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**DEVELOPMENT OF EB-PVD TBC'S:
THE ROLE OF DEPOSITION TEMPERATURE
AND
PLASMA ASSISTANCE**

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To my family,

ABSTRACT

Gas turbine manufacturers have achieved continually improved engine efficiency and thrust-to-weight ratio by designing with increased Turbine Entry Temperature (TET). The protection of High Pressure Turbine (HPT) aerofoils with thin insulating ceramic coatings, referred to as Thermal Barrier Coatings (TBC's), has emerged as the next key technology to allow for further increases in TET. Electron Beam Physical Vapour Deposition (EB-PVD) is today's most promising processing route for the manufacture of TBC's applied on aerofoils.

The purpose of this work was to generate a sound understanding of the relationship between the EB-PVD process and the structure of ZrO_2 -8wt% Y_2O_3 ceramic deposits, which could be exploited to achieve improved TBC performance. In particular, the role of deposition temperature and the potential benefits in using RF and DC plasma assistance of the EB-PVD process were investigated, together with their influence on the erosion performance of EB-PVD TBC's. The significance of particulate erosion as a degradation mode is assessed under conditions representative of the HPT environment. New explorable routes to achieve reduced thermal conductivity of EB-PVD TBC's are identified.

It is shown that EB-PVD TBC's deposited at low temperature contain a massive content of microscopic voidage (~50%) which is responsible for their lack of thermal stability. The growth of EB-PVD TBC's at elevated deposition temperatures is explained in terms of dynamic sintering, whereby diffusion processes compete against the high rate arrival of vapour atoms to overcome the spontaneous defectiveness of the atomic build up. Modelling of the gas discharge physics has highlighted scope for improving the effectiveness of plasma assistance in causing ceramic structural damage, capable of modifying the coating thermal properties.

The erosion rate of EB-PVD TBC's is shown to be controlled by their degree of plastic deformation upon particle impacts, which in turn depends on the ceramic column diameter and inherent porosity.

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INTRODUCTION

The background

To remain competitive in the fierce world market of commercial jet engines, gas turbine manufacturers must aim for ever increased engine efficiencies and thrust-to-weight ratios. These goals can be achieved by designing with higher turbine entry temperatures which necessitates materials having greater high temperature capability. Several generations of superalloys, along with corrosion resistant coatings have been developed over the past decades, which coupled with internal cooling technology have allowed working gas temperatures up to 1700°C to be used. Today's superalloys operate already at 0.85 of their melting point which leaves very little scope for further improvement via alloy base development. As the next generation of turbine materials (ceramics?) is still a long way off, Thermal Barrier Coating technology appears to have a major role to play in pushing the turbine entry temperature a step higher.

The concept of Thermal Barrier Coating (TBC) first appeared some thirty years ago, whereby a ceramic insulating coating is applied to a cooled metallic component to reduce its temperature. The technological challenge was then to apply successfully a ceramic layer capable of surviving large thermal cyclic strains imposed by the thermal expansion mismatch with the metallic substrate. Progress was made through the development of coating processes producing strain tolerant ceramic morphologies, namely thermal spraying and electron beam physical vapour deposition (EB-PVD) and the optimisation of ceramic compositions, the ZrO_2 -8wt% Y_2O_3 being the system on which the industry has standardised. The development of oxidation resistant overlay coatings helped further to render the thermal barrier coating approach viable, as the ceramic coat cannot be made more adherent than the oxide growing at the interface with the metal. Hence, thermal barrier coatings are duplex systems comprising an oxidation resistant alloy bond coat overlaid with an insulative ceramic coating. The durability of such a system depends as much on the immunity of the ceramic coat to thermal cycling, foreign object damage and chemical attack as on the integrity of the oxide growing at the ceramic/bond coat interface.

To date, the use of thermal barrier coatings in aeroengines has been restricted to non-critical applications i.e. where partial ceramic loss does not compromise the integrity of the component protected. Typical benefits of TBC's have been for example to increase the life of combustor parts. Maximum pay-offs are however to be gained with the protection of High Pressure (HP) turbine components such as rotating and nozzle guide vane aerofoils, for which very high levels of coating durability and reliability are required. Of the two types of TBC's currently in use in industry, only the EB-PVD TBC's appear to have the potential to meet the performance criteria in terms of spallation resistance, surface finish retention and erosion resistance required for the protection of HP aerofoils. Still, many technological barriers

are left to be surmounted to access to the promises of EB-PVD TBC's.

The thesis context

Until very recently, the technology of EB-PBD TBC's was exclusively American based with the aero-engine manufacturers Pratt&Whitney and General Electric, along with coatings industries such as Airco Temescal and Chromalloy Research & Technology, boasting both research and manufacturing experience. In Europe, no manufacturing capability was available until the acquisition of an industrial Leybold-Heareaus coater by Chromalloy UK in 1994. Activities in the field of EB-PVD TBC's had been mainly based at research institutions such as DLR in Germany and Hull University in the UK. At a time when the strategic disadvantage of Europe over the United States of America in this technology was most acute, Rolls-Royce set out to develop a PVD TBC technology beyond the American state-of-the-art. Cranfield University, formerly Cranfield Institute of Technology have accompanied Rolls-Royce to achieve this goal since 1990, with first their involvement in the Brite Euram 0141 programme in the exploratory phase and in a UK-based programme in a more competitive stage. The european programme, which terminated in 1994 put together as other european partners MTU (Germany), the research laboratories DLR (Germany) and AEA (UK), and the coatings manufacturer ASET (UK). The UK-based programme, which is still ongoing, was initially organised around the creation of a consortium of interacting science based (Cranfield University, AEA technology) and industry based (Rolls Royce, Chromalloy UK Ltd) institutions, thus bringing together the complementary skills necessary to develop and implement an advanced TBC technology. The present thesis was written from work directed by Rolls-Royce under these two programmes.

To meet up with the challenge of developing and implementing an advanced TBC technology, Rolls-Royce have adopted an all-round approach to the problem by addressing the needs for:

- further developments in the process technology
- a proven TBC lifing methodology
- integrating the technology of TBC's at the initial design stage in order to extract the maximum benefits

Broadly, Cranfield have been involved in three areas of work, all related to the process technology of EB-PVD TBC's (see Figure 1). These are:

- 1 the evaluation of new bond coat chemistries with regard to their oxidation and corrosion behaviour in interaction with the ceramic coat.
- 2 the role of controlled pre-oxidation and *in situ* glow discharge treatments of the bond coat surface on the bonding of the ceramic top coat.
- 3 the development of novel ceramic structures with reduced thermal conductivity and improved durability.

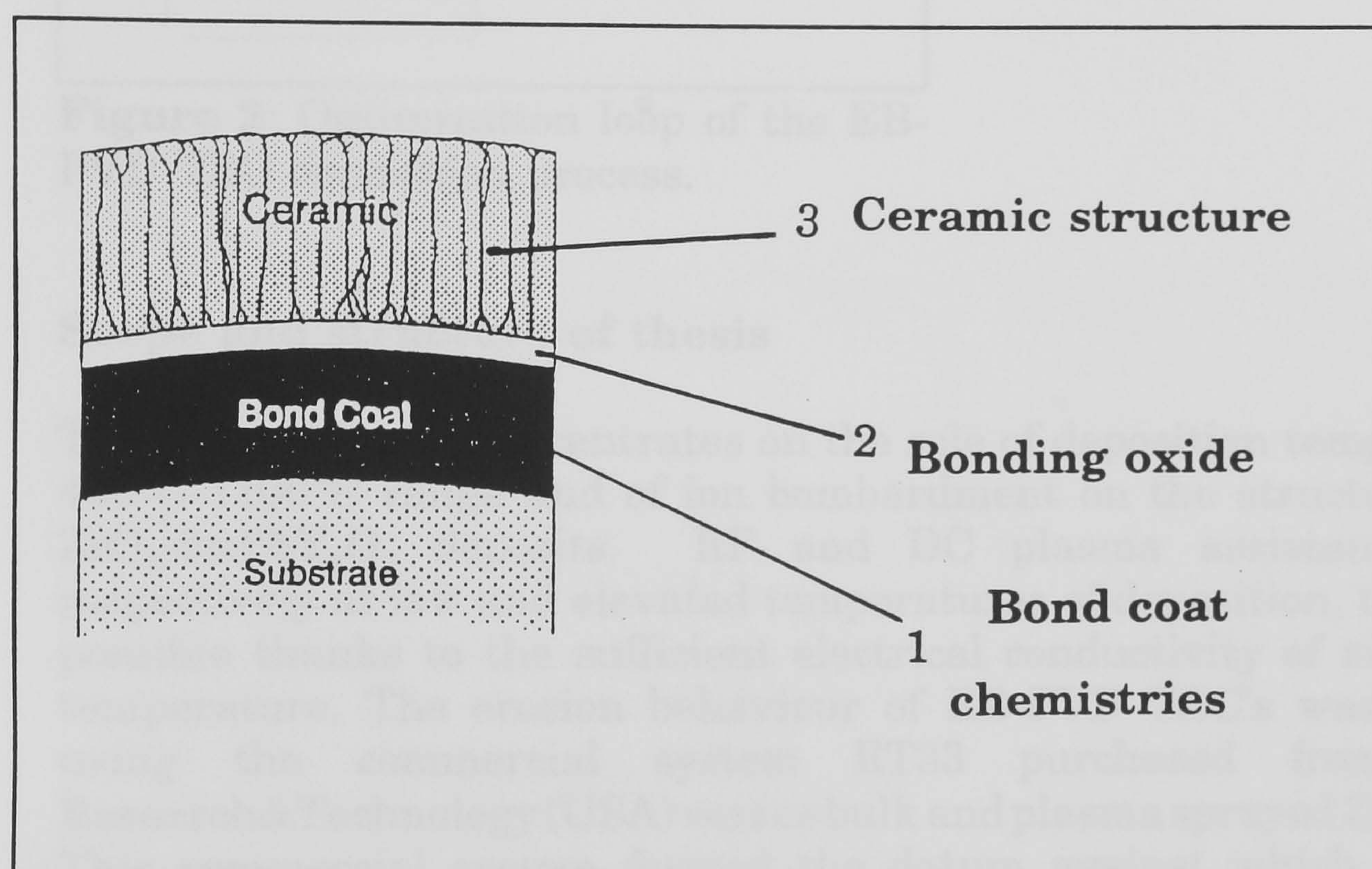


Figure 1: Ongoing developments in the process technology of EB-PVD TBC's.

The work from which this thesis was written relates to the third area. The aim was to generate a scientifically sound understanding of some aspects of the relationship between the deposition process and the structure of the ceramic coat, from which new reasoned processing routes can be identified to achieve enhanced TBC performance (see Figure 2).

The performance aspects covered in this document relate specifically to erosion resistance. The issue of thermal conductivity, being the object of a different study, is discussed here more at a superficial level.

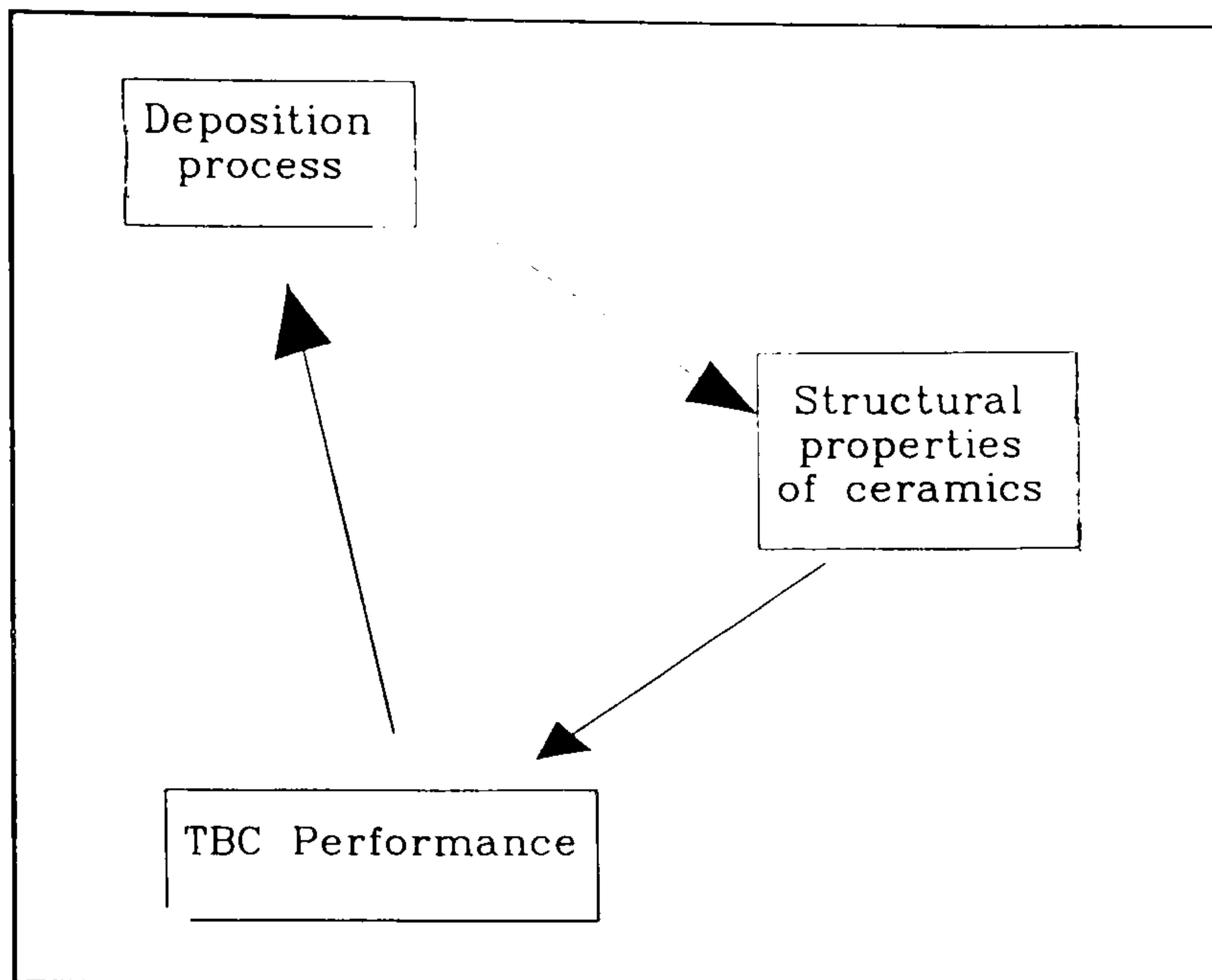


Figure 2: Optimization loop of the EB-PVD TBC deposition process.

Scope and structure of thesis

The present thesis concentrates on the role of deposition temperature in the 400°C-1100°C range and of ion bombardment on the structure of EB-PVD ZrO_2 -8wt% Y_2O_3 deposits. RF and DC plasma assistance were used respectively at low and elevated temperatures of deposition, the latter being possible thanks to the sufficient electrical conductivity of zirconia at high temperature. The erosion behaviour of EB-PVD TBC's was characterised using the commercial system RT33 purchased from Chromalloy Research&Technology(USA) versus bulk and plasma sprayed ZrO_2 -8wt% Y_2O_3 . This commercial system formed the datum against which the structural properties and erosion performance of the Cranfield TBC's were assessed.

The thesis structure is depicted in Figure 3. The background is broad in its content as it required an appreciation of TBC technology from the industry viewpoint (chapters 1 and 2) and of the underlying science encompassing both the materials science of zirconia and PVD films, as well as glow discharge theory (chapters 3 to 5).

The experimental details concerning the deposition process, the characterization techniques and erosion testing used in the study are described in chapter 6. Special efforts were devoted to the commissioning of the erosion test facility so as to render it capable of testing at temperatures and particle velocities comparable to typical engine operating conditions.

As a preliminary to discuss the role of plasma assistance on the structure of EB-PVD TBC's, chapter 7 provides a diagnosis of the ion bombardment regime that applied both in the DC and RF substrate biasing. Chapter 8 then discusses the relationship between the process parameters and the structural properties of the deposits. Although the emphasis is put on deposition temperature and ion bombardment, other important parameters

are highlighted as influential to the ceramic structure. Chapter 9 investigates the erosion mechanisms of EB-PVD TBC's and, in the light of chapter 8, assesses the ceramic structural properties controlling erosion performance.

Considering the whole of the preceding chapters, an appraisal of the contribution of this thesis to TBC technology is then given in chapter 10, with regard to the process optimisation loop depicted in Figure 2 .

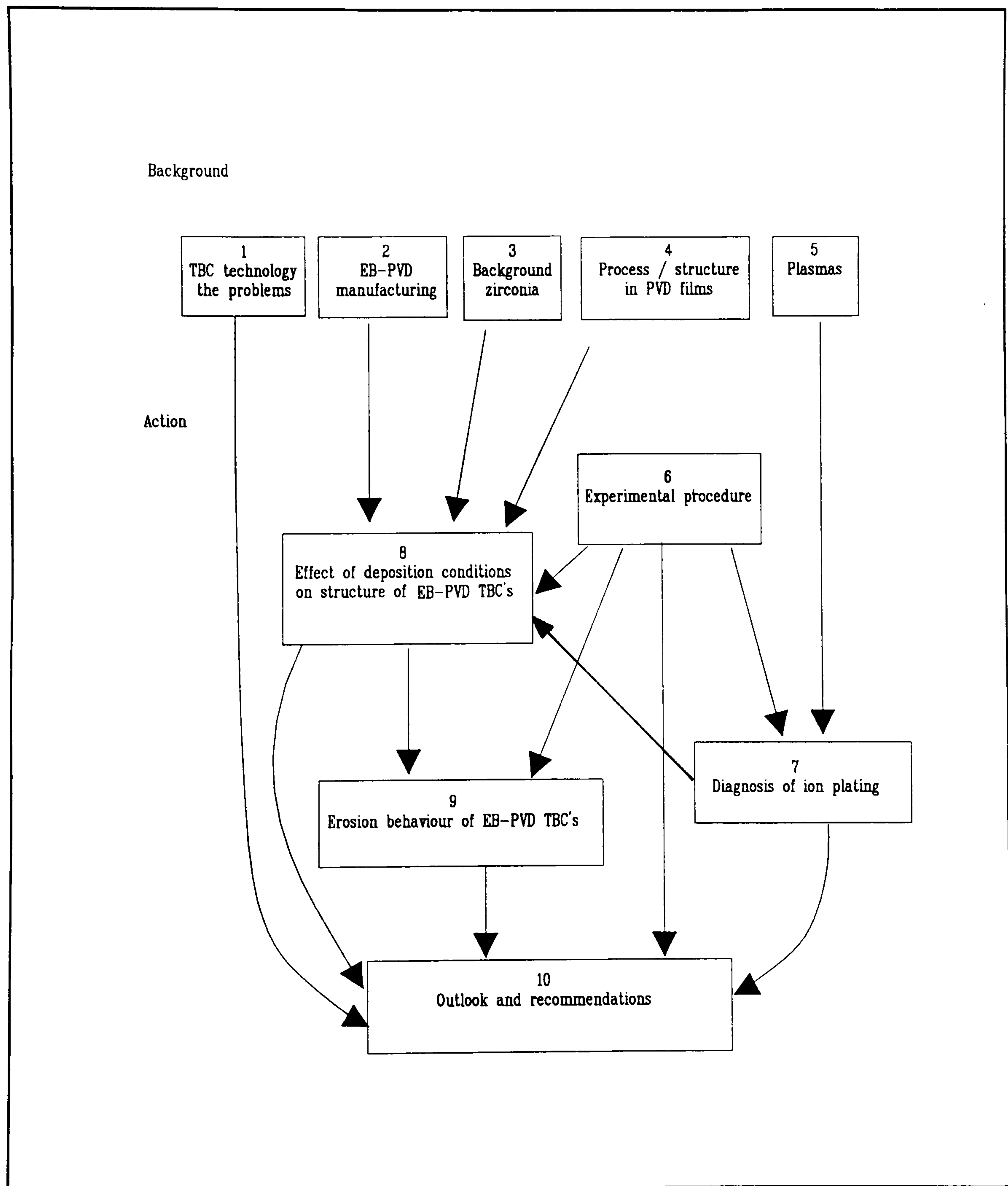


Figure 3: Diagram showing thesis structure.

1 TBC'S FOR THE AERO GAS TURBINE ENGINE

The status of thermal barrier coatings (TBC's) is reviewed with regard to their current and projected incorporation in the aero-gas turbine engine (1). The crucial role of process developments in enabling their successful application is highlighted (2). The degradation mechanisms of TBC's are discussed with special emphasis on solid particle erosion, the significance of which as a TBC life limiting factor must be addressed in the perspective of applying TBC's to aerofoils (3,4).

1.1 NEED, CONCEPT AND IMPLEMENTATION OF TBC'S

1.1.1 The drive for increased temperature capability of turbine materials

The design aims of commercial jet engine manufacturers have been conditioned by commercial and environmental pressures demanding for higher thrust and more cost effective engines within the environmental regulations governing emissions and noise levels. The running costs of a modern turbofan engine split into fuel and maintenance costs. The former, being directly related to the engine Specific Fuel Consumption (SFC), account for over 50% of the direct operating costs of airliners¹. Maintenance costs are so low as the durability of engine parts is high. Typically, service lives in excess of 90,000 hours are being achieved which equates to several years of airline operation.

Improvements in SFC are achievable mainly by reducing the coolant flow requirement of High Pressure Turbine (HPT) aerofoil components (see Figure 4) and/or increasing the engine thermal efficiency, the latter implying increased turbine entry temperatures (TET)¹.

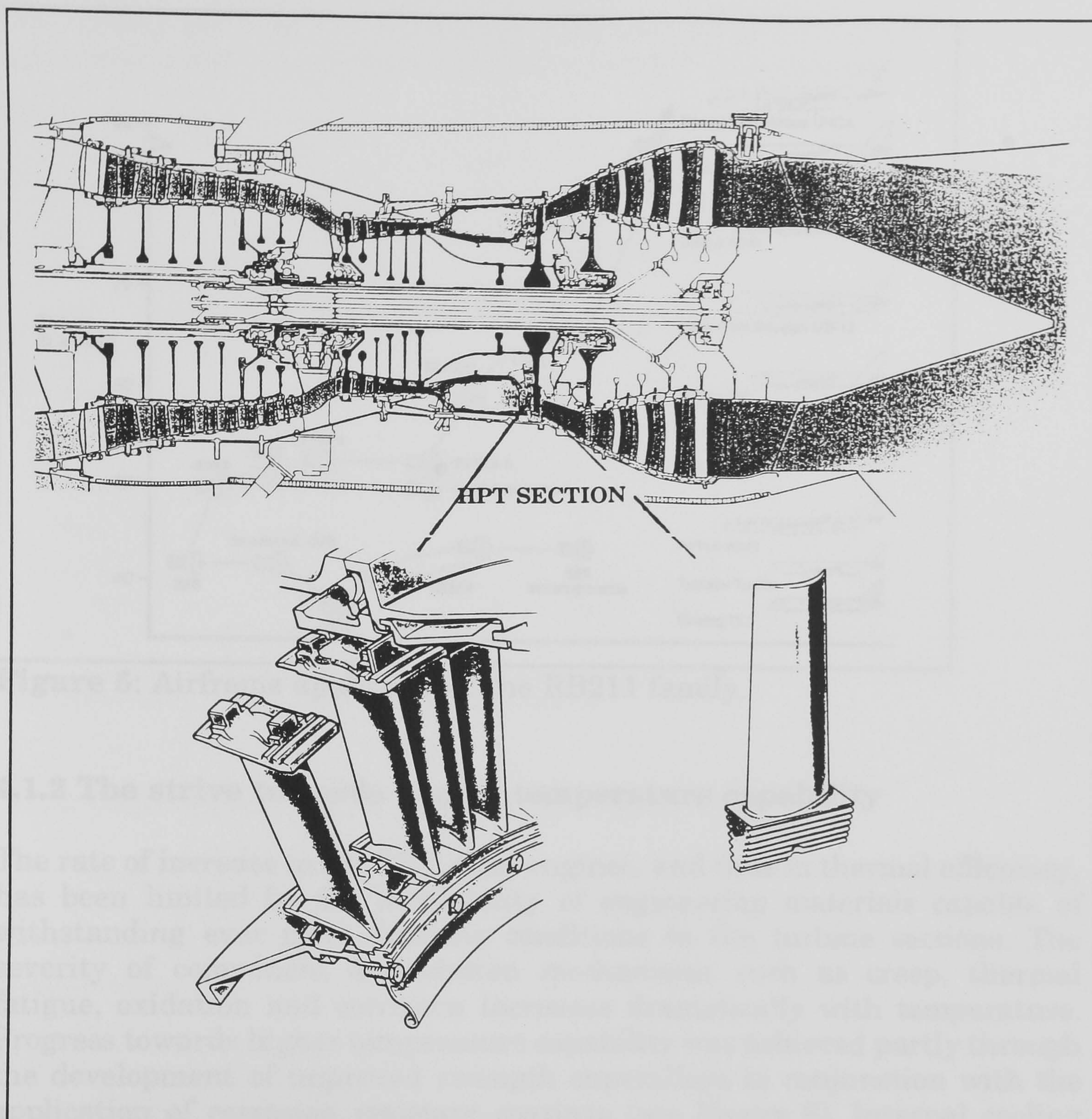


Figure 4: Typical first stage nozzle guide vane (left) and turbine blade (right) and their location in the aero-engine.

In addition to engine efficiency, there is a continuing requirement to develop engines with increased thrust to meet the needs for future aircraft designs (see Figure 5). Such thrust growths are achieved in part by developments in the compressor and combustion module (encompassing low, intermediate and high pressure stages) of the engine, but also by the introduction of new materials into the HP turbine to match the required increases in TET. Although it would be possible to increase the TET by internal cooling of the HPT hardware, extraction of this air from the primary gas path reduces engine efficiency. For example, it has been estimated that a 4% reduction in coolant flow would save 10 millions gallons of fuel annually for a 250 aircraft fleet². Increased thrust and reduction in SFC rely therefore on the capability of gas turbine materials to operate at increased temperatures.

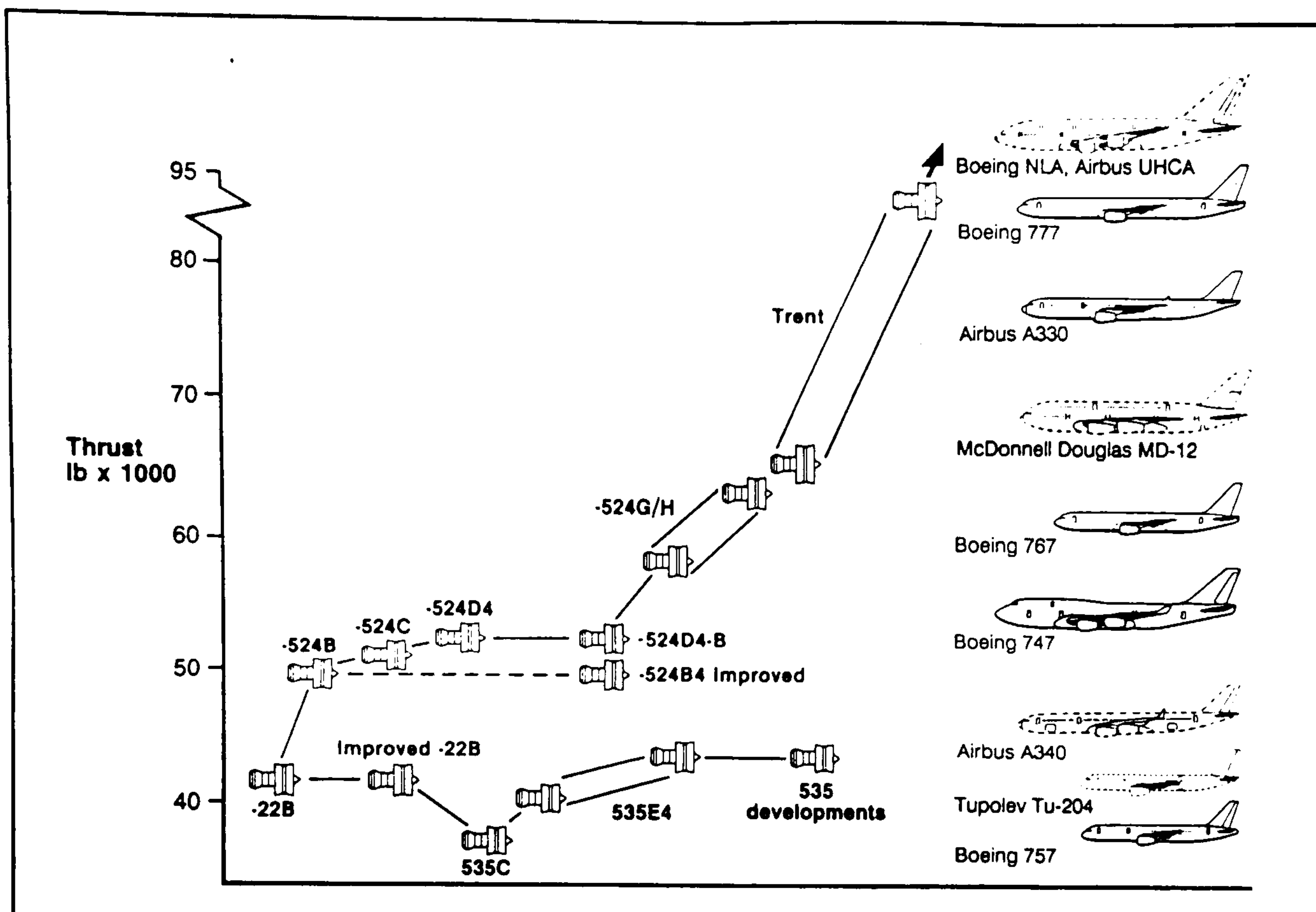


Figure 5: Airframe applications: the RB211 family.

1.1.2 The strive towards higher temperature capability

The rate of increase in the TET of jet engines, and thus in thermal efficiency, has been limited by the availability of engineering materials capable of withstanding ever more exacting conditions in the turbine sections. The severity of component degradation mechanisms such as creep, thermal fatigue, oxidation and corrosion increases dramatically with temperature. Progress towards higher temperature capability was achieved partly through the development of improved strength superalloys in conjunction with the application of corrosion resistant coatings (see Figure 6). Internal cooling technology and later developments in casting technology (directionally cast and single crystal components) helped push further the temperature operating limits of these materials. Today, High Pressure Turbine components with melting points in the range 1230°C - 1315°C typically operate in a combustion gas environment in excess of 1370°C ³. This corresponds to service metal temperatures in the region of 0.85 of the superalloy melting points which leaves virtually no margin for further increase in TET via alloy development. Increasing the coolant flow would require so much compressor bleed air that this would lead to a shortfall in the projected increase in engine efficiency⁴. The potential of economically increasing cooling efficiency by designing more effective heat transfer geometries is equally considered exhausted^{5,6}.

As the substitution of superalloys by the next generation of gas turbine ceramic materials is still remote⁷, there has been an acute need for an alternative technology to allow for the projected increase in TET. The use of $250\mu\text{m}$ insulative ceramic coatings, known as Thermal Barrier Coatings, has

emerged as the next key technology with the potential to realise new major advances in the temperature capability of HPT components.

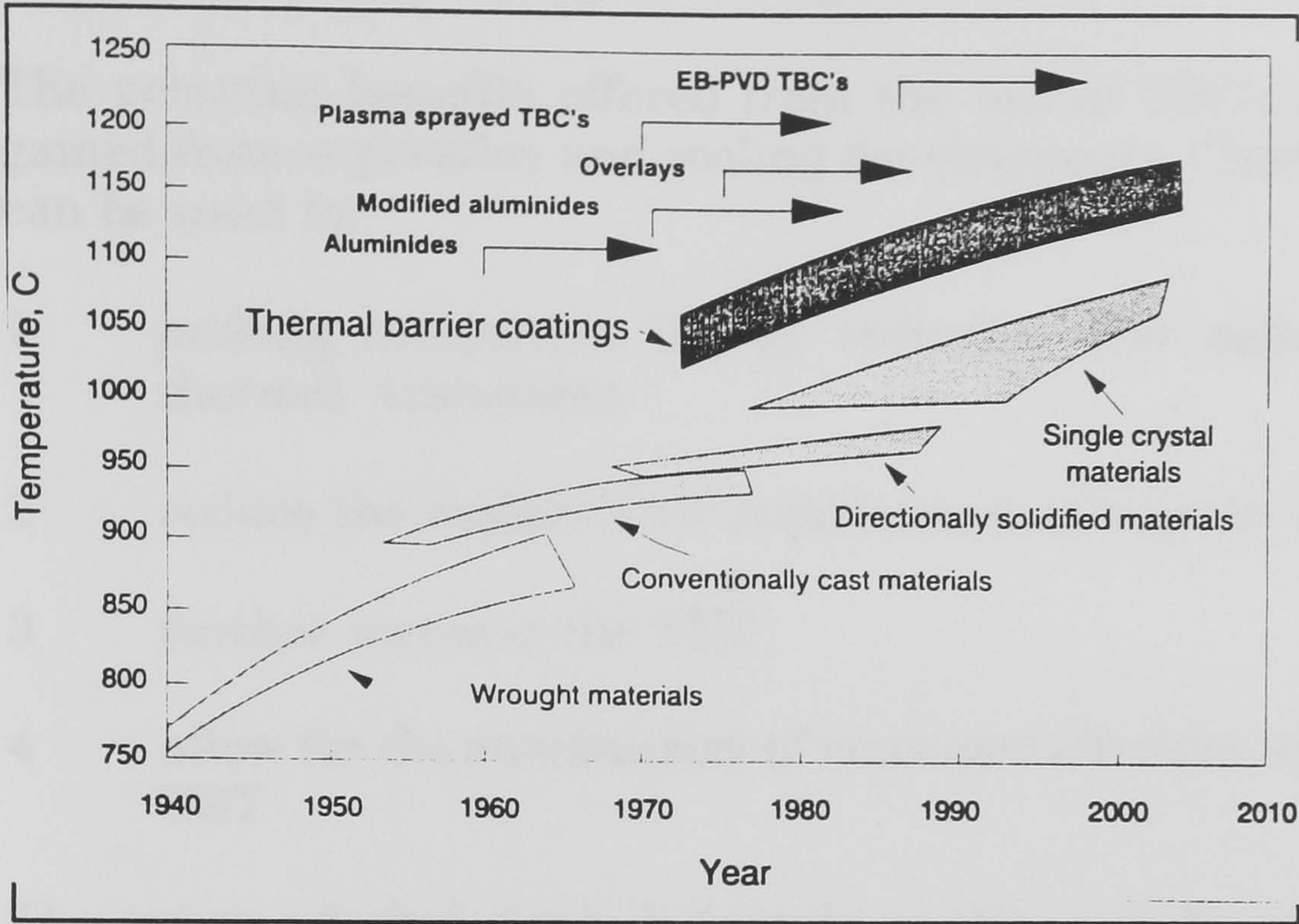


Figure 6:Increase in TET over the years.

1.1.3 Concept and potential benefits from TBC's

The effect of applying a thin ceramic film on a cooled metallic component is shown in Figure 7¹. The temperature at the hot gas/component interface is increased but drops sharply across the ceramic layer so that the metal temperature is reduced.

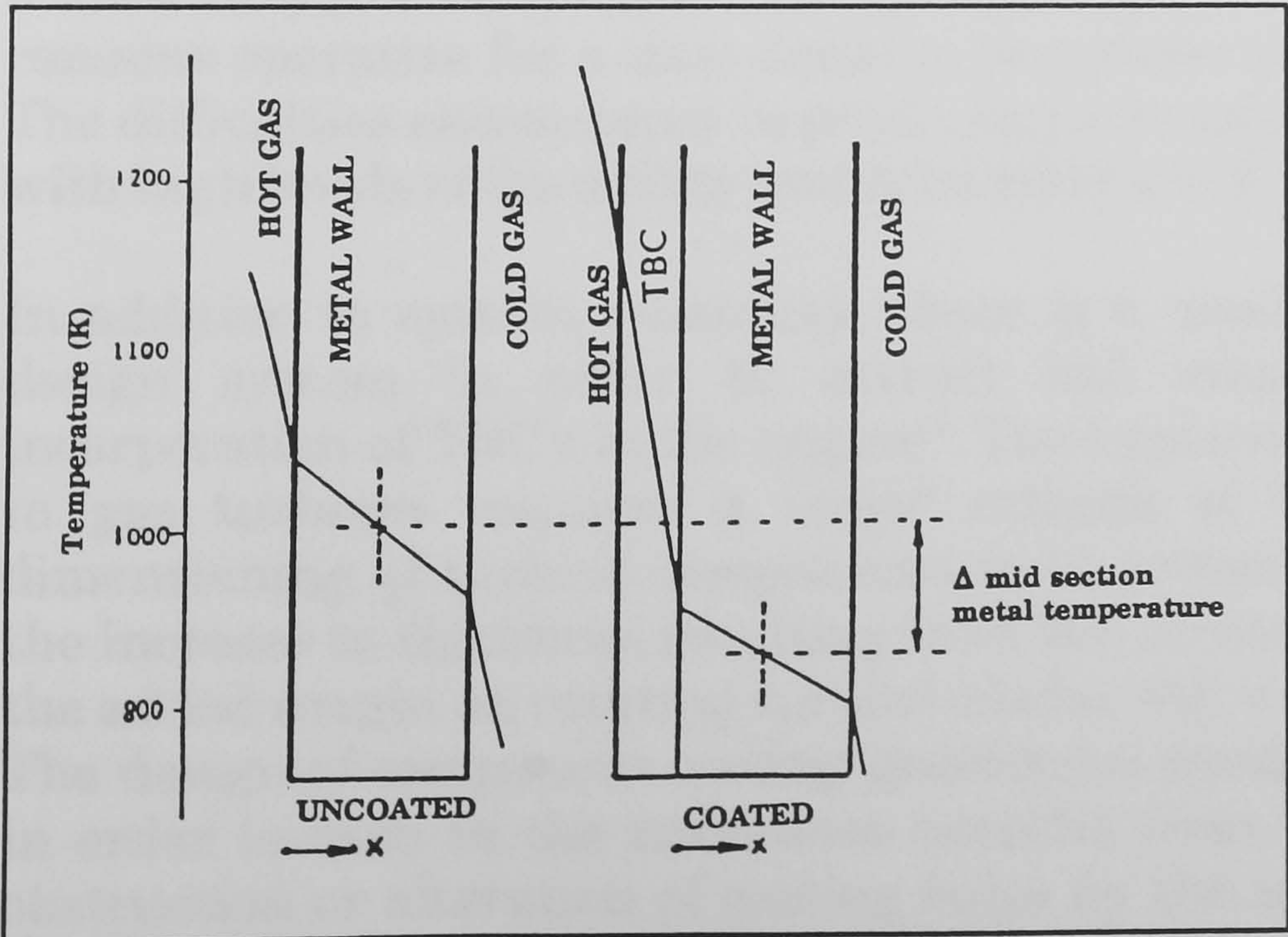


Figure 7:Effect of applying a thin insulating ceramic coating.

Depending on the heat flux, temperature reductions as high as 170°C have been achieved in research gas turbine engines with 250µm thick TBC's. This

represents a leap forward in temperature capability greater than the cumulative gains achieved over the last twenty-five years⁶ from developments in superalloy and cooling technologies.

The potential benefits offered from the use of TBC's are additive to those gained from superalloy and cooling developments. Thermal Barrier Coatings can be used to:

- 1 prolong component life by reducing near metal temperatures and thermal transients
- 2 reduce the coolant flow requirement at a given TET
- 3 further increase the TET
- 4 allow for the substitution of more cost effective substrates at any given TET

The option adopted depends largely on the application. In effect, the choice is, to date, essentially restricted to 1, as still considerable technological barriers are to be surmounted to be able to fully exploit the potential of TBC's (options 2 through 4).

1.1.4 The technological challenges of TBC technology

The application of TBC's involves a very high risk since coating failure would quickly lead to total component loss. Therefore, to achieve this goal, there is a need for a proven reliable TBC system, that is to say a coating system that remains operative for a time equal to or greater than the aerofoil design life. The difficulties encountered in producing a ceramic system effective as a TBC with high levels of durability and reliability are discussed in the next section.

In addition to system reliability, there is a need for a TBC coated aerofoil design system in order to extract the maximum pay-offs from the incorporation of TBC's in the engine³. The implementation of TBC technology in gas turbines requires a major rethink of the existing designs. The dimensioning of turbine components to be protected must take into account the increase in thickness resulting from the ceramic coating and the fact that the added weight on rotating turbine blades will increase the centrifugal load. The design of component cooling geometries needs to be revisited altogether in order to cash in the maximum benefits from TBC application while the obstruction or alteration of cooling holes by the ceramic has to be accounted for. Figure 8 shows a simplified cooling geometry design of a rotating turbine blade resulting from the application on the pressure side only of a 250µm thermal barrier coating⁵. A reduction in the mass average temperature of 125°C is expected from this design.

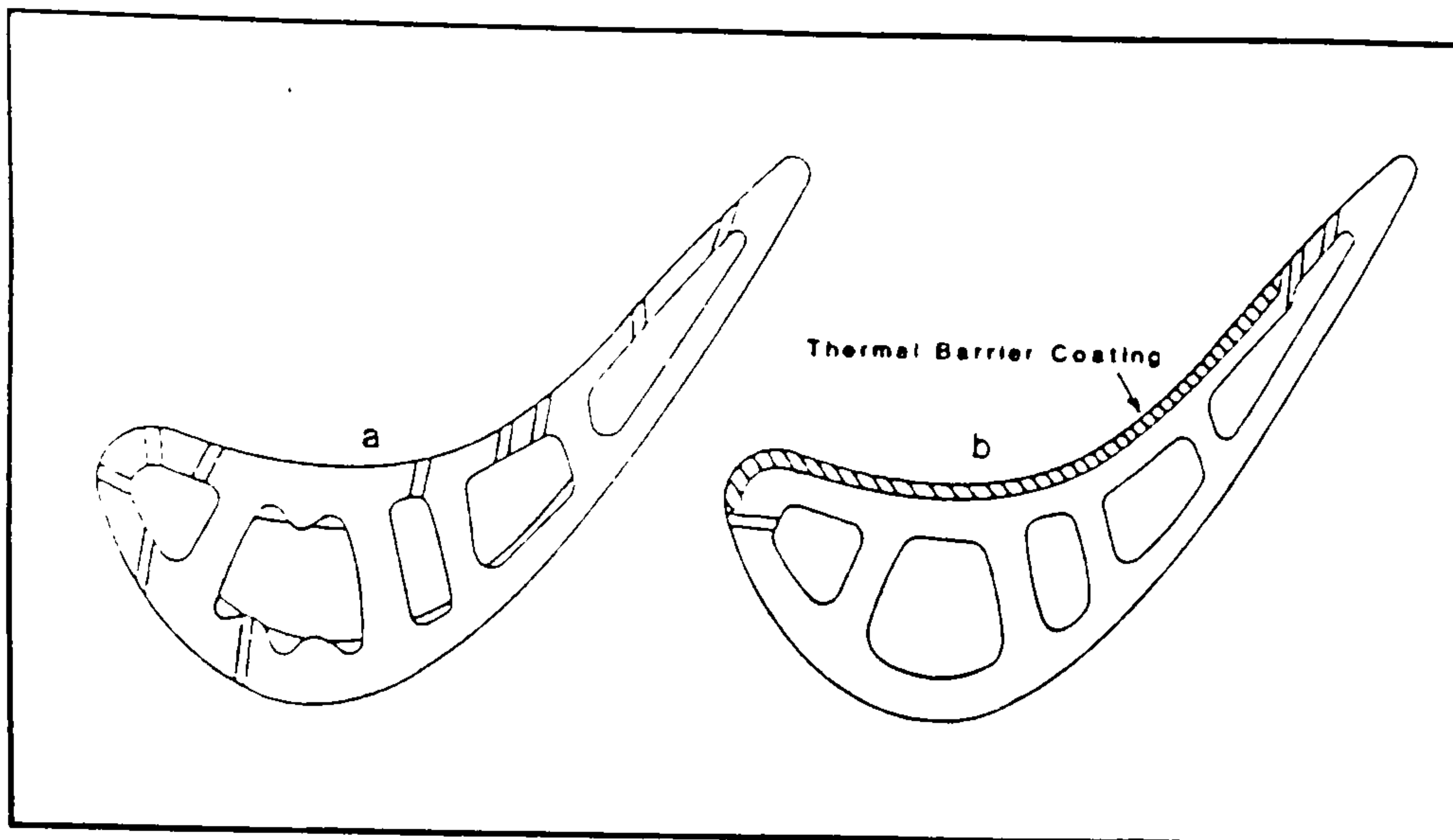


Figure 8: Simplified cooling design using TBC's.

Finally, to assure coating and component reliability, there is a need for a methodology to predict TBC spallation life. Life prediction models that correlate TBC spallation life to time-cycle temperature conditions have been developed by Pratt&Whitney and GTEC with NASA support^{8,9,10}. They are built up on laboratory experiments and calibrated with flight service evaluation data.

1.2 CURRENT STATUS OF TBC's

1.2.1 Development of TBC's

It is interesting to note that the rather simple idea of applying an insulating ceramic coating to a turbine aerofoil, investigated as early as in 1947¹¹, only appeared achievable in the late eighties while, in the mean time, ostensibly more complex technologies such as superalloy composition developments, casting developments and clever concepts of internal cooling were being adopted. This only highlights the complexity of developing a production viable process route capable of rendering a 'repugnant' ceramic layer effective as a TBC in the harsh gas turbine environment.

Thermal barrier coatings have owed their continually improved performance to the concurrent developments in ceramic composition, ceramic deposition technologies and bond coat systems.

Zirconia-based systems are at the forefront of TBC applications for their low thermal conductivity (1-3.5W/m.K compared to 25W/m.K for superalloys) and their relatively high thermal expansion coefficient ($10 \times 10^{-6}/^{\circ}\text{C}$) approaching those of superalloys ($15 \times 10^{-6}/^{\circ}\text{C}$). Early TBC's on combustor parts consisted of magnesia stabilised zirconia. This system has been largely superseded by yttria stabilised zirconia for its superior high temperature mechanical stability and lower thermal conductivity. Research in the optimisation of the ceramic composition has led to the selection of zirconia partially stabilised

with 6-8wt% yttria. This yttria content range resulted in maximum test life times of plasma sprayed TBC's which correlated with the presence of maximum amounts of 'non transformable' tetragonal phase⁸. A more detailed examination of the properties of the yttria-zirconia system is given in chapter3.

The primary drawback however to the practical use of ceramics was their lack of compliance and brittleness. The thermal strain imposed on a ceramic coating upon thermal cycling, induced by the thermal expansion mismatch with the metallic substrate, gives rise to unacceptable stresses leading to coating spallation. This prohibited the use of dense ceramic coatings and addressed the need for strain tolerant ceramic structures. Two deposition technologies have been developed to obtain the improvement in the strain tolerance of the TBC, namely thermal spraying and electron beam physical vapour deposition (EB-PVD). Figure 12 shows the improved strain tolerance from bulk to plasma deposited to EB-PVD structures.

To date, the use of TBC's has been limited to non-critical applications where partial coating loss does not compromise the integrity of the component protected. They are being utilized in service to achieve substantial increases in component durability at current performance level. Combustor parts have been protected with TBC's for over 20 years against hot spots and thermal fatigue cracking, resulting in life improvements over 50%. More recently, plasma deposited TBC's have been used by Rolls-Royce and Pratt&Wittney to enhance the durability of High Pressure Turbine nozzle guide vane platforms (NGV)^{3, 5}.

1.2.2 Plasma sprayed TBC systems

Plasma spraying has been the preferred processing route for TBC's as it proved capable of offering an acceptable TBC service life with high levels of reproducibility at relatively low capital cost⁸. In the plasma spray process, the coating material is injected in a powder form into the high temperature, high velocity plasma arc and propelled on to the surface to be coated. Coating build up results from the accumulation of molten or semi-molten material droplets called splats (see Figure 9).

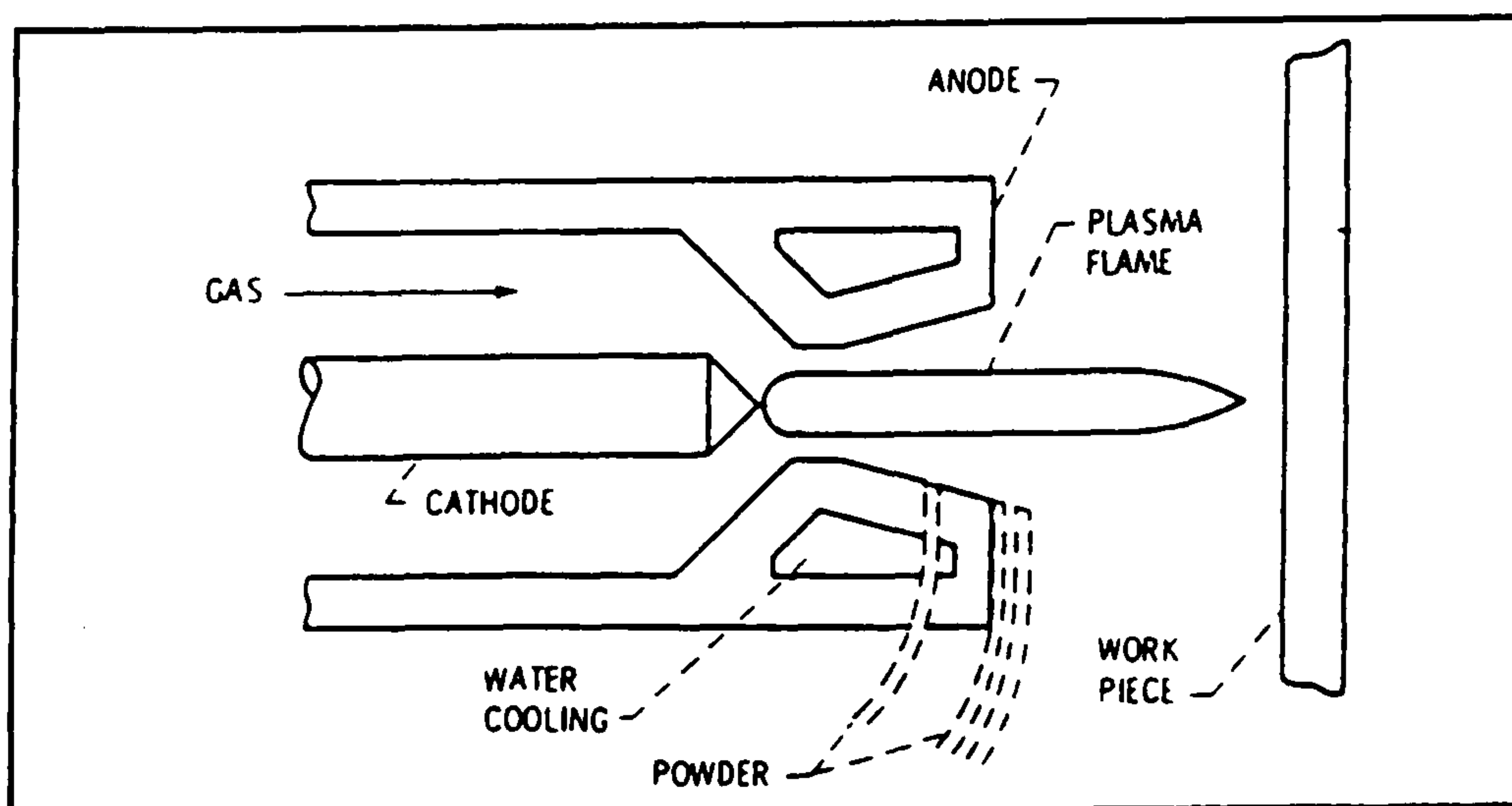


Figure 9: Plasma spray torch.

A plasma sprayed ceramic coating typically has a heavily microcracked structure and contains significant amounts of porosity (5 to 20wt%). The latter results from the entrapment of air during coating build up as the process is carried out at atmospheric pressure (see Figure 10). Microcracking and porosity are beneficial structural features as they contribute to both lower the thermal conductivity and enhance the thermal strain tolerance of the ceramic. Typically, plasma sprayed TBC's have thermal conductivities 33% of that of dense partially stabilised zirconia ².

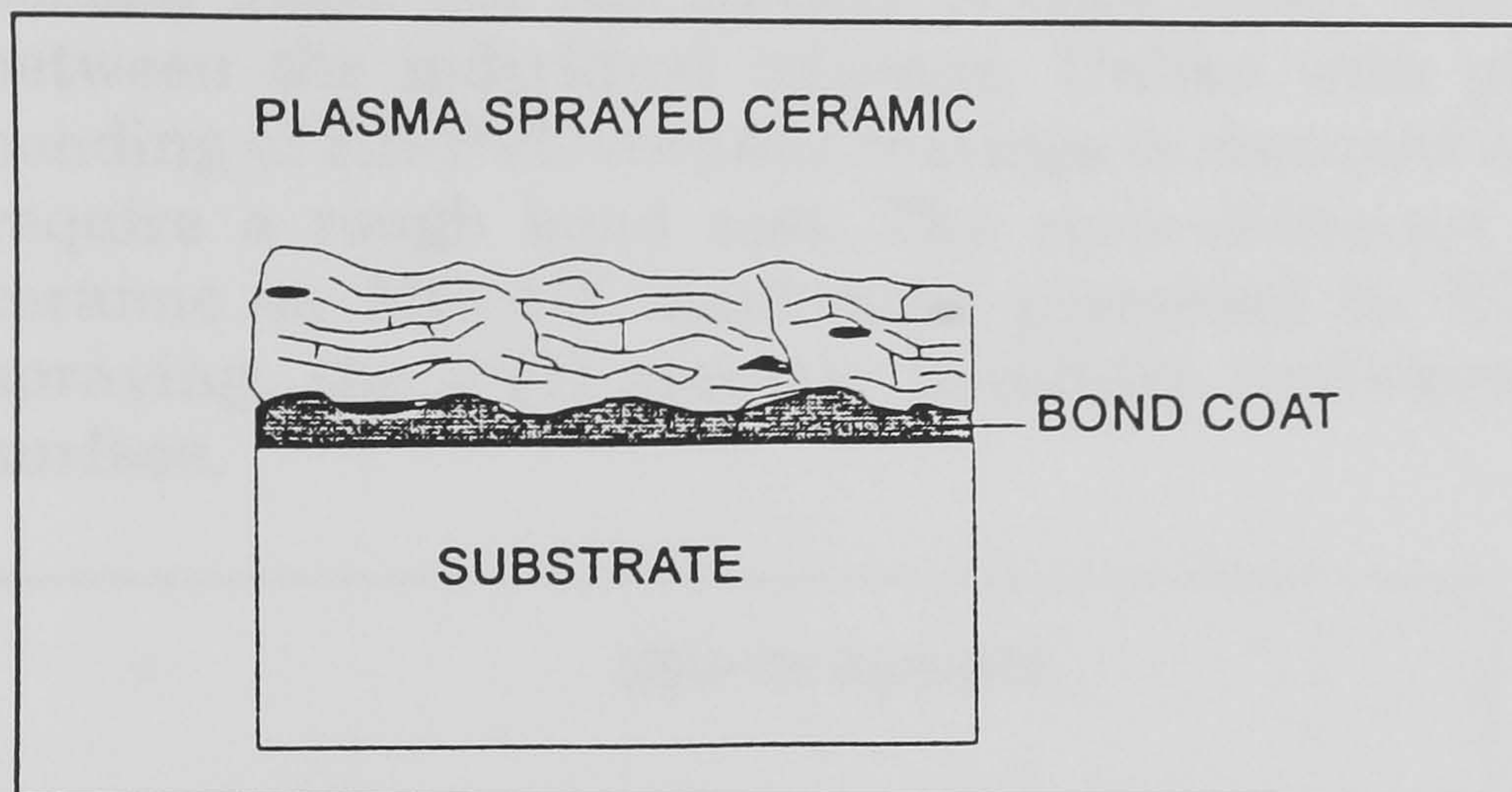


Figure 10: Schematic of the APS TBC structure.

Ceramic segmentation however creates easy paths for oxygen ingress and thus exposes the ceramic/metal interface to oxidation. For this reason, thermal barrier coatings are designed as duplex systems with the ceramic layer being deposited on an oxidation resistant bond coat. Adhesion of plasma sprayed TBC's relies on mechanical keying which requires a bond coat with sufficient surface roughness. In the as-deposited state, plasma sprayed bond coats have a suitable surface topography to provide the necessary interlocking with the ceramic coat.

Early bond coats consisted of NiAl and NiCr compositions. As the operating temperature in combustors increased, bond coats with improved compositions (MCrAlY where M=Ni,Co or both) were substituted. For still higher temperature applications (e.g. 1000°C on NGV platforms), plasma spraying of the bond coat is performed in vacuum (VPS) or in a low pressure gettered argon environment (LPPS). This enhances bond coat oxidation resistance by minimising its porosity and oxide inclusion contents ^{5,6}.

1.2.3 EB-PVD TBC systems

The Electron Beam Physical Vapour Deposition (EB-PVD) process has been established for over 20 years for the manufacture of oxidation resistance MCrAlY coatings on turbine blades. Early efforts to apply the EB-PVD process to ceramics were plagued with 'infant mortality' problems where some coating batches would be of very poor quality with the ceramic coat spalling off as early as during the handling stage³. This dramatic lack of process reproducibility considerably retarded the industrial acceptance of EB-PVD

TBC's. Conserted efforts to improve process reliability were justified by the outstanding thermo-mechanical performance that these systems exhibited. They were introduced for the first time in service in mid-1989 by Pratt&Wittney on second stage turbine vanes⁶. Extensive details on the industrial EB-PVD process are given in the next chapter.

As shown in Figure 11, the EB-PVD TBC has a 'feathered' or 'columnar' morphology, where the columns are firmly attached to the substrate at near normal angle but not bonded to each other. Significant voidage is present between the individual columns. Unlike with plasma sprayed TBC's, the bonding of EB-PVD ceramic coatings is chemical in nature and thus does not require a rough bond coat. The state-of-the-art practice is to deposit the ceramic on MCrAlY bond coats processed by EB-PVD or vacuum plasma spraying, the PVD ceramic faithfully replicating the original bond coat surface.

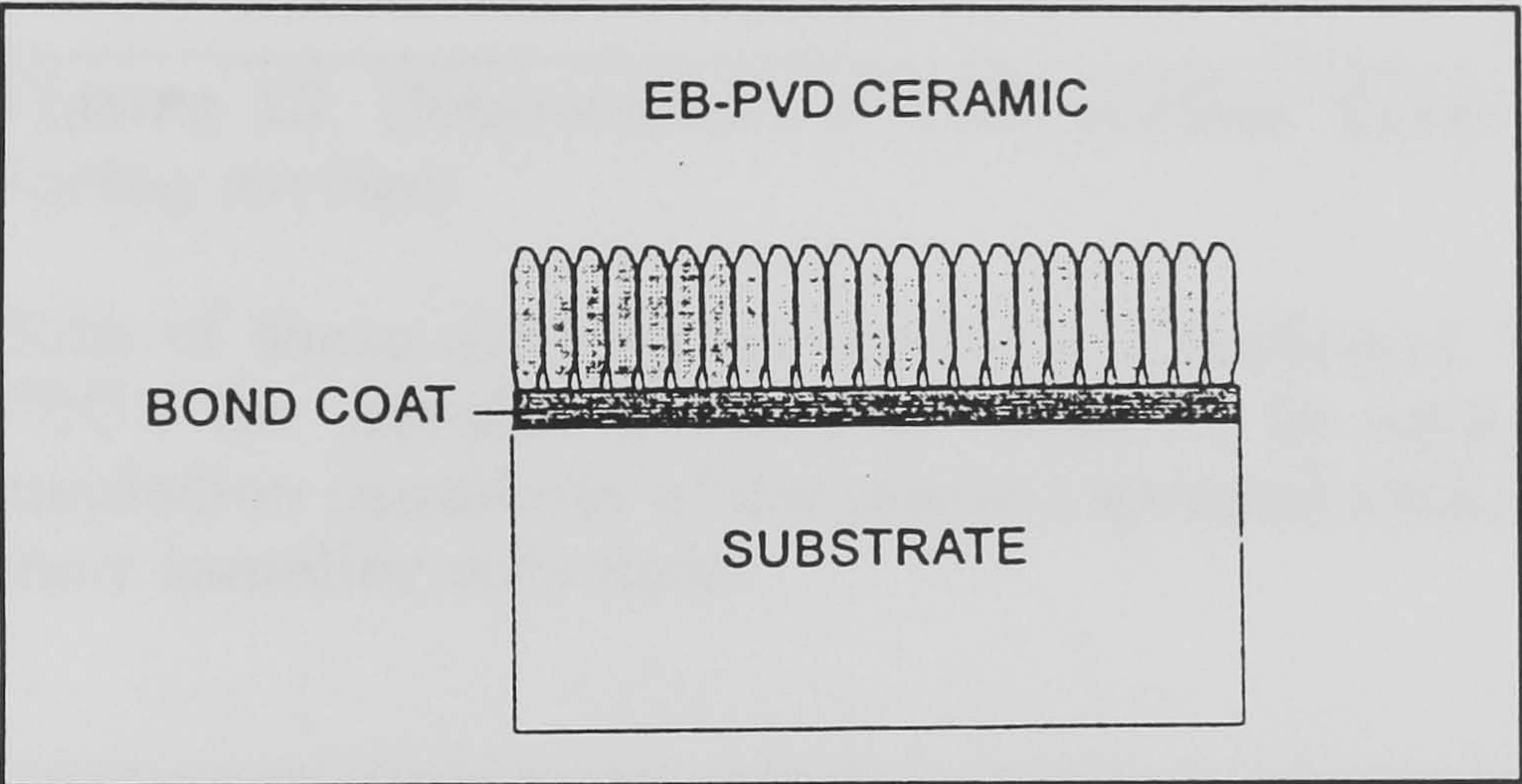


Figure 11: Schematic of the EB-PVD TBC structure.

1.2.4 Performance comparison between APS and EB-PVD TBC's

Optimisation of spray parameters has contributed to substantial increases in the longevity of plasma sprayed TBC's. However, under fierce thermal cycling, it is still largely superseded by the EB-PVD system (see Figure 12).

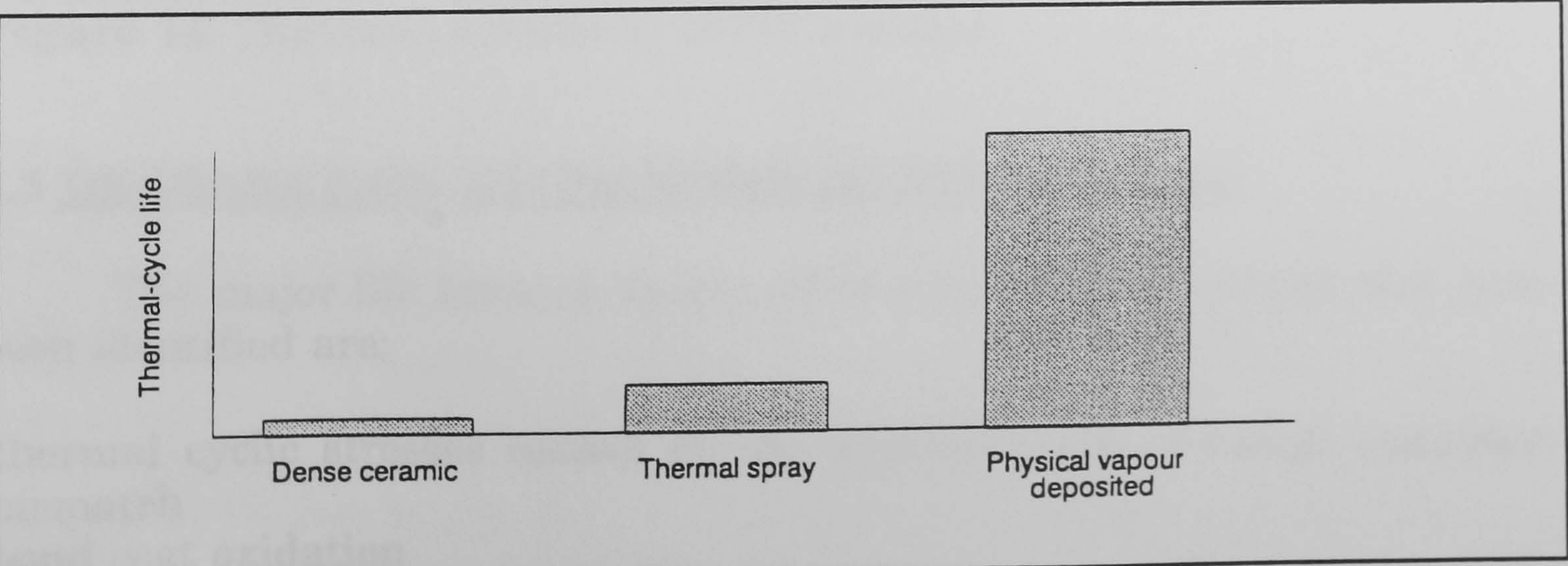


Figure 12: Comparative thermal cyclic lives.

The surface finish of plasma sprayed TBC's is also a major handicap to their use for aerofoil applications. Although the coating can be polished before use, experience shows that it recovers its initial surface roughness during service as a result of particulate erosion. This is in contrast with the smoothness of the EB-PVD TBC and its providential surface finish retention (see Figure 13)

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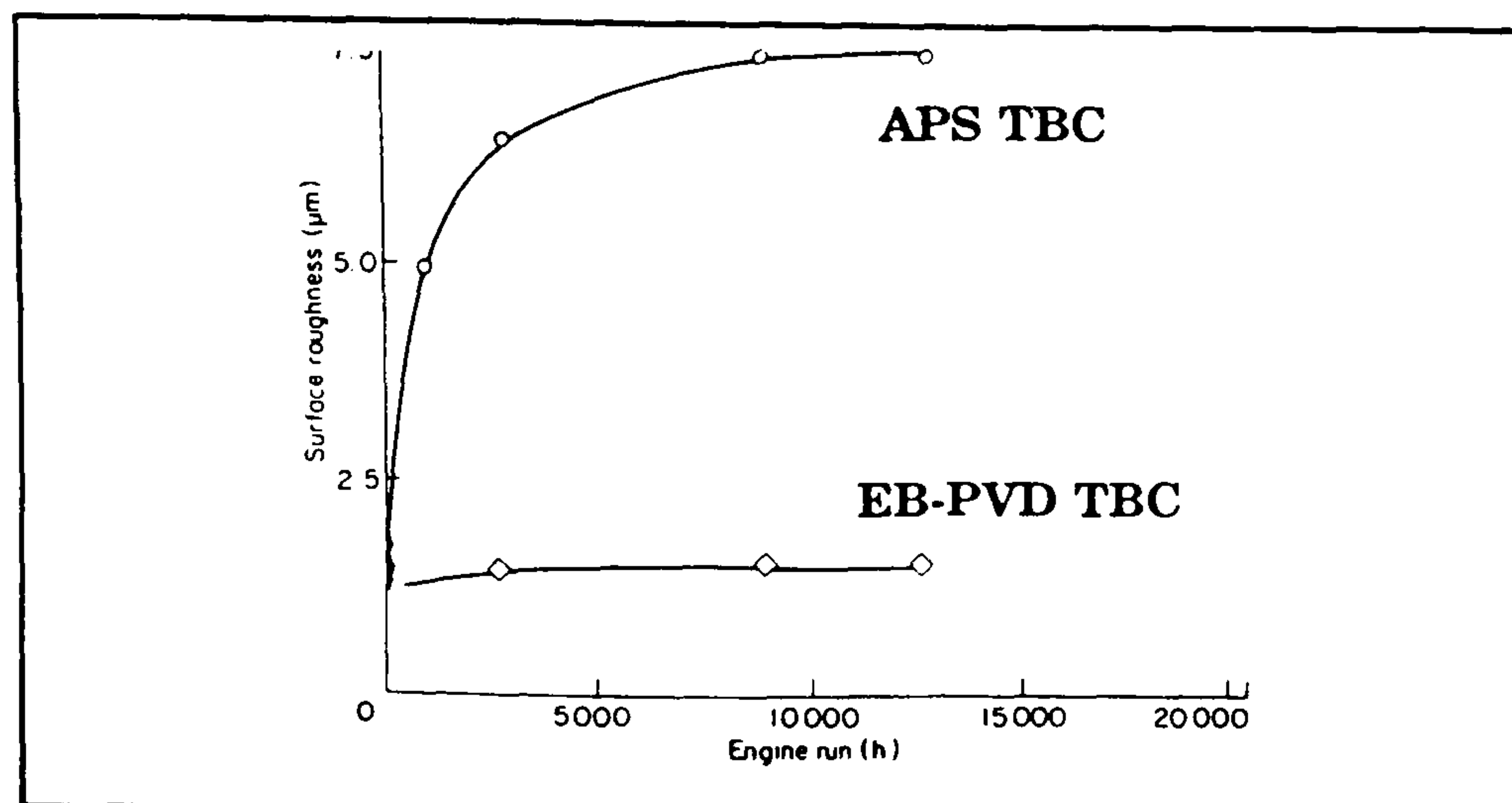


Figure 13: Deterioration of TBC surface finish during service.

Both of these areas of weakness are sufficient to preclude the use of APS TBC's for aerofoil protection. This is in spite of the superior thermal insulation capability of the plasma sprayed systems (Figure 14) imparted by their lamellar structure.

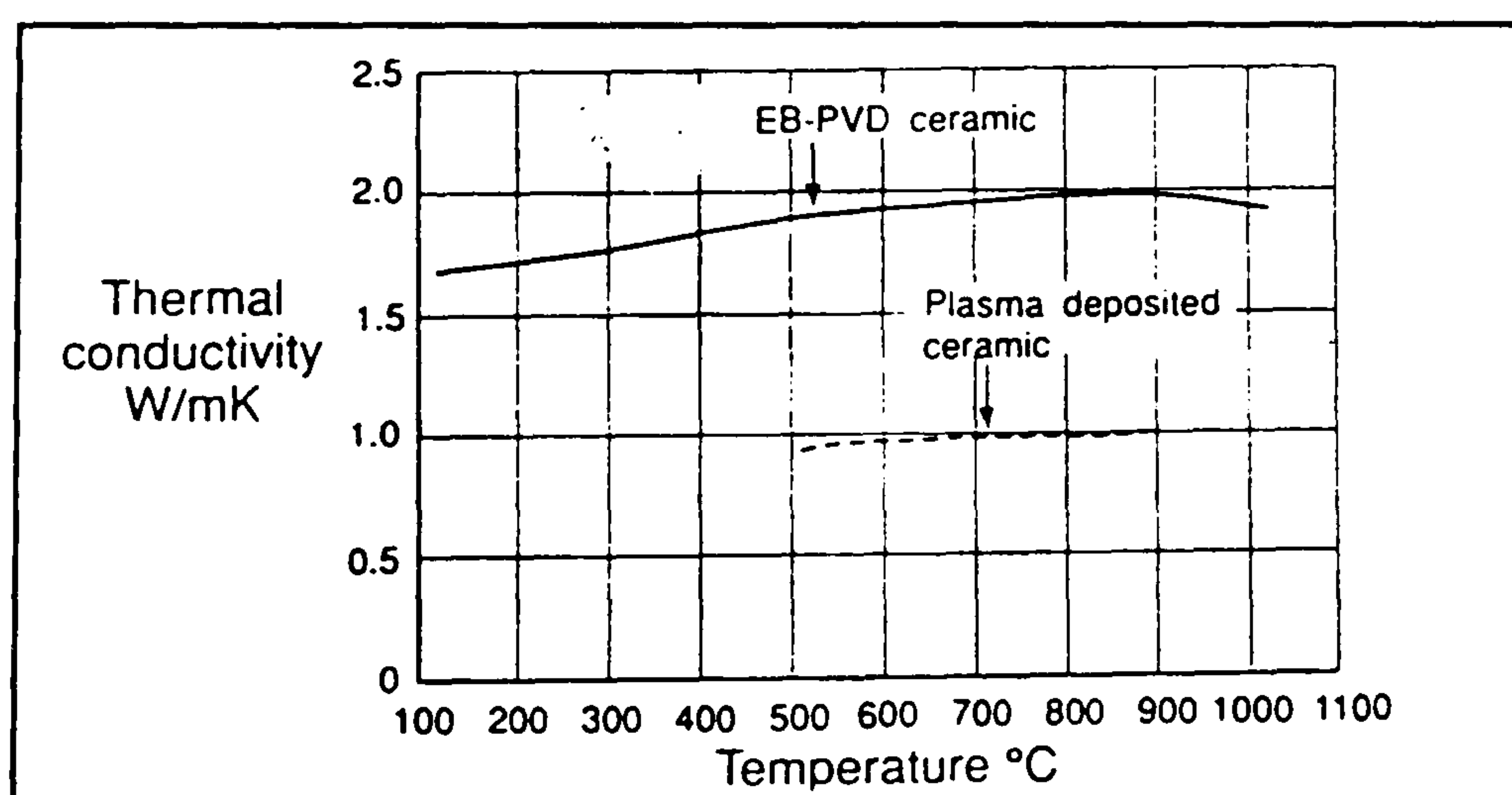


Figure 14: Thermal conductivity of TBC systems.

1.3 DEGRADATION MECHANISMS OF TBC SYSTEMS

The major life limiting factors of thermal barrier coatings that have been identified are:

- thermal cyclic stresses caused by the ceramic/metal thermal expansion mismatch
- bond coat oxidation

- solid particle erosion,
- chemical ceramic destabilisation
- loss of compliance due to the ingress of low melting point deposits

Other factors contributing to failure processes are loading of the turbine blade (centrifugal and bending stresses), component geometry effects on stress-field and growth morphology, sintering of the ceramic, residual stresses resulting from the deposition process,...⁴ Each factor will now be considered in turn.

1.3.1 Thermal expansion mismatch stresses

Ceramic spallation in plasma sprayed TBC's occurs from the propagation of a crack running in the region of the ceramic adjacent to the bond coat interface. This is the end-result of the link-up of micro-cracks near the ceramic/metal interface during repeated thermal cycles¹². The driving force for this mechanism is believed to be the synergistic interaction of cyclic thermal expansion mismatch stresses with bond coat oxidation stresses. The effect of a rough interface on the stress-state was investigated using computer simulation with the sole influence of thermal expansion mismatch stresses taken into account. This study indicated that the ceramic region above any bond coat asperities was subjected to a stress-state of in-plane compression and radial tension which was believed to promote delamination cracking⁸.

The superior thermal-cyclic behaviour of the EB-PVD TBC resides not in different thermal expansion properties but in a much higher compliance. Its elastic modulus in the coating plane was measured at 20GPa at 1000°C compared to 200GPa for the APS system¹³. These figures simply reflect that the columnar morphology imparts more strain tolerance to the ceramic coat than the lamellar structure. Also, the relative absence of asperities at the interface with the bond coat in the EB-PVD system is believed to be partly responsible for its greater durability, while for a same reservoir of protective elements, less bond coat surface area is exposed to oxidation.

1.3.2 Bond coat oxidation

The advent of more strain tolerant ceramic structures such as that of EB-PVD TBC's made bond coat oxidation the major cause for TBC failure. Spallation of EB-PVD ceramics occurs by cracking at the thermally grown oxide/bond coat interface¹³ at a critical oxide thickness of about 5µm¹³. Some authors have concluded that bond coat oxidation was the dominant failure mechanism of plasma deposited TBC's as well¹⁴. Ceramic spallation occurred at the ceramic/thermally grown oxide interface and was associated with the growth of Co,Ni bearing oxides and spinels. NiO and Ni(Cr,Al)₂O₄ spinels formed the weakest points of the bond coat oxide scale and accelerated ceramic spallation. It is generally believed that the formation of a continuous α-alumina scale, growing by inward oxygen diffusion, has to be preferred to

the oxidation of alloy base elements. Oxides of Ni, Co, Cr grow by outward cation diffusion which creates stresses and voids at the oxide/ceramic interface. Their high Pilling-Bedworth oxide/metal volume ratio means that the growth of these oxides generates more stresses than in the case of alumina. Last but not least, they grow at a faster rate than alumina. These points concur to indicate that a critical stress to ceramic spallation is more rapidly attained with the growth of Ni, Co and Cr oxides than with alumina.

It has been experimentally verified that promoting the formation of an alumina scale resulted in enhanced TBC durability. It has been shown that bond coat surface treatments prior to ceramic deposition such as aluminising, pre-oxidation in air, or both could be effective routes in both reducing bond coat oxidation and improving TBC lives^{15,16,17}. Another contributing factor of TBC failure is the bond coat depletion in aluminium due to its diffusion into the substrate during service.

Although bond coat oxidation resistance is a major contributor to TBC durability, it is not the sole influential bond coat parameter. Evidence exists that the use of certain bond coat compositions with poorer oxidation resistance will result in longer times to ceramic spallation². It was proposed that bond coat properties such as modulus, strength, thermal expansion coefficient and compositional effects on adhesion played a significant role in TBC durability. For instance, it was found that bond coats with improved creep strength resulted in longer cyclic lives¹⁸.

1.3.3 Degradation by low melting point deposits

Molten deposits can cause degradation to the ceramic in two ways. They can either react chemically with the ceramic stabiliser and/or infiltrate the ceramic porosity. In the former, the zirconia becomes destabilised and undergoes the detrimental tetragonal-to-monoclinic transformation. In the latter, the ceramic loses its compliance upon solidification of the deposit, generating great compressive stresses.

Such situations occur under hot salt corrosion conditions or with the use of low grade fuel. Fuel contaminants such as sulphur, sodium, vanadium are known to form corrosive products that leach out the zirconia stabilising oxide (Y_2O_3, CeO_2). Alternatively, these corrodents may permeate through the ceramic and cause spallation by forming voluminous corrosion products with the bond coat. It has also been proposed that the molten salts may infill the pores causing TBC degradation due to their thermal expansion mismatch with the ceramic upon cooling, or due to the loss of compliance necessary to combat thermal strains. Similar failure mechanisms can be expected with the deposition of molten silicates at very high temperatures (1600°C) from ingested sand particles¹⁹.

It is generally accepted that a dense outer ceramic surface would be effective in alleviating problems associated with the ingress of hot salt corrodents. The evidence exists that EB-PVD systems are more prone to hot salt corrosion degradation than the APS systems²⁰ due to their more open columnar morphology.

1.3.4 Particulate erosion of TBC's

Jet engines are exposed to damage from the ingestion in the engine inlets of foreign objects such as birds, hailstone, ice slab, etc.... Less spectacular but not less a problem, is the erosion caused by hard particles entrained in the gas flow through the engine sections. Particulate erosion damage in jet engines arise most significantly on the ground from the ingestion of airborne particles such as sand, dust and runway gravel lifted by the massive air intake vortices²¹. Particles generated within the engine, such as carbon particles formed during the combustion process and engine wear residues, also contribute to erosion damage²². The former, although not a major contributor to erosion in the aero-gas turbine today, could become more important with the use of alternate low grade fuels²³.

Erosion from a particle laden flow arises because the inertia forces cause the particles to deviate away from the gas stream lines and hit the wall surfaces turning the flow²⁴. Thermal barrier coatings applied on combustor parts do not suffer from erosion as the gas flows parallel to the surface. However, particulate erosion is potentially a serious problem to TBC's applied on turbine blades and nozzle guide vanes. These components do experience particle impacts, and so under the most exacting conditions in terms of temperature and particle velocities. Flight Service Evaluation trials have showed that erosion damage can be a significant problem on TBC's applied just to the platform of nozzle guide vanes^{5,25}. Therefore, if TBC technology is to be developed to the point where application to HPT aerofoils is possible, it becomes essential to assess the significance of particulate erosion as a life limiting factor.

Erosion damage not only results in the structural degradation and progressive removal of the ceramic coat, but may also lead to the deterioration of its surface finish resulting in significant loss in aerodynamic efficiency and an increase in the heat transfer to the component. Therefore the performance of a TBC system to resist erosion damage should be considered in terms of both erosion rate and surface finish retention. The former is defined as the removed quantity of coating material for a given quantity of erodent impacting.

1.4 A LITERATURE REVIEW OF EROSION TESTING OF TBC'S

There has been limited investigations on the erosion of TBC's, mostly concentrating on plasma sprayed systems. Hanschuh²² tested the erosion behaviour of plasma sprayed 8wt%Y₂O₃-ZrO₂ and 12wt%Y₂O₃-ZrO₂ systems. A gas burner rig was used that could simulate the erosive environment existing in gas turbine sections. Test variables such as particle velocity, temperature and diffusion flux pattern were varied simultaneously by changing the distance from the specimen to the hot gas stream nozzle. In this way both the particle velocity and specimen surface temperature were decreased from 320m/s and 1600°C to 260m/s and 1150°C. Alumina grit with an average diameter of 130µm was used as an erosive medium.

It was found that the erosion rate increased strongly with angle of particle impingement. In spite of the brittle response expected of these systems, some plastic deformation could be observed on the eroded surface. The 90° angle erosion rate was measured at 45g/Kg and was found to be fairly insensitive to ceramic composition, temperature, particle velocity and diffusion flux pattern over the ranges investigated.

A later study on the erosion behaviour of TBC's was published by Davis, Boone and Levy²⁶. The test conditions (room temperature, 30m/s particle velocity) were far remote from those seen in gas turbine engines. However, their work was more aimed at correlating the structural features of the coatings to their erosion resistance. They found that the initial erosion rates of the plasma sprayed systems were much higher than those at steady state and this was related to the surface roughness of these coatings. The as-received surface of a plasma sprayed system is made of protuberances that are preferentially removed weaknesses. The same argument was used to explain why the more porous coatings were the less erosion resistant since the entrapped porosity made the eroded surface topography more protruded. It was also found that an increase in erosion rates corresponded to a decrease in Vickers Hardness Number, as measured on the coating cross section using a 300g load. Erosion rates were in the range 0.05-1g/Kg and did not vary much with angle of impingement (30°-90°). A 20wt%Y₂O₃-ZrO₂ processed by EB-PVD was also tested and performed amongst the best of the coatings. This result was of significance as it meant that the superior thermo-mechanical performance of the EB-PVD system was not obtained at the expense of a poor erosion resistance, as was generally the case with plasma sprayed TBC's.

A similar study was undertaken by Eaton and Novak²⁷ although, in their work, the test conditions used were more representative of gas turbine operating conditions. Testing was conducted at 1300°C using alumina grit with a particle size of 27µm and a velocity of 244m/s at an incidence angle of 15°. Plasma sprayed zirconia systems with varying density, strength, pore morphology and distribution were evaluated. They found that erosion resistance increased with both coating strength and lower pore surface area for a given porosity. Dorfman and Reardon²⁸ reported that the erosion

resistance of ceria stabilised zirconia (CSZ) coatings was poorer than that of YPSZ systems processed under the same plasma spray conditions. Dense plasma sprayed Zirconia-Yttria-Titania systems exhibited an erosion resistance several times greater than that of the two former and could be used as erosion resistant top coats to overlay the TBC's with.

The most important data published to-date originates from work placed by Rolls-Royce Inc at the University of Cincinnati under the direction of Toriz and Tabakoff^{21,29}. A high temperature erosion test rig was used, capable of evaluating systems under similar conditions to those found in gas turbine sections. The facility also allowed the particle velocity to be varied independently from particle size and specimen temperature. Nine ceramic systems were evaluated including the APS YPSZ Rolls-Royce standard and the EB-PVD TBC manufactured by Chromalloy Research and Technology (known commercially as RT33). The test variables investigated were angle of particle impingement, particle velocity, specimen temperature and particle size. The erosion resistance of the systems was evaluated both in terms of erosion rate and surface finish retention. The following table summarizes the test parameters and ranges examined in the study, with test results reproduced in Figure 15.

Table I: Range of parameters investigated in the Tabakoff's study^{21,29}.

Parameter investigated	Range investigated
Particle Velocity	122-305m/s
Impingement angle	20°-90°
Specimen temperature	260-815°C
Particle size	8-130µm (alumina)

The published erosion rate data was normalised relatively to that of the APS TBC standard. The absolute figures were said not to be very meaningful because of the accelerated nature of the testing.

It was concluded that the EB-PVD TBC performed the best amongst the ceramic coatings irrespective of the test condition, but was more prone to erosion damage than the MARM002 substrate. Still, it offered a ten-fold improvement on the performance of the standard YPSZ plasma sprayed coating.

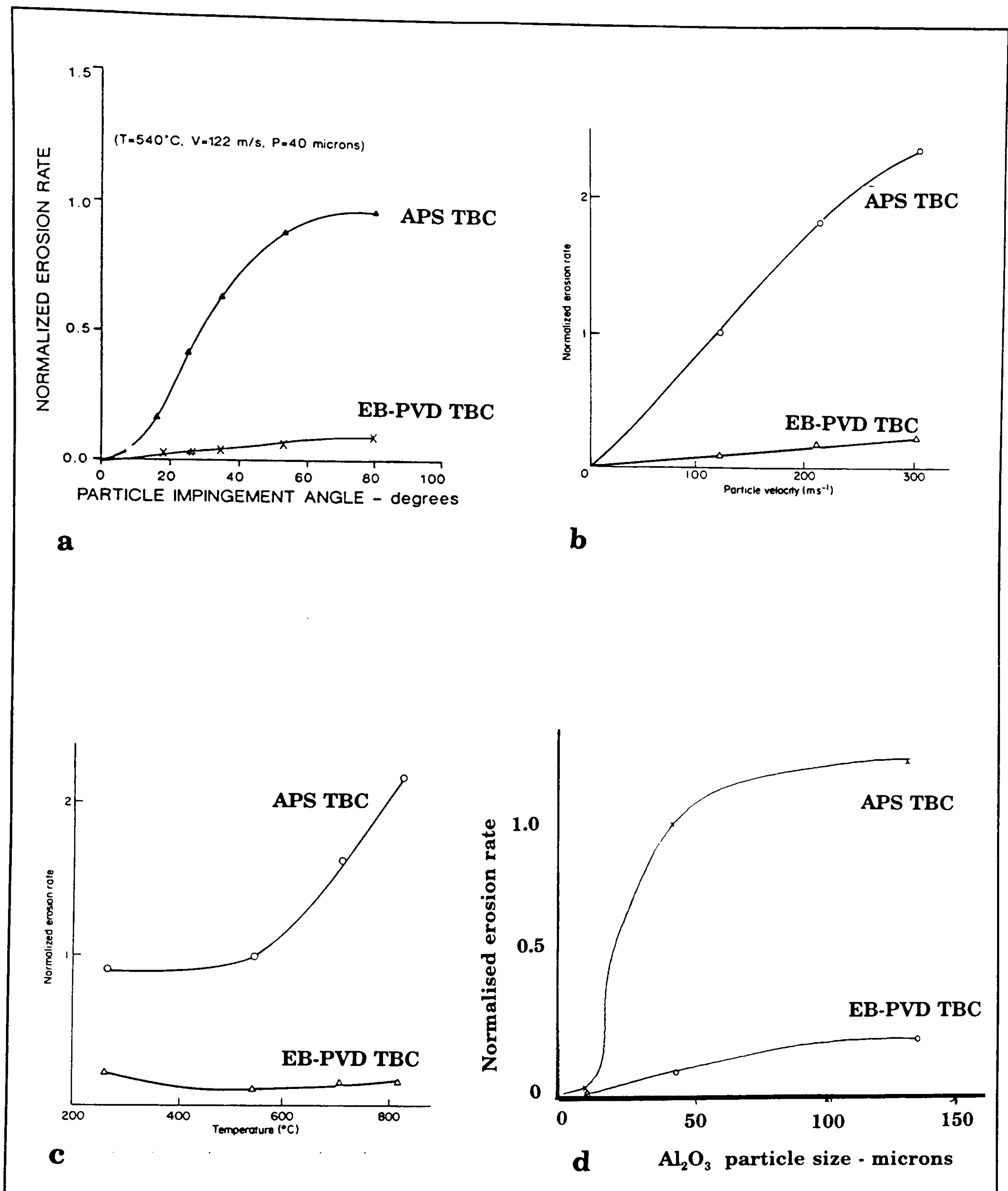


Figure 15: Findings from Tabakoff's study^{21,29}.

Their results may be summarised as follows:

a/

As would be expected, a brittle response was obtained from all the ceramic systems tested at 538°C i.e. their erosion rate increased monotonically with angle of particle impingement (see Figure 15a).

b/

Erosion rate was found to increase with increasing particle velocity (Figure 15b). It should be noted however that the velocity dependence of erosion rate is not as strong as it usually is for ceramic systems. Many authors¹⁵⁸ have reported a power law dependence with exponents much greater than 2. In this work, a near linear dependence is obtained for both the APS and the EB-PVD system.

c/

Erosion rate was reported to increase with specimen temperature (Figure 15c). Nonetheless one could argue that, over the range investigated, temperature does not appear to be very influential to the erosion rate of the EB-PVD system.

d/

Increasing particle size rendered the test more severe but this effect seemed to level off above 100 μ m (Figure 15d). This phenomenon has also been commonly reported for many systems³⁰.

Moreover, the EB-PVD TBC retained its initial surface finish throughout the test whereas the plasma sprayed systems, which were polished prior to testing, gradually recovered their initial roughness (Figure 16). The surface finish data generated from the laboratory testing was found to correlate reasonably well with that from the Flight Service Evaluation trials (Figure 16).

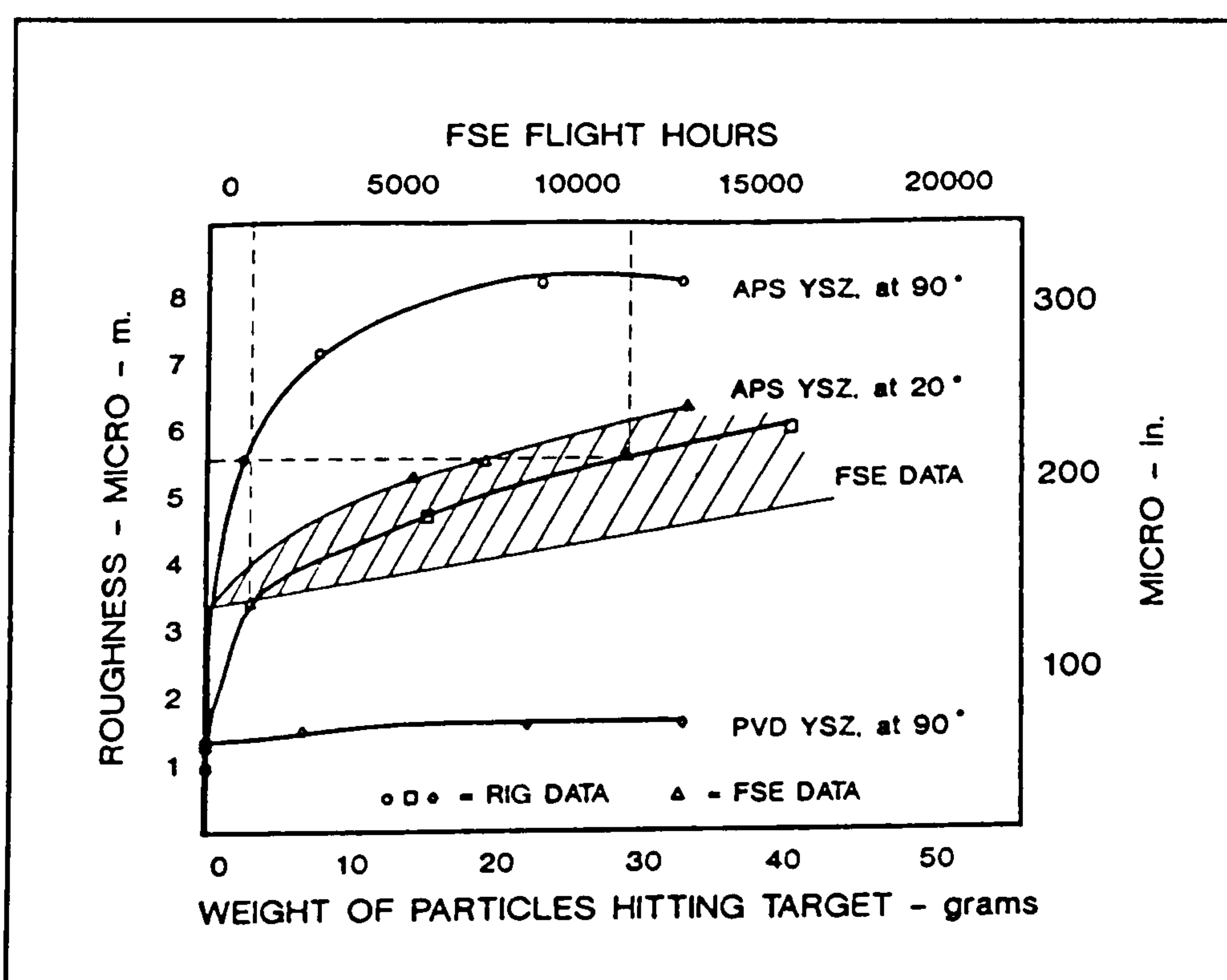


Figure 16: Correlation between laboratory and Flight Service Evaluation TBC surface finish data.

2 ELECTRON BEAM PHYSICAL VAPOUR DEPOSITION OF TBC'S

The object of this chapter is firstly to describe the processing conditions of commercial TBC systems (Chromalloy Research & Technology RT33 and Pratt & Whitney PWA 266), the RT33 coating being the datum in this work. This is necessary to help develop in the later stages of the thesis the picture of how the properties and performance of PVD TBC's relate to the deposition process. Secondly, it is meant to provide some awareness of the reality of an EB-PVD production facility, so that the contrast with the laboratory process is highlighted. In this way, the practicality of adapting a prescribed process optimization to a current production coater design can be appreciated. Thirdly, it provides a collation of previous studies on the process developments of EB-PVD TBC's, which form the starting point of the present work rationale.

2.1 A MANUFACTURING PROCESS PERSPECTIVE

2.1.1 History of EB-PVD coatings manufacture

The manufacture by Electron Beam Physical Vapour Deposition of thick MCrAlY coatings was originally developed in a joint development programme between Pratt & Whitney Aircraft and Airco Temescal in the late 1960's³¹. It became the preferred processing route for the production of high performance protective coatings for turbine blades³². PVD MCrAlY's have been used by jet engine manufacturers for over 20 years for the protection of HPT components⁷. More recently, the process capability to deposit Thermal Barrier Coatings on a production scale was demonstrated. PVD TBC's were used for the first time by Pratt & Whitney in 1989 and General Electric in 1990 to extend the life of HPT components^{7,6}.

2.1.2 Features and requirements of an EB-PVD manufacturing process³³

The PVD coating process involves the transition of the coating source material into the vapour phase, and the condensation of this vapour onto the part to be coated. The process is carried out in a vacuum chamber so that the evaporation of the source material is eased and contamination of the condensate from undesirable gaseous reactants is avoided.

To be acceptable as a manufacturing method, this technique must prove high levels of reproducibility, together with viable production rates. The nature of

the coating process is naturally suited to batch production whereby several parts are simultaneously exposed to the coating vapour. However, the size of the batch is constrained by the difficulty to ensure uniform coating conditions over a number of parts. Uniformity across the batch must be achieved in terms of:

- coating microstructure, adhesion and composition
- coating thickness and thickness profile.

which, in turn, depends on the uniformity of the relevant parameters controlling the EB-PVD process. These are:

- preconditioning of parts (surface finishing, cleaning and degreasing),
- substrate temperature,
- deposition rate,
- vapour chemistry and density,
- substrate motion.

The requirements of process uniformity within the batch of parts and reproducibility from one batch to another are met by careful coater design and necessitates a high degree of automation.

2.1.3 Critical aspects of evaporation³⁴

Vapour characteristics, deposition rate and substrate temperature are all strongly dependent on the evaporation conditions. Therefore, very stringent control on the evaporation process must be met to assure the consistency and uniformity of the coating properties.

2.1.3.1 Features and advantages of EB evaporation

Electron Beam (EB) evaporation is used for evaporating both metallics and ceramics. It offers several advantages over potential alternative thermal evaporation processes.

In the electron beam evaporation process, a focused high energy electron beam is impinged on the surface of the material to be evaporated. The bulk of the kinetic energy of the electrons is dissipated into heat upon impact, melting and evaporating the source material. An EB gun consists of a hot tungsten filament assembly, from which thermionically emitted electrons are accelerated by an electric field and focused into a beam by electromagnets. The beam is directed and scanned onto the surface of the evaporant material using time-varying magnetic fields. The particularities of the electron beam evaporation process are such that:

- the power carried by the beam is delivered directly at the surface of the melt resulting in high melt surface temperatures and thus high evaporation rates.
- the beam power density can be made very high by proper focusing of the beam, allowing evaporation of even the most refractory materials.
- it has a very high heating efficiency (95%).
- contamination of the vapour is kept to a minimum since the energy source itself is clean and no interaction is made possible between the evaporant melt and the water-cooled copper crucible.

The Electron Beam power requirement depends on the number of parts to be coated at one time and on the desired rate of deposition. Generally three EB guns are used with typical beam powers ranging from 150 KW to 300 KW. The melt pool level is maintained constant by continuous replenishing of rod shape feed-stock evaporant material. The speed of ingot replenishing is controlled by feed back of the melt pool level as monitored using laser-based techniques or video cameras.

The evaporator configuration differs depending on whether the coating source material is metallic or ceramic because of their different melt characteristics.

2.1.3.2 Evaporation of metallics

In the case of MCrAlY evaporation, a single melt pool contained in a skull of parent material is formed (see Figure 17). The coating composition is essentially that of the feedstock material. However, as the elements spread differently in the vapour cloud, the total vapour composition must be made slightly different from that of the deposits. Moreover, as the different melt constituents have different vaporization rates, the melt pool composition initially changes with the preferential depletion of the high vapour pressure elements until an equilibrium state is reached. The melt pool temperature is typically in the range 1600-1900°C. The large spread in vapour pressures of the elements means that small fluctuations in beam power densities can lead to unacceptable departures from the desired coating composition. The degree of regulation of the electron beam parameters that is required to meet the specified tolerances is of the order of a few tenths of percent. The quality of MCrAlY systems has been found to improve with increasing deposition rate. However, the maximum deposition rate achievable is constrained by the occurrence of splashing above a certain threshold of beam power density. MCrAlY coatings are deposited at a rate of 25µm/min. The process has to be carried out with a base pressure of the order of 10^{-5} Torr to avoid the formation of non-metallic inclusions in the deposits.

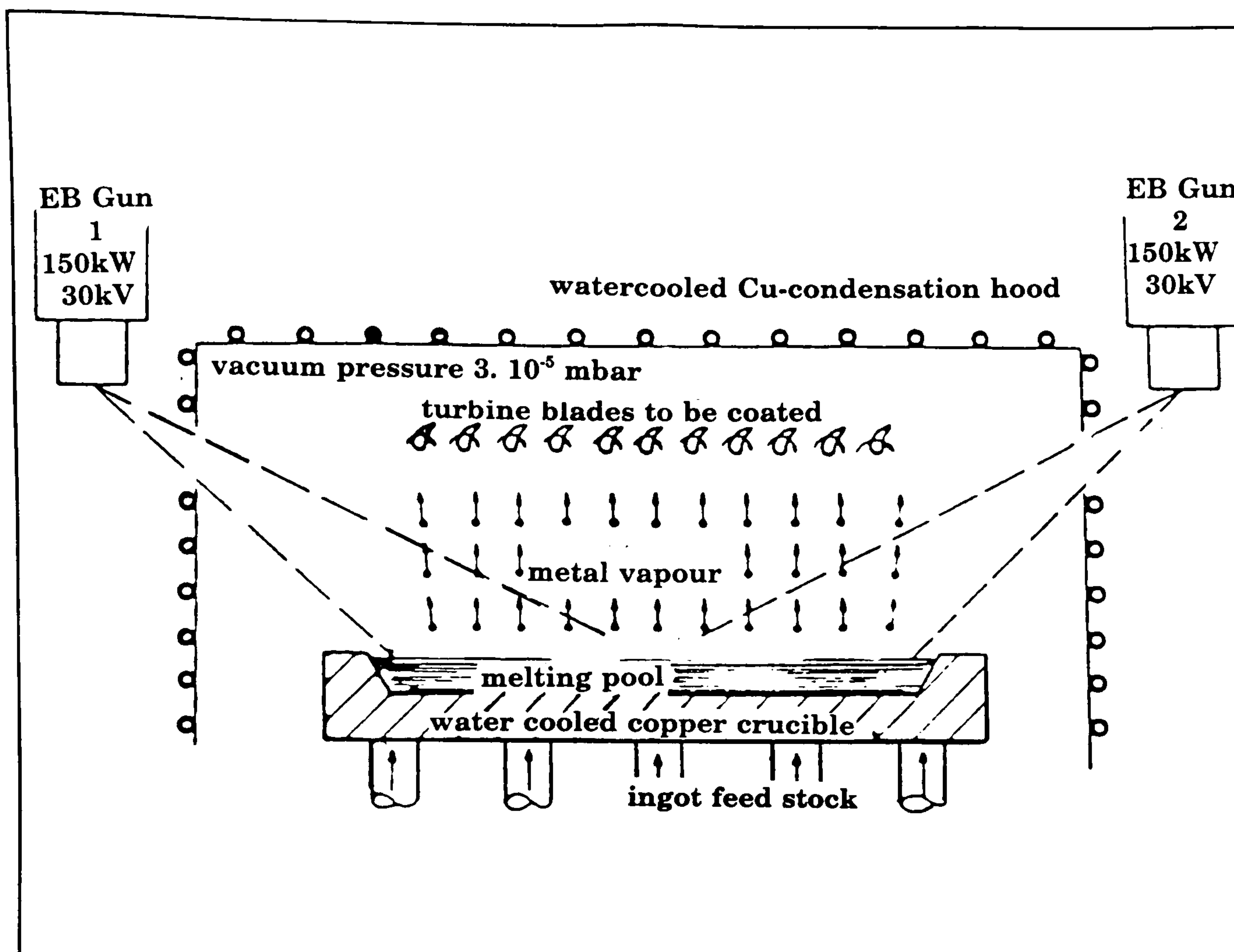


Figure 17: Schematic of evaporator for metallics.

2.1.3.3 Evaporation of ceramics

The problem areas for the evaporation of yttria partially stabilized zirconia are mostly inherent to the very low thermal conductivity of this material. As the heat does not spread out, the melt pool is confined within a depth of 1 to 2 mm, resulting in the use of much smaller crucibles than for metallics (see Figure 18). Practically, three rod-shaped ingots contained in water cooled copper crucibles side by side are used to cover an evaporation source area sufficient to guarantee a uniform vapour density across the batch of parts. The electron beam is directly impinged on the top surface of the rods heating the surface at the point of beam impact to temperatures in excess of 3600°C. The difficulty resides in obtaining an even temperature distribution over the whole of the melt surface. Failure to do so leads to gradients in evaporation rates over the melt surface. This eventually modifies the rods surface geometry, which affects the vapour flux pattern. To obtain the correct melt characteristics imposes extreme constraints on the electron beam scan pattern and power density. Another difficulty of the evaporation of zirconia is its propensity to dissociate leading to non-stoichiometric film compositions. This problem is partially overcome by depositing in a partial pressure of oxygen of 10^{-2} Torr.

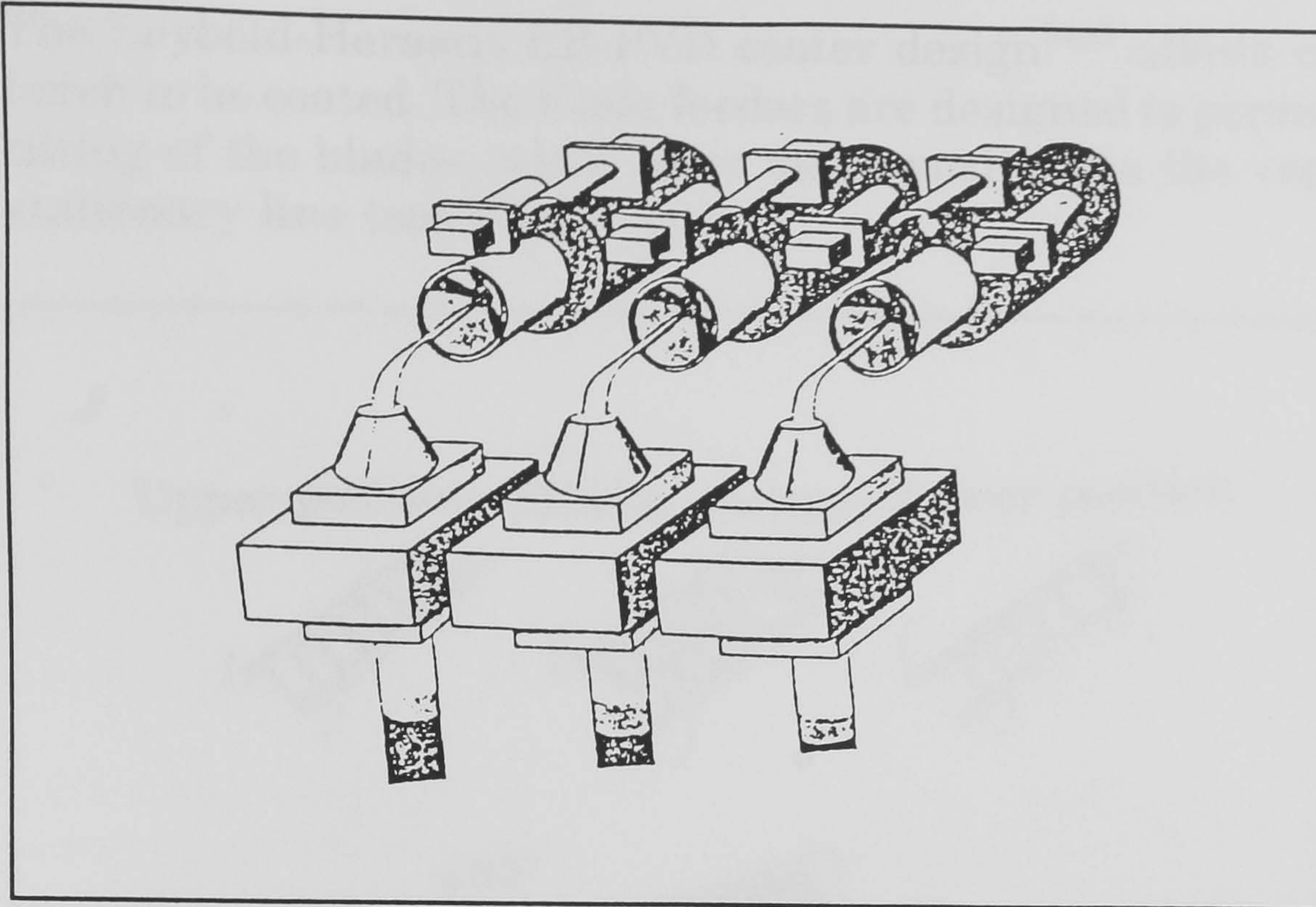


Figure 18: Schematic of evaporator for ceramics.

2.1.4 Part motion

The EB-PVD process is a line-of-sight deposition. Therefore, parts with complicated shapes need to be moved in the vapour cloud to ensure complete coating coverage. In the Airco Temescal design³¹, the blades are rotated with an offset angle of 15° to 30° so that the surfaces that would otherwise be parallel to the vapour flux direction can be coated. Airco Temescal production coaters can coat up to 16 small turbine blades per batch (see Figure 19).

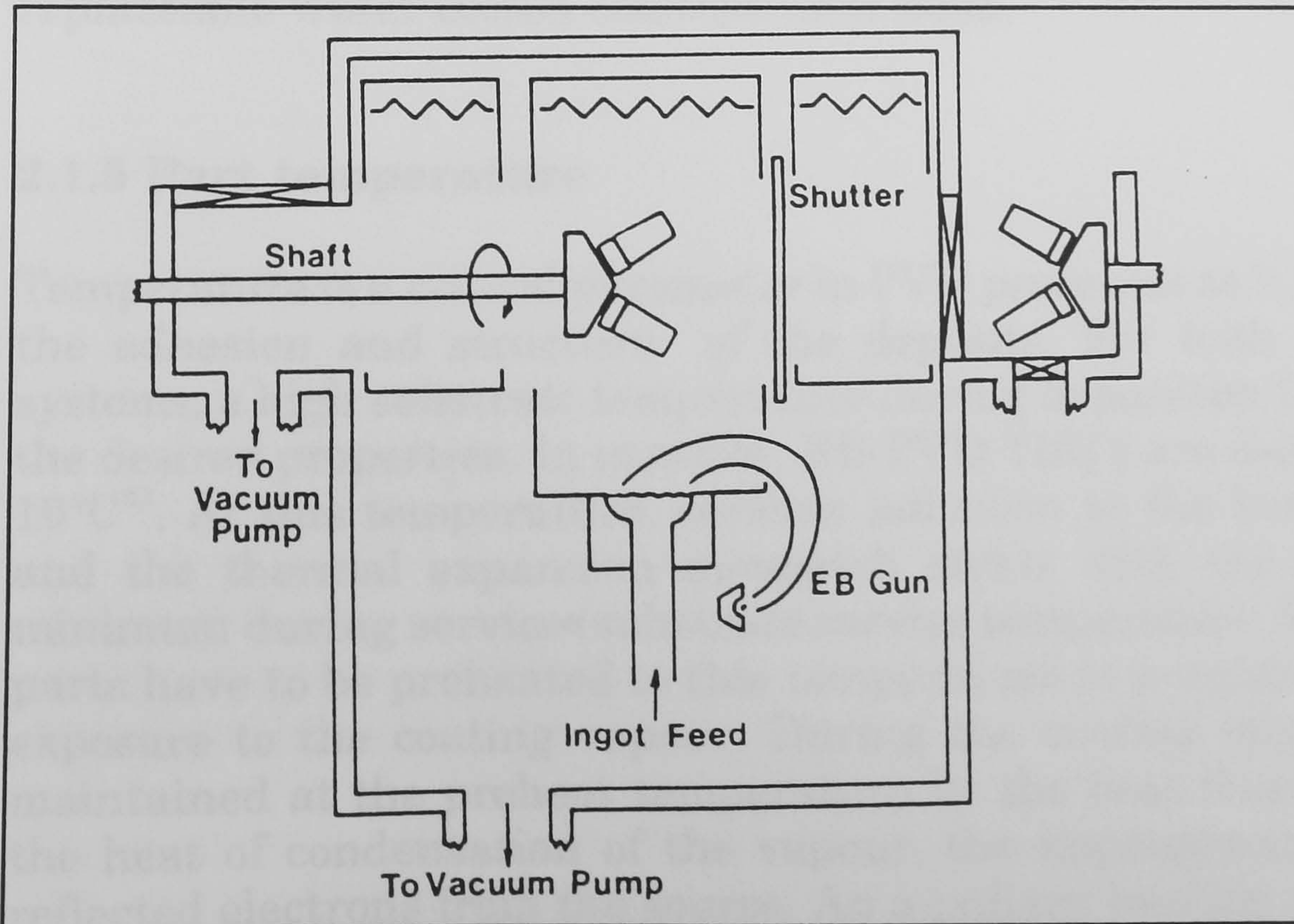


Figure 19: Airco Temescal part holding design.

The Leybold-Heraeus EB-PVD coater design^{34,33} allows up to 11 blades per batch to be coated. The blade feeders are designed to permit both rotation and tilting of the blades, while their mean position in the vapour cloud sits in a stationary line (see Figure 20).

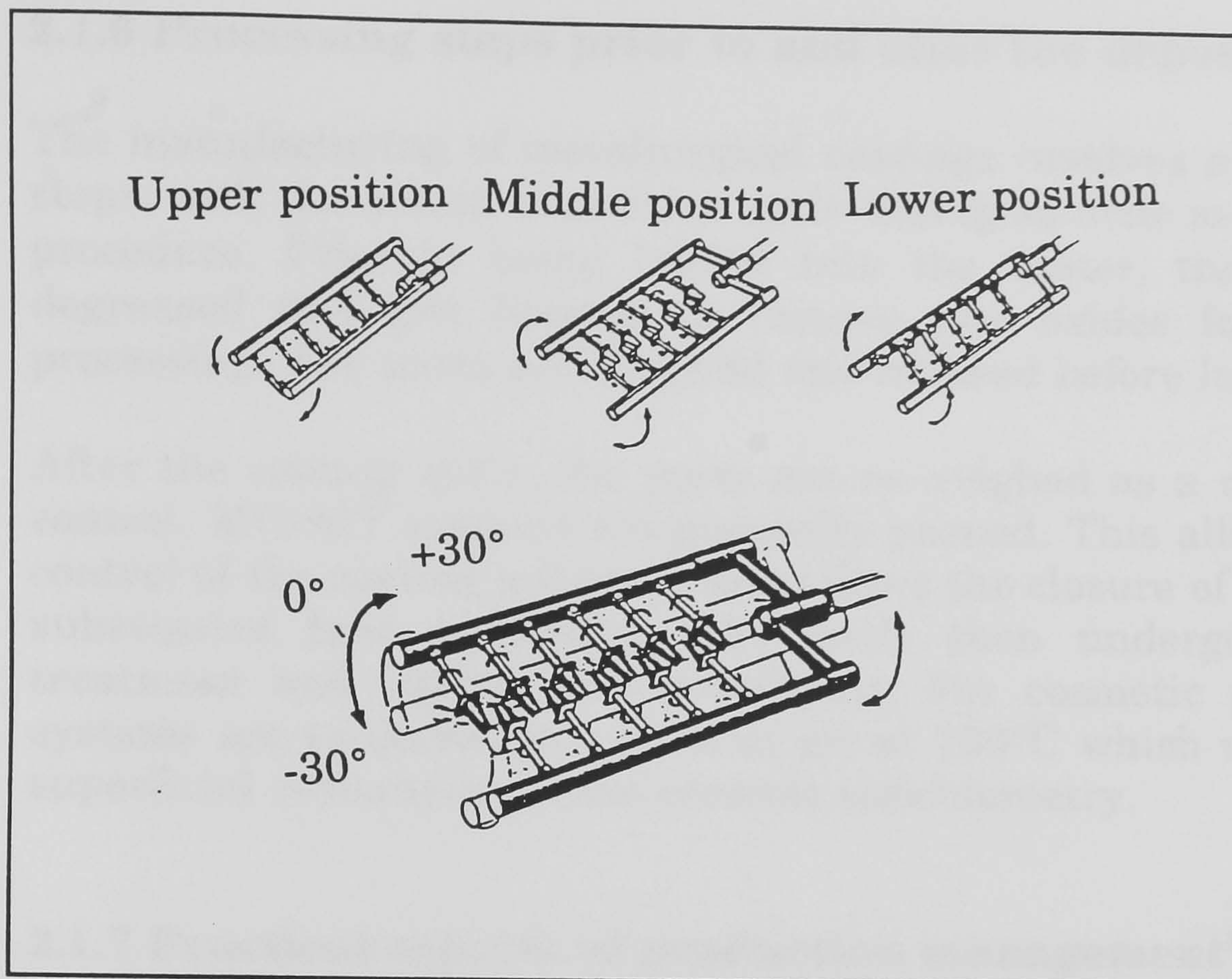


Figure 20: Chromalloy's 'rake-like' feeder.

This design, allowing more flexibility in the substrate motion, can be applied to an extended range of part geometries and makes possible, to a certain degree, the tailoring of coating thickness. Only 5% of the evaporated material is actually deposited on the parts. The rest of the vapour is captured by a replaceable water cooled condensation hood.

2.1.5 Part temperature

Temperature is a critical parameter in PVD processes as it strongly influences the adhesion and structure of the deposits. For both MCrAlY and TBC systems, a high substrate temperature during deposition is required to obtain the desired properties. In practice, EB-PVD TBC's are deposited at $1000^{\circ}\text{C} \pm 10^{\circ}\text{C}$ ³³. At this temperature, ceramic adhesion to the bond coat is favoured and the thermal expansion mismatch stress with the substrate is made minimum during service (substrate service temperature: 950°C - 1000°C). The parts have to be preheated to this temperature in a separate chamber before exposure to the coating vapour. During the coating process, the parts are maintained at the preheat temperature by the heat fluxes originating from the heat of condensation of the vapour, the impingement of radiation and reflected electrons from the source. An auxiliary heating system can be used to allow independent control of the substrate temperature from the evaporation conditions, by means of either radiant heaters or an electron

beam gun. The latter is preferred when depositing zirconia because of its relative immunity to the high partial pressure of oxygen required in the system.

2.1.6 Processing steps prior to and after the deposition cycle

The manufacturing of metallurgical coatings involves numerous processing steps, with the actual deposition cycle taking as little as 40-50% of the total procedure. Prior to being loaded into the coater, the parts have to be degreased and grit blasted to remove any oxides formed during prior processing. The parts are weighed and masked before loading in the coater.

After the coating cycle, the parts are re-weighed as a means for thickness control. MCrAlY systems are generally peened. This allows a quick quality control of the coating adhesion and allows the closure of leader defects after subsequent heat treatment. The parts then undergo a diffusion heat treatment and ageing heat treatment. For cosmetic purposes, the TBC systems are subjected to a bake in air at 700°C which whitens them up by superficial restoration of the ceramic stoichiometry.

2.1.7 Practical aspects of production management³³

The batch to batch reproducibility is achieved by sequentially inserting inside and exiting outside the coating chamber the 'rake-like' feeders while the evaporator runs continuously. In the production of MCrAlY coatings, the process cycle for each individual batch consists of the following steps:

- loading of parts (3 min)
- pump down (5 min)
- preheating (6 min)
- coating (10min)
- cool down (7 min)
- vent and unload (4 min)

With Leybold-Heareaus (LH) equipment, productivity is maximized by using four blade feeders that are synchronized in such a manner that at any time one batch is being coated. This requires two pre-heating chambers and four loading/unloading chambers laid around the central coating chamber (see Figure 21). Maximum productivity can be obtained by using only two blade feeders for the production of TBC's since in this case the coating step is considerably longer (1hour) with typical deposition rates of 3µm/min³⁵.

The coating process runs continuously until the condensate build-up inside the coating chamber becomes critical or the feed stock evaporant material runs out. A production campaign typically lasts between 60 and 80 hours i.e. one working week. After each coating campaign the coating chamber has to

be cleaned, new feedstock material loaded and preventive maintenance work carried out. At the beginning of a coating campaign, the evaporator must be conditioned for an hour to achieve stabilized evaporation conditions.

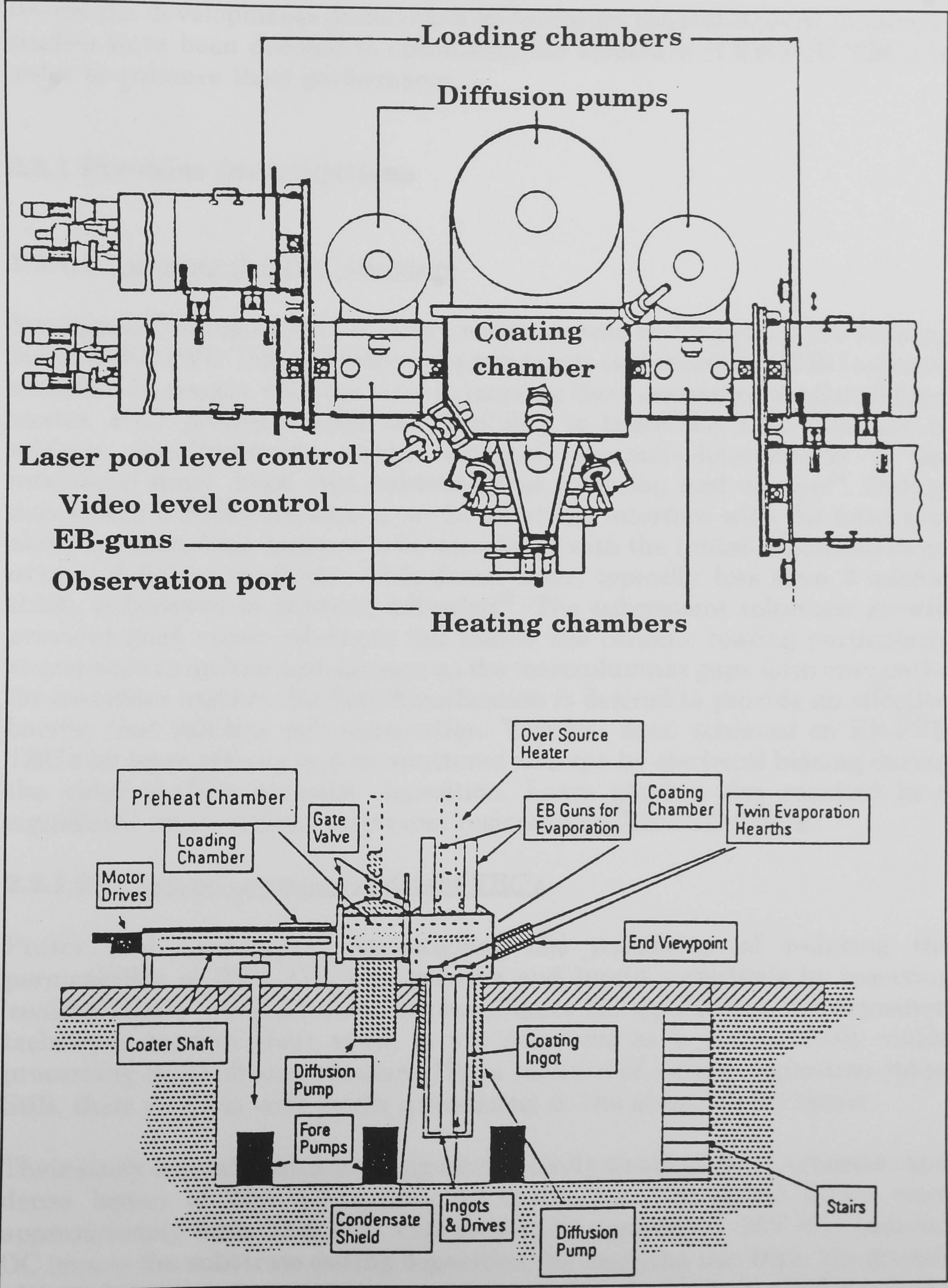


Figure 21: Schematic of EB-PVD coaters: **Top:** top view of Chromalloy's production coater (CR&T). **Bottom:** side view of General Electric's R&D coater.

2.2 RESEARCH IN THE OPTIMISATION OF EB-PVD TBC'S

Beside the developments undertaken by hardware manufacturers, numerous studies have been devoted to optimising the structure of EB-PVD TBC's in order to enhance their performance.

2.2.1 Previous investigations

2.2.1.1 Tailoring the TBC structure

Strangman²⁰ recognised that strain tolerance was no longer the life limiting factor of EB-PVD TBC's. Further improvements in durability of TBC's should therefore be sought with the view to increase their resistance to other failure modes. PVD processes offer the flexibility to tailor the TBC structure to address simultaneously strain tolerance, thermal deterioration of the interfacial bond, bond coat oxidation, hot corrosion and erosion²⁰. During deposition, a dense zirconia layer forms at the interface with the bond coat alumina scale. This appears to be associated with the initial deposition in an oxygen deficient condition. This dense layer, typically less than 2 micron thick, is believed to enhance adhesion³⁶. The subsequent columnar growth provides good strain tolerance but makes the ceramic coating particularly susceptible to molten salt damage as the intercolumnar gaps form easy paths for corrodent ingress. Surface densification is desired to provide an effective barrier that inhibits salt penetration. This has been achieved on EB-PVD TBC's by laser glazing and on sputtered zirconia by electrical biasing during the outer surface material deposition. Laser glazing also resulted in a significant improvement in erosion resistance of EB-PVD TBC's⁹.

2.2.1.2 Improved corrosion resistant TBC's

Prater and Courtright³⁷ investigated the possibility of reducing the permeability of PVD TBC's to gaseous and liquid corrodents by inserting 'sealing' layers into their structure (see Figure 22). Sputtering, the deposition technique used in their work, is not perceived as a commercially viable processing route to manufacture TBC's because of its low deposition rates. Still, their study is well worth considering in the scope of this thesis.

Their study consisted in depositing alternatively strain tolerant columnar and dense layers of 20wt%Y₂O₃-ZrO₂ by sputtering. The dense layers were approximately 5µm thick and were formed by applying a -35V R.F. induced DC bias to the substrate during deposition. By applying this bias, 'the growth of the columnar microstructure was disrupted, and an extremely dense layer was formed'.

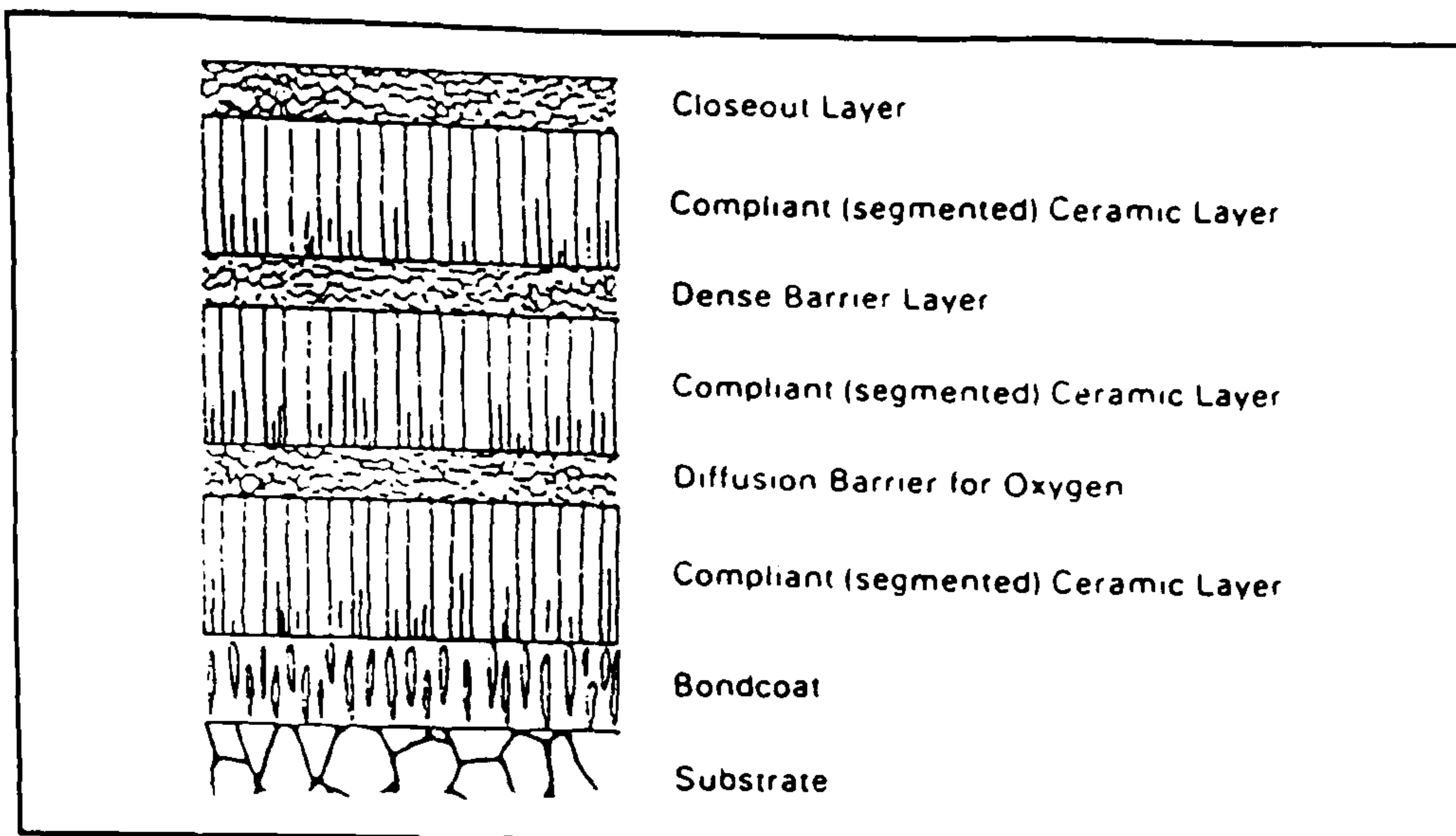


Figure 22: Schematic of improved corrosion resistant TBC's.

The deposition process was carried out at an average temperature of 300°C. Thermal cycling tests revealed that the insertion of dense layers into the columnar ceramic structure was not detrimental to the coating thermo-mechanical resistance. The dense layers were found to be effective in blocking the ingress of liquid Na_2SO_4 but did not retard the diffusion of oxygen to the bond coat. Substituting ceramics with low oxygen diffusivity (e.g. SiAlON , ZrSiO_4) to 20wt% Y_2O_3 - ZrO_2 for the dense layers failed to reduce significantly bond coat oxidation.

2.2.1.3 PAPVD of TBC's

The effect of electrically biasing the substrate in conjunction with the EB-PVD process, a technique commonly called ion plating, was investigated as early as 1986 at the University of Hull (UK)³⁸.

The rationale of these investigations^{38,39,40,41} were to show that some of the benefits of ion plating over simple gas evaporation, such as enhanced adhesion and structural modification, could be used to advantage to produce improved performance PVD TBC's. In contrast with the industrial process, the depositions were carried out at low temperatures (<400°C) because, as the authors put it, 'the influence of ionization on structure is masked if increased temperatures are used'³⁸. Investigating the feasibility of processing TBC's at low temperatures was also justified as 'there is a longer term aim to coat conventional materials (e.g. aluminium alloys)' for automotive applications^{38,42}. In the Hull work rationale, the use of low deposition temperatures would offer obvious benefits in terms of economics of the industrial process.

The deposition facility used in their work had been originally designed for ion plating wear resistant thin films (<5µm) using a 380kHz R.F. generator. The absence of continuous source material feeding meant that it was impossible to deposit thick coatings in one single coating run. The deposition process had to be interrupted to replenish the EB gun crucible and four to eight coating cycles were necessary to attain the desired thicknesses³⁸.

It was found that ion bombardment improved the adhesion of the ceramic coat³⁹, as measured by a critical load using the conventional scratch test method. From SEM observation, it was concluded that ion plated structures were denser and had a smoother surface finish resulting from a better column packing^{38,39}. Coating thickness uniformity was improved using PAPVD resulting from the ability to deposit at higher pressures with no detrimental effect on the structure.

The thermo-mechanical behaviour of the coatings was assessed under burner rig trials. In accordance with the prescriptions by Strangman²⁰, it was found that maximum life was obtained with a structure comprising a dense adherent layer close to the substrate followed by a more open strain tolerant layer. The benefits of ion plating could therefore be combined with those of EB-PVD in a two step process. The former produced a dense thin layer providing adhesion and some degree of oxygen ingress impedance to the bond coat, while the latter imparted strain tolerance to the ceramic coat^{40,41}.

2.2.1.4 Density graded TBC's

DLR in Germany have been involved in the development of EB-PVD TBC's since the late eighties. Their deposition facility, a LH laboratory coater, is probably the nearest system to the actual production coaters, owned by a research institute in Europe. It features a 25kV 60kVA electron beam gun, a preheating chamber capable of bringing the substrates to temperatures up to 1000°C, a substrate rotation system and the possibility to bleed oxygen to pressures of 10^{-2} mbar.

Their work looked at evaluating the performance of EB-PVD TBC's in a hot gas burner rig, as affected by the ceramic deposition process and bond coat systems⁴³.

The columnar structure resulted in a saw-tooth morphology which was attributed to rotation of the substrates during ceramic deposition.

Burner rig tests resulted in gradual weight loss of the TBC's and mud flat cracking of the ceramic. It was concluded that the systems failed because of ceramic sintering arising from large compressive stresses. These stresses were generated both as a result of the deposition process and by the hot gas stream during testing. Sintering caused cracking of the ceramic upon cooling down, and the subsequent excavation of the cracks by abrasion of the ceramic blocks during thermal cycling.

The recommendations from their work were first that the compressive stresses should be minimised in order to increase TBC durability. This should be achieved either by means of bond coats with matched thermal expansion coefficients and/or by tailoring the ceramic apparent density. Apparent density, in their terminology, is an indicator of the compaction of the columns and this should be decreased towards the outer surface of the ceramic coat in order to reduce the compressive stresses during operation. Following this work, their next step was to attempt to produce TBC's with 'density-graded columnar structures' by gradually reducing the process temperature during

ceramic deposition.

The other main conclusion reported was that the rate of TBC weight loss, resulting from internal friction of the segments, was reduced with higher deposition temperatures. This formed the basis of their second recommendation that higher deposition temperatures should be aimed for as TBC's adhered better and were harder, when processed at elevated temperatures.

2.2.1.5 Erosion resistant thermal barrier coatings

In September 1994, General Electric issued a patent (US 5,350,599) which claimed a process modification readily compatible to the current industrial practice and capable of imparting EB-PVD TBC's with improved erosion resistance over current levels. The idea was based on creating a 'banded' ceramic structure with alternate low and high density layers (see Figure 23). The dense layers are claimed to impart erosion resistance with the porous layers procuring the necessary strain tolerance to the ceramic coat. The erosion resistant region is formed by slowing down or even halting the substrate rotation with the surface to be protected facing the deposition source.

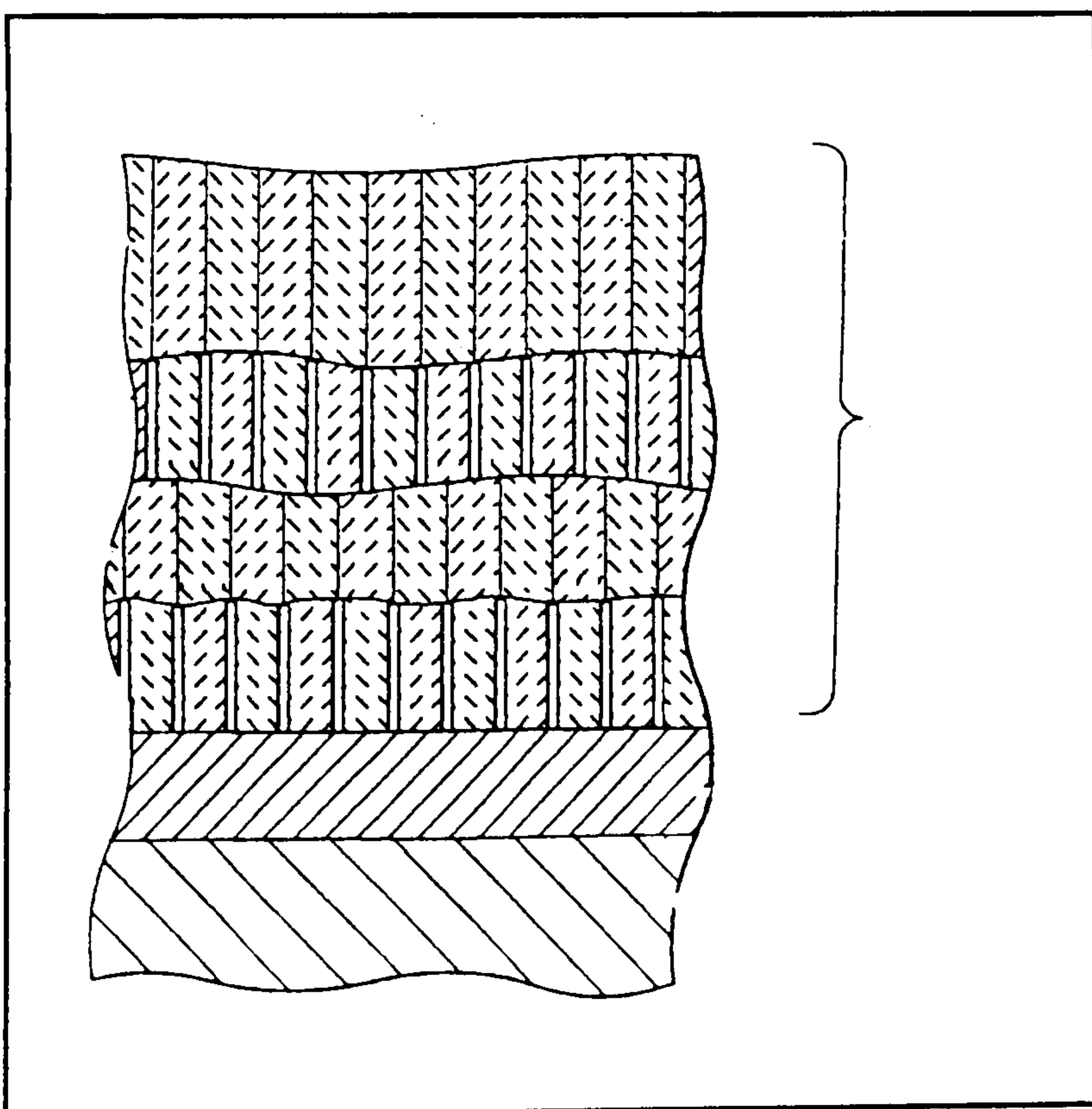


Figure 23: Erosion-resistant thermal barrier coating (US patent 5,350,599)

This way, the deposited region is less columnar and denser by virtue of a higher deposition temperature since the rotation induced cooling is reduced. The low density layers, containing both inter-columnar spacings and some degree of porosity within the columns, are formed by default with substrate rotation.

This patent is very relevant to the present work as it is about the relationship between the deposition process and the coating erosion resistance. The effect of rotation on the ceramic structure is an aspect that will be referred to later in this thesis. It should be noted that no erosion rate numbers were quoted in the patent to substantiate the claimed improved erosion resistance.

2.2.2 Outlook and rationale of the present work

The consensus in industry is to deposit EB-PVD TBC's at temperatures in the range 871-1093°C ³⁶. *Why are low temperature deposited TBC's not viable?* The reason usually invoked is that both the microstructure and adhesion of TBC's is improved with high temperatures of deposition. The present work will attempt to be more extensive on the weaknesses of low temperature deposited EB-PVD TBC's.

Can high temperature of deposition be substituted for ion plating? This is a legitimate question since the peculiarity of plasma assisted PVD processes is their ability to provide 'high temperature benefits' while processing at low temperature. The present work also investigates whether there are any advantages to be gained in combining both high temperatures of deposition and plasma assistance. To the best of the author's knowledge, work on high temperature ion plating of TBC's has not been published before. If ion plating of TBC's is to be performed at temperatures near 1000°C, why then not use DC ion plating given the electrical conductivity of zirconia at high temperature.

A redundant idea is that TBC surface densification is desirable to enhance erosion resistance and provide protection against the ingress of molten salt deposits as long as the thermal strain tolerance is not impaired. This school of thought is somewhat in contrast with the recommendations from DLR, who emphasized the role of thermal compressive stresses as a life limiting factor and the need for less outer compaction of the columns. The present work attempts to generate a basic understanding of how the process parameters such as temperature, plasma assistance and oxygen bleed affect the structure of EB-PVD TBC's. The object is to identify optimised process routes capable of enhancing TBC performance, with regard particularly to erosion resistance and thermal conductivity.

3 BACKGROUND ON ZIRCONIA

The two main sources of zirconia are baddeleyite (80-90% of ZrO_2 with impurities of TiO_2 , SiO_2 , Fe_2O_3) in Brazil and zircon (ZrSiO_4) which is found in India, Australia and America (Florida). With an estimated content of 0.02 to 0.03% in the earth's crust, zirconia is more abundant than many metallic ores⁴⁴.

Zirconia ceramics are finding increasing use in high technology applications. This chapter first gives an account on their selection for Thermal Barrier Coating applications. The structural and physical properties of bulk partially stabilised zirconia are then reviewed. This forms the background knowledge of this material to support the discussion.

Concentrations in doping yttrium oxides are quoted in the literature variably in mol or mass percentage of either $\text{YO}_{1.5}$ or Y_2O_3 . A conversion table is provided in Appendix 1.

3.1 THE SELECTION OF ZIRCONIA

The requirements a material must satisfy to be selected for thermal barrier coating purposes are low thermal conductivity, high temperature chemical stability and good thermomechanical resistance. Ceramics are materials of primary interest with regard to thermal barrier coating applications due to their insulativity and chemical inertness.

Table II compares some of the properties that are relevant to thermal barrier coating applications for several high temperature engineering ceramics^{45,46}. Zirconia-based systems are natural candidates for TBC applications considering their low thermal conductivity and chemical stability at high temperatures. Moreover, their relatively high thermal expansion coefficient approaching those of superalloys combined with their low Young's modulus help minimize stresses induced by the thermal expansion mismatch with the underlying substrate.

To be useful as a structural material, zirconia must be alloyed with a stabilizing oxide to prevent the deleterious effects associated with the tetragonal to monoclinic phase change. Yttria stabilised zirconia is today's state-of-the-art system for TBC applications.

Table II: Comparison of ceramic properties relevant to TBC applications.

Material	k (W/m°C)	α ($10^{-6}/^{\circ}\text{C}$)	E (GPa)	ρ (Kg/m ³)	Ref.
ZrO ₂	3.5	10.6	200	6000	45
HfO ₂	5.8	9.0	200	9700	45
MgO	24	12.6	264	3800	45
Al ₂ O ₃	20	7.5	380	3900	46
SiC	91	4.3	400	3200	46
Si ₃ N ₄	25	3.2	330	3200	46

3.2 STRUCTURAL PROPERTIES OF ZIRCONIA

3.2.1 Polymorphs of zirconia

The oxide of zirconium exhibits three well defined polymorphs that are the cubic, the tetragonal and the monoclinic phases (see Figure 24 and Table III⁴⁷). On cooling down, pure zirconium oxide undergoes a phase change from cubic to tetragonal at 2370°C and from tetragonal to monoclinic at 1170°C. Zirconia can exhibit an orthorombic form if subjected to pressures of the order of 10 GPa.

The high temperature cubic phase can be specified as the fluorine structure, where the cation and anion sublattices are respectively face centered cubic and simple cubic. The two sublattices are positioned in such a way that the Zr⁴⁺ cations occupy the eight-fold coordinated sites in the anion sublattice.

The tetragonal structure is commonly described in terms of face centered tetragonal symmetry to ease the comparison with the cubic phase, although the primitive cell is body centered tetragonal. In this form the Zr⁴⁺ cation has an eightfold coordination with the oxygen anions.

In the monoclinic phase, which is that of baddeleyite, the natural form of zirconia, the Zr⁴⁺ has a sevenfold coordination with the anions.

Table III: Lattice parameters for pure zirconium oxide⁴⁷.

structure	MONOCLINIC	TETRAGONAL	CUBIC
lattice parameter (Å)	a=5.156 b=5.191 c=5.304	a=5.094 c=5.177	a=5.124
angle	98.9°		

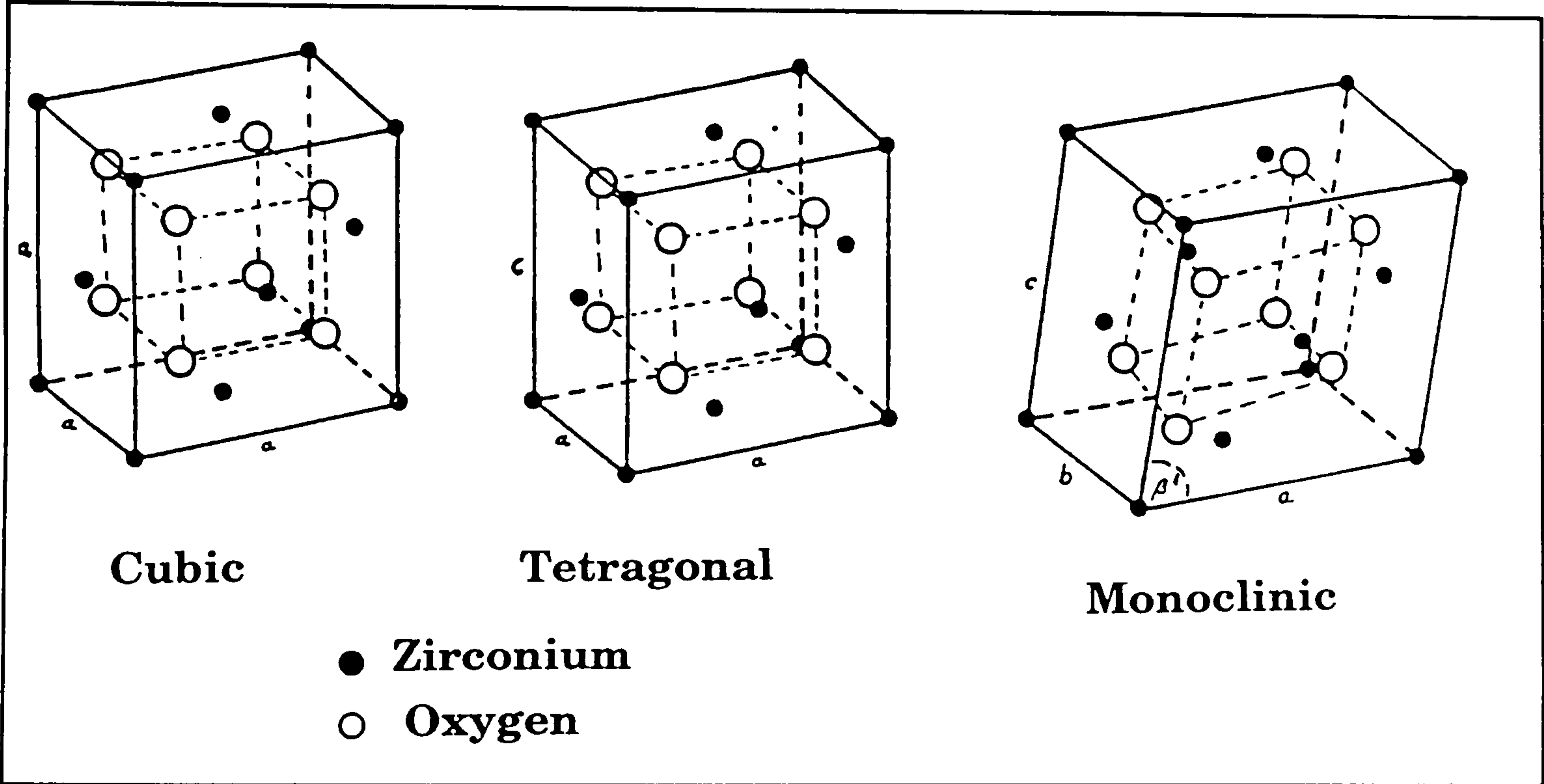


Figure 24: Lattice cells for the polymorphs of pure zirconium oxide⁴⁸.

3.2.2 The Y₂O₃-ZrO₂ binary phase diagram

On cooling down past the temperature of 1170°C, zirconium oxide transforms from the tetragonal to the monoclinic phase. This phase change is accompanied with a volume expansion of a few percent, which is enough to give rise to internal stresses causing the zirconia to crumble away. This characteristic makes impossible the use of pure zirconia for the fabrication of engineering components.

It has been known for over 50 years that the high temperature cubic phase of zirconia can be retained at room temperature by the alloying with particular oxides. Alkali oxides such as CaO and MgO have been the focus as cubic phase stabilizers for mass market applications. However, these systems

are unsuitable for advanced gas turbine applications because of their too high cation diffusion rates⁴⁸. Zirconia systems stabilised with rare earth oxides such as yttria offer better performance.

The $\text{ZrO}_2\text{-Y}_2\text{O}_3$ binary phase diagram after Scott⁴⁹ is considered as today's most reliable. Figure 25 shows a blow up of this phase diagram in the low yttria region. It can be seen that the cubic phase is only fully stabilised for $\text{YO}_{1.5}$ concentrations over 20% in mol. Under this level, the zirconia is said to be partially stabilised (YPSZ).

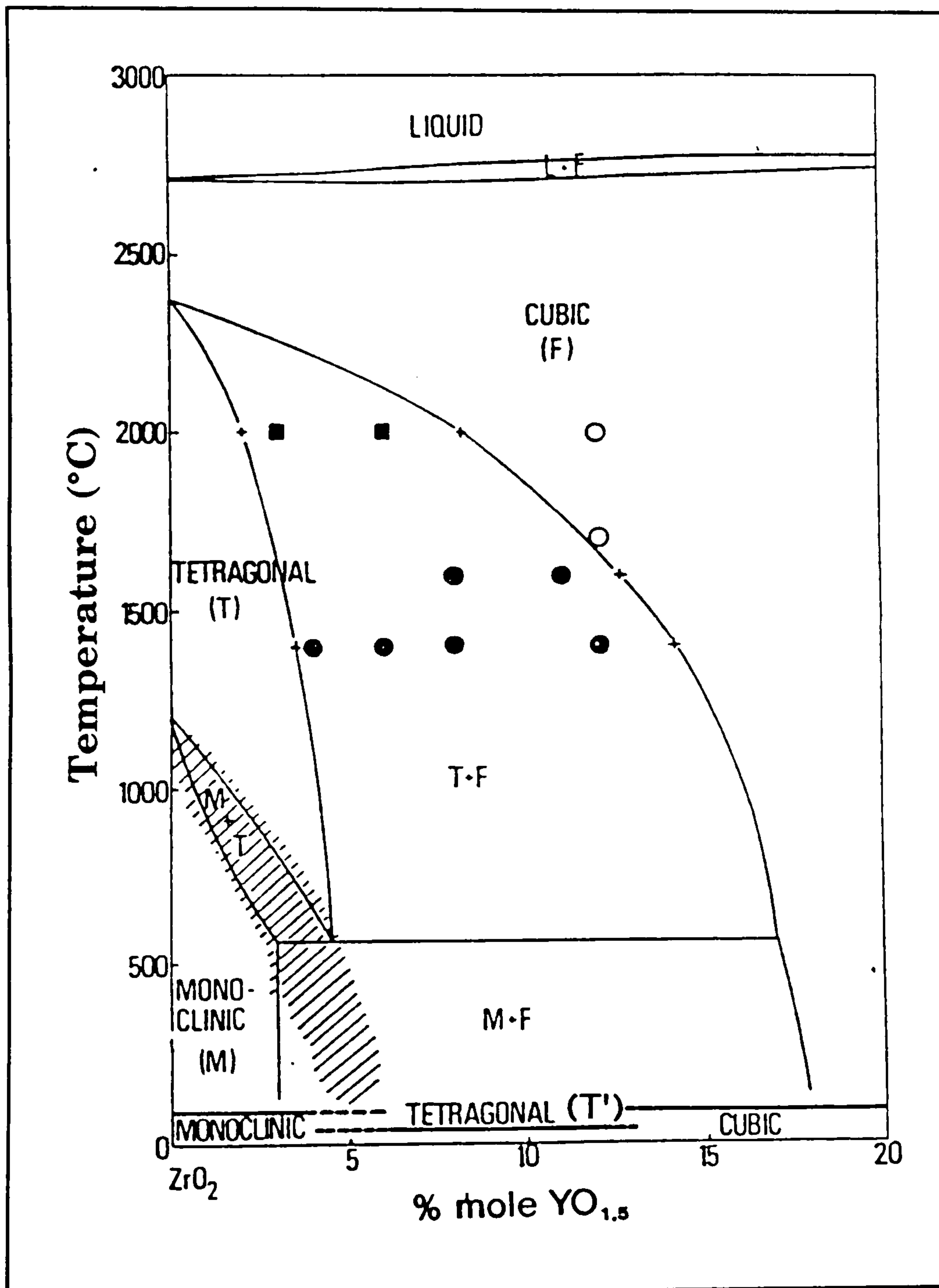


Figure 25:Low yttria region of the $\text{Y}_2\text{O}_3\text{-ZrO}_2$ phase diagram after Scott⁴⁹.

The Scott's diagram shows the equilibrium phases and the metastable homogeneous phases obtained at room temperature (lower margin).

In the 0-5 mol% $\text{YO}_{1.5}$ composition range, the tetragonal to monoclinic transformation temperature decreases down to 565°C and a narrow field of tetragonal + monoclinic exists. Three main equilibrium phase fields can be identified at temperatures above 1200°C. These are the tetragonal phase

field (T), the phase field consisting of a mixture of tetragonal and cubic phases (T+F) and the homogeneous cubic phase field (F).

The non-equilibrium structures recorded at room temperature are not those obtained at the equilibration temperature. This is due to the occurrence of diffusionless phase changes such as the transformation from the cubic to a non-equilibrium tetragonal phase, said 'non-transformable', and the already mentioned tetragonal-to-monoclinic transformation^{49,50}.

The non-transformable tetragonal phase (t') is obtained from the rapid cooling of the cubic phase in the 5-12 mol% YO_{1.5} composition range. For instance, this phase is often encountered in plasma sprayed YPSZ systems. The (c)--->(t') transformation is diffusionless as opposed to the (c)--->(t) transformation. As a result the t' phase is richer in YO_{1.5} than the equilibrium tetragonal phase, hence its stability at room temperature. Upon annealing at 1600°C, it decomposes into the equilibrium tetragonal and cubic phases.

Assume equilibrium is achieved at 2000°C for a 6 mol% YO_{1.5} composition. The system is then a mixture of cubic phase containing about 8 mol% YO_{1.5} and tetragonal phase containing 2 mol% YO_{1.5}. Upon quenching, the cubic phase undergoes a diffusionless transformation into a 'non-transformable' tetragonal structure and the tetragonal phase transforms into monoclinic. Assume equilibration at 1400°C, the same 6 mol% YO_{1.5} system now consists of a mixture of a 4 mol% YO_{1.5} tetragonal phase and a 14 mol% YO_{1.5} cubic phase. Upon quenching, the tetragonal phase transforms readily into monoclinic while the fluorite structure is retained due to its high yttria content.

3.2.3 Lattice parameters for the Y₂O₃-ZrO₂ system

In the yttria-stabilised-zirconia system, the solute Y³⁺ ions sit in substitution sites in the Zr⁴⁺ sub-lattice and the charge neutrality is preserved by a compensating amount of oxygen vacancies⁵¹. The anions vacancies so generated are homogeneously distributed in the crystals, which leads to an increase in lattice parameter and a subsequent decrease in density (the atomic mass of yttrium being slightly less than that of zirconium). Several authors have described analytically the dependence of the lattice parameters and density on the concentration of solute Y³⁺.

The lattice parameters for the tetragonal phase obtained after the rapid quenching of the cubic phase were determined by Scott⁴⁹ as a function of the yttria content (see Figure 26). In this figure, it is shown that for 3<x<13 where x is the YO_{1.5} content in mol%,

$$\begin{aligned} a_t(\text{\AA}) &= 5.08 + 3.58 \cdot 10^{-3} x \\ c_t(\text{\AA}) &= 5.195 - 3.10 \cdot 10^{-3} x \end{aligned}$$

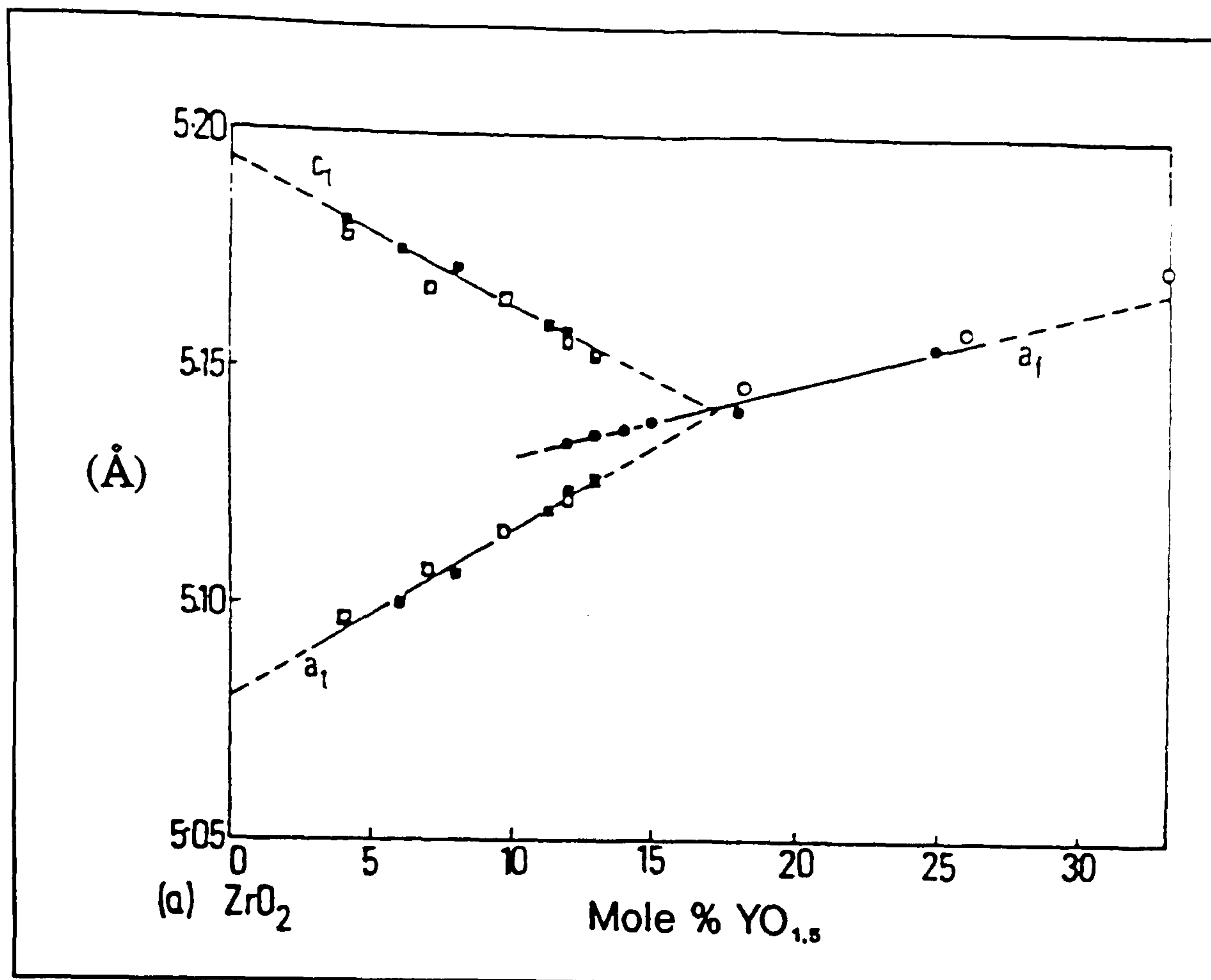


Figure 26: Lattice parameters at room temperature for homogeneous zirconia-yttria phases⁴⁹.

Ingel and Lewis⁵¹ showed that the density as a function of yttria content for the fluorite structure could be predicted from the following equation in the composition range 2-50 mol%Y₂O₃:

$$\rho(\text{Kg/m}^3) = (818.435 - \frac{137.023x}{100+x}) \left(\frac{1}{a_{(nm)}^3} \right)$$

3.2.4 The tetragonal-to-monoclinic transformation

Garvie, Hannink and Pascoe were the first to point out that the (t)-->(m) transformation could be used to advantage to improve both the strength and the toughness of ceramic systems⁴⁷. The following concept of transformation toughening aroused tremendous interest in the understanding of the transformation mechanisms.

It is now broadly accepted that the (t)-->(m) transformation is martensitic in nature. This means it is a displacive shear process (diffusionless) that occurs spontaneously at near sonic velocities. The reaction is athermal i.e. the amount of tetragonal phase transformed depends on the temperature of transformation and not on the time at temperature. The onset of the tetragonal-to-monoclinic transformation has been found to depend on factors such as composition, stress state and microstructure.

Effect of composition

The tetragonal phase (t) becomes unstable when its free energy (F) becomes higher than that of the martensitic phase (m). The effect of stabilizer additions is to decrease the cross-over point temperature where the tetragonal and monoclinic phases have the same free energy⁵². At a given temperature M_s below this critical temperature, the driving force for the transformation is the chemical free energy change:

$$\Delta F_{t \rightarrow m}(M_s) < 0.$$

For this transformation to occur, the driving force must overcome the strain energy associated with the lattice shear and volume expansion, and the creation of interfacial surface energy. Accommodation of the volume expansion and shape change occurs through a shear transformation (twinning) and elastic deformation of the monoclinic and parent phases as well as microcracking of the matrix.

Effect of stress state

The magnitude of the strain energy associated with the transformation as a result of lattice volume expansion and shape change is function of the constraint applied by the surrounding matrix and on the existence of residual stresses.

Phenomenologically, it is known that the constraint imposed on a tetragonal grain by the surrounding matrix can discourage the dilation into monoclinic. A good illustration was provided by Lange who showed that the retention of the tetragonal phase in sintered 2.5 mol% Y_2O_3 - ZrO_2 systems depended strongly on the material density⁵³ (see Figure 27). Porosity lowers the material elastic modulus and introduces free surface. Both these factors reduce the strain energy associated with the transformation, thus allowing more tetragonal grains to transform.

As the stress fields that arise from the martensitic transformation are compressive, residual compressive stresses will further lower the transformation temperature (more driving force being required to surmount the strain energy)⁵⁴. Inversely, tensile stresses are known to favour the transformation since both the dilational and shear components are then assisted^{55,56}.

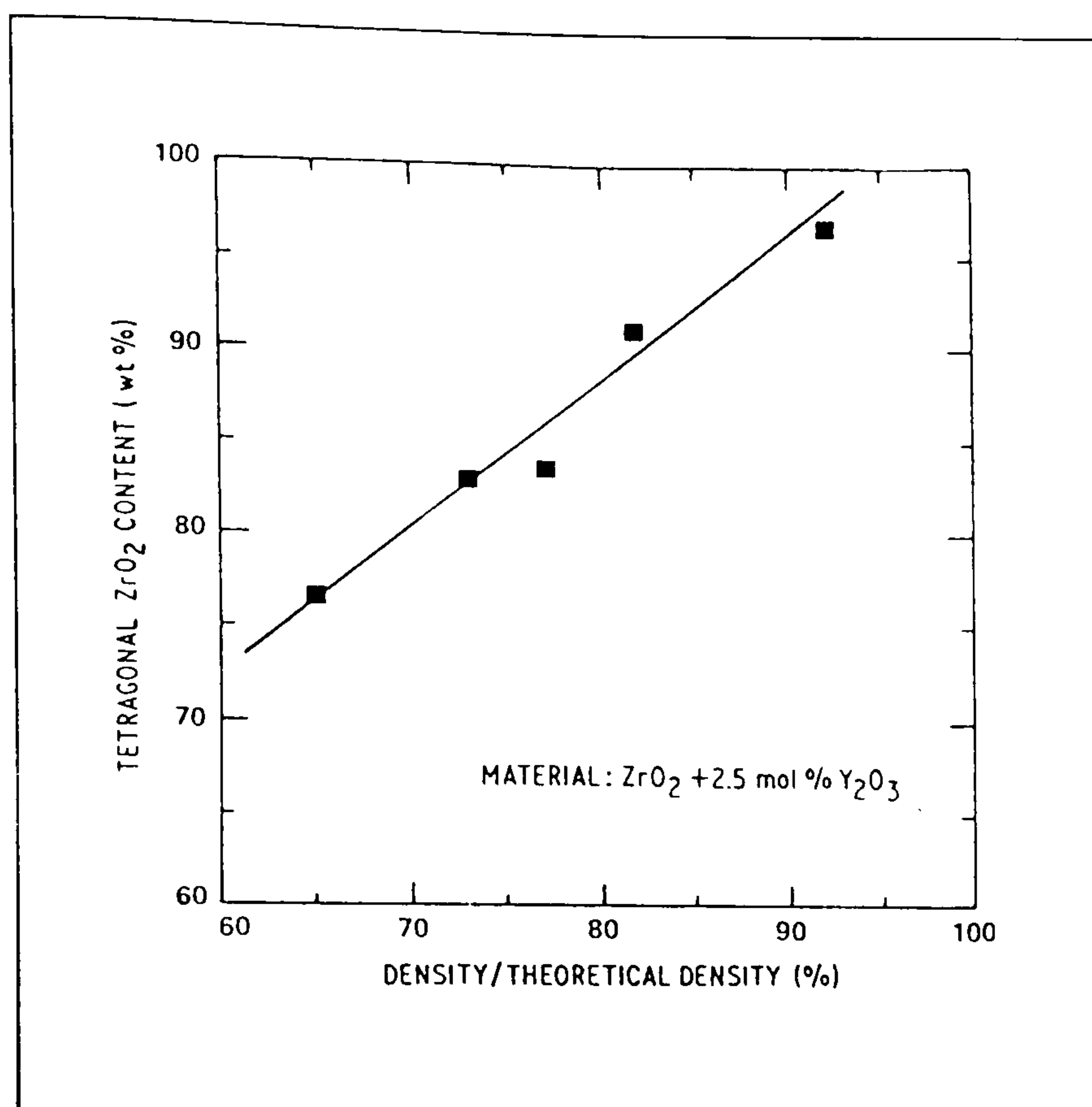


Figure 27: The effect of density on retention of tetragonal $\text{ZrO}_2 + 2.5 \text{ mol\% Y}_2\text{O}_3$.⁵³

Effect of microstructure

Experimental observations on a variety of zirconia materials have shown the dependence of the tetragonal phase stabilisation on grain size, precipitate size and powder size⁵⁵. The critical grain size below which the martensitic transformation is inhibited lies in the 0.1-1 μm range^{55,53} depending on the amount of stabiliser the degree of mechanical constraint and stress state. An explanation for the grain size dependence of the transformation was proposed by Anderson and Gupta⁵⁵. Their theory is based on the idea of the pre-existence of precursor embryos whose potency to grow increases with their size. Lange, along the lines of Garvie, gives an account on the size dependence of the transformation based on the creation of interfacial surface energy⁵⁴. The change in surface energy per unit volume of a spherical tetragonal particle is inversely proportional to its diameter. For a given driving force and strain energy to overcome, there exists a critical grain size below which the surface energy change requirement will discourage the transformation.

Beside the energy-based arguments that precede, there exists a different school for who the martensitic transformation is controlled by nucleation. This means that the onset of the transformation relies on the existence of defects acting as nucleation sites to trigger the transformation. Chen and Chiao state that the matrix constraint exerted on the entire tetragonal particle is essentially irrelevant. Rather, this is the stress field exerted by the tetragonal parent matrix in the vicinity of a nucleating defect (dislocation build-up) that is responsible for the onset of the transformation⁵⁷.

3.3 PHYSICAL PROPERTIES OF ZIRCONIA BASED CERAMICS

3.3.1 Thermal conductivity

In the absence of convection, heat conduction in a solid takes place via three concurrent basic mechanisms that are conduction by electrons, conduction by phonons and radiation by photons. The relative contribution of these mechanisms to the total thermal conductivity depends on the type of material and temperature.

Unlike in metals, the contribution of conduction by electrons is minor in dielectrics such as zirconia as they contain a small amount of free electrons. Conduction by phonons is the major contributor to thermal conductivity for zirconia. A phonon is a quantum of energy associated with elastic waves propagating through lattice vibrations. Conduction by phonons increases with temperature and shows a maximum where phonon-phonon interactions start reducing the mean free path. When the mean free path becomes as small as the lattice spacing, thermal conduction by phonon becomes independent of temperature. The significance of conduction by radiation increases with temperature. It contributes to about 10% of the total conduction term under typical TBC operation conditions⁵⁸.

Overall, the thermal conductivity of bulk zirconia is found to vary little with temperature and with the addition of stabilising oxides⁴⁸. However, microstructural features such as micro-cracking and porosity, characteristics of plasma-sprayed zirconia are known to markedly reduce thermal conductivity. The latter may evolve with thermal cycling and exhibit hysteresis due to microstructural changes caused by sintering⁴⁸, further microcracking⁵⁹, tetragonal-to-monoclinic phase transformation⁶⁰, etc...

3.3.2 Diffusion

Stabilised zirconia is an unusual material in that the rate at which diffusion takes place on the anion sublattice is a millionfold greater than that on the cation sublattice^{48,44}. The implication is that processes controlled by mass transport in PSZ will be controlled by cation diffusion.

The diffusion coefficient of an atomic species is directly related to the diffusion coefficient of the defect species responsible for transport by:

$$D_a = fC_d D_d$$

where

D_a : diffusion coefficient of atomic species

D_d : diffusion coefficient of defect

C_d : defect concentration

f : correlation coefficient

Therefore, it can be seen that the atom mobility can be increased by increasing the concentration of defects⁴⁸. This is an important point to bear in mind considering the defective nature of PVD deposits as will be seen in the following chapters.

3.3.3 Electrical conductivity

Zirconia conducts electricity mainly by oxygen anion transport. Its ionic conductivity follows an Arrhenius behaviour over a wide range of temperature with an activation energy of the order of 1 eV⁴⁴ (see Figure 28). The ionic conductivity of zirconia is dictated by its defect structure i.e. its population of oxygen vacancies⁶¹. Therefore, parameters that control the latter such as temperature, additions of stabilising oxides with lower valence, and a reducing atmosphere can potentially influence the electrical behaviour of zirconia.

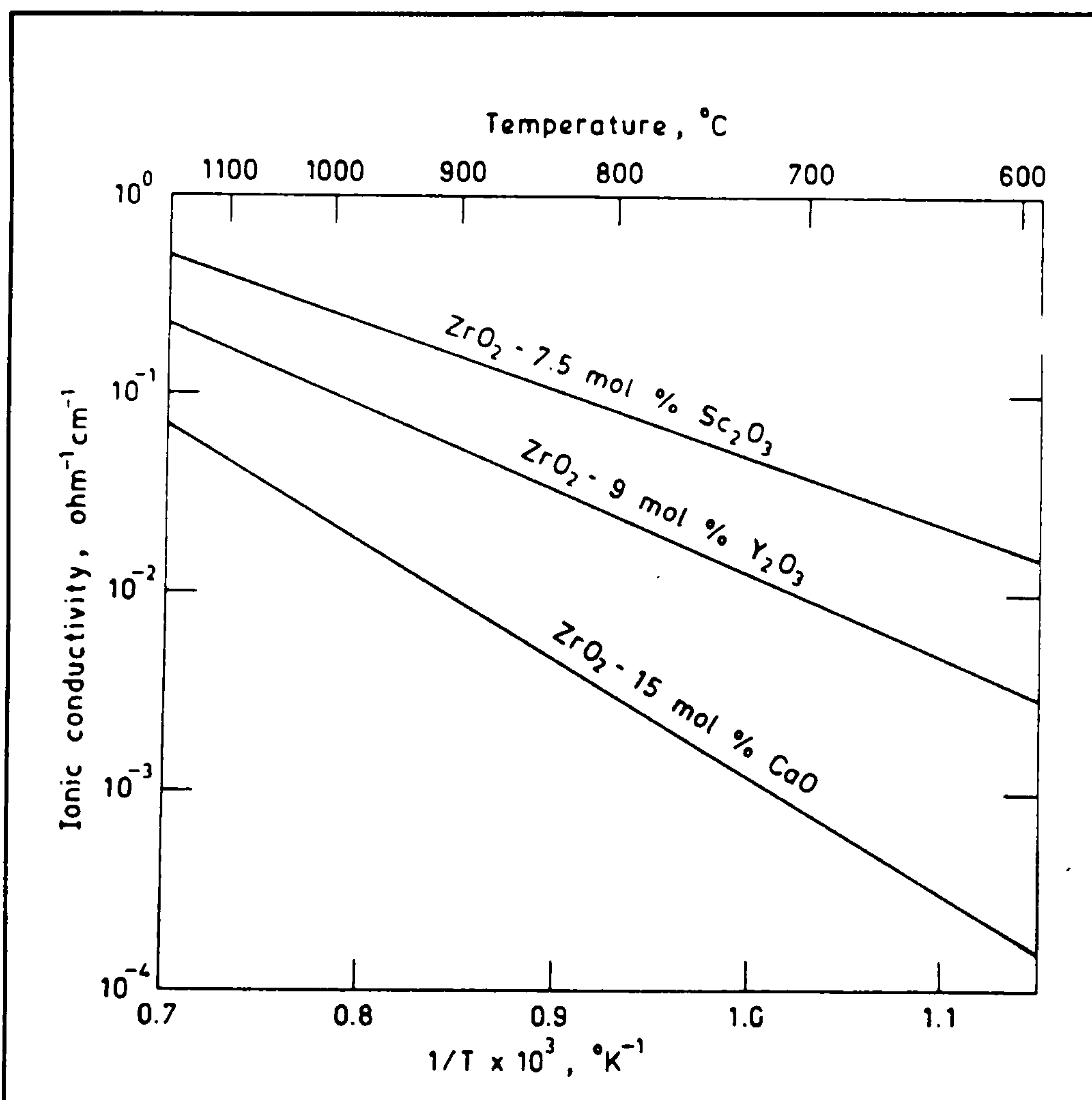


Figure 28: Temperature dependence of ionic conductivities of zirconia doped with Sc_2O_3 , CaO and Y_2O_3 ⁴⁴.

The conduction dependence on dopant concentration is shown in Figure 29.

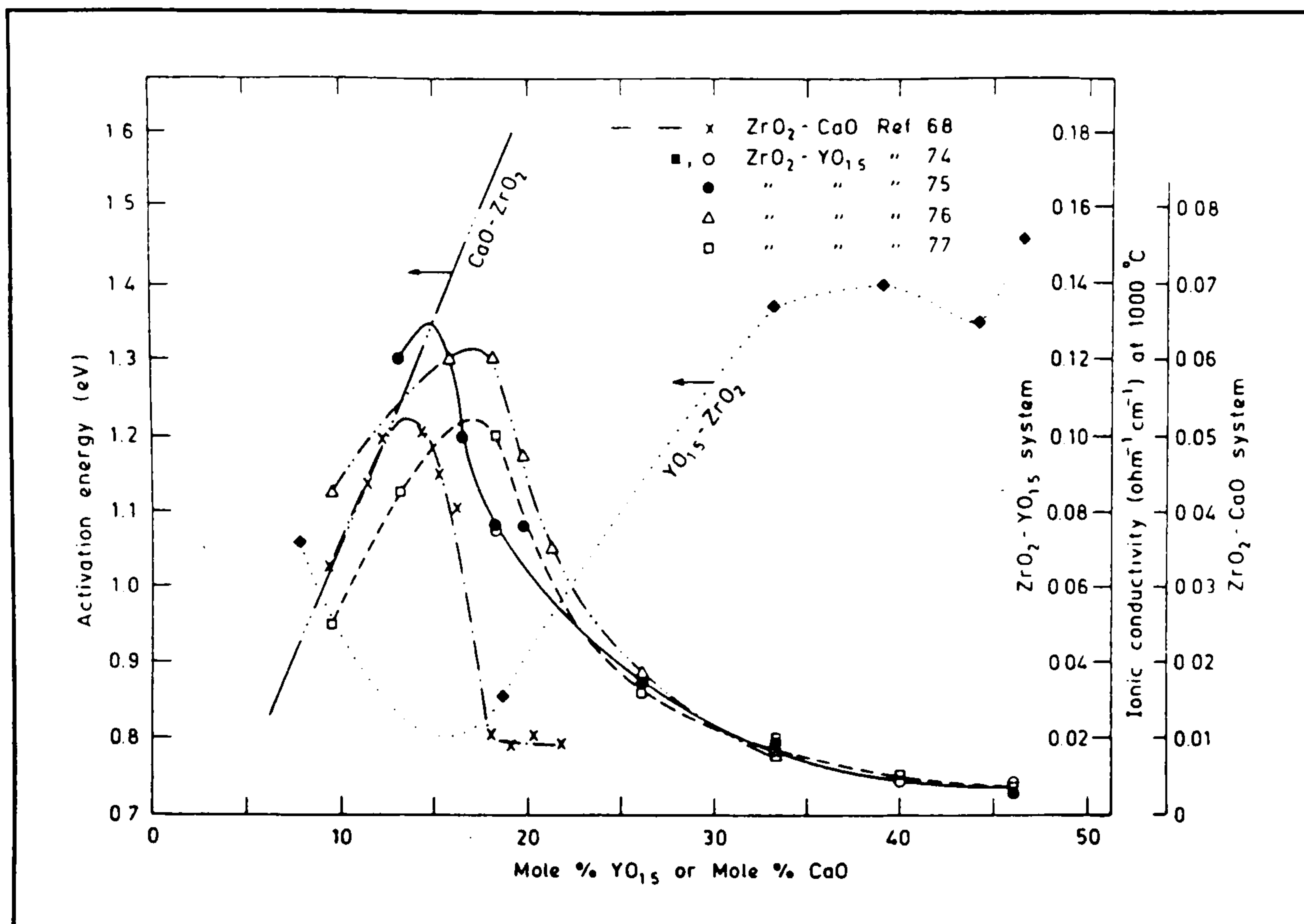


Figure 29: Variation of electrical conductivity and activation energy for conduction with dopant concentration⁴⁴.

It goes through a maximum in the region of 15mol%YO_{1.5} which coincides with a minimum in activation energy, and then decreases with further dopant additions. The main reason invoked for the decrease in conductivity with greater concentration of oxygen vacancies is the ordering of the defects. The transition from order to disorder, which is necessary to set in motion the vacancies, forms a further activation barrier⁴⁸. The ionic conductivity of zirconia is used to advantage in this work as it allows the use of DC substrate biasing for high temperature ion plating. From Figure 29, it can be seen that the resistivity of ZrO₂-8wt%Y₂O₃ (ZrO₂-8.7mol%YO_{1.5}) at 1000°C is in the range of 0.05 to 0.08 (ohm.cm)⁻¹.

It was found that the electrical conductivity of zirconia was unaffected by the oxygen partial pressure down to pressures of 10⁻²⁰ atm⁴⁴. In its reduced state, zirconia exhibits greater conductivities (see Figure 30) and some electronic contribution to the total conduction is observed⁶².

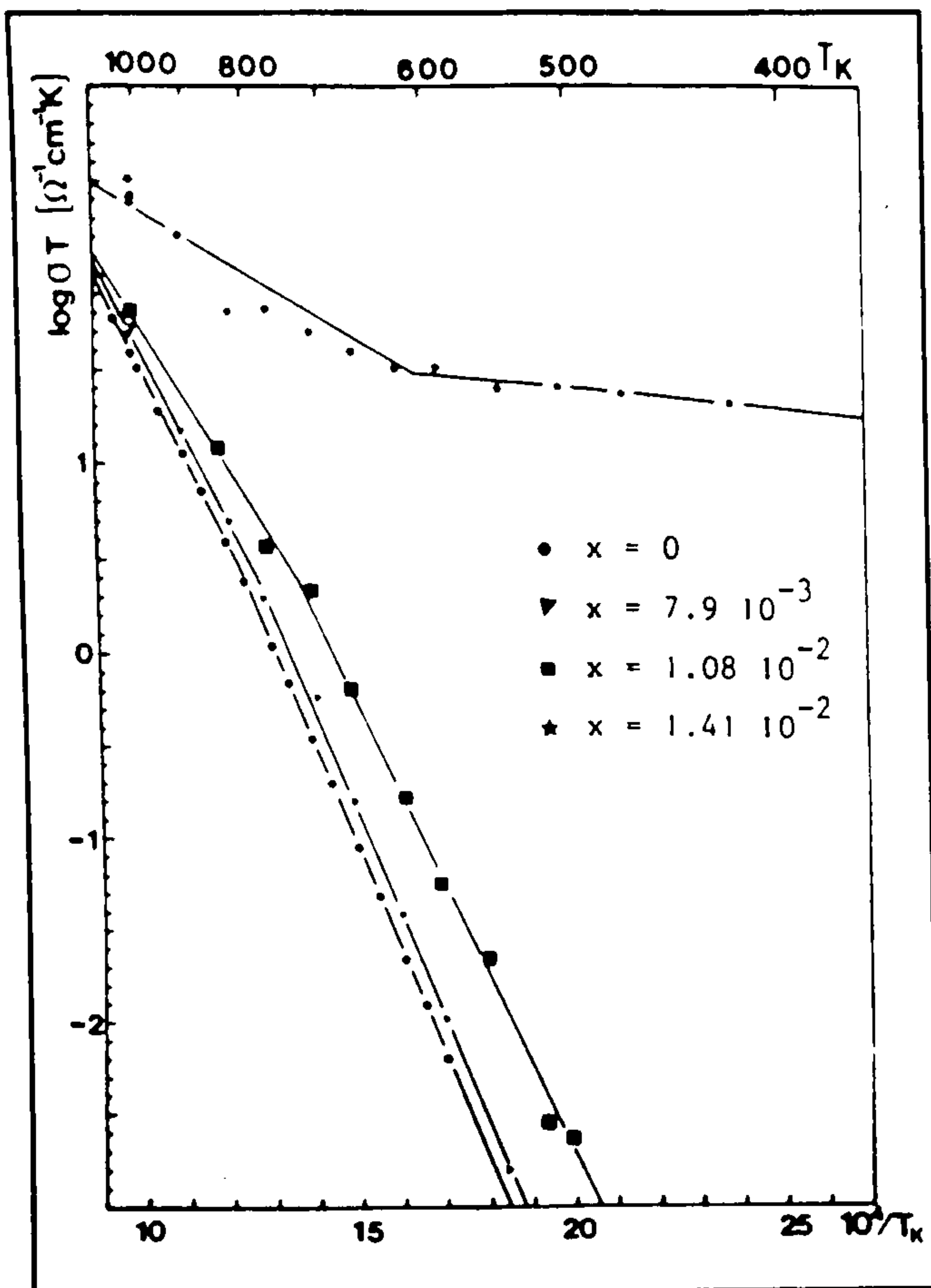


Figure 30: Arrhenius plot of total conductivity of reduced and nonreduced ZrO_2 -9 mol% Y_2O_3 .

4 STRUCTURE/PROPERTY OF FILMS GROWN FROM THE VAPOUR PHASE

Films grown from the vapour phase can exhibit properties that are widely different from bulk materials. This is due to the highly none equilibrium nature of the deposition process whereby individual atoms or clusters of atoms impinge on a surface and build up to form a solid layer. Literally, the PVD process can be described as the transition of bulk material into elemental entities of matter (evaporation) and the construction of a new material by the deposition of the same elements into a different arrangement (condensation). The resulting film structure (physical features of the material) is responsible for the departure from bulk properties.

The present chapter reviews some aspects of the relationship between the process, the structure and the properties of PVD films with particular reference to yttria-alloyed zirconia (YSZ) deposits. The effect of process parameters such as substrate temperature, ion bombardment, pressure... is presented as reported from the literature.

4.1 COATING MORPHOLOGY

4.4.1 Effect of temperature

A salient feature of films grown from the vapour phase is the columnar morphology that they may exhibit when deposited under certain conditions. The effect of temperature on the morphology of PVD deposits was first depicted by Movchan and Demchishin (MD) in 1969⁶³ with the introduction of their original Structure-Zone-Model (SZM). From their study on thick evaporated condensates (250 μ m to 2000 μ m) of Ti, Ni, W, ZrO₂, and Al₂O₃, they identified three zones of coating morphology relating to three temperature regimes relatively to the melting point of the coating material (see Figure 31). In the 'zone 1' low temperature regime ($T/T_m < 0.22$ for ZrO₂), the coating morphology consisted of columnar tapered crystallites with domed tops separated by voided boundaries⁶⁴. The zone 2 structure ($0.22 < T/T_m < 0.5$ for ZrO₂) consisted of parallel densely packed columnar grains defined by metallurgical grain boundaries. The third zone structure consisted of equiaxed grains.

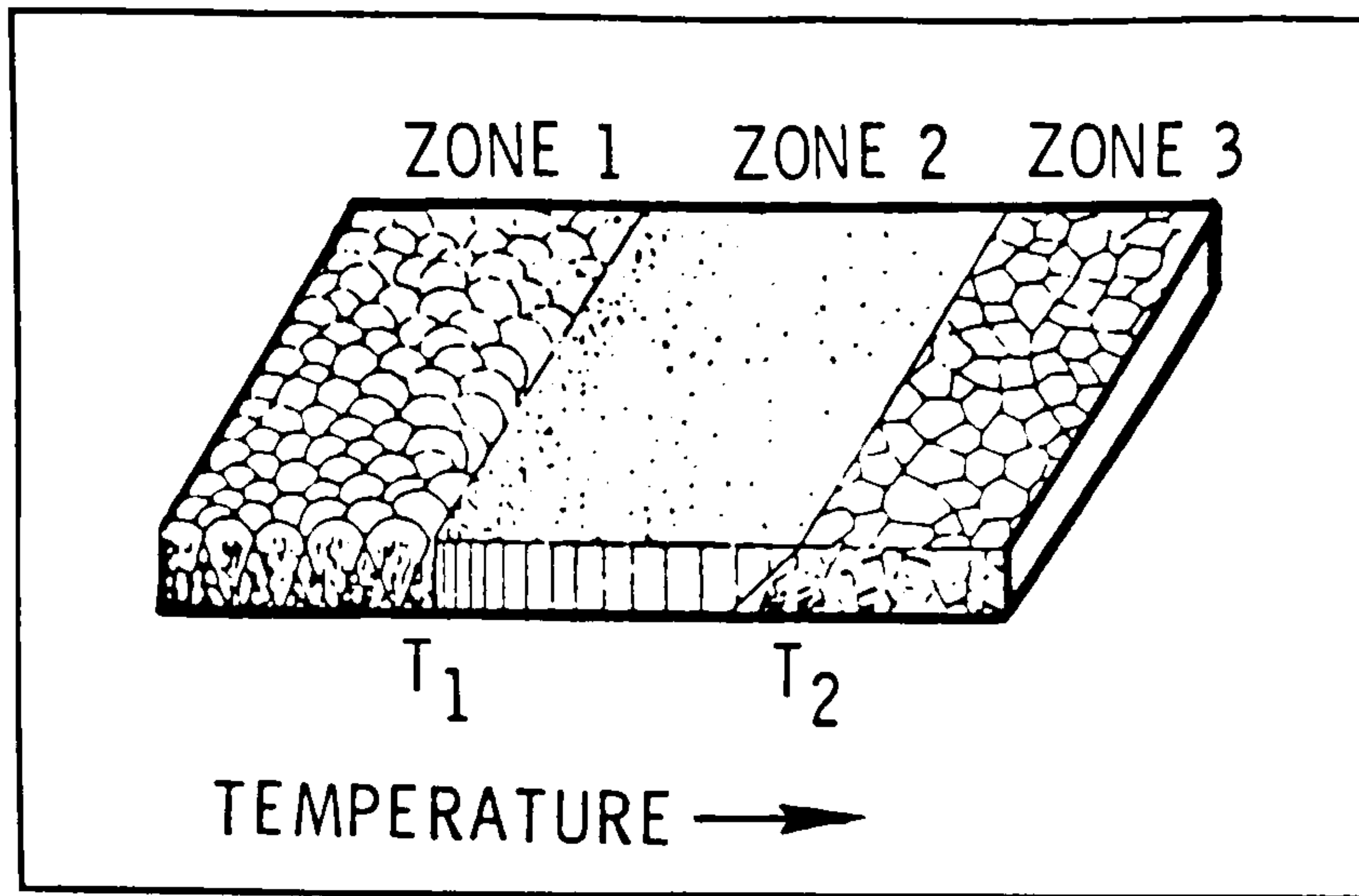


Figure 31: Structure zone model after Movchan and Demchishin⁶³.

According to Thornton⁶⁵, coating growth from the vapour phase involves three critical steps from which the above structure zone model follows (see Figure 32). These are:

- 1- the transport of the vapour atoms to the substrate
- 2- the adsorption of these atoms (adatoms) on the surface of the growing coating, from where diffusion over the surface, incorporation into the coating or desorption may take place.
- 3- movement of coating atoms to their final position in the lattice by bulk diffusion.

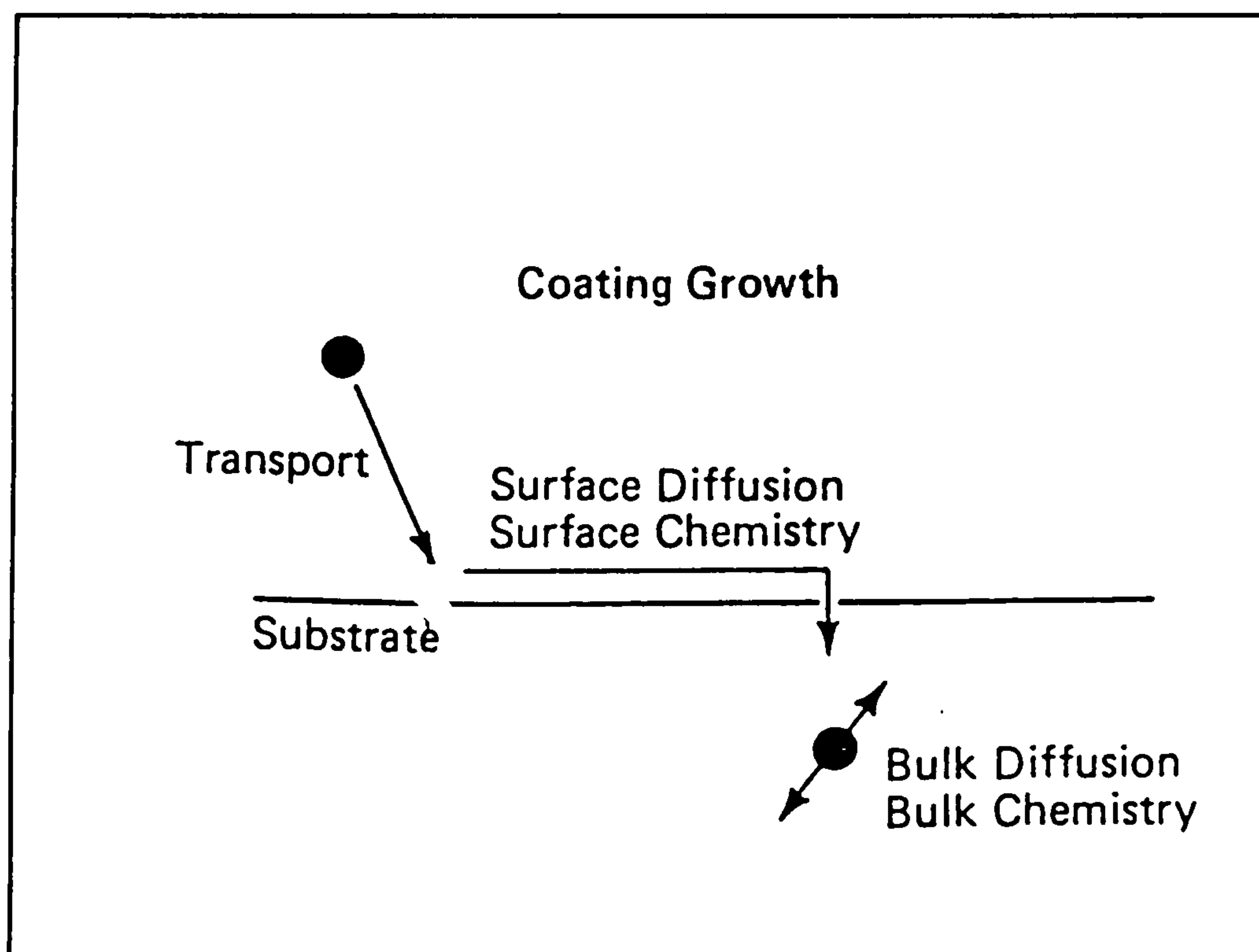


Figure 32: Schematic illustration of vapour condensation during film growth⁶⁵.

At low temperatures where surface diffusion of atoms is hindered, the coating atoms stick close to their site of impingement. As a result, the coating growth pattern is dominated by the transport of the coating species to the substrate

(step 1). This regime applies to the zone 1 of the MD structure zone model, the tapering of the columns separated by voided boundaries being the consequence of vapour flux shadowing. At intermediate temperatures ($0.3 < T/T_m < 0.5$), surface diffusion fluxes dominate over arrival fluxes and the coating atoms loose all memory of their arrival directions (step 2 dominated). The adatoms have enough energy to diffuse along the column boundaries, the voids at the column boundaries disappear and a more closely packed columnar structure is obtained (zone 2 regime). At even higher temperatures ($T/T_m > 0.5$), bulk diffusion overrides the first two steps, grain boundaries and dislocations become mobile allowing recrystallisation and grain growth to occur (zone 3 regime).

4.1.2 Effect of pressure

In 1973, Thornton⁶⁶ extended the scope of the SZM model to magnetron sputtered metallic films by adding a second axis to account for the effect of argon pressure (see Figure 33). A fourth zone consisting of a dense array of poorly defined fibrous grains was identified between the zone 1 and 2 of the MD model. This zone was termed zone T as it was believed to be a transition zone between the two MD zones. The effect of argon pressure is to increase the transition temperature from zone 1 to zone T. Gas scattering of the vapour may be responsible for this effect as this would promote shadowing effects by increasing the oblique coating flux⁶⁷. Another explanation based on a possible reduction in adatom surface mobility in the presence of a gas has also been proposed⁶⁶.

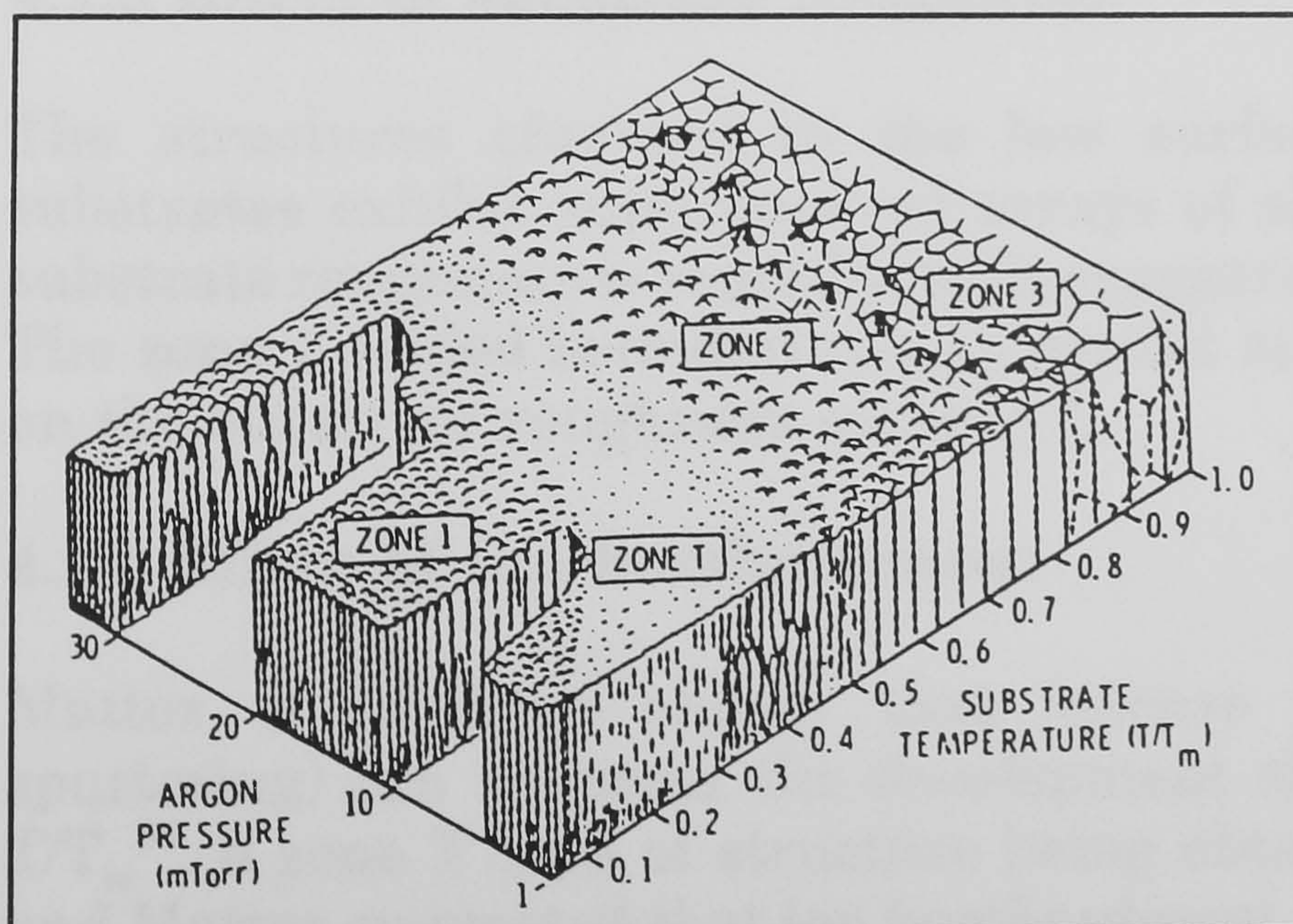


Figure 33: Thornton's Structure Zone Model⁶⁶.

Messier et al have extended these models to include the evolution of morphology with film thickness in the zone 1 regime^{68,69}. Their SZM was derived from TEM and SEM observations of sputtered ceramic films with thicknesses in the range 0.01 to 30 μ m. The column size and associated voids is shown to increase with film thickness in a fractal manner resulting from the clustering of sub-columns into larger columns. In this model, the zone T

morphology recognised by Thornton can be interpreted as a subzone of the zone 1 structures^{69,70}. Messier et al also suggest that it would be appropriate to substitute the pressure axis in the Thornton's SZM by the floating substrate bias as in their interpretation the latter is more relevant to enhanced adatom mobility⁶⁹.

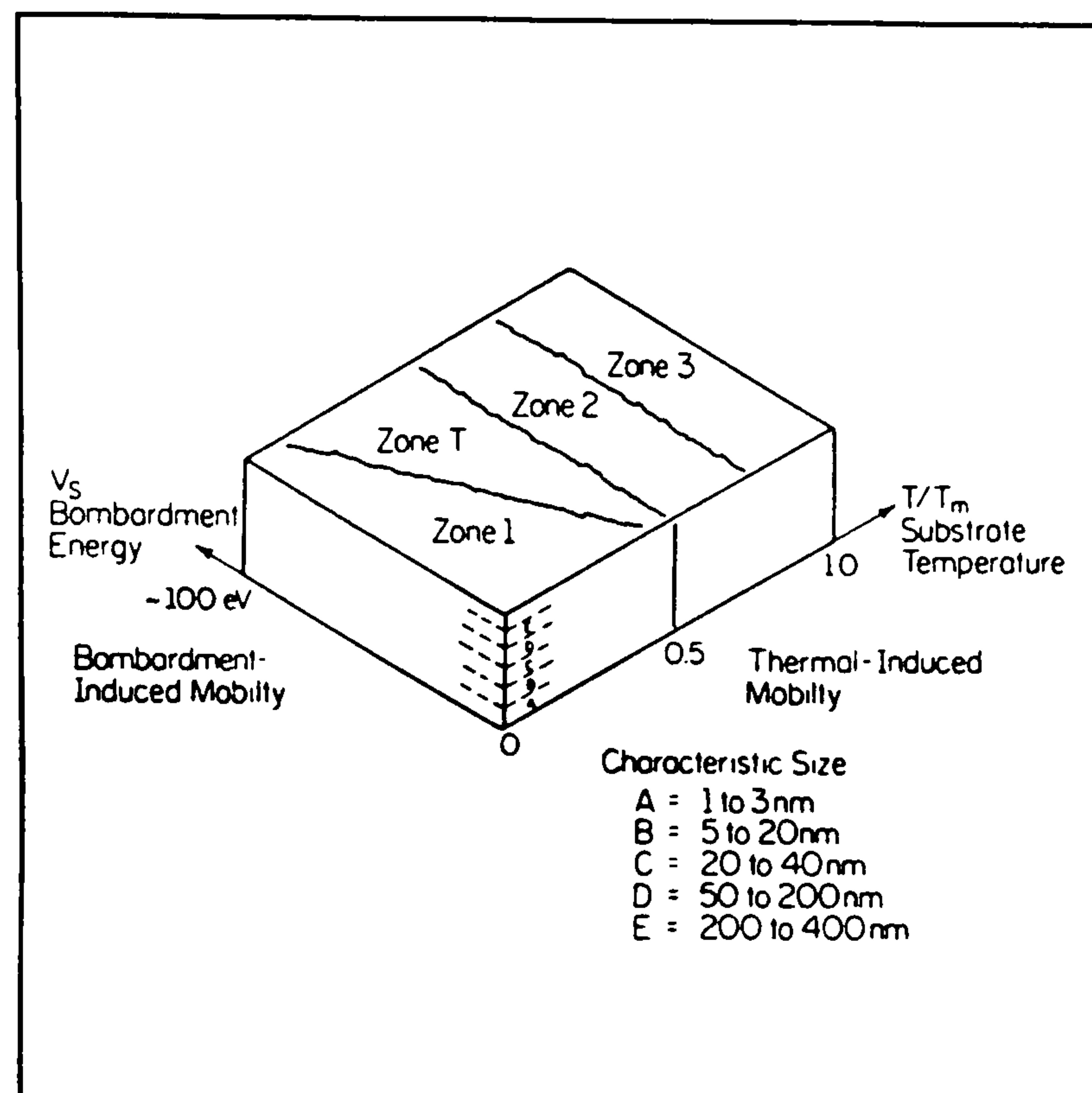


Figure 34: Revised Structure Zone Model after Messier et al⁶⁹.

4.1.3 Effect of substrate roughness

The structures obtained in the low surface diffusion regime on rough substrates exhibit superimposed arrays of shadow-growth boundaries. The substrate roughness is reproduced in exaggerated form on the coating surface. The zone 1 voided boundaries may persist at high values of T/T_m depending on the substrate roughness severity⁶⁴.

4.1.4 Effect of ion bombardment

Mattox et al have shown that intense substrate bombardment (bias sputtering) can suppress the development of open zone 1 structures at low T/T_m ⁶⁴, a zone T type of structure being obtained instead. Bland, Kominiak and Mattox suggested that ion bombardment suppressed the zone 1 structure by eroding surface roughness peaks and redistributing material into valleys from forward sputtering and back-sputtered material returning to the surface⁷¹ (see Figure 35).

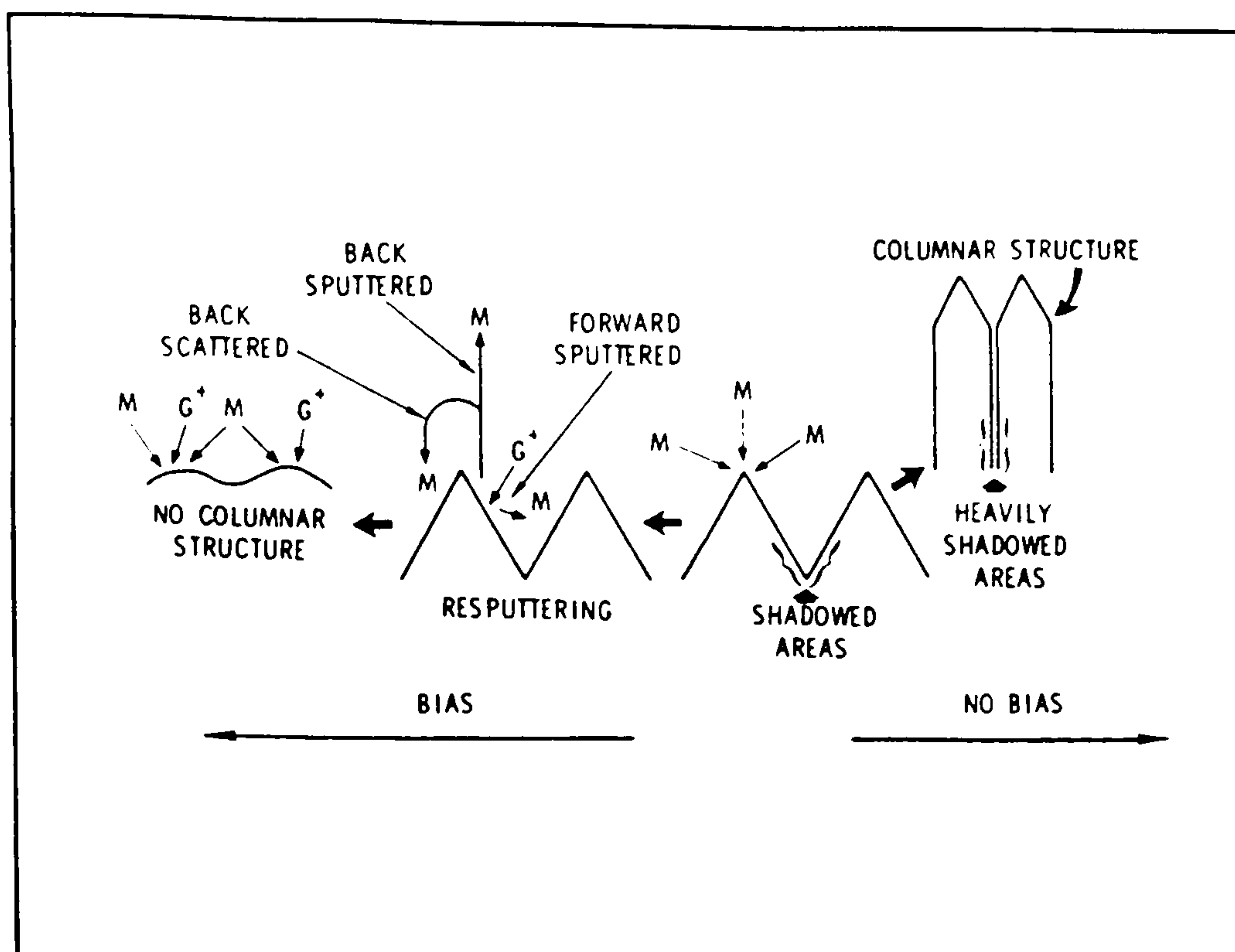


Figure 35: Model of growth modification by ion bombardment during deposition⁷¹.

More recently, investigators such as Rickerby et al, Munz et al^{72,73} also have reported from their work on biased sputtering of TiN coatings, that a dense zone T type morphology could be obtained as a result of ion bombardment.

4.2 COMPUTER SIMULATION OF FILM GROWTH

Beside the structure zone models that have had surprising longevity⁷⁴, computer simulations have been developed from the mid-seventies to elucidate the fundamental processes of film growth. The computer models have substantiated the physical interpretation of SZM's and successfully reproduced the effects of PVD parameters on film properties⁷⁴.

The first computer simulation of film growth appears to have been made by Henderson et al where hard spheres were launched and impinged onto previously deposited spheres assuming different sticking and relaxation conditions. These models were successful in simulating the anisotropic film columnar growth and void formation, although the computed densities could be somewhat unrealistic^{75,76}. More sophisticated models have been developed by K.H.Muller to simulate the effect of temperature, energy of incident coating atom and ion bombardment on the film growth at the atomistic level⁷⁷. Figure 36, Figure 37 and Figure 38 respectively show the isolated effects of kinetic energy exchange between arriving species and film atoms, thermally activated atomic migration and collision cascade induced by ion bombardment on film structure obtained from these simulations. One of the sophistication of the Muller's model is that the trajectories of the impinging atoms are deviated by an attractive potential (Lennard Jones potential ϵ) exerted by the already condensed atoms. As a result, large voids and the onset of micro-columnar growth are promoted by the forces which attract arriving atoms towards adjacent atomic aggregates, which explains the

microporosity present in evaporated films deposited under low thermal excitation conditions. At greater kinetic energies of impingement, the atom trajectories are less deviated by the Lennard Jones potential but interact with the condensed film atoms via a repulsive Molière potential which imparts them with surface mobility of a few lattice spacings. This situation typical of sputtering conditions results into a greater atom packing density (see impact mobility effect in Figure 36). The effect of temperature on film microstructure is simulated by Muller using Boltzmann statistics with a local activation barrier to atomic hopping which is assumed to be function of the number of neighbouring sites (see Figure 37). Ion bombardment during film growth removes overhanging atoms and keeps the void region open until filled by atoms arriving later. Muller's work was significant in that it showed that collision cascade processes were more relevant to the densification undergone with ion bombardment than possible candidates such as enhanced adatom mobility and thermal spikes suggested earlier⁷⁸.

4.3 CRYSTALLINITY OF PVD FILMS

Clearly the crystallinity of a deposit depends on the parameters that affect atomic mobility during film condensation. Temperature, ion bombardment and gas pressure, the latter controlling the kinetic energy of the incident coating atoms are potentially influential parameters to the way a film crystallises.

Yang et al found that sputtered pure zirconia deposited at 60°C was amorphous and that the application of -50V substrate bias resulted into an almost completely crystalline state consisting of the cubic phase with some trace of monoclinic content⁷⁹. Jung et al found that the structure of reactively sputtered zirconia was consistently amorphous for substrate biases of magnitude less than 5V, which they correlated to the Zr-O bond strength in the amorphous phase⁸⁰.

Knoll and Bradley attempted to tailor the phase composition of YSZ thin films using sputtering and investigated a wide range of yttria concentrations (from 3 to 15 mol%Y₂O₃). They found that the deposits were invariably cubic regardless of the yttria content, the substrate bias and the post-deposition heat treatments⁸¹. Fancey and Matthews³⁸ also reported the cubic structure from their work on ion plating of YSZ at low temperature (400°C). Recent investigations^{82,83} concluded that commercial EB-PVD ZrO₂-8wt%Y₂O₃ TBC's consisted of a single phase tetragonal structure.

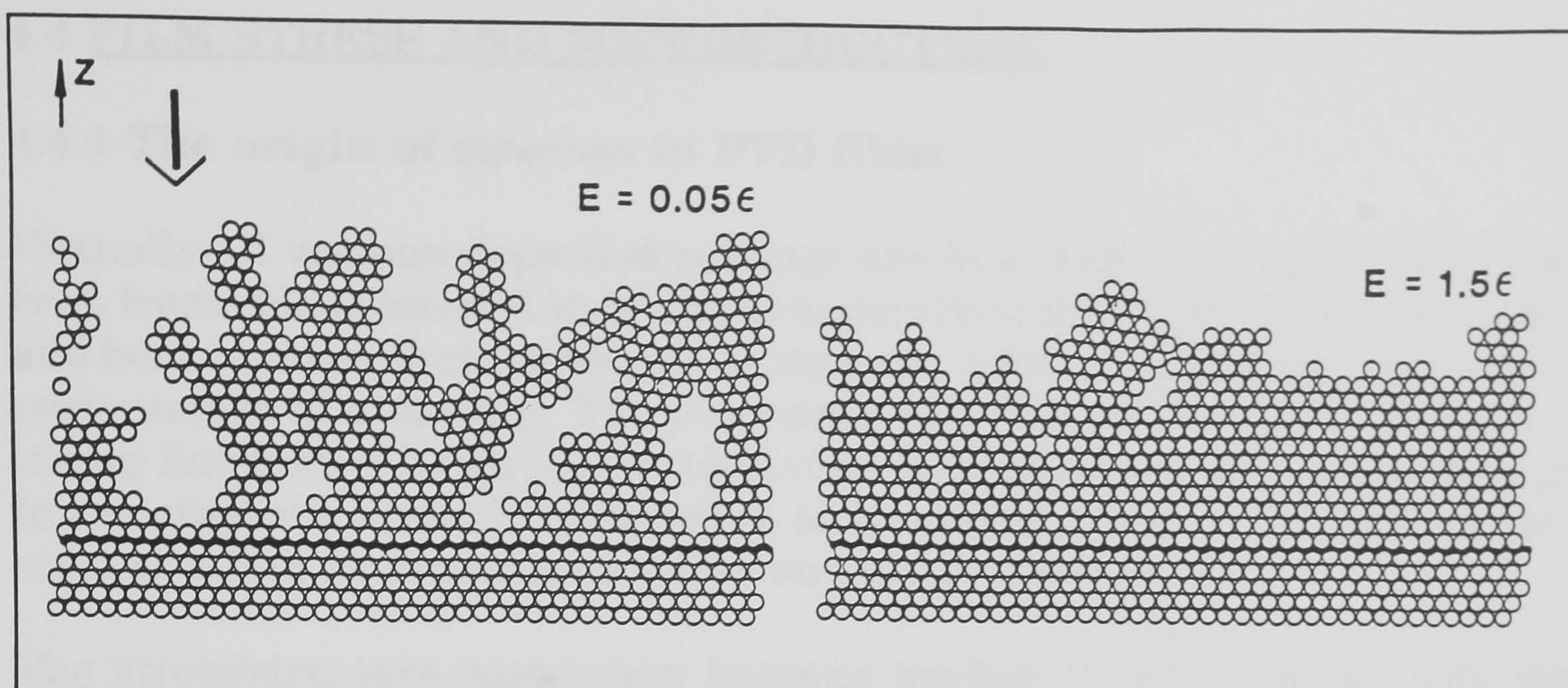


Figure 36: The effect of kinetic energy of arriving atoms on film microstructure⁸⁹ (ϵ : Lennard-Jones potential).

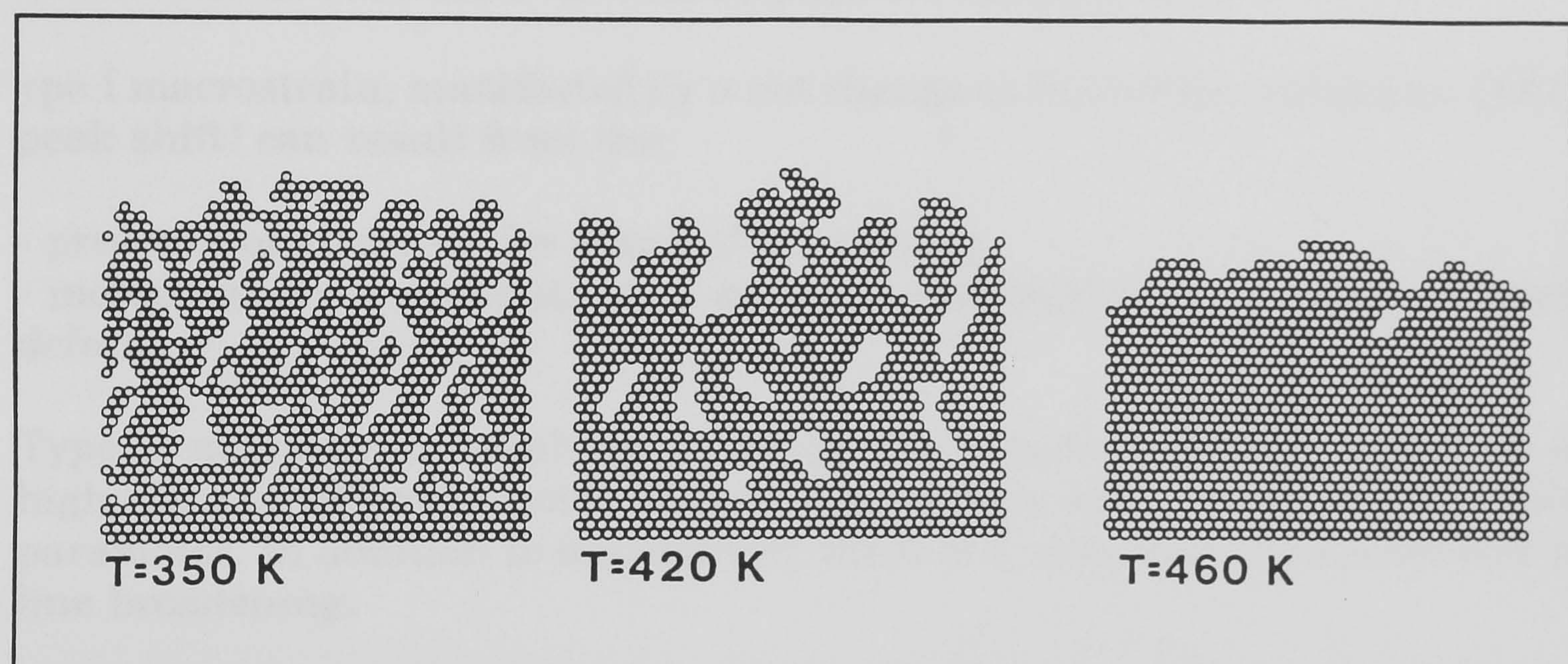


Figure 37: Film microstructure of nickel film at various T/T_m ⁷⁷.

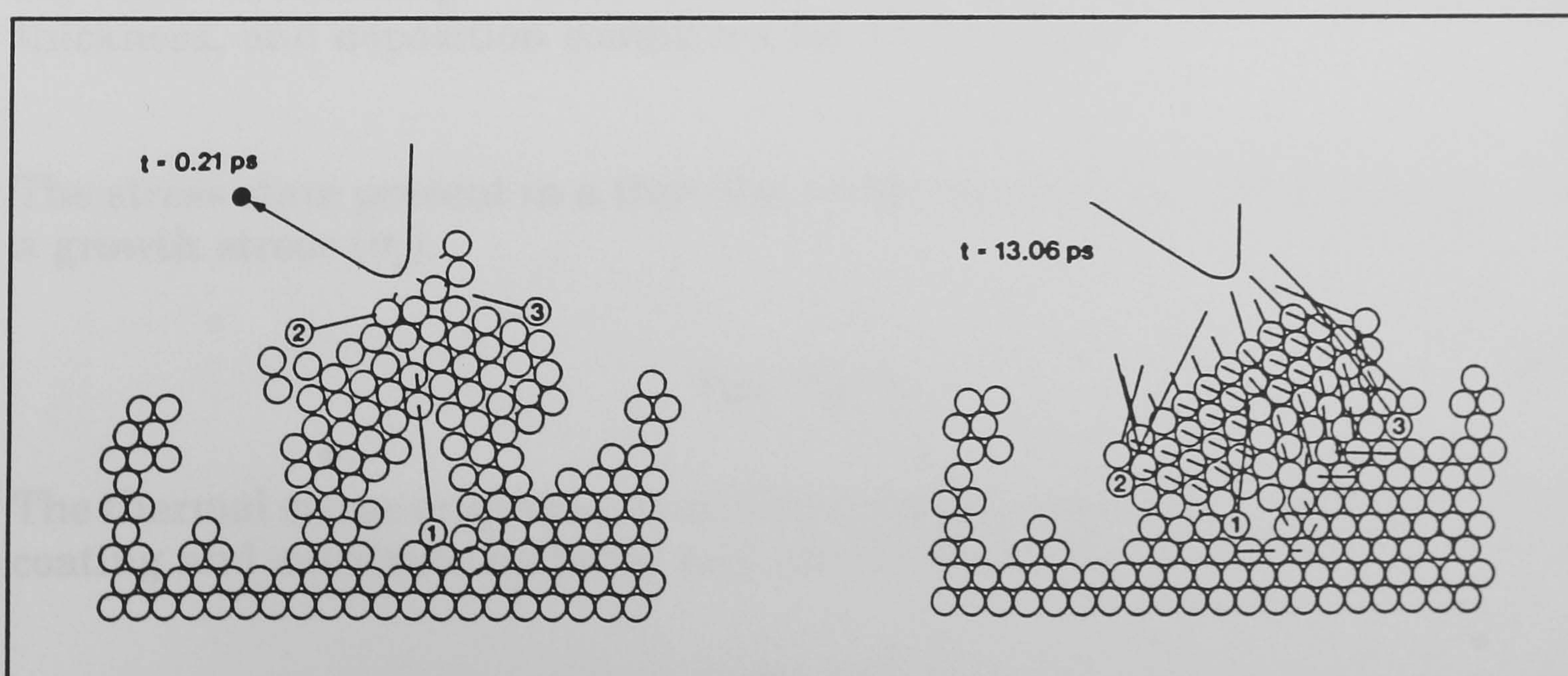


Figure 38: Collision sequence of the impact of a 100eV Ar ion onto a porous Ni film⁷⁷.

4.4 FILM STRESS AND MICROSTRUCTURE

4.4.1 The origin of stresses in PVD films

Virtually all vacuum deposited coatings are in a state of stress⁸⁴. There has been tremendous interest in trying to understand the origin of these stresses, and hence control their influence, as they can affect the adhesion and overall performance of a coating. The propensity of a film to develop a stress is a strong function of its structure, the latter stemming from the morphological to the atomistic scale. It is therefore of peculiar interest to study the stress state of a film as a means to derive structural information.

The stress/structure association becomes evident if one considers that the stress state of a film can be assessed using XRD methods. Rickerby et al⁸⁵ have classified the different lattice strains measurable in PVD deposits using XRD methods with their associated physical interpretations.

type I macrostrain, manifested by a net change in the lattice parameter (XRD peak shift) can result from the:

- presence of stress in the plane of the coating
- incorporation of elements such as argon and high concentrations of point defects

Type II microstrain, resulting in X-Ray line broadening is the reflection of high concentrations of point defects, dislocations etc..., gradients of lattice parameter. In addition to microstrain, there is a contribution of grain size to line broadening.

Type III macrostrains are generally recognised as being the result of structural and yield anisotropy and are characterized by a peak shift and X-ray line broadening. These strains vary with deposition rate, coating thickness, and deposition conditions for PVD coatings.

The stress state present in a thin film is the sum of a thermal stress (σ_{th}) and a growth stress (σ_g).

$$\sigma_{film} = \sigma_{th} + \sigma_g \quad (3)$$

The thermal stress originates from the thermal expansion mismatch between coating and substrate material and can be expressed as:

$$\sigma_{th} = \frac{E}{(1-\nu^2)} \Delta\alpha(T-T_0) \quad (4)$$

where E, ν , $\Delta\alpha$, ΔT are the film Young's modulus and Poisson's ratio, the

thermal expansion coefficient mismatch between coating and substrate material, T_0 the deposition temperature and T the temperature at which the stress is measured.

The growth stress, also called intrinsic stress, can be defined as that component of the total stress that cannot be attributed to thermal stress. It originates from the accumulating effect of crystallographic flaws built into the coating during deposition⁸⁴.

4.4.2 Effect of temperature

From equation (4), it is clear that the thermal stress is a strong function of temperature, and that this stress at room temperature, if supported by the coating material, increases inasmuch as the deposition temperature increases.

A fall in intrinsic stress with increasing substrate temperature is generally observed⁸⁶. The intrinsic stress of evaporated metallic coatings with high melting points is generally tensile⁸⁷ when deposited under low T/T_m conditions. This is believed to be the consequence of constrained shrinkage of condensing matter resulting from the relaxation from an atomic disordered state to a more ordered state during film growth⁸⁸. Low melting point materials do not develop stresses to the same extent as the refractory materials since under practical conditions atomic mobility is sufficient to allow for relaxation mechanisms to take place during film growth.

4.4.3 Effect of pressure

Thornton showed that the intrinsic stress of magnetron sputtered metallic films was a strong function of pressure^{67,84}. The stress varies from a tensile to a compressive state as the pressure is decreased and often a maximum exists in the tensile regime (see Figure 39) as observed for over 15 elemental metals and alloys⁸⁴.

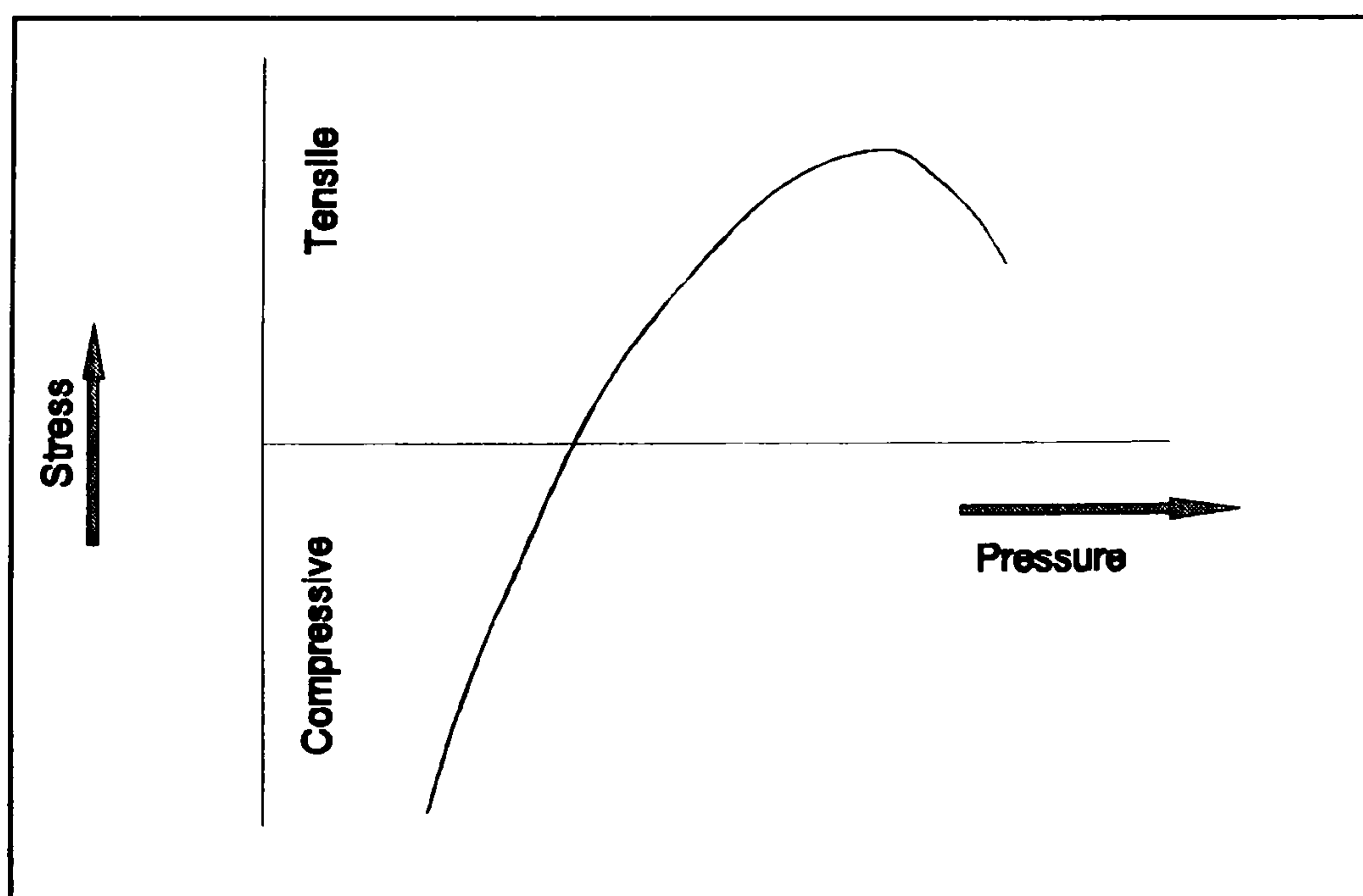


Figure 39: Schematic diagram showing the intrinsic stress as a function of working gas pressure⁸⁹.

Muller⁸⁹ modelled the intrinsic stress behaviour in the tensile regime using a two-dimensional Molecular Dynamics approach. He showed that as the working pressure was decreased, the film microstructure evolved from a porous micro-columnar atomic network to a more densely packed atomic network with closed micropores. The stress passes through a maximum as interatomic forces producing the tensile stress act more effectively in the latter structure, and then decreases as the concentration of microvoids decreases. In this model, the structural change with decreasing pressure was a result of increasing kinetic energy of the incident vapour atoms (see Figure 36). This argument was substantiated with the experimental observation that the transition pressure from the tensile to compressive regime increased with atomic mass of the coating species⁸⁴.

4.4.4 Effect on ion bombardment

Ion bombardment may have a dramatic effect on the stress state of vacuum deposited films. A similar dependence of stress on the energy of bombarding ions or neutrals as that on pressure was found (see Figure 40) which was again successfully simulated by Muller⁸⁹. The latter concluded that Ar bombardment during growth imitated a higher arrival kinetic energy of coating atoms.

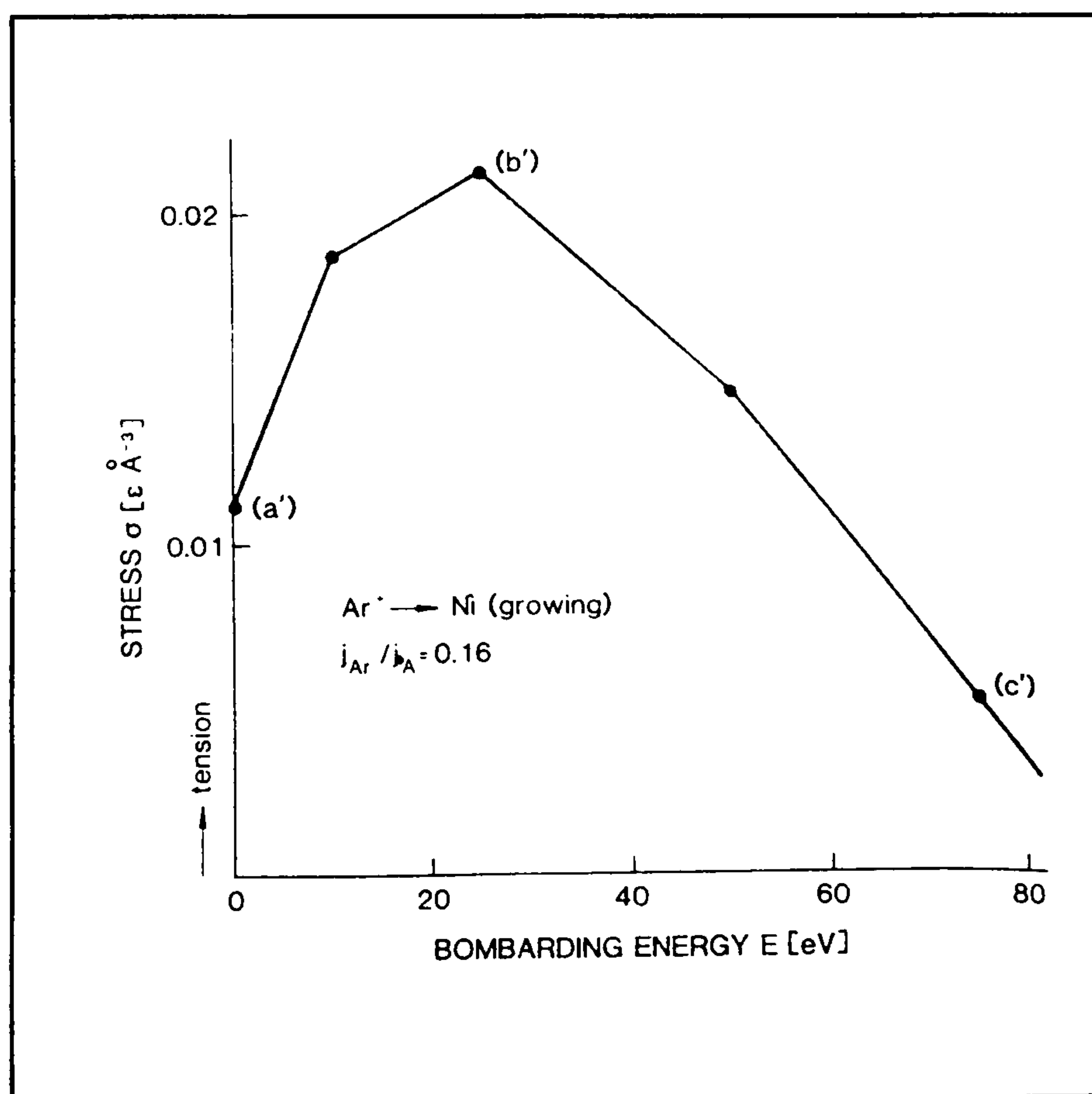


Figure 40: Intrinsic film stress vs Ar bombarding energy E . The Ar-to-atom vapour ratio is $J_{Ar}/J_{vap}=0.16$ ⁸⁹.

Several investigators reported from work on Ion Assisted Deposition that ion bombardment could improve the adherence of evaporated films by reducing the intrinsic stress^{90,91} and measured a critical ion-to-atom arrival ratio. Hirsch and Varga⁹¹ attributed this observation to an annealing effect caused

by atomic rearrangement in bombardment induced-thermal spikes. Brighton and Hubler⁹² modelled the data after Hirsch and Varga and concluded, along the lines of Muller's work, that ion bombardment annealing occurred through atomic displacement in the bulk rather than enhanced adatom surface diffusion or thermal spikes.

A transition from tensile to compressive stress with increasing substrate bias in sputtered films has been reported by many authors. Knoll and Bradley⁹³ found that the stress state of sputtered YSZ on silica substrates could be modified from +600MPa with no bias to -1.7GPa with -200V applied bias (see Figure 41). Given that the thermal expansion coefficient of silica is less than that of YSZ, the thermal stress will be tensile which means that the actual intrinsic stress is greater than the total stress measured. Cléry⁹⁴ and Mesbah⁹⁵ observed a change in the lattice parameter of sputtered YSZ films which was the manifestation of a compressive stress estimated to be of the order of a few GPa.

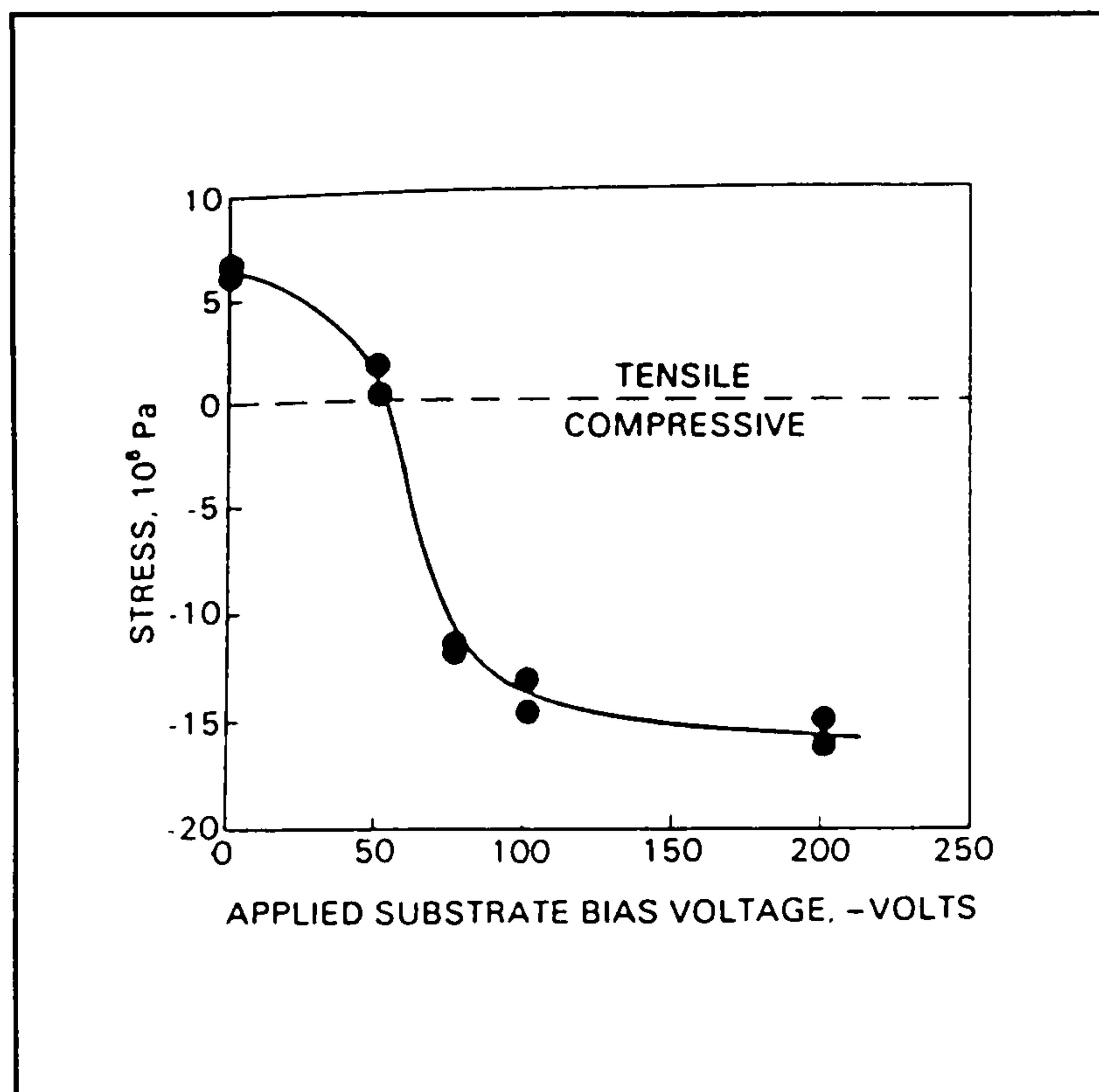


Figure 41: Effect of substrate bias on stress in ZrO_2 -8mol% Y_2O_3 films deposited on SiO_2 substrates at 250°C ⁹³.

Rickerby et al⁹⁶ found compressive stresses in Sputter Ion plated TiN coatings of several GPa for substrate biases up to -60V. As these coatings were deposited on stainless steel substrates at 500°C , a significant compressive thermal stress of the order of 1GPa had to be deduced to obtain the net intrinsic stress. The same author resolved the microstrain measurements into two components, one due to distortion at the grain boundaries and one due to defects in the crystallites⁹⁷.

Compressive stresses in thin films deposited with concurrent ion bombardment are believed to originate from the lodging of atoms into positions that would normally be too small for them⁸⁶. The incorporation of

gas atoms in the film lattice and the knocking of coating atoms into interstitial sites and in grain boundaries have been suggested as possible mechanisms, a model that Thornton referred to as 'atomic peening' ⁹⁴.

4.5 GRAIN SIZE

Hard coatings deposited by PVD owe their good tribological properties to their fine grain size⁹⁶. The grain size in PVD deposits, which is generally less than that for bulk materials, is a function of the deposition conditions.

4.5.1 Effect of temperature

Grain growth is naturally controlled by substrate temperature via surface and bulk diffusion processes during film deposition. Clery⁹⁴ and Stamper⁹⁸ found that the grain size in sputtered YSZ films increased with deposition temperature. In the latter, the grain size in sputtered 11mol%Y₂O₃-ZrO₂ films was reported to increase from 10nm when deposited at 50°C to 50nm when deposited at 600°C. Annealing at 1150°C for 20 hours resulted in an increase of the grain size of the films deposited at room temperature to 28nm. The grain size of YSZ films in the as-deposited state, although not dependent on the yttria composition⁸¹, was found to increase more during annealing with lower yttria contents^{81,95}. It was concluded that increasing the yttria content decreased the cation diffusion rates in YSZ systems.

4.5.2 Effect of ion bombardment

In metallic films, it has been reported that ion bombardment could result in the diminution of the grain size^{99,100}. The reason invoked for this phenomenon was that Ar gas atoms lodged at the grain boundaries hindered grain growth and grain coalescence. In the case of sputtered YSZ films, it was found that grain size was not significantly altered by substrate bias in the range 0 to -200V^{93,101,94}.

4.6 TEXTURE

Vapour deposited films are well known to have preferred orientations in them, the texture in the deposits varying with thickness. The development of texture occurs in three stages¹⁰²(see Figure 42):

Stage 1 (Nucleation): Crystallites are nucleated on the substrates, the distribution, orientation and size of which will depend on the substrate.

Stage 2 (Competitive growth): Certain favourably oriented nuclei will grow faster than the remainder of the crystallites.

Stage 3 (Steady growth): Once a preferred orientation has achieved dominance, steady state growth will occur.

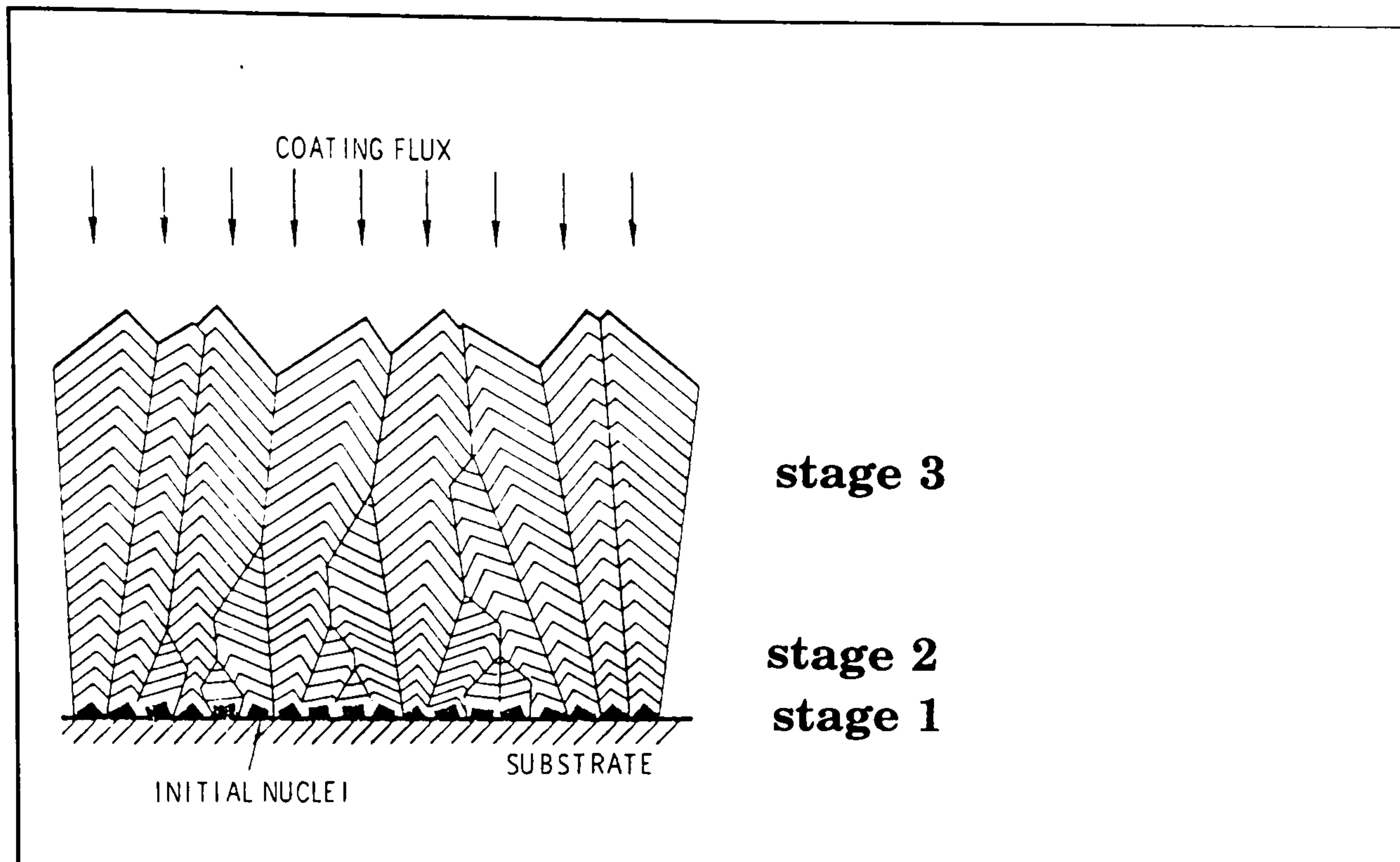


Figure 42: Schematic of development of texture in PVD films.

The preferred crystallographic orientation of a deposit depends on deposition parameters such as the substrate material and surface finish, the deposition temperature, the presence of inert and reactive gases, the angle of vapour flux incidence and ion bombardment¹⁰³. Although models^{104,105,104} attempting to explain the dependence of texture on deposition conditions have been proposed, there is no unified model to account for the overall deposition conditions. It is still obscure as to what controls the development of texture.

Empirically, it is known that thin films with bcc, fcc and hcp structures grow at low T/T_m with their most densely populated planes parallel to the substrate surface⁶⁴. This corresponds to the (111) plane for an fcc structure.

In the case of YSZ films, it has been reported that the texture changed with temperature^{106,98,94}, the $\langle 111 \rangle$ direction corresponding to the low temperature texture. For example, Cléry⁹⁴ observed growth directions in sputtered YSZ changing from near random, to $\langle 111 \rangle$ and $\langle 110 \rangle$ at 250°C, 550°C and 720°C respectively. Substrate bias was found to favour the $\langle 100 \rangle$ texture in pure ZrO_2 ^{101, 106} and in YSZ¹⁰⁷ sputtered deposits. Knoll and Bradley⁸¹ found that the texture of sputtered YSZ was a function of yttria content, ion bombardment, and heat treatment. Mesbah et al⁹⁵ looked at the effect of different oxygen concentrations of the working gas on the properties of sputtered YSZ films and invariably obtained the (111) texture for deposition conditions up to 400°C.

4.7 POROSITY

The porosity in PVD deposits is depicted in the SZM's as inter-columnar voidage^{64,7}. The modelling work after Muller has enforced the idea that porosity develops down to the atomistic scale and the same author coined the phrase that a film grows as a porous atomistic network⁸⁹. Porosity, being the fruit of insufficient atomic mobility is strongly dependent on deposition

parameters such as temperature and ion bombardment.

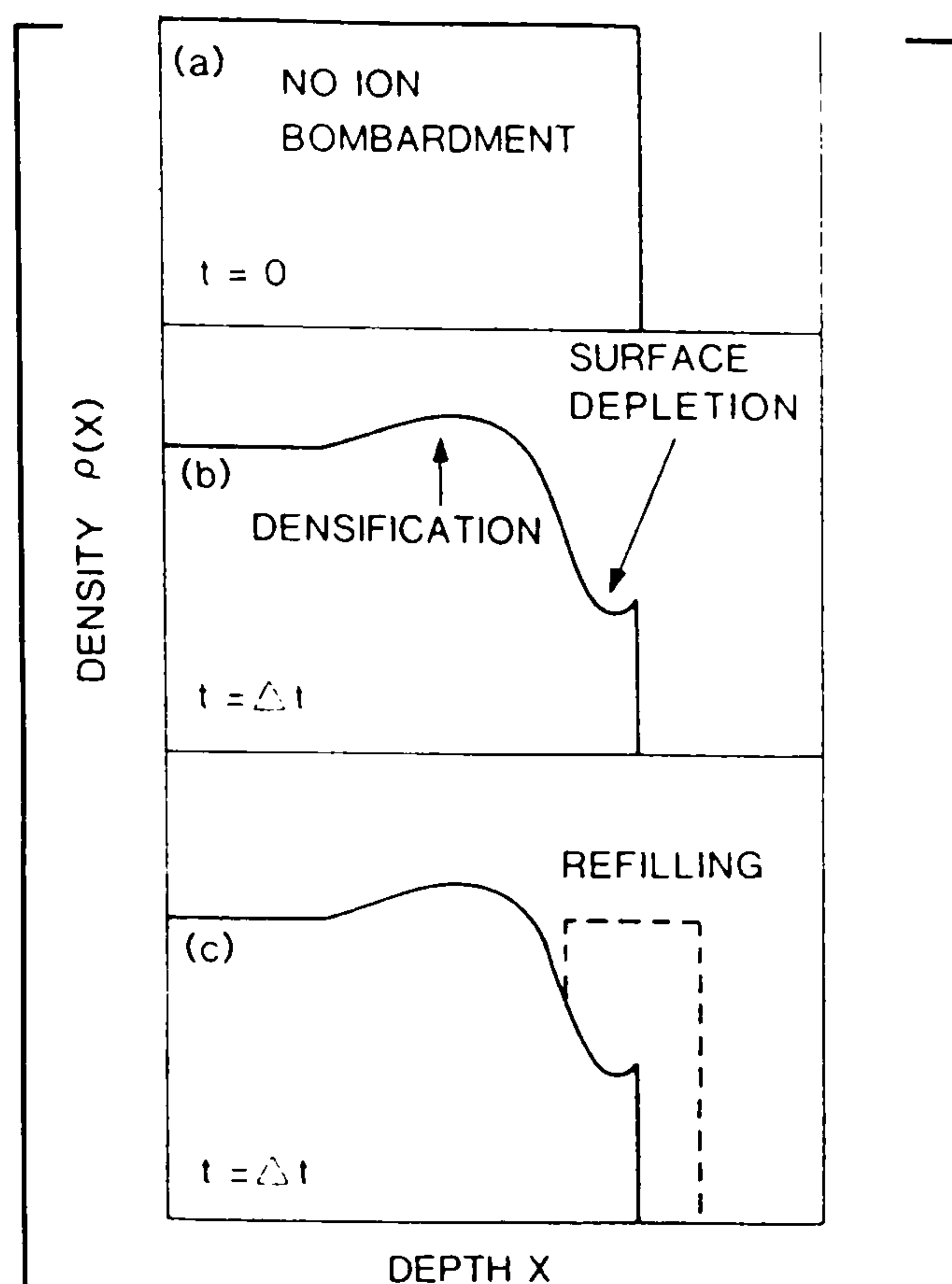


Figure 43: Film density without ion bombardment (a), caused by ion incorporation, sputtering and recoil implantation (b), and refilling of depleted surface (c).

Evidence of intergranular voids (20-40nm⁹³) and large intercolumnar voids using TEM techniques have been found in YSZ and pure ZrO₂ films deposited by sputtering^{93,108,94}. The application of a high substrate bias led to fully dense films with no evidence of columnar growth⁹³. Cléry⁹⁴ measured the density of sputtered YSZ films to be 6000±400Kg/m³ irrespective of the substrate temperature (up to 720°C) and bias (up to -100V). This suggests that the densification undergone with substrate temperature and ion bombardment did not exceed the actual scatter in the density measurements (400Kg/m³). The intergranular voids were found to be resorbed after annealing⁸¹.

Film density is a major concern in the production of optical films as the refractive index is lowered by the presence of microvoids and made unstable with the entrapment of moisture⁷⁸. The relative density of straight evaporated ZrO₂ is about 0.80 as deposited on unheated substrates and can be increased up to that of bulk zirconia with ion assistance⁷⁸. Muller¹⁰⁹ developed further his collision cascade model to quantitatively predict the increase in packing density with oxygen ion assistance. According to this model, ion bombardment causes surface depletion due to sputtering and inwardly recoiled atoms and densification deeper in the bulk because of ion incorporation and recoil implantation (see Figure 43a,b). The surface vacancies which are created by sputtering and driven-in atoms are partially refilled with newly arriving vapour atoms¹⁰⁹ (see Figure 43c).

The above model which predicts a strong dependence of packing density on the ion-to-atom flux ratio yielded a good agreement with the experimental data¹⁰⁹ (see Figure 44).

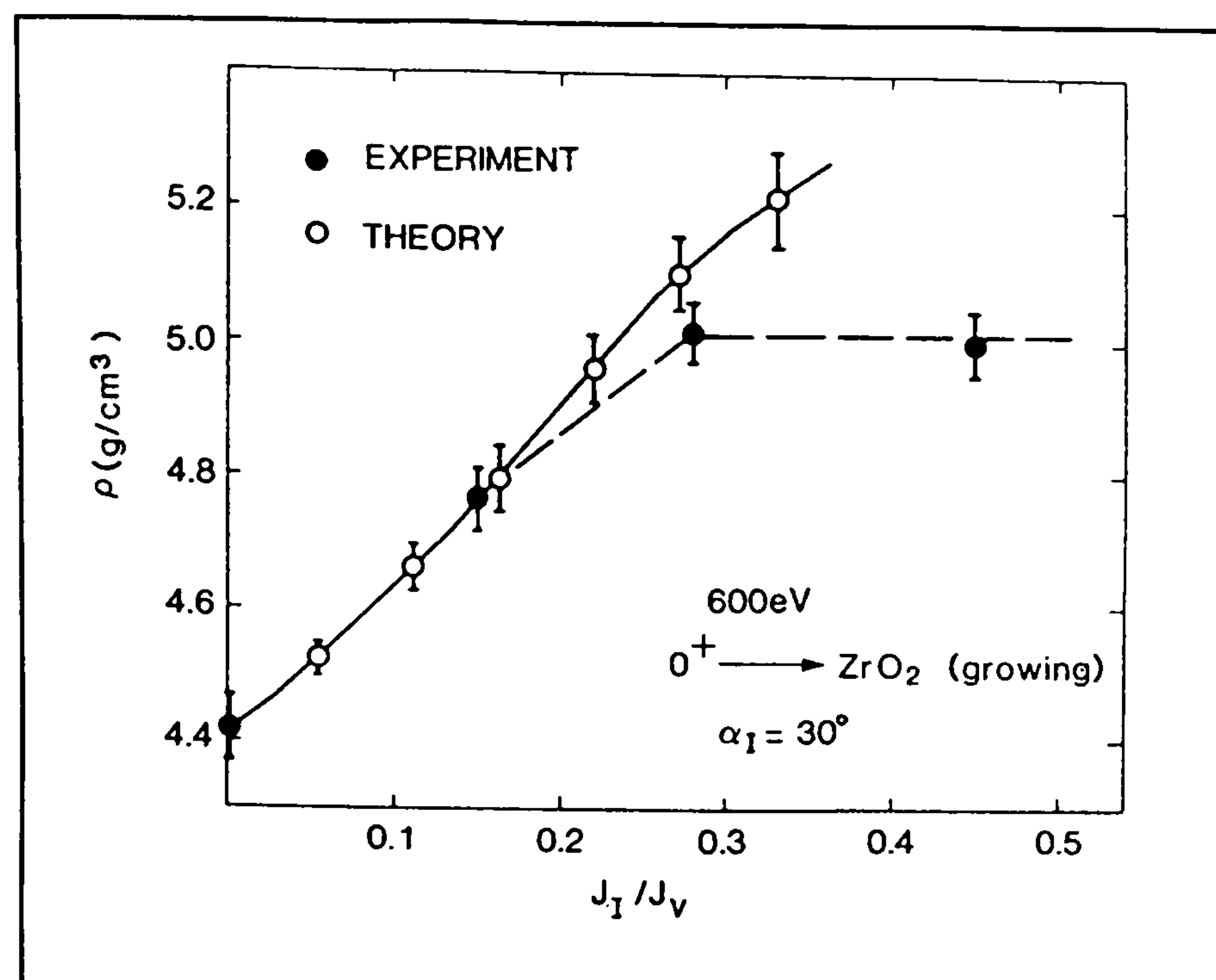


Figure 44: Mass density attained by 600-eV O^+ -assisted zirconia films for different ratios of J_i/J_v (30° angle of ion incidence)¹⁰⁹.

In the light of these previous investigations, the object of chapter 8 is to discuss the role of process parameters such as temperature, ion bombardment, pressure,... on the structure of thick EB-PVD ZrO_2 -8wt% Y_2O_3 deposits in terms of phase composition, texture, morphology, density,... with the aim to further comprehend some aspects of the relationship between the deposition process and the coating structure.

5 GLOW DISCHARGE PLASMAS

There exists many different varieties of plasmas and as many different ways of approaching them. It is beyond the scope of this work to enter the world of plasma physics per se. Rather this chapter concentrates on the glow discharge plasmas from a surface processing point of view. The aim is to lay down the fundamentals that lead to some understanding of DC and RF gas discharges. This theoretical review then forms the basis for the formulation of a way of estimating the ion current density incident on the substrates for both DC and RF ion plating (chapter 7).

This chapter contains five sections. The first is a foreword on gas discharges. The second is a review of the basic phenomena of particle physics involved in the existence of a laboratory discharge. The third describes the electrical behaviour of a gas discharge as painted by Chapman in his work of reference¹¹⁰. The fourth section gives an account on RF glow discharges specifically.

5.1 DEFINITION OF A GLOW DISCHARGE PLASMA

A gas in its ground state is an insulator because of the absence of free charged particles. Partial ionization of a gas can be obtained by the application of heat, the irradiation by a beam of energetic particles or of electromagnetic waves. Such a gas is then called a plasma and consists of a mixture of neutrals, ions and electrons. A plasma is globally neutral, that is to say it contains equal numbers of negative and positive charges. It is a good approximation to consider that those three sets of particles have a Maxwell-Boltzmann energy distribution. The energies of these particles can then be described by their respective temperature.

In Surface Engineering, the plasmas of technological importance split into two categories, namely the *thermal plasmas* and the *non-equilibrium plasmas*. Thermal plasmas are characterized by their high plasma density (density of electrons) and the equality between the temperature of the heavy particles (ions, neutrals) and the electrons (local thermal equilibrium). Such features give these plasmas a very high energy density suitable to thermal spray powders of refractory materials¹¹¹ (see Figure 45).

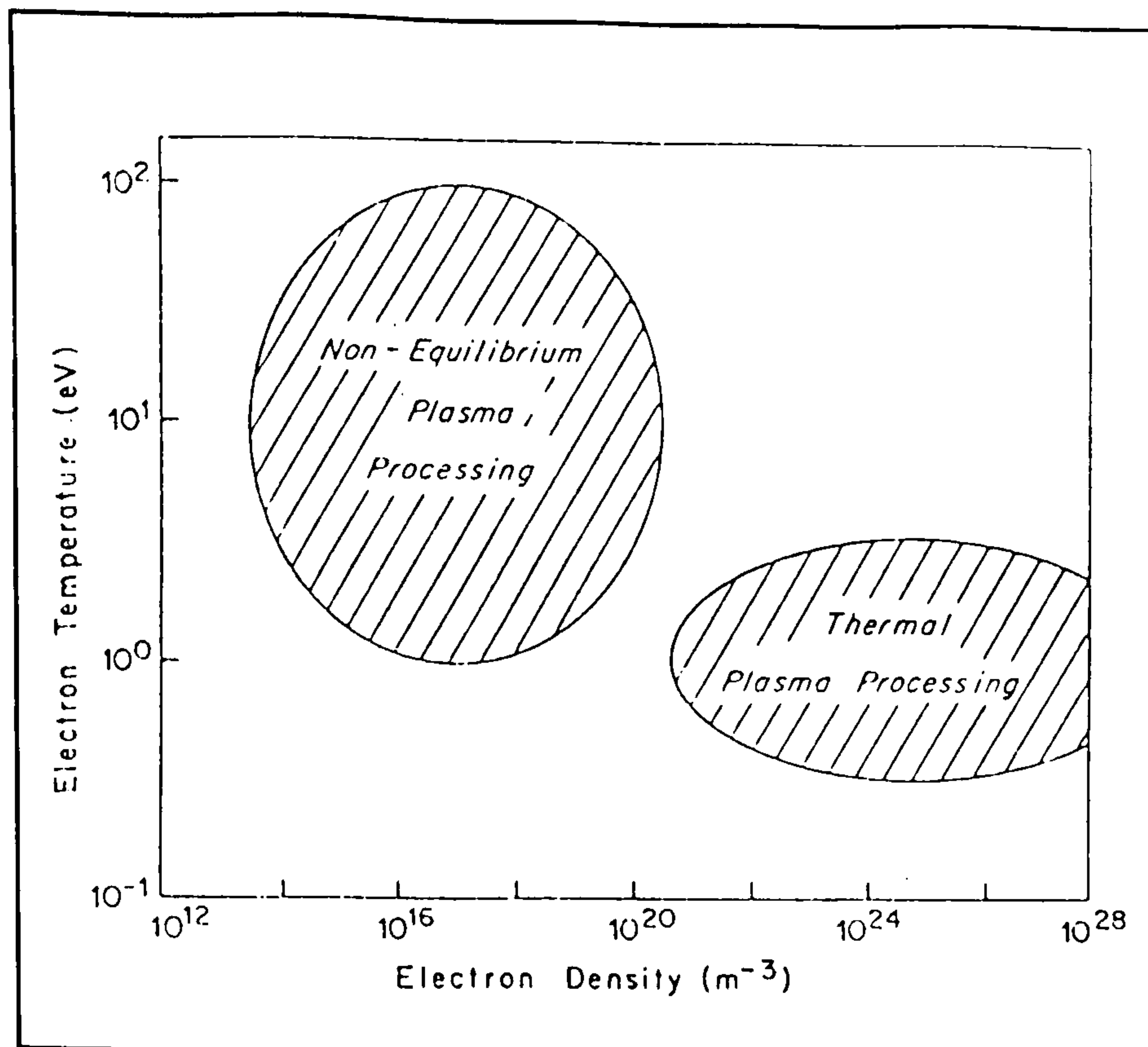


Figure 45: Typical ranges of temperatures and electron densities for thermal and non-equilibrium plasmas¹¹¹.

Non-equilibrium discharges are low pressure plasmas. They have a lower plasma density than the thermal plasmas and are characterized by an electron temperature much greater than that of the heavy particles. Glow discharges belong to this category of plasmas.

Table IV summarizes the typical ranges of plasma parameters for glow discharges.

Table IV: Typical ranges of glow discharge parameters.

pressure	10 ⁻⁴ -10 Torr (1 Torr = 133.7 Pa)
electron temperature	a few eV (1eV≡ 11594 K)
ion temperature	0.03-0.04 eV
gas temperature	300K (0.026 eV)
degree of ionization	10 ⁻⁶ -10 ⁻³
plasma density	10 ⁹ -10 ¹² cm ⁻³

5.2 THE INTERACTION OF PARTICLES WITH A GAS AND A WALL SURFACE

5.2.1 Gas phase collision processes

5.2.1.1 Elastic and inelastic collisions

Collision processes can either be elastic or inelastic. The maximum energy transferable in an elastic collision between two colliding bodies of mass m_1 and m_2 is¹¹⁰ :

$$\frac{4m_1m_2}{(m_1+m_2)^2} \quad (5)$$

Therefore, the more dissimilar the masses, the less kinetic energy can be exchanged in an elastic collision. In the case of an electron colliding elastically with an argon atom, the maximum fraction of energy exchangeable is of the order of 10^{-4} . The effect of elastic collisions between the electrons and the heavy particles is then to scatter the directions of the electrons without altering significantly their energies. This is why at low pressures the electrons can be thermally isolated from the gas: $T_e \gg T_{gas}$ (see Figure 46). At higher pressure, the collision frequency between the electrons and the heavy particles is increased so that the kinetic energy transfer between the two set of particles can no longer be ignored. At high enough pressures, $T_e = T_{gas}$ (thermal plasmas).

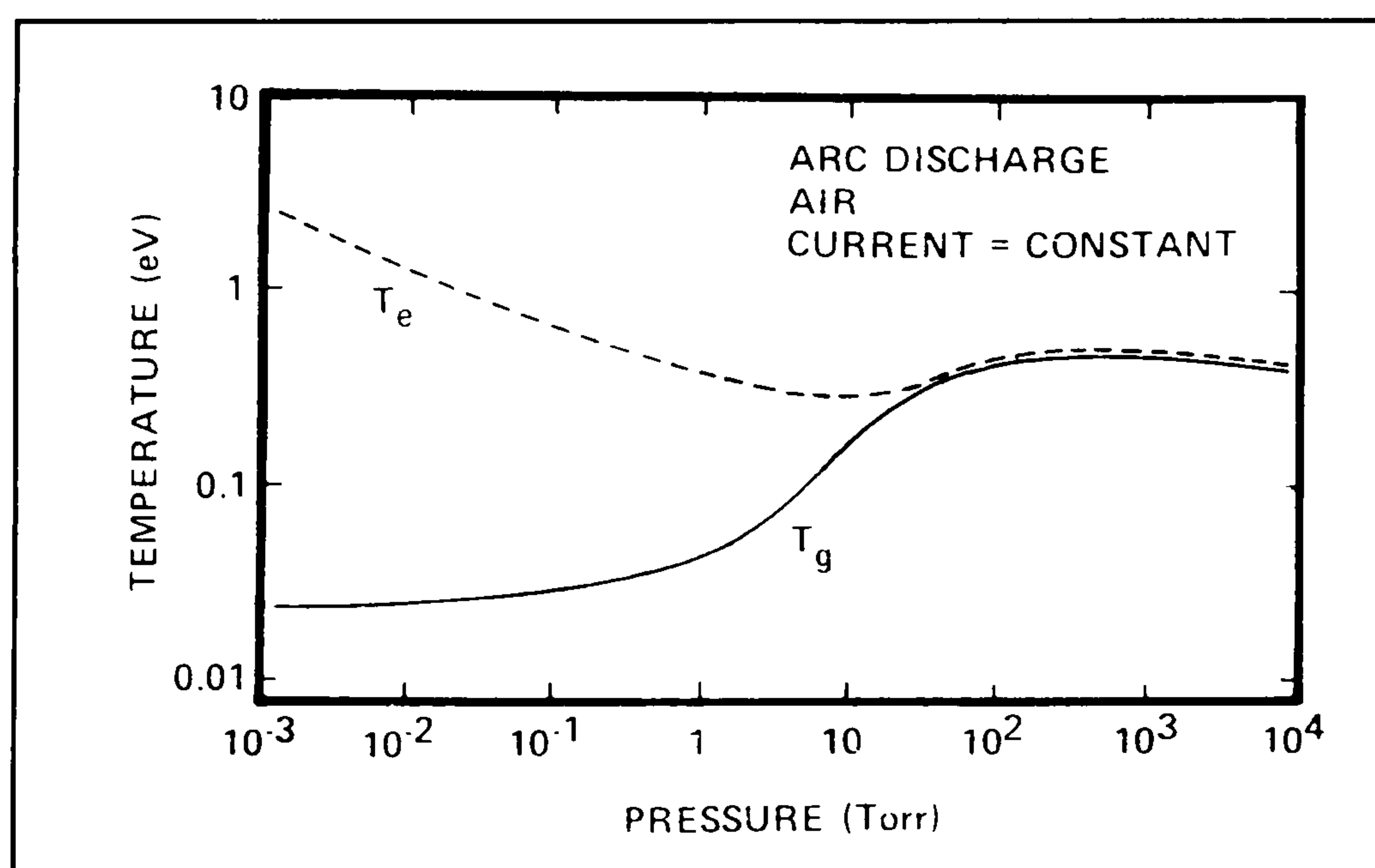


Figure 46: Effect of pressure on electron temperature¹¹².

Inelastic collisions are the basic phenomena that matter in plasma chemistry. The energetic electrons in nonequilibrium discharges can activate chemical reactions that would otherwise necessitate the use of very high process temperatures. Glow discharges are generally used in reactive surface

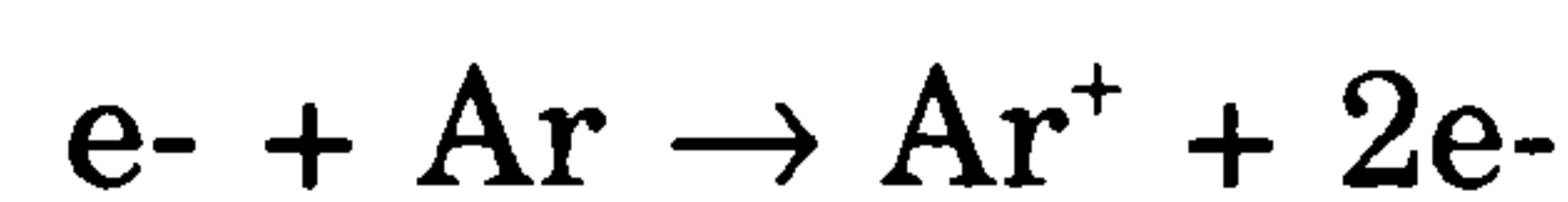
processes to generate metastable species that react with the surface either to form a stable compound (reactive deposition) or volatile products (reactive etching).

In the present work, glow discharge plasmas are used as a source of ion bombardment. The main inelastic collisions of interest, here, are those governing the existence of the plasma, i.e. the ionization and recombination processes respectively.

5.2.1.2 Ionization mechanisms

Ionization is the process of removing an electron from the outer shell of an atom or a molecule and therefore requires work. The major ionization mechanisms in glow discharge plasmas are electron impact ionization, photoionization and excitation.

electron impact ionization:



The effectiveness of electrons in ionizing a gas, as characterized by their cross-section, depends on their energies. To be ionized, a neutral must receive an energy input in excess of its ionization potential which has a value of 15.2 eV for argon. Figure 47 shows the energy dependence of the ionization cross-sections of the noble gases.

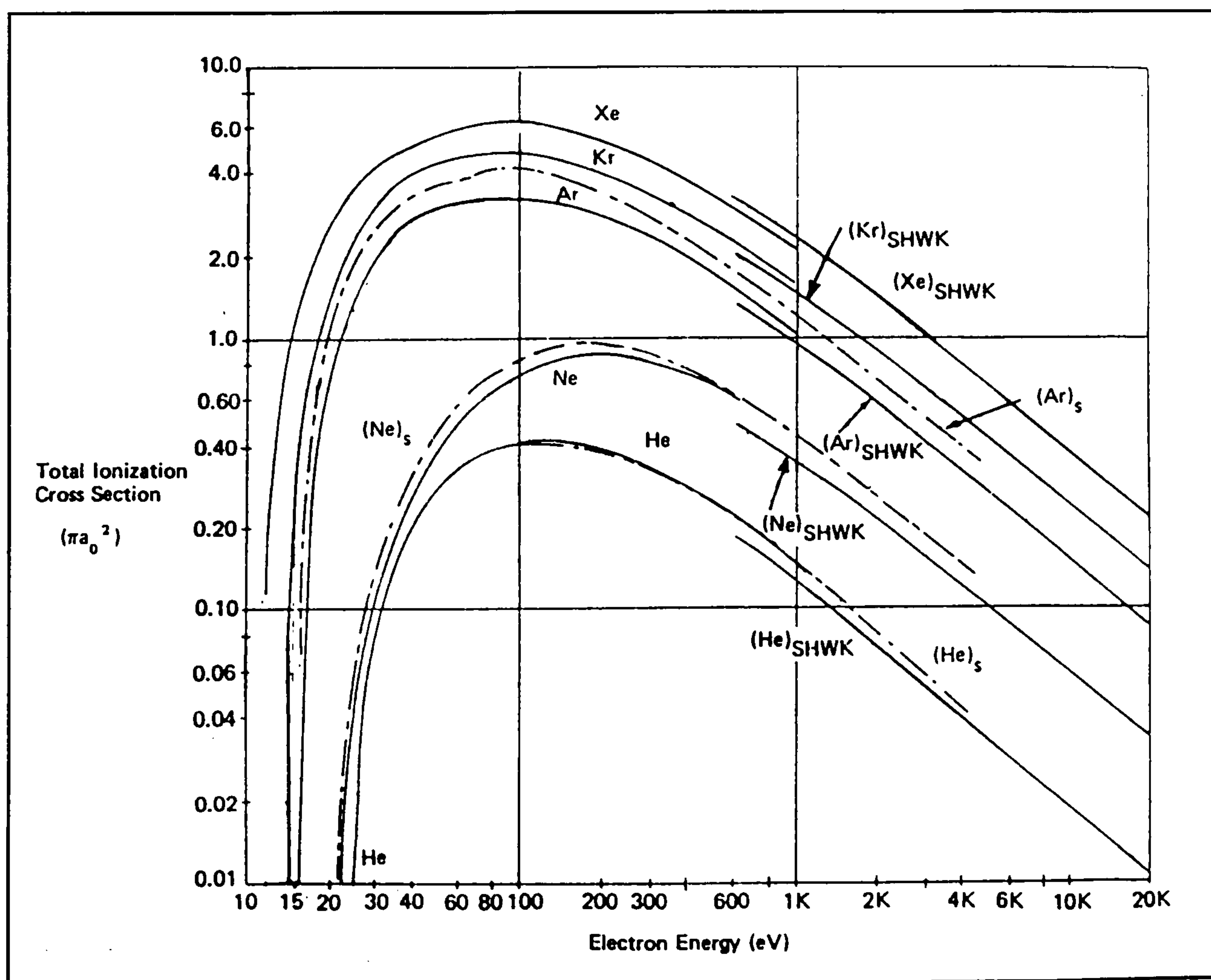


Figure 47: Ionization cross-section of the noble gases¹¹⁰.
 $\pi a_0^2 = 8.82 \times 10^{-17} \text{ cm}^2$

The ionization cross-section increases steeply after the threshold and goes through a maximum. At very high electron velocities, the probability to cause ionization drops off as the time of interaction during the collision decreases.

Electrons with energies less than the ionization potential can induce excitation i.e. raise an outer shell electron to a higher energy level. As with ionization, there is an energy threshold to cause excitation of an atom (11.56 eV for argon). De-excitation or relaxation occurs through the emission of photons and this is responsible for the plasma glow.

Photo-ionization, by the radiation originating from the relaxation of excited species, can be significant. Although the photo-ionization cross sections are less than for electron ionization, photo-ionization is still a major ionizing contributor due to the 'cascade' nature of this mechanism¹¹⁰. The excess energy between the incident radiation energy and that required to cause ionization appears mostly as kinetic energy of the emitted electron .

photoionization:
$$h\nu + \text{Ar} \rightarrow \text{Ar}^+ + e^-$$

The emitted electron leaves the ion with enough energy to cause ionization and the 'hole' left behind can be filled by an electron transition yielding another ionizing radiation.

Ionization through collisions between heavy particles in the plasma body is marginal in the case of cold discharges due to the low energy of the ions and neutrals.

5.2.1.3 Recombination mechanisms

When a gas discharge is established, the ion production rate is balanced by the rate of ion loss via recombinations. In order to recombine with an ion, an electron must lose its excess energy which requires a third body in the vicinity of the electron-ion collision. Recombination occurs mainly at the walls or in the plasma volume through electron attachment. In the former, a solid wall acts as a third body to take up the surplus energy in the form of heat. In the latter, recombination is a two step process. First, the electron attaches itself to a neutral to form a negative ion; then this negative ion collides with a positive ion to form two neutrals.

electron attachment:
$$e^- + \text{O}_2 \rightarrow \text{O}_2^-$$

or dissociative attachment:
$$e^- + \text{O}_2 \rightarrow \text{O}^- + \text{O}$$

ion recombination:
$$\text{A}^+ + \text{O}_2^- \rightarrow \text{O}_2 + \text{A}$$

or
$$\text{A}^+ + \text{O}^- \rightarrow \text{O} + \text{A}$$

To the contrary of noble gases, electronegative gases such as oxygen, chlorine and water vapour are prone to electron attachment¹¹².

The practical implications of this is that, for a given ionization rate, the degree of ionization of an argon discharge potentially depends on the surface-to-volume ratio of the reactor and on the presence of electronegative impurities such as oxygen and water vapour.

5.2.2 Particle-surface interactions

5.2.2.1 Secondary emission

The walls coupled to a gas discharge (chamber walls, electrodes) are subjected to bombardment by energetic electrons, ions and neutrals originating from the plasma volume. Under typical glow discharge conditions, fast ions and electrons upon impact cause secondary emission of electrons from the wall surface. As it will be seen further in the text, these electrons contribute strongly to discharge maintenance.

The energy threshold that must be imparted to an electron so that it has a finite probability to leave the surface is called the work function ϕ . The work function corresponds to the difference between the energy of a free electron E_v and the Fermi level which is the highest energy level that can be occupied by an electron in the surface.

$$e\phi = E_v - E_F$$

The work function has typically a magnitude of a few electron volts.

Action of ions:

Secondary emission of electrons can take place under positive ion bombardment. The energy requirement to eject one electron is then $2e\phi$ since one electron is necessary to neutralize the ion¹¹³.

The secondary emission yield γ_i , defined as the number of electrons emitted per incident ion, depends on the species and energy of the ion as well as on the surface of the emitter. The yield increases with increasing ion energy but, in the ion energy range of interest in glow discharges, it can reasonably be approximated as constant as seen in Figure 48.

The secondary emission yield γ_i does not depend on the temperature of the emitter¹¹³ and is usually taken as 10%.

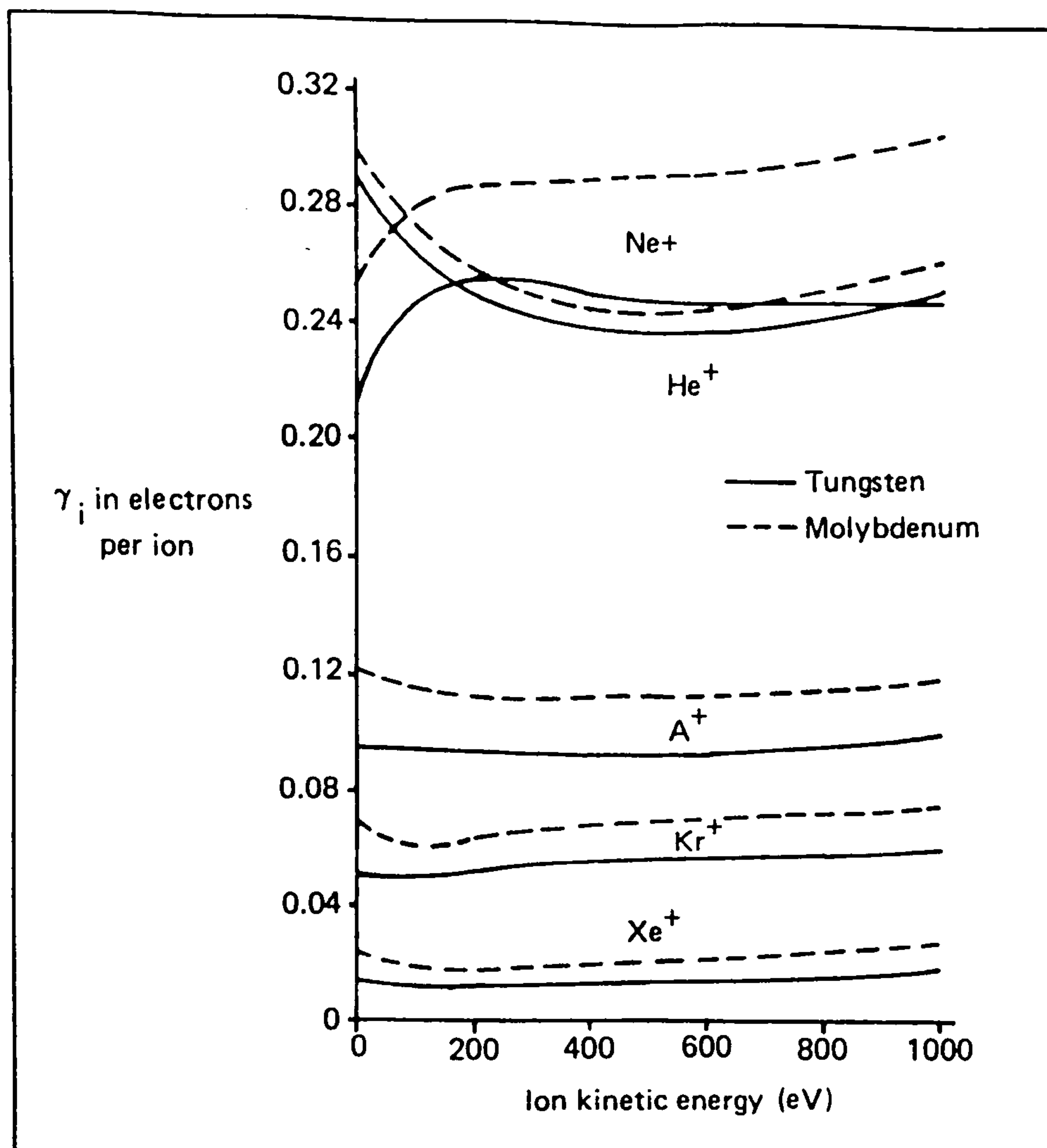


Figure 48: Secondary electron yields γ_i for noble gas ions on atomically clean tungsten and molybdenum¹¹⁰.

Action of electrons:

The energy dependence of the secondary emission yield δ for electron bombardment goes through a maximum. It varies around unity for metals and is higher for insulating materials which leads to the build-up of a positive charge on the surface. The energy distribution of electrons emitted from a surface subjected to beam of monoenergetic electrons consists of the energy distribution of the reflected primaries superimposed on the energy distribution of the secondary emitted electrons¹¹⁴ (see Figure 49). The high energy peak (a) corresponds to the elastically scattered primaries. Secondary electrons are emitted with energies of the order of a few tens of volts irrespective of the energy of the primaries (low energy peak: c).

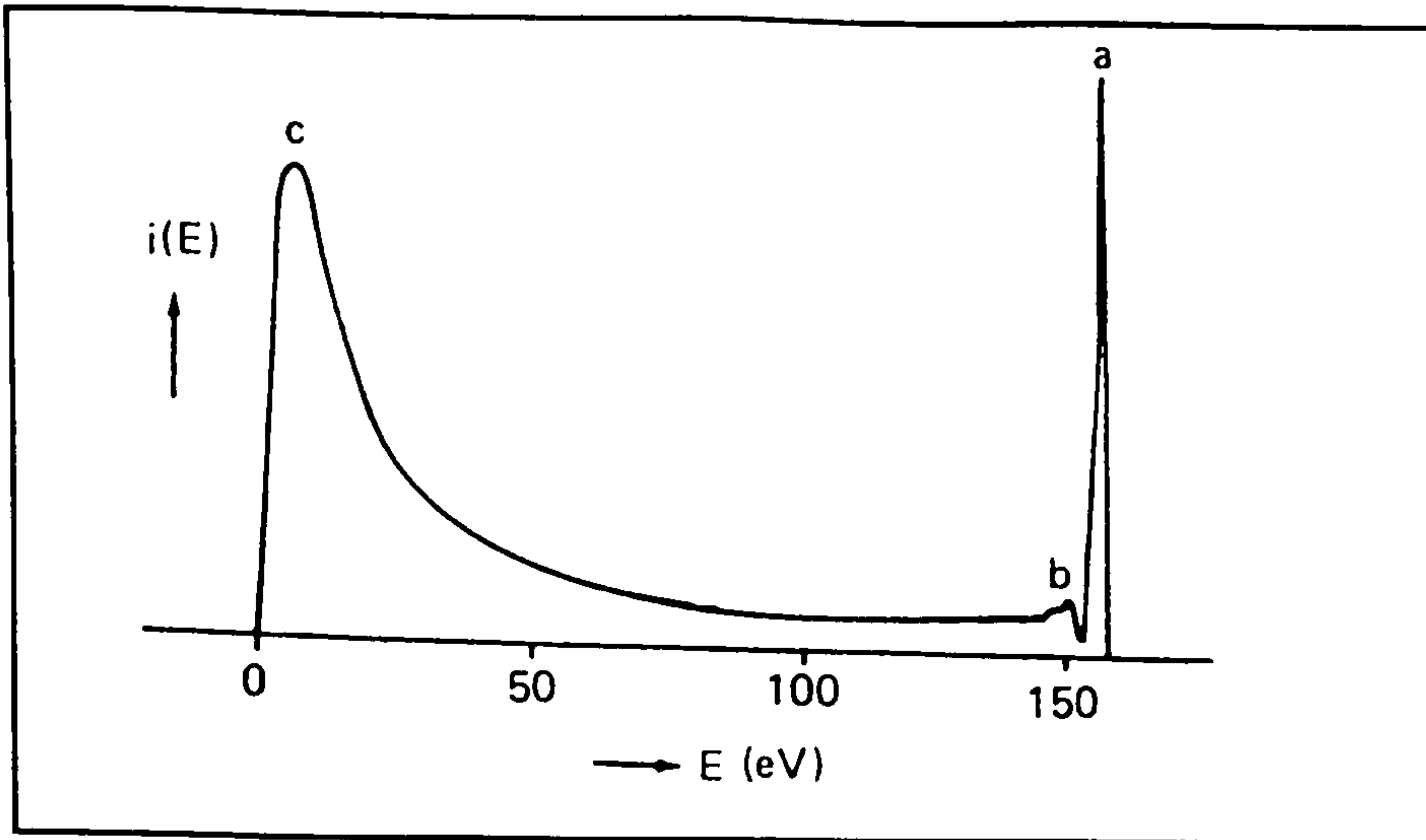


Figure 49: The energy distribution of electrons emitted by silver irradiated with a 150 eV electron beam¹¹⁴

- a: elastically reflected primaries
- b: inelastic reflected primaries
- c: true secondaries

5.2.2.2 Thermionic emission

Electrons can overcome the potential barrier ϕ and escape the surface under the application of heat. This is called thermionic emission. The current density of thermionically emitted electrons increases inasmuch as the magnitude of the work function is low and the energy available to the electron in the form of heat increases. Dushman derived a law that predicts the maximum current density that can be thermionically emitted from a hot surface¹¹²:

$$j_s = AT^2 \exp\left(-\frac{\phi}{kT}\right)$$

where A and ϕ are respectively a constant and the work function, both characteristic of the emitting material. T is the absolute surface temperature and k is the Boltzmann's constant. Dushman's equation predicts the saturation current density which applies when all the emitted electrons actually leave the surface. This situation can be satisfied in the presence of an accelerating electric field. However, departure from this law can be observed for high magnitudes of electric field. Generally, electrons can be drawn out from the surface of a cold material by a very high electrostatic field (field emission). This also holds for a hot surface, thus, a correction must be introduced to the Dushman's law to account for the effect of the field. Schottky demonstrated the field dependence of the thermionic current density to be of the form¹¹⁵:

$$j_{th} = AT^2 \exp\left[-\left(\frac{\phi - \sqrt{e^3 E}}{kT}\right)\right]$$

where E is the electric field in the vicinity of the hot surface and e the elementary charge.

5.3 ELECTRICAL BEHAVIOUR OF A PLASMA

5.3.1 Plasma potential

When a plasma is struck between two electrodes, the potential does not vary linearly across the inter-electrode space. In a glow discharge plasma, the charge concentration is uniformly distributed within the plasma volume. The sum of all the Coulomb interactions tend to cancel and the charges move as free particles. The absence of net electrostatic forces on the charged particles means the plasma is electric field free. In other words, it is equipotential and one refers to the *plasma potential*.

One would expect however that the charge concentrations become uneven down to some scale, leading to local variations in potential. A detailed analysis shows that those potential fluctuations, when they exist, are attenuated over distances of the order of the Debye length¹¹⁰:

$$\lambda_d = \left(\frac{kT_e \epsilon_0}{n_e e^2} \right)^{\frac{1}{2}}$$

where T_e , k , ϵ_0 , n_e , e are respectively the electron temperature, the Boltzmann's constant, the electric permittivity, the electron density and the elementary charge. The electric field is confined in a sphere of a few Debye lengths diameter (tenths of millimeters under typical glow discharge conditions). Outside of this region the plasma is unaware of the perturbation and is equipotential.

5.3.2 Electron and ion energy distributions

Because the electrons are much lighter than the heavy particles, they exchange virtually no energy when they collide elastically with the gas neutrals and ions (see equation (5)). The electron velocity distribution is therefore governed by electron-electron collision events. Given that the plasma is field free, the electrons move at random and their velocity distribution can be considered Maxwellian and thus be described by their temperature. Similarly, given that the ions have the same mass as that of the gas neutrals and that the plasma is virtually field free, the ion velocity follows a Maxwellian distribution characterised by a temperature close to that of the gas. Typically, the electron temperature is 2 eV and that of the gas and ions is 0.03 eV under glow discharge conditions¹¹⁶.

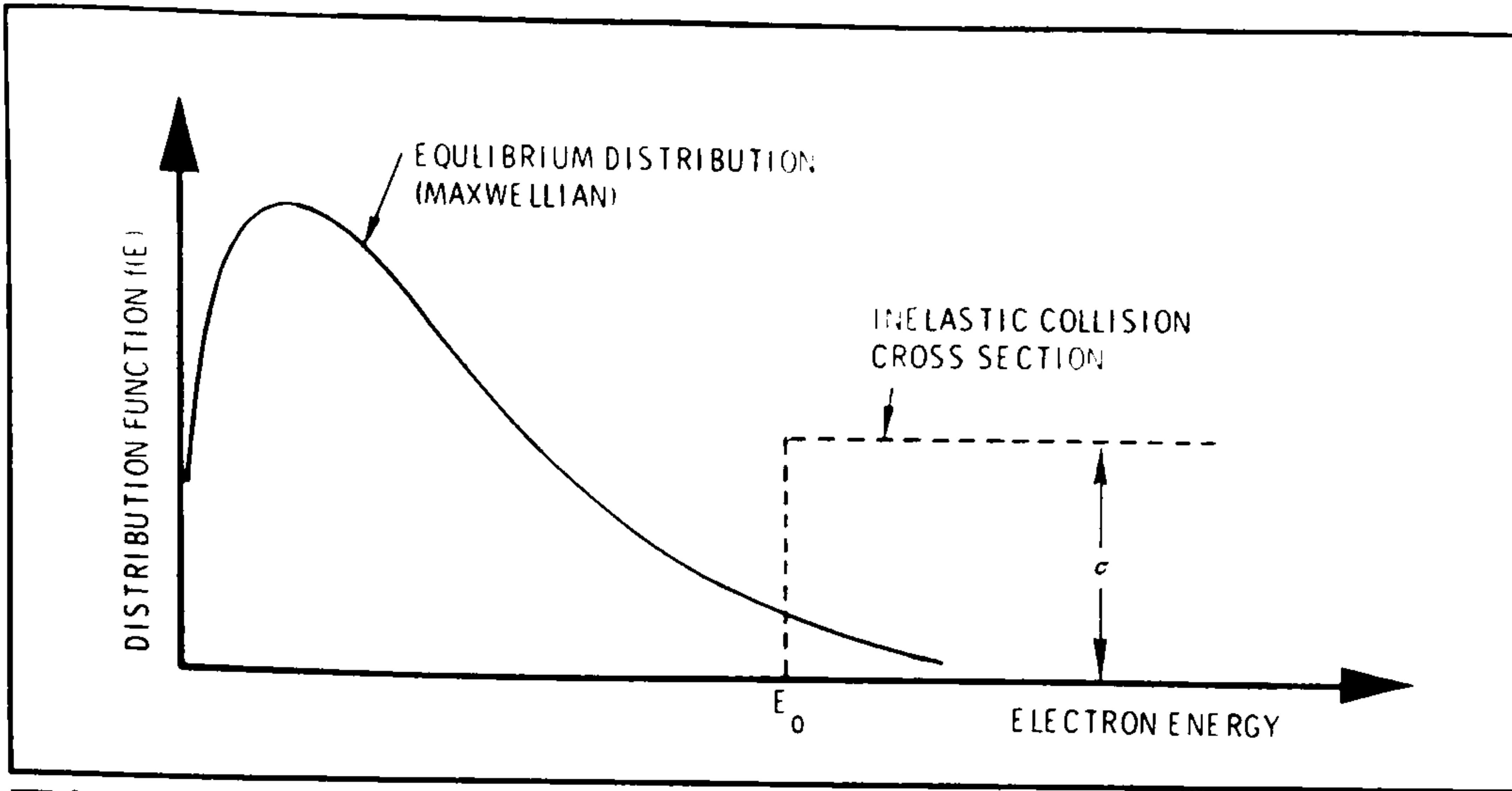


Figure 50: Maxwell-Boltzmann energy distribution¹¹⁷.

The temperature (average energy) of a group of particles relates to their average speed as¹¹²:

$$C = \left(\frac{8kT}{\pi m} \right)^{\frac{1}{2}}$$

where T is their absolute temperature, C their average speed, k the Boltzman's constant and m the particle mass.

In theory, the electron population of the plasma with energies in excess of the ionization threshold should be less than that predicted by the Maxwell-Boltzman distribution given that these electrons loose energy through excitation and ionization collisions (see Figure 50). The effect of these inelastic collisions would be to cut the tail of the electron energy distribution and inflate by an equal amount the electron population around the mean velocity. It is however found experimentally that the electron energy distribution is Maxwellian and this is known as Langmuir's paradox¹¹⁰.

5.3.3 Ion and electron current densities in the plasma

Differences in mass and energy imply that the electrons have much greater velocities than the ions:

$$\frac{C_e}{C_i} = \left(\frac{T_e m_i}{T_i m_e} \right)^{\frac{1}{2}} \quad (11)$$

This ratio is of the order of 10^3 for electron and argon ion temperatures of 2eV and 0.03eV respectively.

The flux density q of a set of particles flowing across an imaginary plane inside the plasma is¹¹⁰:

$$q = \frac{1}{4} n C$$

where n and C are respectively the particle density in the plasma volume and

the mean particle velocity.

As the plasma contains equal concentrations of positive and negative charges, the electron current density in the plasma volume is greater than the ion current density by the same velocity ratio as in equation (11).

5.3.4 Floating potential

Assume that an object is placed in the plasma volume. From the above, it is clear that the electrons will impinge on the surface of the object at a much faster rate than the ions. If the object is floating (electrically isolated), the electrons will collect more quickly than the ions leading to a negative charge build-up. This net negative charge, acting as a potential barrier for the electrons, increases until the electron impingement flux matches that of the ions. Therefore, any floating object in contact with the plasma volume assumes a negative potential relative to the plasma. This potential develops so that the net current flow to the object is zero. It is called the *floating potential* (see Figure 51). The magnitude of the floating potential (potential difference relative to the plasma for which the ion flux balances out the electron flux) can be calculated theoretically and, in practice is no more than a few tens of volts.

5.3.5 Plasma sheath

Due to their high mobility, the electrons tend to leave the plasma to the surrounding walls at a faster rate than the ions, thus creating an electron depleted region at the edge of the plasma in contact with the walls. This positively charged region is no longer a plasma and is called a sheath. The space charge in the sheath allows for the existence of an electric field limiting the outward flow of electrons from the plasma. This raises the plasma potential relative to the wall potential (see Figure 51).

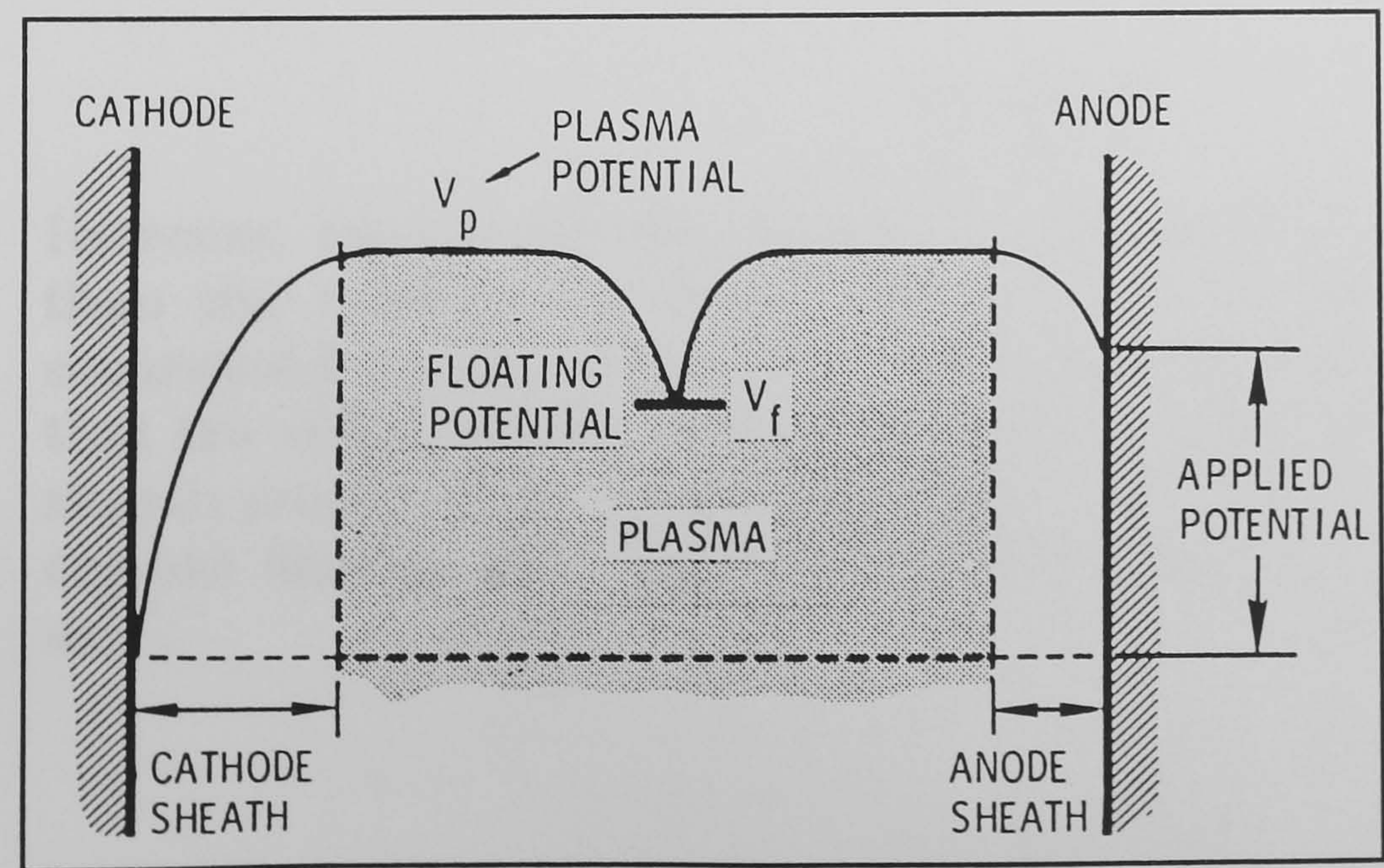


Figure 51: Schematic illustration of the various types of sheaths that form between a discharge plasma and wall surfaces¹¹⁷.

5.3.6 Effect of electric field in the sheath

Note that the effect of the field is to reduce the electron flux impinging on the walls by repelling back into the plasma the electrons that have insufficient energy to overcome the potential barrier across the sheath. The electron current density that impinges on the wall surface is¹¹⁰:

$$J_e = J_{eo} \exp\left(-\frac{V_p - V_{wall}}{kT_e}\right)$$

with

$$J_{eo} = \frac{1}{4} n_e e C_e$$

where J_{eo} is the electron current density crossing the plasma-sheath boundary and $V_p - V_{wall}$ (difference between plasma potential and wall potential) is the potential barrier for electrons also called *sheath potential*.

To the contrary, the electric field in the sheath accelerates every ion that happens to cross the plasma-sheath boundary which results in ion bombardment of the walls. Ionization in the sheath can be ignored¹¹⁰, therefore the ion flux density impinging on the walls equals that entering the sheath.

5.3.7 The Bohm's criterion

One could first expect that the ion current density received by a surface coupled to the discharge corresponds to the random ion current density in the plasma:

$$J_i = \frac{1}{4} n_i e C_i$$

However, the ion current drawn in practice from a DC discharge is greater than the random ion flux¹¹⁰. This is due to the fact that the sheath is separated from the plasma by a quasi-neutral region of low electric field and that the effect of this region is to increase the velocity of ions entering the sheath proper. This is known as the *Bohm sheath criterion*¹¹⁰. The actual ion current density entering the sheath is coupled to the electron temperature as¹¹⁷:

$$J_i \sim 0.6 e n_i \left(\frac{kT_e}{m_i}\right)^{\frac{1}{2}}$$

where T_e , e , k , n_i and m_i are respectively the electron temperature, the elementary charge, the Boltzmann's constant, the ion density in the bulk

plasma and the ion mass (see Figure 52).

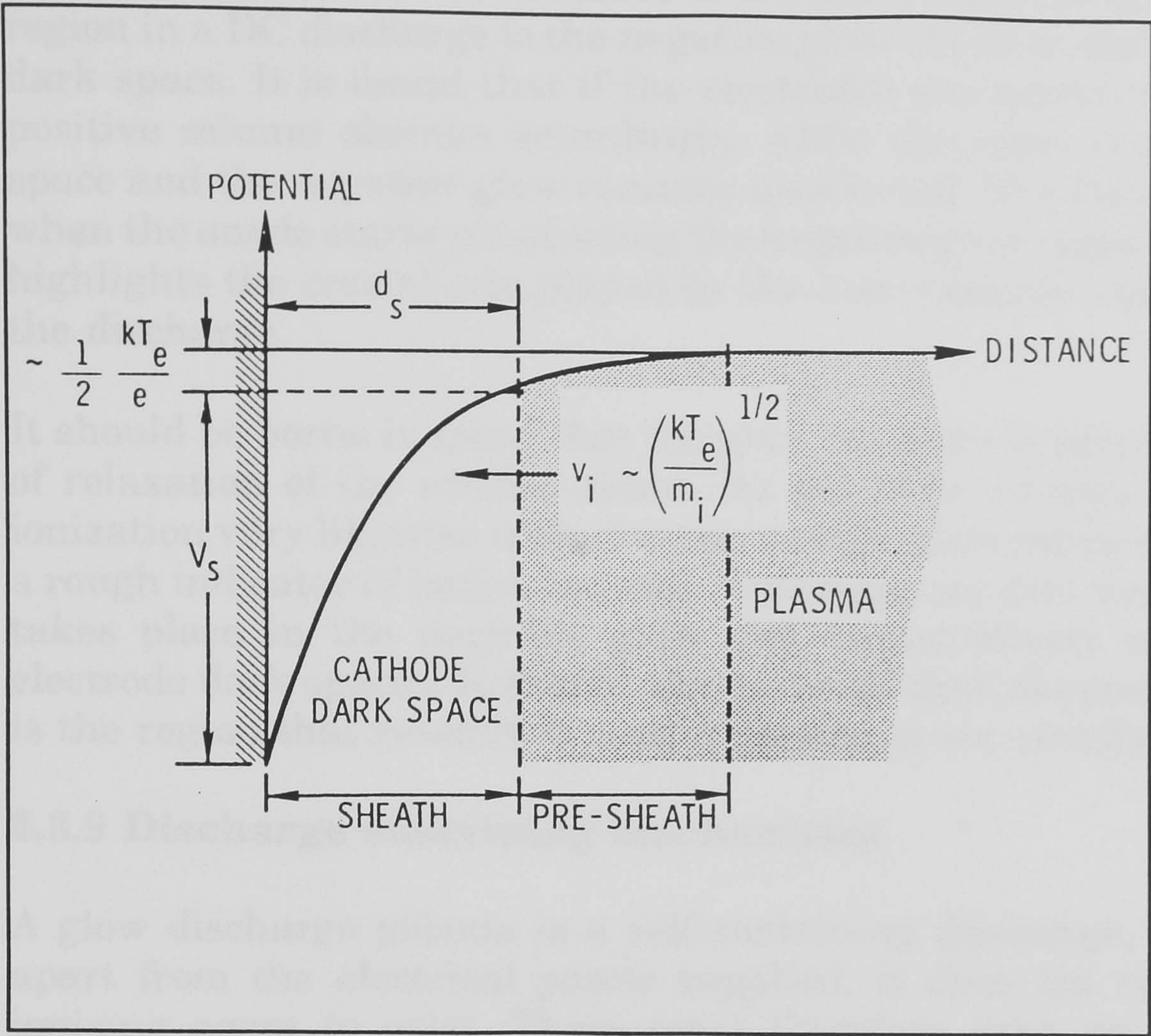


Figure 52: Regions of cathode sheath¹¹⁷

5.3.8 Structure of a DC plasma

In the above, the structure of a glow discharge was described as a two region system consisting of the body of the plasma which is equipotential and the plasma sheaths where the potential gradient is found. Reality is however more complex. Glow discharges generated between two planar electrodes in a glass tube have been used to study the detailed structure of glow discharges. DC discharges consist of alternate light and dark regions. As many as nine distinctive regions were observed¹¹² depending on the gas and the pressure used. Figure 53 shows these regions with their relative glow intensity, voltage and charge distributions.

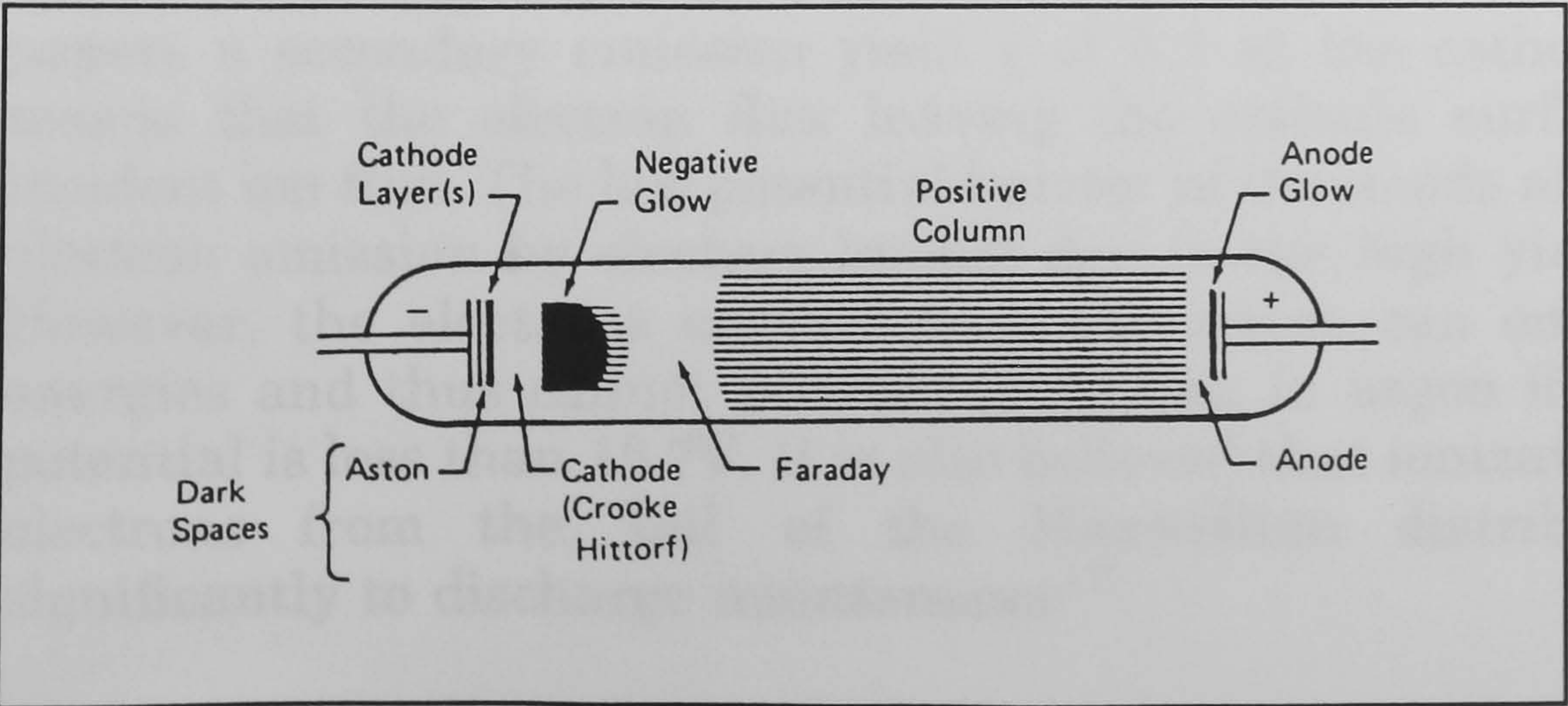


Figure 53: The glow discharge in Neon¹¹².

The plasma sheaths were defined as regions near the walls that are no longer equipotential. These are inclusive of the electrode dark spaces. The brightest region in a DC discharge is the negative glow which is adjacent to the cathode dark space. It is found that if the electrodes are moved closer together, the positive column shrinks accordingly, while the space occupied by the dark space and the negative glow remains unaffected. The discharge extinguishes when the anode starts penetrating the negative glow region¹¹². This behaviour highlights the crucial role played by the near cathode region in maintaining the discharge.

It should be borne in mind that the glow intensity is proportional to the rate of relaxation of the excited atoms. As the cross sections for excitation and ionization vary likewise with electron energy, glow intensity is often taken as a rough indicator of ionization rate. This suggests that most of the ionization takes place in the negative glow and comparatively none occurs in the electrode dark spaces. It should also be noted that the positive column which is the region that resembles most a plasma is not strictly equipotential.

5.3.9 Discharge sustaining mechanisms

A glow discharge plasma is a self-sustaining discharge, which means that apart from the electrical power supplied, it does not require an external ionizing agent to exist. There must therefore exist an ionization process inherent to the discharge to compensate for the charged particles lost by outward flow to the walls and by volume recombination.

The major sustaining mechanism of a DC glow discharge plasma is secondary emission of electrons from the walls originating from ion bombardment. These electrons are accelerated in the sheaths and enter the body of the plasma with high energies undergoing multiple ionizing collisions. Under most situations, the mean free paths of these electrons for excitation or ionization are greater than the sheath length. Hence the 'darkness' of the plasma sheaths. As the secondary emitted electrons do not lose energy in transit through the sheaths, they form a monoenergetic beam with the full sheath potential as energy and the lines of field as directions. The electrons emitted from the cathode acquire energies of the order of the negative bias applied, which varies typically from a few hundred volts to a few kilovolts. In most papers a secondary emission yield γ_i of 0.1 at the cathode is used, which means that the electron flux leaving the cathode surface is 10% of the incident ion flux. The low potential barrier at the anode allows for secondary electron emission by electron impact due to the high yield of this process. However, the electrons emitted from the anode can only acquire limited energies and thus cannot produce ionization in argon if the anode sheath potential is less than 15.7V. It is also believed that ionization by the thermal electrons from the 'tail' of the Maxwellian distribution contributes significantly to discharge maintenance¹¹⁰.

5.3.10 Incident ion energy distribution

If the transit of ions through the plasma sheaths were collisionless, they would all impinge on the surface with the same kinetic energy equivalent to the full sheath potential (assuming rightly that the initial ion energies are negligible comparatively to the sheath potential). In most glow discharge conditions, the sheath length is of the same order of magnitude as the mean free path of the ions¹¹⁸. This implies that a considerable proportion of the accelerated ions undergo collisions with the neutrals and thus impinge on the cathode with reduced energies (see Figure 54).

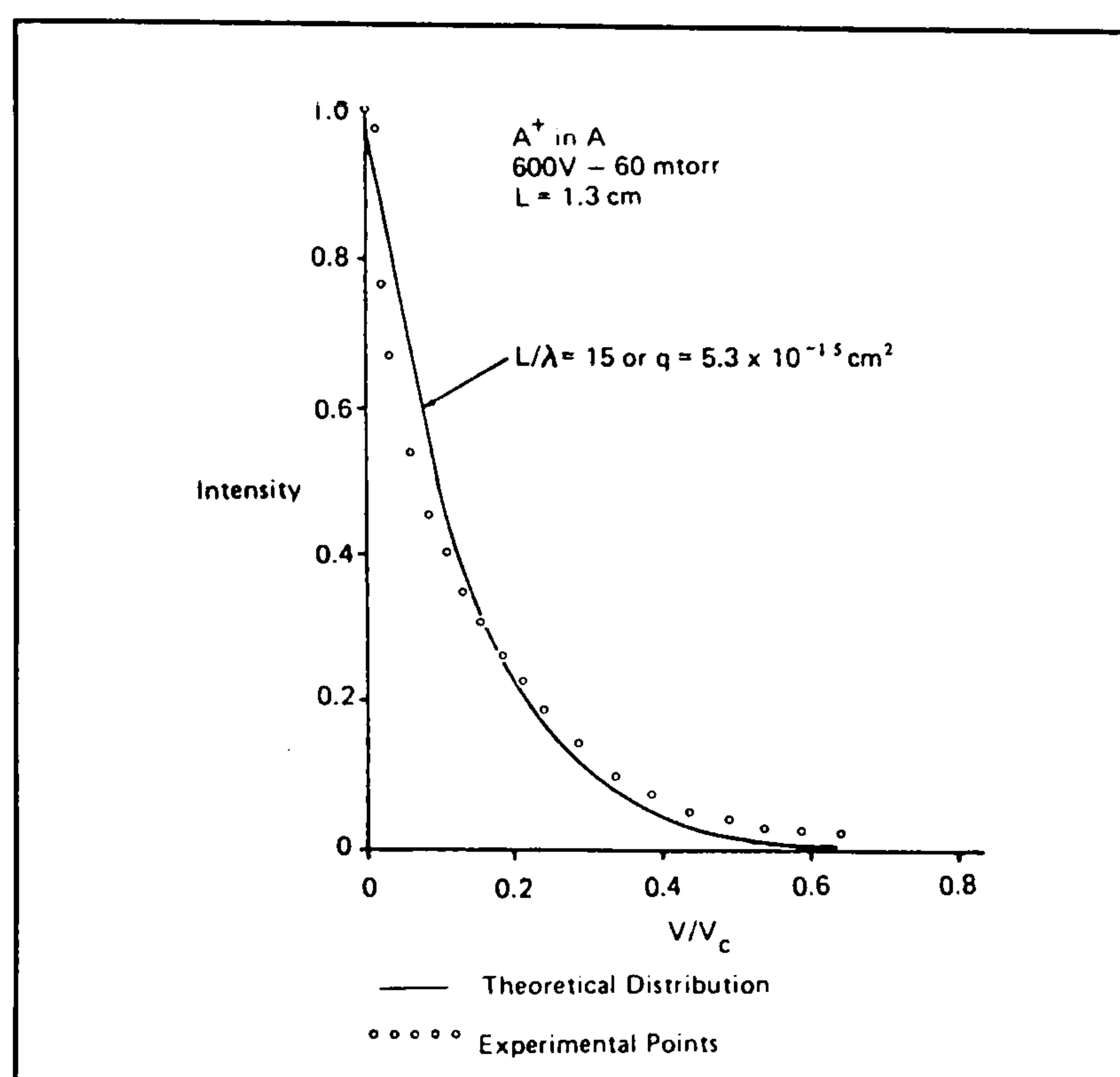


Figure 54: Energy distribution for Ar⁺ from an argon gas discharge¹¹⁹.

The work of reference by Davis and Vanderslice¹¹⁹ demonstrated the dominant effect of charge exchange collisions in reducing the energies of the ions in transit through the sheaths. In a symmetrical charge exchange collision, an accelerating ion yields its positive charge to a parent atom, creating a fast neutral and a newly formed ion:



If this newly formed ion does not collide, it will reach the surface with an energy corresponding to the potential at the point where it originated, which is necessary less than the full sheath potential. If the fast neutrals stay directional towards the surface after colliding, then the effect of charge exchange collisions is to increase the flux of fast particles on the surface, while reducing the average particle energy.

5.4 FEATURES OF RF GLOW DISCHARGE PLASMAS

In practice, glow discharge processes are almost always driven by high frequency power supplies, usually in the megahertz range¹¹⁰. RF discharges have the advantage over DC discharges of allowing plasma processing of non-conducting surfaces which is why low temperature ion plating of ZrO_2 cannot be envisaged using DC biasing. The treatment of RF discharges is more complex than DC discharges and in spite of increasing research activities in this field, there remains much that is poorly understood or even misunderstood¹²⁰. The object of this section is to describe some of the features of RF discharges that are broadly accepted in the literature and that are relevant to chapter 7.

5.4.1 Effect of frequency on discharge maintenance

If the frequency of the applied voltage is increased, it is observed that the minimum pressure at which the discharge can operate is gradually reduced, the effect being detectable from about 50kHz and leveling off for frequencies of a few MHz¹²¹. This indicates that there is an additional source of ionization other than secondary electron emission as in the case of a DC plasma. The additional sustaining mechanism invoked for RF plasmas is the ability of electrons to gain energy from colliding with the oscillating plasma sheath boundary. The greater the frequency, the greater the sheath velocity and thus the greater the velocity gained by the electrons colliding with the sheath. Low frequency discharges (such as 380kHz) are believed to be maintained primarily by secondary electron emission from ion impact of electrode surfaces^{122,123,124}. The sustaining voltage is high at low frequency and low at high frequency. This is because the loss of the charged particles from bulk plasma is small at high frequencies, as compared with the loss at low frequency, so that high voltages are not required to sustain the plasma¹²⁴.

5.4.2 DC offset

When an RF discharge is struck via an external capacitor or an electrode covered with a dielectric surface, it is found that a negative DC self bias develops on the electrode to which the RF voltage is applied (see Figure 55). This DC potential, a result of a negative charge build-up, reduces the portion of time of the RF period over which electrons from the plasma can impinge on the driven electrode, so that the net flow of charges over a complete RF cycle is zero.

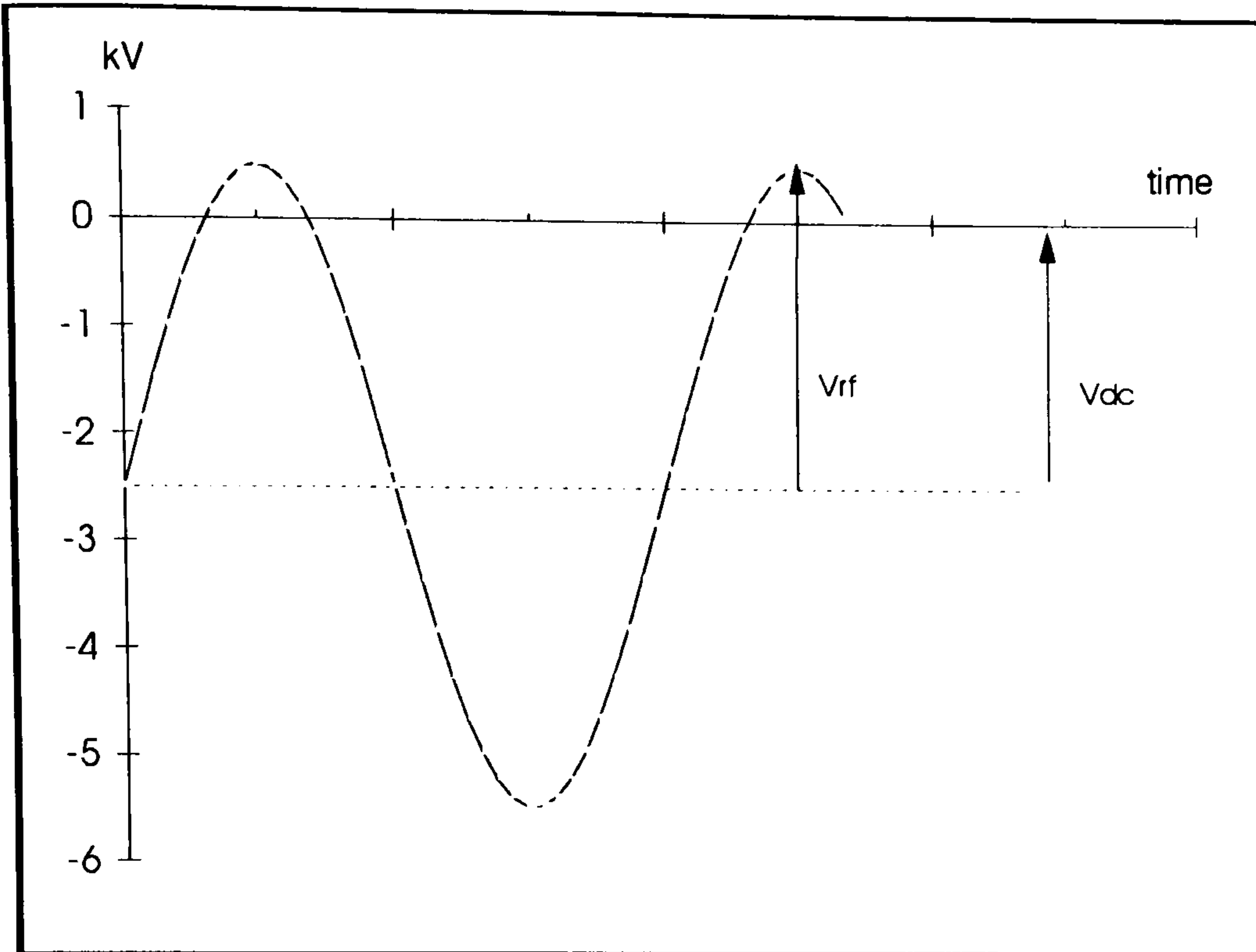


Figure 55: Electrical potential on a capacitively RF driven electrode showing the effect of the self DC bias.

Koenig and Maissel¹²¹ derived a relationship between the time-averaged sheath potentials and the electrode areas, well known as the fourth power law. However, it has been shown that the fourth power law is not obeyed experimentally^{110,125}.

More recently, Song, Field and Klemperer¹³³ formulated a relationship between the applied RF voltage and the DC offset to the relative electrode areas:

$$\frac{V_{DC}}{V_{RF}} = \sin\left(\frac{\pi}{2} \times \frac{A_{ANODE} - A_{CATHODE}}{A_{ANODE} + A_{CATHODE}}\right) \quad (17)$$

which was substantiated with success for a range of experimental data from independent investigators. The implication of the DC offset on the power dissipation will be discussed in chapter 7 where a formulation of the power density of bombardment is proposed for low frequency RF discharges. Also the basis of the derivation of the above equation after Song et al will be used in the same chapter in order to discuss the interaction between the RF discharge and the electron beam source.

5.4.3 Effect of frequency on ion energy and fluxes

There has been a powerful drive in the last ten years to better predict the ion energy distribution (IED) incident on surfaces processed using reactive ion etching. Bruce¹²⁶ studied the effect of excitation frequency on the maximum energy achieved by the ions accelerated in the RF sheath and thereby

highlighted the significance of the ion transit time (ITT) on the energy achieved by the ions. At low frequencies, the ions cross the sheath in times short comparatively to the oscillation period and are accelerated by the instantaneous sheath fields. As the frequency is increased, the maximum ion energy achievable is reduced as the ions are increasingly subjected to time averaged fields (see Figure 56).

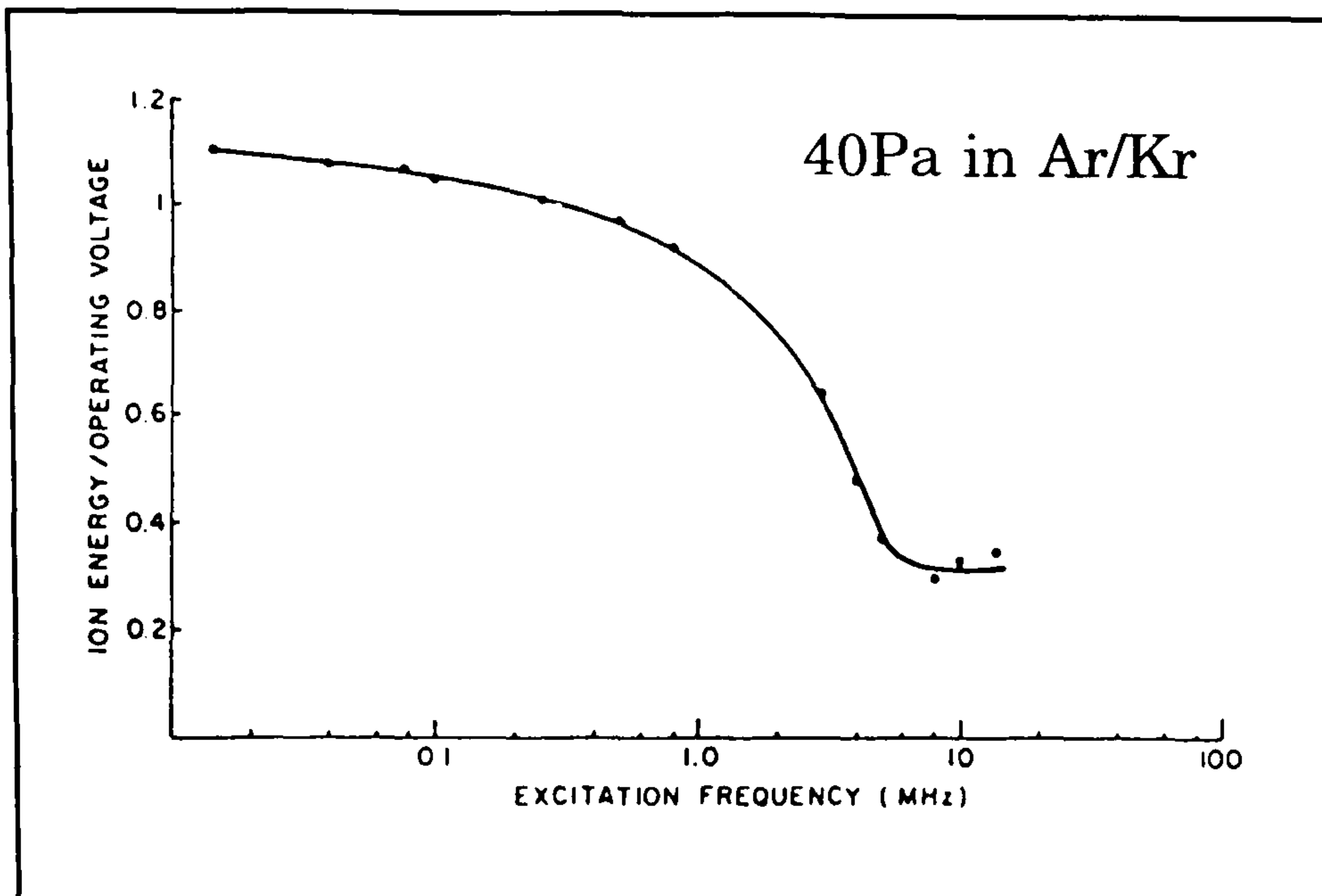


Figure 56: Ratio of maximum ion energy incident on grounded electrode to the applied voltage amplitude versus frequency¹²⁶.

It can be seen from the above figure that at 380kHz, it is reasonable to assume that the ions sense the instantaneous sheath field ($ITT < RF$ period). This assumption will be used in chapter 7. The role of ITT on the ion energy distribution has also been highlighted at a set frequency using different ion masses (see Figure 57).

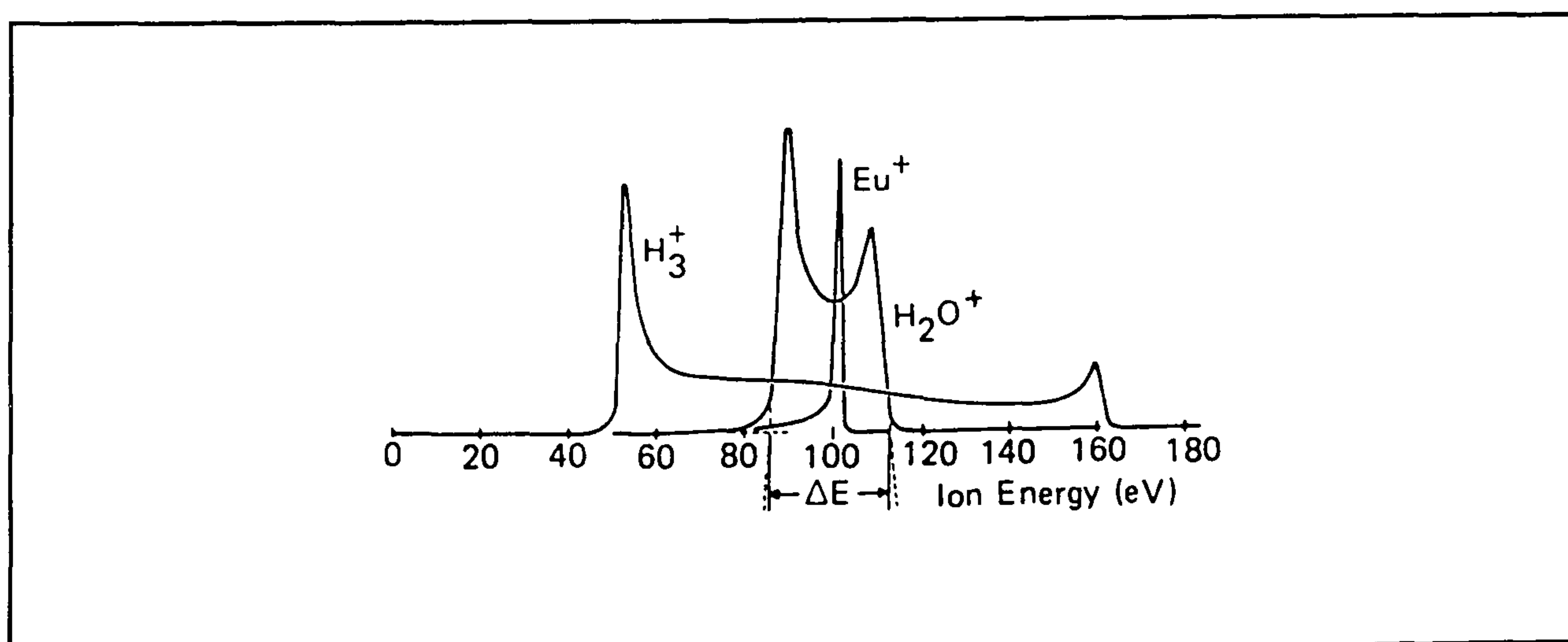


Figure 57: Energy distributions of H_3^+ , H_2O^+ and Eu^+ at the substrate from a 13.6MHz discharge¹¹⁰.

For a given RF voltage and frequency, the ion transit time decreases with decreasing ion mass which results in broadening of the ion energy distribution. This effect is referred to as RF modulation¹³⁴. The effect of ITT on

current is that at a low frequency, the ion current is strongly modulated and that at high frequencies the ion current shows little modulation^{127,2}. At a low frequency (e.g. 380 kHz), the ion current is believed to increase in phase with the sheath voltage and this is because the ions in transit through the sheath are accelerated by the increasing sheath field¹²⁸. Besides these studies focused on IED's, May, Field and Klemperer¹²⁹ modelled the effect of both momentum transfer and charge exchange collisions between ions and neutrals and concluded that the fast neutrals in the RF sheath formed the overwhelming contribution to the numbers of energetic particles striking the cathode. The role of fast neutral bombardment must be therefore taken in earnest.

The RF sheaths may be represented electrically by a non-linear resistor in parallel with a capacitance. Charge flow across the sheath constitutes the conduction current whereas the cyclic charging and discharging of the capacitance constitutes the reactive current^{122, 128}. At high frequencies, the sheaths are primarily capacitive whereas at low frequencies, the sheaths are more resistive in nature[?].

The plasma potential is no longer constant in RF discharges. The functional form of the plasma potential ($V_p(t)$) is sinusoidal for purely capacitive sheaths ($>10\text{MHz}$) whereas, at lower frequencies, $V_p(t)$ tends to follow the positive excursions of the electrode voltage $V(t)$ (see Figure 58).

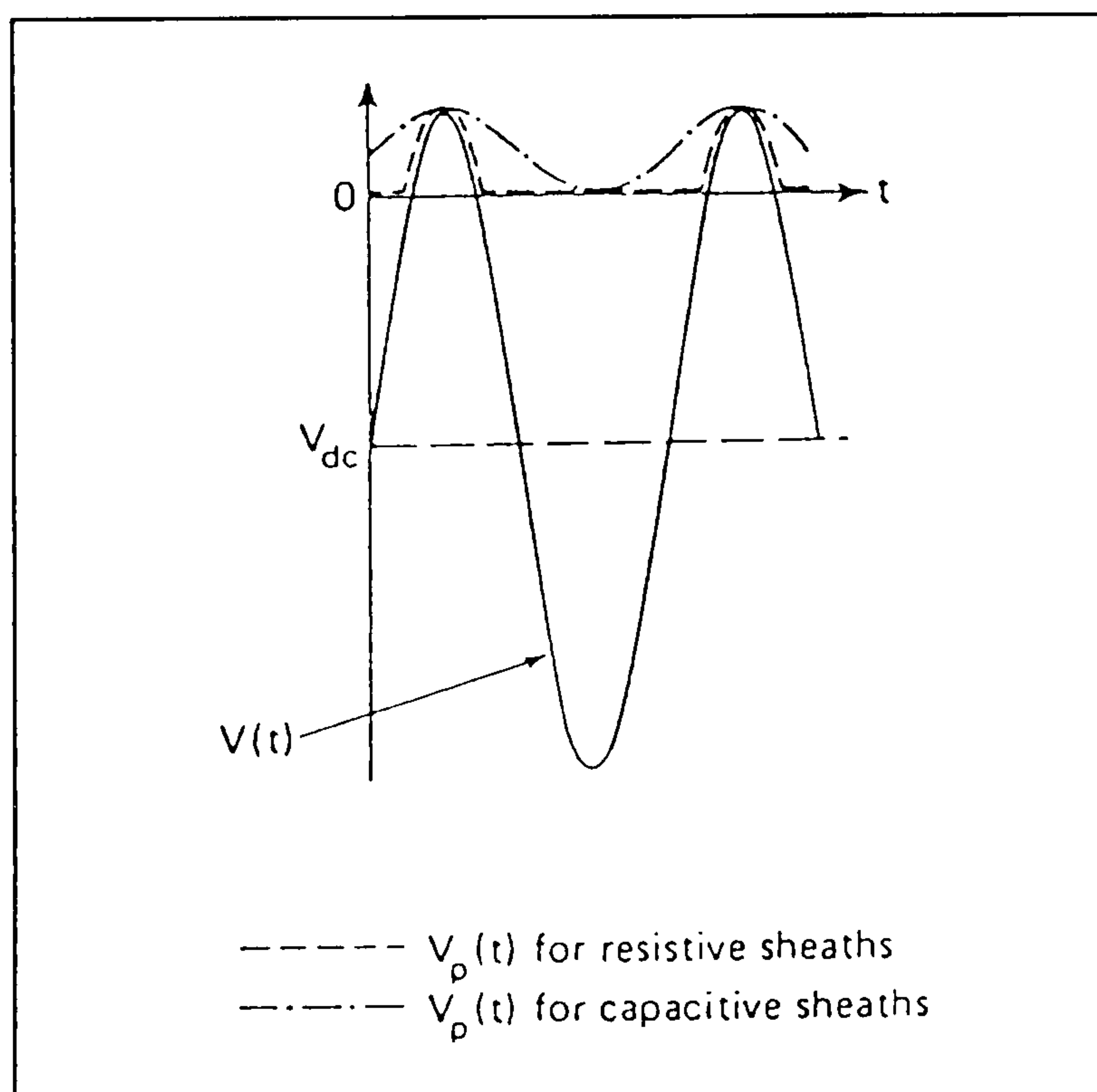


Figure 58: Illustration of the plasma potential for both resistive and capacitive sheaths in a capacitively coupled RF discharge.¹³⁴

6 EXPERIMENTAL PROCEDURE

6.1 DETAILS OF COATING PROCESS

6.1.1 The Electrotech CL ion plater

The Cranfield ion plater was designed and built by Electrotech in the early eighties. It consists of a commercial CL evaporator, customized to incorporate a differentially pumped electron beam gun assembly (see Figure 59). The processing chamber consists of a 1mx1mx1m cube with stainless steel walls. The chamber walls are earthed and the power is capacitively coupled and fed to the driven electrode from the top of the chamber. The RF power supply is a 380kHz Electrotech generator nominally capable of delivering 6kW power. The tuning of the impedance matching network was set from the time the ion plater was commissioned and no further tuning was made available to the operator.

Gases such as argon and oxygen can be bled via mass flow controllers to chamber pressures up to 10^{-2} Torr monitored by a Baratron. To allow evaporation at such high pressures, the electron beam gun assembly is placed in a separate chamber underneath the reactor, which is differentially pumped to below 10^{-4} Torr. For each chamber, pumping relies on a diffusion pump in line with a rotary pump.

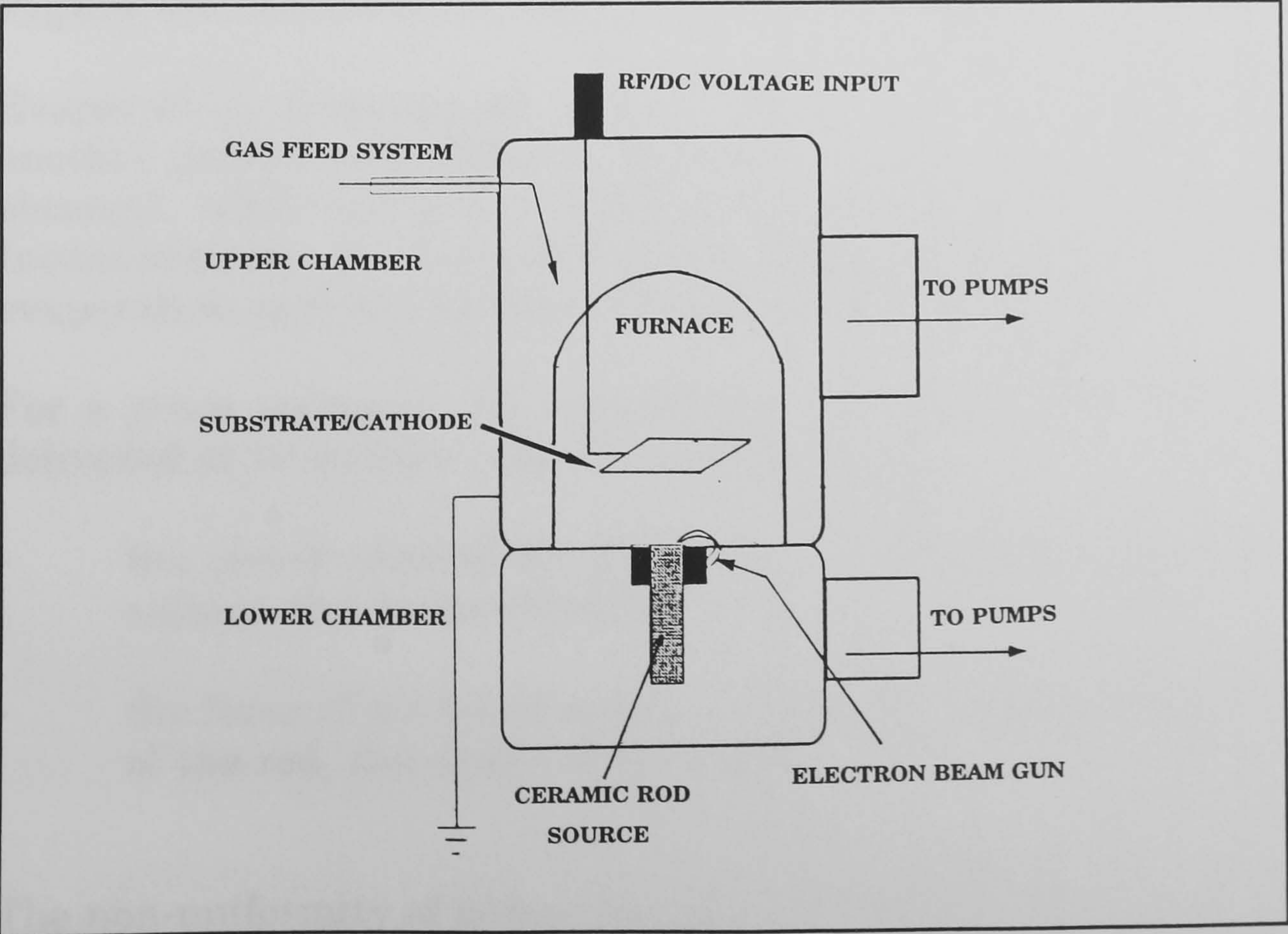


Figure 59: Schematic of the Cranfield ion plater.

6.1.2 Evaporation source

The evaporant source material was 8wt%Y₂O₃-ZrO₂ ingot rod (2.54cm diameter) purchased from Daichi in Japan.

The rod sits in the center of a water-cooled copper hearth and is clamped at its bottom to a driving mechanism allowing simultaneous rotation and upright translation (see Figure 60). The electron beam gun is of the 270° type, which means that it is out-of-sight of the vapour generated. It can operate nominally at a beam current of 1.5A and at an accelerating voltage of 10kV. The beam can be scanned over the rod surface longitudinally and laterally.

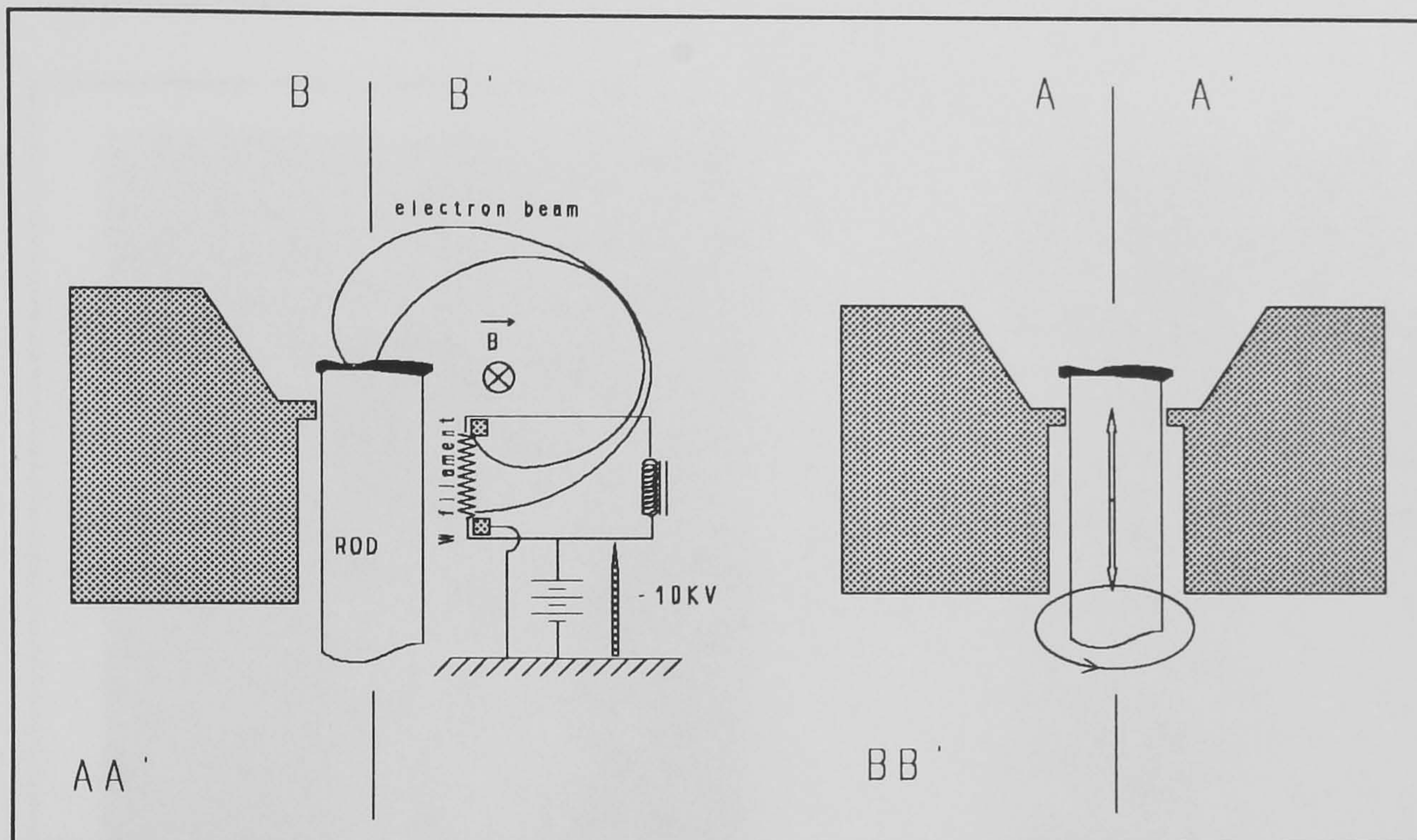


Figure 60: Schematic of rod-fed electron beam gun.

Evaporating at consistent rates throughout a run and from one run to another proved very difficult. Extreme scatter in deposition rate could be obtained while using the same accelerating voltage and beam current. Inconsistencies in deposition rates originated from variations both in evaporation rate and in directionality of the vapour flux.

For a given material, the evaporation rate depends on the power density delivered at its surface, which is a function of:

- the power carried by the beam i.e. the product of the accelerating voltage and beam current.
- the focus of the beam on the rod surface, which depends on the height of the rod, the shape of the beam, etc...

The non-uniformity of power density and time of residence of the beam over the melt surface leads to the formation of peaks and troughs, due to the low thermal diffusivity of zirconia. Once the melt surface geometry is no longer

planar, a significant amount of the vapour flux is emitted away from the substrates. As a result, the deposition rate is lowered as less vapour flux is intercepted by the substrates.

The key to consistency in deposition rate, for a given beam power level, is to maintain the melt surface even and at a constant height. This was achieved by proper longitudinal scanning of the beam over the rod surface in conjunction with rod rotation. The melt level was monitored by eye through a port and the rod was raised accordingly to compensate for the amount of rod evaporated. Figure 61 compares from left to right the surface melt geometries resulting from hectic and satisfactory evaporation conditions respectively.

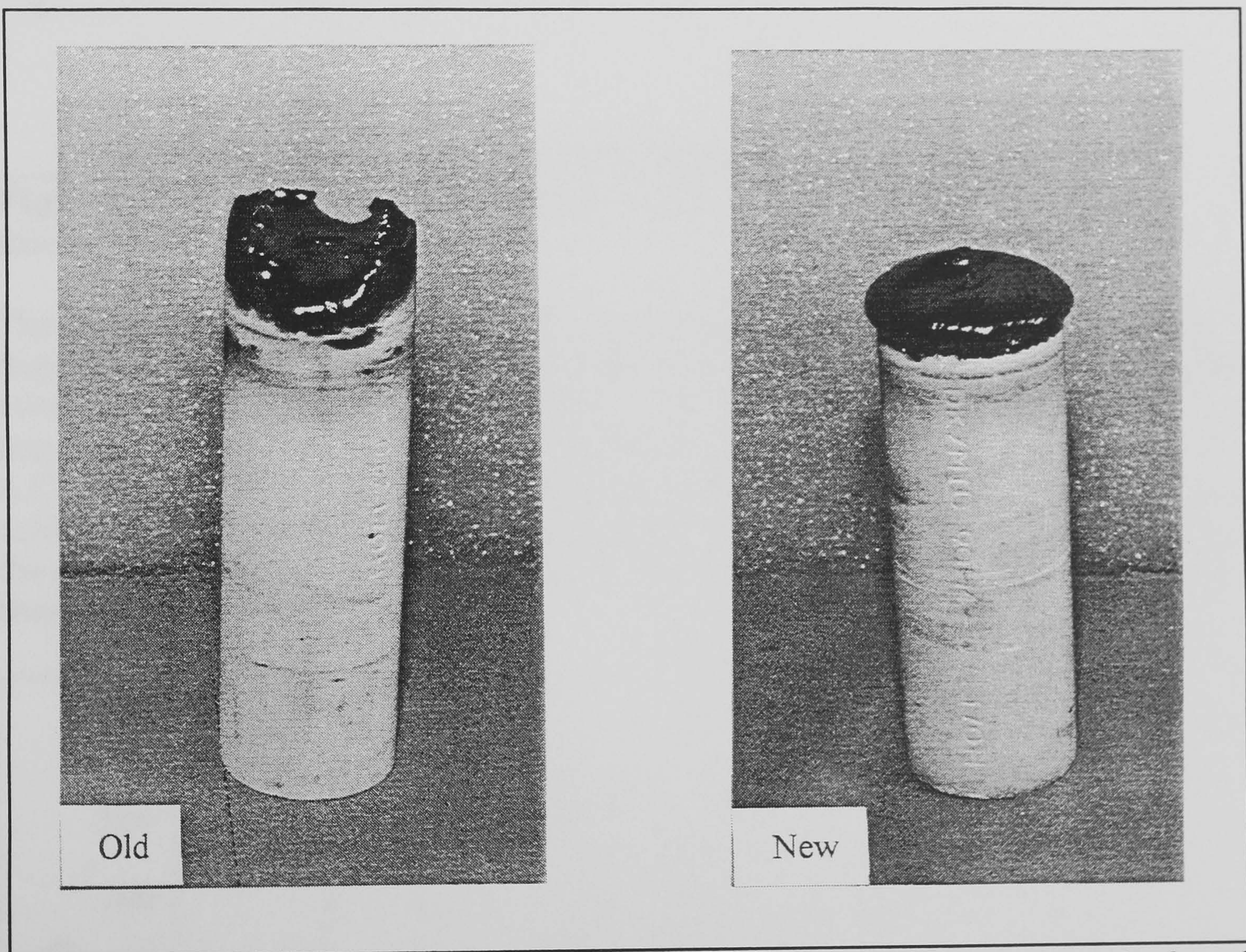


Figure 61: Comparison of melt surface geometries resulting from bad and ideal evaporation conditions.

6.1.3 High temperature deposition capability

6.1.3.1 Resistive heating of substrates

In the early stages of the work, the Cranfield coatings group did not possess a high temperature facility to carry out vacuum depositions with. To study the effect of temperature on the properties of the deposits, the approach usually used is to mount the specimens on a resistively heated support^{66,63}.

The approach chosen in the present work differed slightly in that the substrate itself was resistively heated. The constraint imposed on the specimens is that they need to have a small cross-section. In order to investigate the role of temperature over a range, the substrates were made tapered so as to generate a temperature gradient across them. The dimensions of the so-called 'dog-bone' shaped substrates, cut out from 1.5 mm thick Nimonic 75 sheets, are given in Figure 62.

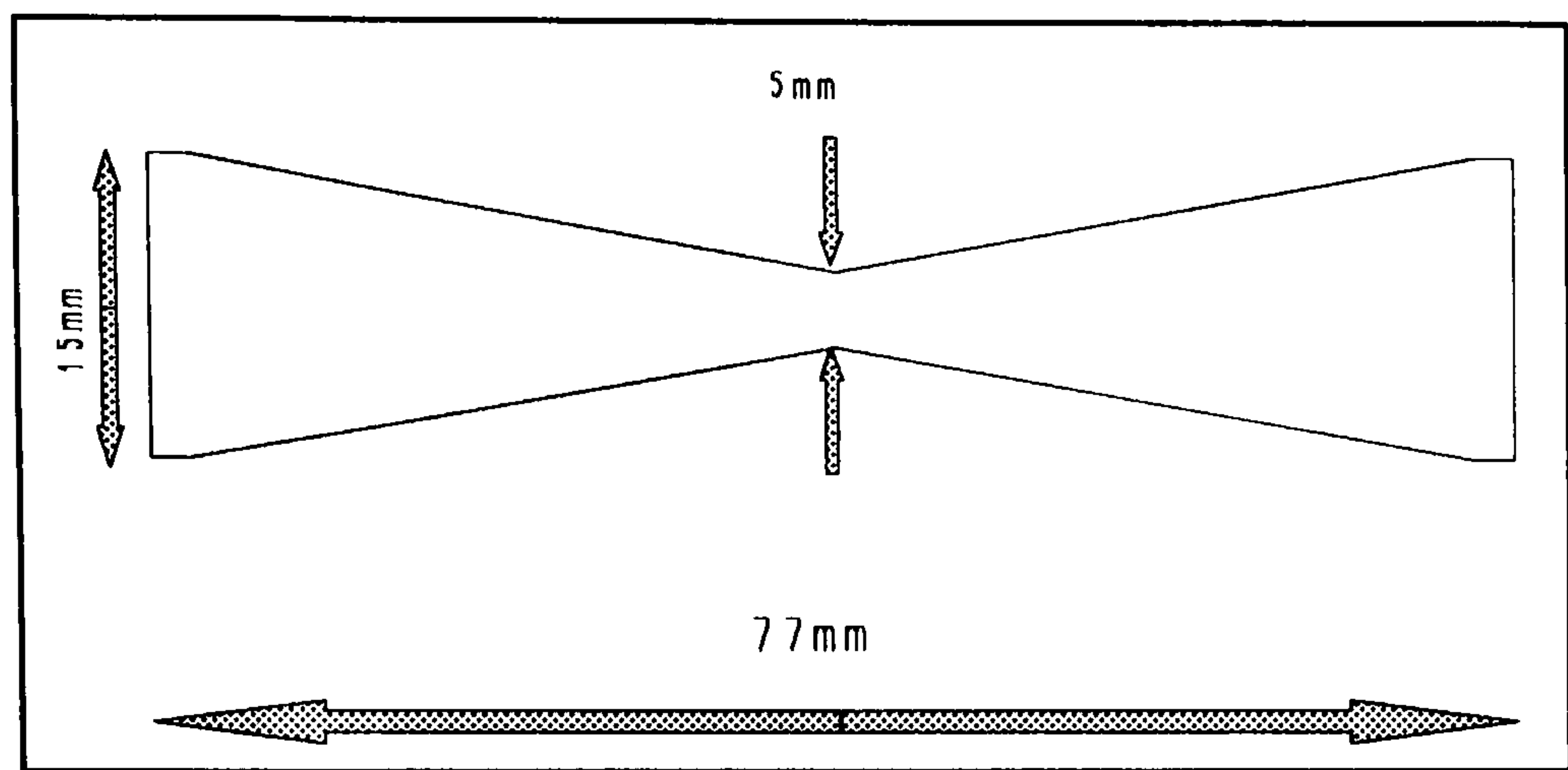


Figure 62: Dimensions of 'dog-bone' substrates, thickness = 1.5mm.

The specimen holder jig consisted of two bulky copper electrodes clamping the dog-bone from both ends. These clamps had the same geometry and overlapped with the substrate material by 3mm each (see Appendix 2). The dog-bone substrates were heated using a low voltage (5V), high current (150A) A.C. supply. The temperature profile obtained across the specimen was calibrated in vacuum for different current levels, using K-type 0.5mm wire thermocouples spot welded on the surface. Figure 63 shows the results from these calibration runs.

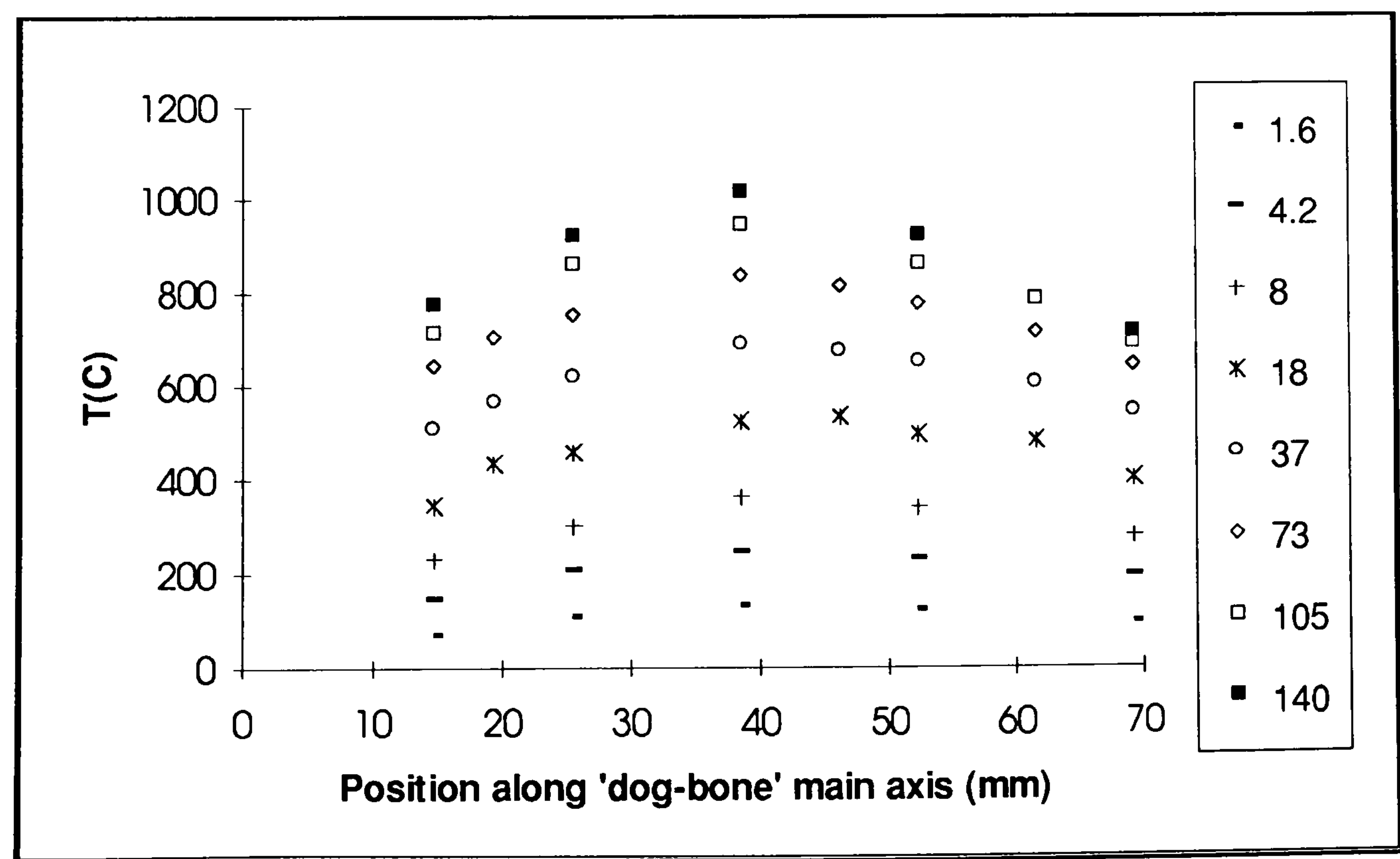


Figure 63: Temperature profile over 'dog-bone' substrates as a function of heating current (A).

The maximum current (140A) was used in practice generating a [650-1000°C] working temperature range.

Applying high RF voltages to the substrate meant that the heating power supply had to be isolated from the mains. To achieve this, the heating transformer was floated and powered by an isolation transformer with an RF filter in between (see Figure 64).

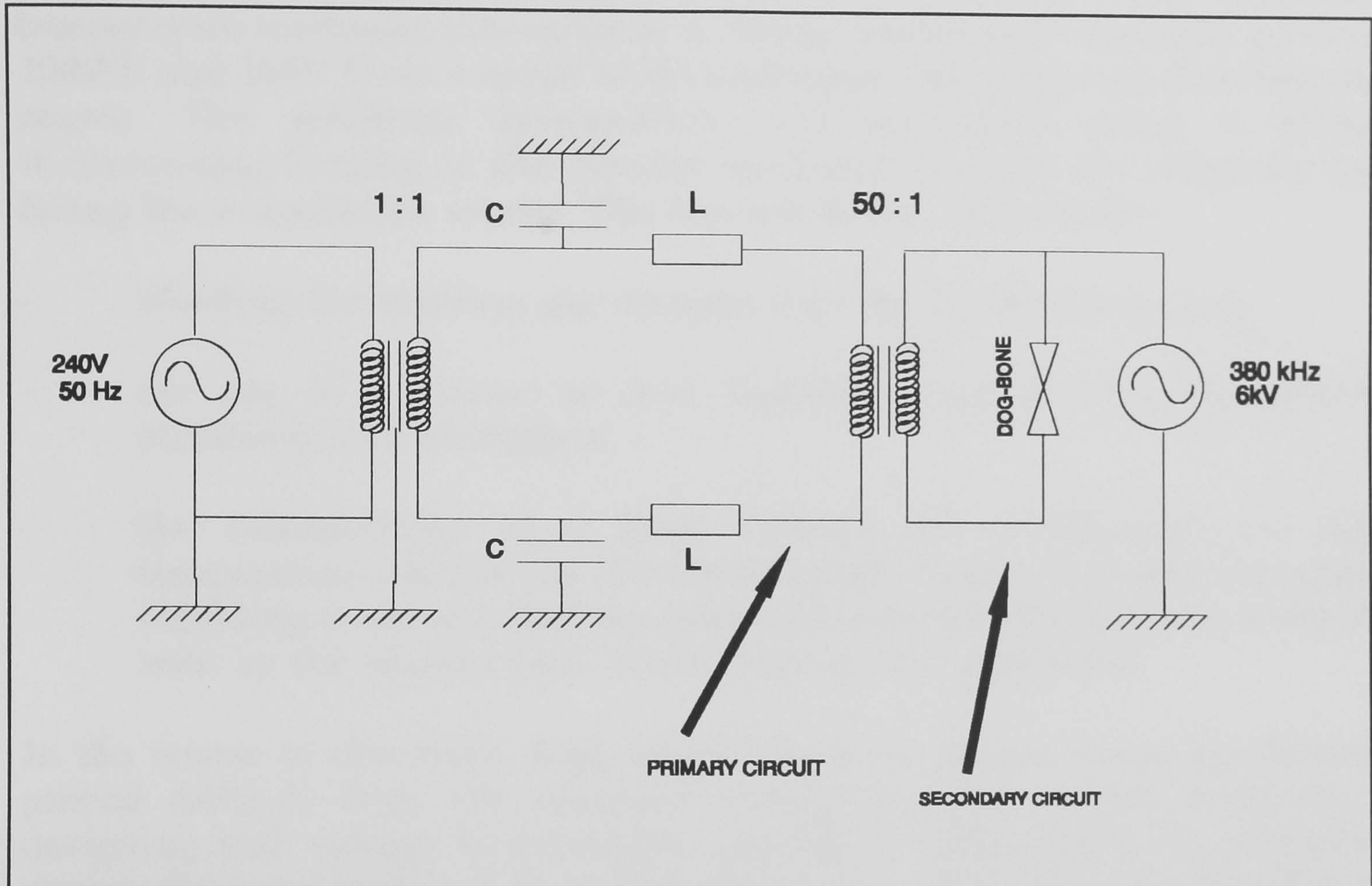


Figure 64: Diagram showing filtering of the RF bias applied on the heating circuit

The filter could not be placed in the heating circuit because of the high heating current required and the inevitable introduction of a high resistance from the coils compared with that of the dog-bone (0.035Ω). The filter was designed to meet a minimum attenuation ratio of 10K assuming a 1 to 1 RF coupling between the secondary (heating) and the primary circuit. The design specifications of the filter were as follows:

Coil breakdown voltage > 5kV peak-to-peak at 380 KHz.

Coil inductance (L) > 4.2 mH

Coil current rating: 4A RF

Capacitance > $1\mu\text{F}$

Capacitor break down voltage > 10V

The chokes (coils) were custom built by Aluminium Inductors Ltd with the following ratings: air cored, 10mH inductance, 1Ω DC resistance, 15A DC capacity.

6.1.3.2 Vacuum furnace for high temperature gas evaporation and DC ion plating

In a later phase of the programme, the Cranfield coatings group acquired a vacuum furnace which was co-designed between Rolls-Royce, Cranfield and Severn Furnace Limited, and built by the latter. This facility allowed to carry out coating runs on large flat plate coupons with typical substrate temperatures of 950°C at the start of the deposition. The deposition temperature increased thereafter to a steady temperature typically between 1000°C and 1050°C, as a result of the additional radiative heat flux from the source. The substrate temperature was monitored using a K-type thermocouple floating in the furnace environment aside the substrate and facing the evaporation source. The furnace design allowed for:

- bleeding the working gas straight into the furnace enclosure.
- the use of a shutter so that deposition started with the already stabilised melt conditions.
- the incorporation of a High Voltage DC feedthrough for high temperature ion plating. The feedthrough design incorporated proper shielding to ensure that the substrate was the only tangible electrode seen by the plasma from which current was monitored.

In the course of this work, high temperature ion plating using the furnace proved difficult from the practical standpoint, due to the necessity of designing high voltage feedthroughs capable of withstanding the combined electric field and high temperature environment. Although, the manufacture of a high temperature DC feedthrough capable of withstanding voltages up to 3kV and temperatures up to 1050°C was successful, thanks to expertise gained in past experience at AEA Technology, no success was met in designing an equivalent RF feedthrough for use in the vacuum furnace. This is because RF excitation puts much more exacting demand on the dielectric strength of insulating materials comparatively with direct current. This made impossible, in this work, the use of the vacuum furnace for high temperature RF ion plating.

6.1.4 Monitoring of plasma electrical parameters

In order to diagnose the power density of bombardment incident on the substrates, the ion plater was instrumented to measure the RF voltage, the RF current and the self DC bias during deposition. The term 'power density of bombardment' is defined and its relevance discussed in chapter 7.

A Tektronix voltage probe was used to monitor the RF voltage amplitude on the driven electrode using an oscilloscope (see Y2 in Figure 65). The probe attenuation ratio, function of the frequency, was experimentally measured by

means of a low voltage signal generator.

The RF current was monitored using a toroidal current transformer (C.T.) with a 20:1 ratio. A 15Ω resistor was placed across the terminals of the secondary circuit allowing the induced RF current to flow. The RF current wave form was revealed by monitoring the voltage across the resistor using the oscilloscope (see Y1 in Figure 65). The true amplifying ratio of the current transformer was calibrated using a dummy 380 kHz sine wave current by means of a signal generator. The voltage across the 15Ω resistor relates to the RF current drawn from the power supply as: $I_{RF} = 1.6 V_{15\Omega}$ (with I_{RF} in A and $V_{15\Omega}$ in V). A dual display of the RF voltage and RF current on the oscilloscope allowed to estimate the phase shift.

The DC offset induced on the driven electrode was measured by means of a resistive potential divider with a design attenuation ratio of 1000:1 (see Figure 65). A DVM was used to monitor the divided voltage across the bottom resistor. A shunting capacitor was placed across the bottom resistor to filter out potential errors on the DVM induced by the RF signal. The actual attenuation ratio (974:1) was determined by measuring the top and bottom DC resistance of the divider using a DVM.

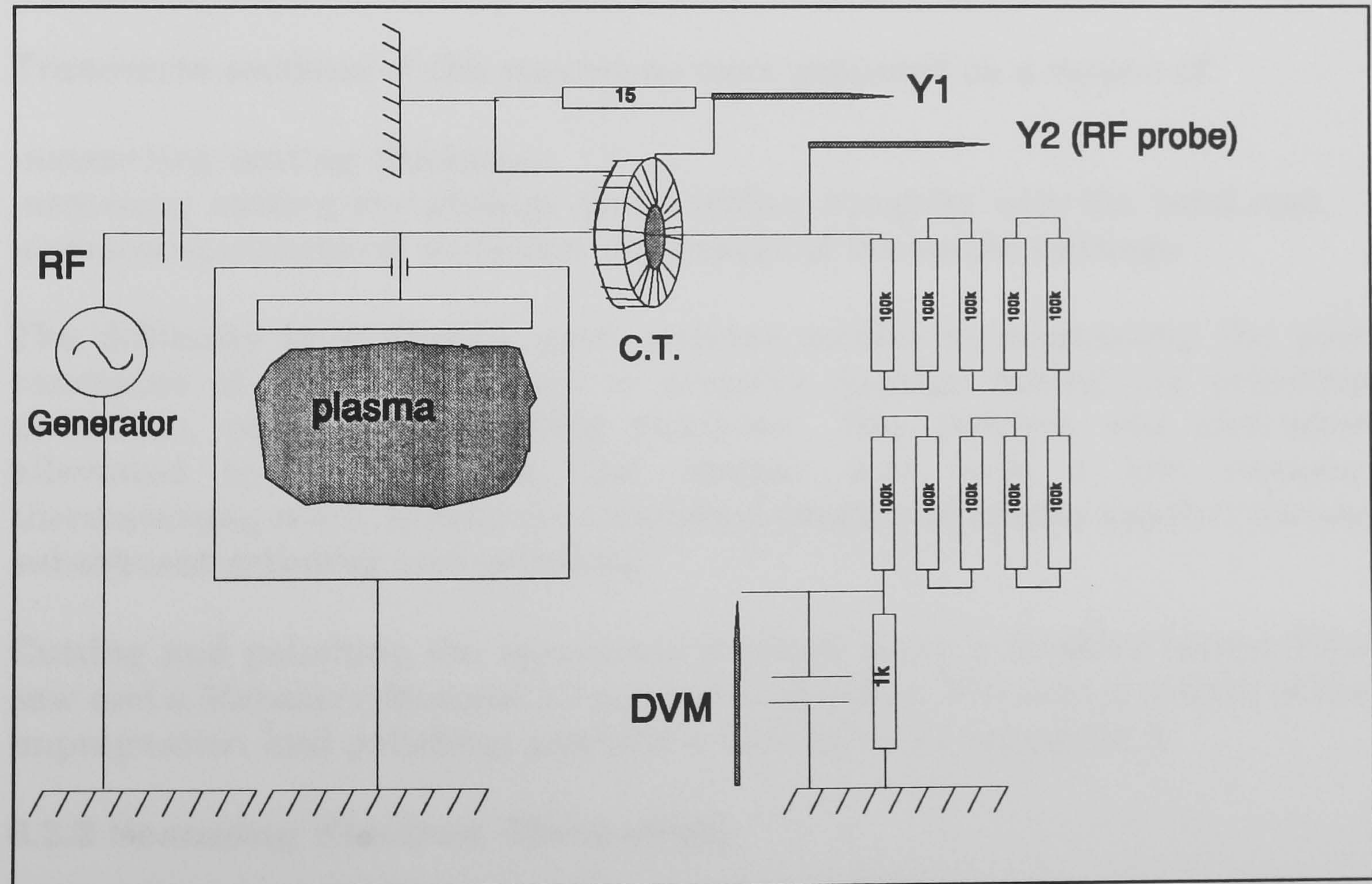


Figure 65: Monitoring of cathode voltages and RF current drawn from the power supply.

6.1.5 Routine of deposition process

The substrate materials used in this study, other than the 'dog-bone' specimens, consisted of 2mm Nimonic 75 flat coupons, overlayed with a glass bead peened VPS NiCoCrAlY bond coat.

Prior to coating, the substrates were washed with a detergent and degreased in inhibisol and isopropanol with ultrasonic agitation.

The chamber was evacuated to a base pressure between 10^{-5} to 10^{-4} Torr before heating the substrates and admitting the working gases. In the runs that did not involve using the vacuum furnace facility, the substrates were given a sputter clean in gettered argon for 20 minutes, using the maximum RF power.

Once the deposition was completed, the substrates were let to cool down in high vacuum, before venting the chamber.

6.2 CHARACTERIZATION TECHNIQUES

6.2.1 Preparation of coating transverse sections

Transverse sections of the specimens were prepared as a means of:

- measuring coating thickness.
- assessing coating morphology and interface integrity with the bond coat.
- examining structural evolution or damage of the tested coatings.

The difficulty in preparing good sections resides in overcoming the poor resistance of the ceramic coat to abrasive damage during the polishing procedure, resulting in coating pluck-out. This problem was somewhat alleviated by impregnating the ceramic coat with a low viscosity thermosetting resin, to hold the individual ceramic segments together during subsequent grinding and polishing.

Cutting and polishing the specimens involved using a Buehler Isomet Plus saw and a Metaserv Motopol 12 automatic polisher. The actual details of the impregnation and polishing procedures are given in Appendix 3.

6.2.2 Scanning Electron Microscopy

A Cambridge 250 Stereoscan scanning electron microscope was used to assess the morphology of the deposits from surface topography, transverse polished section and fractured edge observations. Both back-scattered and secondary electron imaging were used in order to highlight structural features such as column boundaries and variations in coating density. The specimens were coated with a film of gold-palladium or carbon, prior to observation in order

to avoid charging up.

The use of optical microscopes was restricted mainly to the thickness measurement of the ceramic, oxide and bond coat layers.

6.2.3 Coating density measurements

Coating density was determined from mass and volume measurements in two different ways.

1. The coating mass was measured by weighing the substrate prior to and after ceramic deposition. Coating thickness was measured optically on a polished transverse section of the same specimen.
2. The deposit was isolated by dissolving the substrate away in methanol 5% bromium then weighed. Coating thickness was measured on a polished transverse section of a mate coupon of the density specimen.

The relative error on density measurements arising from variations in coating thickness, specimen area and coating mass can amount to 15%.

6.2.4 Microhardness testing

Microhardness testing was carried out on the surface and on a polished transverse section of the coatings using a Vickers indenter. The properties so measured will be referred to in the text as *surface indentation resistance* and *transverse indentation resistance* respectively, and quoted in kg/mm^2 . Test loads in the range 50-300g were chosen with two concerns in mind:

- 1- the indentation depth should not exceed one tenth of the coating depth
- 2- the indent size should be made sufficiently large to minimize reading errors from the operator.

The potential dependence of hardness magnitude on the applied load (Indentation Size Effect) was not verified in this work over the range of loads used.

6.2.5 Chemical analysis

The chemical composition of the deposits was determined using the EDAX system available on the Cambridge 250 Stereoscan scanning electron microscope. A electron beam accelerating voltage of 20keV was used and the $K\alpha$ spectra were analysed using the ZAF method. The analysis was carried out on polished coating cross-sections, coated with an arc evaporated thin film of carbon.

6.2.6 X-Ray Diffraction Analysis

X-Ray Diffraction studies were performed at AEA TECHNOLOGY from which the phase, lattice parameter, texture, stress-state and crystallite size of the deposits were determined.

6.2.6.1 Operating conditions

A Siemens D500 fully automated powder diffraction system was utilized with CuK α radiation (1.5406Å). The experimental specimens were placed at the center of the diffractometer circle and rotated in synchronisation with the detector so that the diffracting planes were those parallel to the plane of the deposit. Typically, a cathode accelerating voltage of 40kV and a tube current of 30mA were used. The range of 2Θ scan was $[10^\circ, 148^\circ]$ with an incremental step of 0.05° held for 8 seconds. The count rate data was logged in and processed using a computer.

The XRD traces were printed superimposed on the diffraction patterns of a RT33 powder sample (tetragonal) and baddeleyite (monoclinic). This allowed an expedient assessment of the structure and texture of the deposits.

6.2.6.2 Texture

The degree of crystallite orientation for a given reflection (hkl) can be assessed by means of the texture coefficient:

$$T_{hkl}^* = \frac{\frac{I_{hkl}}{I_{ohkl}}}{\frac{1}{n} \sum \frac{I_{hkl}}{I_{ohkl}}}$$

where I_{hkl} and I_{ohkl} are the integrated intensities of (hkl) reflections measured for an experimental specimen and the standard powder sample (randomly orientated) respectively, n being the total number of reflection planes.

6.2.6.3 Hall-Williamson analysis

The contributions of microstrain and crystallite size to diffraction line broadening were decoupled by line breadth Hall-Williamson analysis. The broadening due to crystallite size (β_c) and lattice strain (β_e) are respectively:

$$\beta_c = K \frac{\lambda}{L \cos \Theta}$$

and

$$\beta_e = 4\epsilon \tan \Theta$$

where K is the crystallite shape factor (taken as unity), λ the wavelength of the radiation used, Θ the bragg angle, L the mean crystallite size and ϵ the

lattice strain.

The instrumental broadening, arising from X-ray beam divergence and departure from the monochromatic nature of the radiation, was determined experimentally as a function of angle using a fully annealed ceria standard. The total broadening corrected for the instrumental broadening is the sum of the former two contributions:

$$\beta = \beta_c + \beta_e$$

which can be rewritten as:

$$\beta \frac{\cos\Theta}{\lambda} = \frac{1}{L} + 4\epsilon \frac{\sin\Theta}{\lambda}$$

The contribution of CuK α 2 to the line breadth is deducted in the calculation of β .

The plot of $(\beta \cos\Theta/\lambda)$ vs $(2\sin\Theta/\lambda)$ is a straight line which slope (2ϵ) and Y-intercept $(1/L)$ yield estimates of the lattice strain and mean crystallite size respectively. Crystallite size up to 0.2 μ m can be estimated by means of a diffractometer.

If the lattice structure is not cubic, a Hall-Williamson plot should be made strictly with bragg angles from reflection planes of the same family i.e. (nh,nk,nl) planes where n is a positive integer. However, even when the structure was found to be tetragonal, reflections from different families were used for Hall-Williamson plots. The validity of this approach is justified by the fact that the difference in the 'a' and 'c' lattice parameters of the tetragonal structure is only slight for zirconia.

6.2.7 Image analysis

A Joyce-Loebl Image Analyser was used to measure the particle size distributions of the erosive media. Both spherical and angular particles were sized.

The diameter of a spherical particle is simply:

$$D = \left(\frac{4A}{\pi} \right)^{\frac{1}{2}}$$

where A is the area measured by the instrument.

Angular particles were assumed to be cylinder shaped with L and d their length and base circle diameter respectively. The quoted particle size (D) corresponds to the diameter of a spherical particle having the same volume as the cylindrical particle.

$$D = \left(\frac{3}{2} \sqrt{\frac{d}{L}} \right)^{\frac{1}{3}} \times A^{\frac{1}{2}}$$

where A, the area measured, is related to d and L as $A = Ld$. Typically, a sample population of 100 objects was chosen to compute the particle size distribution and statistics.

6.3 EROSION TESTING

6.3.1 Testing objectives

The object of the erosion studies were:

1 to assess the significance of particle erosion as a TBC life limiting factor.

The aim was to evaluate the erosion behaviour of the datum coating RT33 under test conditions representative of the gas turbine environment seen by an HPT aerofoil. The specifications were to carry out testing at particle velocities in excess of 300m/s with varying angles of impingement and at specimen temperatures as close as possible to 1000°C.

2 to rank the development coatings under the most severe testing condition as defined in 1.

3 to generate an understanding of how the coating structure and properties influence the erosion response. With this aim in mind, the scope of tested materials was broadened to plasma sprayed and bulk YPSZ.

6.3.2 Tested Materials

Commercially available TBC systems, coatings developed under this programme, and bulk 5wt%YPSZ were tested. These are:

- RT33 which is the EB-PVD TBC datum purchased from CR&T in Orangeburg (USA).
- APS TBC supplied by Rolls-Royce.
- Cranfield development coatings.
- Bulk 5wt%YPSZ coupons bought from Morgan Matroc.

TBC erosion test pieces consisted of 25.4x25.4x2.5mm square coupons cut off from pre-coated paddle plates. The bulk YPSZ coupons were 35x31x9mm in size.

6.3.3 Erosive media

Alumina is usually preferred to sand for high temperature erosion testing as the latter can become soft and sticky at elevated temperature. Both types of particles were used in this work. The value in using sand is that it is a realistic erodent for jet engines, while the effect of hard particles at high temperature can be investigated using alumina.

The solid particles that flow through the HPT sections of a jet engine vary between 2 to 150 μm in diameter. Newer designs are reducing this range to below 50 μm ⁵. Particles with diameters less than 30 μm tend to follow the deviated stream lines in the flow field surrounding the target. As a result, the particles that do actually impact the test specimen are fewer and have a broad range of incident angles with reduced velocities¹³⁰. For this reason, it is recommended to use particle size in excess of 30 μm ²².

Silica beads (Honite18 from Guyson) and alumina grit particles were selected in this study. Figure 66 shows micrographs of these particles. Particle sizes were in the 20-100 μm range (60 μm average) for the silica and 80-120 μm range (100 μm average) for the alumina, as determined by image analysis. The size distribution plots and statistics are given in Appendix 4.

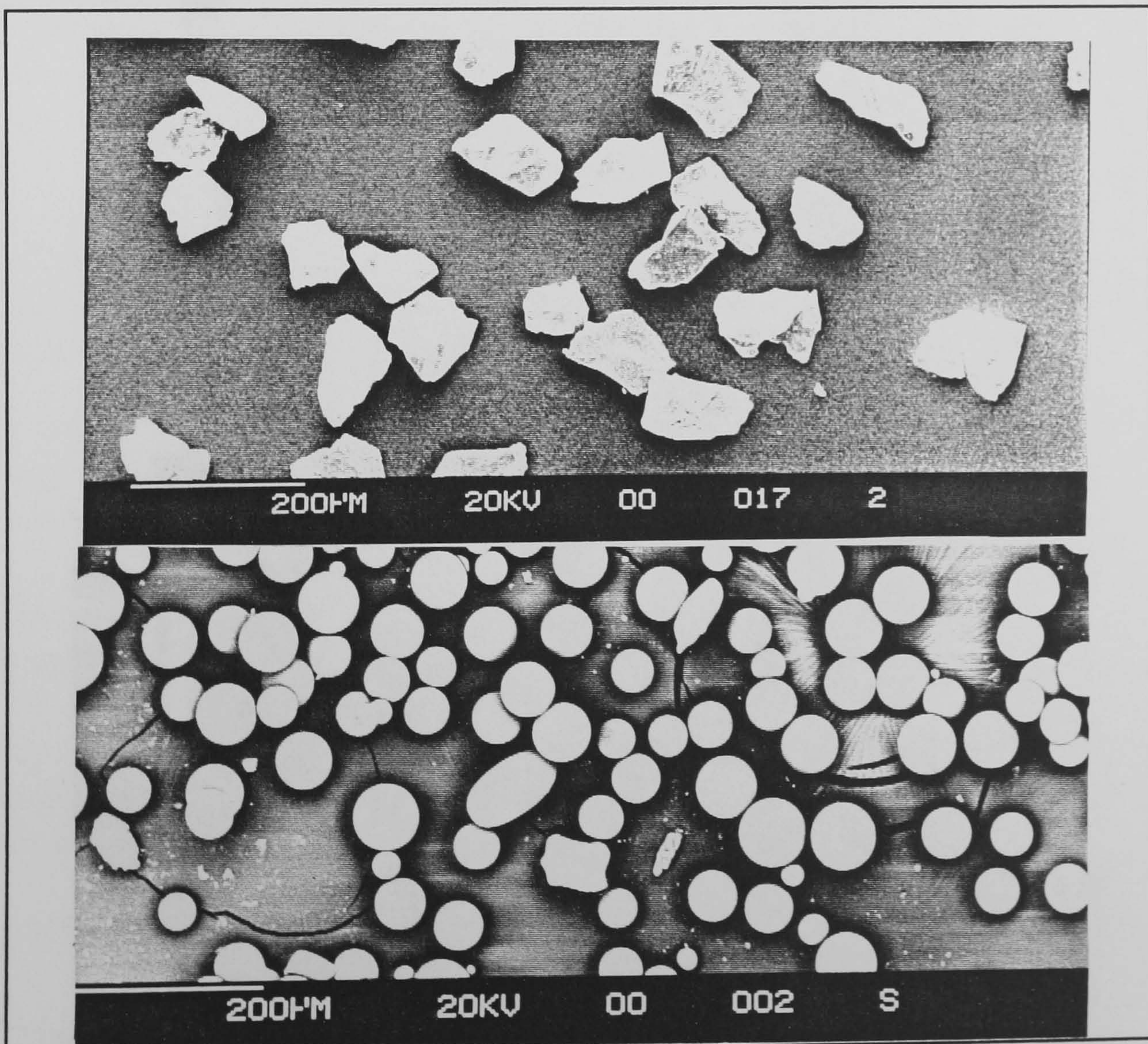


Figure 66: Micrographs of silica beads and alumina grit.

6.3.4 Commissioning of erosion rig

6.3.4.1 Decription of erosion rig

The Cranfield High Temperature High Velocity erosion rig was originally designed to achieve a specimen temperature of 700°C with a gas velocity of 200m/s. The design was based on a gas gun approach where upon particles are accelerated down a tube by a hot gas carrier to impact the test specimen heated by the gas. Figure 67 is a schematic of the rig. The air, pressurized by the compressor (C) is heated up as it passes through an air heater (H) and expands in the acceleration tube down to ambient. Particles are fed into the tube by a helix feed hopper (F). The pressure tank (T) smooths out the pressure fluctuations from the compressor and provides reserve of gas for rig operation.

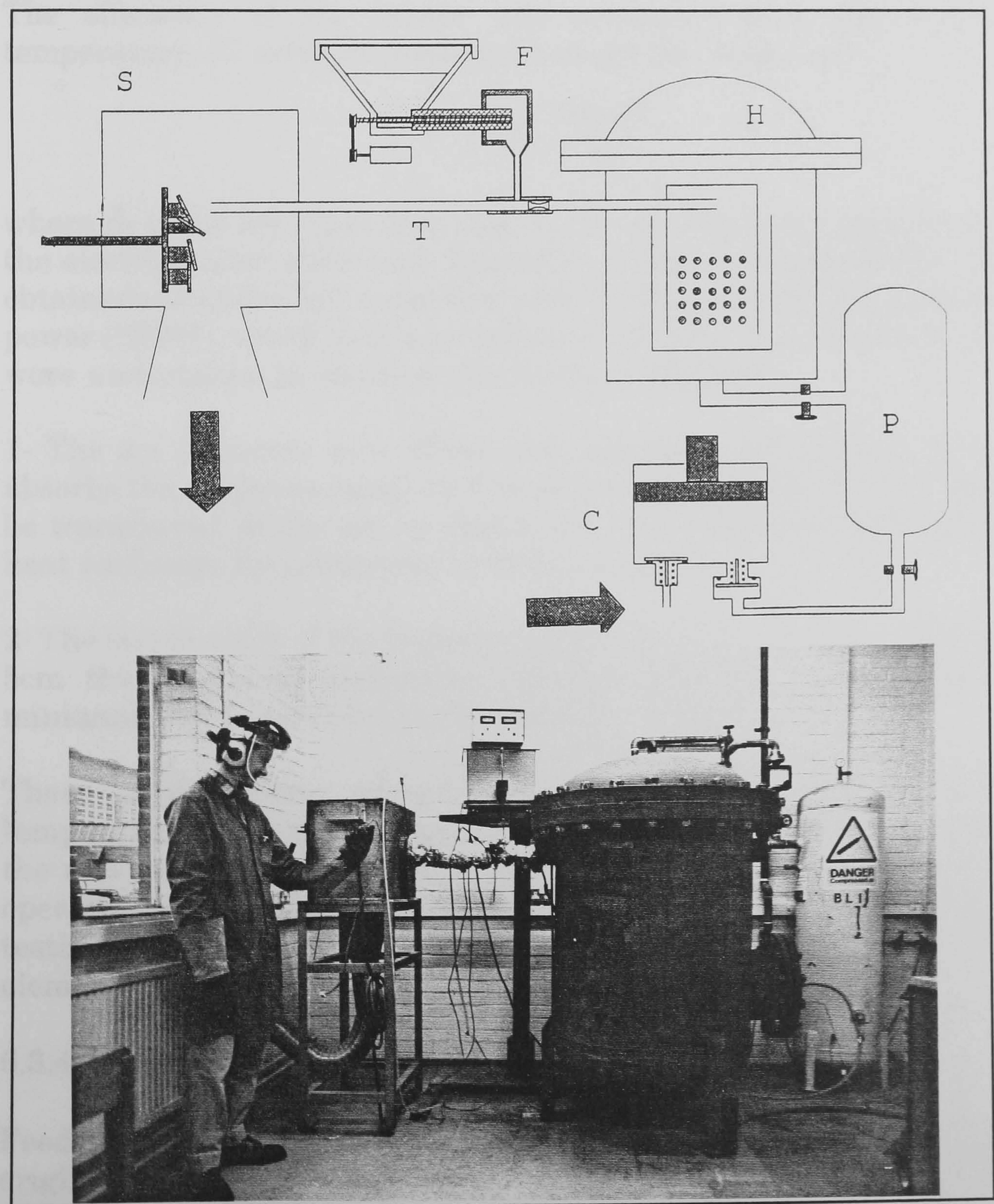


Figure 67: Schematic of Cranfield High Temperature High Velocity Erosion Rig.

In its inherited state, the rig proved incapable of reaching the specified specimen test temperature and particle velocity. Considerable design modifications were required to upgrade both the temperature and particle velocity capabilities of the rig.

6.3.4.2 Temperature capability upgrading

The air heater consists of a series of wound elements capable of dissipating into heat an electric power of 35 kW. It is contained in a metal box positioned at the core of the pressure vessel. The cool air enters the vessel from the bottom, flows up and down through the baffled coaxial channels and enters the metal box via the bottom. There, it sweeps the hot elements and finally exits into the acceleration tube. Heating of the gas relies on convective heat transfer as the gas sweeps the hot channel walls and the elements.

The efficiency of the heater was estimated from the increase in gas temperature ΔT after its passage through the vessel as:

$$\eta = \frac{\dot{m} c_p \Delta T}{W_e}$$

where $\dot{m}$ is the air mass flow rate, c_p the specific heat capacity of air and W_e the electric power delivered. Typically, a gas exit temperature of 700°C was obtained using the full mass flow rate (0.034 Kg/s) and the maximum electric power (35 kW), which yields an efficiency of 60%. The following modifications were undertaken to increase the heating efficiency:

1- The air channels were filled with stainless steel metal wool. The latter absorbs the radiative heat, otherwise lost to the vessel walls, which can then be transferred to the air by convection. Also, the wool enhances convective heat exchange by promoting turbulent air flow.

2- The inside walls of the pressure vessel were lined with an aluminium foiled 5cm thick mineral insulation blanket (Rockwool Fire Barrier) to keep minimum the heat losses to the outside.

These modifications proved very effective in boosting the specimen temperature. A maximum specimen temperature of 960°C was achieved using the maximum gas flow rate which, was this time limited by the maximum operating temperature of the elements (1050°C). It was decided to carry out testing at a specimen temperature of 910°C so as to avoid to operate the element at its limits.

6.3.4.3 Particle velocity upgrading

Feeding particles into a pressurized gas jet can prove very difficult. In the original design, particles were fed by means of a bent tube facing downstream and positioned in a constriction (Venturi) of the acceleration tube (see Figure 68).

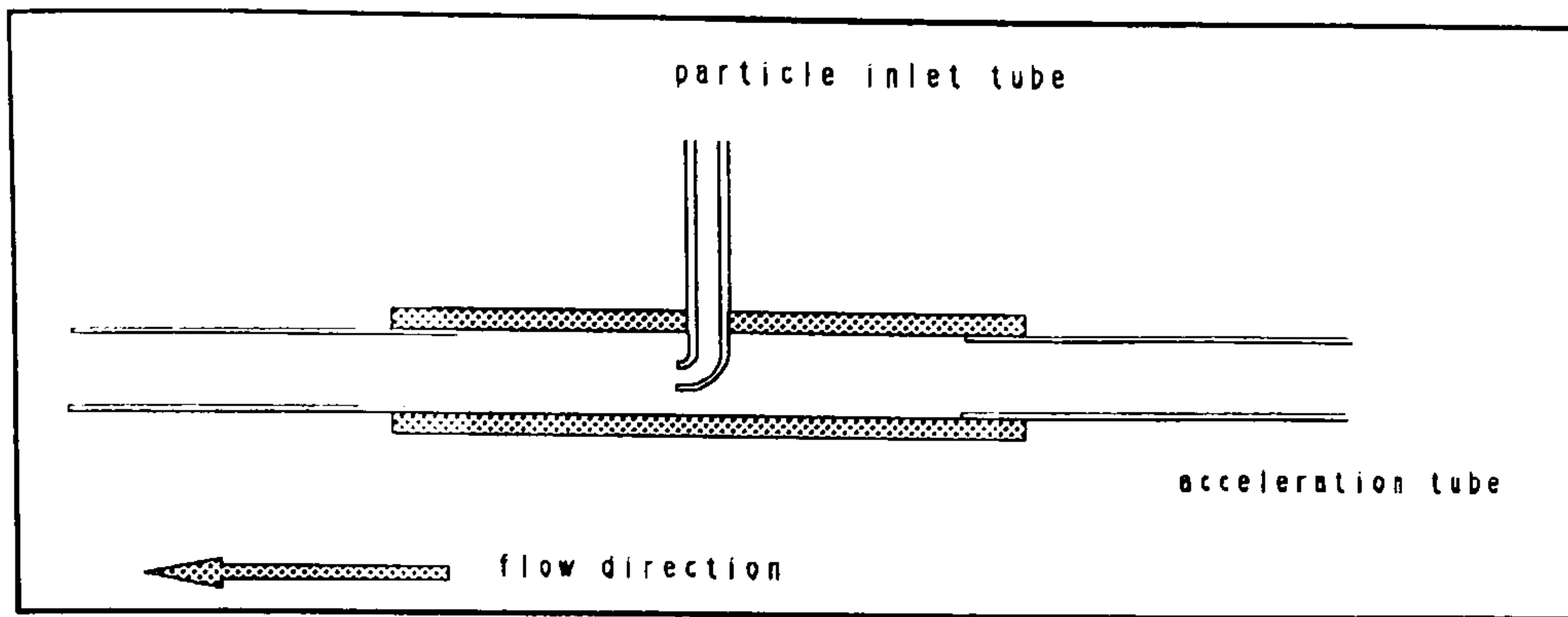


Figure 68: Schematic of original particle feeding design.

This design proved impractical when using the maximum air flow rate and heating power as the static pressure was then so high, that it would cause air to blow up the feeding tube and repel the particles away. Solutions involving pressurizing the hopper and the feed line were ruled out for cost considerations.

Success lied in the ability to generate a static pressure less than atmospheric at the particle inlet section so that the erodent could be ingested by suction into the hot gas stream. This was achieved by placing a converging-diverging nozzle upstream to the particle inlet section. If the ratio of pipe diameter to nozzle throat diameter is suitably chosen, supersonic flow is induced downstream from the constriction which is accompanied by a dramatic pressure drop. Figure 69 is a sketch of the new design with the predicted pressure profile.

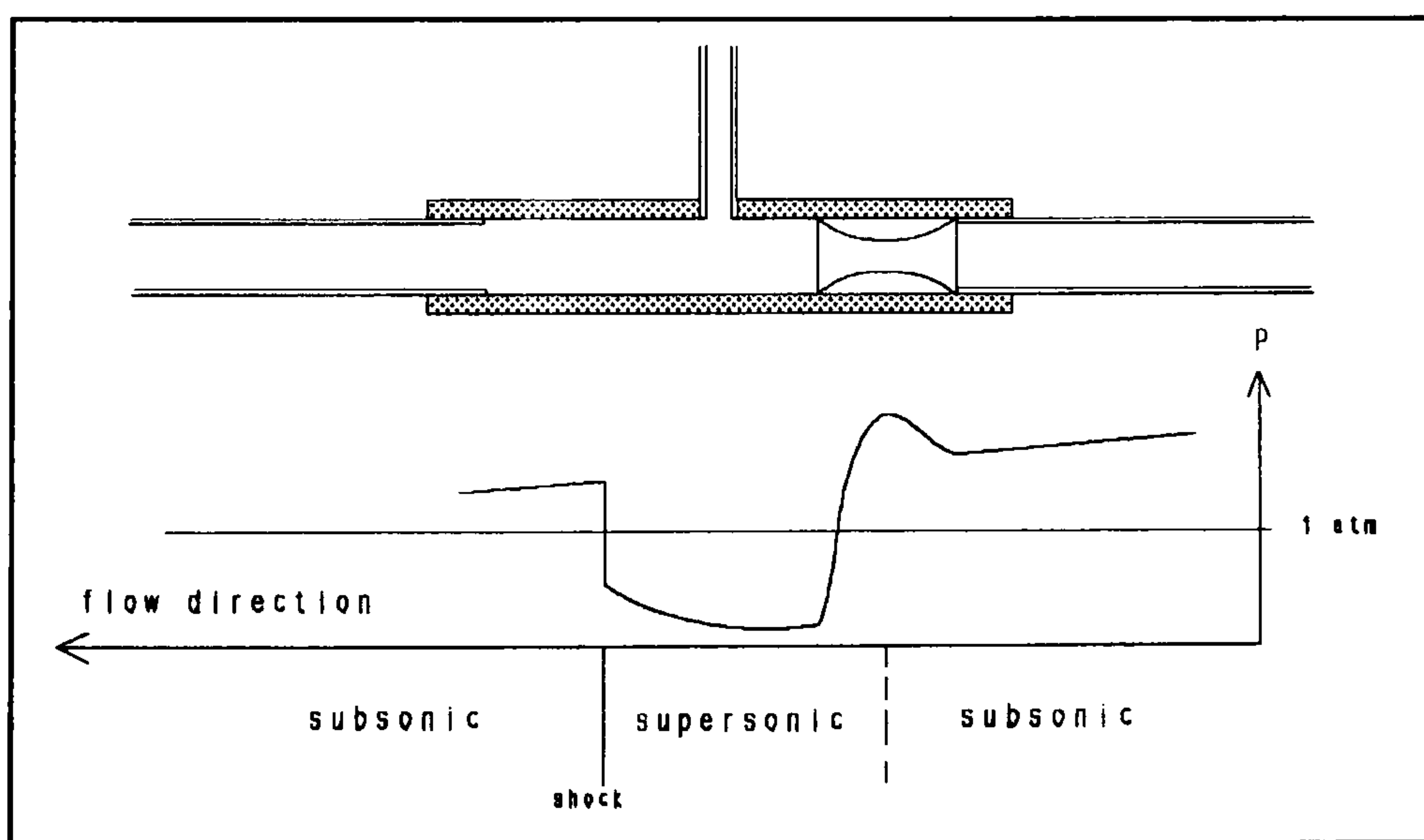


Figure 69: Schematic of new particle feeding design.

6.3.4.4 Particle velocity prediction

Particle velocity is of crucial importance in erosion studies since it controls the magnitude of impact undergone by the specimen surface. Measuring velocities in the range 200-400m/s of particles entrained in a gas jet at 900°C is a serious technological challenge well beyond the scope of the project. Fortunately, the geometry of the system was simple enough to allow the prediction of particle velocity on theoretical grounds.

The methodology developed to calculate particle velocity comprises two steps. The first one is the choice of a simple flow model that describes satisfactorily the gas flow parameters (velocity, pressure, density) over the tube length travelled by the particles. The second is the derivation of particle velocity from the aerodynamic drag force which depends on the flow parameters inferred from the first step.

The gas flow properties were described using Fanno Line Flow theory¹³¹ which is a monodimensional model assuming adiabatic flow with friction in a constant area duct.

The aerodynamic drag to which the particles are subjected is taken as¹³⁰:

$$\frac{1}{2}C_D\rho A(V-V_p)^2$$

where V and V_p are the gas and particle velocity respectively, ρ the gas density, A the cross-sectional area of the particle and C_D the drag coefficient. Justification and details on the derivation of particle velocity are given in Appendix 5.

6.3.4.5 Instrumentation of the rig

The rig is instrumented to ensure reproducibility of testing conditions, and to measure parameters used for the calculation of particle velocities.

The specimen temperature is monitored using a K-type wire thermocouple, spot-welded at the center of the flow facing side of a 1"x1" Nimonic 75 dummy specimen. This dummy specimen is mounted on the carrousel at an angle of 90° with the flow direction.

Two static pressure taps are fitted at two different points along the acceleration tube.

6.3.4.6 Specimen test cell

The high thermal mass of the air heater unit implies that two to three hours are needed for both heating up and cooling down. A design was produced allowing a batch of up to 6 specimens to be loaded in the specimen box and tested one after the other by swapping them round *in situ* while keeping the rig running. The specimen holders are mounted on a disc (see Figure 70) that can be rotated from outside the specimen box, and set to a fixed angle so that all the particles exiting the acceleration tube impact the individual specimen surfaces. The angle of particle impingement is set by the geometry of the individual specimen holders.

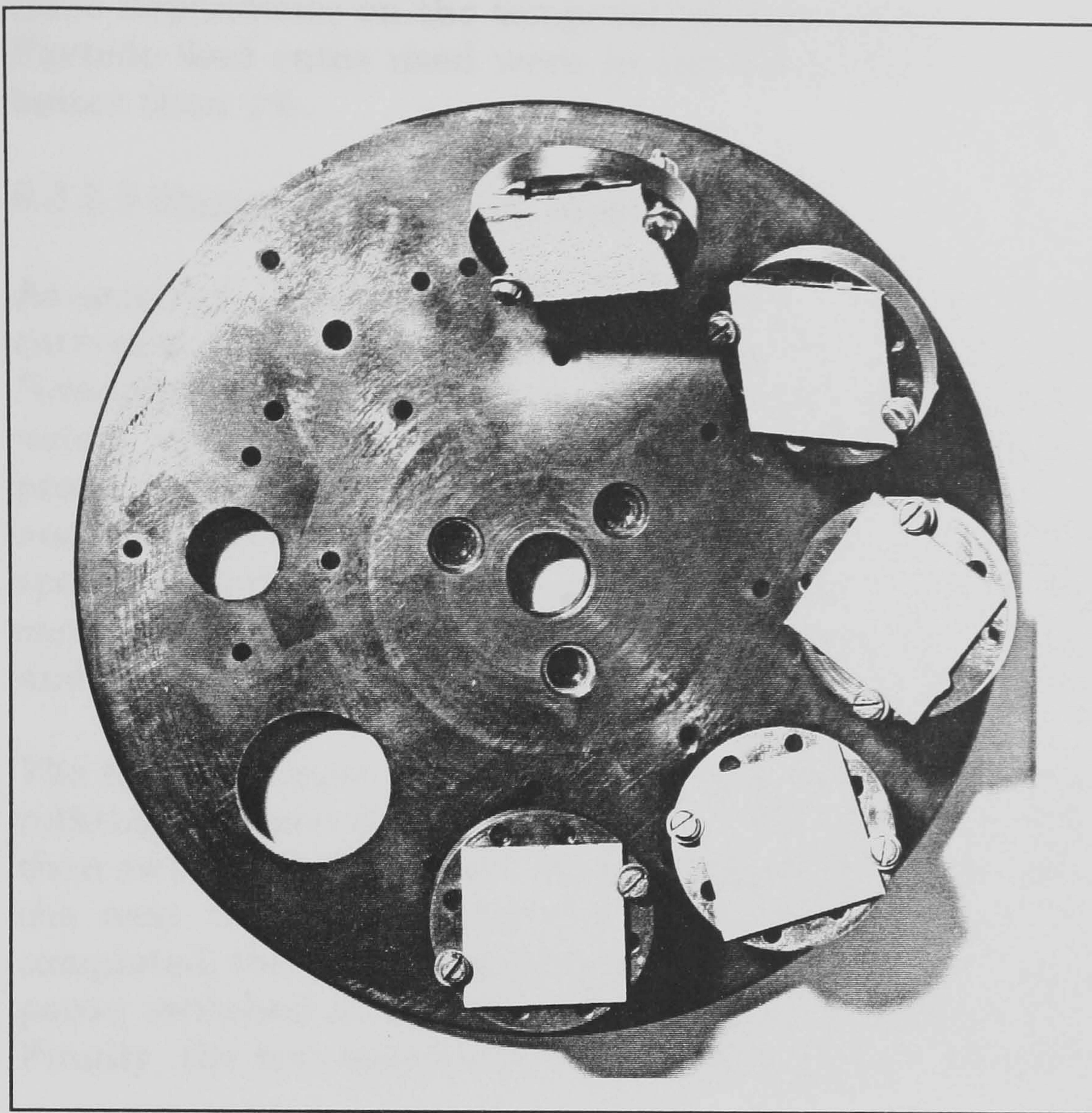


Figure 70: Specimen carrousel.

6.3.5 Testing procedure

6.3.5.1 Weight loss measurements

A Sartorius microbalance capable of measuring weight to the 10^{-5} g was used. Prior to weighing, the test pieces were dusted off, soaked in hot acetone, flushed with isopropanol and dried off with an air blower. This procedure was used prior to and after the test. Some ceramic loss of the order of 10^{-5} g could be incurred when mounting the specimens on the carrousel caused by the stress exerted by the washers on the ceramic coat. This however remained negligible compared to the erosion weight loss. Weight gain from oxidation during high temperature testing was also negligible.

6.3.5.2 Particle loading

One of the source of potential scatter in erosion rate measurements is the accuracy with which the particle load is known. In the present test configuration, the erosion scar is confined within the test piece i.e. every particle fed into the acceleration tube impacts the test specimen. The error in particle loading is therefore solely dependent on the accuracy in the amount of particle fed. To optimise accuracy in particle loading, the hopper feed rate was systematically recalibrated before testing, as the latter showed

some dependence on the temperature and dampness of the laboratory room. Particle feed rates used were in the 0.5 to 6g/min range with a precision better than 1%.

6.3.5.3 Sequence of erosion testing

As-received test pieces were weighed as in 6.3.5.1 and mounted on the carousel. The carousel was then fitted in the specimen test cell with the Nimonic 75 dummy specimen facing the exit of the acceleration tube. The air valves were then fully opened and the flow conditions, monitored by the pressure readings, left to stabilise. The heating unit was then switched on and the power turned to 100%. Two hours were necessary to achieve a specimen temperature of 910°C. Calibration of the hopper feed rate was carried out fifteen minutes before the test temperature was reached. Pressure and temperature readings were recorded after which testing could commence.

The test specimens were positioned in front of the acceleration tube outlet by rotating the carousel from the back of the specimen test cell. The hopper was then switched on for a set duration, then the carousel was rotated to place the next test piece in front of the gas jet, and so on. Once testing was completed, the dummy specimen was placed back in the gas flow, the heating power switched off and the system left to cool down for another four hours. Finally, the test specimens were taken out and weighed as in 6.3.5.1.

7 DIAGNOSIS OF ION PLATING

The structural changes expected to be induced by plasma assistance are the result of atomic displacements in the film lattice caused by the collision of surface atoms with energetic ions and/or neutrals. The mechanisms invoked to account for this 'ion-induced' mobility have been thermal spikes, surface diffusion of adatoms and atomic displacements in the bulk. Whatever the mechanism considered, the influence of ion bombardment on the structure of a film is a function of the nature of the bombarding species, their energy distribution, and their flux relatively to the flux of depositing vapour atoms. The first objective of this chapter is to attempt to characterize the 'ion bombardment' regime relevant to plasma assisted EB-PVD TBC's with regard to the ion current and substrate accelerating voltages. An analysis was undertaken based on readily measurable parameters for both DC and RF biasing. This then forms the preliminaries for discussing the significance of ion plating compared to other plasma assisted techniques such as bias sputtering in chapter 8. In the present work, RF ion plating was hampered with the difficulty in maintaining the plasma in conjunction with the evaporation source. Some considerations are given to account for this phenomenon.

7.1 DC GAS DISCHARGE CHARACTERISTICS (RESULTS)

The current drawn by the power supply was monitored as influenced by the substrate bias, gas pressure, temperature and electron beam current. These current characteristics are presented and modelled with the aim of dissociating the ion current impinging on the substrate from the total current measured in practice. An estimate of ion current density is derived, typical of the ion plating conditions used in this work.

7.1.1 Current/voltage characteristics at low temperature

The current-voltage characteristics of the plasma coupled with the DC power supply were plotted for a range of pressures and voltages. A Nimonic 75 flat plate with a total surface area of 50cm^2 , typical of the substrate to be used for depositions was used as the cathode. The temperature was monitored by an earth sheathed K-type thermocouple floating in the furnace environment during these trials. Figure 71 shows the current drawn (I) for different substrate acceleration voltages and chamber pressures.

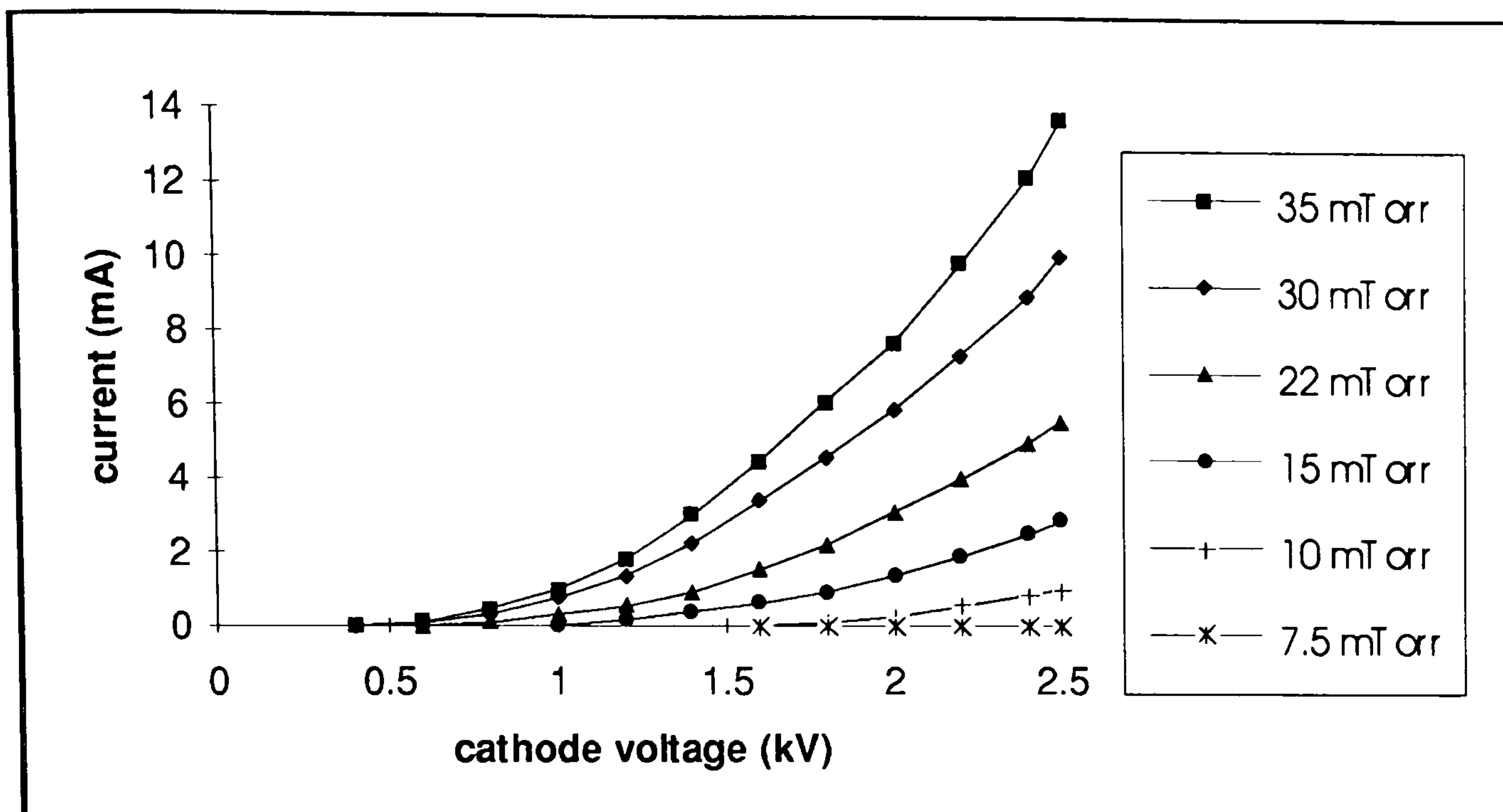


Figure 71: Current/voltage characteristic of DC glow discharges in furnace enclosure ($T_F=60^\circ\text{C}$).

7.1.2 Effect of furnace temperature

The furnace was switched on and the variation of current drawn with temperature recorded for a pressure and accelerating voltage set to 12mTorr and -2.5KV respectively (see Figure 72).

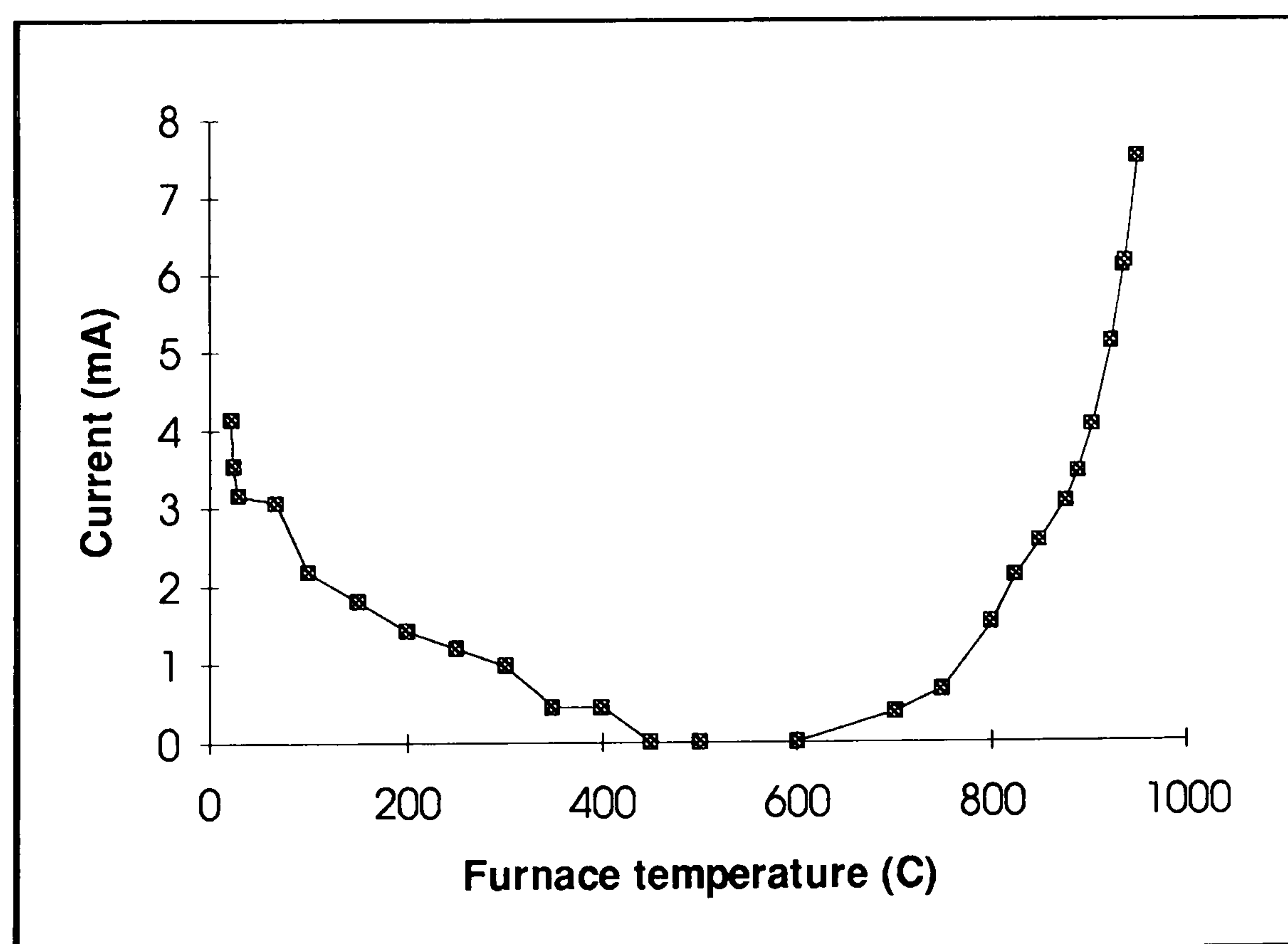


Figure 72: Evolution of current drawn with furnace temperature at a set cathode voltage (-2.5kV) and chamber pressure (12mTorr of argon).

The furnace temperature is found to influence strongly the current drawn from the power supply.

7.1.3 Current/voltage characteristics at elevated temperature

The current drawn (I) was recorded for different substrate acceleration voltages and chamber pressures at a steady temperature of 810°C .

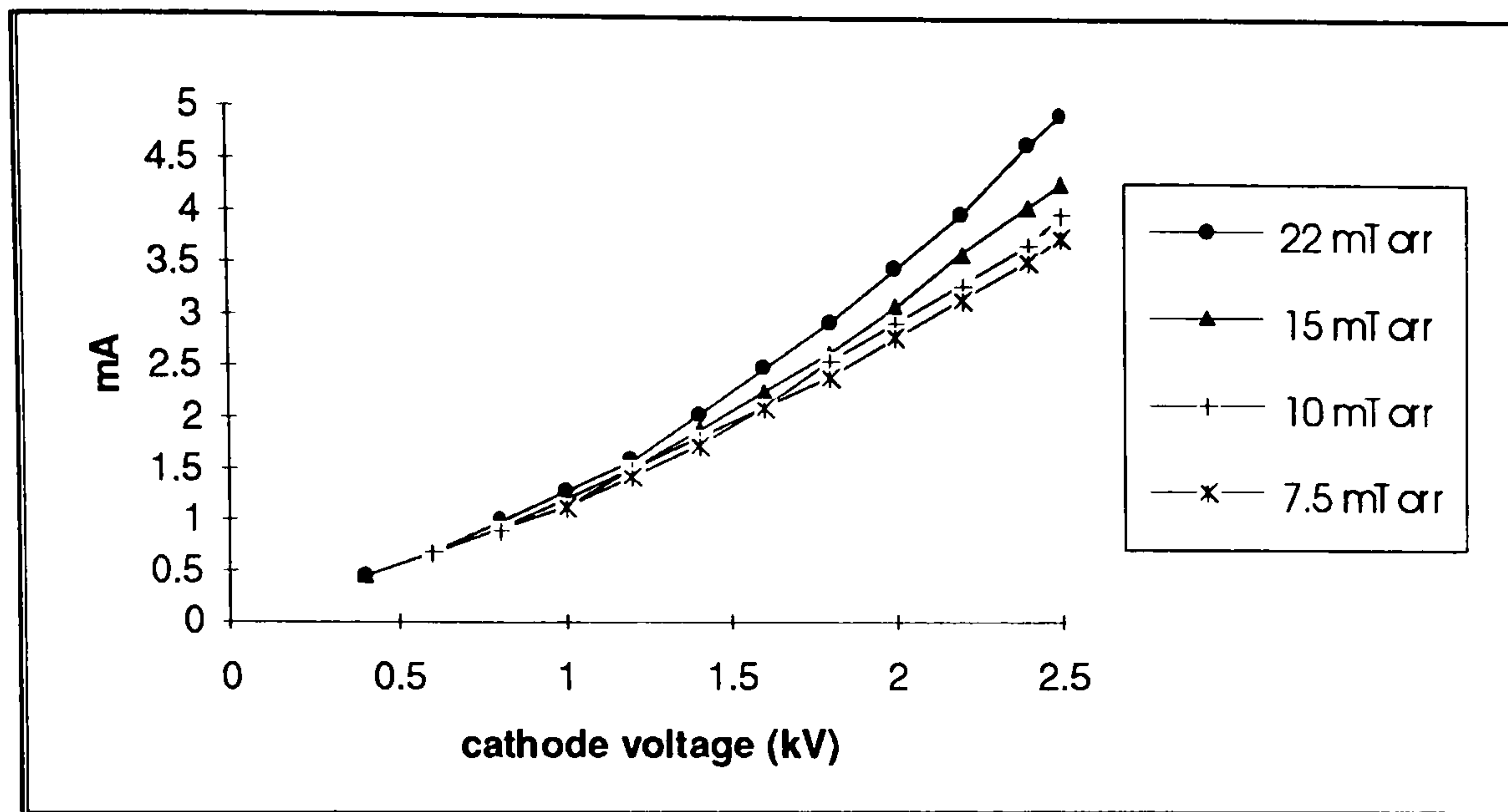


Figure 73: The influence of gas pressure on the current/voltage characteristics at 810°C .

The shape of the characteristics differs sharply with those obtained at 60°C (see Figure 71). The effect of pressure on the current drawn is less dramatic and the slope of the characteristics at 0kV seems no longer horizontal.

7.1.4 Effect of EB current on current drawn from the discharge

The current monitored was found to increase with increase in electron beam current (see Figure 74). Inevitably, the furnace temperature also increases readily with the rod surface temperature and this will contribute to the increase in current monitored (see Figure 72).

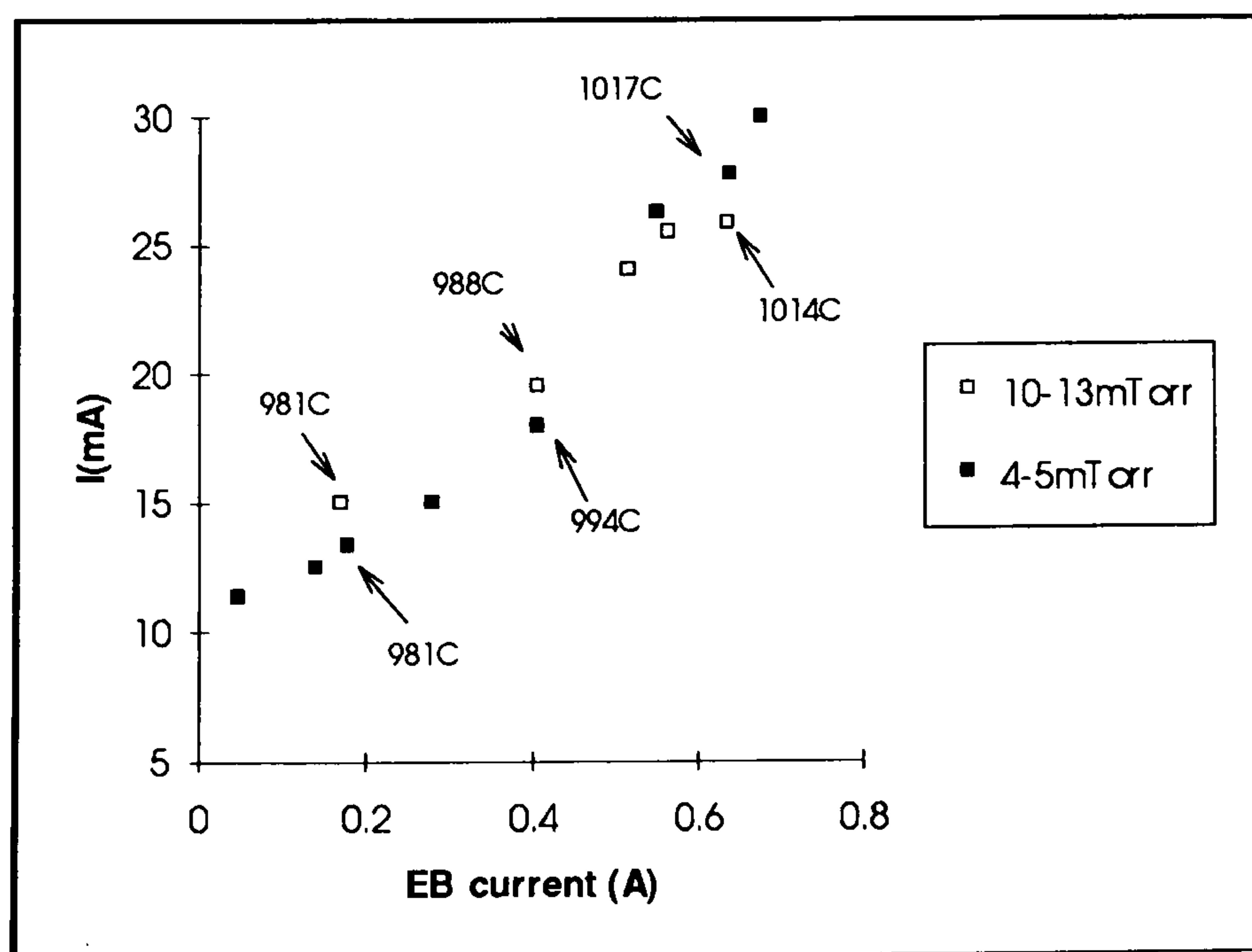


Figure 74: Effect of electron beam gun on current drawn from the discharge at 2.5kV (Gun H.T: 7kV).

7.1.5 Effect of EB evaporation on I-V characteristics

Current-Voltage characteristics were recorded while evaporating zirconia at a set electron beam current of 0.6A and HT of 7kV. These are overlaid with the characteristic obtained with the gun off on cooling after evaporation (see Figure 75). The current measurements were taken in a consistent narrow band of temperatures so as to minimise the effect of the latter on the shape of the characteristics.

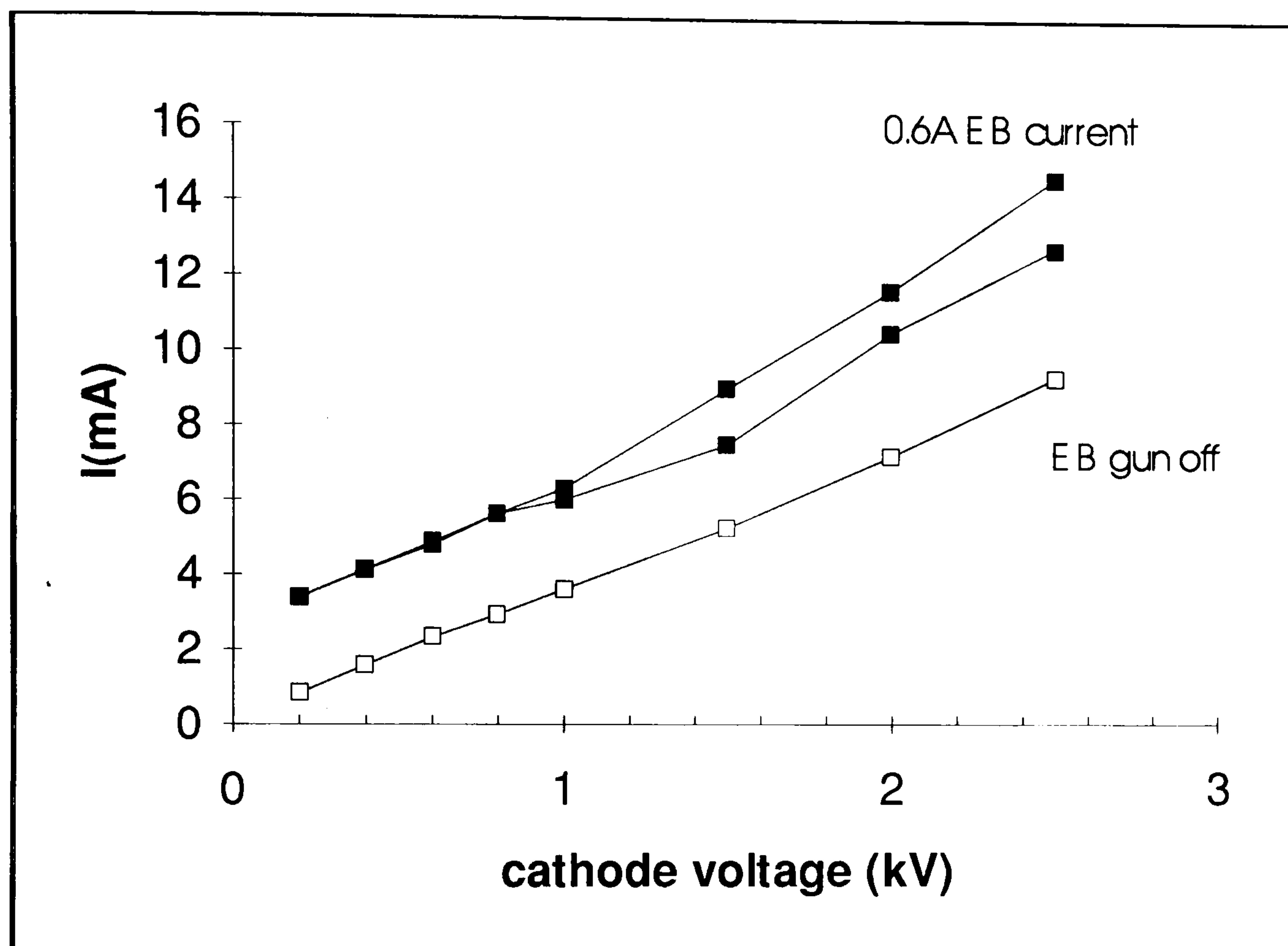


Figure 75: Effect of electron beam evaporation (EB) on the I-V characteristics for a cathode temperature in the 1014-1023°C range and a chamber pressure of 10mTorr.

The onset of evaporation seems to result in the upward translation of the 'gun-off' characteristic (no apparent change in slope).

7.2 MODELLING OF DC GAS DISCHARGE (DISCUSSION)

7.2.1 Currents drawn from a DC glow discharge

Figure 76 is a schematic of the substrate DC biasing during ion plating. The substrate to which the high negative voltage is applied is referred to as the cathode in this section.

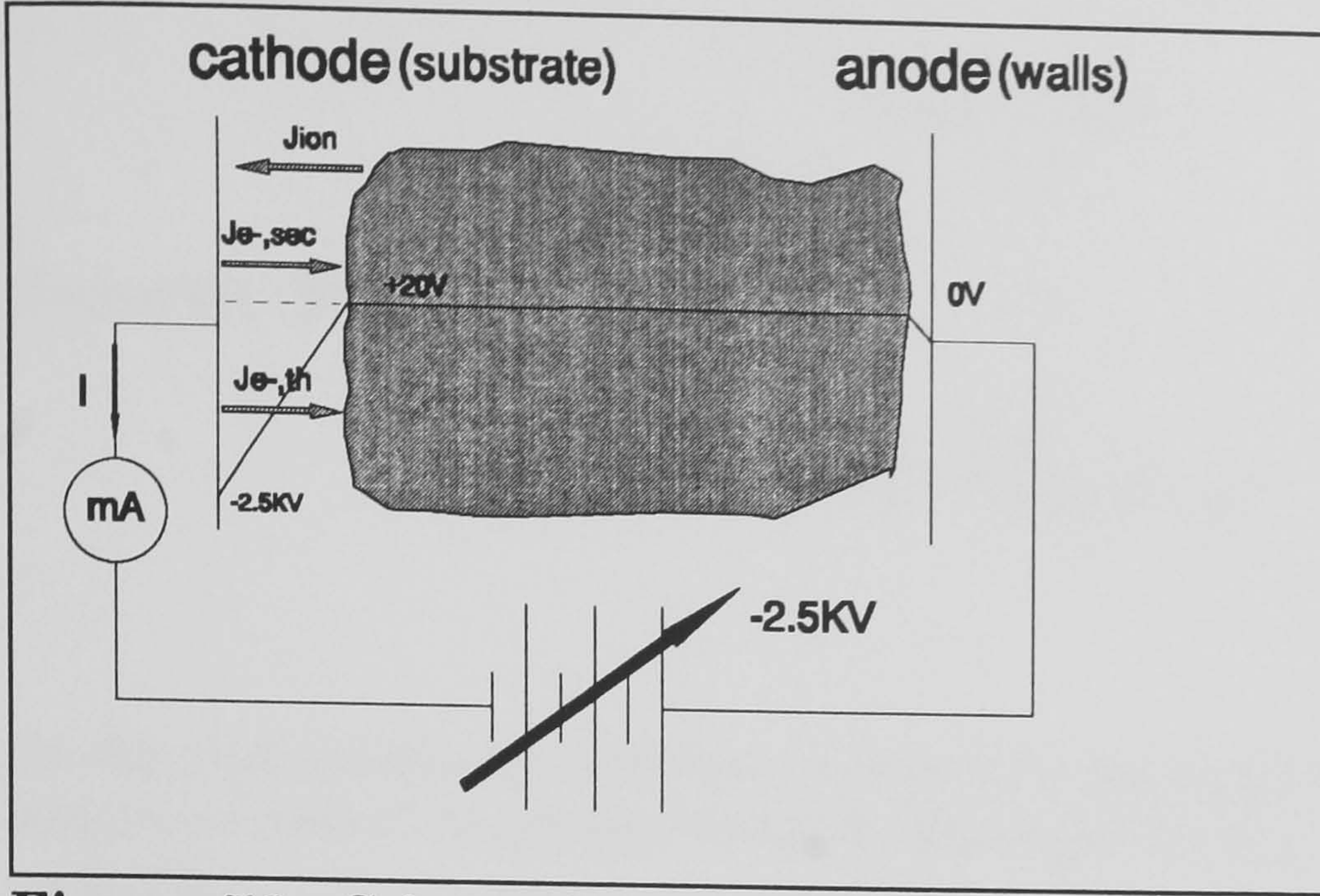


Figure 76: Schematic of a DC glow discharge plasma showing the flow of charged particles at the cathode.

The current measured in the external circuit (I) is the algebraic sum of the ion current bombarding the cathode (J_{ion}), the current of secondary electrons induced by ion bombardment and leaving the cathode ($J_{e-,sec}$) and the current of thermionically emitted electrons emitted by the cathode ($J_{e-,th}$):

$$I = A_c(J_{ion} + J_{e-,sec}) + A_T J_{e-,th} \quad (27)$$

where A_c is the area of the cathode fully immersed in the plasma and A_T is the area of cathode at temperature. It will be assumed in the rest of the analysis that $A_c = A_T$:

$$I = A_c(J_{ion} + J_{e-,sec} + J_{e-,th}) \quad (28)$$

Thermionic emission, being a thermally activated phenomenon, is not usually taken into consideration in glow discharge surface processes. Plasma assistance is used in gas phase processes generally as a substitute for temperature and the substrate temperatures achieved are therefore moderate.

The scope of this work is however to operate a glow discharge in the hot environment of a furnace with temperatures in the region of 1000°C . The possible occurrence of thermionic emission should therefore be borne in mind.

The secondary emission electron current relates to ion current by the yield (γ_i) as:

$$J_{e-,sec} = \gamma_i J_{ion} \quad (29)$$

Equation (28) becomes then:

$$I = A_c((1 + \gamma_i)J_{ion} + J_{e-,th}) \quad (30)$$

In the case where thermionic emission is negligible, the current drawn in the external circuit is proportional to the current density of ions impacting the cathode.

7.2.2 Discharge sustaining mechanisms

7.2.2.1 Gas discharge characteristics at low temperature:

From Figure 71, it can be seen that:

1 for a given pressure, the current drawn increases exponentially with the accelerating voltage i.e. the discharge conductivity increases with voltage.

2 for a given accelerating voltage (V_c), the current drawn increases with pressure.

3 the minimum cathode voltage at which the plasma is sustainable decreases with pressure,

These three points are characteristic of DC glow discharges sustained by secondary electron emission from the cathode (see Chapman¹¹¹).

The energy of the secondary electrons emitted by the cathode increases as the accelerating voltage is increased. This enables them to undergo more ionizing collisions as they traverse the plasma volume. Hence the current increases with voltage because the degree of ionization is increased.

At a set accelerating voltage, the energy of the secondary emitted electrons that enter the plasma volume is constant. Increasing the pressure results in more charge carriers. Figure 77 shows a plot of current versus pressure for set accelerating voltages.

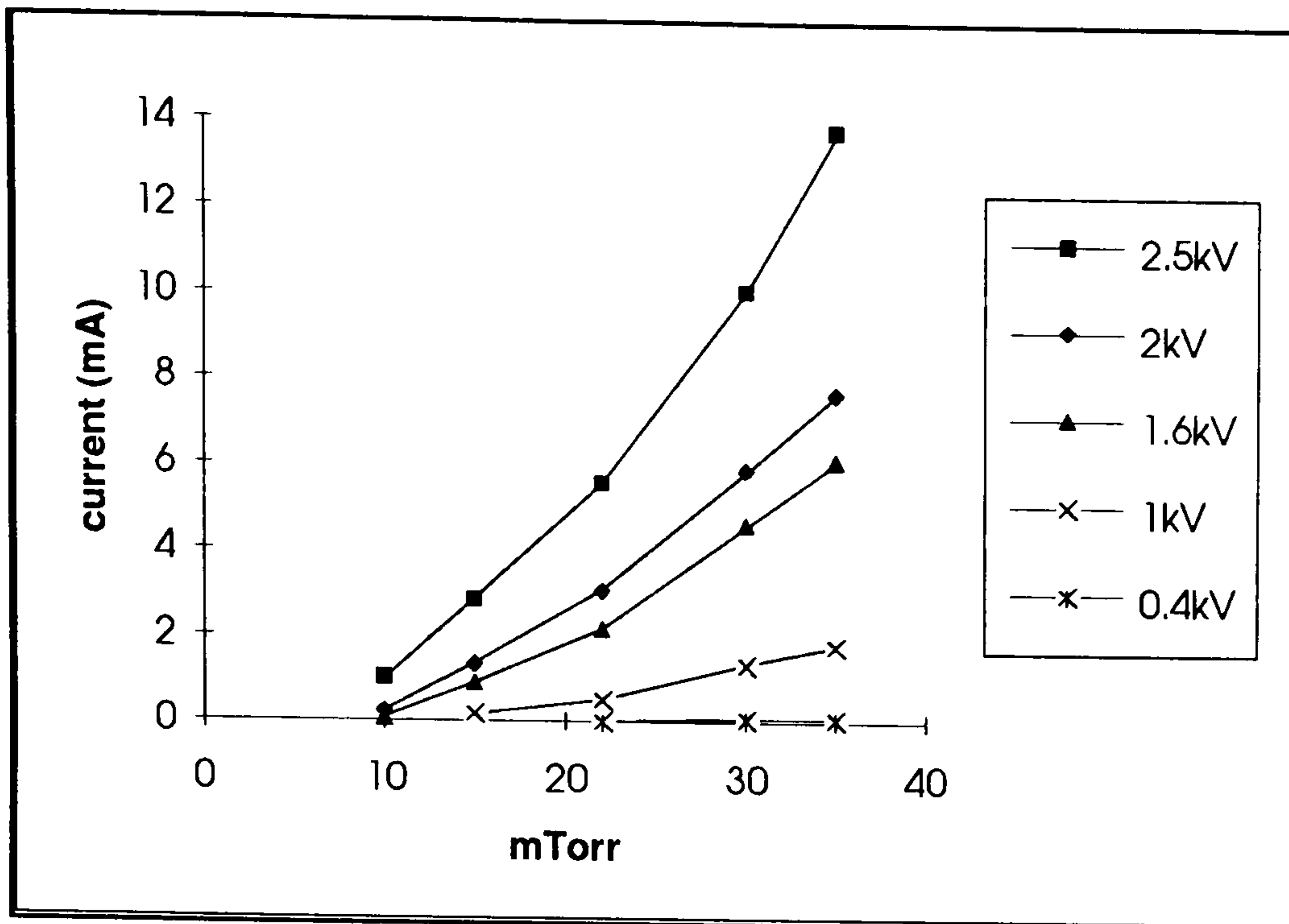


Figure 77: Current/pressure characteristics for different cathode voltages at 60°C (replot of Figure 71).

The convex shape of these characteristics means that as the gas pressure is increased, the degree of ionization also increases.

7.2.2.2 The decrease of current with furnace temperature:

The temperature dependence of the current drawn has been split into the decreasing and increasing regimes for discussion. The experiment was repeated in order to produce a large number of data points for each temperature regime. Figure 78 is a detailed plot of the decrease in current drawn with furnace temperature over the room temperature to 500°C range at 22mTorr.

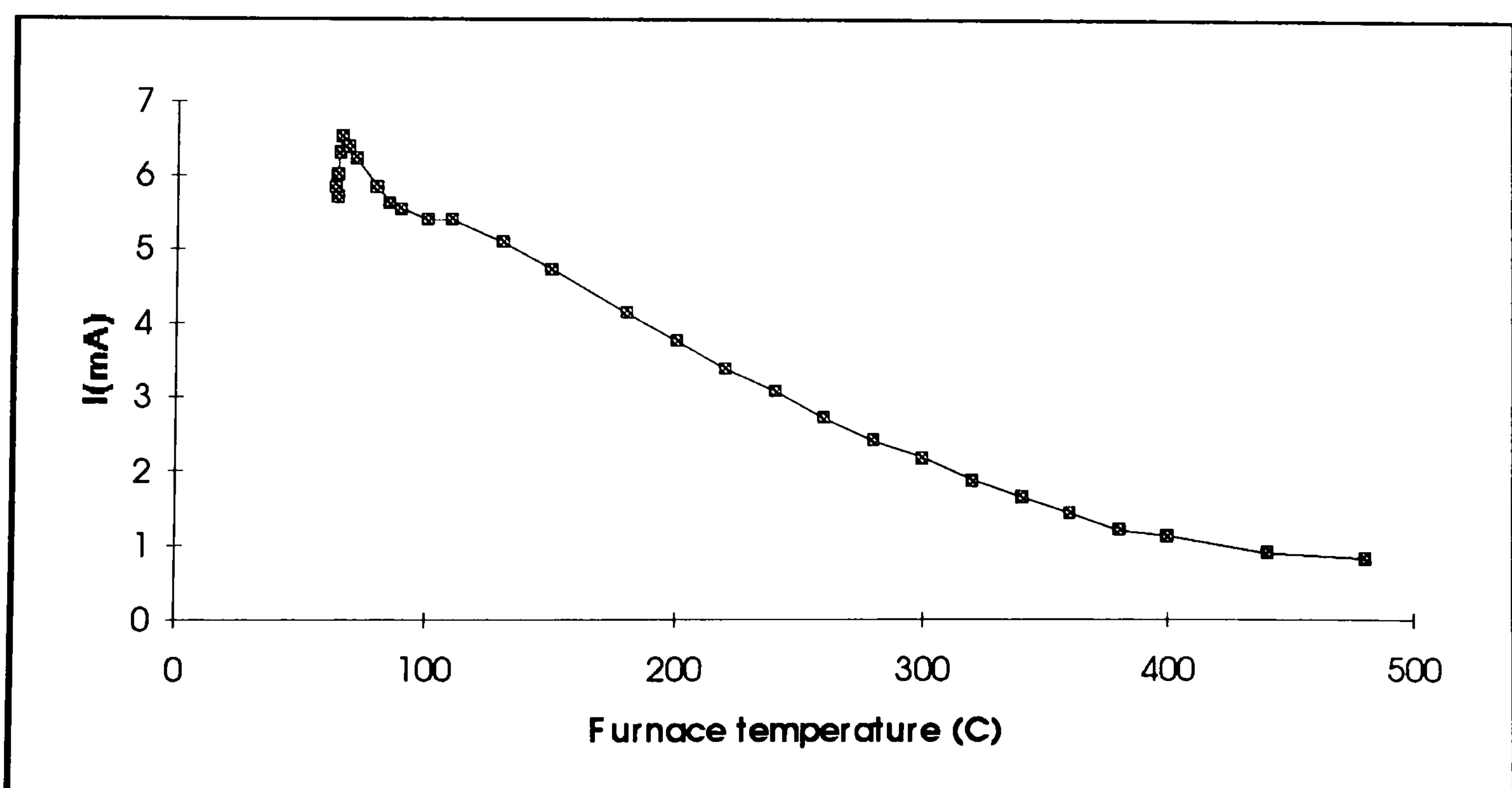


Figure 78: Evolution of current drawn with furnace temperature ($V_c = -2.5$ KV, $P = 22$ mTorr).

Since ionization in the sheath is negligible¹¹⁰, the ion current density impacting the cathode is the same as that entering the plasma sheath and can be written (see chapter 5):

$$J_{ion} = 0.6en_{ion}\left(\frac{kT_e}{m}\right)^{\frac{1}{2}} \quad (31)$$

where n_{ion} , m , T_e , k and e are respectively the ion concentration in the bulk plasma, the ion mass, the electron temperature and the elementary charge.

As the furnace enclosure is not sealed, when increasing the furnace temperature, the density of the hot gas inside the furnace needs to be less to equilibrate to the pressure set inside the chamber by the cold gas. The evolution of gas density (n) inside the furnace can be predicted from the gas law:

$$n = \frac{P}{kT} \quad (32)$$

where T is the gas temperature inside the furnace and P the furnace pressure which equates to the chamber pressure. Using the degree of ionization α (ratio of plasma density to gas density), equation (31) may therefore be written as:

$$J_{ion} = 0.6e\alpha \frac{P}{kT} \left(\frac{kT_e}{m}\right)^{\frac{1}{2}} \quad (33)$$

It is a good approximation to assume that the degree of ionization α is independent of the furnace temperature considering that:

- ionization of the gas relies on secondary electron emission and the yield γ_i is independent of temperature¹¹³.
- the degree of ionization was found not to depend significantly on gas density for pressures less than 22mTorr at 60°C (see Figure 77). Therefore, decreasing the gas density by increasing the furnace temperature at 22mTorr should not affect the degree of ionization.

The dependence of the electron temperature (typically 20000K) on the furnace temperature is unknown. As the gas becomes rarer inside the furnace upon heating, the electron/gas atom collision frequency decreases and, as a result, the electron temperature potentially increases. Two cases are envisaged here, the first assuming that the electron temperature does not vary with furnace temperature ($T_e = \text{constant}$) and the second assuming that it increases inversely with the gas density ($T_e \propto T$). Given these assumptions and the fact that the chamber pressure did not vary with furnace temperature, according

to equation (33), the ion current density (J_{ion}) should decrease inversely with the furnace temperature for $T_e = \text{constant}$ and with the square root of the furnace temperature for $T_e \propto T$.

In order to test the validity of the above reasoning, the current drawn was plotted as a function of $1/T$ (see Figure 79) and $1/\sqrt{T}$ (see Figure 80).

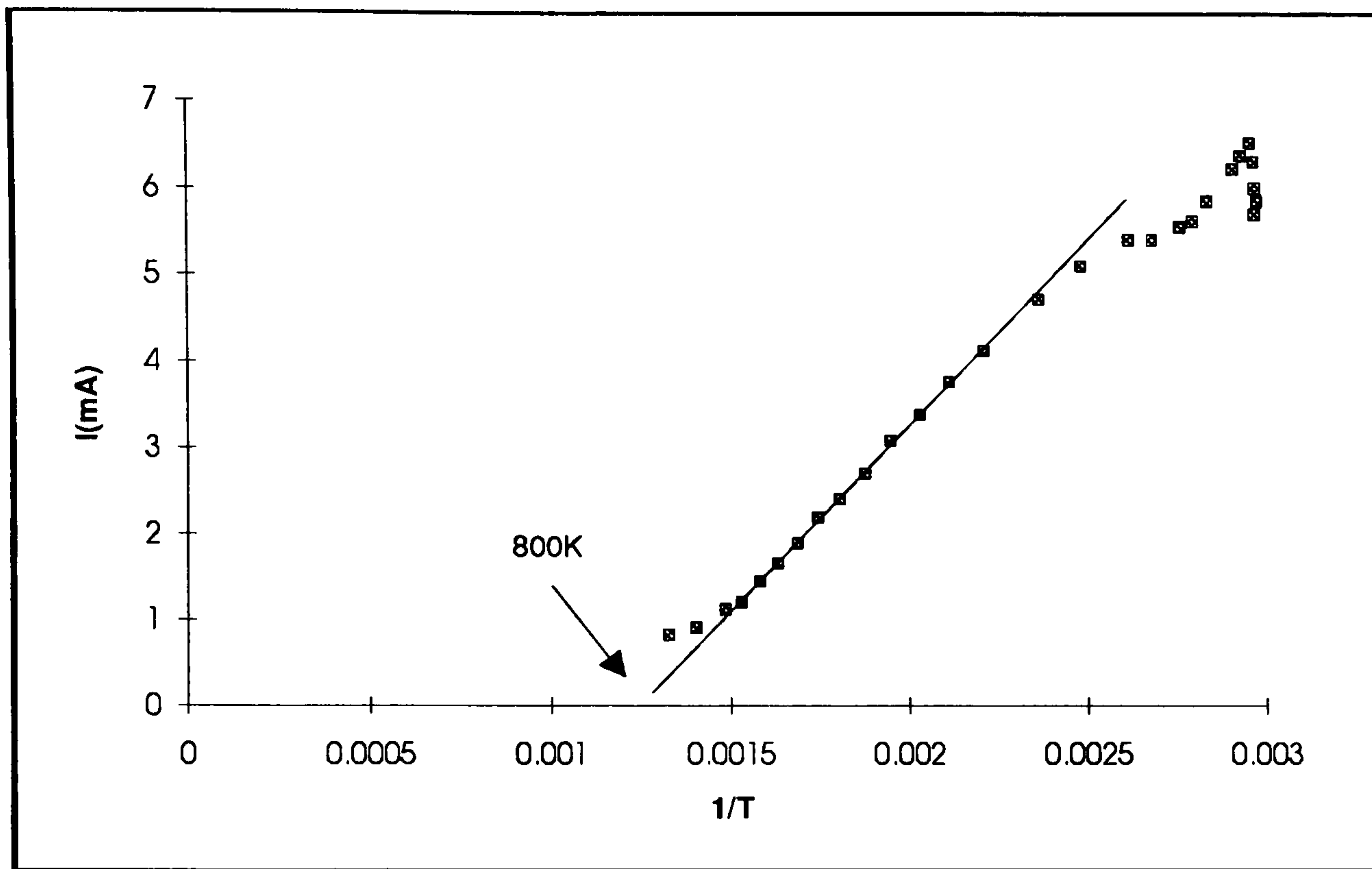


Figure 79: Replot of data from Figure 78 with T in Kelvin (assuming $T_e = \text{constant}$).

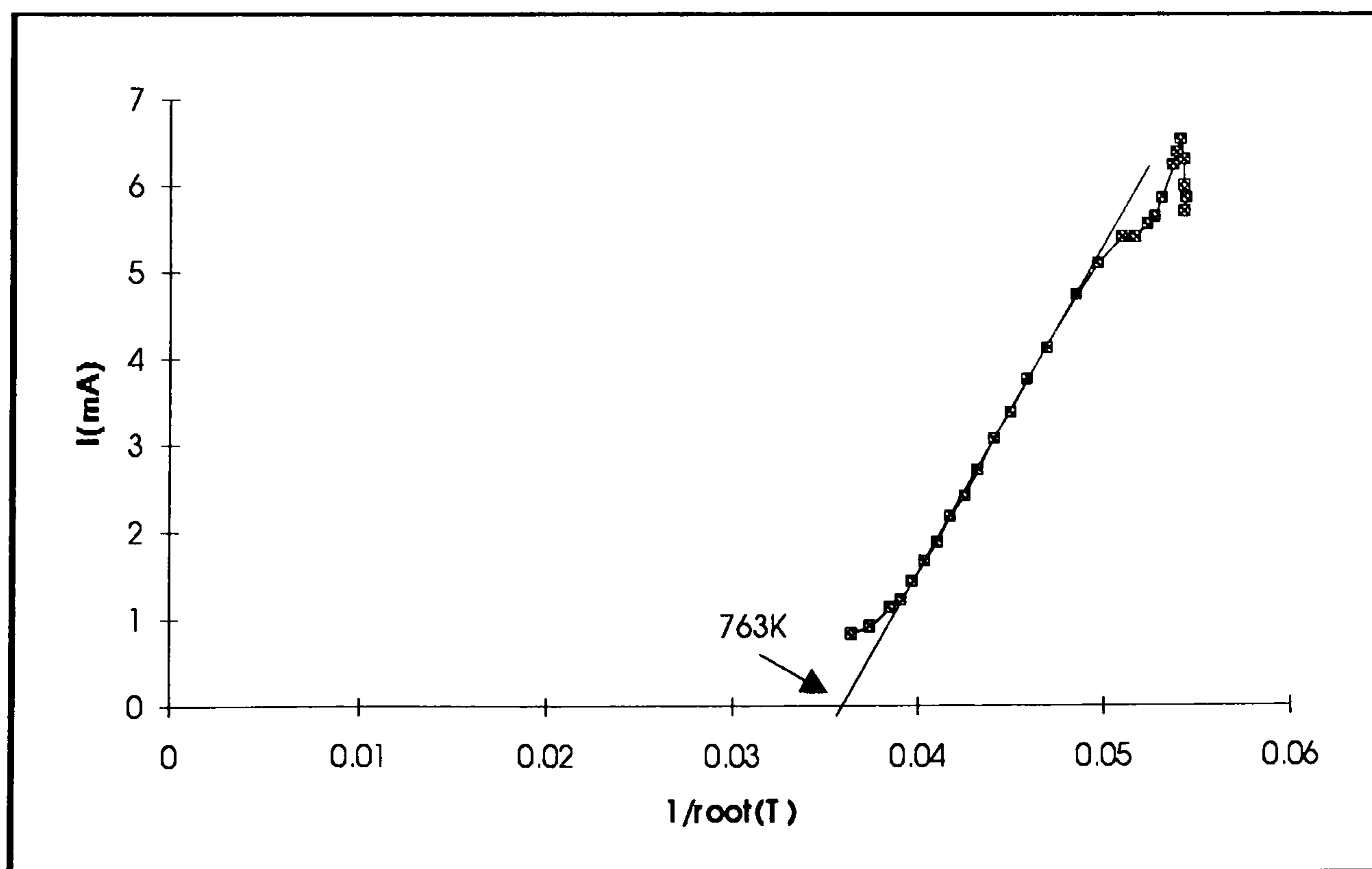


Figure 80: Replot of data from Figure 78 with T in Kelvin (assuming $T_e \propto T$).

The above plots substantiate the hypotheses that the current drawn is proportional to the ion current density and that the latter decreases with

temperature as the gas density inside the furnace decreases. The straight lines can be extrapolated to the x-intercept which is the temperature above which a DC glow discharge plasma is no longer sustainable at 22mTorr and -2.5KV. This critical furnace temperature corresponds to a gas density threshold below which the emitted secondary electrons cannot undergo enough ionizing collisions to maintain the plasma.

The implication of the above is that for a given working gas pressure, cathode voltage and furnace geometry, there is a critical temperature above which a DC plasma cannot be generated in the furnace as maintained by secondary emitted electrons.

7.2.2.3 High temperature I/V characteristics:

Figure 73 shows the current-voltage characteristics obtained at a furnace temperature of 810°C (above the critical temperature identified above) for a set of chamber pressures. It contrasts with the low temperature I-V characteristics in that:

- 1 there is no voltage threshold below which current cannot be drawn.

- 2 relatively high currents can be drawn at chamber pressures for which a glow discharge could not be struck at room temperature (7.5mTorr).

These two points indicate that there is a discharge sustaining mechanism other than secondary electron maintenance. This is consistent with the above analysis which predicted that a glow discharge plasma maintained by secondary emission could not be generated at temperatures above 500°C for cathode voltages and chamber pressures less than -2.5KV and 22mTorr respectively.

The nature of the current drawn at high temperature can be further assessed by examining its dependence on furnace temperature (see Figure 81). It can be seen that the current increases sharply with furnace temperature.

Although the thermocouple is not attached to the cathode, it is assumed here that the temperature read by the thermocouple is the same as the cathode temperature. This hypothesis is valid so long as the substrate is subjected to the same heating as the thermocouple. The validity of this assumption depends on the significance of ion bombardment heating of the cathode.

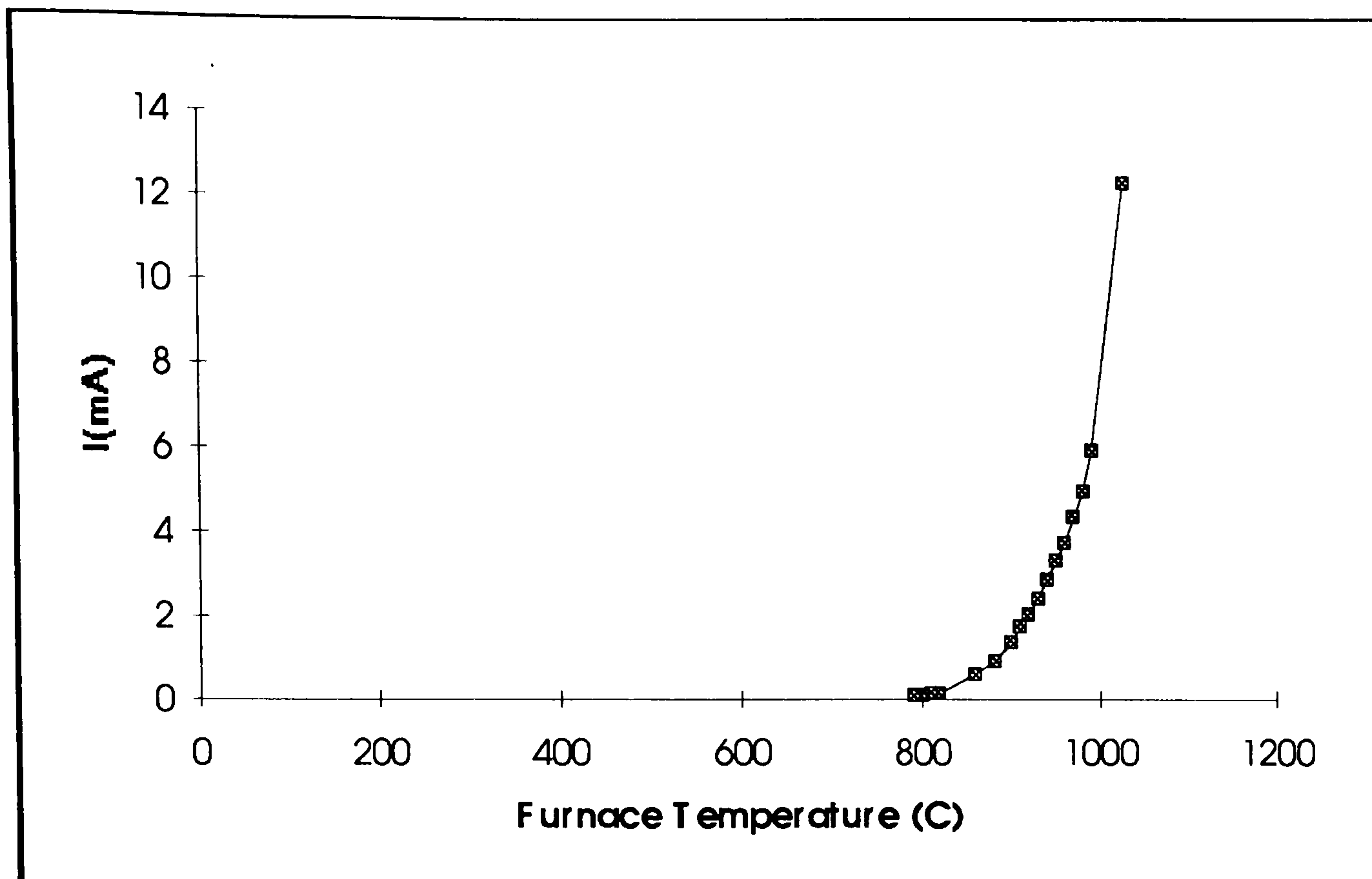


Figure 81: Dependence of current drawn on furnace temperature. (VC=-2.5KV, P=5mTorr).

If this assumption is right, Figure 81 can be read as the rise of current drawn with cathode temperature which points to possible thermionic emission (see chapter 5).

Schottky's law predicts the current density that can be thermionically emitted from a hot surface with the enhancement by an electric field as:

$$J_s = aT^2 \exp\left(-\frac{\varphi - \sqrt{e^3 E}}{kT}\right) \quad (34)$$

where a and φ are respectively a temperature-independent-parameter and the work function, both a function of the emitting material, and E is the electric field in the vicinity of the surface.

If the current drawn was purely due to thermionic emission, then the current density measured I/A_c should follow equation (34), which can be rewritten as:

$$2\ln(T) - \ln(J) = \frac{\Phi}{kT} - \ln(a) \quad (35)$$

where:

$$\Phi = \varphi - \sqrt{e^3 E} \quad (36)$$

Figure 82 shows the plot of $(2\ln(T) - \ln(I))$ vs $1/T$.

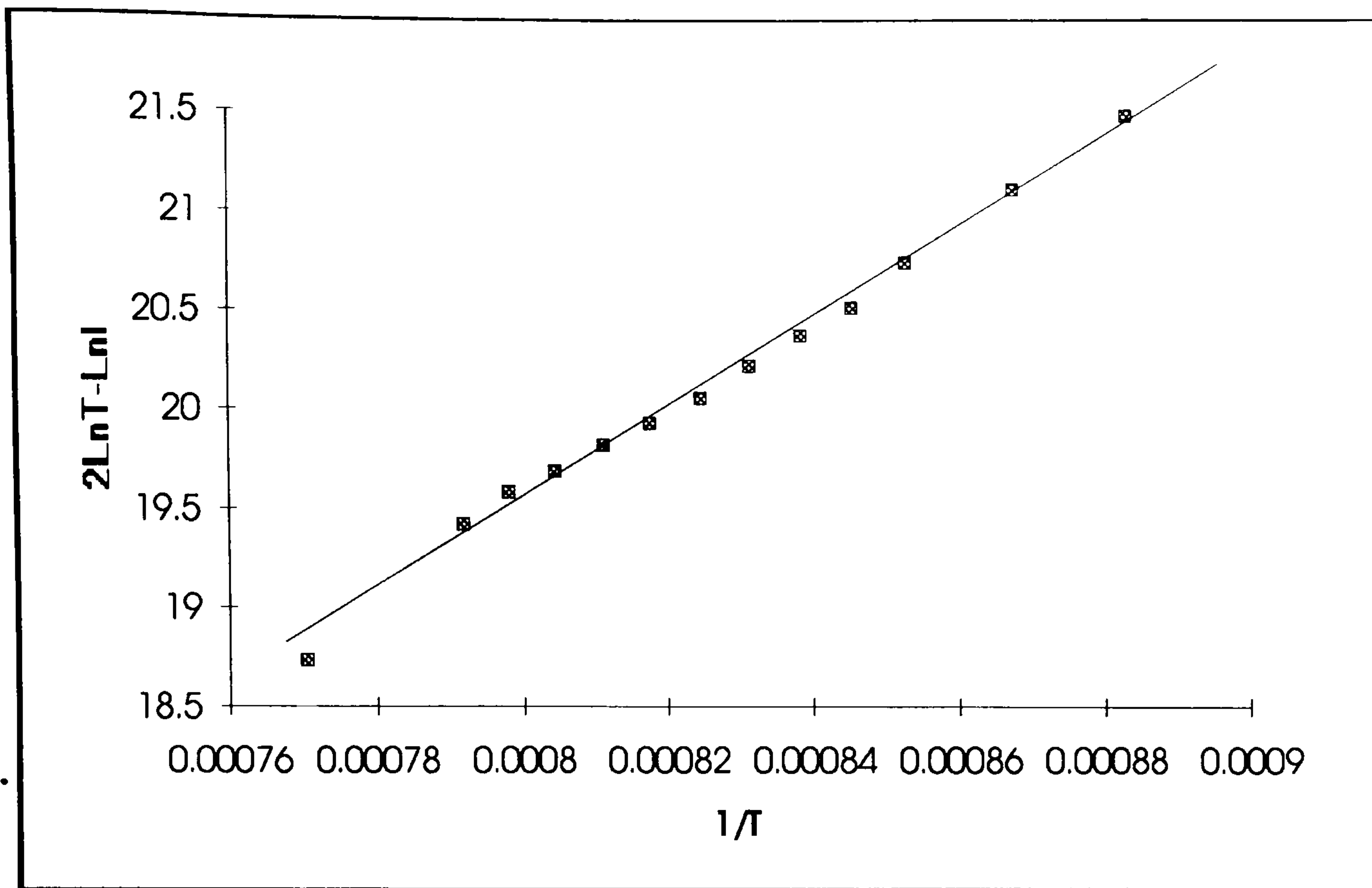


Figure 82: Replot of data from Figure 81, T in Kelvin and I in Amps.

This is a straight line with a correlation factor R of 0.996 and a slope corresponding to an effective work function of $\phi=2.0\text{eV}$. The work function of ZrO_2 for thermionic emission without field enhancement is $\phi=3.4\text{eV}$ (Ref. 112). The above plot proves that thermionic electron emission of the hot cathode is significant and that the total current drawn at elevated temperatures can be approximated as being proportional to the thermionic electron current. Given equation (30), this is equivalent to say that the ion current drawn from the plasma, if any, is also proportional to the thermionic electron current:

$$J_{ion} = \beta J_{e-th} \quad (37)$$

The thermionic current is independent of gas pressure. Therefore, the rise in current with pressure seen in Figure 73 is the manifestation of an ion current originating from ionization by the energetic thermionic electrons. This is what the above equation predicts. The implication is that as the furnace temperature is increased from room temperature to elevated temperatures, the discharge sustaining mechanism shifts from secondary electron emission to thermionic electron maintenance.

7.2.3 Estimation of ion currents

7.2.3.1 Ionization from thermionic emission

Having established that the discharge is sustained by thermionic emission from the substrate at elevated temperature, it is now necessary to separate out the thermionic current from the induced ion current.

The ionization coefficient β can be roughly estimated theoretically as:

$$\beta = n\sigma l$$

where n , σ , l are respectively the gas density, the electron ionization cross-section of the gas, and the distance travelled by the ionizing electrons.

For a gas pressure of 10mTorr and a temperature of 1000°C, the gas density inside the furnace enclosure is $7.6 \times 10^{13} \text{ cm}^{-3}$ (from equation (32)). The ionization cross-section of argon for electron energies of 2.5keV is $4.41 \times 10^{-17} \text{ cm}^2$ (see Figure 47 in chapter 5). Assuming a mean cathode-to-anode distance of 30cm (overestimate) yields a gas ionization of 10%. The bulk of the current monitored at 1000°C would therefore consist mainly of an electron current. This was experimentally verified by varying the argon pressure at set temperature and cathode accelerating voltages (see example in Figure 83).

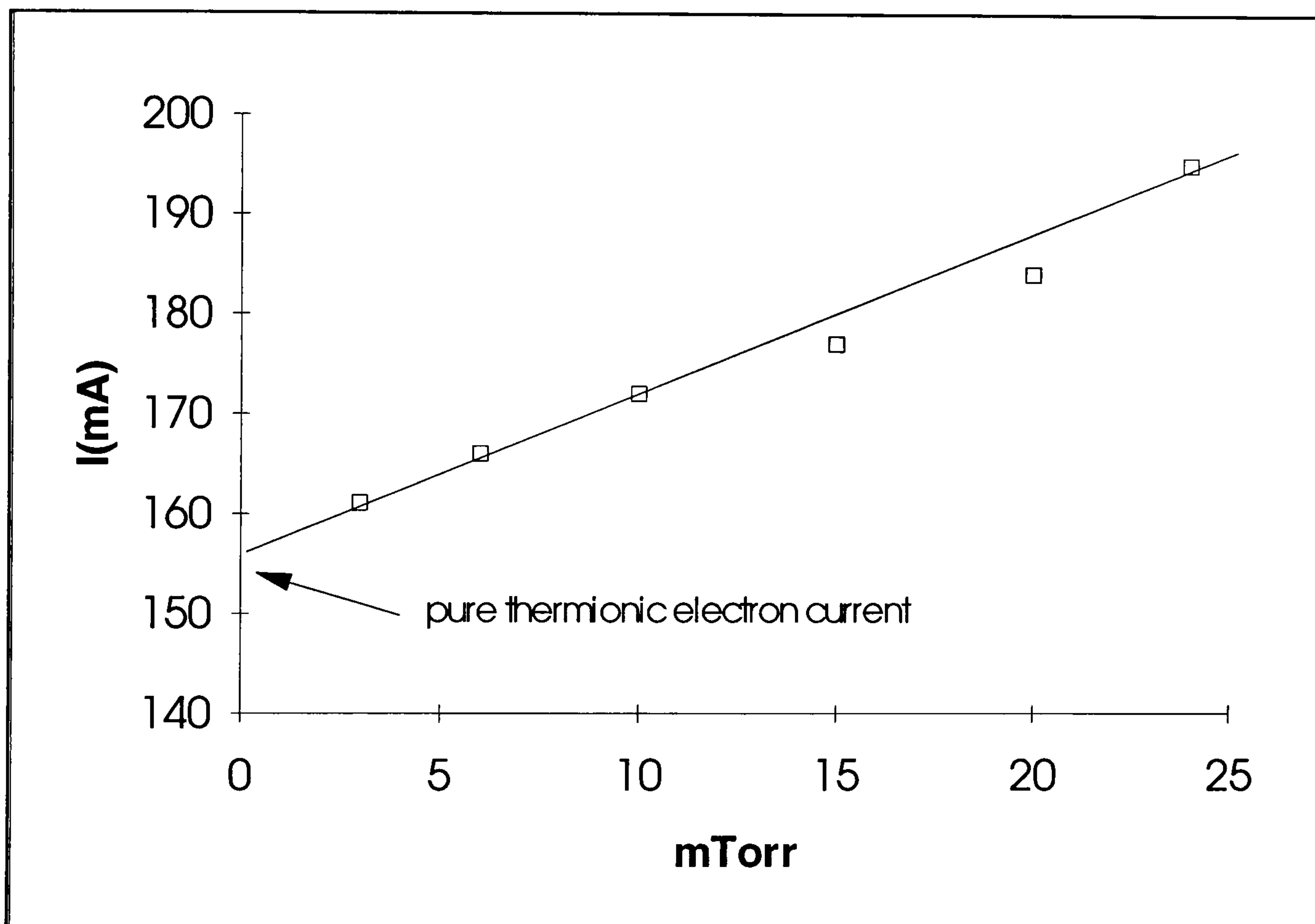


Figure 83: Dependence of current on argon pressure at 1000°C and 2.5kV substrate bias.

The Y-intercept is a measure of the sole thermionic electron current $J_{th,e-}$. The coefficient of ionization at a given pressure p can be determined graphically as:

$$\beta = \frac{\Delta I(p)}{A_c J_{th,e-}}$$

Using this method, the ionization coefficient was measured as a function of the chamber pressure for a series of accelerating voltages at 1000°C (see Figure 84).

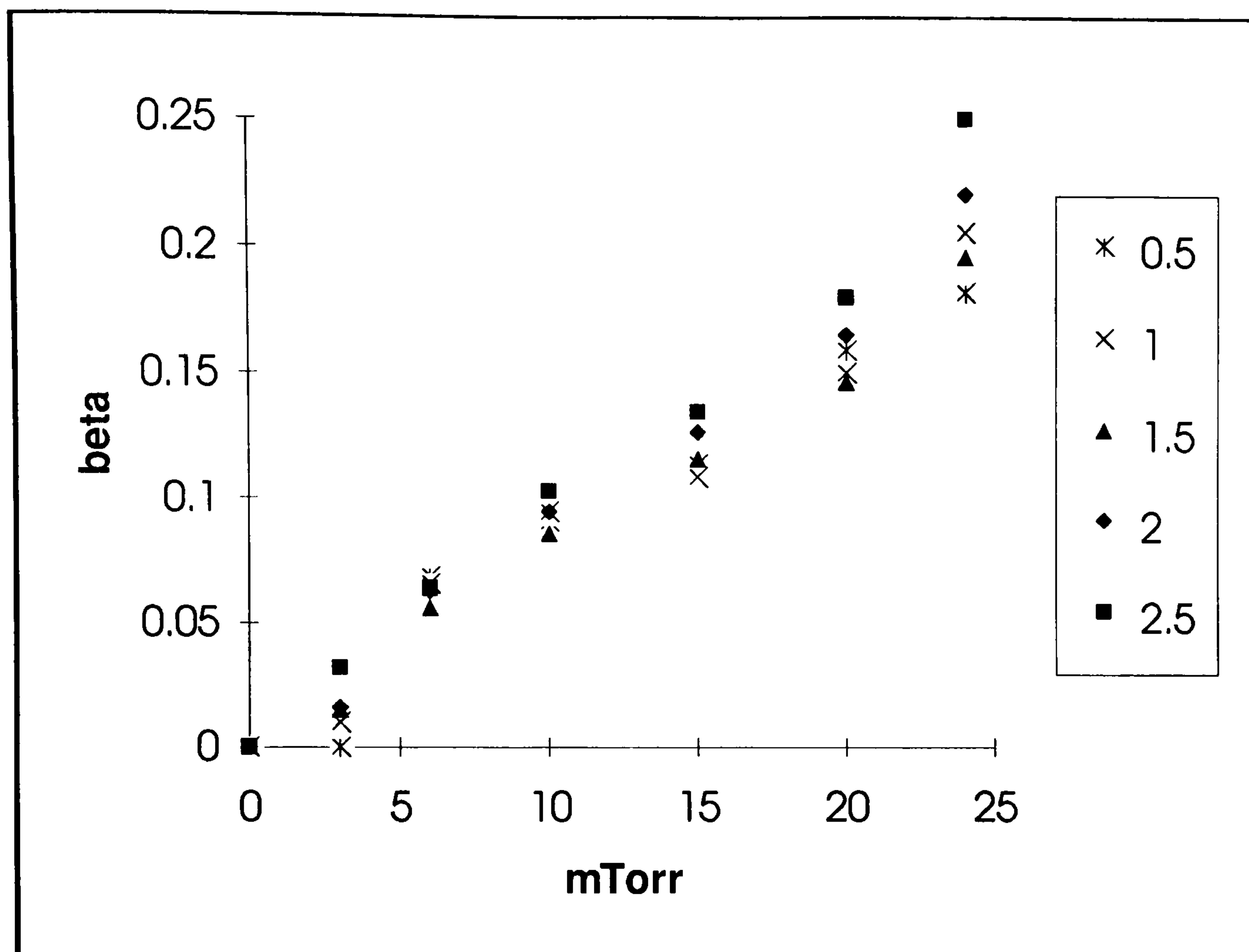


Figure 84: Dependence of thermionic ionization coefficient on argon pressure and accelerating voltage (kV) at 1000°C.

The thermionic ionization coefficient seems to increase with accelerating voltage, but the significance of this effect decreases with working pressure (e.g. 10mTorr). In order to determine an overestimate of the ion current density that applied for the depositions carried out at 10mTorr, a thermionic ionization coefficient of 15%, independent of substrate bias, will be assumed in the rest of this analysis.

7.2.3.2 Ionization from Electron Beam gun:

The onset of the electron beam gun may create additional ions via four possible mechanisms that are:

- 1 ionization of the vapour by thermionic electrons from the cathode (substrate).
- 2 ionization of the background gas by the gun electron beam
- 3 ionization of the vapour by the gun electron beam.
- 4 thermal ionization of the vapour

The total current drawn (I) can be expressed as:

$$\frac{I}{A_C} = J_{th,e^-} + \beta_{gas} J_{th,e^-} + \beta_{vap} J_{th,e^-} + \beta_{tot} \frac{I_{EB}}{A_C} \quad (40)$$

where:

J_{th,e^-} is the thermionic electron current

β_{gas} is the thermionic ionization coefficient of the background gas (15%)

β_{vap} is the thermionic ionization coefficient of the vapour (mechanism 1)

β_{tot} is the ionization efficiency of the Electron Beam gun encompassing mechanisms 2 to 4.

I_{EB} is the gun Electron Beam current

A_c the cathode area.

It should be noted that the contribution to the total current monitored of secondary electrons emitted from the cathode as a result of ion bombardment has been neglected in equation (40). This is justified considering the typically low secondary emission yields (10%).

Clearly, the mechanisms 2 to 4 should in principle be independent of the substrate bias. An interaction could be expected if the high substrate bias voltage affected the shape of the gun electron beam. There was no evidence of such a phenomenon and one should recall the potential screening from the plasma in between. Therefore, the ion current attributable to mechanisms 2 to 4 at -2.5kV should be the same as that at zero substrate bias. Given that at 0kV the thermionic induced ionization is eliminated, the current at the Y-intercept of the I-V characteristics (see Figure 75) is a measure of the net flux of charged particles from the vapour and the gas ionized by the EB-gun. These characteristics are reproduced in Figure 85.

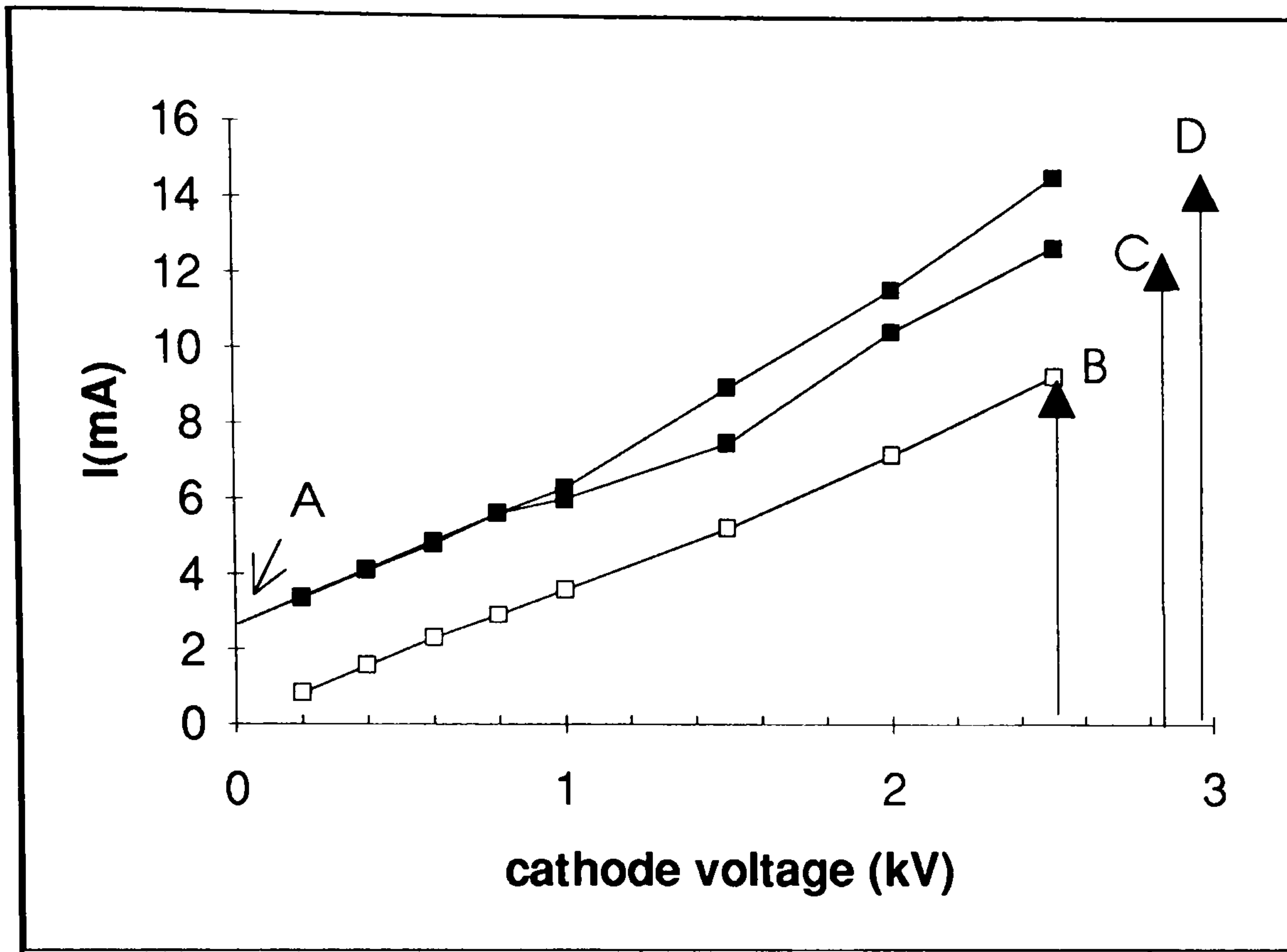


Figure 85:Current-voltage characteristics in the range 1014-1023°C and a chamber pressure of 10mTorr (see Figure 75).

The Y-intercept of the characteristic slope at -50V substrate bias should correspond to an ion current considering that the secondary electrons emitted from the source have insufficient energies (no more than a few tens of eV's)^{132,113} to overcome the repelling substrate potential while the fast reflected primaries (up to several keV) are deviated away by the magnetic field in the vicinity of the hearth.

The total ion current may therefore be estimated as follows:

- the ion current attributable to mechanisms 2 to 4 corresponds to the Y-intercept, point A, ($I_A=2.6\text{mA}$)

- The gas thermionic ionization current can be derived from the current at point B as: $I_B \cdot \beta_{\text{gas}} / (\beta_{\text{gas}} + 1) = 9.3 \times 0.13 = 1.2\text{mA}$

- The vapour thermionic ionization current can be derived from the currents at points C and D i.e. in the range $[I_D - I_B - I_A, I_C - I_B - I_A] = [0.85 - 2.7\text{mA}]$

The total ion current drawn impinging on the substrate is the sum of these three contributions: 4.8-6.5mA which corresponds to current densities in the 0.10-0.13mA/cm² range (50cm² substrate area). These values derived from the assumption that $\beta_{\text{gas}}=15\%$ correspond to an upper bound of ion current density for high temperature DC ion plating of YSZ. The ion current density for low temperature RF biasing is in turn estimated in the following section.

7.3 CHARACTERISTICS OF LOW FREQUENCY RF GAS DISCHARGE (RESULTS)

Unlike with the DC power supply, where the cathode voltage was the controllable parameter, with the RF generator, the 'output power' was the parameter setting the discharge conditions. In this work, the system was operated at its maximum power level i.e. 6kW nominally. The current/voltages characteristics obtained are presented in the result section as a function of chamber pressure and electrode area. Deriving the ion current impinging on the substrates is a more complex issue in the RF case than in the DC case. This is because the RF current monitored consists of the sum of an ion current and a displacement current, the latter being associated with the capacitance of the oscillating sheath. In order to isolate the ion current density incident on the substrates, a semi-empirical methodology was employed. A simple model of ion bombardment in low frequency RF gas discharges is first formulated from which the ion current density is then derived using ion cathode heating considerations. In the latter part of this section, it was attempted to explain why the RF plasma extinguished in conjunction with the evaporation source.

7.3.1 Current/voltage waveforms

Figure 86 shows a record of the voltage and current waveforms obtained using the maximum power output from the generator at a chamber pressure of 10mTorr. The waveform of the voltage resembles a pure sine wave. The current which is the 'response' to the driving voltage has a waveform noticeably different from a pure sine wave in that it incorporates a sharp peak and some high frequency modulation. The RF current quoted in the text corresponds to half of the maximum peak-to-trough amplitude of the waveform monitored on the oscilloscope. A more appropriate approach would be to use the root-mean-square current but this was discouraged by the complexity of the current waveform. It will have to be remembered in the rest of the text that the RF current quoted does not correspond to but is proportional to the RMS current. The RF current monitored is the sum of a displacement current and a conduction current. Only the latter contribution is of interest here as it relates to the ion current incident on the substrates. This is the object of the present work to estimate the magnitude of the conduction term.

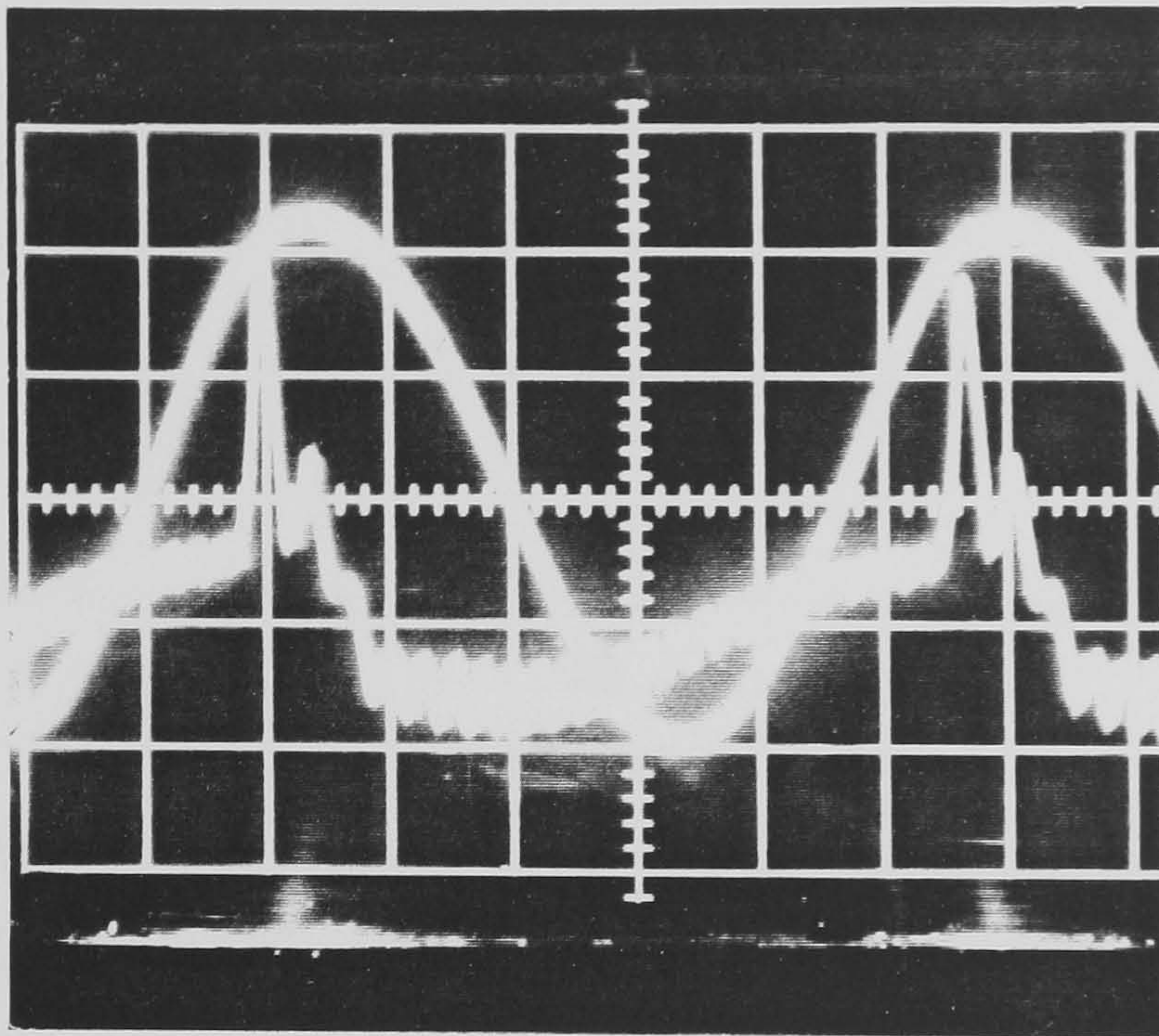


Figure 86: Picture of the RF voltage and current waveforms as displayed on the oscilloscope.

7.3.2 Current/voltage characteristics

At the set nominal 6kW power level, both the RF voltage and RF current were found to decrease with increasing chamber pressure as seen from Figure 87 and Figure 88. For pressures less than 8 mTorr in argon, the current seemed to saturate or even drop (see Figure 88).

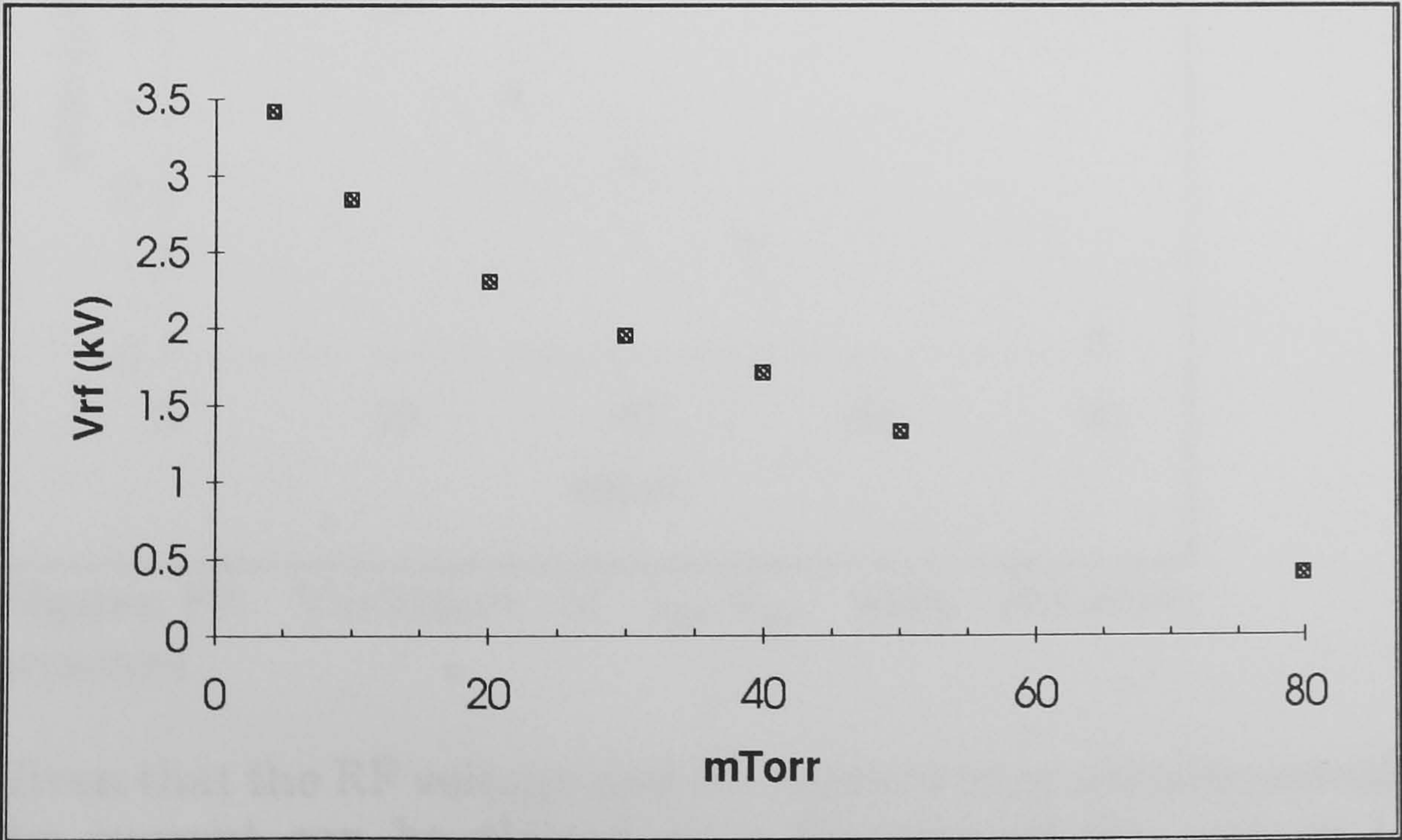


Figure 87: Dependence of RF voltage on chamber pressure for a set nominal RF power of 6kW.

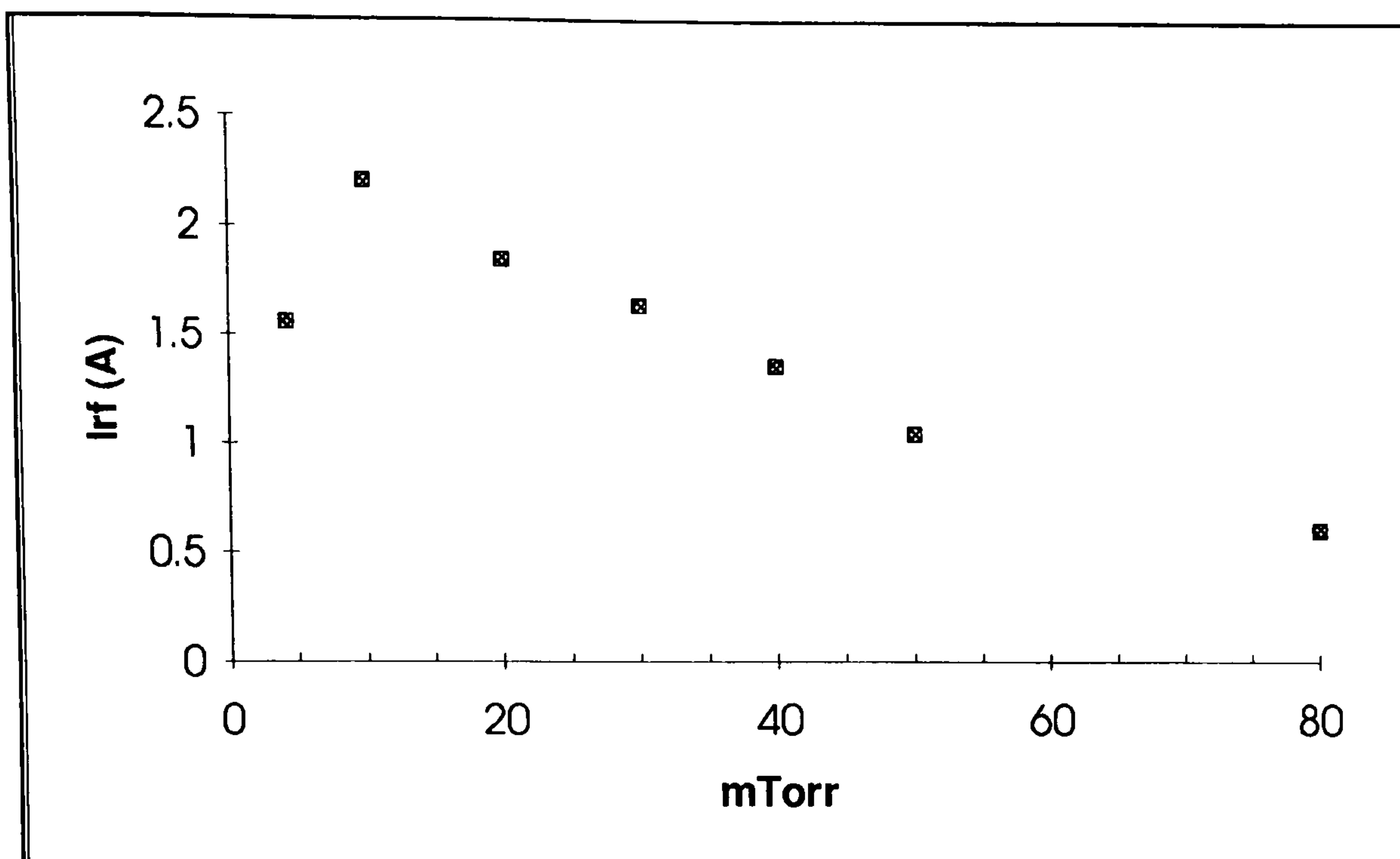


Figure 88: Dependence of RF current on chamber pressure for a set nominal RF power of 6kW.

The current/voltage phase shift did not appear to change noticeably with pressure, therefore it can be inferred from Figure 87 and Figure 88 that the power delivered by the generator decreased with chamber pressure (see Figure 89).

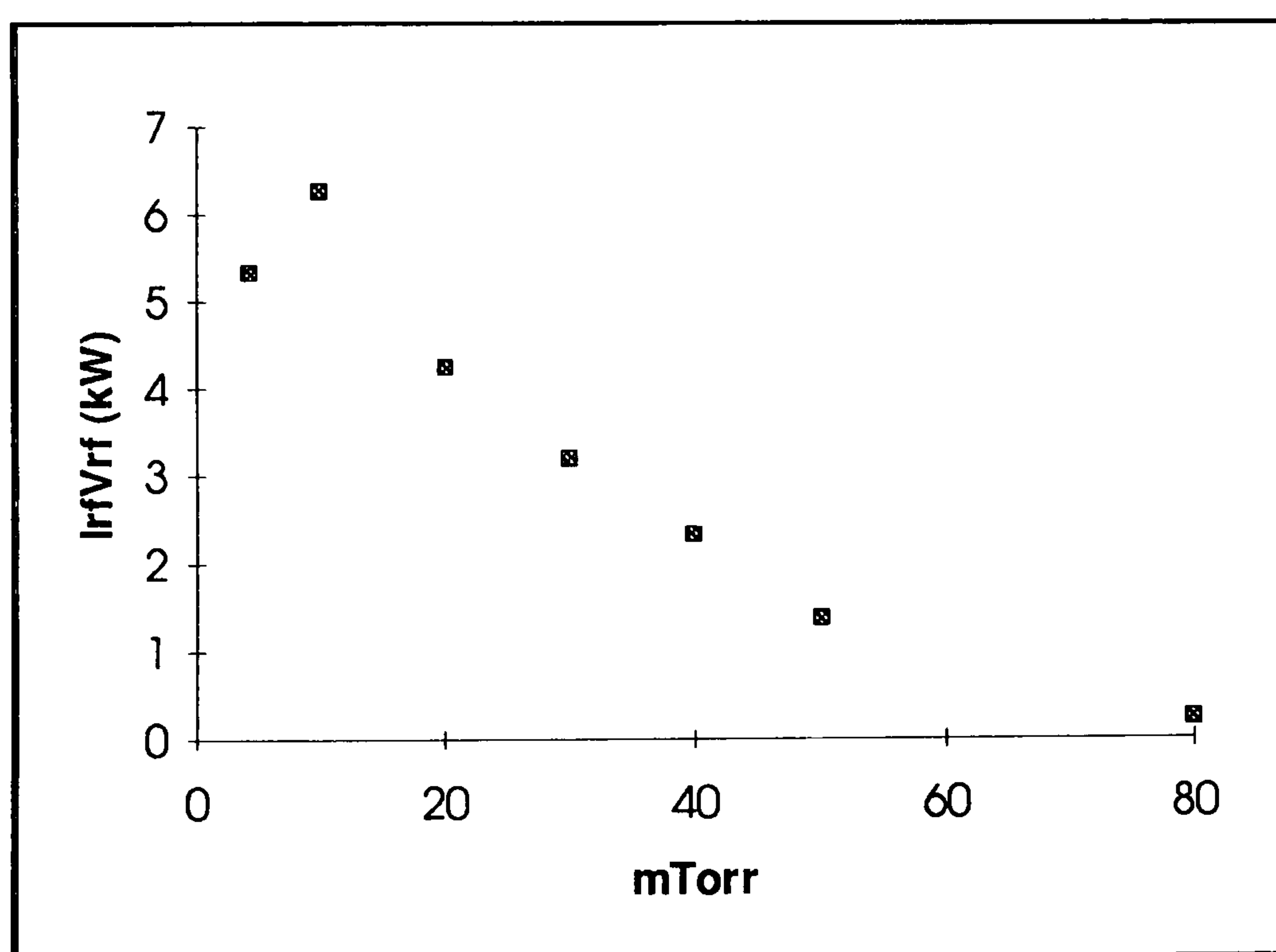


Figure 89: Variation of $I_{RF} \cdot V_{RF}$ with chamber pressure.

Given that the RF voltage and RF current vary simultaneously with pressure, the current can be plotted as a function of the voltage by changing the chamber pressure (see Figure 90).

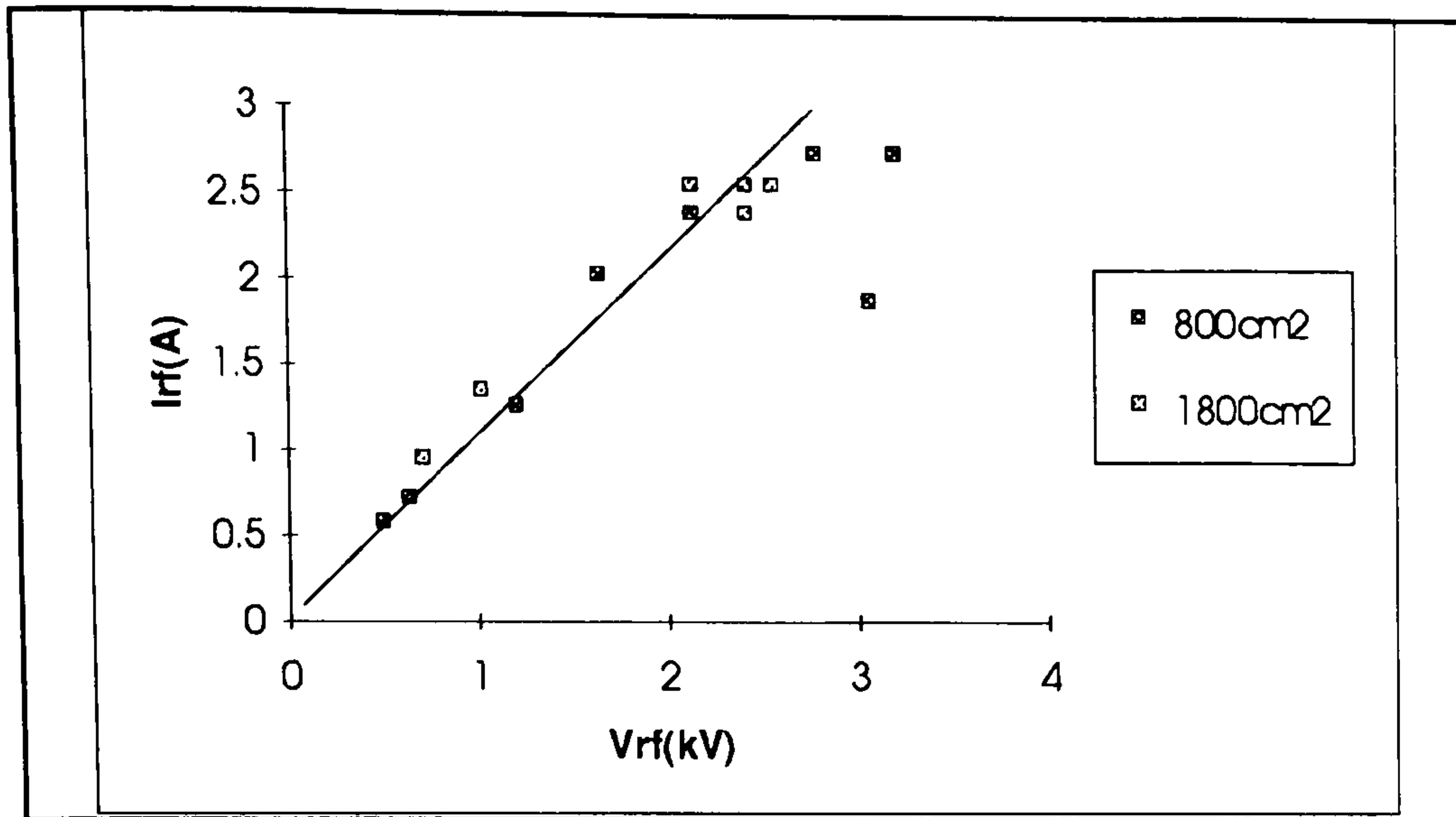


Figure 90: I-V characteristics as a function of the cathode surface area (plot obtained over typical pressure range of 5 to 100mTorr).

The RF current amplitude is found to be proportional to the RF voltage amplitude with changing pressures. The inference is that, overall, the plasma impedance does not vary with chamber pressure.

The I-V characteristic is found to be independent of the electrode size over the range considered. This means that for a set output power from the generator, the RF power density delivered to the substrates is inversely proportional to the cathode area. This result is of significance as it means that a consistent electrode surface area must be used in order to aim for reproducible bias conditions.

By increasing the pressure, the DC offset measured on the driven electrode was found to decrease simultaneously with the RF voltage amplitude. A linear dependence is found between the DC offset magnitude and the RF voltage amplitude (see Figure 91). A slope of 0.96 and an X-intercept of about 350V were found. These parameters do not seem to change significantly with cathode size in the range considered.

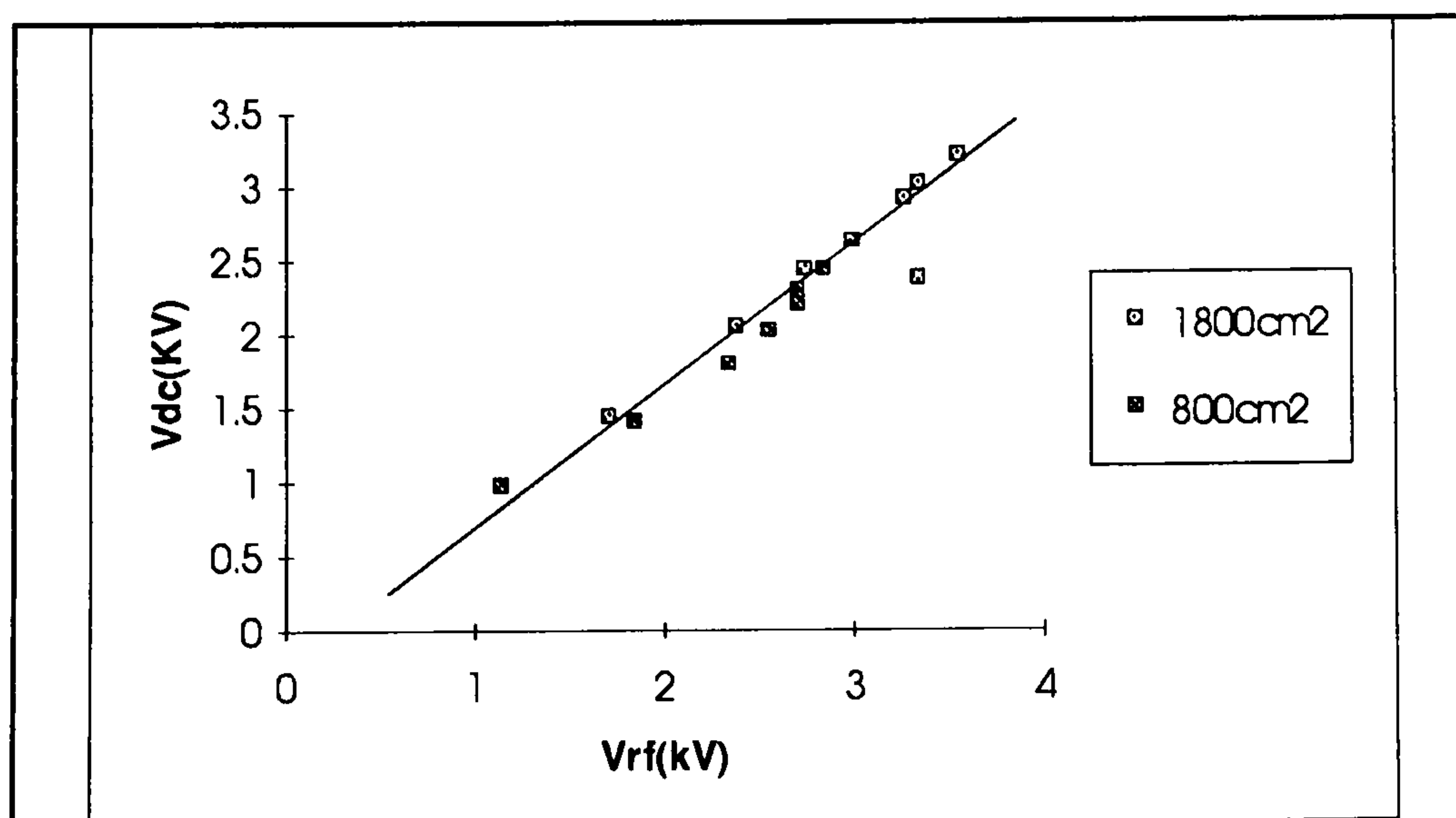


Figure 91: Dependence of the DC offset magnitude (<0) on the RF voltage amplitude (plot obtained over typical pressure range of 5 to 100mTorr).

7.3.3 Interaction between EB gun and RF plasma:

The RF plasma was found to extinguish ($V_{DC}=0$, $I_{RF}=0$) above a certain threshold of Electron Beam current, and this threshold was found to decrease with deposition time. In order to ion plate 'throughout', the gun current had to be constantly stepped down so as to maintain the plasma. The threshold values were found to vary from run to run.

7.4 MODELLING OF LOW FREQUENCY RF GAS DISCHARGE (DISCUSSION)

7.4.1 Derivation of ion current density: the approach.

The ions that enter the plasma sheath undergo multiple collisions with gas neutrals on their acceleration path to the substrate. The effect of collisions, that can be either elastic scattering or charge transfer collisions was discussed in the introductory 'plasma chapter' of this thesis (chapter 5). Some of the power that would be carried by the ions, if their transit through the cathode sheath were collisionless, is transferred to the neutrals via collisions. The end result of these collisions is therefore to increase the flux of fast particles to the substrate, consisting of both neutrals and ions, while reducing the average particle energy. The power density delivered to the substrate by the bombarding particles (ions and neutrals), defined as the product of particle energy by their flux density, can be expressed mathematically as:

$$P_b = \phi_i \int_0^{\infty} f(E_i) dE_i + \phi_n \int_0^{\infty} f(E_n) dE_n \quad (41)$$

where ϕ , E , $f(E)$ are respectively the flux density, the energy and the energy distribution of the bombarding ions (i) and neutrals (n).

The following assumption will be made in this analysis:

Assumption 1:

The bombardment power density delivered by both the ions and neutrals is the same as the bombardment power density that would be delivered by the ions only, if the sheath was collisionless.

This assumption is valid so long as the power sharing between neutrals and ions is conservative i.e.

- all the fast neutrals generated by collisions in the sheath bombard the substrate.

- ionization within the sheath is negligible.

Consider now a DC plasma with the collisionless sheath condition. The ions will impinge on the cathode with a same energy corresponding to the cathode sheath potential (ignoring subtleties such as the pre-sheath field, the Bohm's criterion etc...). Then, the bombardment power density can be expressed as:

$$P_b = J'_i V_{c,sheath} \quad (42)$$

where J'_i is the ion current density and $V_{c,sheath}$ the cathode sheath potential. Since there is charge conservation in the sheath (ionization negligible), the ion current density in the would-be collisionless sheath is the same as that in the real situation.

$$P_b = J_i V_{c,sheath} \quad (43)$$

where J_i is the ion current density in the plasma sheath with collisions.

Therefore, if the power density of bombardment and the cathode sheath voltage are known, the ion current density impinging on the substrates can be determined using the above equation. Equation (43) forms the basis of the methodology used herein to estimate the ion current density. The difficulty is that in an RF gas discharge, both the sheath potential and the ion current density are modulated. Time-averaged values will therefore be considered. The power density of bombardment (P_b) will be estimated experimentally using cathode heating considerations.

7.4.2 RF sheath voltages and their implication on power dissipation

7.4.2.1 Voltages at electrodes

When an RF potential of frequency f is capacitively applied to an electrode relatively to ground, with the grounded surface area greater than that of the driven electrode, ($A_{cathode} < A_{anode}$) a negative self DC bias develops on the driven electrode (see equation (44) and Figure 92).

$$V_{CATHODE} = V_{RF} \sin(2\pi ft) - V_{DC} \quad (44)$$

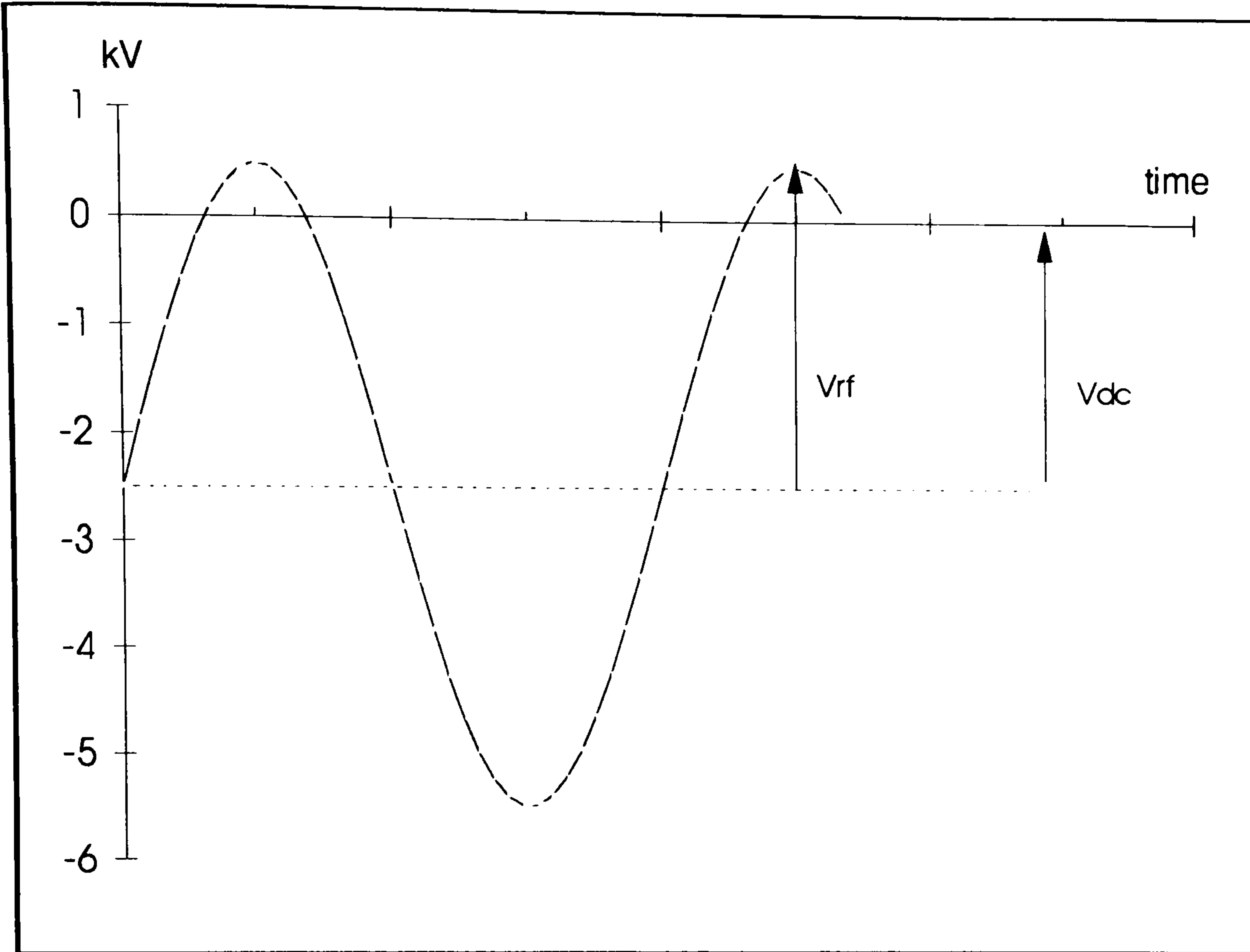


Figure 92: Cathode potential typical of the RF discharge conditions used in this work.

The origin of this DC offset has been discussed in chapter 5. It is known that its magnitude is related to the asymmetry in electrode surface area as predicted by the recent model after Song, Field, Klemperer¹³³ who proposed the following analytical expression:

$$\frac{V_{DC}}{V_{RF}} = \sin\left(\frac{\pi}{2} \times \frac{A_{ANODE} - A_{CATHODE}}{A_{ANODE} + A_{CATHODE}}\right) \quad (45)$$

Their model was successfully validated using experimental data generated from a hollow cathode RF discharge. It can be seen that the DC offset increases with smaller cathode area relatively to the grounded area and that in the extreme case where:

$$\frac{A_{cathode}}{A_{anode}} \approx 0$$

the DC offset equates the RF voltage amplitude:

$$V_{DC} = V_{RF}$$

In the context of the present work, the anode consisted of the earthed chamber walls with surface area (15000cm² approximately) much greater

than that of the electrode on which the substrates were clamped. This accounts for the high DC offset voltage measured in the operating conditions of this study. From equation (45), a coefficient of linearity of 0.96 between V_{DC} and V_{RF} would correspond to a cathode surface area 10% that of the anode, which by enlarge concurs with the cathode sizes investigated. It should be noted however that their model does not allow for the X-intercept observed in this work.

The straightforward effect of this DC offset is to increase the portion of the period time t during which the driven electrode is negative relative to ground (see Figure 93). Its consequence on power dissipation is discussed below.

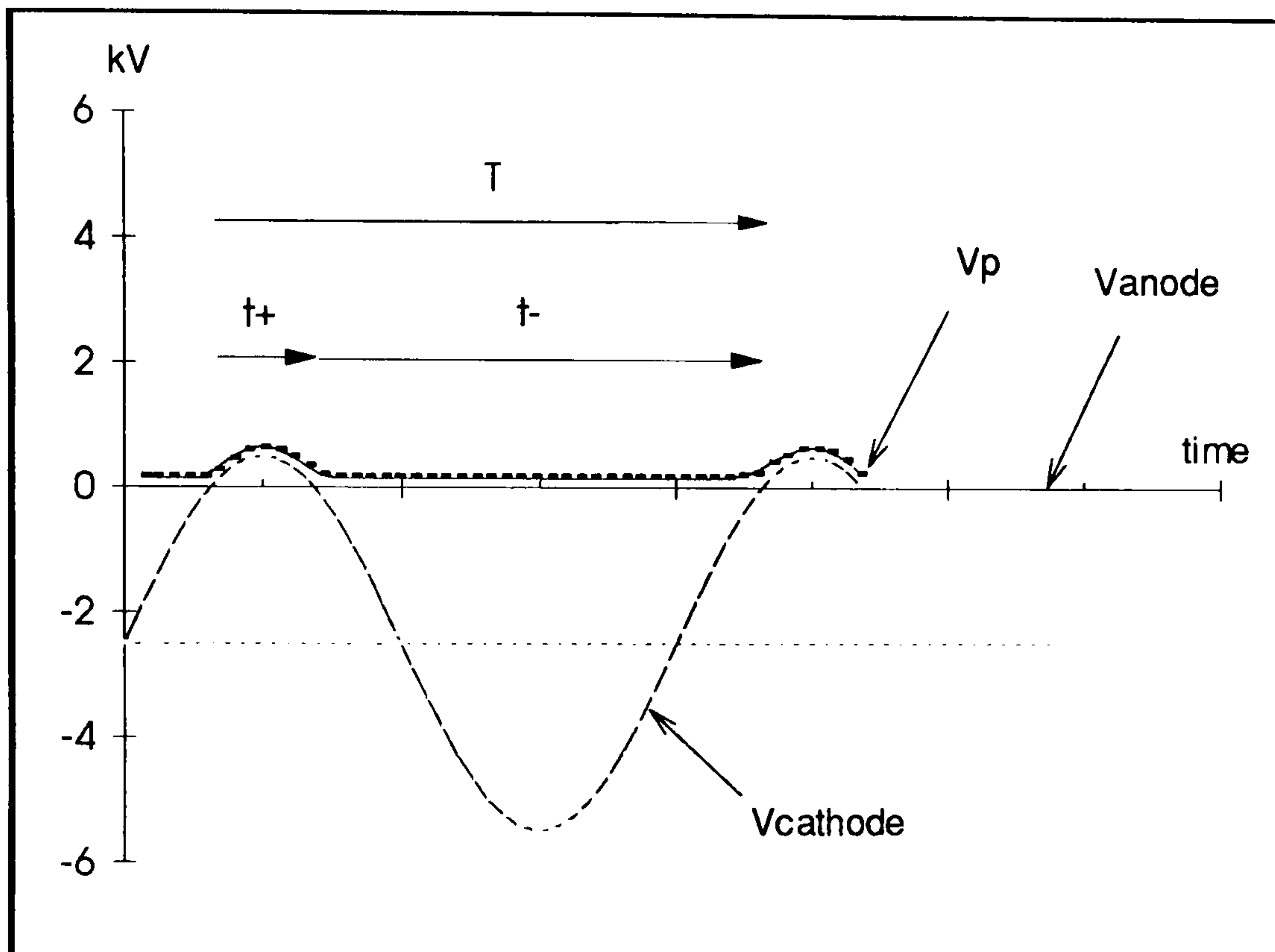


Figure 93: Diagram showing simultaneously the time dependence of the potential at both electrodes and the plasma potential (V_p).

7.4.2.2 Sheath voltages

The sheath voltage represents the drop in potential from the plasma to the electrode:

$$V_{sheath} = V_P - V_{electrode}$$

At 380kHz, the plasma potential follows the potential of either of the two electrodes that has the greater potential at a given time (see chapter 5 and Figure 93).

The time dependence of the cathode and anode sheath voltage follows from Figure 93 (see Figure 94 and Figure 95 respectively). Given that the sheath voltages are responsible for accelerating the ions to their respective electrode.

in a situation where the DC offset is zero, the power carried by the bombarding ions is equally shared between, and alternatively delivered to the two electrodes. The role of the self DC bias is therefore to allocate the most of the available power of ion bombardment to the driven electrode (greater acceleration voltage and longer time t^- of bombardment). At the limit $V_{DC} = V_{RF}$ ($A_{cathode} \ll A_{anode}$), virtually all the power is delivered to the cathode.

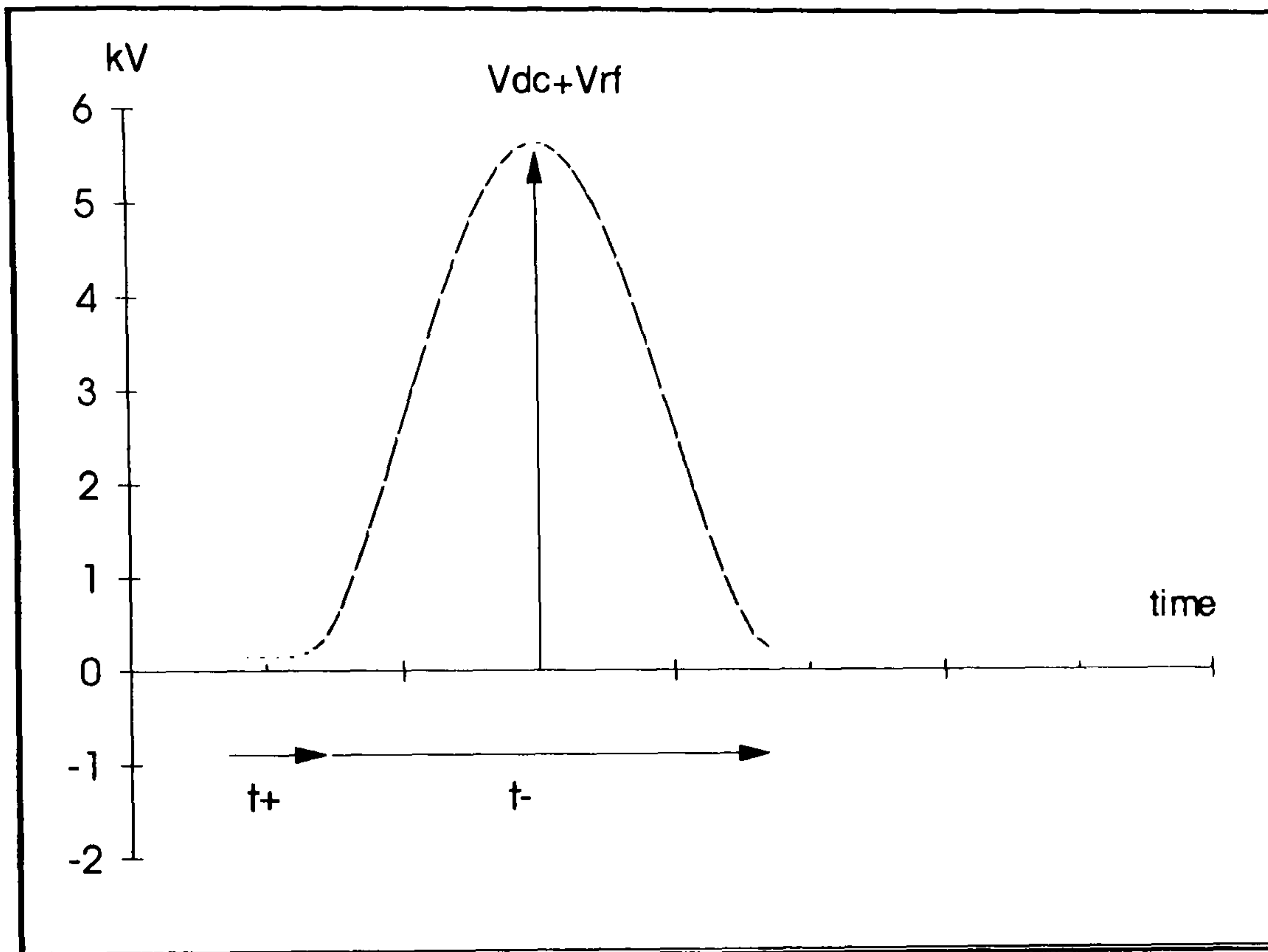


Figure 94: Time dependence of the cathode sheath potential.

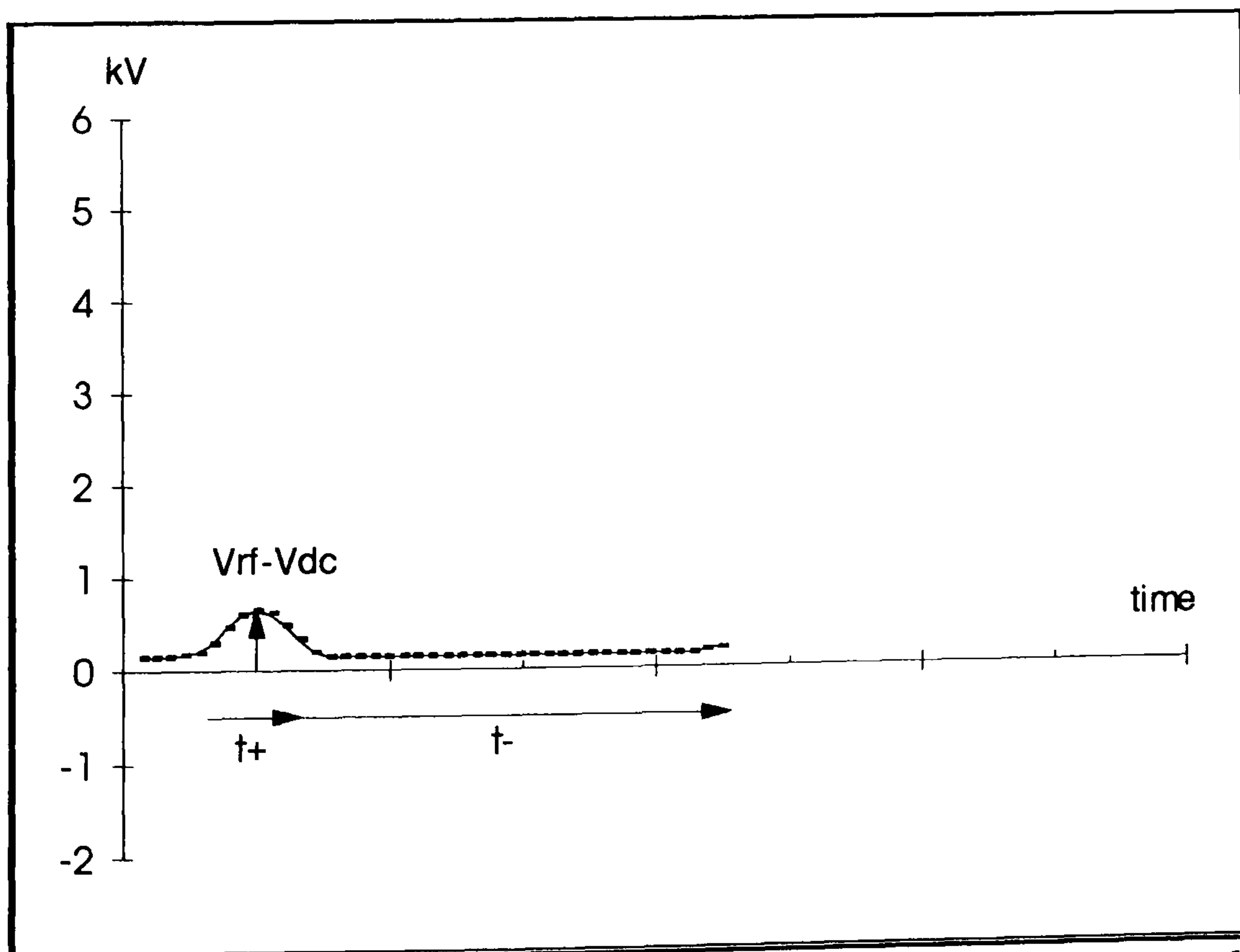


Figure 95: Time dependence of the anode sheath potential.

Now that the qualitative concepts relating to the allocation and time dependence of ion bombardment have been introduced, a formulation of time averaged power density of ion bombardment on the cathode is proposed.

7.4.3 Formulation of bombardment power density

7.4.3.1 Definition of bombardment power density

In an RF discharge, the sheath length varies in phase with the sheath voltage. As the voltage magnitude increases with time, the sheath expands exposing an increasing number of ions to the electric field in the sheath. At 13.56 MHz, the ion transit time (ITT) through the sheath is larger than the RF period. Therefore, the ions in transit in the sheath are swept back and forth by the moving plasma-sheath boundary and drift towards the cathode with an energy corresponding to the time-averaged sheath field. In those circumstances, both the current density and the energy of the ions are little modulated and can be reasonably considered steady. This scenario however does not apply to 380 kHz discharges. When the frequency is reduced, the ITT becomes less than the RF period and the ions sense the instantaneous sheath field. In a situation where the ion transit time through the sheath is small compared to the RF period, it is reasonable to assume that the ion energy at impact corresponds to the sheath voltage at the time the ion crossed the moving plasma-sheath boundary, bearing in mind the assumption of collisionless sheath. This is the second assumption.

Assumption 2:

The ion energy of impact at time t corresponds to the sheath voltage amplitude at time t .

It is clear from Figure 94 that the energy of the ions impinging on the cathode over t^+ is negligible comparatively to the ion energies over t^- . This implies that ion bombardment over t^+ will be insignificant relatively to that over t^- which is the third assumption:

Assumption 3: The power carried by the bombarding ions over t^+ is negligible.

Following the above assumptions, the time averaged power density of bombardment delivered by the ions to the cathode can be written:

$$P_b = \frac{1}{\tau} \times \int_{t^-} V_{c,sheath} \times J_{ion} dt \quad (49)$$

where τ is the RF period, t^- the portion of time over which ion bombardment of the cathode is taken into account, J_{ion} is the ion current density and $V_{c,sheath}$ is the instantaneous sheath voltage.

The time dependence of the ion current density is an unknown. It is generally believed that the ion current increases in phase with the sheath voltage for low frequency gas discharges^{122, 128, 127}. Here, a linear dependence will be assumed as that taken by Köhler, Horne and Coburn¹³⁴ (*Assumption 4*):

$$J_{ion} = g \cdot V_{c,sheath} \quad (50)$$

where g is a time independent constant (in Ω^{-1}/m^2).

From equation (49), it can be derived that the time averaged power density of bombardment is proportional to the square of the quadratic time averaged sheath potential $\langle V_{c,sheath} \rangle$:

$$P_b = g \langle V_{c,sheath} \rangle^2 \quad (51)$$

with:

$$\langle V_{c,sheath} \rangle = \left(\frac{1}{\tau} \int_{t^-} V_{c,sheath}^2 dt \right)^{\frac{1}{2}} \quad (52)$$

$\langle V_{c,sheath} \rangle$ will be referred to as sheath voltage in the rest of the text as opposed to instantaneous sheath voltage.

7.4.3.2 Formulation of ion current density

The object is to determine the ion current density impinging on the cathode. This will be done by considering the quadratic time-averaged ion current density:

$$\langle J_{ion} \rangle = \left(\frac{1}{\tau} \int_{t^-} J_{ion}^2 dt \right)^{\frac{1}{2}} \quad (53)$$

which, by combining equation (49), (50) and (51) can be expressed as:

$$\langle J_{ion} \rangle = \frac{P_b}{\langle V_{c,sheath} \rangle} \quad (54)$$

This equation is analogous to equation (43) established for a DC bias. $\langle J_{ion} \rangle$ will be referred to as ion current density thereafter. The remaining steps to determine the ion current density using equation (54) are now to estimate the power density P_b as a function of $\langle V_{c,sheath} \rangle$. The latter is calculated from the measurement of V_{DC} and V_{RF} as described below.

7.4.3.3 Calculation of the cathode sheath voltage:

The cathode sheath voltage is the difference between the plasma potential and the cathode potential.

$$V_{c,sheath} = V_P - V_{cathode}$$

Assumption 5: Over t , the magnitude of the plasma potential is negligible compared to the cathode potential (see Figure 93). The sheath voltage becomes then:

$$V_{c,sheath} = V_{RF} \sin(2\pi ft) - V_{DC} \quad (56)$$

From equation (52) and (56), it is demonstrated in Appendix 6 that the sheath potential can be explicitly expressed as a function of V_{DC} and V_{RF} as:

$$\langle V_{c,sheath} \rangle^2 = \left(\frac{1}{2} + \frac{a}{\pi} \right) (V_{DC}^2 + \frac{V_{RF}^2}{2}) - \sin(2a) \frac{V_{RF}^2}{4\pi} + \cos(a) \frac{2V_{DC}V_{RF}}{\pi}$$

with

$$a = \arcsin\left(\frac{V_{DC}}{V_{RF}}\right)$$

7.4.3.4 Estimation of power density of bombardment

One would expect that most of the power delivered to the cathode by ion bombardment is dissipated into heat. The power consumption from sputtering, electron secondary emission and lattice structural modifications should be minor compared to the heat dissipation. However, some of the incident bombardment power may be reflected from the surface, in the case for instance where fast neutrals bounce off elastically. In any case, the ion heating power density (Q) is proportional to the power density of ion bombardment (P_b):

$$Q = \eta P_b \quad (59)$$

where η is the heating efficiency (<1).

Provided that the heating efficiency is known, the power density of ion bombardment may be monitored by measuring the heat input from the plasma (see equation (59)), presupposing that:

Assumption 6: Radiation and electron heating from the plasma is negligible compared to ion heating. This is justified partly because the electrons impinging on the cathode have low energies comparatively to the accelerated ions.

Assumption 7: Heating from ion bombardment over t^+ is negligible compared to ion bombardment over t^- . This assumption follows assumption 3.

7.4.4 Substantiation of model and estimation of ion current densities

7.4.4.1 Experimental procedure

The heat input received by the cathode from the plasma was monitored for different sheath potentials ($\langle V_{c,sheath} \rangle$). The output power from the generator was set to 6kW, and the RF voltage and DC offset were varied by changing the chamber pressure as in Figure 87. A substrate consisting of a 25.4mmx25.4mmx2mm pack-aluminized Nimonic 75 coupon was clamped in the middle of a cathode plate with a surface area of 800cm². This cathode plate was the same as that used to carry out the deposition of the low temperature RF ion plated coatings in this work. The substrate temperature was monitored using a K-type thermocouple, sheathed with ceramic beads and spot-welded on its surface. As the thermocouple was connected to the cathode via the substrate, the temperature could not be monitored while the RF power was on. For each pressure, the plasma was left on for 15 minutes allowing the cathode to reach its steady-state temperature. The substrate temperature was read just after turning off the RF power.

The experiment was set up to ensure that the cathode plate, the substrate and the thermocouple were subjected to the same heating from the plasma. Being aware of the possible influence of the electrode shape on the incident ion current density, the thermocouple wires in the vicinity of the substrate were laid against the cathode plate so as to form a planar plasma sheath adjacent to the hot thermocouple junction.

Under conditions of even plasma heating, conductive heat transfer between the substrate and the cathode plate or the thermocouple wires are not expected. Considering that convection heat losses can be neglected in a soft vacuum environment, only radiative heat transfer can play a part as a substrate cooling mechanism. The substrate temperature at equilibrium can then be related to the heat input from the plasma as:

where σ is the Stefan-Boltzmann constant ($56.7 \times 10^{-9} \text{ W/m}^2\text{K}^4$), E is the emissivity of the substrate, F is the heat radiation view factor from the

$$Q = \sigma F E (T_E^4 - T_0^4) \quad (60)$$

specimen to the chamber walls (which is unity in the present case), T_0 the background temperature seen by the substrate and T_E is the substrate temperature achieved at equilibrium. If the above derivation of ion bombardment power density is valid (see equations (51), (59) and (60)), a plot of T_E^4 versus $\langle V_{c, sheath} \rangle^2$ should yield a straight line provided that:

Assumption 8: η is independent of the sheath voltage amplitude i.e. the heating efficiency does not vary significantly with the energy of the bombarding species.

Assumption 9: E is independent of temperature, which is a good approximation considering the temperature range of interest.

7.4.4.2 Results

Table V shows the temperature achieved by the substrate as heated from the plasma for different degrees of bias.

Table V: Results from cathode heating experiment.

Pressure (mTorr)	$V_{RF}(V)$	$V_{DC}(V)$	$I_{RF}(A)$	$T_E(^{\circ}C)$	$\langle V_{c, sheath} \rangle (V)$
140	497	224	.51	90	437
100	639	506	.64	100	721
60	1200	1026	1.12	157	1400
39	1633	1300	1.8	192	1850
23	2130	1550	2.1	230	2312
12	2556	1790	2.3	260	2726
10	2770	2000	2.4	284	2996
8	3053	2435	1.66	290	3460
3.5	3195	2143	2.43	286	3340

The temperature attained was plotted against $\langle V_{c, sheath} \rangle^2$ as the latter should be proportional to the power density received by the cathode according to equation (51) (see Figure 96).

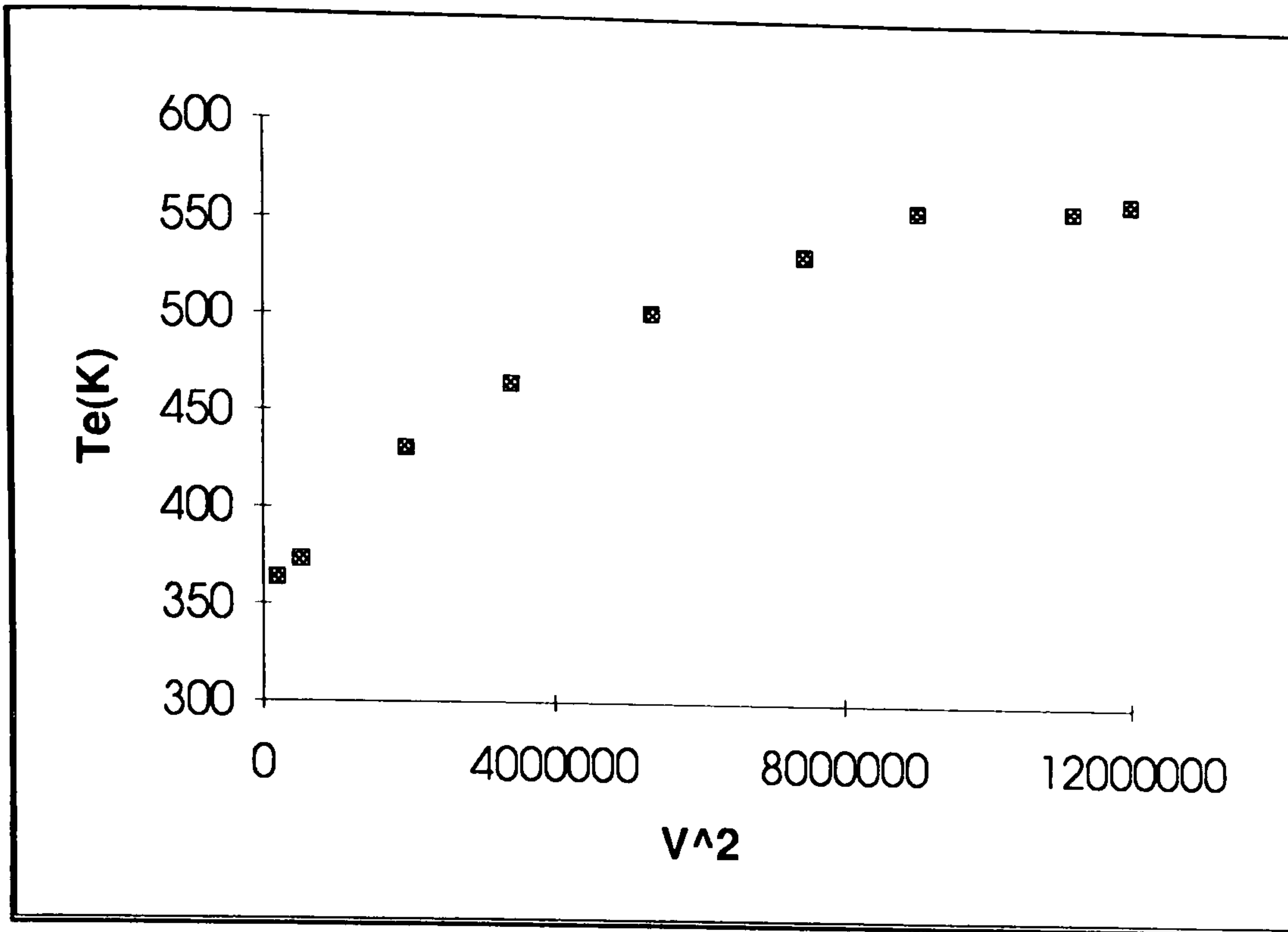


Figure 96: Plot of T_E versus $\langle V_{c,sheath} \rangle^2$.

Figure 97 is a replot of the data presented in Figure 96.

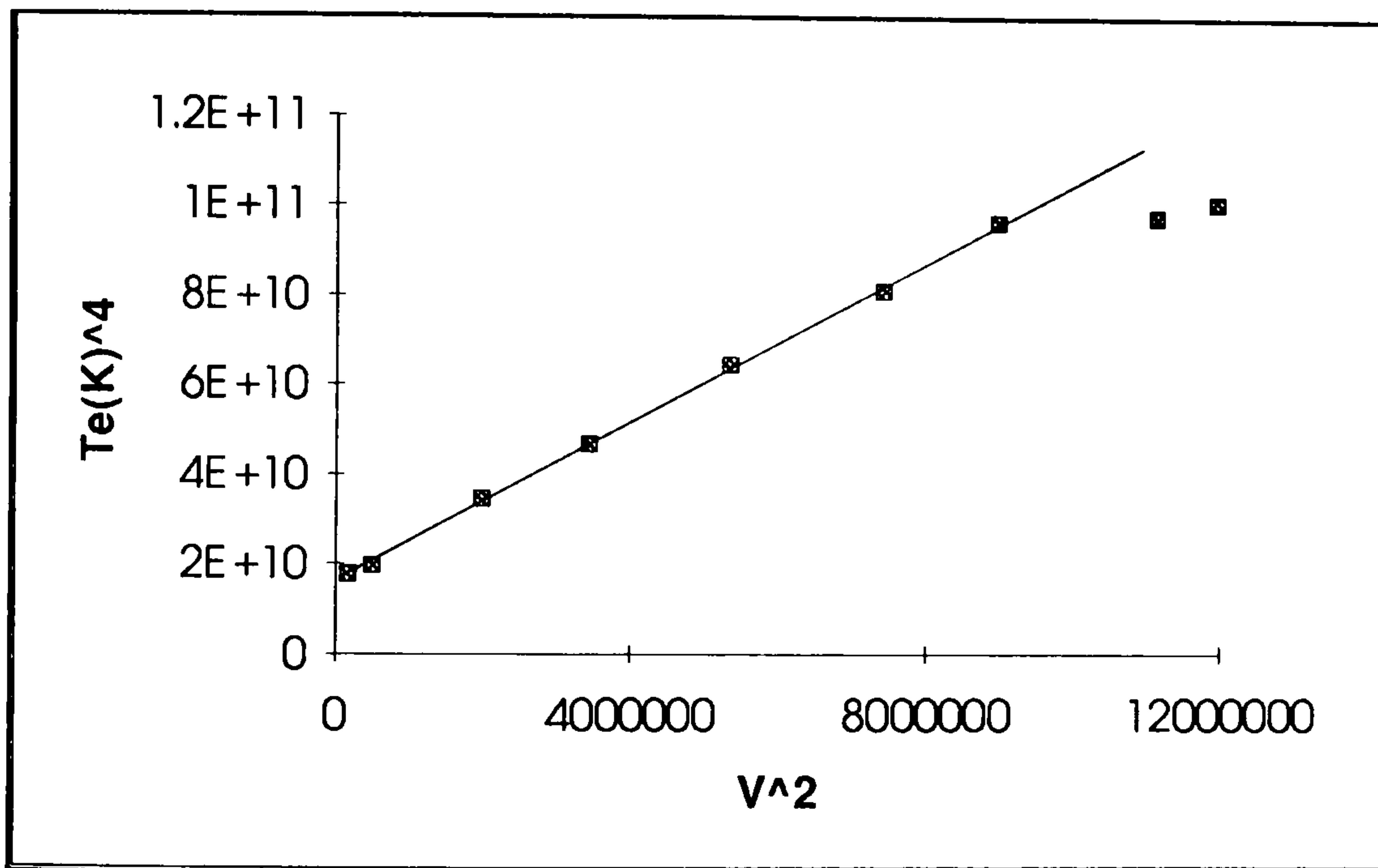


Figure 97: Plot of T_E^4 versus $\langle V_{c,sheath} \rangle^2$ showing linear dependence.

A straight line is obtained for sheath voltages up to 3kV. The two points beyond that are off the line and this is related to the RF current dropping at chamber pressures less than 8mTorr as depicted in Figure 88. Figure 97 shows that the heating power received by the substrate from the plasma is proportionnal to $\langle V_{c,sheath} \rangle^2$ as it was expected from equations (51), (59) and (60). It thereby demonstrates the relevance of $\langle V_{c,sheath} \rangle$ as a power density controlling parameter and substantiates the pertinence of the above model from which it was derived. In particular, this result is consistent with the assumption that the instantaneous ion current density was proportionnal to the instantaneous cathode sheath voltage (*Assumption 4*). The time averaged ion current density may now be estimated.

7.4.4.3 Estimation of ion current densities.

There are two unknowns in the determination of the bombardment power density that are namely the heating efficiency and the substrate emissivity. Given equations (59) and (60), the power density of bombardment can be written:

$$P_b = m \cdot \sigma \cdot (T_E^4 - T_0^4) \quad (61)$$

where

$$m = \frac{E}{\eta}$$

Glang and Maissel¹³⁵ quote that 75% of the power applied to a sputtering target is dissipated as heat by the ions and energetic neutrals that strike it. Given that P_b is a fraction of the applied power, the implication is that $\eta > 0.75$. An upper m value of 1.33 ($E=1$, $\eta=0.75$) will be used for overestimating the ion current density impinging on the substrates.

The background temperature T_0 can be determined from Figure 96 by extrapolating the curve to the Y-intercept which yields a temperature of 360 K. Table VI shows the power densities of bombardment calculated using $T_0=360\text{K}$ and m values ranging between 0.1 to 1.33 as a function of $\langle V_{c,sheath} \rangle$.

Table VI: Power densities for a range of m values using $T_0=360\text{K}$.

$\langle V_{c,sheath} \rangle$ (V)	$P_b(m=1.33)$ (W/cm ²)	$P_b(m=1)$ (W/cm ²)	$P_b(m=0.5)$ (W/cm ²)	$P_b(m=0.1)$ (W/cm ²)
437	~0	~0	~0	~0
721	0.015	0.011	0.006	0.0011
1404	0.12	0.096	0.048	0.0096
1850	0.22	0.17	0.84	0.017
2312	0.35	0.27	0.13	0.027
2726	0.48	0.36	0.18	0.036
2996	0.60	0.45	0.22	0.045
3340	0.61	0.46	0.23	0.046
3460	0.63	0.47	0.24	0.047

From this table, ion current densities can be calculated for different m values using equation (54). These are plotted as a function of the accelerating voltage ($\langle V_{c, \text{sheath}} \rangle$) in Figure 98.

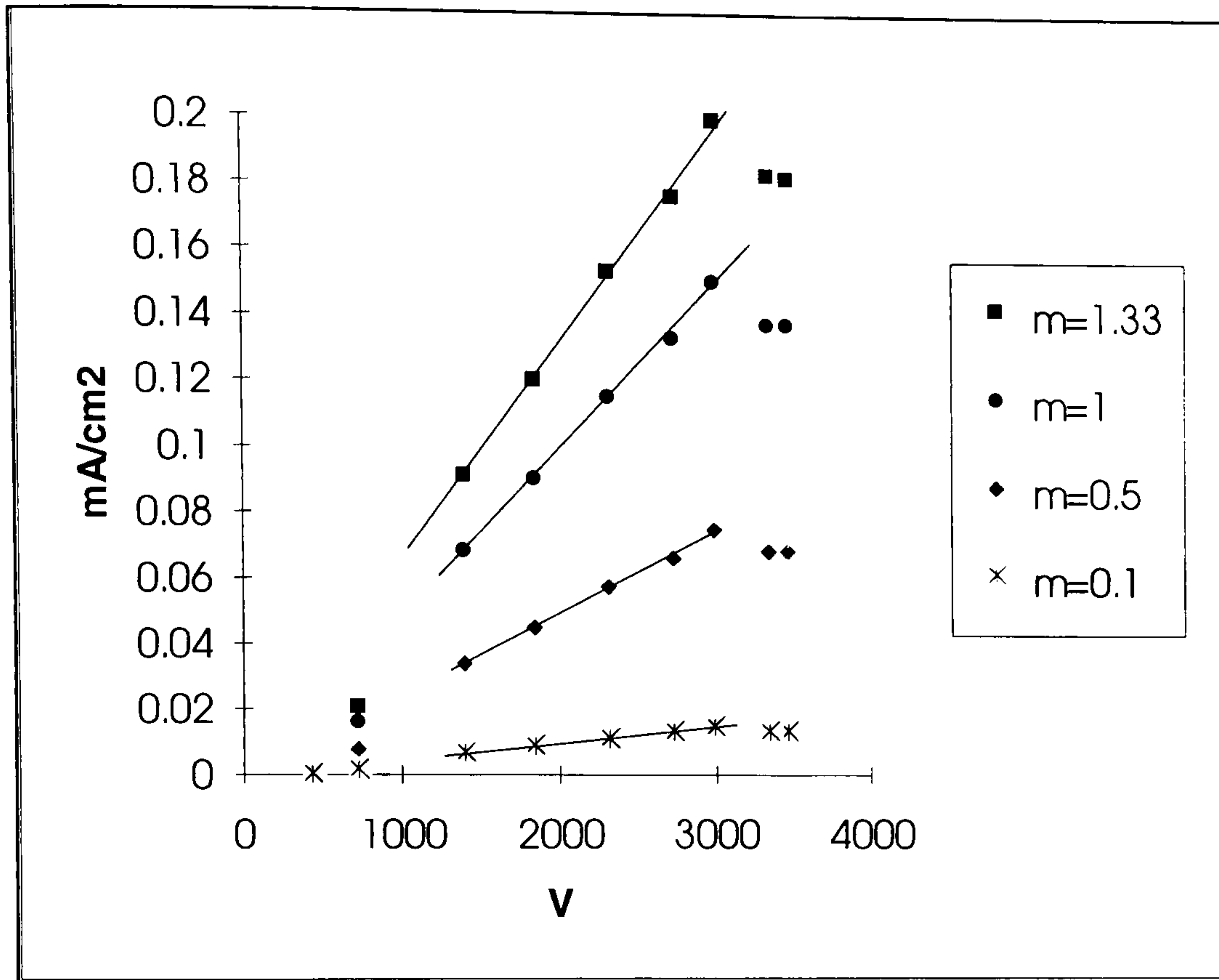


Figure 98: Plot of ion current density ($\langle J_{\text{ion}} \rangle$) as a function of sheath voltage ($\langle V_{c, \text{sheath}} \rangle$) for a cathode area of 800cm^2 .

The ion current density is found to be proportional to the sheath voltage in the sheath voltage range 1500-3000V. At lower voltages, the computed current density becomes more sensitive to the error made in estimating the background temperature T_0 which is probably why the low voltage points are off the line. Although the exact m parameter is not known, this graph allows to quote a window of ion current densities relevant to this study. At the operating conditions used ($P \approx 10\text{mTorr}$, $\langle V_{c, \text{sheath}} \rangle \approx 3\text{kV}$), an upper ion current density bound of 0.2mA/cm^2 can be defined using $m=1.33$ ($E=1$ and $\eta=0.75$) and a lower bound of 0.02mA/cm^2 using $m=0.1$ ($E=0.1$, $\eta=1$). The upper bound corresponds to an ion current of 0.16A which is more than ten times less than monitored by the RF coil (see Table V). It can therefore be concluded that the bulk of the current drawn from the RF plasma corresponds to a displacement current as opposed to an ion conduction current. The power density of ion bombardment (P_b) was plotted against the product of RF current with RF voltage ($I_{\text{RF}} \cdot V_{\text{RF}}$) as this quantity is proportional to the power delivered by the generator (see Figure 99). It can be seen that the power density delivered by the ions to the cathode (P_b) varies linearly with the power delivered by the generator. It is however not possible to assess the efficiency of this process given the uncertainty on m , I_{RF} and the voltage/current phase shift.

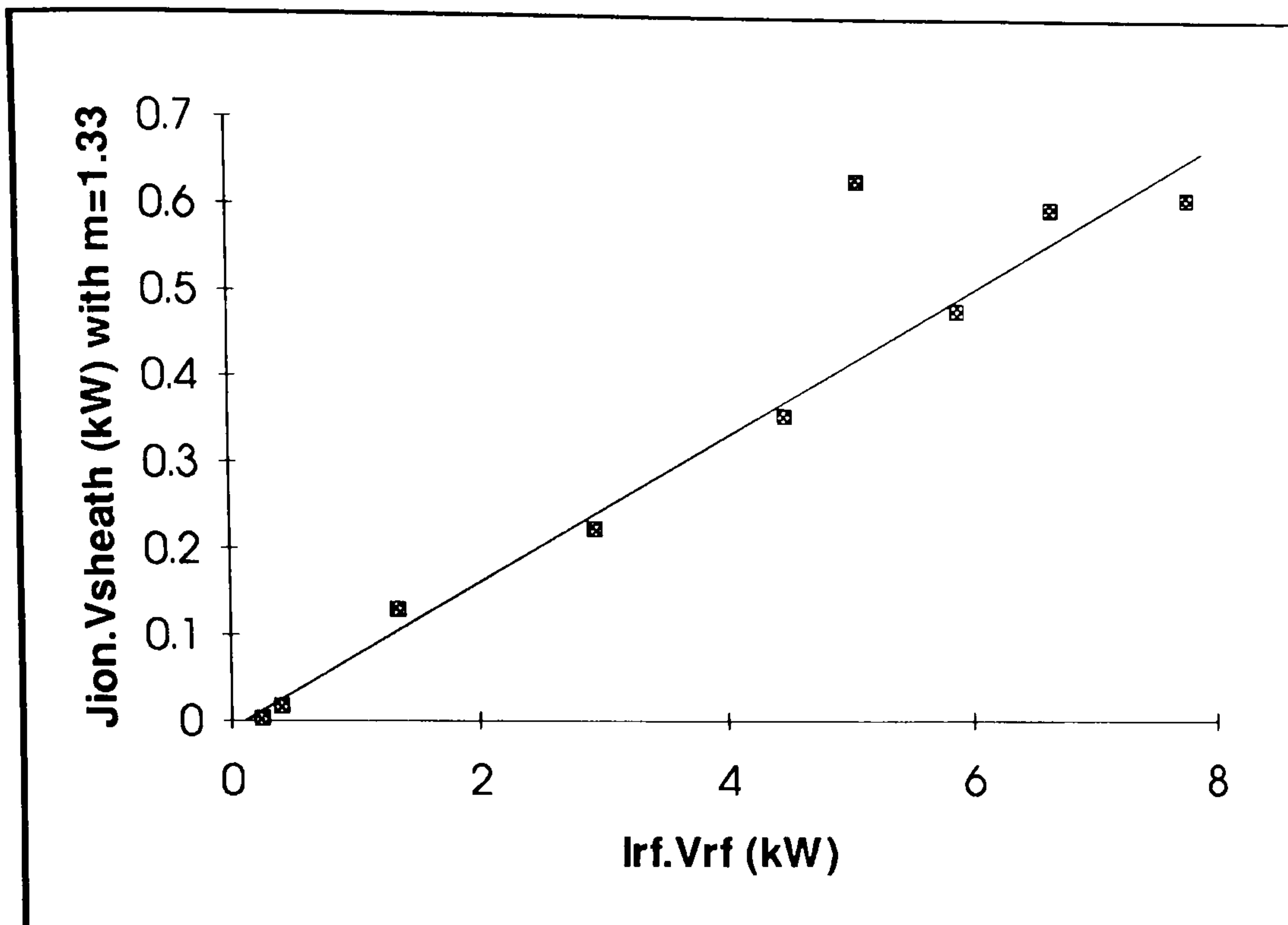


Figure 99: Plot of power density of bombardment using $m=1.33$ versus $I_{RF}.V_{RF}$ from the data in Figure 98 and Table V.

7.4.5 Non-dependence of $J_{ion}/\langle V_{c,sheath} \rangle$ relationship on pressure

It should be noted that the linear relationship between the ion current and the sheath voltage shown in Figure 98 was established in spite of the chamber pressure changing about tenfold over the range of voltages considered (see Table V). This behaviour is analogous to that of the RF current varying linearly with the RF voltage (see Figure 90) by changing the chamber pressure from 5 to 100 mTorr.

It should be remembered that the ion current density formula in equation (31) was established for DC plasmas by Bohm and recent investigators have expressed concern about the applicability of the Bohm criterion to RF discharges. In modelling the sustaining mechanisms of 380kHz discharges, Gill^{122, 128} derived a mean ion current density that was proportional to the random ion current density in the plasma. This result will be used here, the ion current can then be written:

$$\langle J_{ion} \rangle = K \alpha n e C_{ion} \quad (63)$$

where α , n , C_{ion} are the degree of ionization, the gas density and the mean velocity of the ions, and K the constant of proportionality. Since the ions are in thermal equilibrium with the gas neutrals ($T = T_{ion}$), equation (63) may be rewritten:

$$\langle J_{ion} \rangle = K' \frac{\alpha p}{\sqrt{T}} \quad (64)$$

where K' is another constant of proportionality, P and T are respectively the gas pressure and temperature.

Given that low frequency RF discharges (e.g. 380 kHz) are maintained primarily by secondary electron emission from the cathode (see chapter 5), the degree of ionization (α) can be expected to increase strongly with the cathode sheath voltage as in DC discharges. Although the pressure is increased, the degree of ionization will be decreased as a result of the decreasing sheath voltage with pressure.

The pressure dependence of the sheath voltage can be estimated from a logarithmic plot of the data in Table V (see Figure 100):

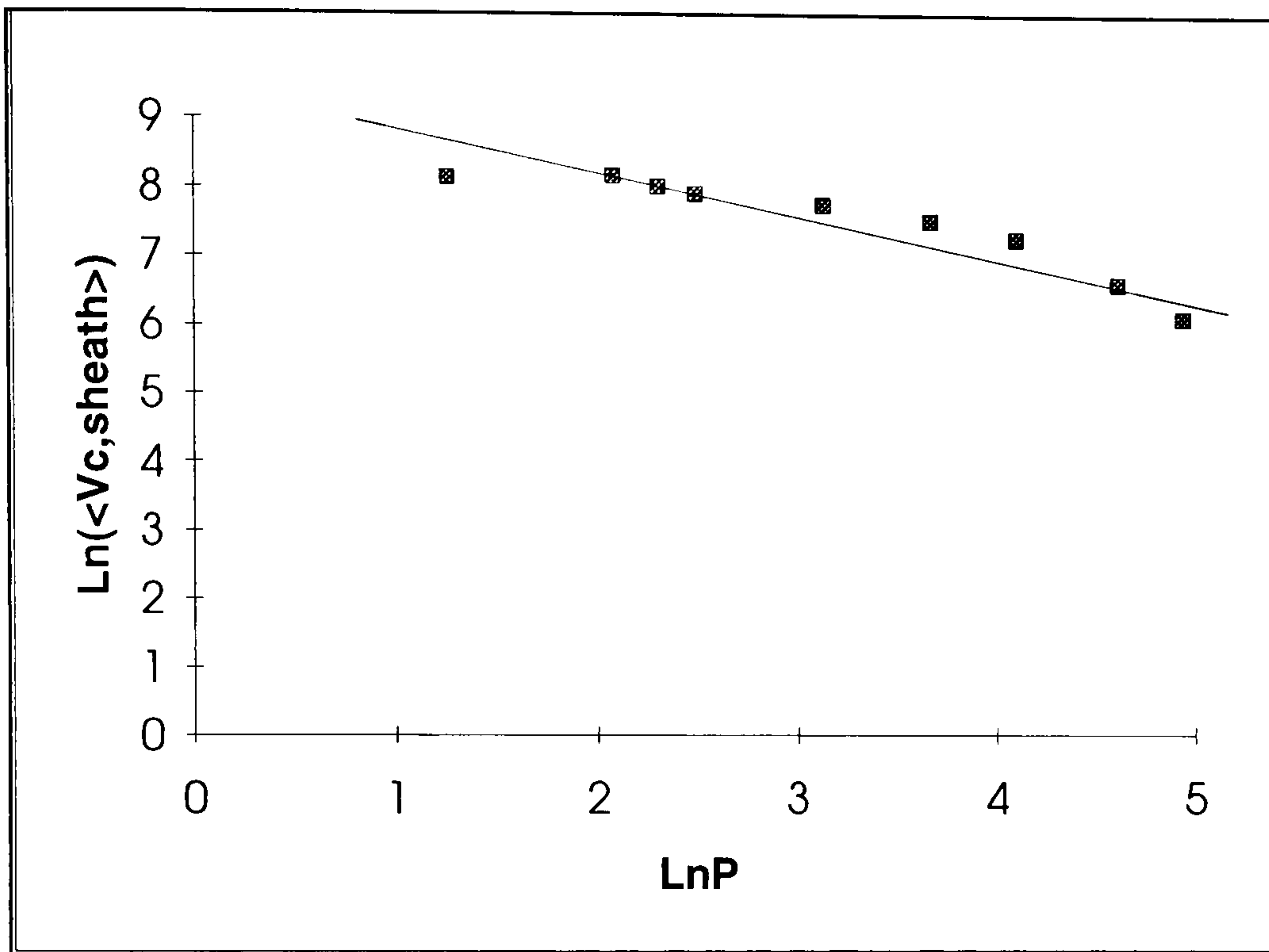


Figure 100: Logarithmic plot of $\langle V_{c,sheath} \rangle$ versus pressure from Table V.

Assuming that the sheath voltage depends on pressure via a power-law, one has:

$$\langle V_{c,sheath} \rangle \propto p^{-0.5} \quad (65)$$

or inversely:

$$p \propto \langle V_{c,sheath} \rangle^{-2} \quad (66)$$

In the case of a DC plasma, the effect of sheath voltage on the degree of ionization can be appreciated by considering Figure 71. If a first order approximation is used that the degree of ionization follows a power law dependence with the sheath voltage, the 'power law' exponent can be estimated by replotting the data in Figure 71 on a logarithmic scale:

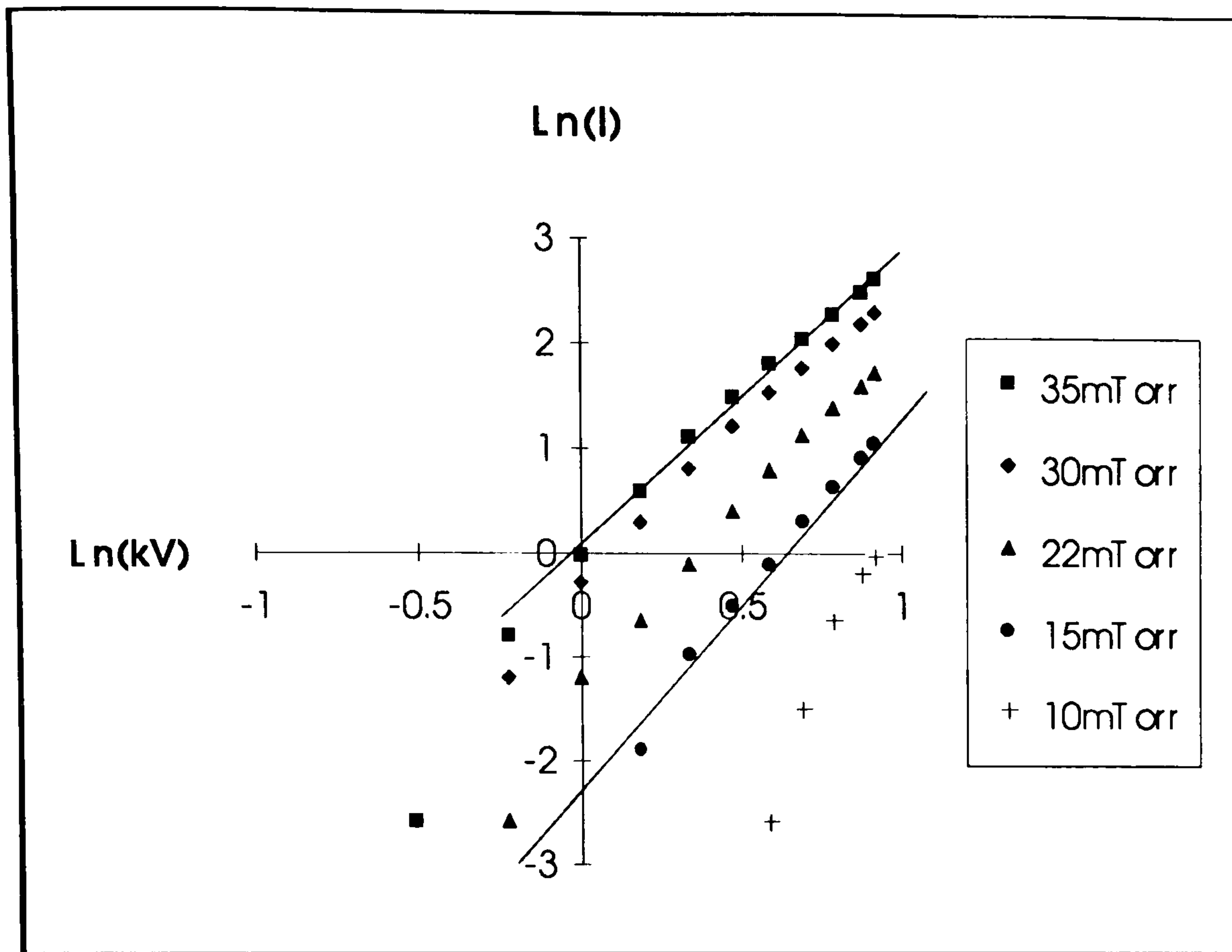


Figure 101: Plot of $\ln(I)$ versus $\ln(kV)$ for different chamber pressures (replot of Figure 71).

Considering that at a set pressure and temperature the current is proportional to the degree of ionization (see equation (64)), from Figure 101 the sensitivity of α on sheath voltage can be approximated as:

$$\alpha \propto V_{sheath}^{3.5} \quad (67)$$

If it is assumed that the sensitivity of the degree of ionization on sheath voltage established for a DC plasma is valid for a 380kHz RF plasma, then by substituting equations (67) and (66) into (64), the ion current density is found to depend on sheath voltage as:

$$J_{ion} \propto \langle V_{c,sheath} \rangle^{1.5}$$

This is in reasonable agreement with the linearity shown in Figure 98, given the assumptions taken regarding the power laws.

7.4.6 Interaction between Electron Beam gun and RF discharge

It was found that after a certain time of evaporation the RF plasma extinguished i.e. the DC offset and RF current dropped abruptly to zero. The plasma could be re-established by reducing the electron beam current but would extinguish again after a while. Effectively, the EB current threshold above which the plasma extinguished was found to decrease with deposition time. The reason for this phenomenon could not be absolutely elucidated. Qualitative considerations are given here as a starting point for discussion

and further experiment.

As far as the plasma is concerned, the onset of evaporation can modify the operating conditions in three ways. First, it gives off a vapour that blends with the working gas thus locally modifying the composition and the density of the gaseous species between the source and the substrates. Second, it provides an additional heat input into the system. Third, the gun electron beam potentially enhances ionization of the gas as in a triode system. There are two salient features of the phenomenon that must be discussed here:

- 1 is it inherent to RF plasmas?
- 2 why it is time dependent?

In order to establish whether the extinguishing of the plasma was a phenomenon inherent to the RF set up, an experiment was carried out to compare the effect of the EB source on both DC and RF ion plating using the same conditions with regard to pressure, temperature and cathode geometry. This was done at 'low temperature' (no supplementary heating other than that from the plasma and the source) using stainless steel 316 as an evaporant. It was found that over the 40 minutes of evaporation, the RF plasma continuously went out and could be re-established by reducing the evaporation source electron beam current. When using DC biasing, the plasma never extinguished (i.e. a non-zero current could be monitored) using the same range of EB gun currents. This experiment therefore indicated strongly that the collapsing of the plasma occurred more easily with the low frequency plasma and that the phenomenon occurred with metallic evaporants as well.

The time dependence of the phenomenon, i.e. the decrease with time in the gun current threshold above which the plasma collapses, could point to a temperature effect. It was found for instance that increasing the furnace temperature resulted in the decrease of the gas density within the furnace enclosure to the point where a DC glow discharge could no longer be sustained as maintained by secondary electrons. Could such an argument be applied to the whole of the deposition chamber, as exposed to radiative heating from the source? In order to answer this question, first it must be considered that the gas was bled into the chamber at a set flux q (molecules bled per sec) using mass flow controllers. Typically, the pressure rose right after the onset of the evaporation source, then decreased steadily towards its initial value. The pressure rise is believed to be the result of:

- the desorption of gases from the evaporant rod (entrapped water vapour and other gases)
- the desorption of gases from the wall surfaces close to the evaporation heat source

- the dissociation of zirconia into oxygen species

The desorption of gases is a transient phenomenon and after a certain time of evaporation the gas input into the chamber from the gas bleed and zirconia dissociation may be approximated as steady (q_{steady}). At equilibrium, the rate of gas input is balanced out by the gas pumping rate.

$$q_{steady} = pS$$

where P is the chamber pressure and S is the pumping speed (volume per time). The chamber pressure is a function of chamber temperature and gas density and may be written:

$$p = n_{ch} k T_{ch} \quad (70)$$

where n_{ch} , T_{ch} and k are respectively the density and the temperature of the gas averaged over the chamber volume and k the Boltzmann's constant.

The mean gas density may then be written:

$$n_{ch} = \frac{q_{steady}}{S k T_{ch}} \quad (71)$$

Given that at a set temperature, the pump speed is constant over several decades of pressure¹³⁶, the pump speed can be considered constant over a large range of gas densities. This is equivalent to say that, at a set pressure, S is independent of gas temperature. From equation Figure 102, this means that the mean chamber gas density is expected to decrease inversely with the mean chamber temperature.

Effectively, the chamber temperature decreases strongly with distance from the source. Given that pressure is *a priori* a uniform parameter, the gas density can be expected to decrease closer to the source according to equation (70). Therefore, at a set electron beam power density, the proportion of vapour density to gas density is expected to increase with deposition time.

The steady temperature achieved by the substrates 15cm above the source is about 600°C from the radiative heating of the latter. Therefore at a given gas bleed rate and chamber pressure, the gas density between the source and the substrates is decreased by a minimum factor of $n(600^\circ\text{C})/n(20^\circ\text{C})=3$. In the light of Figure 71 and Figure 88, such a drastic reduction in gas density at 10mTorr could potentially cause a plasma to extinguish given that this is equivalent to having a pressure of about 3mTorr at room temperature. However, one should bear in mind the potential ionization enhancement from the gun electron beam current. Also, it is difficult to argue that gas density is the sole driver to the extinguishing of the RF plasma as, if it were, one should expect the DC plasma to extinguish as well. This is because the minimum pressure at which a DC plasma is sustainable is greater than that

for an RF plasma and it is not readily explainable as to why the potential ionization enhancement from the gun electron beam should change this order.

Even if the gas was rarefied in the region of the substrates to the point where a discharge could no longer exist, with DC biasing a current would still be monitored and ion bombardment still occur by virtue of the vapour forming a weakly ionized plasma¹³⁷ by default. The situation is different with the capacitive coupling of RF power since no net current can be drawn from the plasma over a complete RF cycle. This is of significance considering that the emission of ionized vapour species impinging on the substrates may potentially upset the electric charge balance. In order to investigate the effect of this ionized vapour flux, the derivation after Song et al¹³³ was revisited by taking into account the impingement of a vapour ion flux $I_{ion,v}$ constant over the RF period (τ) adding to the ion flux J_{ion} from the RF plasma. The build up of this positive charge on the cathode over a complete RF cycle must be matched by the electron flux over t^+ , i.e. when the potential barrier for electrons is minimal:

$$J_{ion}A_c\tau + I_{v,ion}\tau = J_eA_c t^+ + I_{v,e}t^+ \quad (72)$$

where A_c , J_e and $I_{v,e}$ are respectively the area of cathode exposed to the RF plasma, the electron current density originating from the RF plasma and the electron current originating from the vapour. The latter could be incorporated into J_e as these electrons are not easily distinguishable from the RF plasma electrons. To the contrary, the vapour ions differ from the Ar ions from mass, energy and directionality considerations. However, written in this form, the above equation covers the eventuality that the RF plasma no longer exists above the source.

Over t^+ , the plasma must remain neutral, therefore, the outflow of positive charges must equate the outflow of negative charges:

$$I_{v,e}t^+ + J_eA_c t^+ - J_{ion}A_c t^+ = J_{ion}A_a t^+ \quad (73)$$

where A_a is the earthed area exposed to the plasma (anode). Combining equation (73) with equation (72) yields:

$$I_{v,ion} = J_{ion} \left[A_a \frac{t^+}{\tau} - A_c \frac{t^+}{\tau} \right]$$

substituting for J_{ion} , one has:

$$I_{v,ion} = K' \frac{\alpha p}{\sqrt{T}} \left[A_a \frac{t^+}{\tau} - A_c \frac{t^+}{\tau} \right] \quad (75)$$

where T and α are the averaged chamber pressure and degree of ionization of the RF plasma. Equation (75) summarises the combined effects of chamber

temperature and vapour ion flux from the source on the existence of the RF plasma. It can be seen that greater vapour ion fluxes must be matched by an increased degree of ionization and/or a decrease in the DC offset (i.e. increase in t^+). This fragile balance is perturbed by an increasing chamber temperature. Equation (75) agrees qualitatively with the experimental observation that there exists a vapour ion flux/temperature regime for which an RF plasma may no longer exist. Passed a certain threshold of gas density, the degree of ionization saturates (see Figure 98) and for a given $I_{v,ion}$, a certain temperature can be reached for which equation (75) can no longer be satisfied and the plasma be sustained.

8 THE INFLUENCE OF DEPOSITION CONDITIONS ON THE STRUCTURE AND PROPERTIES OF EB-PVD TBC'S

In this chapter, the role of deposition conditions on the properties of 8wt%Y₂O₃-ZrO₂ deposits is examined. The coating properties considered are listed below with the terminology used:

- chemical composition
- phase composition
- lattice parameter
- texture (preferential crystallographic orientation)
- lattice microstrain
- crystallite size or grain size (size of diffracting domains)
- morphology (structural features observable from SEM)
- density (coating mass/volume)
- indentation resistance

Although the emphasis in this chapter is put on process conditions such as deposition temperature and plasma assistance, other important parameters are highlighted as influential to the ceramic structure. How these coating properties may relate to TBC performance is an issue that will be addressed in following chapters.

8.1 RESULTS

8.1.1 Chemical composition

The chemical composition of the deposits was examined by comparison with that of the source ingot and of a commercial coating (RT33) using X-Ray Energy Dispersive Spectroscopy. Within the error of the analysis, the composition of Zr, Y and O within the deposits was found to be the same as that of the ingot and of RT33 irrespective of the ion plating condition (see Table VII). This result is consistent with the work by Knoll&Bradley on sputtered YSZ who found that substrate biasing did not lead to the preferential sputtering of yttrium or zirconium⁸¹.

Table VII: Results from EDS elemental analysis.

	ZrO ₂ -8wt%Y ₂ O ₃	RT33	RF ion plated	Relative error (%)
Zr (at.%)	28.57	28.34	29.47	±0.8
Y (at.%)	5.72	5.99	4.83	±3.5
O (at.%)	65.71	65.87	65.89	

8.1.2 Phase composition

8.1.2.1 Effect of deposition temperature

The coatings deposited at temperatures less than 600°C yielded X-Ray diffraction spectra that corresponded to either the tetragonal or cubic symmetry (for example see Figure 105 and Figure 107). The ambiguity arose whenever peak broadening made it impossible to resolve the peak doublets characteristic of the tetragonal structure. Upon annealing at temperatures up to 1100°C, the breadth of the diffraction lines could be decreased to the point where the doublets became apparent.

Thanks to sharper diffraction lines, the systems deposited at elevated temperature were found to unequivocally consist of the tetragonal structure. In some instances however, the high temperature deposits were found to contain some monoclinic phase as well, the significance of which increased with deposition temperature (see Figure 102). It is difficult to quantify the relative proportions of tetragonal to monoclinic due to the high degree of texture of these coatings. The formation of monoclinic was found to also depend on parameters other than temperature such as oxygen bleed during deposition, heat treatment in air and coating depth. These effects are identified and discussed below.

8.1.2.2 Effect oxygen partial pressure

The coatings deposited at high temperature (1000-1100°C) in the presence of 90%O₂/10%Ar as opposed to pure argon did not show the monoclinic phase (see for example Figure 108). In no depositions since bleeding oxygen in the system, was the monoclinic phase identified.

8.1.2.3 Effect of ageing in air

The monoclinic phase content of the as-deposited coatings was found to almost disappear after ageing in air at temperatures as low as 700°C for 30 minutes (see Figure 103).

8.1.2.4 Dependence on coating depth

X-ray diffraction of the coating interface after dissolving the substrate away showed that the content of monoclinic phase was greater near the bond coat interface than near the free surface (see Figure 104). It should also be noted that the texture at the coating/substrate interface was generally more random irrespective of whether the structure was monoclinic or tetragonal.

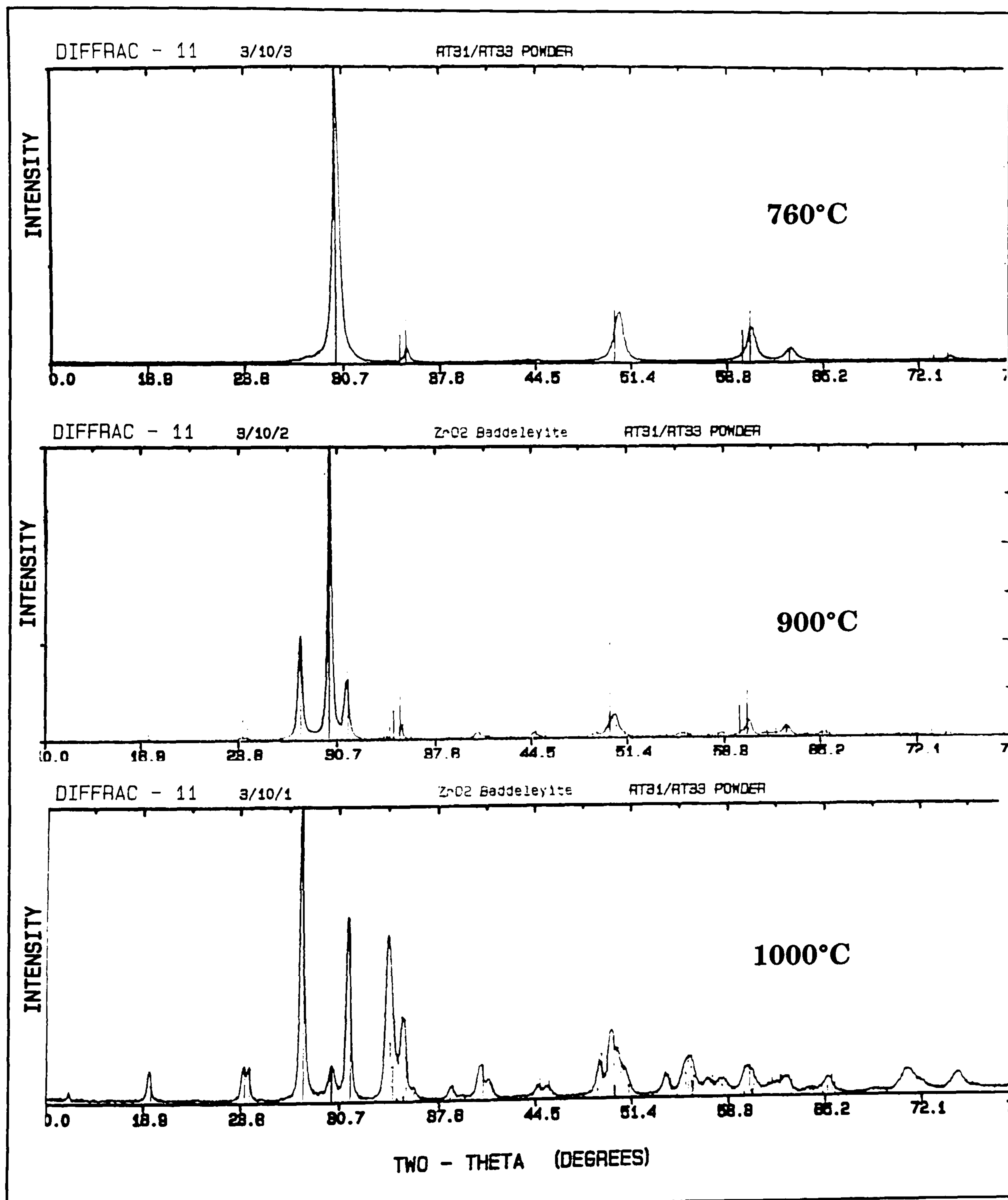


Figure 102: Effect of deposition temperature on the formation of the monoclinic phase.

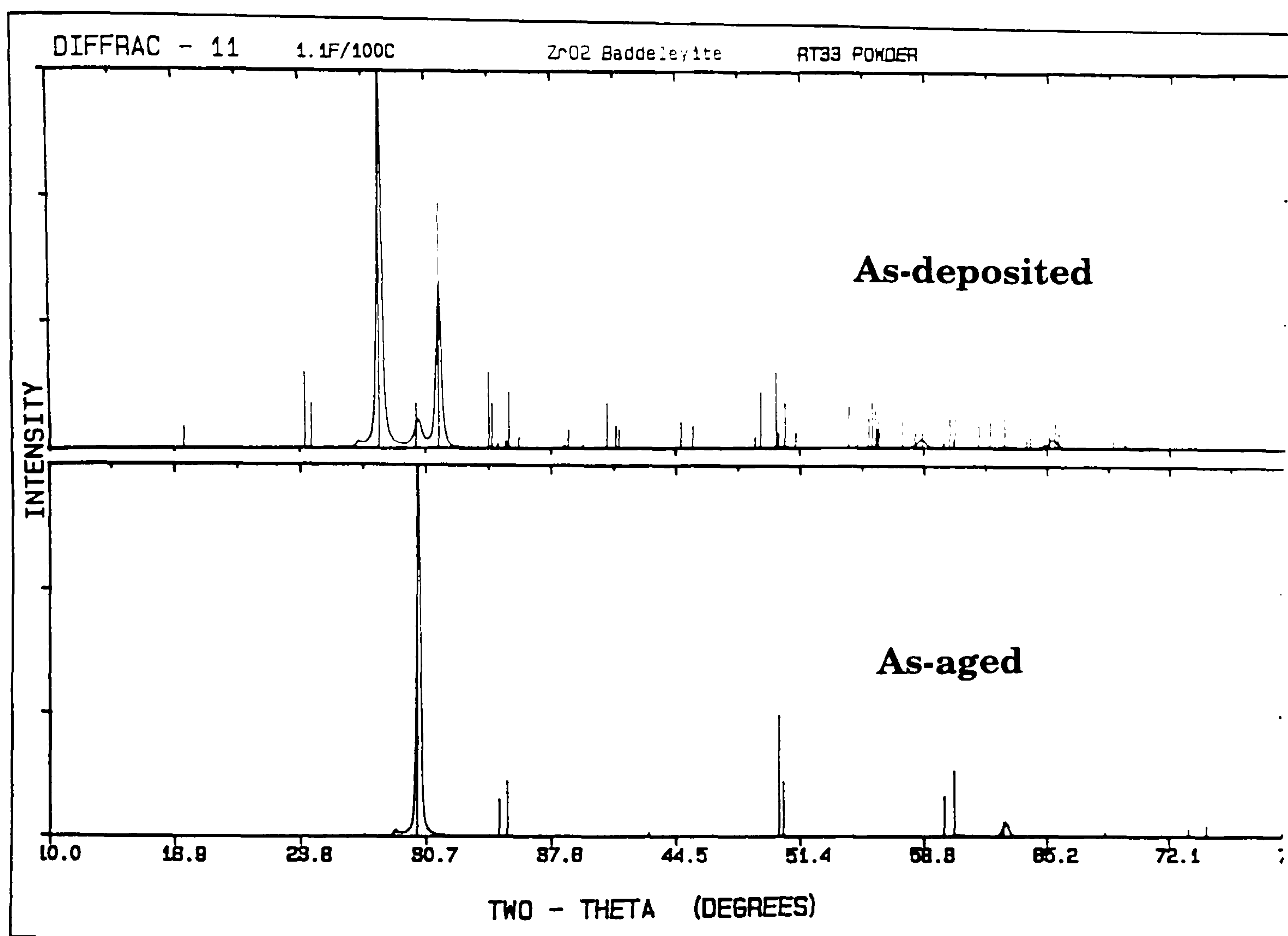


Figure 103: Effect of ageing in air at 700°C for 30 minutes on the crystal structure of a gas evaporated coating deposited at 960°C in pure argon.

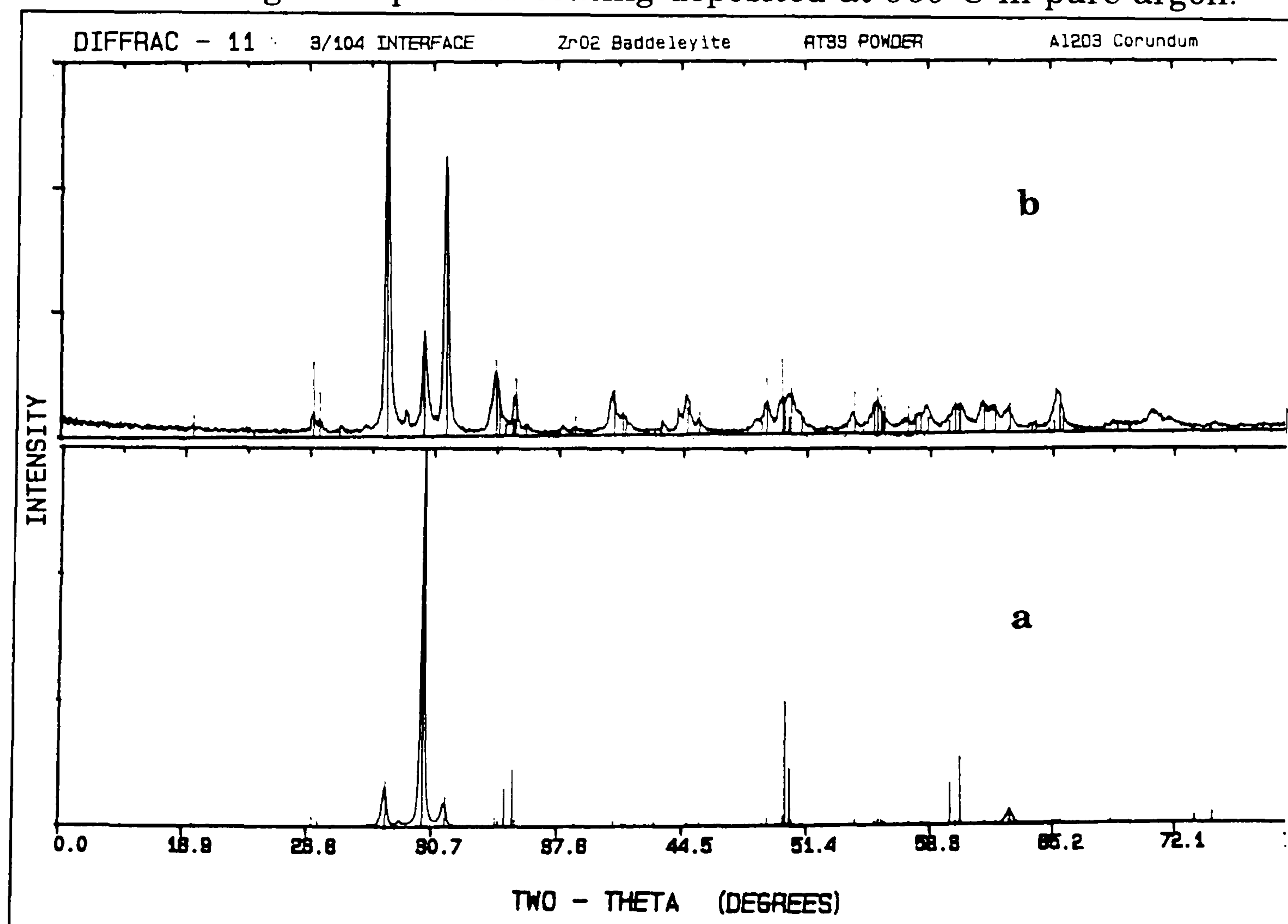


Figure 104: XRD spectra of the top surface (a) and of the interface (b) of a free standing gas evaporated coating deposited at 960°C in pure argon.

8.1.3 Lattice parameter

8.1.3.1 Lattice parameter of datum coating

Table VIII shows the room temperature lattice parameters of the as-deposited RT33 coating and of the RT33 coating powder obtained after dissolving the substrate away. The lattice parameters calculated from Scott's formula⁴⁹ (see chapter 3) are included for comparison.

Table VIII: Room temperature lattice parameters of RT33 in the as-deposited and powdered states.

	a	c
RT33 coating	5.1096±0.0009Å	5.170±0.009Å
Powdered RT33	5.1116±0.0009Å	5.176±0.009Å
Calculated from Scott's formula (8.7mol% YO _{1.5})	5.111Å	5.168Å

The lattice parameters of the commercial EB-PVD TBC match those of the (t') tetragonal phase in bulk YPSZ reported by Scott⁴⁹. This concurs with the work by Lelait et al^{139,83} who also found an excellent agreement between the measured lattice parameters of an EB-PVD TBC supplied by Airco Temescal and those calculated from the Scott's formula.

The substrate is found to have no significant influence on the lattice parameter of RT33.

8.1.3.2 Lattice parameter of development coatings

The lattice parameters of the deposits were assessed both qualitatively, by comparing the position of the diffraction lines relatively to the baton pattern from the RT33 powder and quantitatively, by using the larger Bragg angles available. By enlarge, the lattice parameters of the deposits produced in this work were found to be very close to those of RT33 for all deposition temperature and ion plating regimes investigated. For example, no peak shift was found whether the deposits were ion plated or gas evaporated at low (see Figure 105) or at around 1000°C (see Figure 106). The fluctuations in the quantified lattice parameters shown in Figure 106 (slightly larger 'c' parameter) could not be related to the controlled deposition parameters.

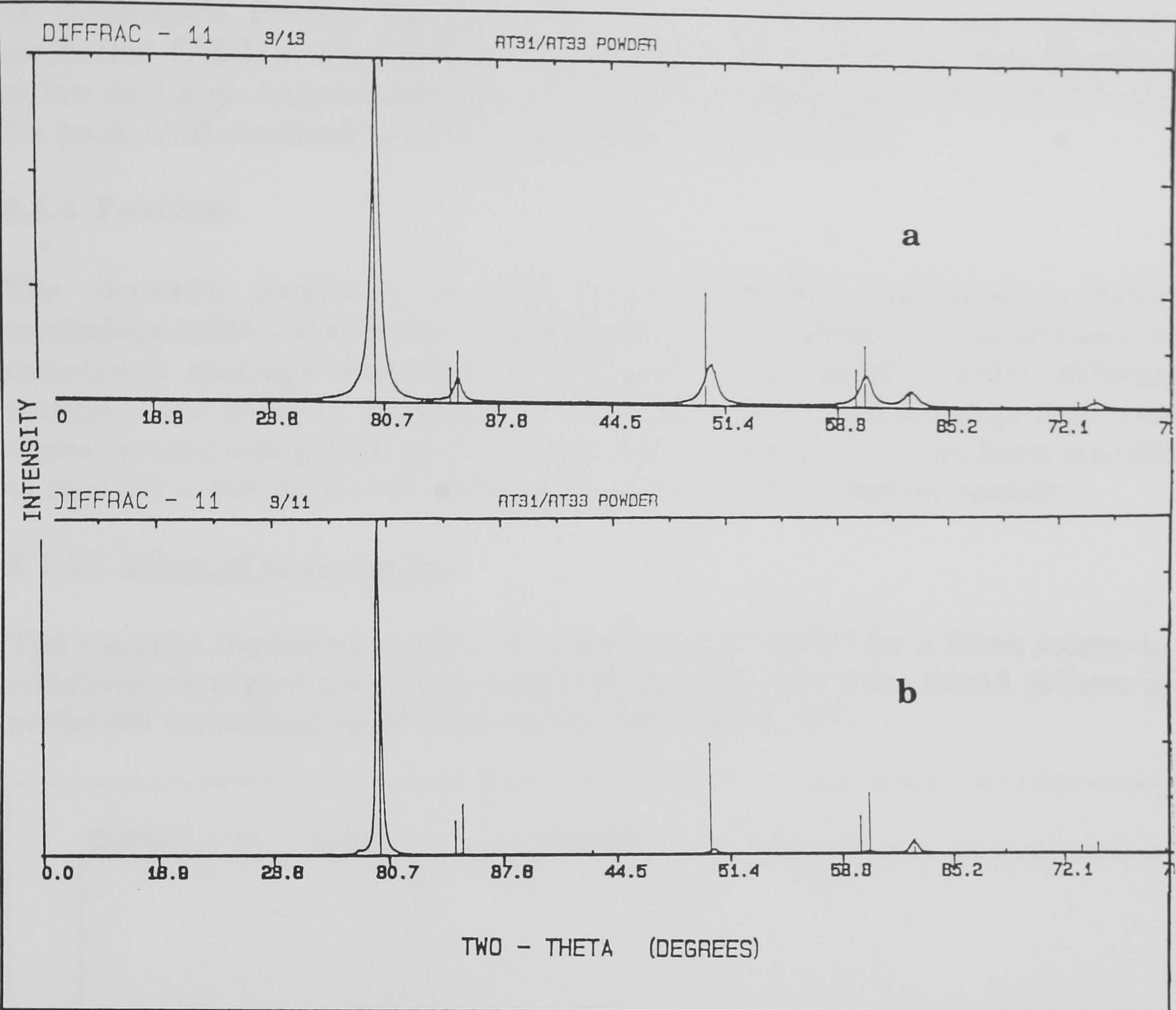


Figure 105: XRD spectra of coatings deposited in pure argon at a temperature of 500°C (a:gas evaporated coating, b:RF ion plated).

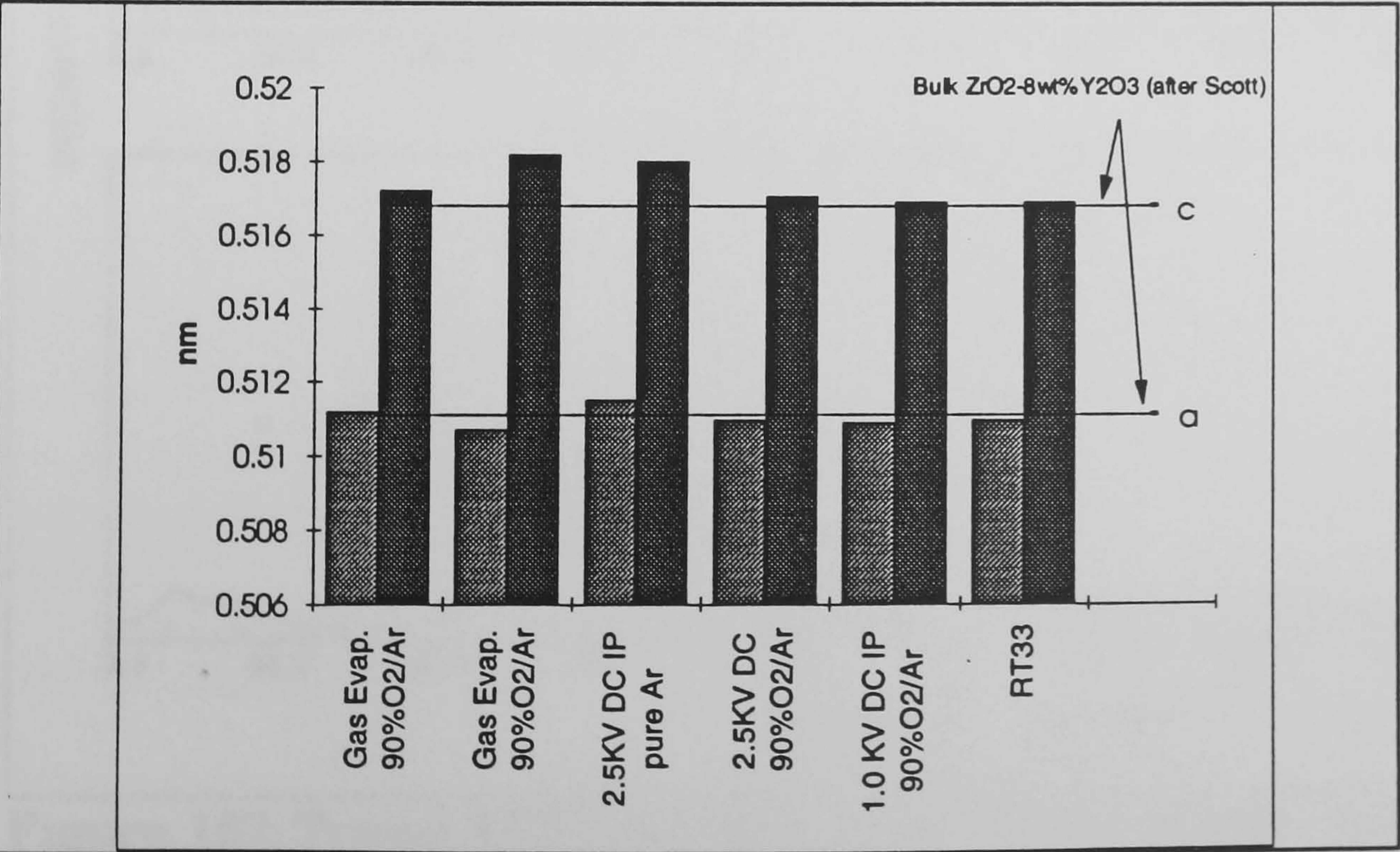


Figure 106: Comparison of calculated lattice parameters of high temperature deposits (950-1030°C) (error on a and c~0.0001nm).

To investigate further the potential role of substrate thermal expansion coefficient (TEC) on the build up of a thermal stress, coatings were deposited at low and high temperatures on stainless steel substrates (TEC: $18 \times 10^{-6}/^{\circ}\text{C}$). No peak shift resulted from increasing the substrate TEC.

8.1.4 Texture

The deposits produced in this work generally exhibited preferred crystallographic orientations. These however were not always predictable as sometimes coatings deposited in the same batch would exhibit different textures (see 3/302 in Appendix 7). Still, from the many deposits that were characterized using XRD in this study (see Appendix 7), it has been possible to identify a few salient features as to what controls coating texture.

8.1.4.1 Effect of temperature

The coatings deposited at very low temperature (300°C for a 22cm source-to-substrate distance) under gas evaporation conditions were found to have no preferred crystallographic orientation (see Figure 107).

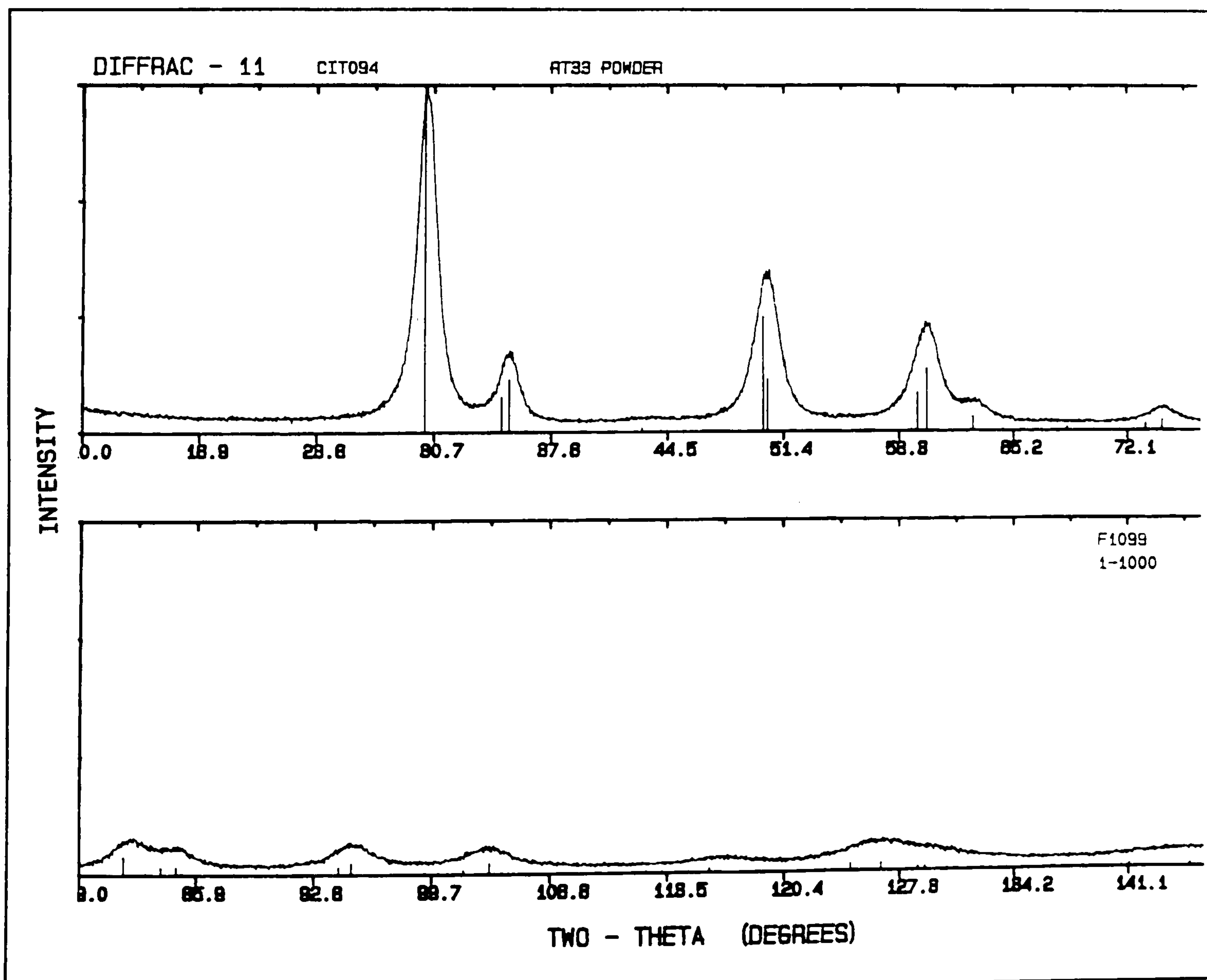


Figure 107: Typical XRD trace of low temperature deposits ($T=300^{\circ}\text{C}$, source-to-substrate distance: 22cm).

The coatings deposited at moderate and high temperature were generally highly textured, the prevailing preferred orientations being the $\langle 111 \rangle$ and $\langle 100 \rangle$ directions (see Appendix 7 and details below).

8.1.4.2 Effect of oxygen partial pressure

The textured gas evaporated coatings that were deposited in pure argon consistently exhibited the $\langle 111 \rangle$ preferential orientation. Some of the deposits (runs 3/M1/1,2,3 and L) exhibited no texture at temperatures up to about 1030°C. Preferred orientations such as the $\langle 100 \rangle$ and the $\langle 001 \rangle$ only started to appear when the bleed of 90%O₂/10%Ar was introduced inside the chamber furnace (see Figure 108 and Appendix 7). These textures were obtained even when the depositions were initiated in pure argon prior to bleeding 90%O₂/10%Ar.

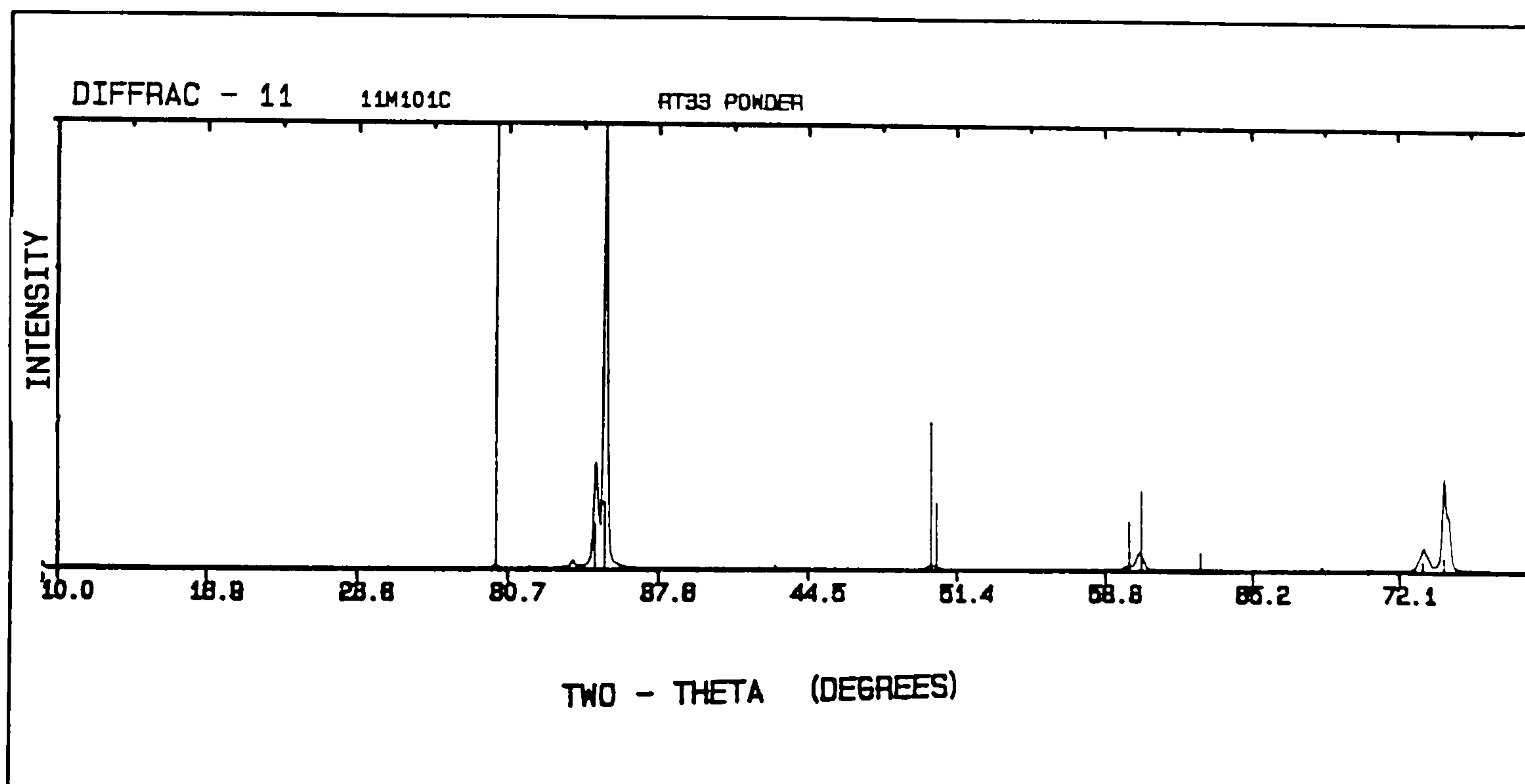


Figure 108: XRD trace of a gas evaporated coating deposited at 1000°C in 90%O₂/10%Ar.

8.1.4.3 Dependence of texture on coating depth

XRD evaluation of the coating interfacial region obtained after dissolving the substrate away showed that the coating crystallites were more randomly oriented nearer the substrate. This was highlighted in section 8.1.2.4 when discussing the relative proportions of tetragonal to monoclinic.

8.1.5 Lattice strain and grain size

The width of the diffraction lines was found to decrease strongly with deposition temperature. Peak broadening may either arise from a small crystallite size ($<0.1\mu\text{m}$) and/or from lattice microstrain. In order to decouple these two contributions, Hall-Williamson plots were produced for different deposition temperatures and ion plating regimes (see Figure 109). In this

figure, the Y-intercept and the slope represent respectively the crystallite size (nm) and the lattice strain (%) as explained in chapter 6.

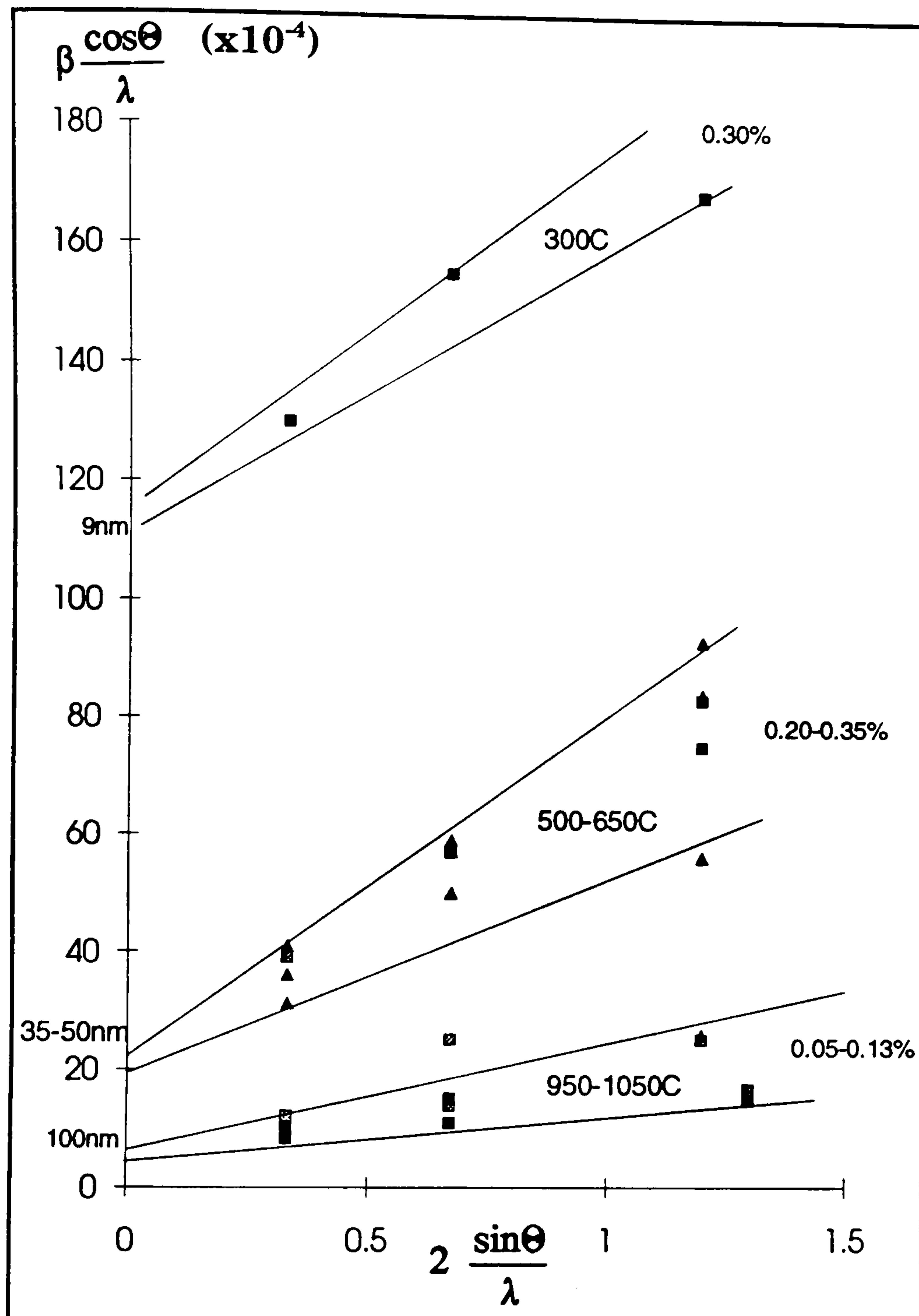


Figure 109: Hall-Williamson plots of coatings deposited under different deposition temperature and ion plating regimes (■: gas evaporation, ▲: ion plating)

It can be seen from this graph that ion plating, using either DC or RF biasing, does not affect significantly the lattice strain nor the grain size of EB-PVD YSZ deposits. The grain size and lattice strain are found respectively to increase and decrease strongly with deposition temperature.

8.1.6 Morphology

8.1.6.1. Influence of substrate surface finish/ion plating

On metallographically polished substrates, ion plating at low temperature was found to result in coating morphologies consisting of an array of fibrous-

like columns (see Figure 110 and Figure 111). However, on grit blasted substrates a coarse columnar morphology was obtained in spite of the ion plating, comparable to that of straight gas evaporated systems on smooth substrates (see Figure 112 comparatively to Figure 111 and Figure 110). In this work, the bulk of the coatings were deposited on substrates with a surface finish typical of those used for metallurgical coatings ($0.5\mu\text{m} < \text{Ra} < 1\mu\text{m}$). Hence, the potential effects of ion plating on morphology were found to be overridden by the surface finish.

8.1.6.2. Influence of temperature

The coatings deposited at low temperature exhibited a coarse column size with little inter-columnar porosity as seen in cross-section (see Figure 116). As the deposition temperature was raised, the mean coarse column diameter was not found to change. However, a transition temperature of about 850°C was found from which the coarse column would transform into bundles of finer or fibrous columns (see Figure 113, Figure 114 and Figure 115). At elevated temperatures of deposition ($>900^{\circ}\text{C}$), a fibrous or refined columnar morphology was generally obtained featuring well pronounced inter-columnar voidage (Figure 117, Figure 118 and Figure 119) which is comparable to that in the commercial TBC datum (Figure 120 and Figure 121). At deposition temperatures greater than 950°C , the coating crystallinity becomes clearly identifiable as seen from the faceted column tops using SEM at high magnifications ($>X10,000$) (see Figure 122 and Figure 123). This concurs with the coating crystallites being larger on average than 200nm when deposited at a temperature of 1000°C (see Figure 109).

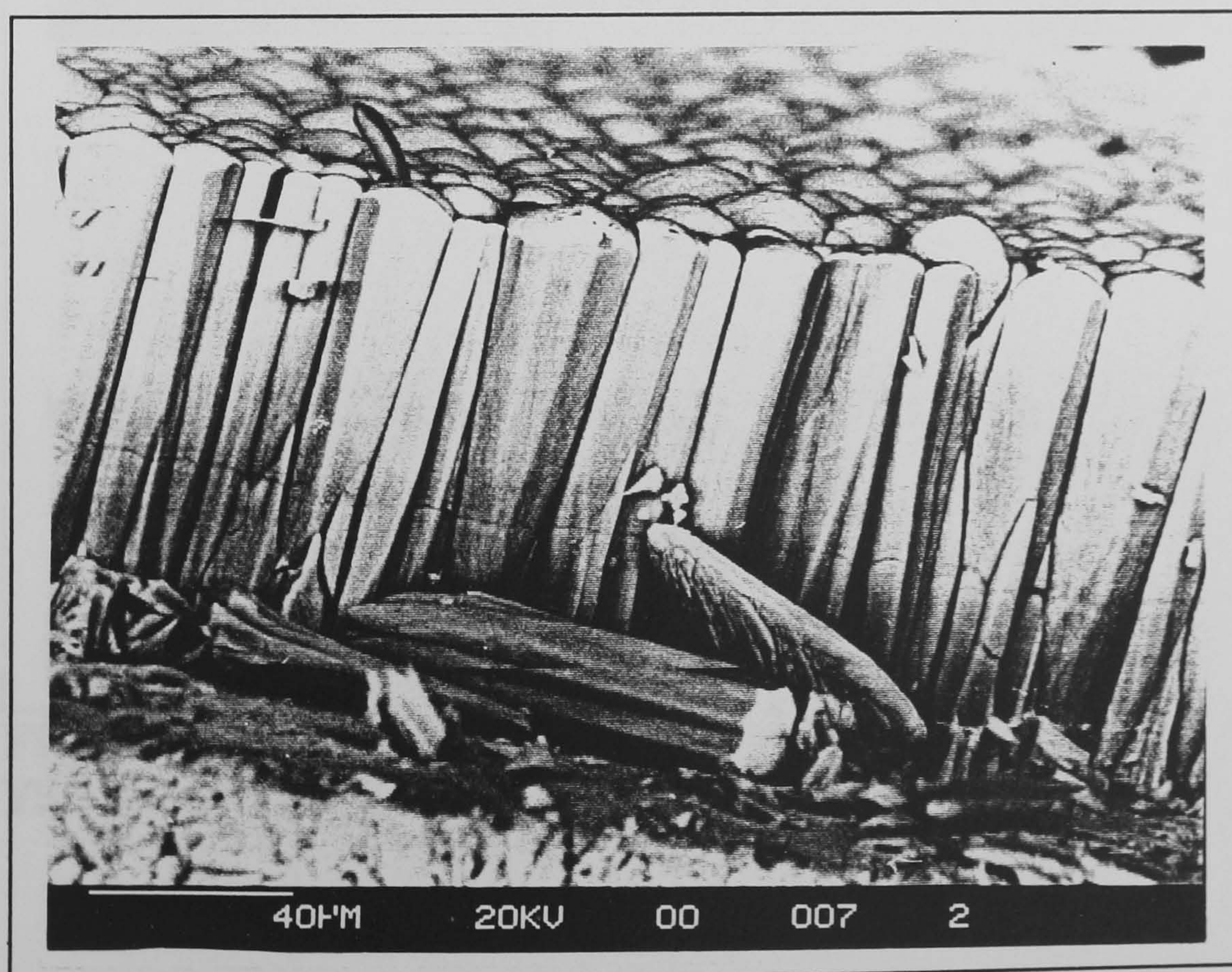


Figure 110: Low temperature ($300\text{-}400^{\circ}\text{C}$) gas evaporated YSZ on metallographically polished substrate.

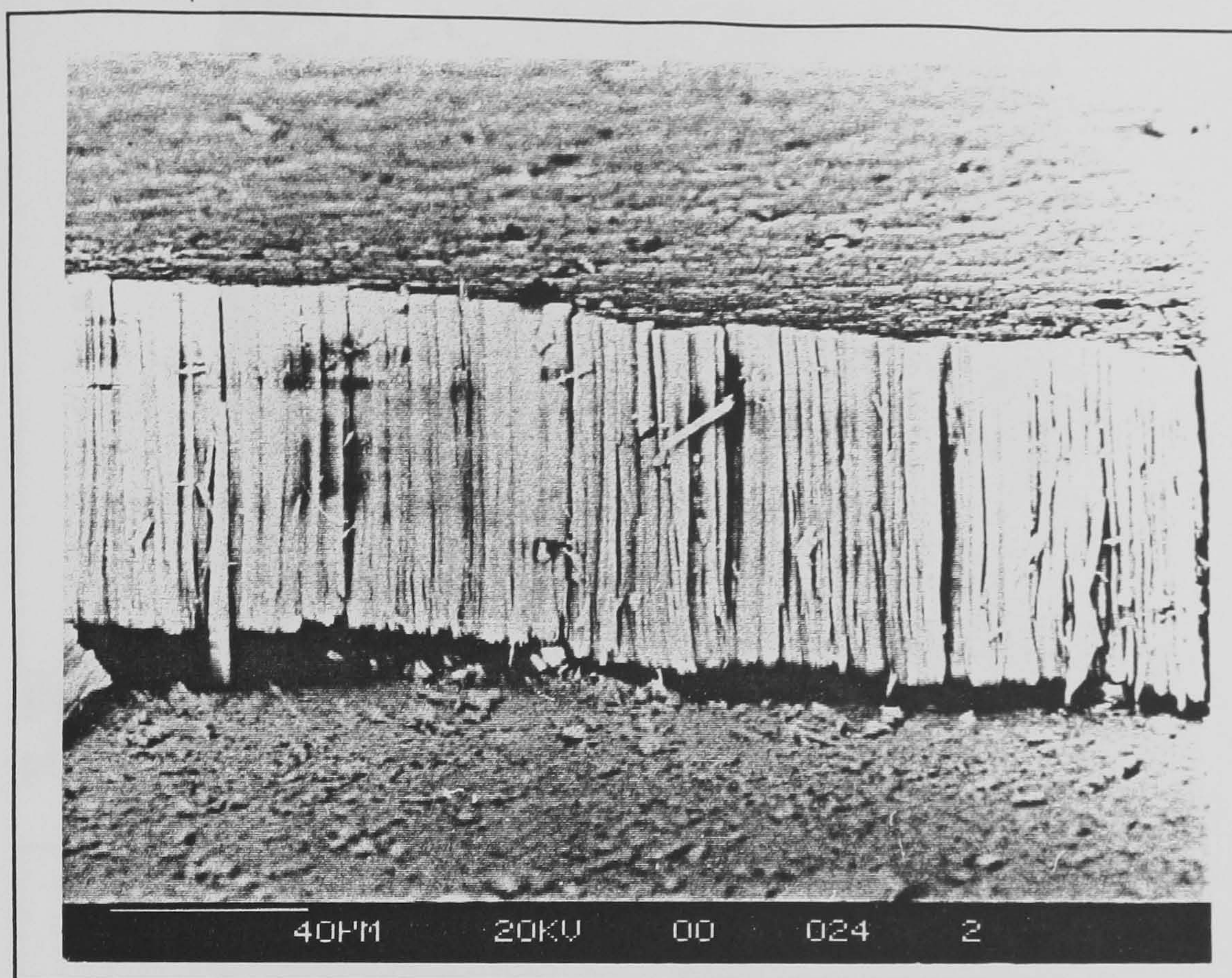


Figure 111: Low temperature (300-400°C) RF ion plated YSZ on metallographically polished substrate.

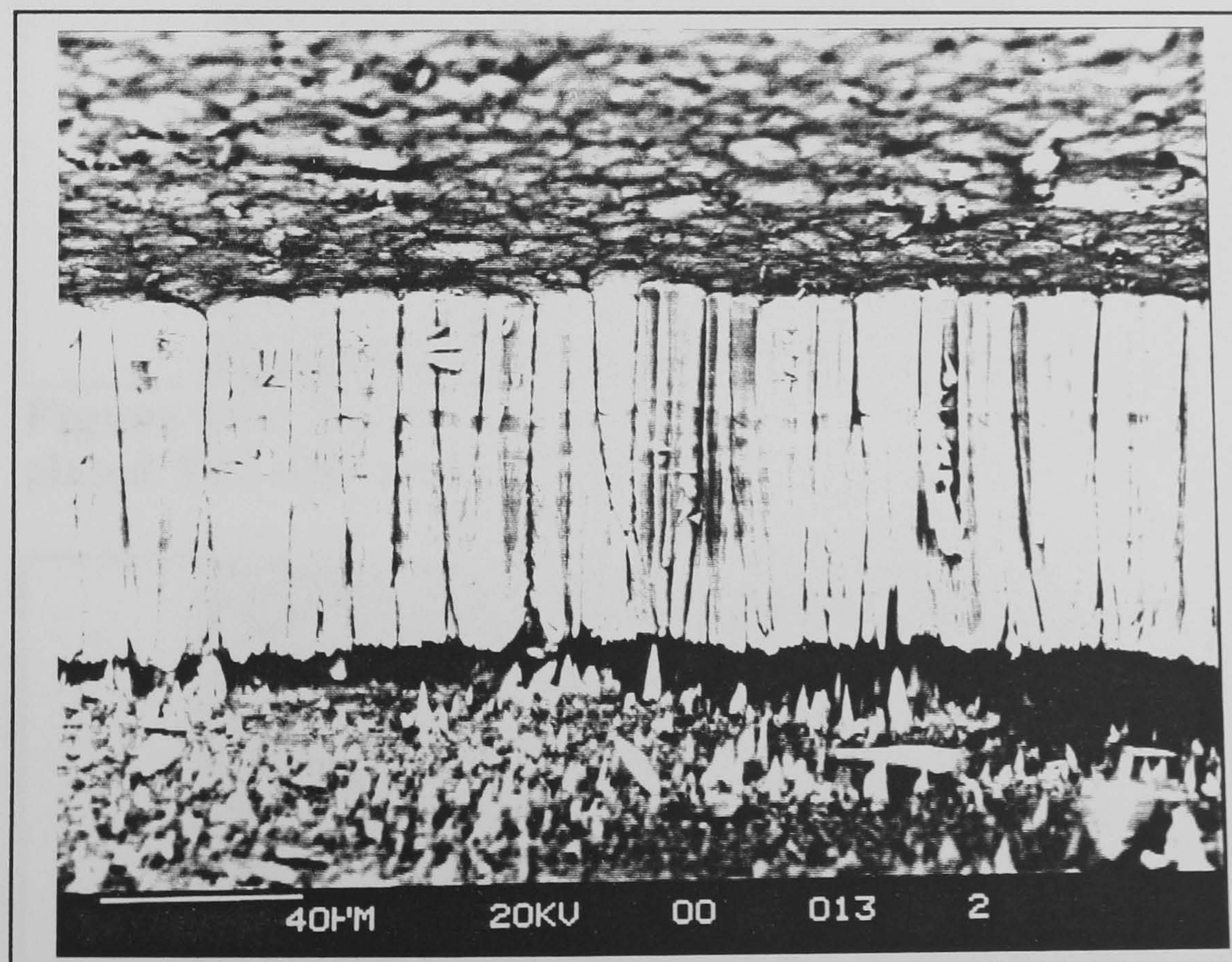


Figure 112: Low temperature (300-400°C) RF ion plated YSZ on grit blasted substrate.

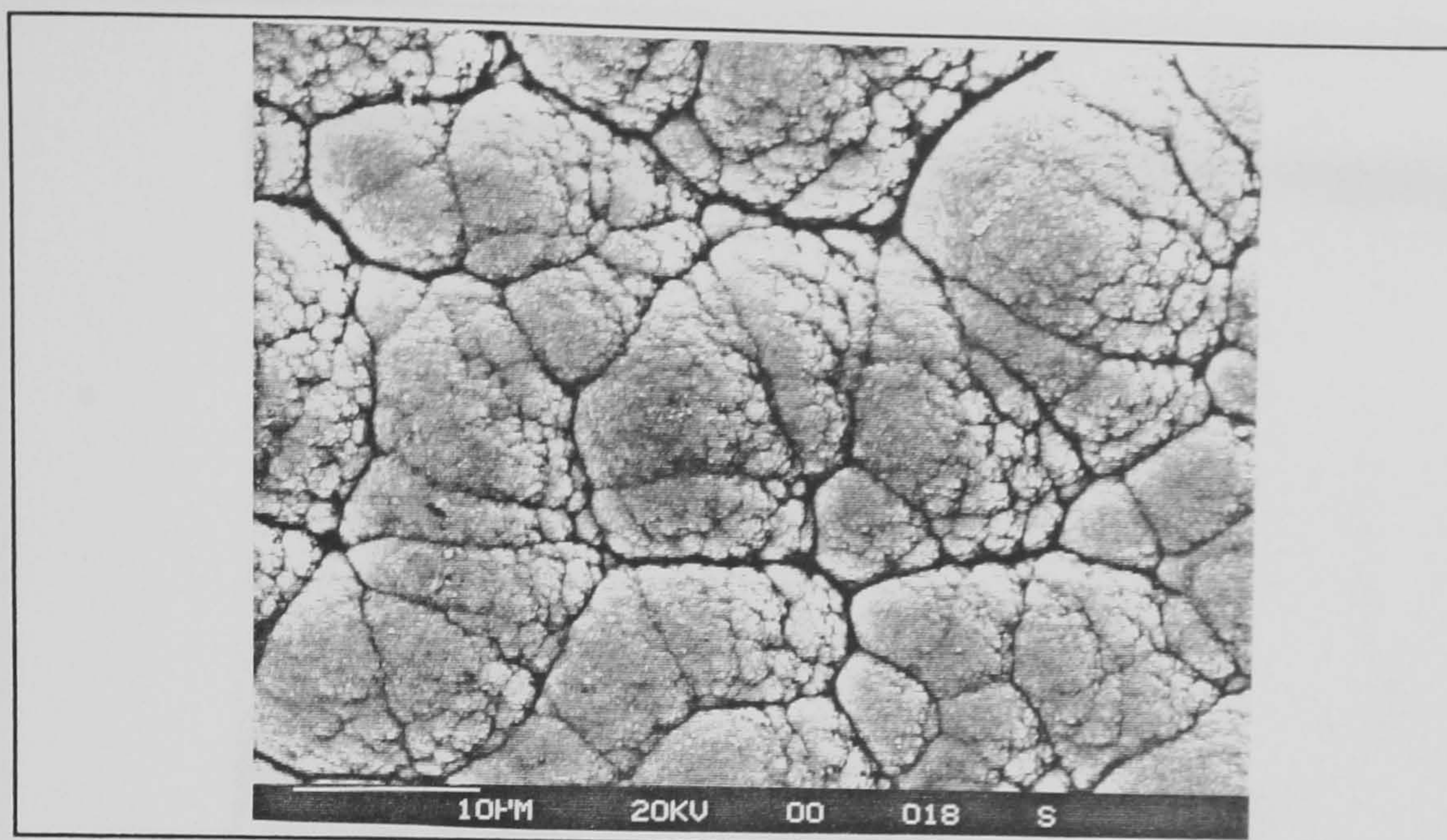


Figure 113: Surface topography of low current density ion plated YSZ deposited on 'dog-bone' substrate at 650°C.

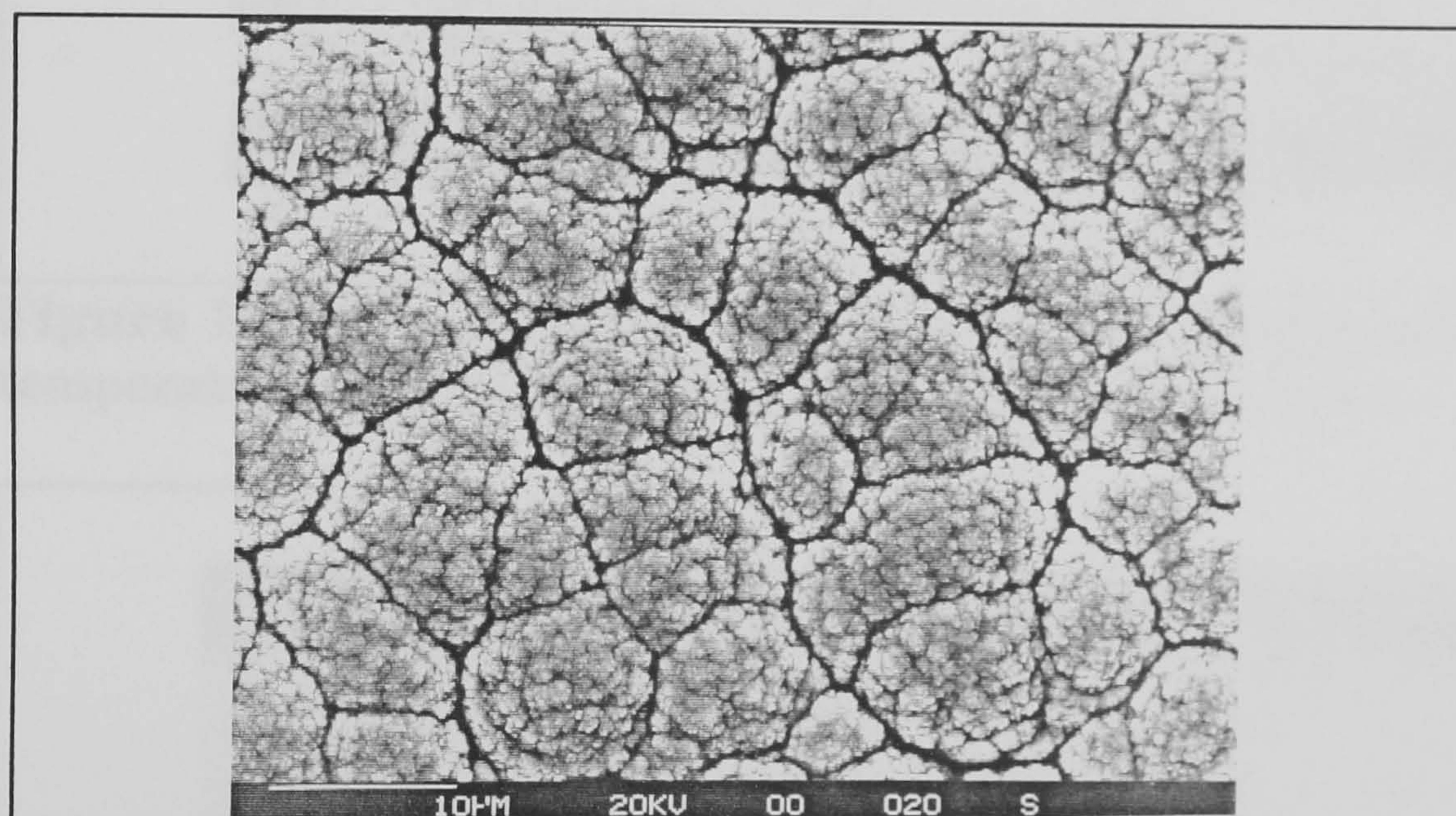


Figure 114: Surface topography of low current density ion plated YSZ deposited on 'dog-bone' substrate at 850°C.

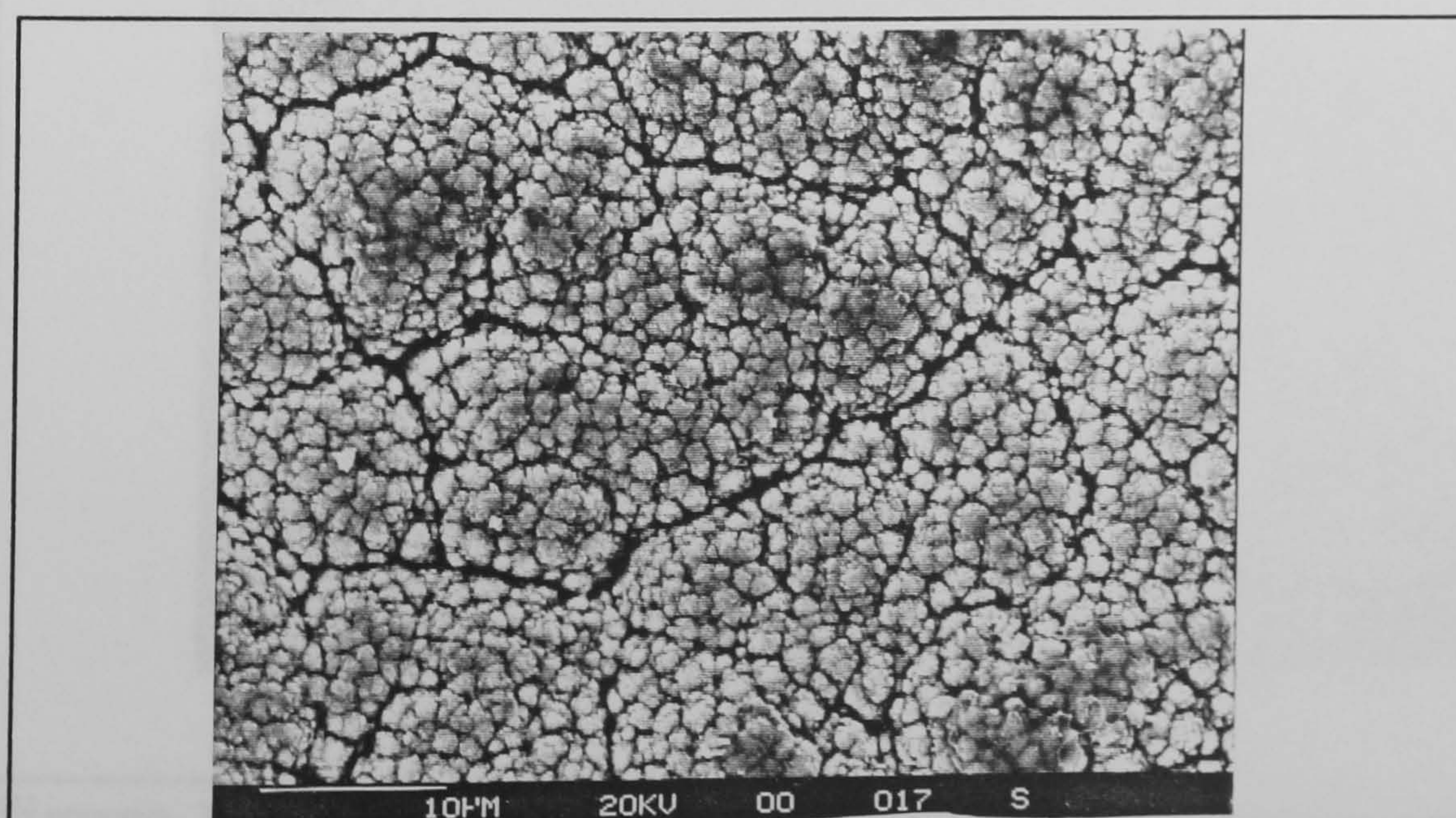


Figure 115: Surface topography of low current density ion plated YSZ deposited on 'dog-bone' substrate at 1000°C.

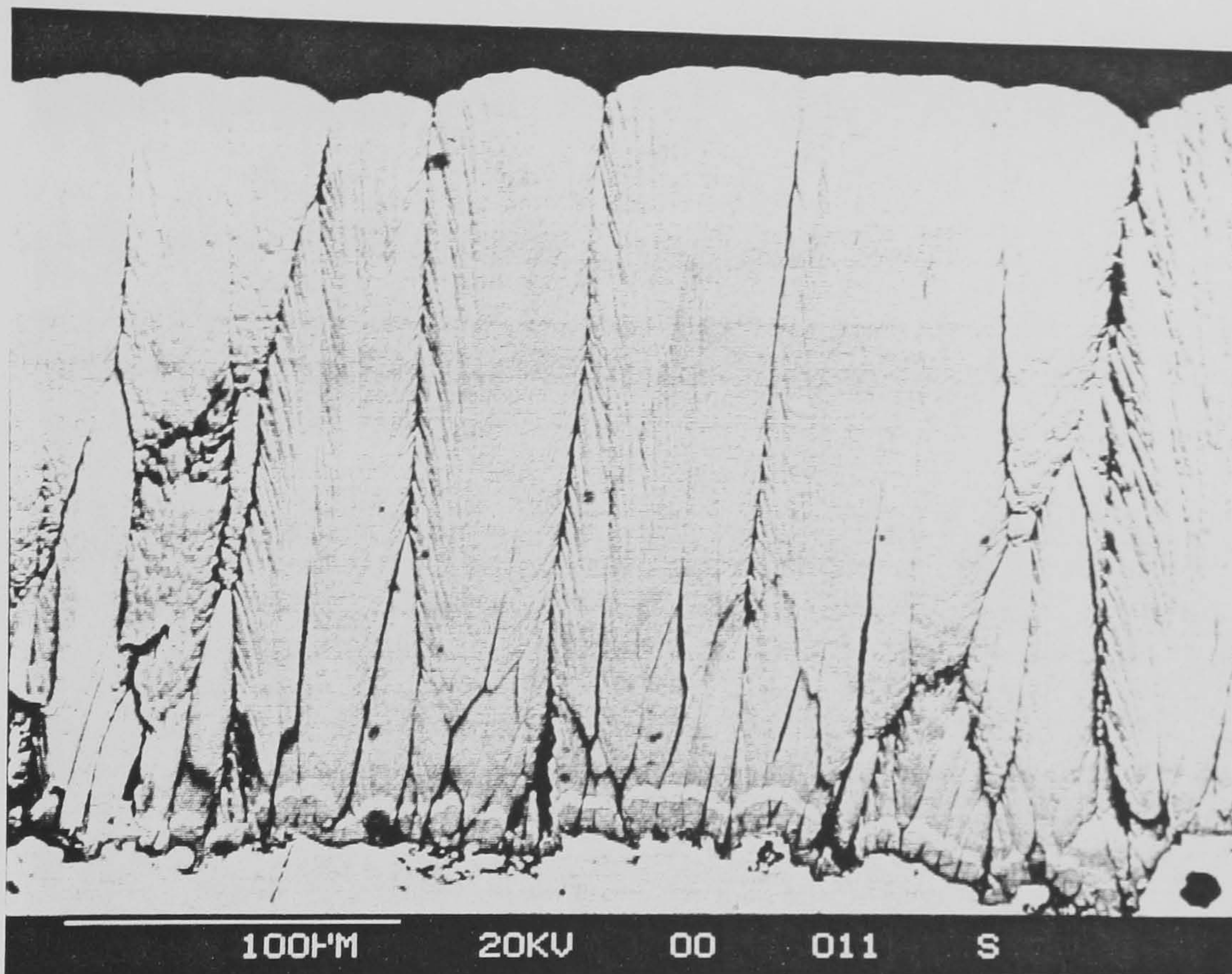


Figure 116: Cross-section of an EB-PVD YSZ deposited in the 500-650°C temperature range (back-scattered electron micrograph).

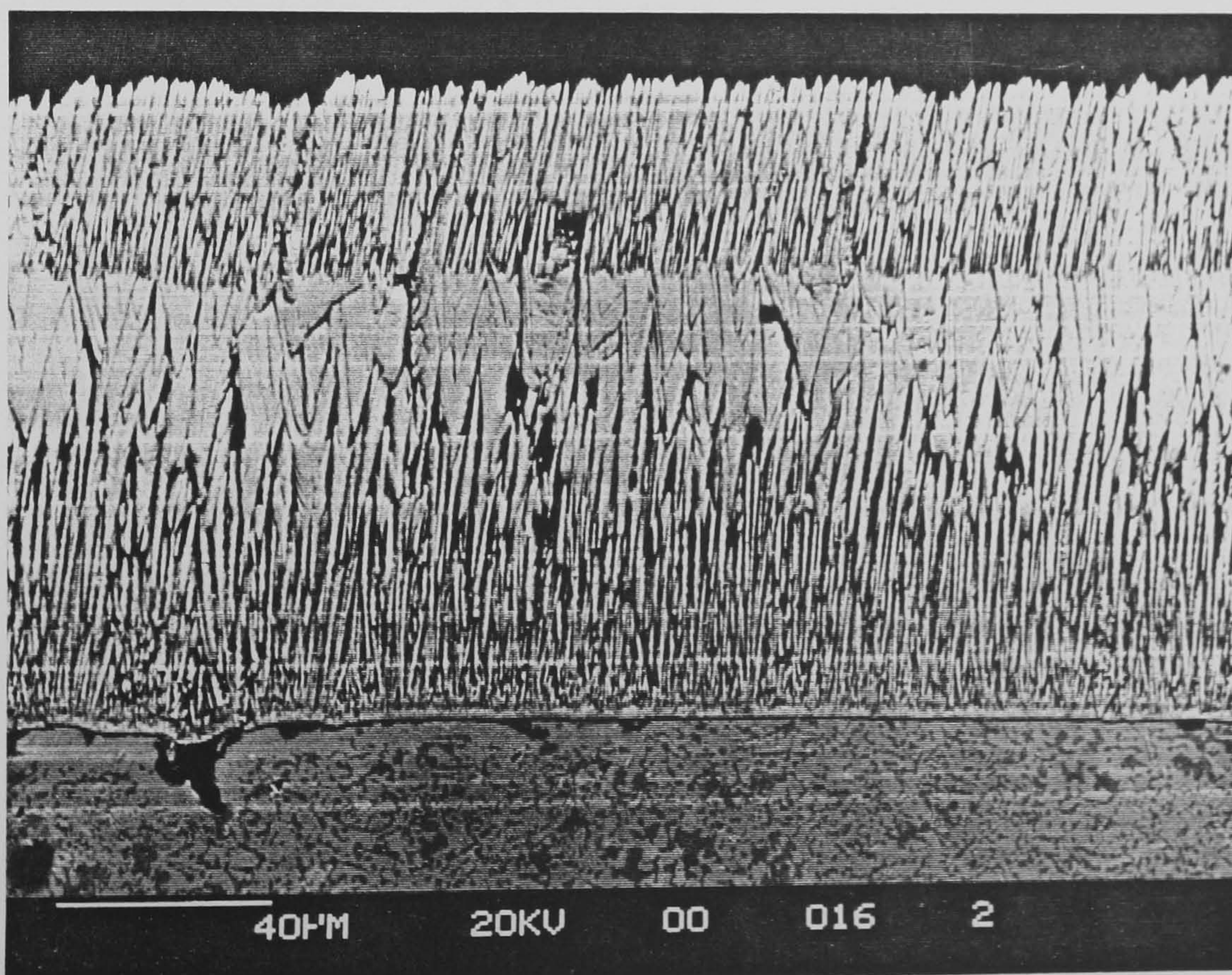


Figure 117: Cross-section of an EB-PVD YSZ deposited at 1000°C (back-scattered electron micrograph).

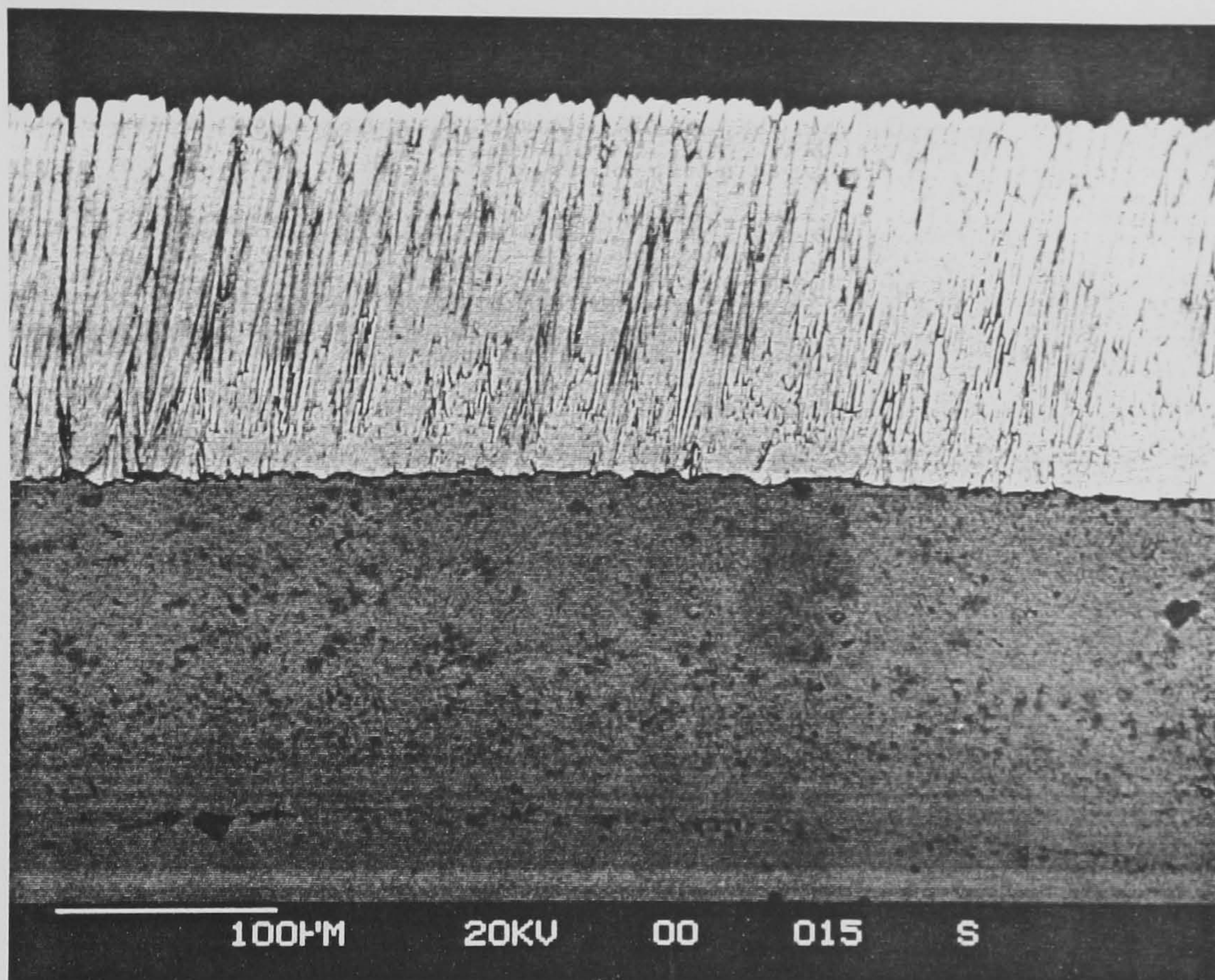


Figure 118: Cross-section of a -2.5kV DC ion plated YSZ deposited at 1000°C (back-scattered electron micrograph).

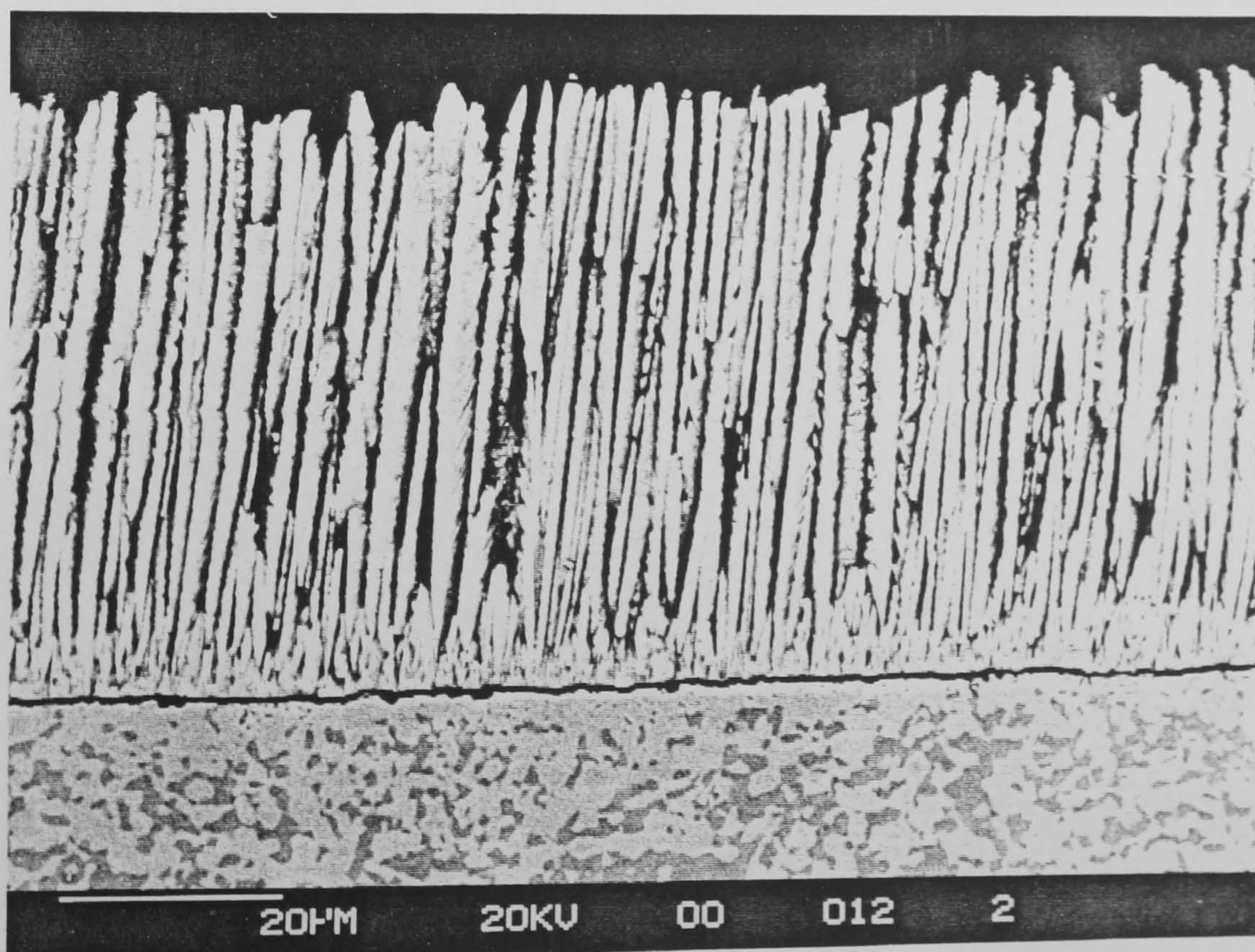


Figure 119: Cross-section of a -3kV DC ion plated YSZ deposited at 1000°C (back-scattered electron micrograph).

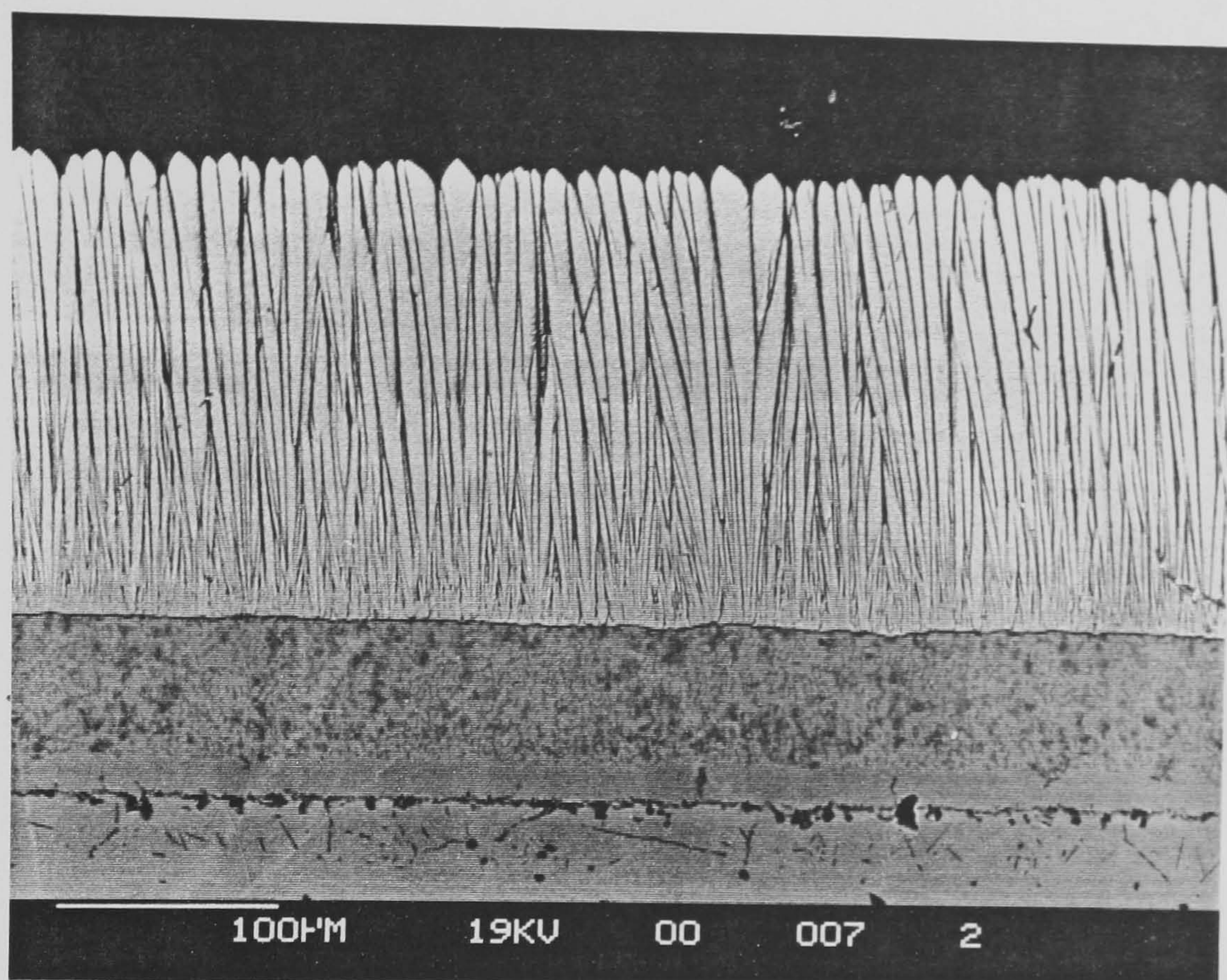


Figure 120: Cross-section of commercial EB-PVD TBC (RT33) purchased from CR&T (USA) (back-scattered electron micrograph).

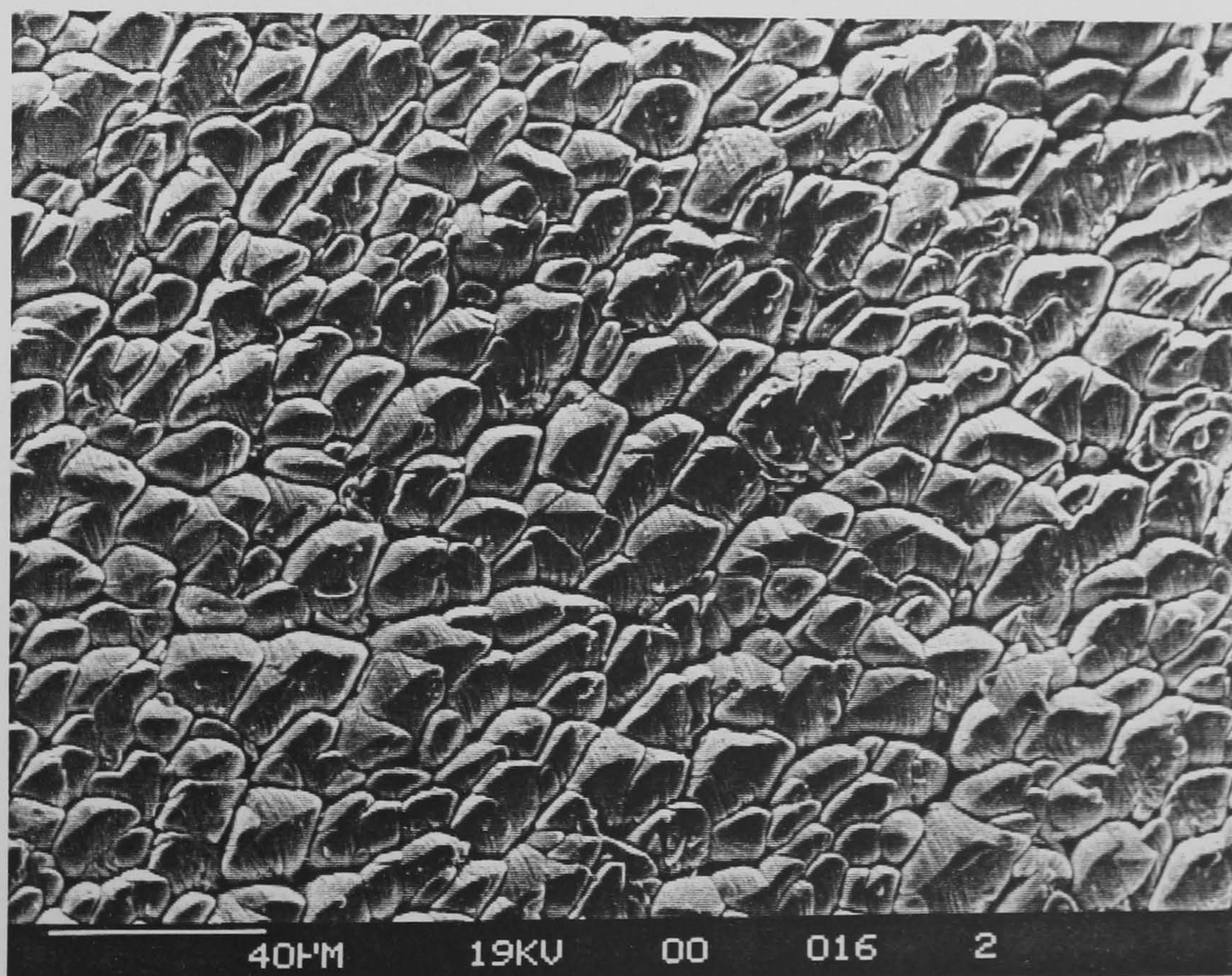


Figure 121: Surface topography of commercial EB-PVD TBC (RT33) purchased from CR&T (USA) (secondary electron micrograph).

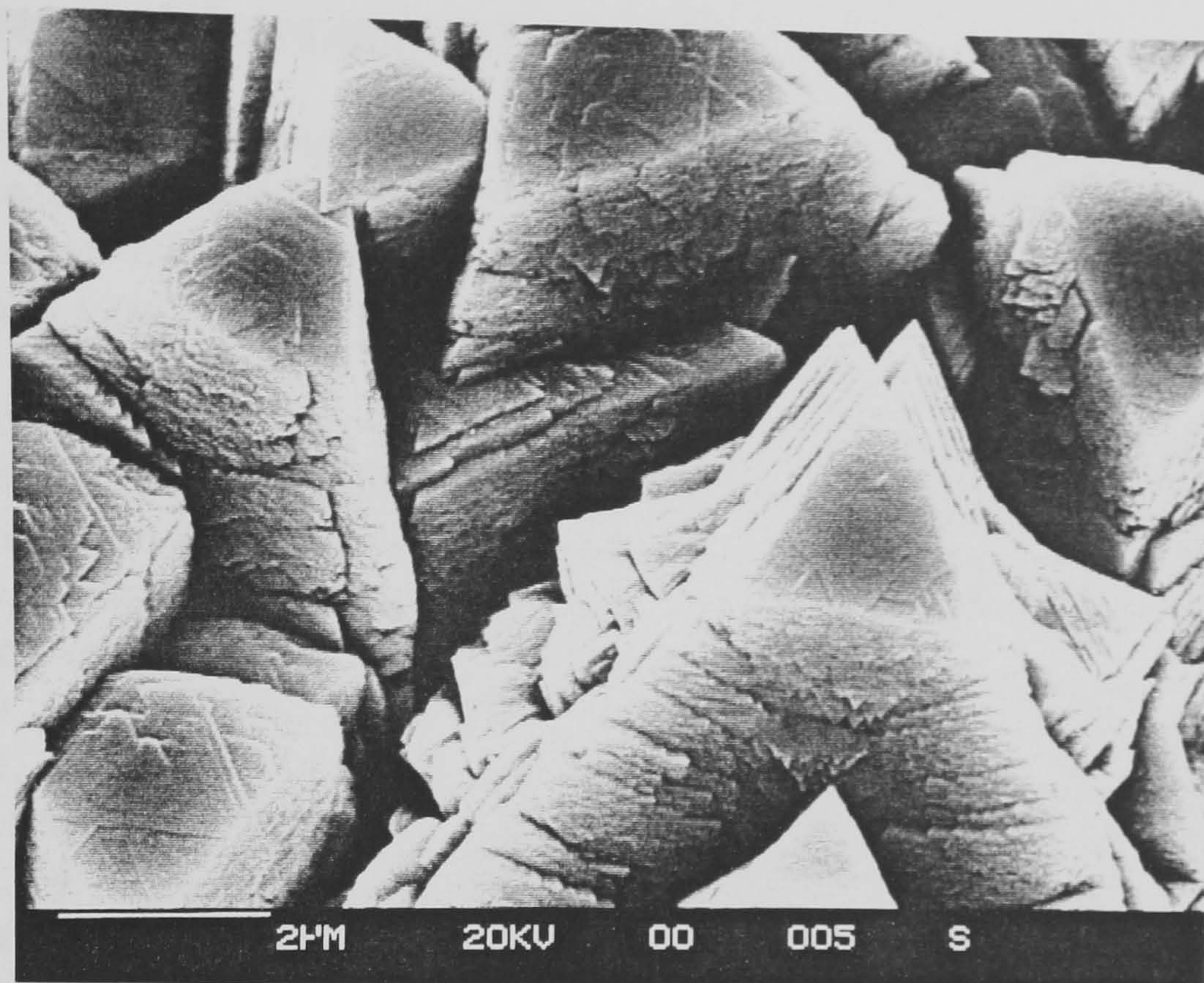


Figure 122: High magnification secondary electron micrograph of the surface topography of EB-PVD YSZ deposited at 1000°C showing <111> texture morphology.

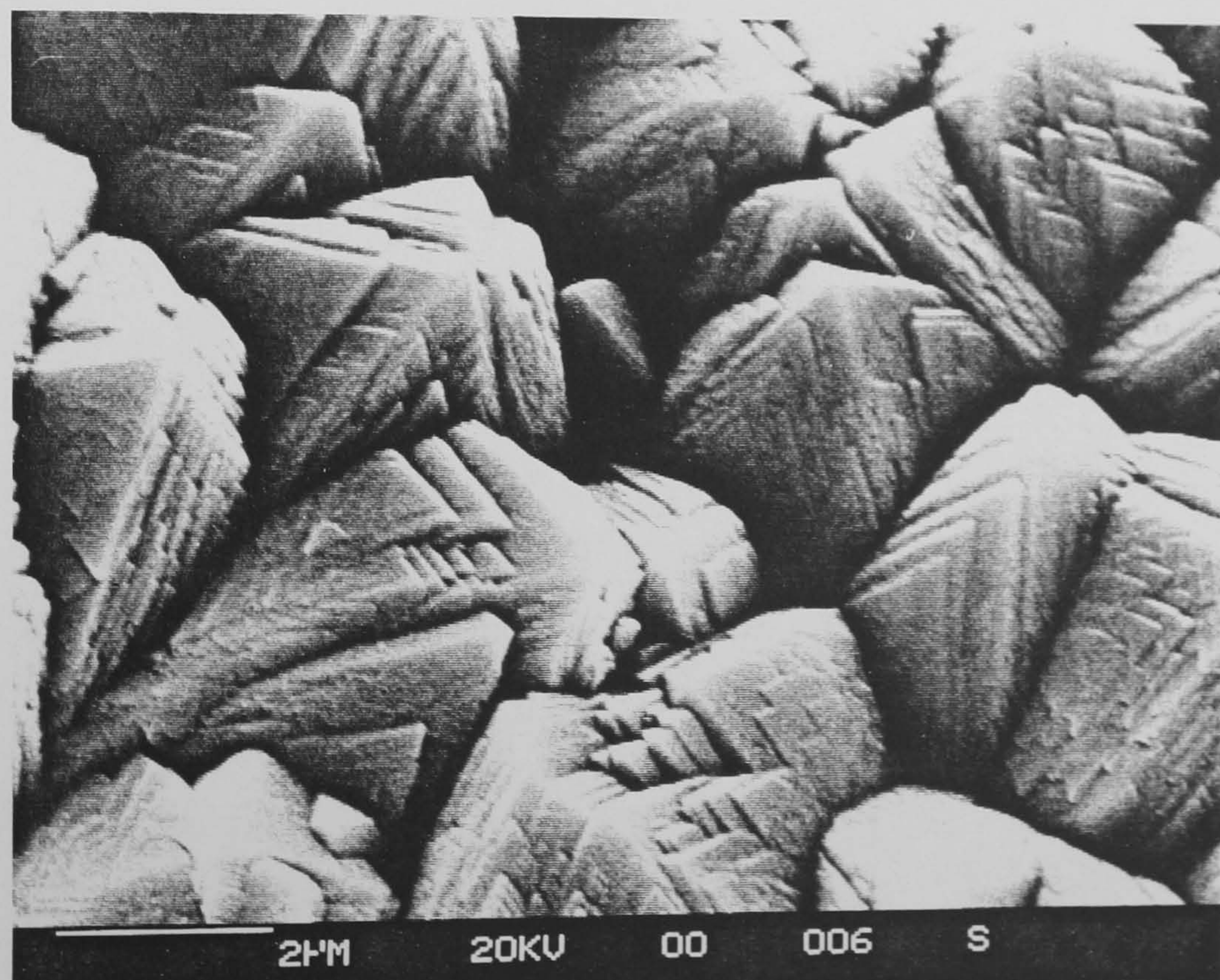


Figure 123: High magnification secondary electron micrograph of the surface topography of EB-PVD YSZ deposited at 1000°C showing <100> texture morphology.

8.1.7 Indentation resistance

8.1.7.1 Influence of deposition temperature

The coatings that were deposited at a source-to-substrate distance of 22cm and at a temperature of about 300°C exhibited a surface indentation resistance in the 7 to 14Kg/mm² range. These figures are probably the lowest hardness data ever recorded for YSZ deposits.

The effect of deposition temperature on coating indentation resistance was unequivocally demonstrated by the temperature-graded substrates ('dog-bone specimens') as, in these coating runs, the same evaporation conditions applied over a range of deposition temperatures. Indentation resistance of the coating surface and cross-section was found to increase monotonically with temperature irrespective of the ion plating regime (see Figure 124 and Figure 125). In these figures, the terms 'high current density' and 'low current density' refer to a low and high RF cathode area (substrate area) respectively. A high cathode area was obtained by placing additional substrates above the source that were unheated resistively but connected electrically to the 'dog-bones'. Given the calibration runs of substrate temperature vis-a-vis source-to-substrate distance (15cm and 22cm), the substrate temperature achieved for 18cm in this particular run is believed to be about 450°C. The indentation resistance of the coatings deposited on these substrates was determined at 65Kg/mm² and are shown in Figure 124. By virtue of a more intense ion bombardment, the 'high current density' coating might have been deposited at higher temperature than the 'low current density' ones.

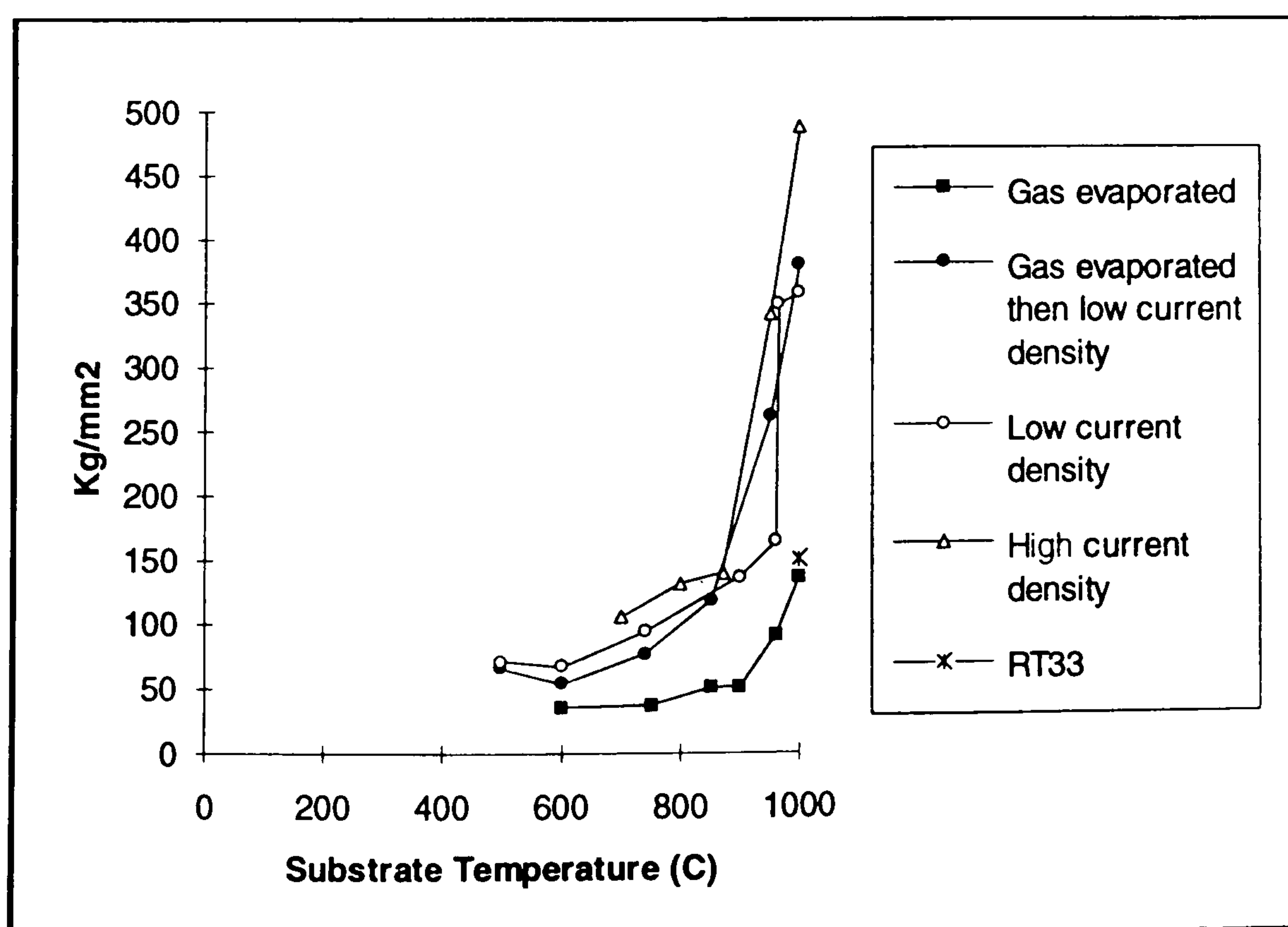


Figure 124: Surface indentation resistance as a function of deposition temperature and ion plating regime.

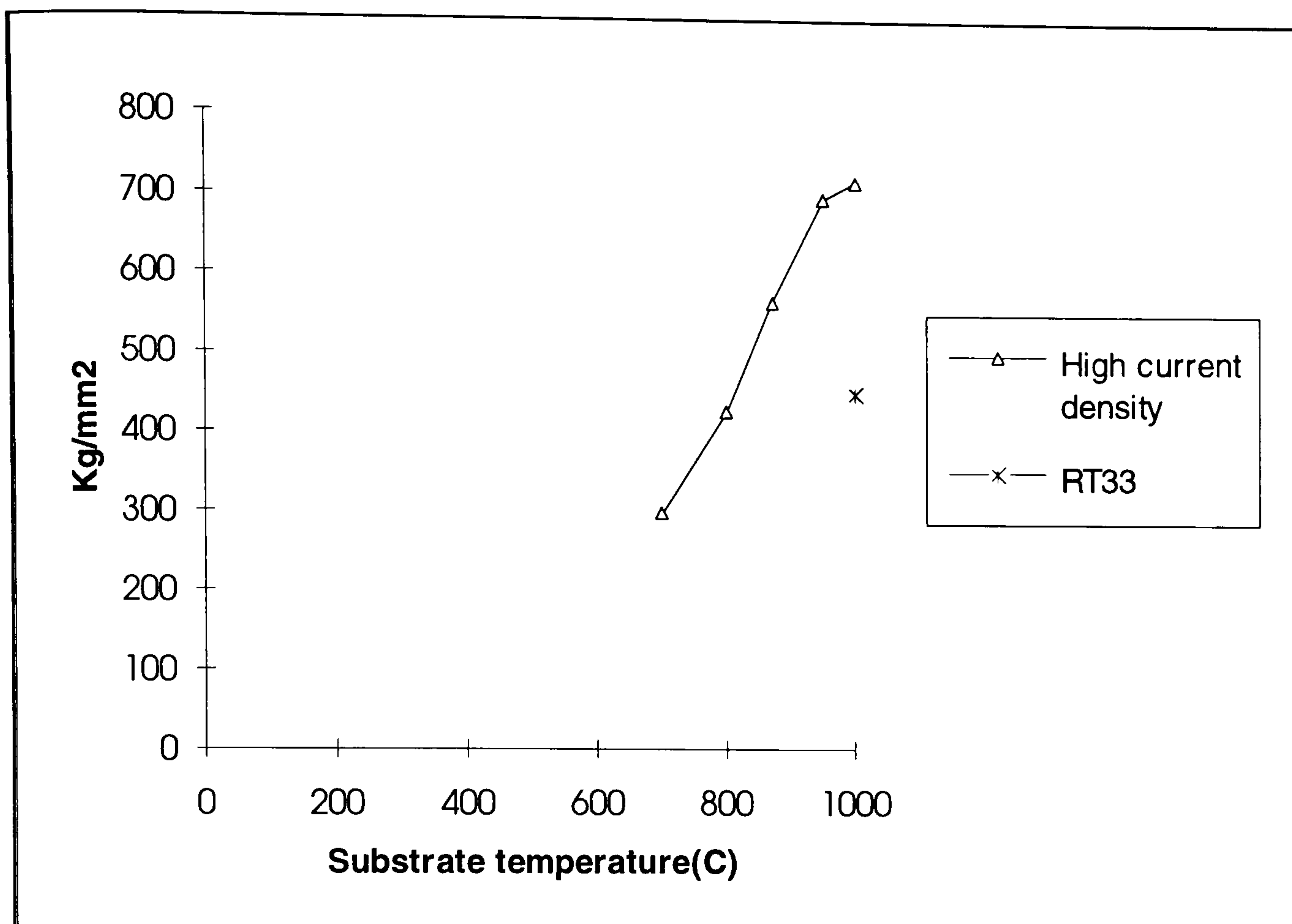


Figure 125: Cross-section indentation resistance as a function of deposition temperature.

It should be borne in mind that the surface topography of the commercial datum (RT33) is significantly rougher than that of the development coatings (see for example Figure 121 and Figure 113 to Figure 115). The rougher surface of RT33 could artificially lower its measured surface indentation resistance relative to that of the development coatings due to the resulting apparent increase in projected area. Twigg and Page¹⁶⁸ reported that the hardness of a commercial EB-PVD TBC was 380kg/mm², as measured on the as-polished coating surface.

8.1.7.2 Influence of plasma assistance

In order to identify the role of plasma assistance on indentation resistance, microhardness testing on a coating cross-section was carried out on a sample of the three gas evaporated and six RF ion plated deposits. These coatings were deposited under similar conditions in terms of source-to-substrate distance, RF cathode area and temperature range. All the depositions were started at a substrate temperature of 300°C, as achieved from ion cleaning for 20 minutes in argon. Although the substrate temperature was not monitored in every run, previous experience had showed that for a source-to-substrate distance of 15cm, the substrate temperature achieved could vary between 500°C and 650°C depending on the evaporation conditions. Poor evaporation conditions are synonymous of a low melt surface area, as seen by the substrates, and are associated with lower substrate temperature and deposition rates.

In the case of the RF ion plating runs, the situation was further complicated by the propensity of the plasma to extinguish as the deposition proceeded due to interactions with the evaporation source. It was found that there was a critical electrom beam current level above which the plasma would extinguish, and that the magnitude of this beam current threshold decreased with run time (see chapter 7). Consequently, the ion plating coatings were deposited with deposition rates that were decreased throughout the run in order to maintain the plasma on. These erratic plasma conditions coupled with fluctuating deposition rates due to unsteady evaporation conditions resulted in deposits with multilayered structures (see Figure 126). Each different layer had a different indentation resistance.

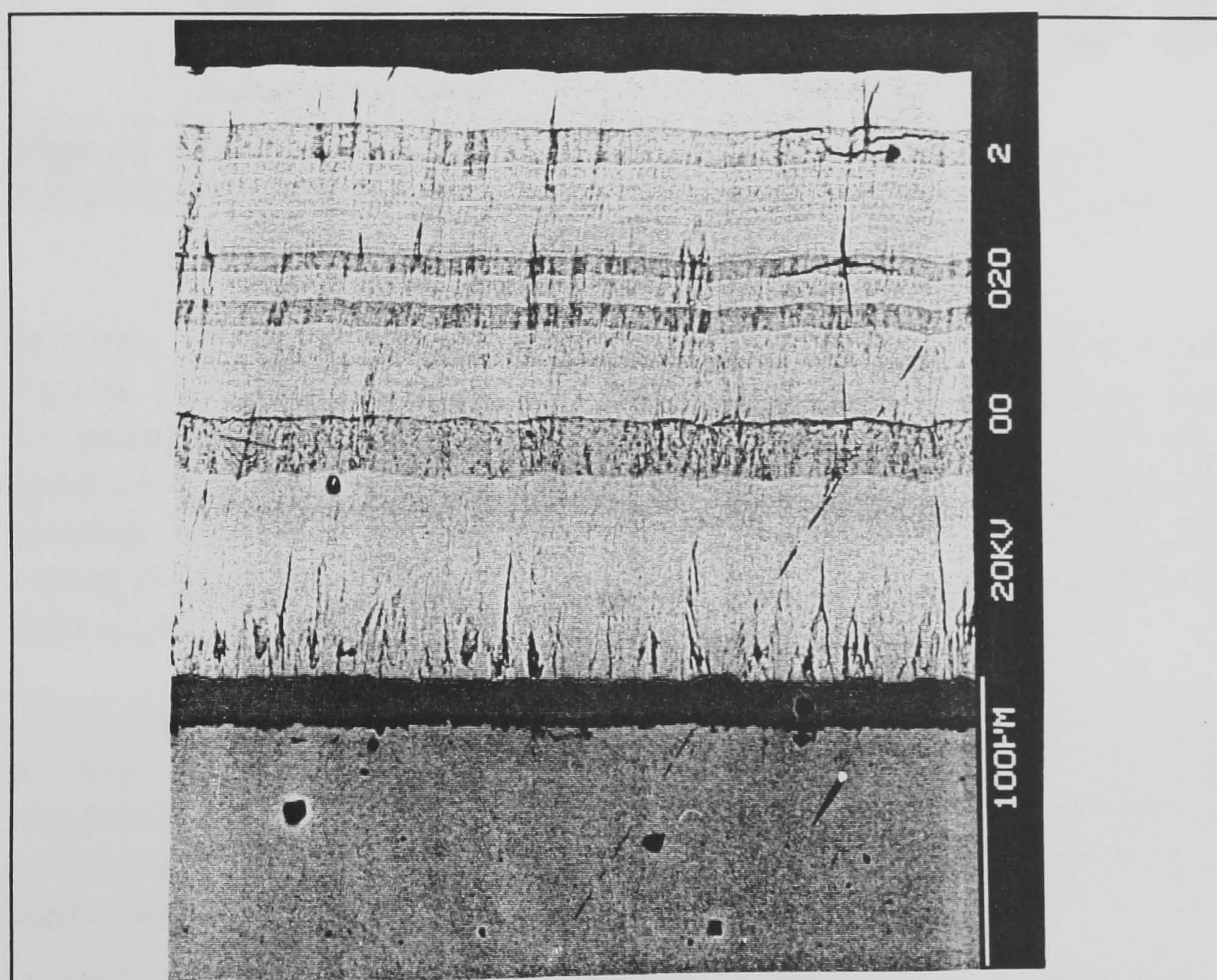


Figure 126: Typical RF ion plated coating deposited in the 500-650°C deposition temperature range showing the effect of RF plasma switching on and off.

The indentation resistance data quoted in Figure 127 is the average of the hardness number obtained for each layer, with the bars giving the standard deviation in values. The massive scatter exhibited by the ion plated coatings is the consequence of the various layers having different hardnesses. In contrast, the gas evaporated coatings exhibited a much more consistent indentation resistance. The scatter for these coatings arises mainly from the fact that the indentation resistance increased closer to the coating free surface. This is believed to be due to the substrate temperature increasing monotonically as the deposition proceeded.

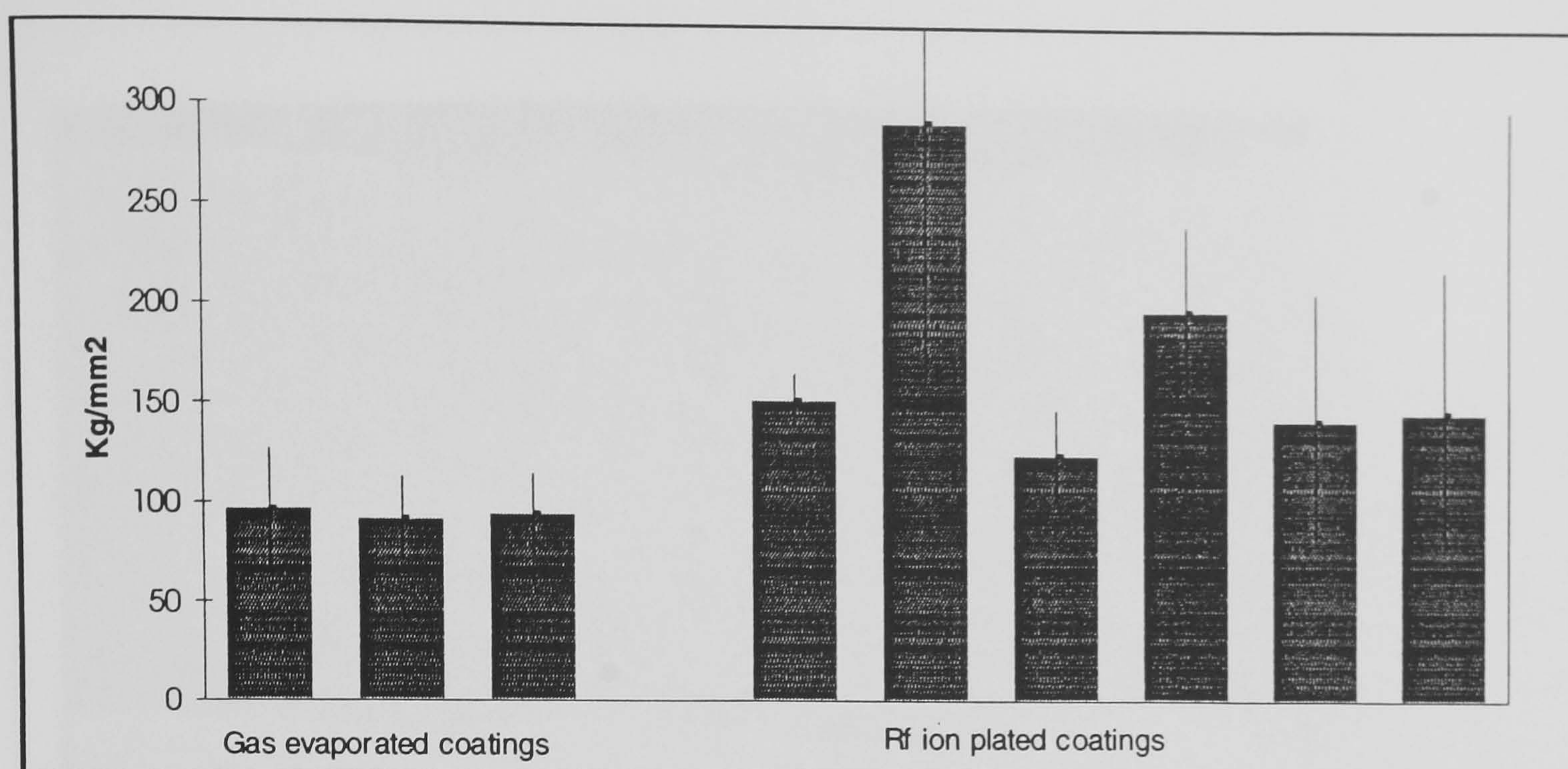


Figure 127: Influence of ion bombardment on the indentation resistance of EB-PVD YSZ deposited in the 500-650°C temperature range.

In spite of these non-ideal deposition conditions, it can be concluded from Figure 127 that plasma assistance enhances coating indentation resistance. To prove this point further, an experiment was conducted to deliberately produce a two layer coating system by initiating the deposition using RF ion plating followed by straight gas evaporation conditions after the self-extinguishment of the plasma. The processing conditions differed from those described above in three respects:

First, the experiment was carried out at a time late in the programme, when a very good control of the electron beam evaporation source had been acquired. The deposition was run with a constant electron beam current level and beam scan pattern, while the rod rotation was uninterrupted and the ingot feeding operational.

Second, the cathode area was less than that previously used (100cm² as opposed to 800cm²) which resulted in a greater power density of ion bombardment, as discussed in the previous chapter, and a greater starting substrate temperature.

Third, the deposition was carried out in the enclosure of the chamber furnace. Although the latter was not powered, it had the consequence of limiting the radiative heat loss, thus significantly raising the deposition temperature over that for the previous situation where radiation from the source was lost to the water-cooled chamber walls. The chamber temperature monitored by a floating thermocouple increased up to 700°C.

Figure 128 is a back-scattered electron micrograph of the coating cross-section obtained from this deposition run.

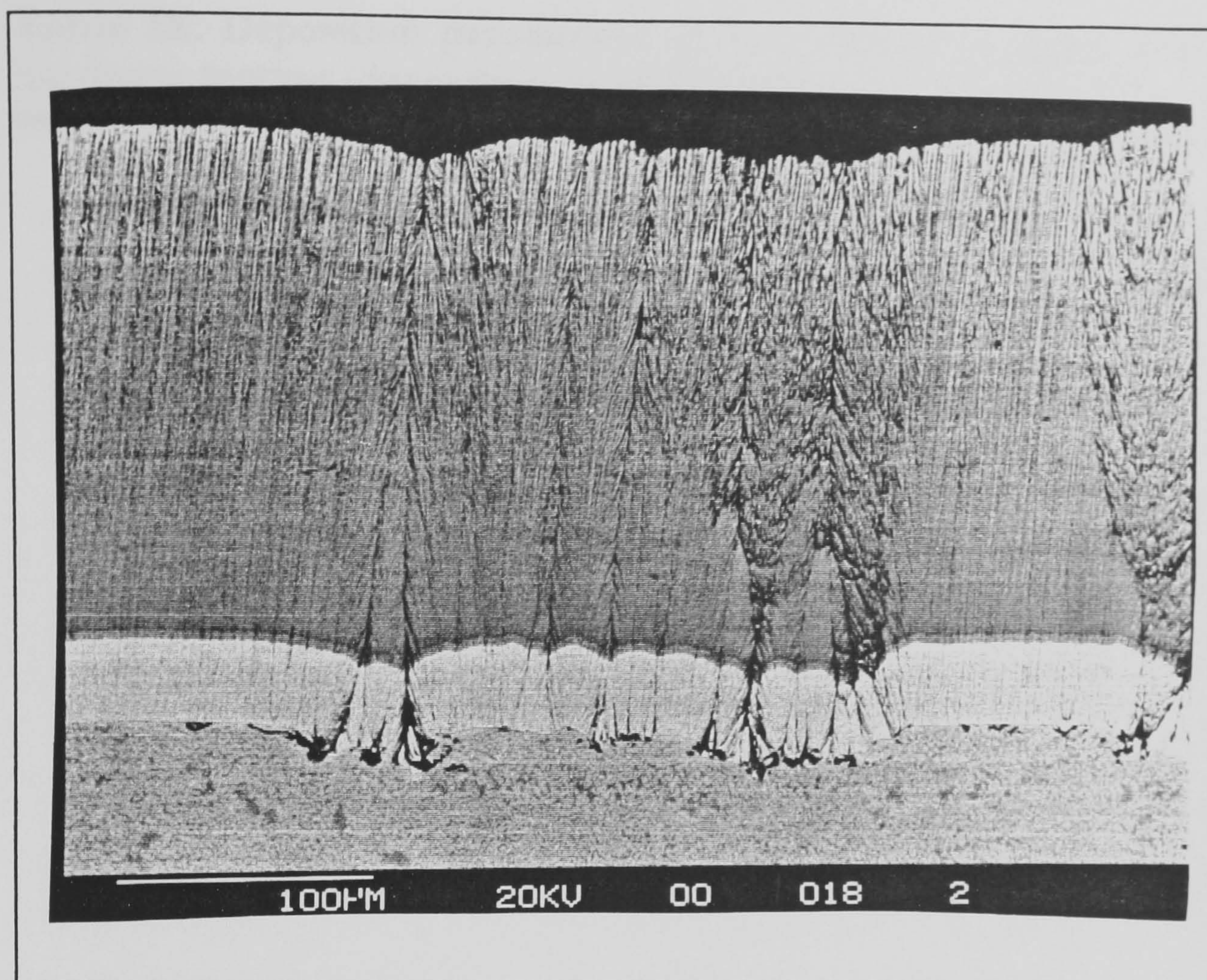


Figure 128: Cross-section of coating initially ion plated then straight gas evaporated showing the effect of interrupting ion bombardment.

Microhardness testing of the section using a 100g load yielded indentation resistance data of $460 \pm 50 \text{ Kg/mm}^2$ and $170 \pm 20 \text{ Kg/mm}^2$ for the ion plated (lighter) and gas evaporated (darker) layers respectively. These figures illustrate the extent to which indentation resistance can be increased using ion plating.

8.1.7.3 Influence of high temperature DC ion plating

The effect of DC ion plating on the coating surface indentation resistance was investigated on a sample of three gas evaporated and five DC ion plated coatings. These systems were deposited in a similar narrow temperature range using the vacuum furnace. The coating runs were carried out with the bleed of 90%O₂/Ar inside the furnace and the operation of a shutter, so that deposition started under stabilised melt conditions.

The designation and deposition details of the eight specimens evaluated are listed in Table IX. The temperature increased from the time the shutter opened due to the added heat flux from the source. The temperatures quoted in Table IX correspond respectively to that at the time the shutter opened and that at equilibrium.

Table IX: Deposition parameters of development coatings evaluated using hardness testing (deposition in 90%O₂/Ar).

Desig.	Time (min)	I(mA) at 1000°C	Bias (kV)	T(°C)	Gun%	thick (µm)
3/302	15	30	2.5	943-980	46	50
AG	10	45	3	966-997	43	60
AH	10	22.5	1.75	960-997	48	45
AJ	10	37.5	3	960-994	44	40
AN	60	22.5	2.5	967-982	42	200
Z	60	0	0	960-998	46	200
3/300	20	0	0	960-996	64	80
AO	60	0	0	960-978	42	200

The surface indentation resistance of the systems in Table IX is presented in Figure 129.

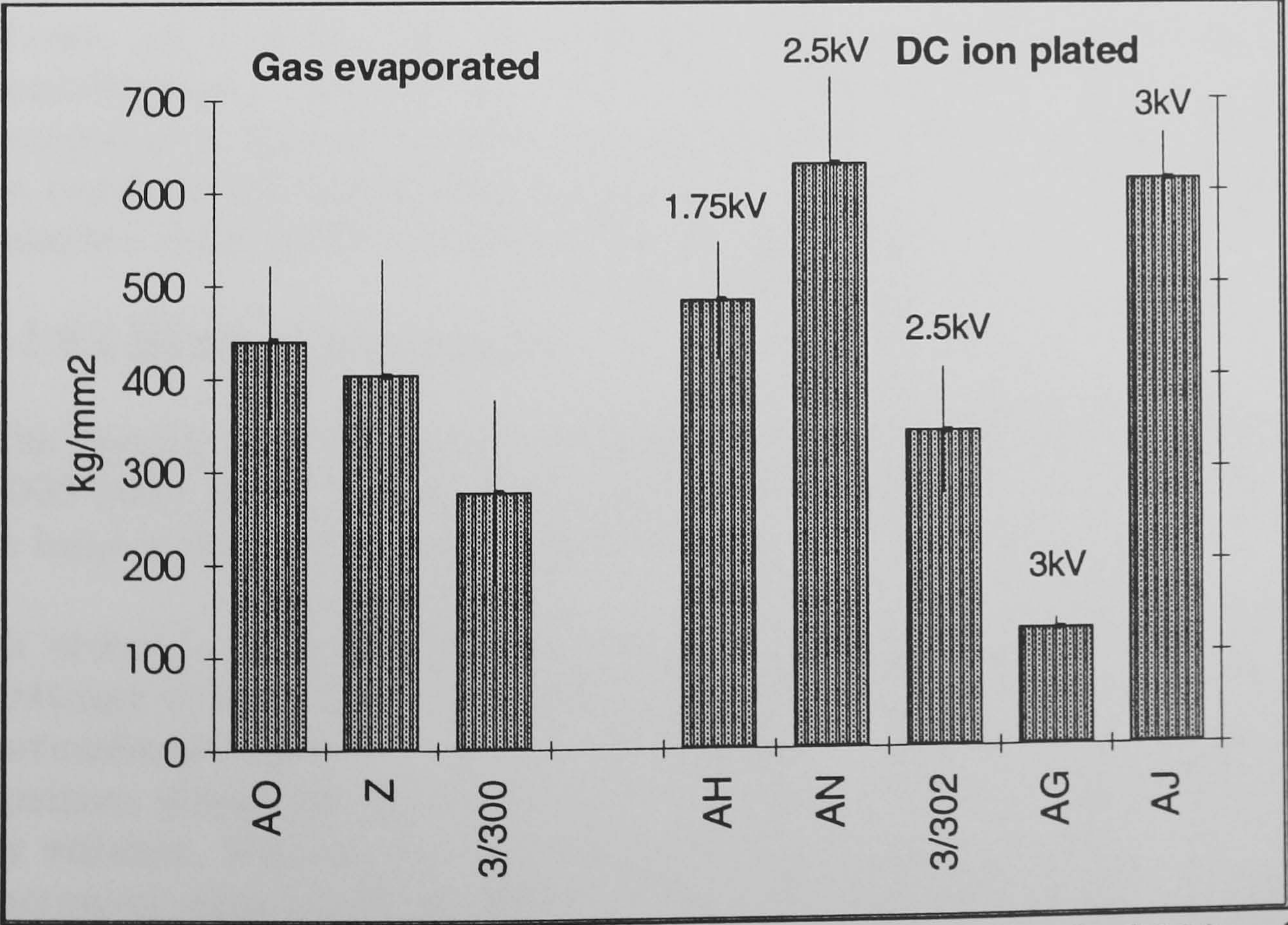


Figure 129: Surface indentation resistance for a load of 300g of gas evaporated and DC ion plated systems in Table IX.

The effect of DC ion plating on the indentation resistance of the deposit does not appear to be as marked as that obtained with RF ion plating, as seen in Figure 127 and Figure 124. There could be two possible reasons to account for this difference. The first one is that greater ion current densities were achieved in the RF ion plating runs than in the DC ion plating runs. This argument cannot be conclusively defended given the uncertainties in derivating the ion current densities in chapter 7. The second argument is that, with DC ion plating, the bombarding gas ions and neutrals consisted mainly of oxygen species as opposed to argon species in the RF ion plating runs. This aspect will be discussed further, later in the text.

The other striking feature of Figure 129, is that the indentation resistance of the gas evaporated deposits is much higher than that exhibited by the system gas evaporated on the 'dog-bone' substrate in Figure 124. The two major differences in the deposition conditions are the composition of the working gas, i.e. oxygen as opposed to argon, and possibly a lower gas density in the furnace environment than that surrounding the 'dog-bone' substrate. This follows from the considerations in chapter 7. How such differences in deposition conditions could be accountable for this difference in indentation resistance will be discussed in chapter 10.

8.1.8 Density

8.1.8.1 Effect of ion plating

The abrupt image contrast between the gas evaporated and ion plated layers shown in Figure 128 is evidence that ion plating results in coating densification, considering that these layers have the same elemental composition. However the densification undergone using ion plating could not be conclusively quantified and is believed to be less than the experimental relative error (15%) in determining these densities.

8.1.8.2 Effect of temperature

The density of the coatings deposited at about 300°C was found to be in the 2000-3000 Kg/m³ range. Coatings deposited at 1000°C were found, as RT33, to have a density of about 5000 Kg/m³.

In order to investigate this matter further, the thickness of some of the coatings deposited on the temperature graded-substrates ('dog-bones') was normalised relatively to the thickness at 1000°C and plotted against the position along the dog-bone main axis (see Figure 130). It can be seen that, by enlarge, the coating thickness decreases as the deposition temperature increases (the initial increase at the low temperature end is attributable to vapour flux shadowing from the copper clamps). Considering that the hottest point of the substrate (center of the dog-bone) was sitting closest to the evaporation source during the deposition, this decrease in thickness with

temperature cannot be explained on the basis of a non-uniform distribution in coating flux.

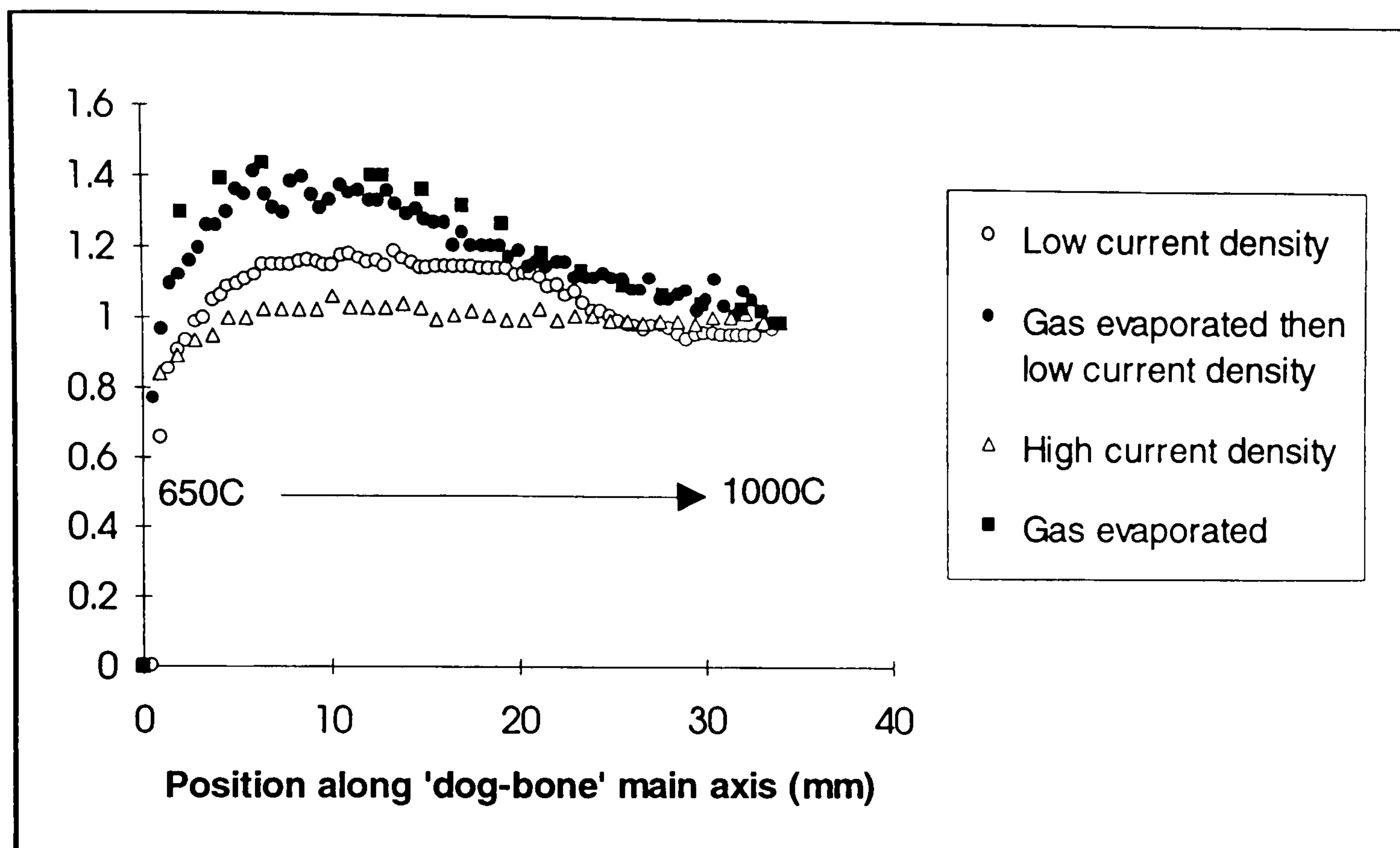


Figure 130: Dependence of coating thickness on deposition temperature (the variation in the low temperature bound is due to vapour flux shadowing from the copper clamps).

Raghuram&Bunshah¹⁵⁴, in their work on Activated Reactive Evaporation of TiC coatings, also observed a decrease in thickness with deposition temperature by some 25%, over the same temperature range as above. They interpreted this result as a decrease in deposition rate with substrate temperature. The argument proposed to account for this phenomenon was that the net condensation rate decreased with increased substrate temperature as a result of a greater desorbing rate of the adatoms. They still qualified as 'debatable' the application of this model to strongly bonded TiC coatings. The relevance of this argument to the present case cannot be ruled out. However, considering that the density of the evaporated deposits was estimated at 3000 and 5000 Kg/m³ for deposition temperatures in the 500-650°C range and 1000°C respectively, such variations in thickness can be more realistically explained in terms of coating density increasing with deposition temperature.

8.2 DISCUSSION

8.2.1 The effect of deposition conditions on phase composition:

8.2.1.1 Cubic or tetragonal?

In this work, the coatings deposited in 90%O₂/10%Ar environment were found, as RT33, to be single phase tetragonal. This concurs with recent publications^{82,83} but is in apparent disagreement with the conclusions from earlier investigations^{138,38}. Unal¹³⁸ reported that commercial EB-PVD TBC's made from 8wt%Y₂O₃-ZrO₂ ingots consisted of the cubic structure. According to Lelait et al⁸³, the latter conclusion was erroneous and was attributable to the experimental difficulty in resolving the coating tetragonality due to a texture with the 'c' direction being parallel to the coating plane. Concerning the work of Fancey and Matthews³⁸, the case is different in that the coatings were deposited at low temperature (400°C). In the present work, it has not been possible to categorically conclude that the coatings deposited at low temperature had the tetragonal structure since the peak doublets could not be resolved as a result of peak broadening. Upon annealing however, the diffraction lines could be narrowed to the point where the peak doublets became apparent (see Figure 131).

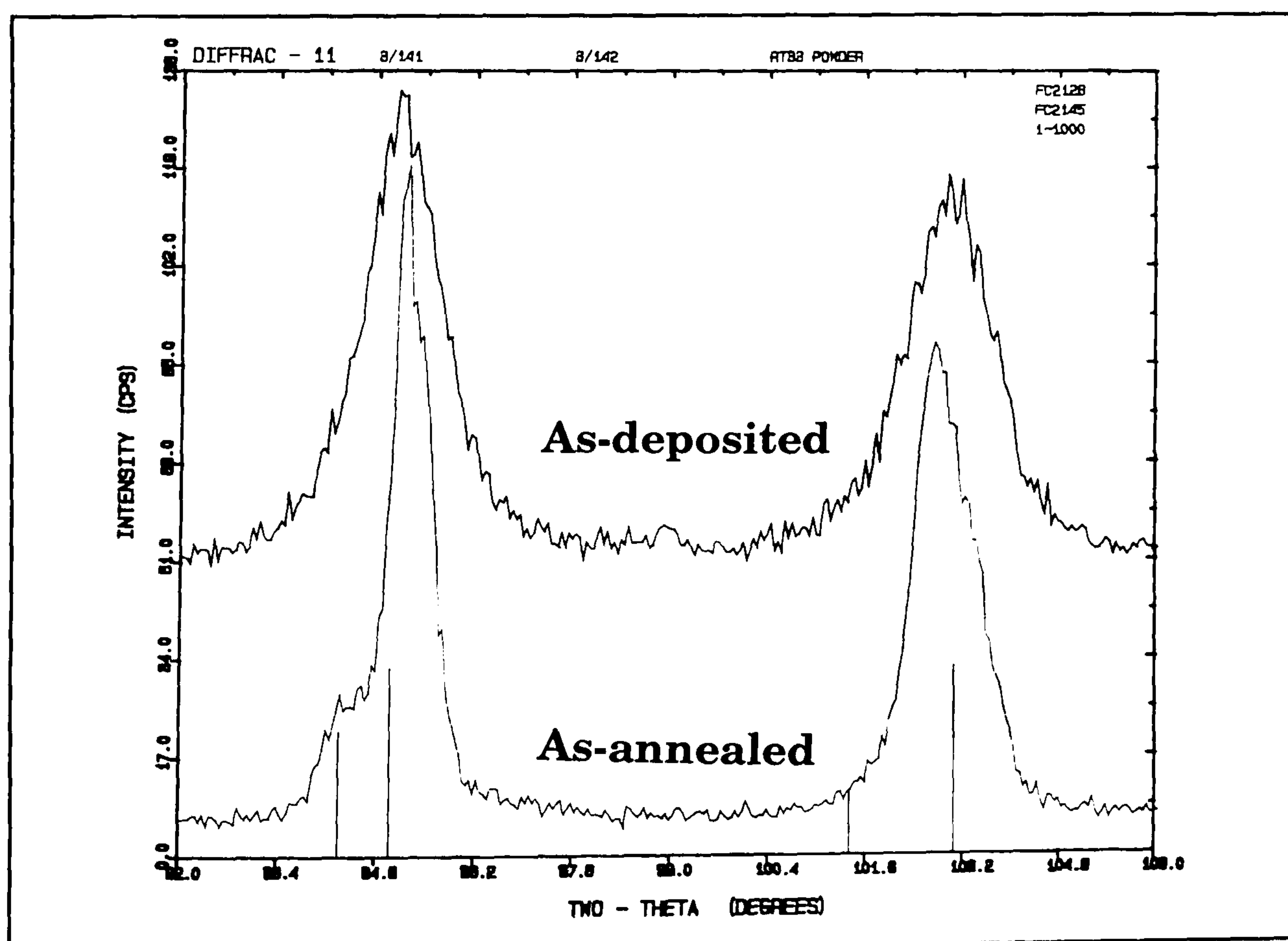


Figure 131: Effect of annealing at temperatures up to 1100°C on the X-ray diffraction pattern.

This does not necessarily mean that the coatings were tetragonal in the as-deposited state since one could argue that the cubic phase might form during deposition and transform into the tetragonal phase during subsequent

annealing. The $c \rightarrow t'$ transformation is diffusionless, reversible¹³⁹ and may be inhibited for grains under a critical nucleation size¹⁴⁰. In this work, the crystallite size of the low temperature deposits (300-400°C) was estimated to be less than 10nm and to increase up to 100nm for annealing temperatures of 1100°C. Therefore, a critical nucleation size in the 10 to 100 nm range could be evoked as an argument to claim that low temperature deposited TBC's do have the cubic structure as-deposited. The present study does not therefore conflict with the conclusions of Fancey and Matthews.

8.2.1.2 On the tetragonal phase

The sharper diffraction peaks, characteristic of the coatings deposited at moderate and high temperature, unequivocally corresponded to those of the tetragonal structure. There exist two sorts of tetragonal phases in the Yttria-Zirconia system that are namely the non-transformable tetragonal phase (t') and the equilibrium tetragonal phase (t) (see chapter 3 on zirconia). These two phases are distinct in that the (t') phase results from the diffusionless transformation of the cubic phase upon rapid cooling and thus contains a higher yttrium content than the equilibrium tetragonal phase. As a consequence, the (t') phase is stable at room temperature, hence its qualification as 'non-transformable tetragonal'. After Scott's diagram (see chapter 3 on zirconia, page 39), the 'non transformable' tetragonal phase may form for yttria concentrations in the range 5 to 12 mol%YO_{1.5}. Considering that the coating composition was found to be the same as that of the ingot using EDS analytical techniques and that the latter contained nominally 8.7mol%YO_{1.5} (8wt%Y₂O₃), the occurrence of the (t') phase would not disagree with the phase diagram after Scott. It would however be premature to conclude that the tetragonal phase of the deposits is of the non-transformable type (t') on the basis that it is stable at room temperature. Given that the critical grain size below which the martensitic transformation is inhibited lies in the 0.1-1µm range (see chapter on zirconia) and that the crystallite size of the deposits was estimated to be less than 10nm to well under a micron, the equilibrium tetragonal phase could be retained at room temperature by virtue of its small grain size.

Whether this tetragonal phase is of the equilibrium or the non-transformable type depends on the ability of cations to migrate. It is generally accepted that equilibrium phases in the YSZ system can only be obtained at temperatures greater than 1200°C, as below this temperature cation diffusion is too slow⁴⁹. With an uppermost deposition temperature of 1100°C, the condensing zirconia vapour is in effect rapidly cooled to a temperature where the equilibrium tetragonal phase cannot be obtained via bulk diffusion. If there are no gradients nor time fluctuations in the vapour yttrium content during the deposition process, the condensate should build up with an homogeneous yttrium distribution (the author is unaware of publications reporting gradients or fluctuations of the yttrium concentration in the yttria-zirconia vapour produced by electron beam evaporation). At the deposition temperatures involved, the coating atoms have enough energy to organise

themselves into an ordered structure but still insufficient mobility for long range migration. Therefore the coating structure should be consistent with that of an homogeneously alloyed yttria-zirconia i.e. the 'non-transformable' tetragonal phase. The fact that the coating's lattice parameters are very close to those of the t' phase related by Scott in rapidly cooled YSZ supports the idea that the tetragonal phase identified is of the non-transformable type.

8.2.1.3 The formation of monoclinic

Coatings deposited in pure argon at substrate temperatures greater than 760°C were found to contain some monoclinic phase, the significance of which increased with deposition temperature (see Figure 102). The formation of monoclinic phase in EB-PVD TBC's had never been reported before. The absence of oxygen bleed during deposition would appear to be responsible for this behaviour given that coating manufacturers and research institutes⁴³ evaporate zirconia at a high oxygen partial pressure (5mTorr to 10mTorr) and do not report the occurrence of the monoclinic phase.

The strong dependence of monoclinic formation on the deposition temperature first pointed to a possible change in the coating yttrium composition with process temperature. Electron Probe Micro Analysis on the surface of a temperature-graded specimen did not show a change in the yttrium content with temperature over the range [650-1000°C]. It could still be argued that the volume of analysis sampled using EPMA was still too coarse to detect variations in the yttrium concentration from grain to grain which would be responsible for the transformation of low yttrium content crystallites. However, the fact that the tetragonal phase can be fully reestablished and be stable at room temperature after a mere ageing in air at 700°C for 30 minutes, a heat treatment for which cation diffusion can be neglected, showed that the formation of monoclinic was not related to the coating yttrium distribution.

8.2.1.4 Its relation to oxygen deficiency

Both the effect of oxygen bleed during deposition and ageing in air post deposition would indicate that the formation of monoclinic is related to the coating deficiency in oxygen. How can this phase transformation be possible at such a low temperature and over such a short period of time?

First it must be considered that the tetragonal to monoclinic transformation is reversible, diffusionless and involves atomic displacement less than the inter-atomic distance. This transformation does not therefore rely on cation diffusion which would be precluded at 700°C. This temperature is however sufficient to allow oxygen diffusion in the bulk and this is demonstrated by the fact that zirconia is electrically conductive at 700°C due to anion transport (Figure 28). Therefore, upon heating at 700°C, the as-received monoclinic phase should convert into the tetragonal phase (the t $\rightarrow$ m

transformation temperature being about 570°C for 8wt%Y₂O₃ concentrations) as the ambient oxygen diffuses into the coating. Once the oxygen depletion is eliminated, the tetragonal phase is retained upon cooling down to room temperature.

From the above, it would appear possible that oxygen depletion be at the origin of the destabilisation of the so called 'non-transformable' (t') phase. This is somewhat of a paradox considering that this is the defect structure (oxygen vacancies) resulting from the addition of solute ions with a lower valence which is responsible for inhibiting the transformation into monoclinic of zirconia based ceramics. Why then should added oxygen vacancies destabilise the tetragonal phase? First, it should be realised that the mechanisms of stabilisation by oxide alloying are still not well understood⁴⁴. A qualitative assessment will be given here as a substitute to an absolute explanation of this paradox.

There is a fundamental difference between the oxygen vacancies introduced by Y₂O₃ alloying and those due to the lack of oxygen bleed. The difference is now that for each oxygen vacancy formed, two Zr⁴⁺ cations will be replaced by two Zr³⁺ in order to compensate for the negative charge deficiency. Therefore, the more oxygen vacancies are formed during the deposition process and the more cations with lower positive charge the ceramic contains. As a result, the ionic bonds are weakened¹⁴¹ and this would favour the formation of a less closely packed structure such as the monoclinic.

8.2.1.5 Its dependence on deposition temperature

Given that the formation of monoclinic phase is related to the presence of oxygen vacancies, the question must be addressed as to whether the temperature dependence seen in Figure 102 can be explained in terms of oxygen deficiency increasing with deposition temperature. The oxygen content of the coating surface was analysed using X-Ray Photon Spectroscopy (XPS) and was not found to vary over the deposition temperature range [650-1000°C]. It could be argued that the amount of oxygen vacancies necessary to trigger the transformation into monoclinic is less than the sensitivity of the analysis, and that the latter cannot measure subtle changes with deposition temperature. Qualitatively however it is debatable as to why oxygen depletion should increase with temperature in the range up to 1000°C considering that the oxidation of free zirconium is thermally activated and that the decomposition of zirconia takes place at much more elevated temperatures.

There is however a much stronger argument to account for the dependence of monoclinic phase formation on deposition temperature. This involves the coating crystallite size. It is well documented that for zirconia ceramics there exists a critical crystallite size, function of composition and stress, below which the tetragonal-to-monoclinic transformation is inhibited. Many authors have reported a critical nucleation size in the 0.1 to 1 µm range. In this work, the crystallite size was found to increase strongly with deposition

temperature (see Figure 109) from 10nm at the lower temperature end to over 200nm at the highest temperature investigated. It is therefore believed that as the deposition temperature is increased, the fraction of crystallites with a size greater than that required to undergo the (t)-->(m) transformation increases. The coatings deposited at low and moderate temperature (<600°C) do not undergo the (t)-->(m) transformation due to their small grain size, no matter their oxygen deficiency.

8.2.1.6 Its dependence on coating depth

The content of monoclinic phase was found to be greater nearer the interface with the bond coat. In the light of the above, this could be interpreted as a more significant oxygen depletion and/or a greater crystallite size nearer the interface. It is debatable as to why the coating should build up with a greater oxygen deficiency during the early stages of growth. It has been found that the oxygen content in the vapour of zirconia produced by electron beam evaporation decreased steadily with time¹⁴².

Another potential reason may be that the affinity of aluminium with oxygen is higher than that of zirconium. In fact, Lelait et al came to this conclusion from their work on the oxidation of APS TBC's that the thermally grown alumina scale reduced to some extent the adjacent YPSZ¹⁴³. Therefore, given a limited reservoir of oxygen in the ceramic and its environment, while the deposition proceeds at temperatures near 1000°C the oxygen in the ceramic will diffuse towards the bond coat through the zirconia to preferentially oxidise bond coat aluminium to an alumina scale. This mechanism could be responsible for a greater oxygen depletion near the interface with the bond coat.

Matrix constraint within the ceramic may also be evoked to account for the dependence of monoclinic formation on coating depth. The columns in the high temperature deposits are finer nearer the interface with the bond coat and are separated by voids running normal to the coating plane (see 8.1.6.1). Therefore, the matrix constraint exerted on the crystallites making up the columns may therefore be expected to decrease with increasing depth into the coating and thus preferentially ease the dilation into the monoclinic phase of the crystallites nearer the bond coat.

8.2.2 The effect of deposition conditions on texture

Two deposition parameters were identified as influential to the crystallographic texture of the deposits in this work. These are the deposition temperature and oxygen bleed (see results section).

The coatings deposited at low temperature (<500°C) exhibited a random texture. In the modelling of film growth at low temperature, a sticking coefficient of one is generally assumed, which means that every impinging atom sticks where it lands¹⁴⁴. In other words, the probability of a vapour atom

to condense is unity whatever the crystal plane on which it impinges. This absence of anisotropy in condensation rate at low temperature (no dependence on crystal orientation) naturally limits the scope for the development of a preferred crystallographic orientation during coating growth. This could account for the absence of crystallographic texture in the low temperature deposits.

As the substrate temperature is raised, the crystallites are found to grow with the $\langle 111 \rangle$ preferred orientation, that is with the most densely populated planes parallel to the coating plane. This result is consistent with what would be expected from a film forming at low T/T_m (<0.3) (see chapter 4). The same texture however is found to persist at temperatures greater than 1000°C ($T/T_m > 0.43$). This contrasts with the shift from the (111) texture to the (110) and (100) textures observed respectively by Cléry⁹⁴ and Stamper⁹⁸ in sputtered YSZ. Their deposits were however processed in a mixed oxygen/argon environment (20%O₂/Ar). In this work, it was found that the introduction of oxygen bleed to a pressure of about 10^{-2} Torr at elevated deposition temperatures was effective to switch the crystallographic texture from the $\langle 111 \rangle$ orientation to most often a (100) or (001) texture. This effect was observed even when the coating deposition was initiated in pure argon, which suggests that the sudden introduction of oxygen bleed can disrupt the coating growth habit *in vivo*. For a coating to grow with the $\langle 100 \rangle$ or $\langle 001 \rangle$ orientations, planes such as the (400) or the (004) that are purely and the most densely composed of oxygen atoms, must form parallel to the coating plane (see Figure 132). The orientation of such planes towards the main growth direction may only be allowed with the provision of a sufficient impingement rate of oxygen atoms. Under oxygen deficient conditions, the formation of the (100) and (001) textures are potentially discouraged. This could explain the persistence at elevated temperature of the (111) texture in the deposits evaporated in pure argon.

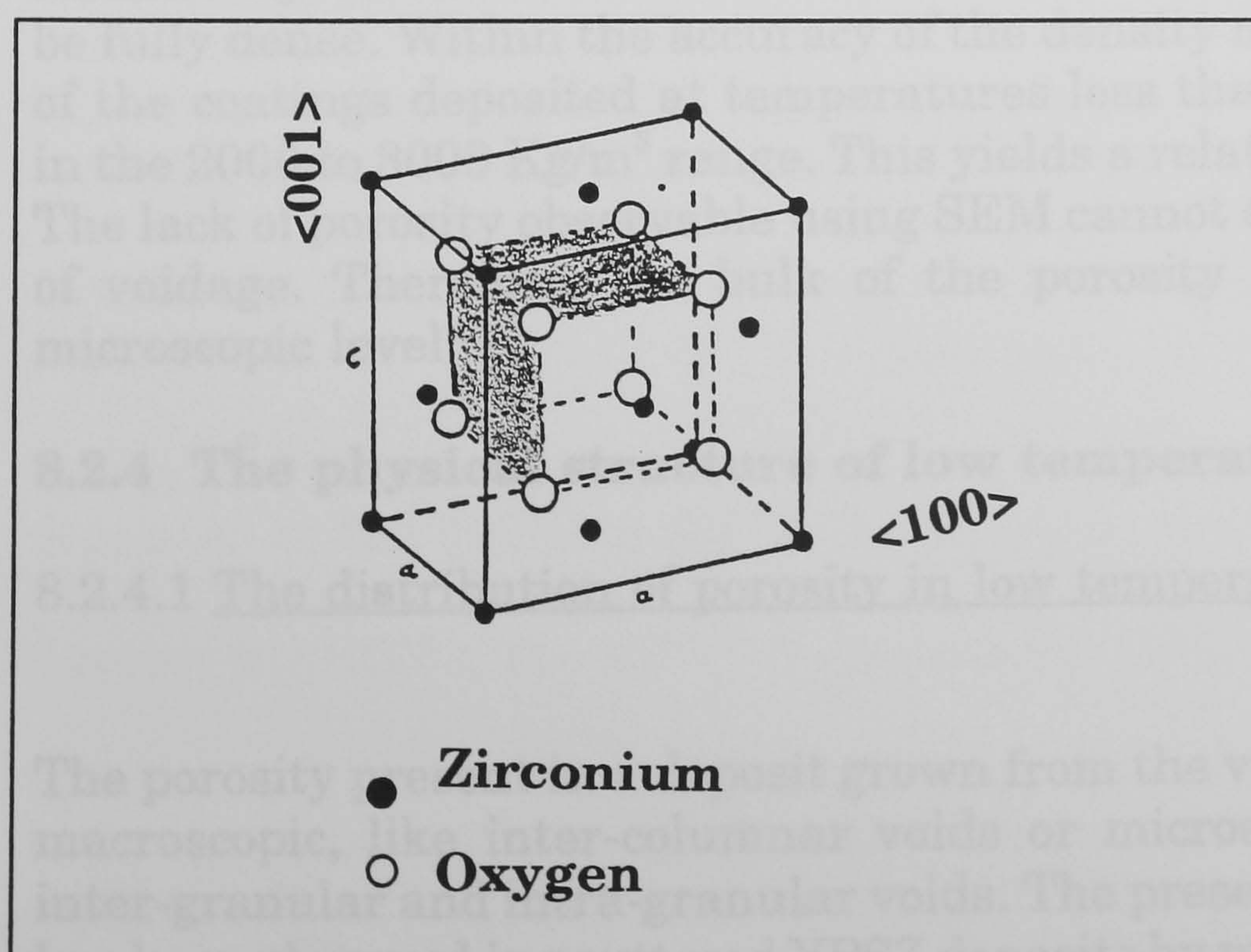


Figure 132: Examples of oxygen planes in the zirconia tetragonal structure and their relation with crystal orientation.

8.2.3 Stress in EB-PVD TBC's

If the ceramic coating was subjected to a macrostress, then the lattice parameters would be expected to change after removing the constraint from the underlying substrate⁹⁷. In this work, the lattice parameters of the datum coating RT33 were found to be the same as that of the powdered RT33 coating obtained after dissolving the substrate away. This implies that the former was virtually free of stress in its as-deposited state. The fact that the coating cell dimensions exactly match those of bulk YPSZ predicted from Scott's formula is another evidence of the absence of stress in the commercial coating. This result is somewhat surprising considering that upon cooling down from 1000°C to room temperature, the ceramic must undergo a thermal expansion mismatch strain of 0.5% imposed by the substrate (assuming $\alpha_{\text{sub}}=15 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ and $\alpha_{\text{coat}}=10 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$). This can only be explained in terms of a low column packing density of the high temperature deposited coatings, the thermal strain being accommodated by bringing the columns closer together without straining the columns themselves.

In this work, the coatings deposited at temperatures greater than 850°C exhibited very well pronounced inter-columnar voidage. Therefore, the argument of low column packing density to account for the absence of macrostress (no peak shift as seen in Figure 106, Figure 103, Figure 104 and Figure 108) can be applied to all the high temperature deposited coatings. In contrast, the low temperature deposits revealed no obvious intercolumnar voidage (see for example Figure 116 and Figure 126). These coatings deposited at temperatures as high as 600°C still must undergo a considerable thermal strain of about 0.3% upon cooling down to room temperature. No peak shift was observed in spite of their dense morphology, apparently amenable to support thermal stresses. Given the absence of intercolumnar voidage, the columns themselves must now deform by 0.3% while leaving the ceramic crystals unstrained. This statement implies that the columns cannot be fully dense. Within the accuracy of the density measurements, the density of the coatings deposited at temperatures less than 600°C were found to lie in the 2000 to 3000 Kg/m³ range. This yields a relative density less than 50%! The lack of porosity observable using SEM cannot account for this magnitude of voidage. Therefore, the bulk of the porosity must be distributed at a microscopic level.

8.2.4 The physical structure of low temperature EB-PVD TBC's

8.2.4.1 The distribution of porosity in low temperature deposited coatings.

The porosity present in a deposit grown from the vapour phase may be either macroscopic, like inter-columnar voids or microscopic, encompassing both inter-granular and intra-granular voids. The presence of inter-granular voids has been observed in sputtered YPSZ deposits by previous investigators using TEM techniques⁸¹. The kinetic energy of the arriving species in the EB-PVD

process is much less than in sputtering. In the absence of thermal agitation, the formation of voids should be even more significant in the EB-PVD process. The presence of inter-granular voids in EB-PVD TBC's processed at temperatures up to 600°C appears therefore unavoidable. Possible intra-granular voids that have been proposed consist either of vacancies, clusters of vacancies or dislocation loops. These atomistic structural defects voiding the lattice would, if present, inevitably lead to XRD peak broadening.

Experimentally, a considerable lattice strain of 0.3% (see Figure 109) was found in the coatings deposited both at 300-400°C and 600°C. Rigorously, this strain may either consist of type II (lattice defects) or type III (lattice distortion due to interaction with neighbouring grains) or combination of the two. Type III lattice strain is generally associated with the existence of a macrostress⁹⁷. In the light of the above, a type III contribution to the total lattice microstrain is highly unlikely. Therefore, the measured 0.3% lattice microstrain is believed to purely reflect the lattice defectiveness of the coating grains. This lattice defectiveness may encompass the voiding defects mentioned above and other stacking faults such as interstitials. Considering that these coatings were deposited under very low atomic mobility conditions, the modelling work after Muller and other investigators (see chapter 4) would suggest that the bulk of the lattice defects present in the coating crystallites consists of quenched-in single vacancies and/or clusters of vacancies.

8.2.4.2 Influence of porosity on thermal stability

The fine crystallite size, high voidage content and lattice defects characterising the low temperature deposits should impart these systems a high specific energy by virtue of a high grain boundary and free surface area. At elevated temperature, one might expect the structure of such deposits to evolve towards one of a lower energy state.

In order to investigate the thermal stability of EB-PVD thermal barrier coatings, heat treatments in air of the following specimens were undertaken:

Specimen 1: Gas evaporated YSZ on a plain grit blasted Nimonic 75 substrate deposited in the 300°C to 400°C temperature range.

Specimen 2: Gas evaporated YSZ on a pack aluminised Nimonic 75 substrate deposited in the 500°C to 650°C temperature range.

Specimen 3: RT33, the EB-PVD commercial TBC.

Specimens 1 and 2 were subjected to cumulative annealing treatments for 1 hour at temperatures of 700°C, 800°C, 900°C, 1000°C and 1100°C respectively. RT33 was heat treated at 1150°C for 50 hours. Structural parameters such as the morphology, grain size and microstrain were monitored as a function of annealing temperature.

SEM examination showed that the specimens 1 and 2 underwent 'mud-flat' cracking, the mud flat cracks coinciding with the intercolumnar boundaries. The inter-spacing between the ceramic blocks so formed was found to increase with annealing temperature (see Figure 137 and Figure 138). A reduction in the coating thickness was also recorded after completion of the annealing treatments. No such change in morphology was observed for RT33. It was found that the mean coating crystallite size and lattice microstrain in specimens 1 and 2 respectively increased and decreased with annealing temperature (see Figure 134, Figure 135 and Figure 136). This behaviour was in sharp contrast with that of RT33 for which no reduction in the XRD line width was obtained, as measured by the Full Width Half Maximum (see FWHM's in Table X).

Table X: Evolution of peak broadening in RT33 after annealing.

	As deposited	After 50 hours at 1150°C
FHWM of (111) reflection	0.143±0.130	0.186±0.136

If an increase in grain size and/or a reduction in lattice microstrain had occurred upon annealing, a reduction in the peak broadening would have been observed. Therefore, the coatings deposited at 1000°C appear unaffected by the above annealing treatments.

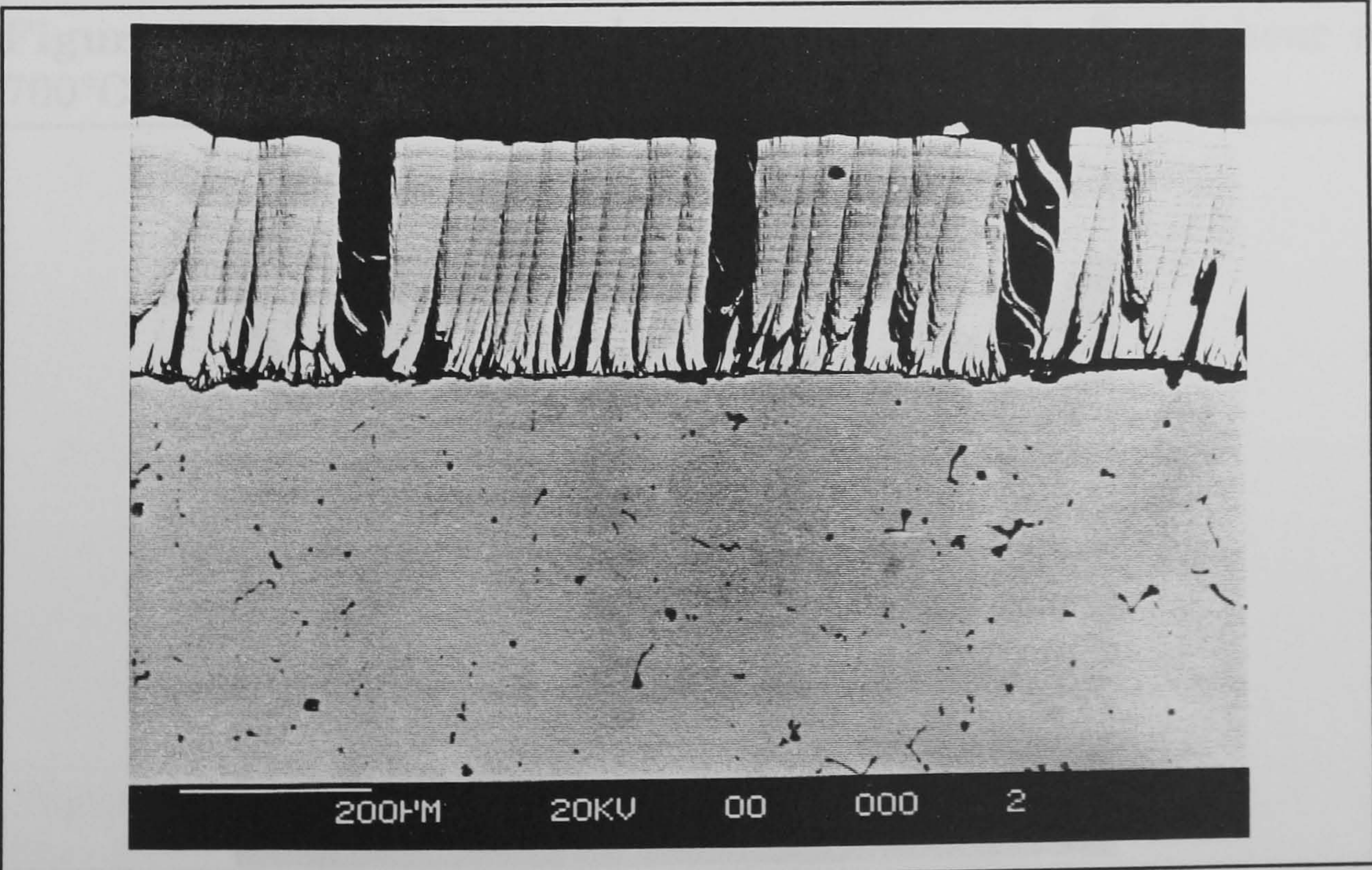


Figure 133: Typical cross-section of an as-annealed TBC deposited in the 500-650°C temperature range (mud-flat cracking).

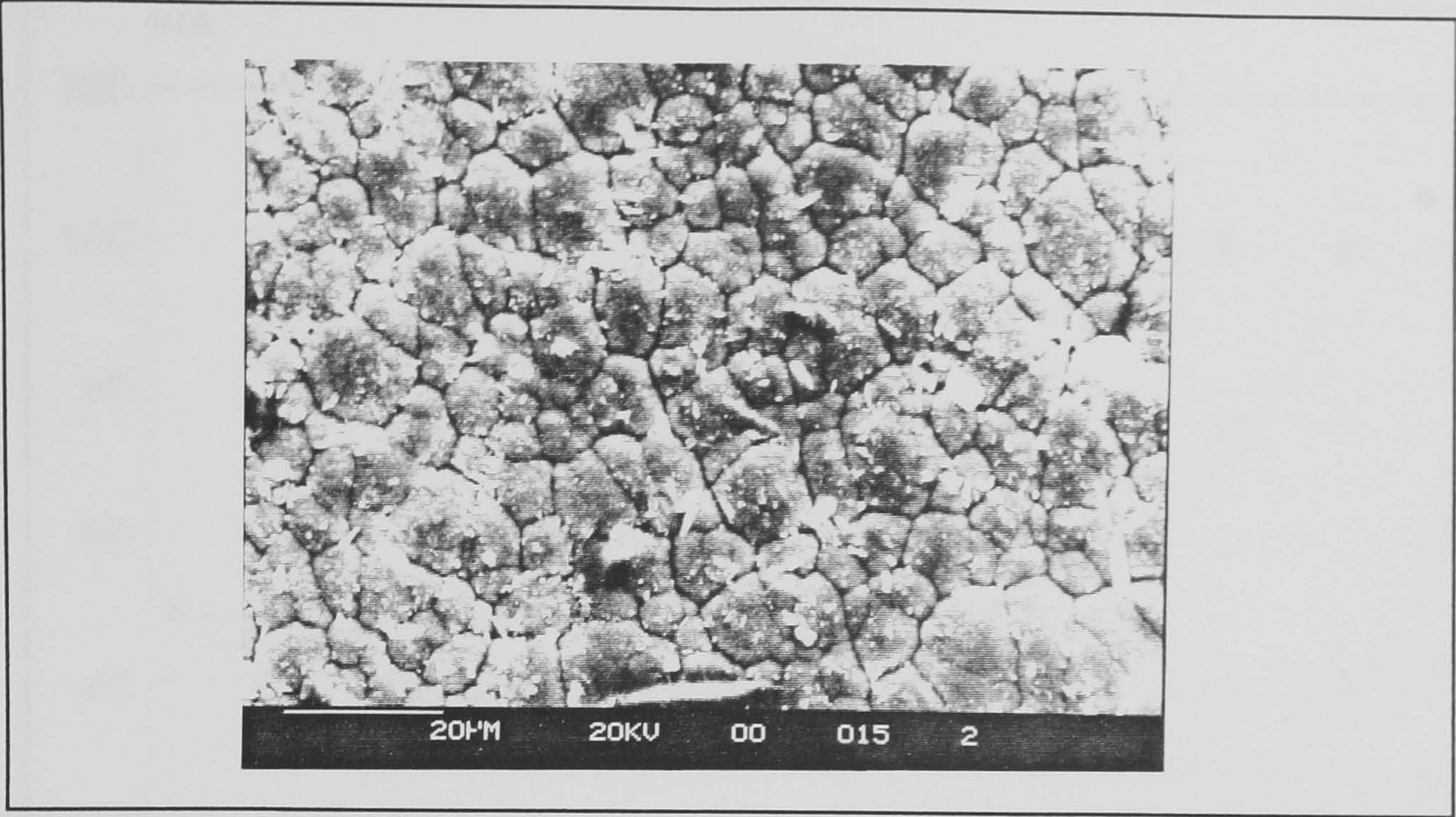


Figure 134: As-received surface topography of specimen 1

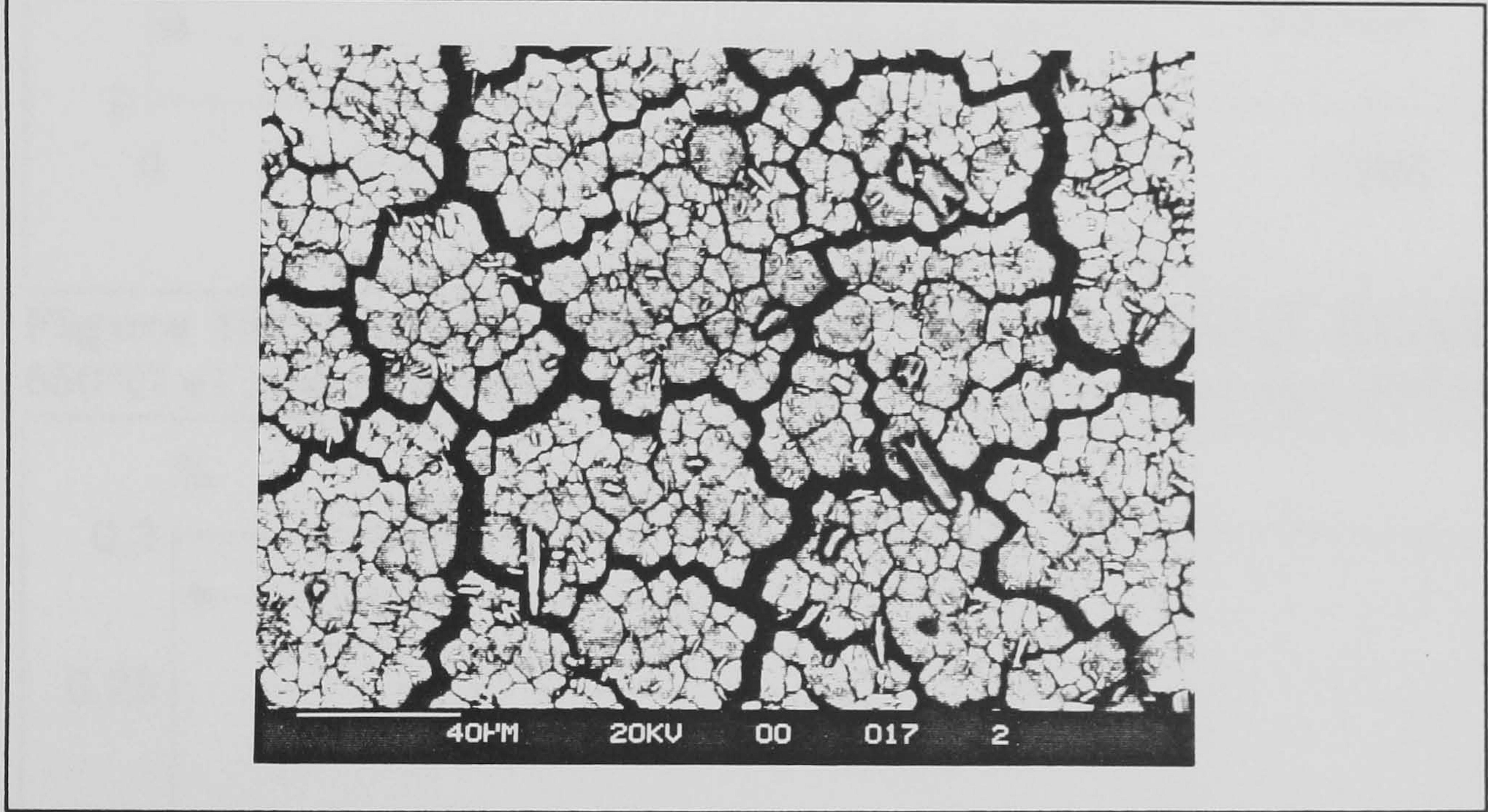


Figure 135: 'Mud flat' cracking in specimen 1 after 1 hour at 700°C

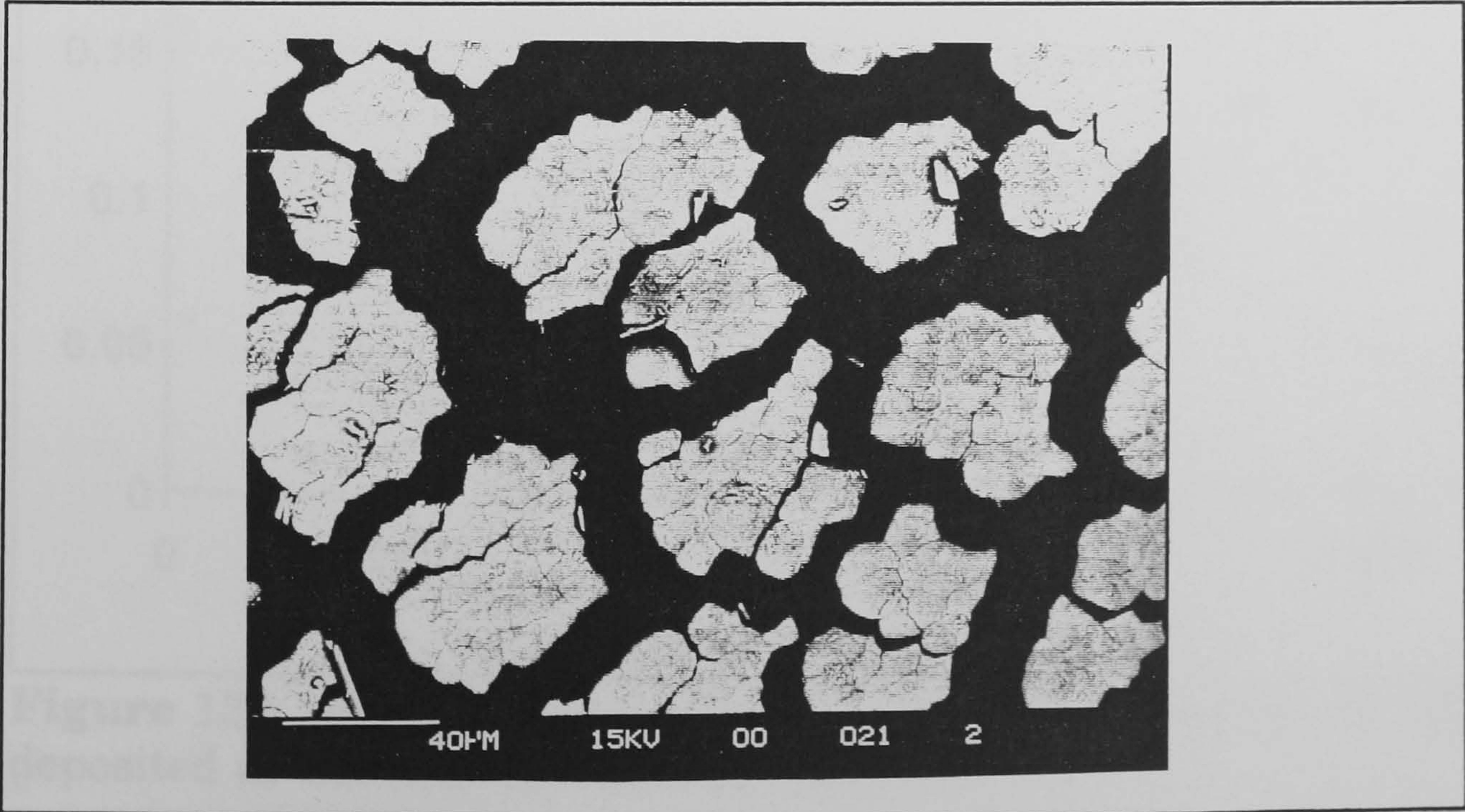


Figure 136: 'Mud flat' cracking in specimen 1 after completion of heat treatments

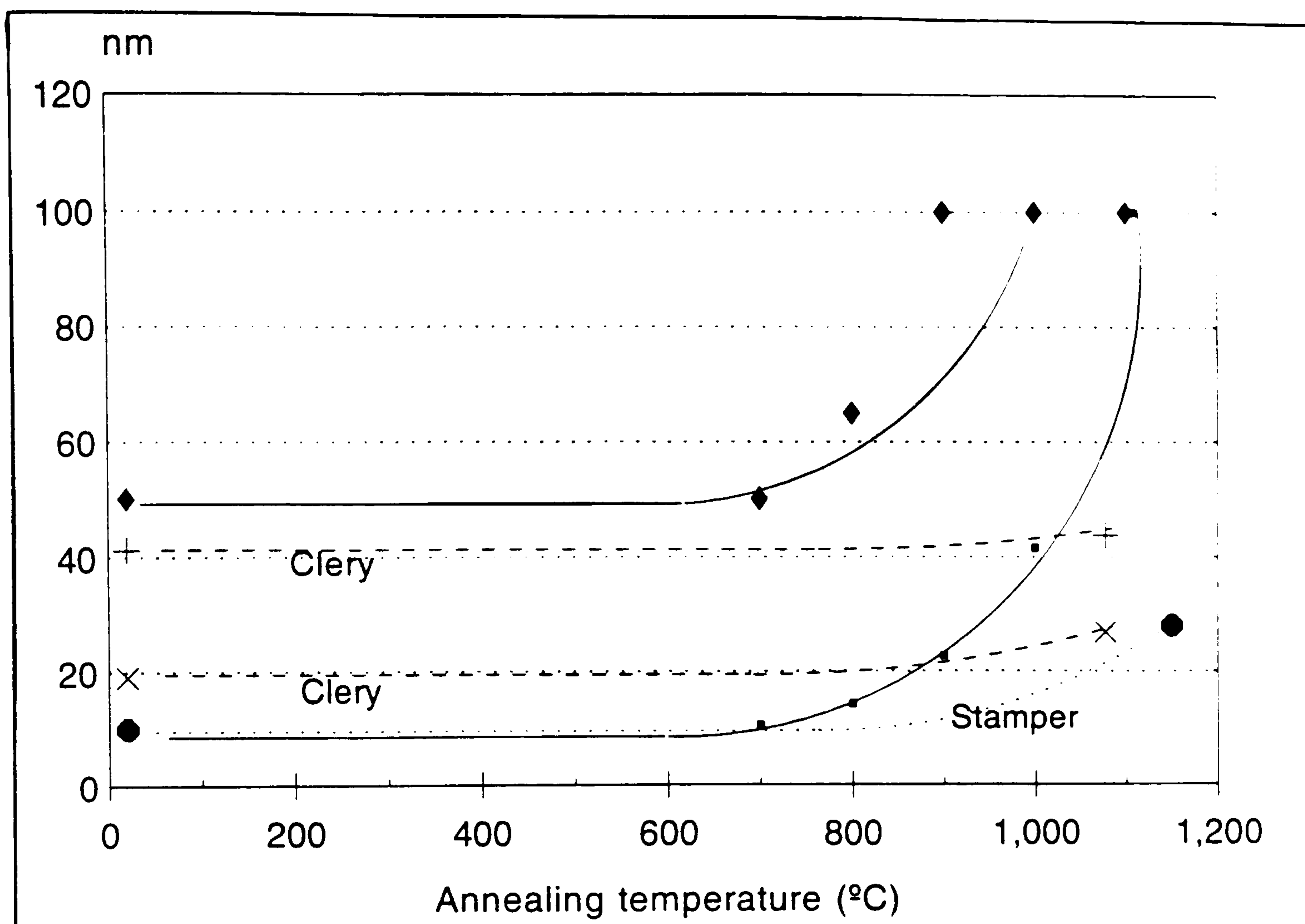


Figure 137: Grain growth in EB-PVD YSZ deposited at 300-400°C(■), 500-650°C(◆) and of sputtered YSZ at 550°C(x), 720°C(+) and 50°C(●).

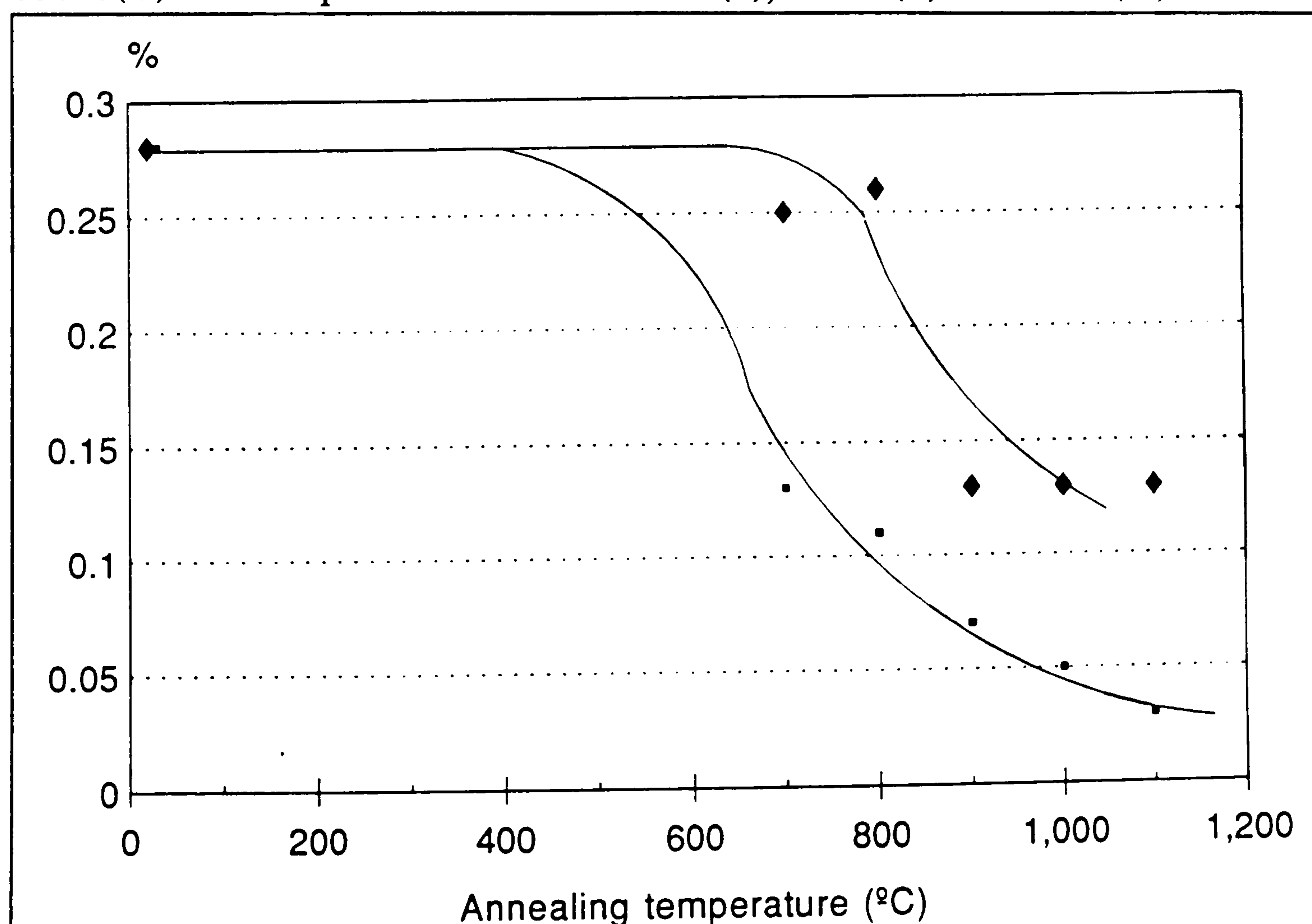


Figure 138: Effect of annealing on the lattice strain of EB-PVD YSZ deposited at 300-400°C(■) and 500-650°C(◆).

8.2.4.3 Grain growth

The increase in grain size upon annealing observed in the low temperature deposits is consistent with the work of previous investigators on sputtered YSZ (Cléry⁹⁴, Stamper et al⁹⁸ and Knoll&Bradley⁹³). It should be noted however that the grain growth achieved in sputtered YSZ after 18 hours at 1077°C (Cléry⁹⁴) or 20 hours at 1150°C (Stamper⁹⁸) was not as marked as that obtained in the low temperature EB-PVD YSZ after the 5 cumulative isochronous annealing treatments up to 1100°C (see Figure 137). In fact, little grain growth was observed in sputtered YSZ with an as-deposited grain size of 40nm (see Figure 137). Given that, in Cléry's work, a similar ceramic composition was investigated (7%wt Y₂O₃) and that the grain size was determined using identical XRD methods (Hall-Williamson plots), it would appear that this discrepancy in annealing behaviour is a genuine effect of the deposition process.

The driving force for grain growth was interpreted as the reduction in grain boundary surface area (Cléry⁹⁴). This driving force for a 40nm grain size in the sputtered deposits and for a 50nm size in the gas evaporated deposits would be expected to be similar. However, little grain growth occurred in the sputtered deposits whereas in the low temperature gas evaporated deposits, the grains were found to coarsen from 50nm to 100nm. This implies that the kinetics for mass transport are more favourable in the low temperature EB-PVD YSZ than in the sputtered YSZ. This result can be explained by considering the level of porosity in the deposits. The above sputtered YSZ films⁹⁴ had densities near that of bulk YPSZ (6000Kg/m³) whereas the low temperature gas evaporated deposits in the present work were found to contain 50 to 60% of microporosity. The coarsening of grains upon annealing requires that some crystallites grow at the expense of others. In bulk ceramics, grains grow via grain boundary migration i.e. the atoms jump from a shrinking grain across the boundary to an adjacent coarsening grain¹⁴⁵ (see Figure 139).

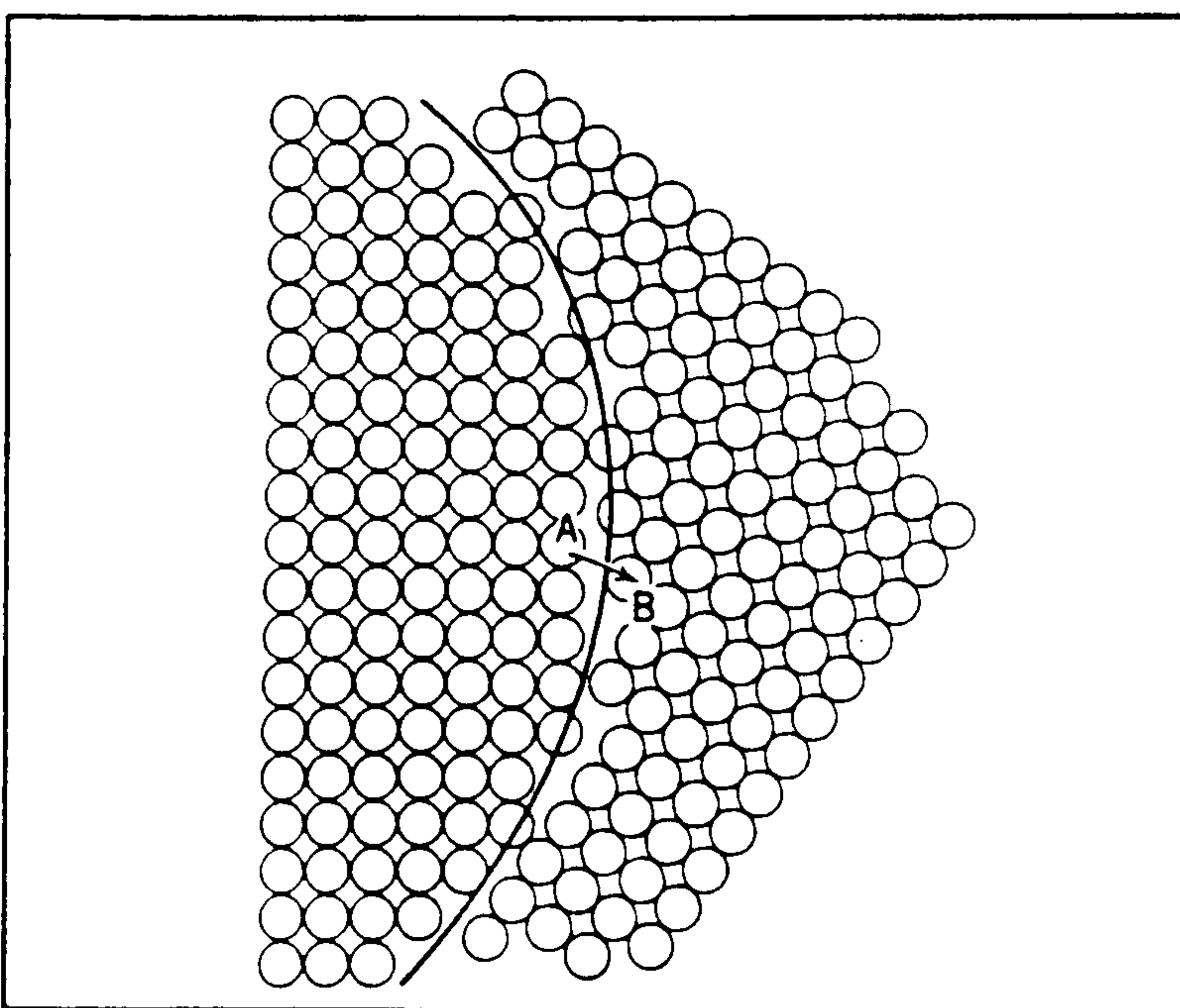


Figure 139: Atomic jump mechanism for grain boundary migration¹⁴⁵.

In the present situation, this mechanism is not believed to be the only mechanism and is not thought to be the most relevant considering that the grain boundaries are voided in the as-deposited state. It is more likely that a mass transport mechanism closer to surface diffusion will be the main contributor to the coalescence of crystallites. Only once the inter-crystallite porosity is evacuated in the later stages of sintering, may grain boundary migration as depicted in Figure 139 play a significant role in grain growth. Given that the activation energy for surface diffusion is less than that for grain boundary migration, grain coalescence in the porous gas evaporated deposits may take place to a much larger extent and at lower temperatures than in the dense sputtered YSZ.

In order to test the above hypotheses, the data obtained from the annealing of specimen 1 in Figure 137 was processed so as to highlight the thermal activated processes involved in grain coalescence. If it is assumed that the driving force for grain coalescence is the reduction in surface energy, the rate of grain growth should be inversely proportional to the grain size ¹⁴⁵, i.e.

$$\frac{dL}{dt} = \frac{D(T)}{L} \quad (76)$$

where L is the grain size, t is the time of annealing and D is the diffusivity at a temperature T .

By integrating equation (76), the increase in grain size from L_i to L_{i+1} resulting from the annealing for a time t at temperature T_i may be written:

$$L_{i+1}^2 - L_i^2 = 2D(T_i)t \quad (77)$$

Considering equation (77), the plot of $\ln(L_{i+1}^2 - L_i^2)$ versus the reciprocal temperature should yield the Arrhenius plot of the diffusion processes involved in grain coalescence. This plot is shown in Figure 140 with its associated tabulated data (Table XI) from Figure 137.

Table XI: Grain size data from isochronous anneal treatments.

Annealing temperature (T in K)	Grain size after 1 hour at T (L in Å)	$L_{i+1}^2-L_i^2$
As deposited	90	
973	105	2925
1073	143	9424
1173	227	31080
1273	415	120696
1373	1000	827775

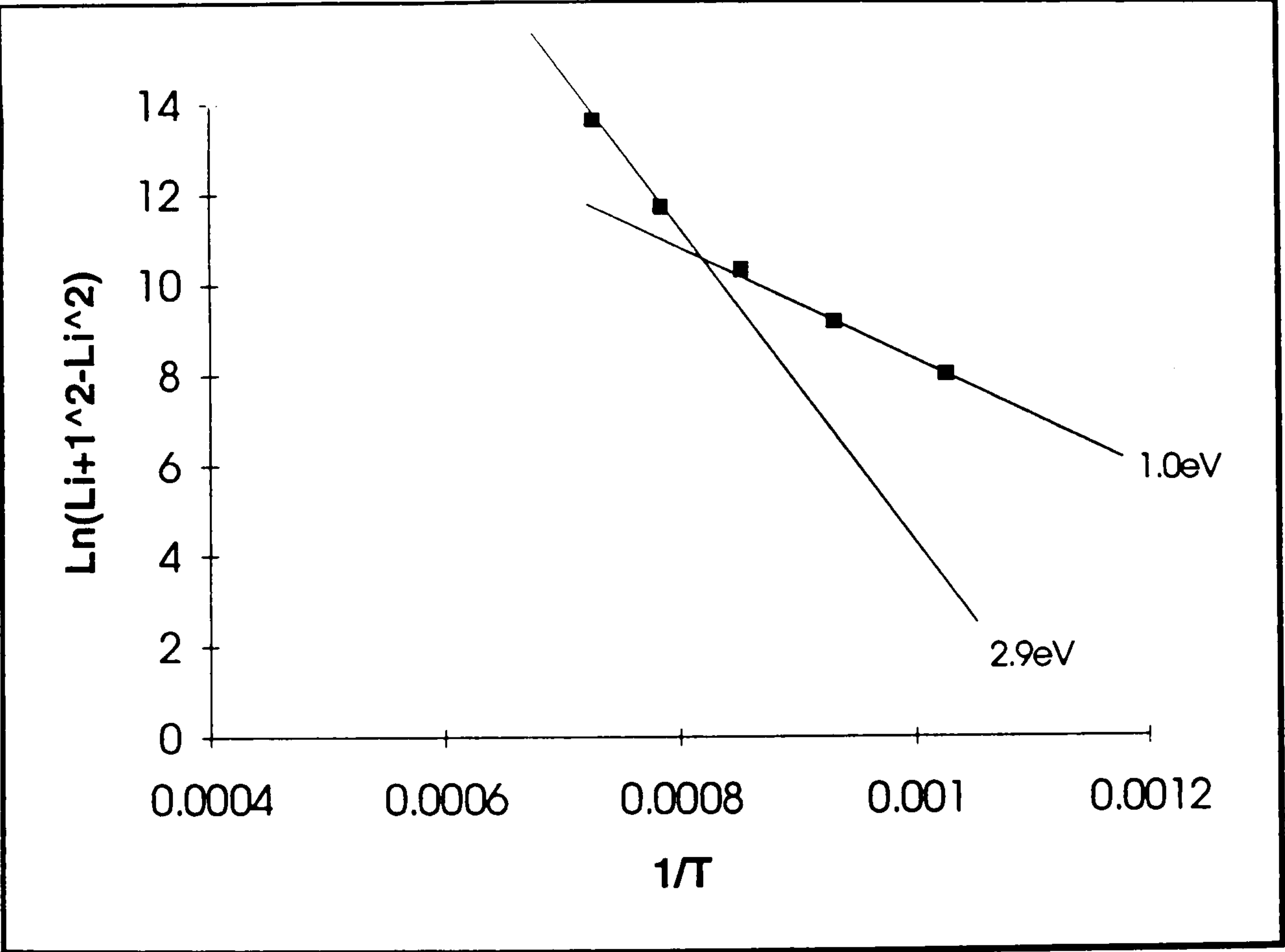


Figure 140: Arrhenius plot of $L_{i+1}^2-L_i^2$ versus annealing temperature observed in specimen 1 from Figure 137.

If a single straight line was drawn through these data points, an activation energy of 150kJ/mol (1.6eV) would be obtained. However, the monotonic curvature suggests that there is not a single mechanism responsible for grain coalescence. Rather, the trend shown in Figure 140 would suggest that the overriding transport mechanism shifts from one of a lower to one of a higher activation energy as the annealing temperature is increased. This would concur with the above considerations that, as the grain boundaries are

densified, the activation energy required for grain coalescence increases from one close to that of surface diffusion to one near that required for atomic jumps in grain boundary migration. Such a behaviour can be mathematically modelled as:

$$D=(1-f).D_1\exp(-\frac{E_{surf}}{kT})+f.D_2\exp(-\frac{E_{g.b.m}}{kT})$$

where D is the apparent diffusivity at a temperature T, k is the Boltzmann's constant, E_{surf} and $E_{g.b.m}$ are respectively the activation energies for surface diffusion and grain boundary migration ($E_{surf} < E_{g.b.m}$), D_1 and D_2 are the pre-exponential constants for each respective diffusion mechanism, and f is the fraction of densified grain boundary surface area. The parameter f depends on the temperature/time history of the specimen and is assumed to be small at the start of the annealing treatments.

In the low temperature regime, the grain boundary migration mechanism plays a minor role and $f \approx 0$, hence:

$$D \approx D_1 \exp(-\frac{E_{surf}}{kT})$$

At higher temperatures, f tends towards 1 and the exponential term for grain boundary migration becomes significant, hence:

$$D \approx D_2 \exp(-\frac{E_{g.b.m}}{kT})$$

If this model were valid, the slope of the asymptotic lines shown in Figure 140 would relate to the activation energies for surface diffusion and grain boundary migration as follows:

$$E_{surf} \leq 1.0\text{eV and } E_{g.b.m} \geq 2.9\text{eV.}$$

The cation species are the slowest moving species in zirconia systems. The kinetics of sintering phenomena are therefore controlled by the rate of cation diffusion. Table XII is a collation of activation energies for zirconium diffusion in zirconia systems.

Table XII: Activation energies for zirconium cation diffusion in zirconia systems.

	kJ/mol(eV)
Surface diffusion	~200(2.0) see text
Grain boundary diffusion	pure ZrO ₂ : 286(3.0)
Volume diffusion	pure ZrO ₂ [?] : 430(4.5)
	12mol%Ca-PSZ ⁴⁸ : 390(4.0)

Little success was met to collate activation energies for surface diffusion. As a rough guideline, the activation energy for surface diffusion can be approximated to about one half of that for lattice diffusion (Ref. 145 page 250). This would give a value of 2.0eV which is twice that found in this work. A better agreement is found concerning the activation energy for grain boundary migration. The activation energy for the atomic jump illustrated in Figure 139 corresponds roughly to that for grain boundary diffusion¹⁴⁵. The value quoted by Ashby⁷ for pure zirconia (3.0eV) coincide with that found in this work (2.9eV) for ZrO₂-8wt%Y₂O₃. However it must be remembered that the nature of the solute stabilising cation and its concentration may have marked effect on these activation energies. Thus cross-comparisons can only be relative. Diffusion data concerning specifically the 8wt%yttria-zirconia system would have to be considered in order to conclude on the validity of the above model.

8.2.4.4 Lattice microstrain reduction

The residual lattice strain in specimen 1 (300-400°C deposition temperature range) after completion of the annealing treatments is that of a near equilibrium structure (0.03%). This is significantly less than that achieved in specimen 2, which was deposited in the 500-650°C deposition temperature range (see Figure 138). Moreover, it seems that the annealing temperature required to initiate a reduction in the lattice microstrain increases with the deposition temperature (see Figure 138). These observations point to the conclusion that higher deposition temperatures make the lattice defects more stable. Why should this be?

To answer this question, one must consider the nature of the lattice defects and the possible mechanisms of annealing them out. As discussed above, the bulk of the lattice defects present in EB-PVD TBC's are believed to consist of single vacancies, microvoids and dislocations. As pointed out by Nakahara¹⁴⁶,

grain boundaries and preexisting microvoids act as sinks for vacancy coalescence. Annealing may therefore result into the following processes:

- 1- the restoration of any oxygen deficiency. This mechanism may happen at relatively low temperatures considering that diffusion on the anion sub-lattice is one millionfold greater than on the cation sub-lattice.
- 2- the migration of vacancies (anion and cation) to the grain boundaries.
- 3- the coalescence of vacancies into intra-granular voids.
- 4- the coalescence of small micro-voids into larger intra-granular voids
- 5- the migration of microvoids to the grain boundaries
- 6- the migration of dislocations to the grain boundaries

The phenomena 2 to 6 are controlled by the rate of cation diffusion.

A perfect as-annealed crystallite would be one for which every single vacancy, microvoid and dislocation has migrated to its boundary. However, the ability of vacancies and microvoids to reach the grain boundary decreases with increasing grain size. The longer these defects have to travel through the grain lattice, the more chance they have to coalesce into larger intra-granular microvoid. As the microvoids grow larger, they become less mobile¹⁴⁷. Based on the above argument, it is proposed that the residual strain observed in the annealed specimen 2 reflects the presence of entrapped intra-granular microvoids that have reached a critical size such that their mobility is insufficient to migrate to the boundary. If the crystallite size is small enough (specimen 1), the vacancies and other microvoids reach the boundary before coalescing beyond the critical size. For a grain size less than 10nm, the defects can be annealed out almost completely leaving the lattice unstrained (0.03%).

8.2.4.5 Ceramic densification

'Mud-flat' cracking, as observed upon annealing of the low temperature gas evaporated deposits (see figures 13 to 17) has not been reported in the sputtered YSZ films^{94,81,98}. The substrate dimensions at room temperature are independent of the annealing treatments since no substrate sintering nor creep are involved. Also, it can be seen that each ceramic segment mates its neighbours as in a 'jig-saw' puzzle indicating that the crack spacings are not the consequence of ceramic loss (see Figure 134 to Figure 133). Therefore, the observed thickness reduction and open mud-flat cracks in specimens 1 and 2 are undoubtedly the symptoms of ceramic shrinkage upon annealing. The volume change undergone in specimen 1 at the end of the annealing treatments was estimated assuming that the ceramic consisted of straight columnar segments. A reduction in coating thickness of 15% and a voidage

area of 40% ('mud-flat' cracking) as measured from the coating surface translate into a densification rate of 100%. This must be read against a specimen density in the as-deposited state evaluated at 2100Kg/m^3 .

It should be noted that in the classical theory of sintering, surface diffusion alone leads to neck formation between particles but cannot not result in shrinkage i.e. the distance between the particle centres stay the same¹⁴⁵. It is somewhat striking therefore that, in this work, densification arose at temperatures as low as 700°C (see Figure 135) where the mass transport mechanisms were found to have activation energies similar to those for surface diffusion (see Figure 140). Most of the literature however refers to the sintering behaviour of green compacts consisting of dense particles which differs from the present situation in two respects. First, the analogous particles considered herein (crystallites) do not have bulk densities and second, they are separated by voided grain boundaries as opposed to comparatively massive inter-particle gaps. The diffusion of the quenched-in lattice voiding defects to the grain boundaries effectively 'deflate' the crystallites and fuels the inter-crystallite boundaries with vacancies. This retards the densification of the grain boundaries which facilitates the evacuation of vacancies and symmetrically favours the in-filling of the grain boundaries via a transport mechanism close to surface diffusion. When two crystallites separated by a voided boundary coalesce to form one single crystallite, the end result is the elimination of the porosity that was separating them. It can therefore be appreciated that the annealing of lattice microstrain and the coalescence of grains depicted in Figure 138 and Figure 137 respectively, are necessarily accompanied by the densification of the ceramic and the parallel segregation of porosity. In other words, ceramic densification is the macroscopic consequence of the structural changes depicted in Figure 137 and Figure 138, occurring at the microscopic scale. Effectively, most of the inter-crystallite porosity is 'evacuated' at the edges and at the top surface of the ceramic blocks. The fact that the shrinkage is more significant in the coating plane than in the thickness direction is consistent with the typical anisotropic distribution of inter-crystallite porosity in PVD films.

It can be envisaged that as the inter-crystallite boundaries become denser upon coalescence, the easy diffusion paths become rarer. Therefore, if the densification of grain boundaries takes place faster than the migration of the lattice defects, these defects will be trapped in the ceramic as coalesced intra-granular and inter-granular porosity. It is therefore expected that the sintered ceramic blocks seen in Figure 136 and Figure 133 still contain a significant amount of residual porosity (see Figure 141).

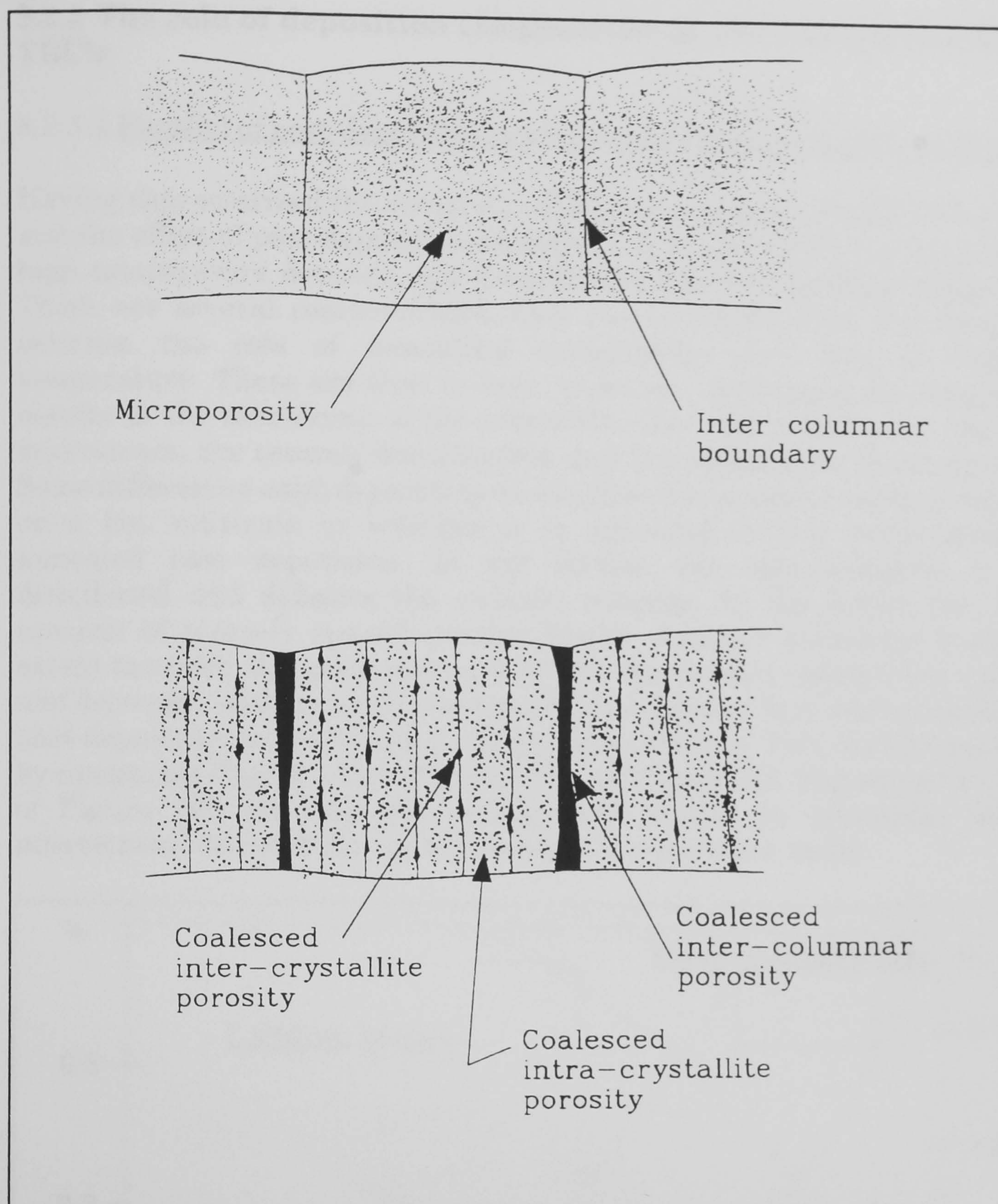


Figure 141: Schematic showing the structural evolution of the low temperature deposits upon annealing.

To conclude, it has been demonstrated from density measurements that the EB-PVD coatings deposited at low temperature contained very high levels of porosity (>50%). The fine intra-granular and inter-granular distribution of the porosity in the deposits was highlighted by their sintering behaviour involving both dramatic grain growth and densification at temperatures less than 0.45 of the ceramic melting point.

8.2.5 The role of deposition temperature on the structure of EB-PVD TBC's

8.2.5.1 Parallel of post-deposition annealing and high temperature deposition

Having characterized the structure of the low temperature EB-PVD coatings and the effect of post-deposition annealing, it is now of interest to turn to the high temperature deposits and consider the role of deposition temperature. There are several commonalities that can be drawn from the comparison between the role of annealing temperature and that of deposition temperature. These are that in both instances, increasing the temperature results in the coarsening of the crystallite size, the reduction in the lattice microstrain, the ceramic densification and the appearance of macroporosity. Some differences exist depending on whether the ceramic coating is deposited on a hot substrate or whether it is deposited at low temperature and annealed post deposition. In the former, the macroporosity is finely distributed and delimits the ceramic columns. In the latter, the coating consists of coarsely spaced ceramic blocks. Another difference is that the extent to which the grain size and lattice microstrain respectively increases and decreases with deposition temperature is greater than that achieved from post-deposition annealing at the same temperatures. This can be appreciated by comparing Figure 142 to Figure 137 and Figure 138. Figure 142 is a replot of Figure 109 showing the average and scatter in crystallite size and microstrain obtained for each deposition temperature range.

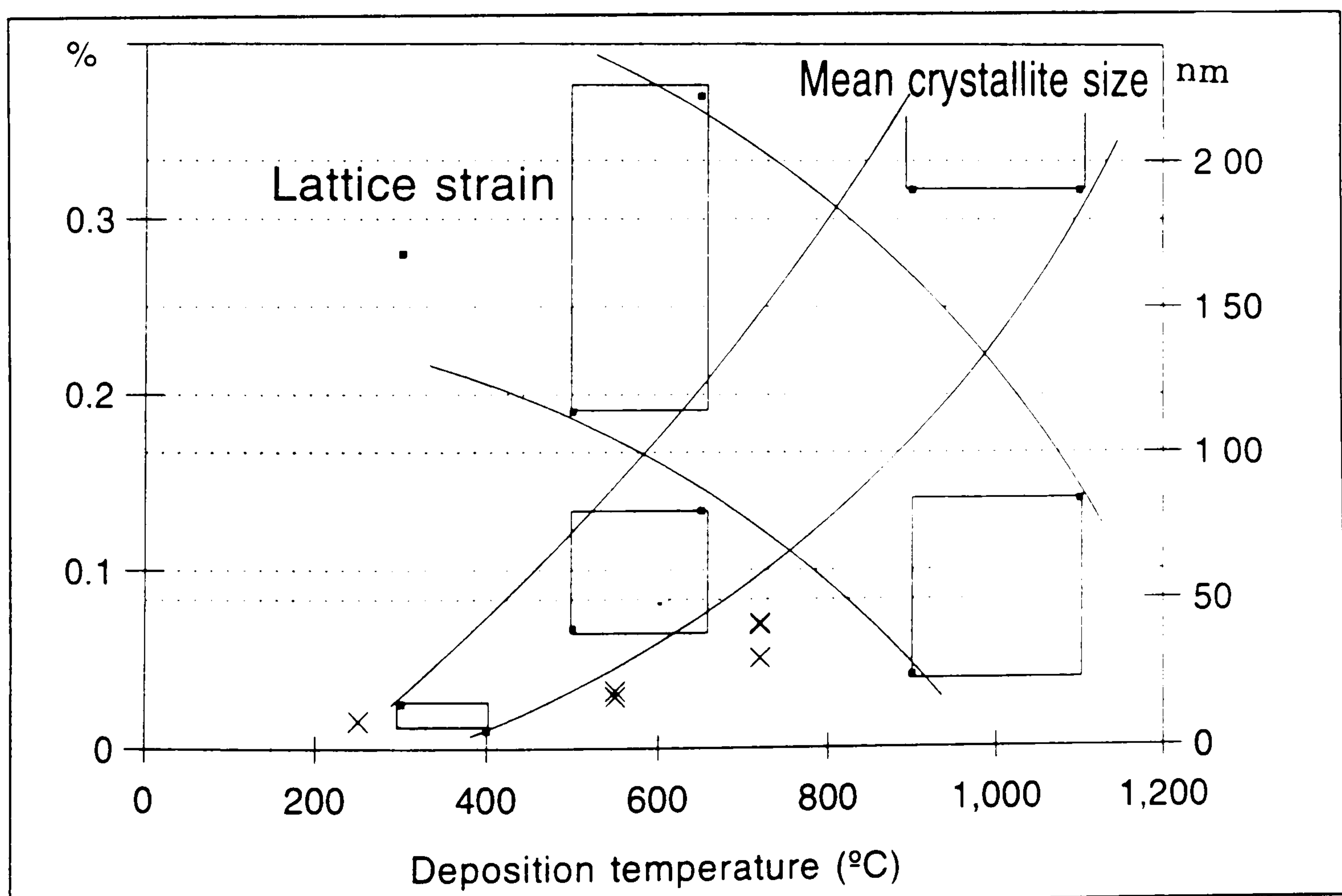


Figure 142: Dependence of lattice microstrain and grain size on deposition temperature in EB-PVD TBC's and of grain size in sputtered YSZ (x from Cléry⁹⁴).

8.2.5.2 Model of high temperature growth of EB-PVD TBC's

The value of the low temperature deposits is that they provide a record of how the coating builds up in the absence of thermal excitation. A heavily defected structure results, containing micropores, vacancies, etc... This structure, typical of what Muller describes as 'a porous atomic network' is the consequence of atomic shadowing and low kinetic energy of the arriving vapour atoms. At elevated substrate temperatures (e.g. 1000°C), the ceramic should tend to spontaneously build up as a porous atomic network considering that the coating flux characteristics are *a priori* the same. However, thanks to the mobility imparted by thermal excitation, the microporosity contained in the freshly deposited atomic layers is annealed out concurrently to the condensation of new vapour atoms. Therefore, the sintering mechanisms modelled for the post-deposition annealing of the low temperature deposits equally apply to the high temperature deposits. The difference is that in the latter, the ceramic deposition and ceramic sintering are two concurrent mechanisms. Grain growth and lattice defect reduction are more significant with high deposition temperatures than with post-deposition annealing probably because, in the former, the proximity of the coating free surface to the sintering volume facilitates the evacuation of the voiding defects and allow surface diffusion to play a bigger part. Furthermore, the inter-columnar porosity characteristic of the high temperature EB-PVD deposits can now be interpreted as the result of microscopic porosity being segregated upon sintering of the columns as the deposition proceeds (see Figure 143).

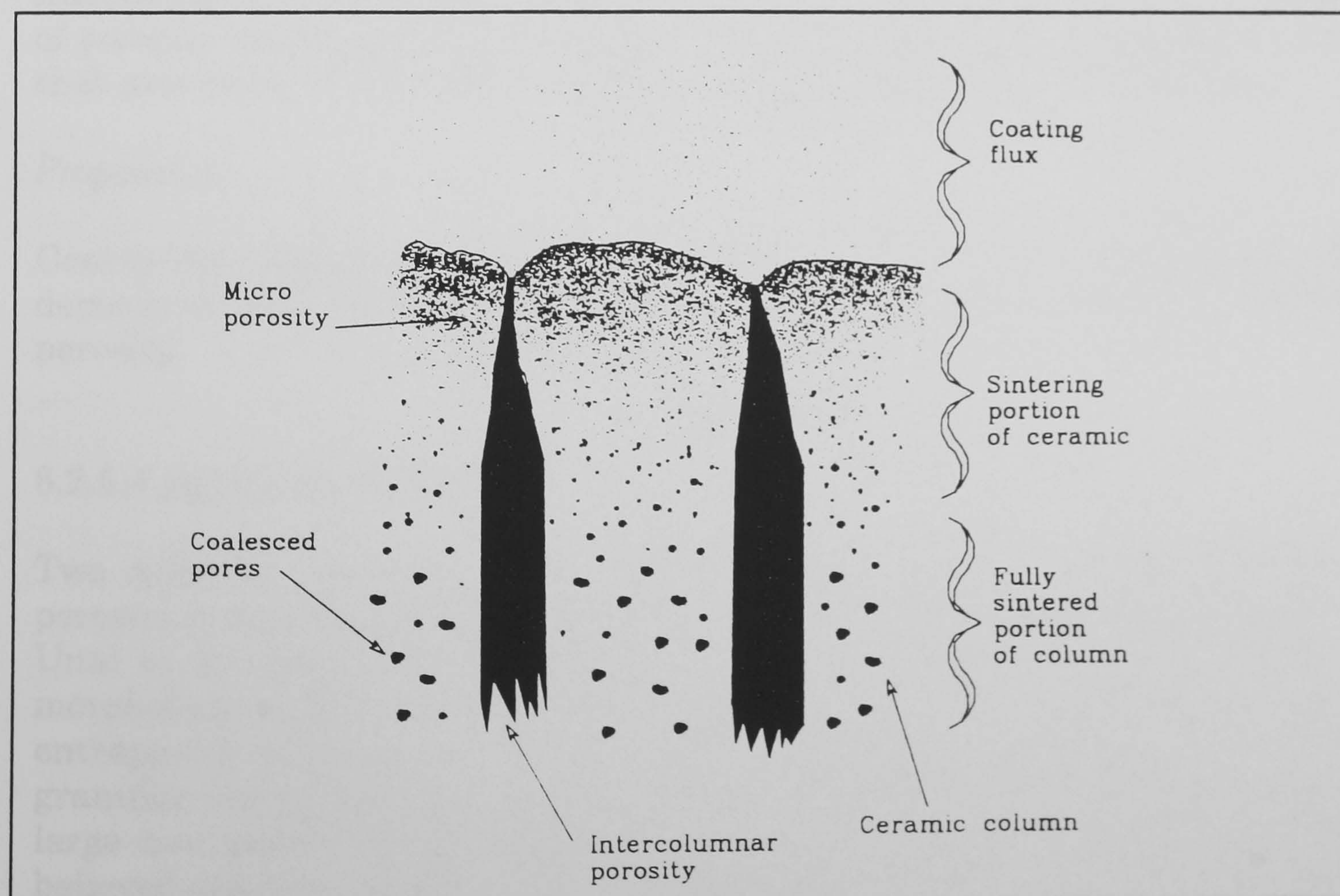


Figure 143: Schematic showing the dynamic sintering of the ceramic coating at elevated substrate temperature.

Both the pertinence and the weaknesses of the coating growth model proposed above will be discussed in the rest of the text.

8.2.5.3 Implications of the model

From the above model of the role of temperature on the growth of EB-PVD deposits, a few predictions can be formulated regarding the influence of other PVD parameters such as kinetic energies of the coating atoms, ion bombardment and deposition rate.

Proposal 1:

The amount of residual porosity in the high temperature deposits, both intra-columnar and inter-columnar, is proportional to the amount of microporosity that would be obtained in the absence of thermal excitation. Process modifications such as increased kinetic energies of the incident coating atoms or ion bombardment potentially increase the density of the deposit without thermal agitation (see chapter 4). Therefore, it is expected that greater kinetic energies and/or ion bombardment will tend to reduce the overall porosity content of the high temperature deposits as well.

Proposal 2:

For a set deposition temperature (i.e. set kinetics of diffusion mechanisms), increasing the deposition rate should tend to result in an increased amount of porosity entrapped within the columns. This follows from the observation that annealing is less effective post-deposition than during deposition.

Proposal 3:

Conversely, increasing the deposition temperature while maintaining the deposition rate constant will yield ceramic columns with less residual porosity.

8.2.5.4 Substantiation of the model

Two different investigators have reported the presence of intra-columnar porosity in high temperature deposited EB-PVD TBC's using TEM techniques. Unal et al reported evenly distributed 25nm pores with a 'Swiss cheese' morphology in ZrO_2 -20wt% Y_2O_3 TBC's, which they attributed to the possible entrapment of gases during deposition¹⁴⁸. Lelait et al observed both inter-granular and intragranular pores in ZrO_2 -8wt% Y_2O_3 TBC's that ranged on a large size scale^{83,139}. The pores had a cuboidal or faceted shape and were believed to be possible precipitates of vacancies and/or gas atoms¹³⁹. Moreover, pores seemed to align at regular intervals ($\approx 0.5\mu\text{m}$), perpendicular to the grain growth axis⁸³. It is interesting to note that the same authors also observed the presence of alternate dark and light layers with the same

periodicity ($\approx 0.5\mu\text{m}$) using SEM back-scattered electron imaging¹³⁹. Although this was not stated by the authors, one could be tempted to believe that the dark layers coincided with the regions of aligned porosity.

The above observations made by independent investigators are very important to the present argument. First, they provide the experimental evidence of the presence of intra-columnar porosity in the high temperature deposits. According to the coating growth model, these pores result from the coalescence of vacancies and microvoids to above a stable critical size upon sintering and not as 'entrapment of gas' which was suggested by Unal¹⁴⁸. Secondly, the stratification of the EB-PVD deposit (alternate light and dark layers) is data against which the proposals 1 and 2 of the coating growth model can be tested. It is known that the stratification in commercial EB-PVD TBC's is the consequence of substrate rotation above the evaporation source, with the dark layers corresponding to the substrate facing away from the vapour source direction¹⁴⁹. The industrial practice³⁵ is to use a substrate rotation speed of 6 r.p.m. with a deposition rate of $3\mu\text{m}/\text{min}$ which concurs with the 0.5 micron intervals reported by Lelait et al. Given that the darker layers are the less dense, the inference is that more porosity is formed when the substrate faces away from the main vapour flux than towards it. This is consistent with the recent patent from General Electric¹⁵⁰ (see chapter 2) in which it is stated that the density of the ceramic can be altered with substrate rotation speed. Slowing down substrate rotation has the effect of reducing both the inter-columnar gaps and intra-columnar voids of the coating deposited on the side facing towards the evaporation source. In the GE patent train of thoughts, the TBC stratification (alternate dark and light layers) is explained as a result of the deposition temperature on the front facing side being greater than that on the back facing side. However, there are other parameters that fluctuate with substrate rotation which should not be overlooked at this stage.

When the substrate faces away from the evaporation source, only the thermalised fraction of the coating vapour can contribute to ceramic deposition. Therefore, both the deposition rate and the kinetic energies of the coating atoms are reduced. The thermalised vapour atoms are those that are in thermal equilibrium with the gas. This means that their direction is isotropic and that their mean kinetic energy approaches 0.1eV which corresponds to the temperature of the gas (assumed to be 1000K). In contrast, the vapour atoms leaving the source are directional and have a mean kinetic energy which is related to the temperature of the rod surface (T_s) as¹⁵¹:

$$E = \frac{3}{2}kT_s$$

where k is the Boltzman's constant. The melt surface temperature of zirconia evaporated by electron beam is estimated to be 3500°C (see chapter 2) which yields a mean kinetic energy of 0.33eV. As the vapour species approach the

substrate they suffer collisions with the gas which reduces their energy and scatters their directions. Therefore, the coatings impinging on the front facing side of the substrate have a mean kinetic energy greater than 0.1eV, but less than 0.33eV against an energy of about 0.1 eV for those impinging on the back facing side.

Proposal 1 would predict an increase in porosity content with the substrate facing away from the source since the kinetic energy of the incident atoms is potentially manyfold less than those in the main vapour stream. *Proposal 3* would also predict an increase in porosity content with the substrate facing away from the source by virtue of a lowered deposition temperature. To the contrary, *Proposal 2* would predict a reduction in porosity due to the lower deposition rate on the back face. The experimental evidence however suggests that the combined effects of deposition temperature and kinetic energy of the incident coating atoms override that of deposition rate.

8.2.6 The indentation resistance of EB-PVD TBC's

Given the structure of EB-PVD TBC's modeled above, how can the indentation resistance data be interpreted?

8.2.6.1 Effect of deposition temperature:

The indentation resistance of a given material potentially depends on numerous factors. These are for instance the crystallographic structure and texture, the presence of toughening phases, the grain size, the porosity content, the presence of internal stresses and also the microstructural texture which is particularly relevant to PVD films⁷².

In this work, the crystallographic texture was not found to vary with temperature in the 650-1000°C range while no significant internal stresses were found in the deposits. This rules out a possible contribution of these two factors to the variation in indentation resistance with deposition temperature. An argument based on the presence of toughening phases is unlikely given that this would require the presence of metastable tetragonal precipitates (equilibrium tetragonal phase) and that the coating's tetragonal structure was identified to be of the 'non-transformable' type (non-equilibrium). The monoclinic phase composition was found to sometimes increase with increasing deposition temperature. This factor could be a potential contributor to the change in hardness with temperature given that the monoclinic symmetry offers less slip systems for dislocation motion than the tetragonal symmetry. However, the fact that two of the deposits exhibited an identical temperature dependence of indentation resistance in spite of one (high current density ion plated) containing no monoclinic phase to the contrary of the other (low current density ion plated) suggests that the presence of monoclinic does not significantly affect the indentation response (see Figure 124 and Figure 102). The grain size was found to increase significantly

with deposition temperature. If grain size affected the indentation behaviour of the deposits, its contribution would be expected to decrease the indentation resistance (Hall-Petch behaviour). The reasons invoked to account for the Hall-Petch behaviour are that the motion of dislocations is restrained by increasing the density of grain boundary area and that, in ceramics especially, the critical flaw size decreases with decreasing grain size. According to the above structural model, the size of the flaws (microvoids) increases with increasing grain size (coalescence). Therefore, in the logic of the Hall-Petch behaviour, the indentation resistance of EB-PVD TBC's should indeed decrease with increasing deposition temperature. The experimental data however does not follow the Hall-Petch argument. This can be explained by considering that, at the same time as the size of the flaws (microvoids) increases with deposition temperature, their concentration is reduced as seen from the increase in density. It is believed therefore that it is the amount of porosity, or density, that controls the indentation resistance of EB-PVD TBC's, overriding the other potential factors reviewed above. Figure 144 illustrates the compaction undergone by a low temperature deposit underneath a Vickers indenter for a load of 50g.

To investigate this further, the role of annealing temperature on the indentation resistance of a low temperature deposit was investigated (see Figure 145). A low load was chosen so as to confine the indent within the sintered ceramic blocks. It can be seen that the role of annealing temperature on indentation resistance is analogous to that of deposition temperature in Figure 124. The increase in hardness with annealing temperature is believed to reflect the densification undergone upon sintering.

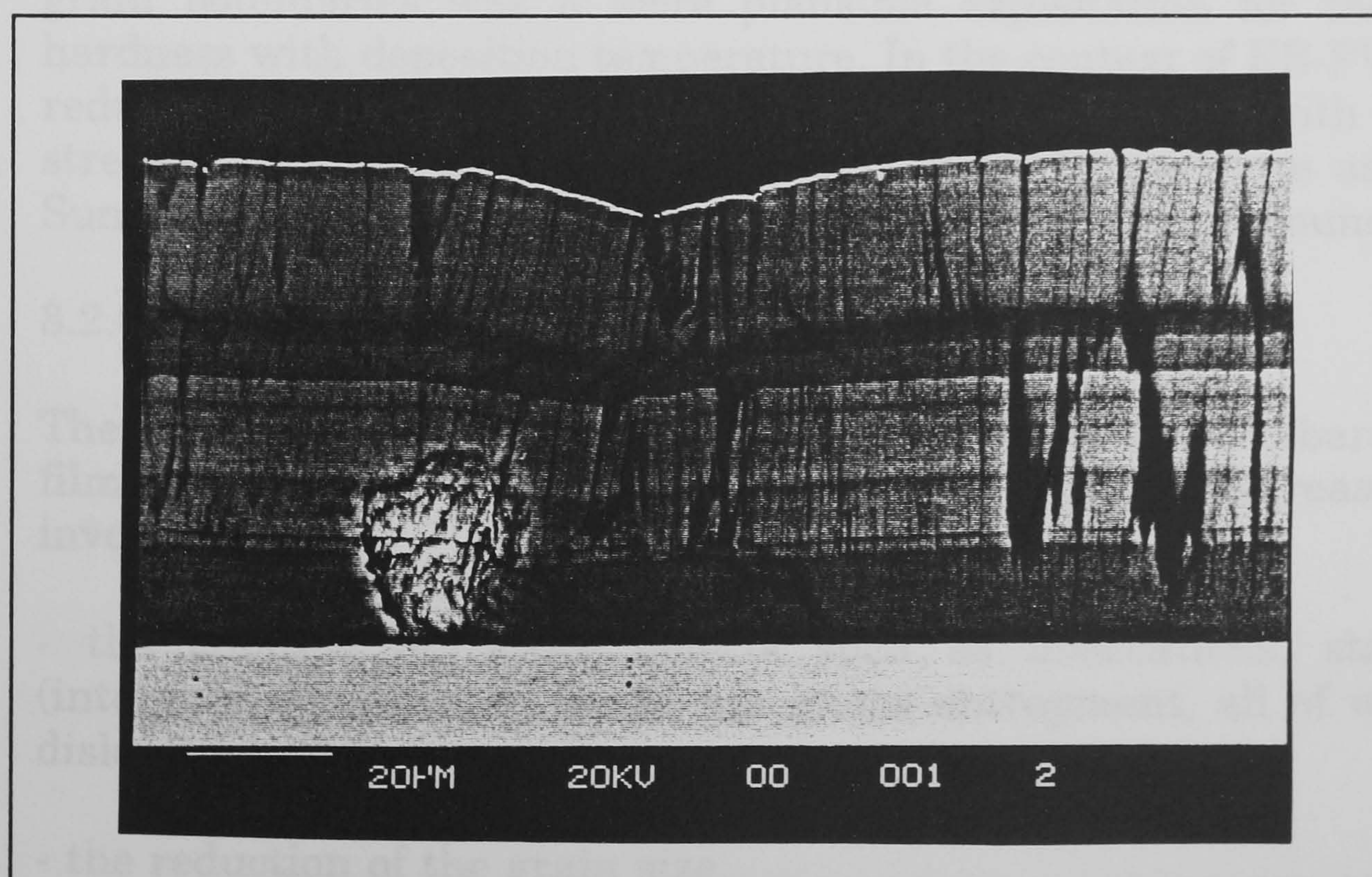


Figure 144: Cross-section of a surface indent in an EB-PVD YSZ coating deposited at 400°C with a surface indentation resistance of the order of 10Kg/mm².

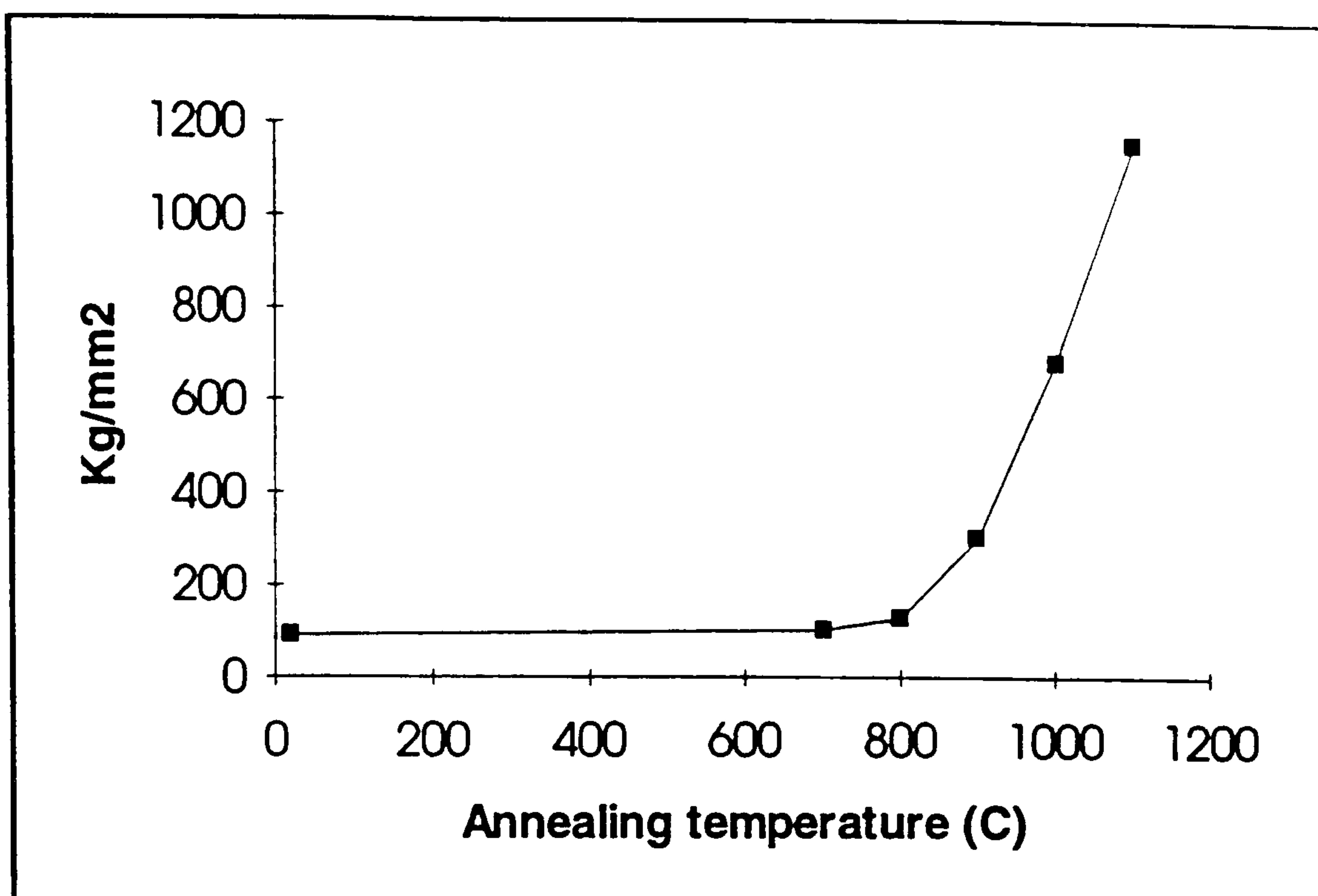


Figure 145: Cross-section indentation resistance of low temperature deposited EB-PVD YSZ as a function of annealing temperature (Load=10g).

Many authors have observed an increase in the hardness of PVD ceramic deposits with deposition temperature^{63,153,154}. Bunshah¹⁵⁴ evoked a reduction in the defect content with deposition temperature to account for this effect. There was still some vagueness about the nature of these defects. Sundgren¹⁵² explained that these strength-reducing defects had been perceived to typically consist of deviations from stoichiometry and vacancies on either of the sub-lattices. The same author however believed that an increasing strength of grain boundaries was a more plausible explanation for the increase in hardness with deposition temperature. In the context of EB-PVD TBC's, the reduced micropore content proposed herein is consistent with the increased strength of grain boundaries with deposition temperature as proposed by Sundgren, given the presence of microvoids at the grain boundaries.

8.2.6.2 Effect of ion plating

There is unanimous evidence in the literature that ion bombardment during film growth increases the hardness of PVD deposits. The reasons generally invoked are:

- the creation of lattice defects such as dislocations, stacking faults (interstitials for example) and gas atoms entrapment, all of which hamper dislocation motion,
- the reduction of the grain size,
- the generation of internal stresses,
- the densification of the deposit.

In this work, no difference in the crystallographic structure, texture, grain size and lattice microstrain could be identified whether the deposits were straight gas evaporated or ion plated. Nor was ion bombardment found to result in the generation of internal stresses. Therefore, the increase in indentation resistance with ion plating appears to simply reflect coating densification.

8.2.7 Comparisons with the work after Movchan&Demchishin and Bunshah

The role of deposition temperature on the structure of EB-PVD zirconia deposits has been studied probably for the first time by Movchan and Demchishin (MD)⁶³ in 1969. Their work on thick vacuum condensates of metals and oxides was a milestone in the science of PVD films as it was the first report that the structure of vacuum deposits could be categorised in three distinct zones relating to the deposition temperature regime (see Figure 146). Good agreement with the MD Structural Zone Model was found a few years later by Bunshah on Y_2O_3 and TiC films deposited by the Activated Reactive Evaporation technique^{153,154}.

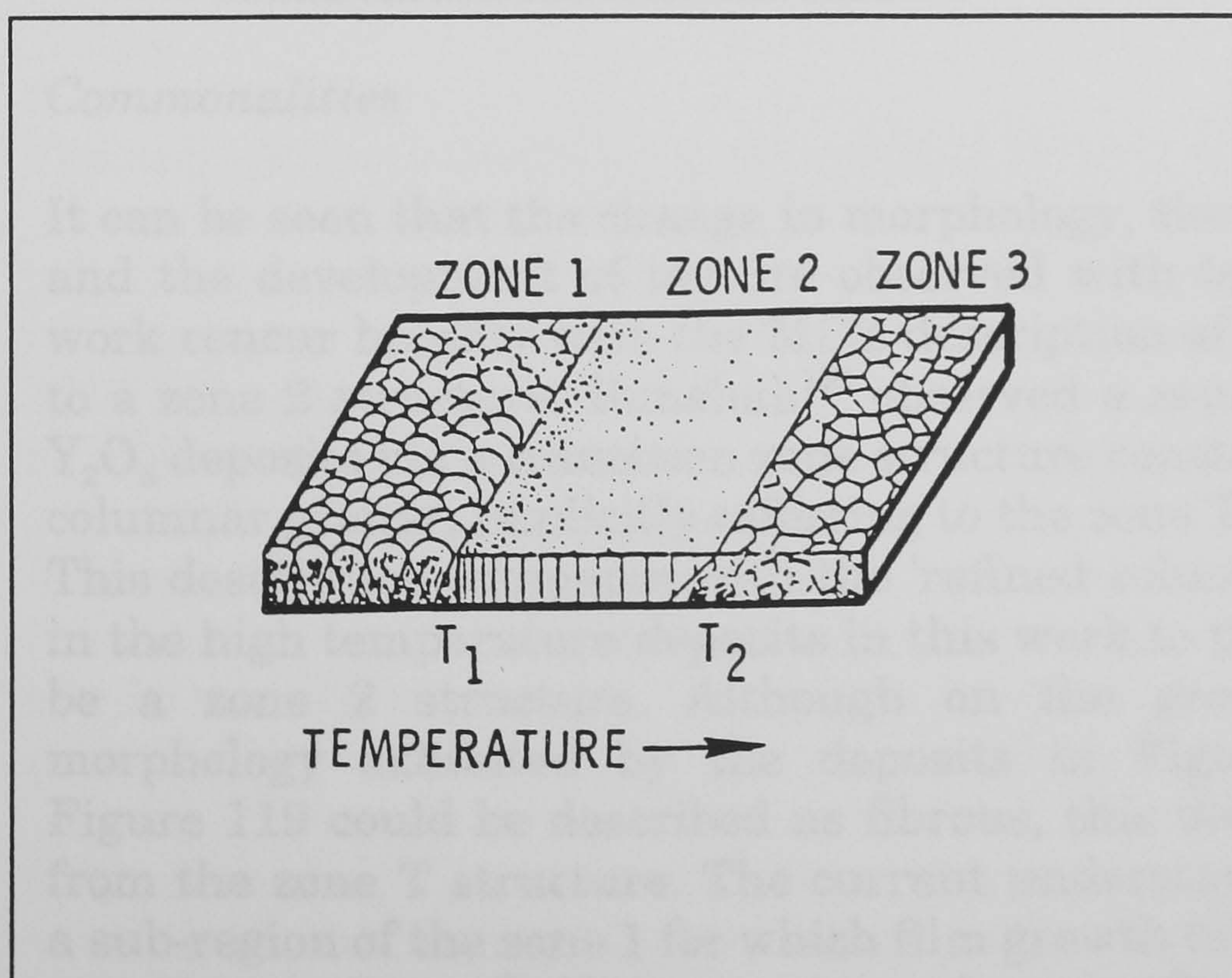


Figure 146: Movchan and Demchishin's Structure Zone Model with $T_1=0.22T_m$ and $T_2=0.45-0.5T_m$ for zirconia⁶³.

These early studies on the role of temperature on the structure of thick PVD coatings are very relevant to the present work. It is the object of this section to compare the findings of these earlier workers with the present results and coating growth model.

8.2.7.1 Role of temperature on the structure of thick vacuum condensates after MD

The description after MD of the role of temperature on the structure of evaporated thick films is reported below as extracted out with scrutiny from the english translation of their original publication⁶³. It should be noted that in the MD terminology and in that employed by Bunshah subsequently, crystallite and grain both refer to column or macrocolumn in the terminology used in the present work.

Movchan and Demchishin reported that the zone 1 deposits consisted of tapered crystallites (columns) with domed tops without any very pronounced boundary zones. This contrasted with the zone 2, which distinctive feature was the presence of well defined grain boundaries. At about T_1 (648K for ZrO_2), some coarsening of the internal structure of the zone 1 crystallites (columns) occurred leading to a gradual changeover to the clearly defined columnar structure characteristic of the second zone. The diffraction patterns in the zone 2 condensates reflected the presence of quite large diffracting domains and a growth texture. In contrast, the diffraction became broadened towards low temperatures of deposition (zone 1), 'probably because of a reduction in the size of the sub-structure elements'.

8.2.7.2 Comparison with present work

Commonalities

It can be seen that the change in morphology, the increase in crystallite size and the development of texture observed with temperature in the present work concur broadly with the MD's description of a transition from a zone 1 to a zone 2 structure. Bunshah¹⁵³ observed a zone 1 to zone 2 transition in Y_2O_3 deposits via a transition zone structure consisting of 'fully dense fibrous columnar grains', implicitly referring to the zone T introduced by Thornton⁶⁶. This description compares with the 'refined columnar morphology' observed in the high temperature deposits in this work to describe what is believed to be a zone 2 structure. Although on the grounds of appearance, the morphology exhibited by the deposits in Figure 114, Figure 115 and Figure 119 could be described as fibrous, this does not mean that they are from the zone T structure. The current understanding is that the zone T is a sub-region of the zone 1 for which film growth takes place under low atomic mobility conditions⁷⁴. For example, such a zone T structure has been observed in the low temperature ion plated YSZ deposited on smooth substrates (see Figure 111).

To the contrary, the refined columnar morphology observed in Figure 115, Figure 117, Figure 118 and Figure 119 is believed to be the result of dynamic sintering typified by symptoms such as the grain growth, the reduction in lattice microstrain and the densification occurring in parallel.

Differences

Three major discrepancies were found between the results of the present work and the findings of MD and Bunshah, regarding the zone1-to-zone2 transition temperature, the porosity and the indentation resistance of the deposits:

1-

A transition temperature T_1 of about $0.37T_m$ (850°C) was found in this work as opposed to $0.25T_m$ after MD and Bunshah^{153,63}.

2-

Thornton^{74,64}, when describing the SZM after MD, mentions inter-columnar voids for the zone 1 type and dense columnar boundaries for the zone 2 type of morphology. This is in contradiction with the observation in this work where the zone 1 deposits exhibit less obvious intercolumnar voidage than the zone 2 deposits. Although porosity is usually mentioned when describing SZM's, it must be pointed out that the original MD's publication does not contain any mention of porosity, whether intra or inter-columnar whatever the temperature regime. The porosity separating the columns in the high temperature deposits observed in this work are replaced by 'well defined boundary zones' in the zone 2 structure typified by MD. Bunshah observed that the zone 1 Y_2O_3 condensates were less than fully dense but did not report porosity in the zone 2 region¹⁵³.

3-

The indentation resistance data reported by both MD and Bunshah are much greater than that found in the present work (see Figure 147). Care must be taken however, as there are some uncertainties on the indentation technique and load used in the study of Movchan and Demchishin. The data quoted for ARE Y_2O_3 correspond to Knoop hardness numbers (KHN). Bunshah¹⁵⁴ showed on TiC coatings using indentation loads of 50g that Knoop hardness numbers were typically 55 to 75% greater than those yielded when using a pyramidal indenter similar to that utilised in the present work. There is no reference to the indentation technique used in the MD work, but even if a correction factor of 1.55 to 1.75 is allowed, their indentation data is overall still significantly greater than that measured on the Cranfield systems.

It is interesting to note that the three discrepancies highlighted above appear to be consistent with each other. A higher T_1 transition temperature indicates a lesser atomic mobility which could account for the presence of porosity in the Cranfield deposits to a much larger extent than that in the MD's deposits, if any. The presence of porosity in the Cranfield deposits in turn translates into a lowered indentation resistance.

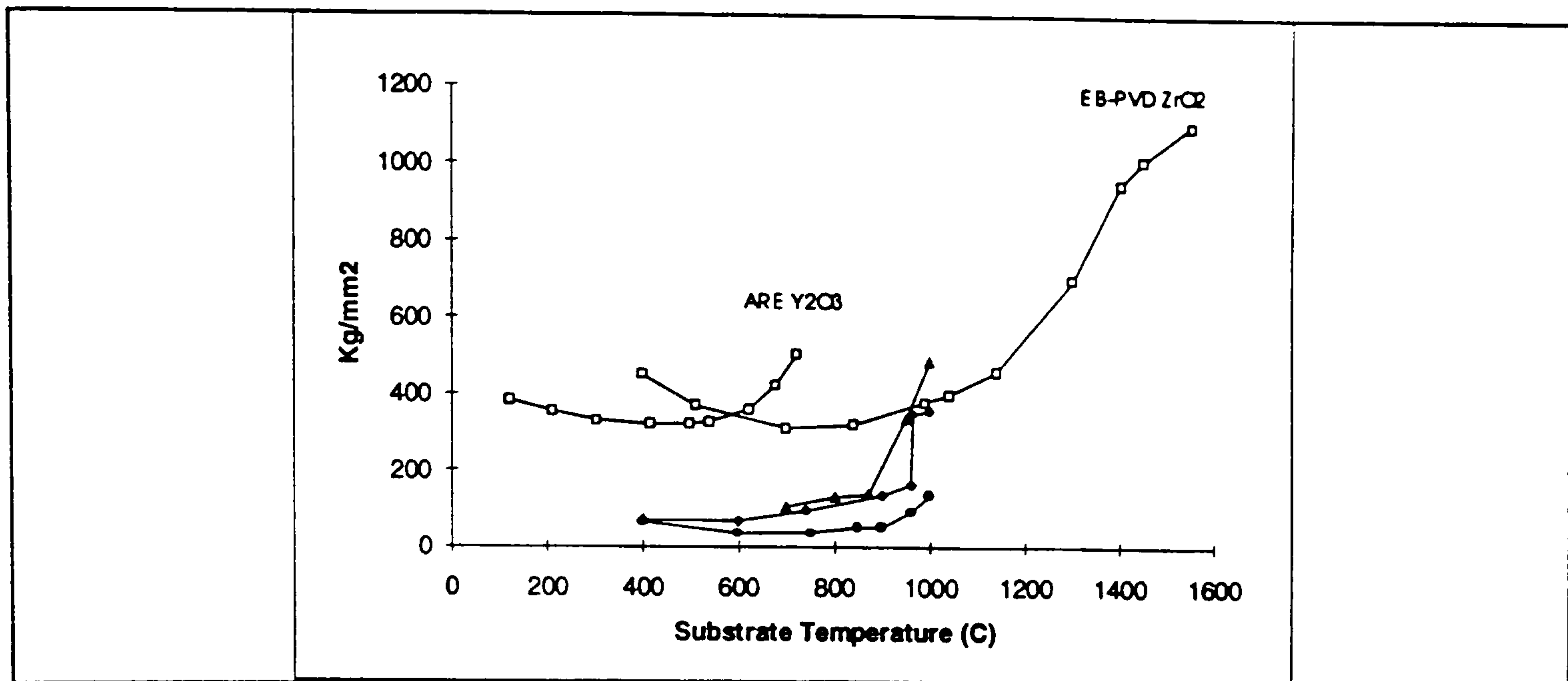


Figure 147: Indentation data of the gas evaporated (●), High (▲) and Low (◆) current density RF ion plated coatings overlayed with data after MD (zirconia) and Bunshah (yttria).

In order to find possible reasons for these differences between the MD work and the present work, the deposition details of each separate study have been tabulated for comparison, as available in the papers (see Table XIII).

Table XIII: Comparison of deposition details between the study from MD and the present work.

	Cranfield	MD ⁶³
Coating material	ZrO ₂ -8wt%Y ₂ O ₃	'stabilised' ZrO ₂ graded pure
Deposition process	Electron beam evaporation	Electron beam evaporation
Vacuum (Torr)	10 ⁻² in Ar	10 ⁻⁴ base pressure
Deposition rate	1-3μm/min	1.2-2.4μm/min
Source-to-substrate distance	18cm	25cm
Deposit thickness	40-250μm	300μm
Substrates	Pack-aluminised or NiCoCrAlY bond coated Nimonic 75	lamellar Cu-Nb
Substrate surface finish	Ra = 0.5μm	optical surface finish ?

Although this was not stated in the papers, it is strongly felt by default that the substrates used in the Bunshah and MD investigations had smooth surface finishes. It is implicit from the fundamental character of their studies that the extrinsic influence of substrate roughness on the film properties was to be avoided.

According to the coating growth model exposed above, it is believed that the density of a ceramic deposit is function of first its 'green density' i.e. the density it would achieve in the absence of thermal excitation, and second of the extent to which diffusion processes can take place simultaneously to ceramic deposition. From the above table, three potential reasons can be evoked to account for the difference in the properties between the Cranfield and MD coatings. These are respectively the working pressure, the substrate surface finish and the ceramic composition.

Amongst the parameters influencing the 'green density' of the deposits, there are those setting the coating flux pattern in terms of angle of incidence and kinetic energy of the depositing atoms. The topography of the substrate also influences the green density by promoting the formation of voids from the shadowing of the oblique coating flux. It can therefore be concluded that the green density achieved in the Cranfield deposits was most probably less than that in the MD study by virtue of gas scattering and surface roughness both promoting the formation of porosity. Martin⁷⁸ reported relative densities of about 0.8 for ZrO_2 films evaporated in high vacuum without ion assistance onto optically smooth substrates at 300°C. Given that at this deposition temperature diffusion processes cannot be significant, the density reported by Martin can be considered as a measure of the maximum coating green density achievable by thermal evaporation. The porosity enhancement from gas scattering and substrate surface finish can be appreciated by comparing the density quoted by Martin with the densities achieved in the low temperature deposits in this work (less than 0.5).

In addition to the working pressure and the substrate surface finish encouraging the entrapment of porosity in the Cranfield coatings comparatively to the MD's, one must evoke the possible role of ceramic composition on the diffusion processes. For example, Knoll&Bradley⁸¹ demonstrated with sputtered YSZ deposits that the extent of grain growth achievable from post deposition annealing decreased with increasing Y_2O_3 content. Unfortunately, no precise reference regarding the stabilising oxide used was available in the MD's publication. Given the vintage of their work (1969), it is most likely that the stabilising oxide consisted of either CaO or MgO considering that these systems were then the most extensively used in bulk zirconia systems. It is known that cation diffusion in calcia and magnesia alloyed zirconias is greater than in YSZ⁴⁸, which is why the latter system has been chosen for optimised thermal stability in thermal barrier coating applications (see chapter 3). Based on these considerations, ceramic composition could be a third contributor to account for the greater density of the MD deposits by virtue of diffusion processes being more significant than

in the Cranfield systems at equivalent deposition temperatures.

8.2.8 Appraising further the coating growth model

In this work, an approach inspired from powder metallurgy processes i.e. dynamic sintering has been used to describe the role of deposition temperature on the structure of EB-PVD ceramic deposits. It is believed that this approach further allows to assess the role of other deposition parameters such as kinetic energy of coating species, ion bombardment, substrate surface finish and deposition rate on the structure of the deposit. The former three affect the coating 'green density', defined as the density achieved in the absence of thermal excitation whereas the latter, with deposition temperature, determine the extent to which diffusion processes can anneal out the microvoids. This model built from the annealing behaviour of the low temperature deposits in this study can explain the fine residual porosity observed in high temperature deposits using TEM by independent investigators. It was shown that the model could also account for the differences observed between the MD investigation and the present work.

The analogy of the role of temperature on ceramic growth with that in powder metallurgy processes is further supported by the fact that the coating lattice parameters were found to be identical to those of bulk YPSZ, thus indicating an equilibrium structure. It should be noted that Movchan and Demchishin did consider the occurrence of sintering in the growth of thick vacuum oxide deposits for temperatures greater than T_2 ($T/T_m > 0.5$), as in bulk ceramics. The novelty of the present model is that it conveys the idea that the structure of EB-PVD ceramic thick films deposited at high rate is determined from pseudo-volume sintering processes of the freshly deposited atomic layers. Pseudo-volume sintering can take place at temperatures lower than $0.5T_m$ because the atomic layers spontaneously build up in a very defective manner with the entrapped atomic porosity enhancing manifold the diffusion processes responsible for sintering. Early growth models have emphasized the role of surface diffusion in dictating the structure of PVD films. The present model is more encompassing in that it considers diffusion in the bulk via short-circuit diffusion paths rather than simple surface diffusion. It is thought that the present model is particularly relevant to situations where the rate of condensing atoms competes against the rate of microvoid annealing whereas the early models simply based on surface diffusion constitute a limiting case for low deposition rate film growth (i.e. the depositing atoms adsorb on a fully annealed film structure).

The coating growth model, as depicted in Figure 143, was deliberately oversimplified in order to highlight the concept of dynamic sintering. In its present form, it contains two major weaknesses, these are the omission of both the individual crystallites making up the columns and the role of the film nucleation stage on the coating physical structure. PVD films are said to

be 'grown' from the vapour phase, such a terminology implies that the initial stages of deposition affect the subsequent film build up. In the above schematic of dynamic sintering, the inter-columnar porosity was depicted as originating from the shrinkage of the sintering portion of the columns (see Figure 143). This was a reasonable proposition considering that the coatings deposited at low temperature on substrates with the same surface finish did not show inter-columnar porosity to the same extent. However, it is believed that the role of surface finish has been so far overlooked in the present text, given that it influences film growth from the early deposition stage.

The substrate surface finish was seen to have a tremendous effect on the coating morphology of the low temperature deposits (see Figure 111 and Figure 112). The effect of surface finish on zone 1 morphology is classically explained on the basis that the peaks intercept more coating flux than the troughs, and thus the coating surface replicates the interface topography in an exaggerated form with shadow growth boundaries^{67,71}. It is believed that this argument is equally valid at elevated deposition temperatures as vapour flux shadowing between columns promotes macroscopic voidage to a scale that is unrecoverable by atomic mobility. Secondly, the surface finish, in dictating the growth morphology at the initial stage of film build up potentially affects the overall coating morphology. It was stated earlier that the substrate surface finish affected the coating green density. Substrate surface topography is not however believed to affect the spontaneous microporosity contained in the freshly deposited atomic layers during film growth. More realistically, its role is believed to reside in seeding the growth morphology of the deposit thereby influencing the column shape and associated intercolumnar voidage.

It was shown that the morphology of the high temperature deposits could vary between a fibrous and a columnar type irrespective of the controllable deposition parameters with regard to the substrate surface finish, the temperature and substrate bias (see Figure 117, Figure 118 and Figure 119). Although it is not clear as to what is the cause for these inconsistencies in coating morphology, it is believed that they originate from combined subtle changes at the early stages of film growth. Different deposition conditions with regard to substrate temperature, deposition rate and vapour flux pattern will affect the dynamic sintering behaviour of the crystallites at film nucleation. Large scale collective coalescence of the elementary crystallites at the nucleation stage will yield a columnar morphology whereas more discrete crystallite coalescence will yield a fibrous morphology. Once the columnar growth pattern is seeded in terms of column diameter and intercolumnar spacings, it is difficult to envisage how the morphology could be changed from a columnar to a fibrous type, or *vice versa*, during subsequent deposition and growth.

Although tremendous improvement on the control of the evaporation conditions had been acquired, inclusive of the use of a shutter (see chapter 6),

it is a fact that the deposition runs still suffered from a significant scatter in deposition rate. It is probable that the inconsistency in coating morphology from a fibrous to a columnar structure reflects inconsistencies in the deposition rate/vapour flux pattern at this crucial stage of film nucleation.

To finish, the influence of the type of deposit material is considered with regard to the applicability of the above coating growth model. This model is believed to be particularly relevant to refractory materials spontaneously exhibiting low green densities under thermal evaporation conditions as was the case for zirconia. It may be postulated that the propensity of a deposit to build up with a high degree of porosity may depend on the type of bonding of the material considered. Muller explains the onset of micro-columnar porosity as a result of arriving atoms being deviated from their trajectory by the attractive force exerted by atomic aggregates. One would expect this effect to be even more significant in the case of ionically bonded systems considering the long range and isotropic nature of the electrostatic forces involved in an ionic bond. Raghuram and Bunshah¹⁵⁴, in their work on ARE TiC, found that a low temperature deposit, as annealed *in situ* at 1180°C for 1 hour, exhibited a hardness and a structure equivalent to that of a high temperature deposit. In the same study, they observed that the deposit thickness decreased with deposition temperature. Such similarities with the present work suggest that the model can be extended to metallically bonded compounds as well.

8.2.9 The role of plasma assistance on the structure of EB-PVD TBC's

The effect of ion bombardment on the structure of YSZ PVD deposits has been studied by previous investigators using bias sputtering^{94,93,81,37,101, 106}, Ion Assisted Deposition⁷⁸ and ion plating^{41,40,39} (see chapters 2 and 4). It is therefore of interest to compare the outcome of the present work with the results from the past investigations.

In this work, the chemical composition, phase composition and grain size of YSZ evaporated deposits was found not to be altered by ion bombardment. This concurs with the findings of previous investigations^{81,101, 106}. At low temperature, plasma assistance was found to increase the density of EB-PVD YSZ deposits but still was incapable of eliminating the massive microporosity content. This was revealed by density measurements and the sintering behaviour upon annealing, that were similar to those of the low temperature straight evaporated deposits (see Figure 148). Ion bombardment, in this study, did not result in the generation of a stress within the evaporated TBC's and this contrasts with the report of compressive stresses increasing with bias in sputtered YSZ⁹³. The persisting porosity content in the ion plated TBC's forbids the build up of stress unlike in the sputtered deposits where the porosity was completely resorbed with the application of substrate bias⁹³.

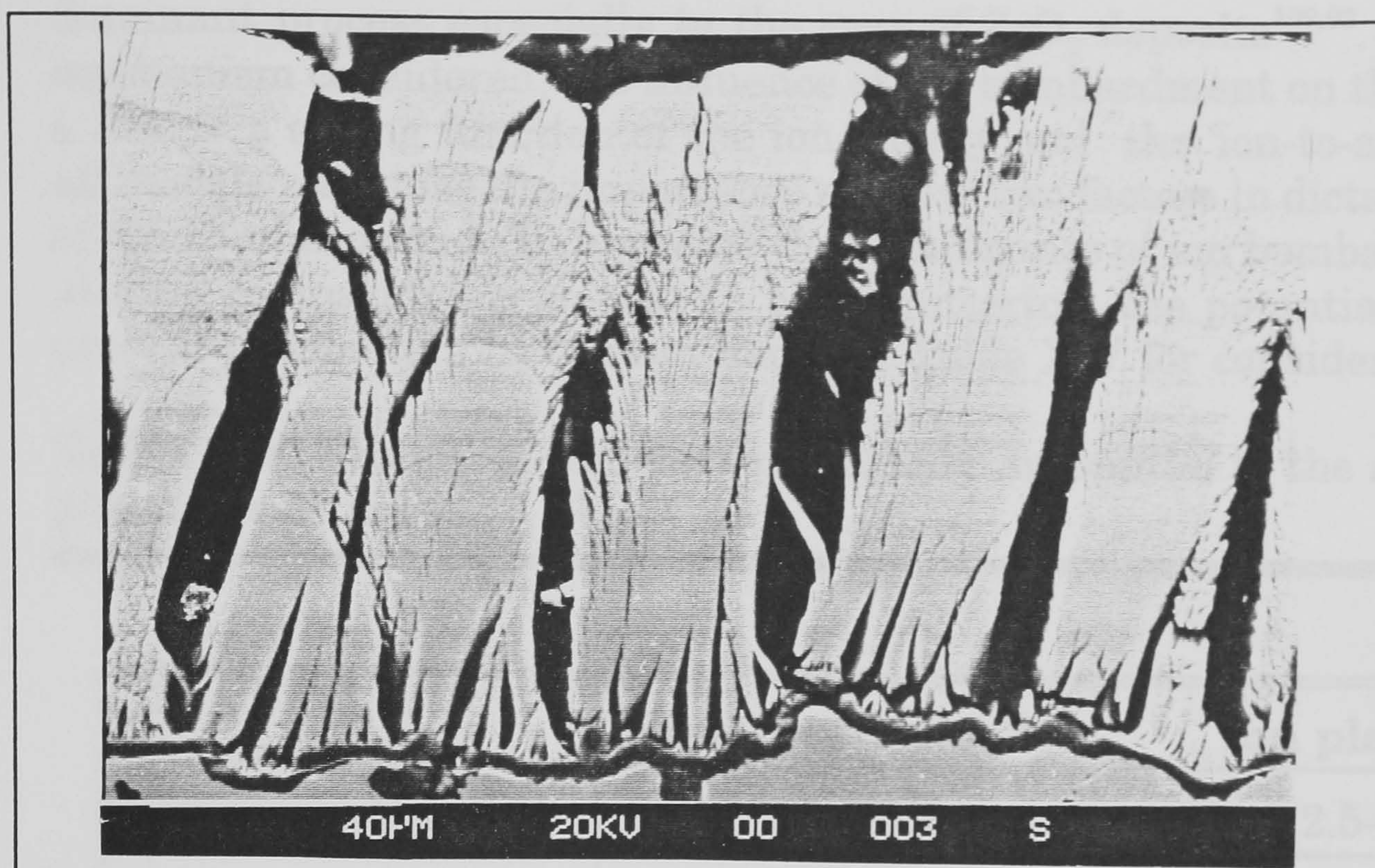


Figure 148: Cross-section of RF ion plated TBC deposited at 500-650°C annealed at 1100°C for 10 hours.

The increasing stress with bias was also accompanied with XRD line broadening which Knoll&Bradley interpreted as atomic disorder induced by ion bombardment. In the present case, no significant effect of ion plating on lattice microstrain was found. Finally, it was reported that ion bombardment could disrupt the columnar growth of sputtered YSZ which clearly is not the case for ion plated TBC's³⁷.

To conclude so far, the structural changes incurred in EB-PVD TBC's by ion bombardment at low and elevated deposition temperatures are found not to be significant with the exception of a slight increase in density. This contrasts in many respects with the role of ion bombardment in sputtering. It should be pointed out that the substrate bias levels used in sputtering, up to a few hundred volts at the maximum, are about an order of magnitude less than those used in the present work (a few kilovolts). It is therefore paradoxal that in spite of greater ion energies, ion plated YSZ deposits suffer minute structural changes compared to bias sputtered coatings. In order to elucidate this paradox, one needs to scrutinise the parameters controlling the effectiveness of ion bombardment in these two different deposition processes. Not only the parameters relating to the plasma, but the whole of the deposition parameters must be considered.

The structural changes induceable by ion bombardment are the result of atomic displacements caused by the collision of an energetic ion or neutral with the film lattice. The mechanisms invoked to account for this 'ion-induced' mobility have been thermal spikes, surface diffusion of adatoms and atomic displacements in the bulk. Modelling works suggest that, of these three mechanisms, the 'thermal spike' contribution is the least significant^{92,155}. Atomic displacements in the bulk, via collision cascades is thought to be the

dominant process especially in the case of ZrO_2 deposits^{109,92}. Whatever the mechanism considered, the influence of ion bombardment on the structure of a film is a strong function of the ion energy and the 'ion-to-atom' ratio, i.e. all models recognise the importance of these two factors in dictating the effect of ion bombardment. To appraise the significance of ion bombardment in ion plating comparatively to that in bias sputtering, the potentially influential process parameters have been listed in Table XIV for consideration.

Table XIV: Process parameters potentially influential to the significance of plasma assistance.

	Bias sputtering^{81,93}	Ion plating
Substrate bias (kV)	up to 0.2	2.5-3
Deposition rate ($\mu\text{m}/\text{min}$)	0.01*	1-3**
Working gas	$\text{Ar}/20\%\text{O}_2$	$\text{Ar}/0-90\%\text{O}_2$
Pressure (mTorr)	20	6-10
Source-to-substrate distance (cm)	5	15-22
Ion flux density (mA/cm^2)	>0.2	≤ 0.2
Ion energies (eV)	?	?
Incident energy of coating atoms (eV)	a few	0.03-0.33
*: deposition rate corresponding to a coating density of about $6000 \text{ kg}/\text{m}^3$		
**: deposition rate corresponding to a coating density of about $5000 \text{ kg}/\text{m}^3$		

The data listed for bias sputtering refers to the experimental conditions used by Koll&Bradley^{81,93} as available from their publications. Unfortunately, the ion current densities that applied in their studies are unknown. In the case of reactive RF sputtering of Ti in N_2 , Sundgren¹⁵⁶ quotes ion current densities varying between 0 to $0.9 \text{ mA}/\text{cm}^2$ for DC substrate bias voltages in the 0-700V range at a total pressure of 5×10^{-3} Torr. The same author¹⁵⁷ quotes ion current densities of $1.6 \text{ mA}/\text{cm}^2$ for a substrate bias of 300V when using a magnetron reactor still at a pressure of 5mTorr in N_2 . These current densities are greater than those relevant to the present study using ion plating which, in the

preceding chapter (Chapter 7: Diagnosis of ion plating), were estimated to be of the order of 0.2mA/cm^2 at the maximum, for both RF ion plating and high temperature DC ion plating. Given the working pressures and substrate biases used by Knoll&Bradley and in the light of the figures quoted by Sundgren, it can be reasonably assumed that the current densities in the sputtering studies of YSZ were at least equal to or greater than those in ion plating of YSZ in the present work. Hence, a current density of 0.2mA/cm^2 will be used in the 'bias sputtering' column of the above table as a conservative assumption.

It is known that the incident ion energies are strongly scattered as a result of both ion/neutral collisions in the plasma sheath and RF modulation (see chapter 5). The ultimate approach to assess the significance of ion bombardment would be to determine the fluxes and energy distributions of both the ions and the fast neutrals impinging on the substrates. This is very difficult to realise either experimentally or using computer modelling¹²⁹ and well beyond the scope of this work. However, the inference from the derivation of the ion current density with RF biasing (see chapter 7) is that it is justified to consider that the ion/neutral collisions in the plasma sheath do not affect the overall power density of bombardment delivered by the heavy particles. In other words, the power density of ion bombardment carried by the ions to the substrate in a would-be collisionless sheath is the same as that carried by both the ions and fast neutrals in a sheath with collisions. The effect of collisions is to increase the flux of fast particles while reducing the average particle energy without altering the overall incident power density. This approach is very practical since it allows to estimate the power density of bombardment from measurable parameters (see chapter 7):

$$P_b = J_{ion} V_a$$

where V_a is the ion accelerating voltage which can be approximated to the substrate bias voltage in the DC case, to the RF bias-induced DC offset in a 13.6MHz plasma as used by Knoll&Bradley, and to $\langle V_{c,sheath} \rangle$ in a 380kHz plasma as explained in chapter 7.

It is proposed that the significance of the 'ion' bombardment regime can be assessed by considering the average incident energy from ion/neutral bombardment per condensing atom, defined as:

$$E = \frac{P_b}{J_{vap}}$$

where J_{vap} is the flux density of condensing vapour atoms/molecules. E can be explicated as:

$$E = \frac{J_{ion}}{J_{vap}} V_a$$

The flux density of vapour atoms/molecules impinging on the coating surface is:

$$J_{\text{vap}} = \rho \frac{N}{M} D$$

where ρ is the coating density in g/cc, N the Avogadro's number, M the mass of a mol of depositing molecules and D the deposition rate in cm/s. The vapour flux quoted later in the text will assume that the evaporant consists of pure zirconia and that dissociation is negligible ($M_{\text{ZrO}_2}=72\text{g}$).

Using the data in Table XIV and the above equations, E can be estimated for both bias sputtering and ion plating of YSZ (see Table XV). To be pedantic, E should refer to the average incident energy from ion/neutral bombardment per condensed atom as this is the rate of depositing atoms and not the rate of arriving atoms which is measured in practice due to the concurrent sputtering of film atoms.

Table XV: Comparison of incident energy of bombardment per condensing atom (E) for both ion plating and bias sputtering.

	Bias sputtering	Ion plating
J_{vap} ($\text{cm}^{-2}\text{s}^{-1}$)	8×10^{14} (0.01 $\mu\text{m}/\text{min}$)	2×10^{17} (3 $\mu\text{m}/\text{min}$)
J_{ion} ($\text{cm}^{-2}\text{s}^{-1}$)	$>10^{15}$	$\leq 10^{15}$
V_a (V)	200 (RF induced V_{DC})	3000 ($<V_{\text{c,sheath}}>$)
E (eV)	>300	≤ 20

It is clear from this table that, although greater substrate bias voltages are used in ion plating than in sputtering, the actual incident energy of bombardment per condensed atom is greater by more than an order of magnitude with bias sputtering. This is because in ion plating, the 'ion' bombardment is effectively diluted due to the high deposition rate of the vapour atoms.

The concept of average incident energy of bombardment per condensing atom (E) may be extended to Ion Assisted Deposition (IAD). Martin⁷⁸ reported that the density of evaporated ZrO_2 deposited at a substrate temperature of 300°C could be increased from 4.4g/cc without ion assistance to 5g/cc with 600eV oxygen ion bombardment using an ion-to-atom ratio of 0.3 (see Figure 44 in chapter 4). This corresponds to $E=180\text{eV}$ which is manyfold greater than the ion bombardment regime in the present work, even if the low angle of ion

incidence (30°) in IAD is allowed for. The data after Martin can now account for why, in the present work, ion plating was found incapable of resorbing the bulk of the microporosity inherent to the low temperature evaporated YSZ deposits, with typical E values less than 20eV. The densification undergone in the ion plated YSZ was not quantifiable using the density measurement procedure described in chapter 6, with a typical experimental error of $\pm 15\%$.

The above considerations substantiate the experimental observation that ion plating has no significant effect on the structure of EB-PVD YSZ deposits other than some coating densification. This is because the ion bombardment regime characterised in chapter 7 is found to be incapable of resorbing the high content of porosity in EB-PVD YSZ, and that coating densification is a prerequisite for the generation of stress and peak broadening typically induced with ion bombardment. The energy delivered by an ion in a collision cascade will be preferentially expended in filling the atomic voids before creating interstitial sites for which exist a high repulsive potential barrier. In principle, such a reasoning could be extended to ion plating of TiN for which similar E values as that in ion plating of zirconia should apply. However, it is known that substrates bias voltages in the 500-2000V range can generate stresses in ion plated TiN of several gigapascals similar to the stress levels in bias-sputtered TiN⁷². This would imply that the E criterion is not the sole argument for the ineffectiveness of ion plating in YSZ, in causing peak broadening (atomic disorder) and generating internal stresses. Why should the role of ion plating in TiN be so dramatically different to that in YSZ? There are two possible arguments that are:

1- evaporated YSZ build up with an atom packing density much lower than that in evaporated TiN, thus rendering ion plating ineffective in causing atomic disorder and stress generation. Again, it is reiterated that the ionic type of bonding in zirconia may be responsible for its propensity to build up as an atomically porous network, by virtue of long range electrostatic forces promoting the onset of microcolumnar porosity (cf. Muller's modelling in chapter 4).

2- the transmitted fraction of the incident energy of bombardment (E_t) to the film lattice is greater in TiN than in YSZ. The maximum transmittable energy is a function of the relative masses of ion to target atom and decreases the more dissimilar the masses. With this argument in mind, it can be expected that Ar/N₂ ion bombardment in TiN will be more effective than Ar/O₂ ion bombardment in ZrO₂. This argument will be developed further in chapter 10.

Given the first argument, it is legitimate to expect that high deposition temperatures would in principle assist the significance of ion bombardment by virtue of an annealed lattice structure being more prone to the inducement of atomic disorder by ion bombardment ('ion peening' see chapter 4). However,

it has been emphasized earlier that the atomic layers do not build up spontaneously in a perfect manner. Therefore, the microporosity contained in the freshly deposited atomic layers can be expected to act as a buffer to the generation of bombardment induced structural defects such as interstitials. Still, ion bombardment seems to accelerate the high temperature annealing of microporosity, as suggested by the enhanced indentation resistance of the high temperature RF ion plated deposited over the gas evaporated YSZ (see Figure 124). Therefore, there should exist a temperature/ion bombardment regime for which 'ion peening' may indeed be incurred in YSZ. The fact that the indentation resistance of the DC ion plated deposits is not conclusively different to that of the gas evaporated deposits (see Figure 129) may be due to the atomic oxygen ions, used in DC ion plating, being less effective than Ar ions used in RF ion plating, due to their lower mass. This will be discussed further in chapter 10.

9 THE EROSION BEHAVIOUR OF ELECTRON BEAM PHYSICAL VAPOUR DEPOSITED THERMAL BARRIER COATINGS

The object of the work of Toriz and Tabakoff²⁹ was to rank the erosion resistance of several TBC systems and to assess the effect of changing the erosion conditions (velocity, temperature up to 815°C and particle size) on erosion rate. No description of the erosion damage undergone by these systems was given, nor was it attempted to relate erosion performance to coating structure. Previous investigators^{26,27} were interested in the link between coating process/microstructure and erosion behaviour for plasma-sprayed TBC's. To date, a published understanding of the failure mechanisms of EB-PVD TBC's under erosive wear is still lacking. This is the object of the present work to characterize the erosion behaviour of EB-PVD TBC's from a mechanism standpoint, and to give some account on the structural properties controlling the coating response to erosion wear.

This chapter contains two sections. In the first section, the erosion rate and damage morphology of the commercial EB-PVD TBC is assessed relatively to that of the plasma sprayed and bulk YPSZ systems. The response to changing the erosion conditions such as the temperature/velocity regime, the angle of particle impingement and particle type is discussed in relation to coating structure. In the second section, the erosion behaviour of the Cranfield deposits is assessed relative to that of the commercial datum (RT33) using the same high temperature test conditions. Aspects of the relationship between the structure and the response to erosion wear of EB-PVD YSZ coatings are then discussed.

9.1 RESULTS

9.1.1 Erosion rate data

9.1.1.1 Computation of particle velocities:

The results from the particle velocity computation described in Appendix 5 are given below (see Figure 149).

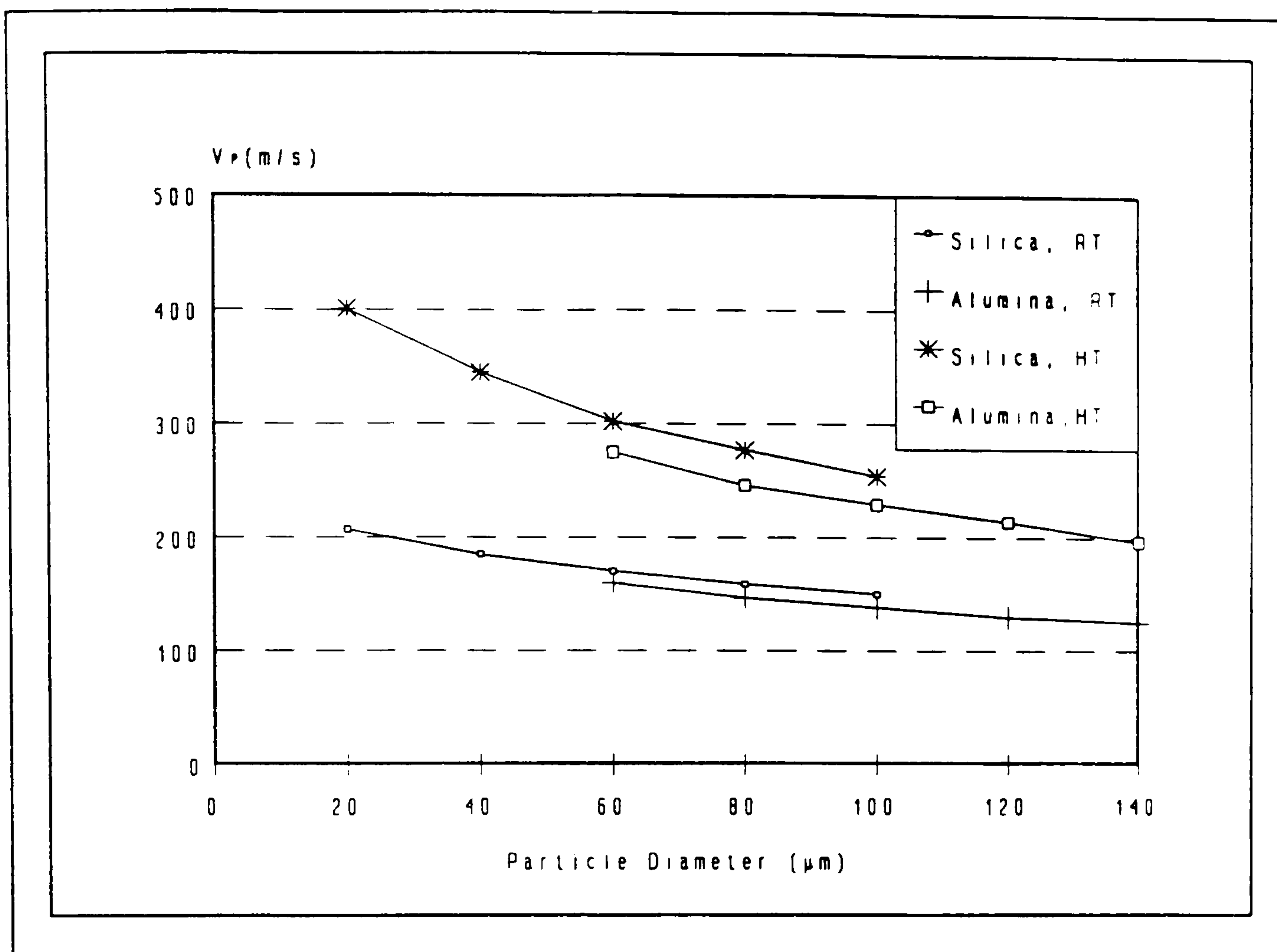


Figure 149: Predicted particle velocities at the acceleration tube exit as a function of particle size and temperature regime.

As the particle size distribution for both silica beads and alumina grit is symmetrical around the mean and that the variation of velocity with particle diameter is roughly linear, the mean particle velocity can reasonably be approximated to the velocity of the mean diameter particle (see Table XVI).

Table XVI: Particle velocities quoted in the text as a function of particle type and test temperature.

	RT	910°C
Mean silica bead velocity	170m/s	300m/s
Mean alumina grit velocity	140m/s	230m/s

9.1.1.2 Note on RT33 coated hardware

The RT33 coated paddles supplied for erosion testing were delivered in two batches spaced in time by over a year. The paddles in the early batch (batch 1) were coated on one side whereas in the later batch (batch 2) the paddles were coated on both sides. The batch 1 coatings were tested at room temperature whereas high temperature testing was performed on batch 2 coatings.

9.1.1.3 Computation of erosion rates

The erosion rates quoted in this work correspond to the slope of the line that best fits the data points of ceramic weight loss versus mass of erodent (see example Figure 150).

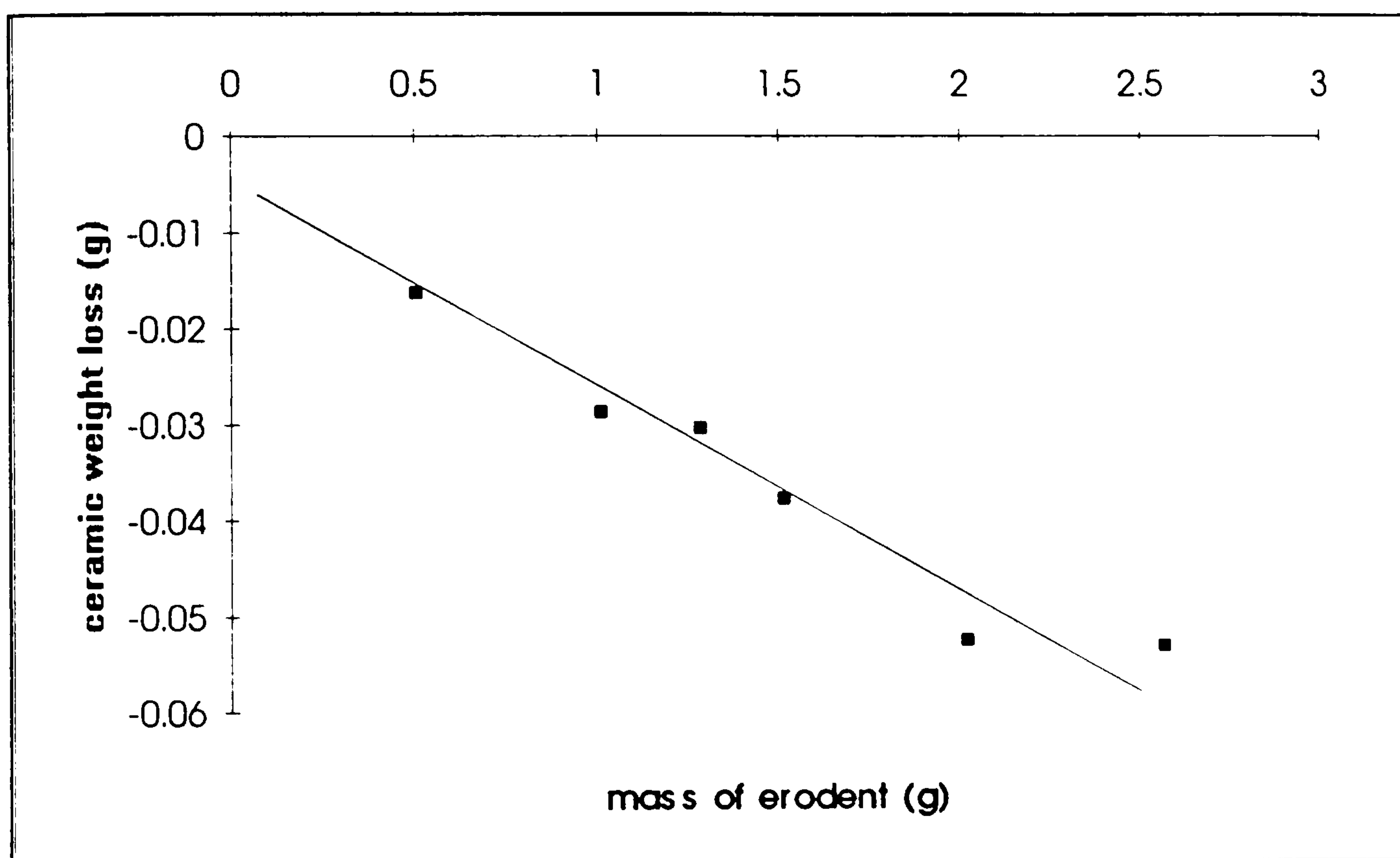


Figure 150: Plot of coating weight loss versus erodent mass for 'batch 2' RT33 tested at room temperature using silica beads (90°).

The above plot was obtained from a room temperature test of RT33 at 90° angle of particle impingement. Six data points were produced exceptionally in this instance in order to assess the scatter in erosion rate. The latter, taken as the standard error in the X-coefficient (slope), is computed from a linear regression using statistical software. From the above data, an erosion rate of $19 \pm 2.3 \text{ g/Kg}$ was obtained which represents a relative error of 12%. Due to the limited availability of testable hardware, only three to four particle loadings were used for erosion rate measurements. The erosion rate data presented in this thesis are tabulated in Appendix 8.

9.1.1.4 Effect of particle type on ceramic erosion rate:

The influence of particle properties on erosion response was assessed by using two types of particles, namely alumina grit and silica beads. The EB-PVD coating was found to erode more than bulk YPSZ but considerably less than the APS system with both types of erodent. The sensitivity of erosion rate to particle type differs quite markedly depending on the structure of the ceramic (see Figure 151). It should be borne in mind that, in the room temperature condition, the velocity of the silica beads is 20% higher than that of the alumina grit.

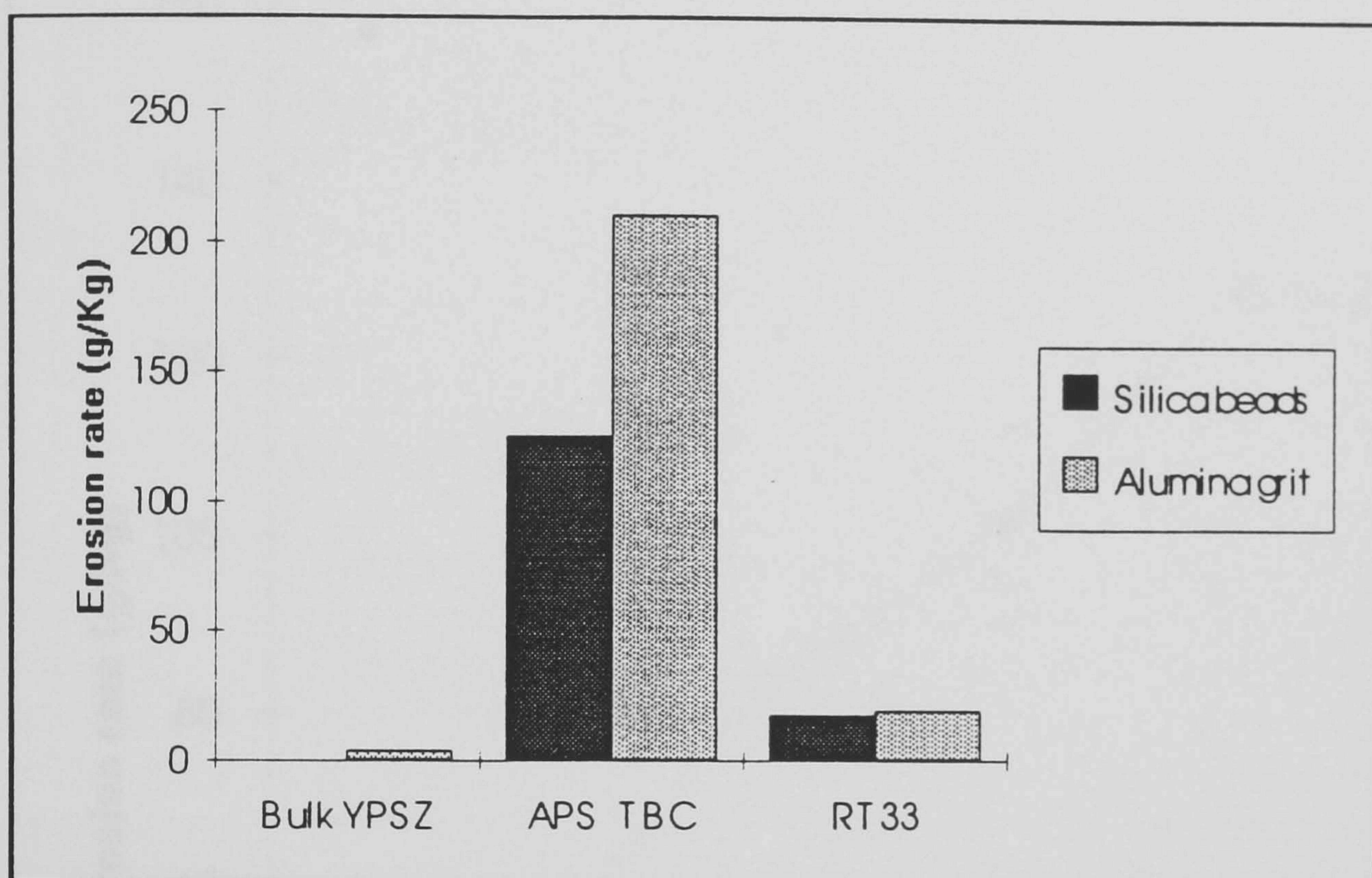


Figure 151: Dependence of erosion rate on ceramic structure and erodent type (room temperature, 90° impingement angle, 'batch 1' RT33)

The erosion rate of RT33 increased only marginally when using alumina. This is in contrast with the plasma sprayed TBC and bulk YPSZ for which the use of alumina resulted in a considerably more severe test. No weight loss could be detected for bulk YPSZ with silica beads using particle loadings up to 30 g over a specimen test area of about 1 cm².

9.1.1.5 The effect of attack angle at room temperature with silica beads:

Room temperature testing at 30°, 45°, 60°, 75° and 90° angles of impingement was carried out on RT33 and the plasma sprayed TBC system using silica beads. Four particle loadings were used on four 25x25mm testpieces cut out from the same paddle for each angle. A brittle-like response was obtained for both systems i.e. the erosion rate increased with increasing angle of particle incidence. RT33 eroded 5 to 7 times less than the APS system over the range of angles investigated (see Figure 152). It can be seen that an abnormally high erosion rate was obtained at the 45° test angle and

this was associated with the test paddle used for that angle being heavily populated with nodular defects ('flakes'). SEM evaluation showed that these defects were readily removed after impact, leaving a hole through to the bond coat and effectively increasing the coating surface area exposed to the obliquely impacting particles (see Figure 153, Figure 174). This artificial erosion enhancement from the flakes is extrinsic to the basic angular dependence of erosion rate. It was therefore chosen to disregard this data point when fitting the RT33 erosion rate data set.

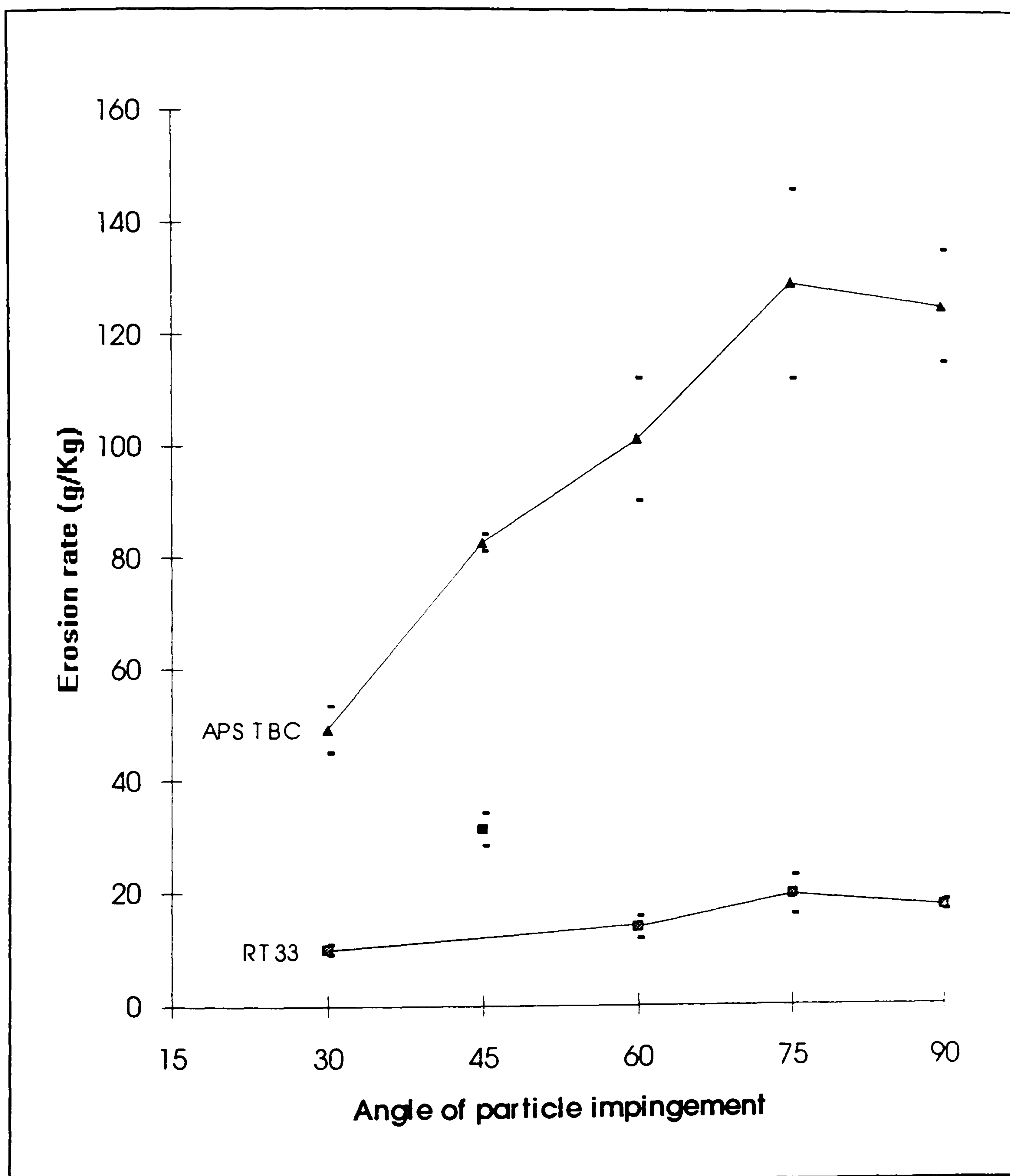


Figure 152: Erosion angular dependence of the EB-PVD TBC (■, 'batch 1' RT33) and the APS TBC (▲). Room temperature, 60µm silica beads, 190m/s.

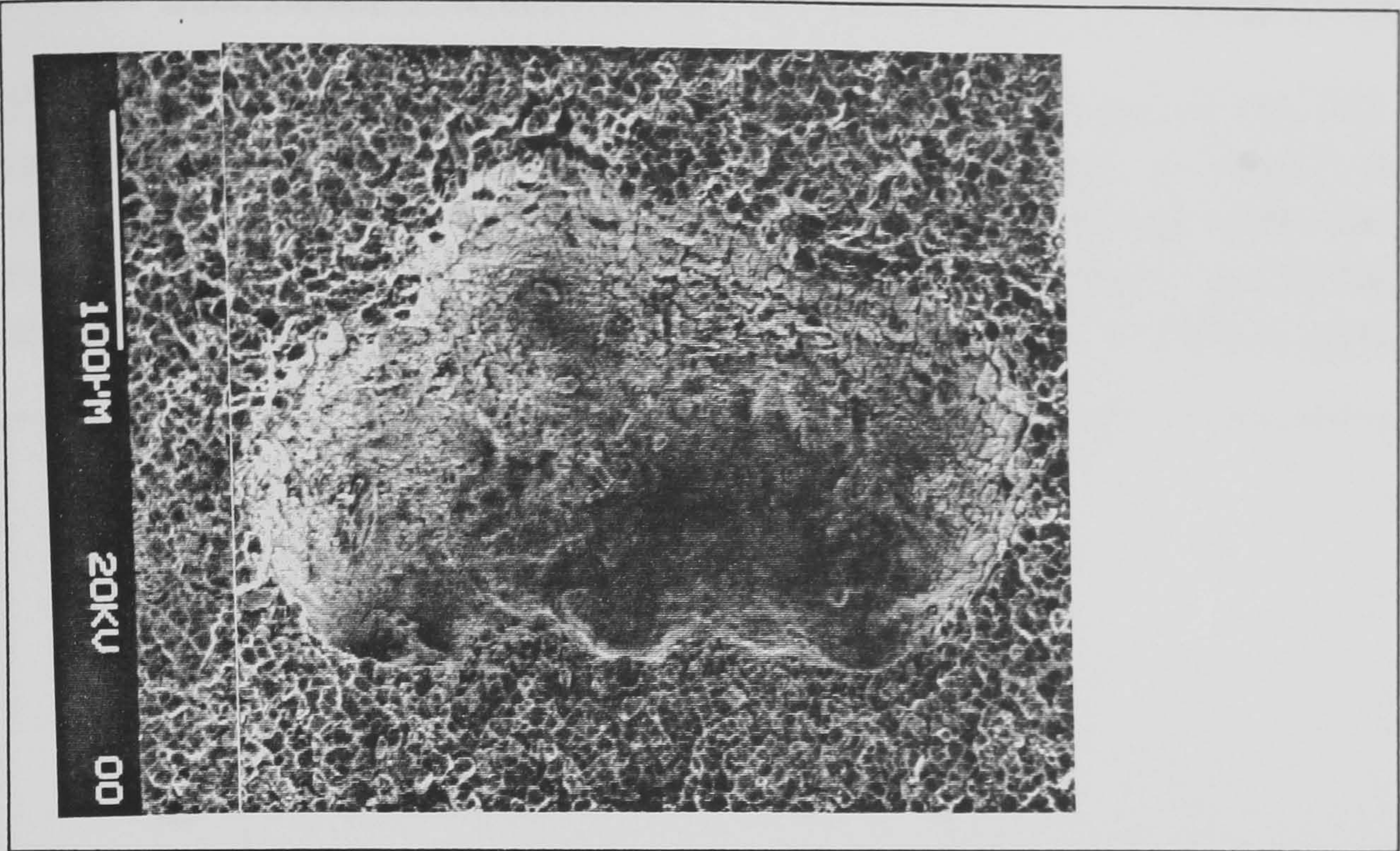


Figure 153: Pit in the commercial EB-PVD TBC formed from the particle impacts of pre-existing nodular defects (flakes) in the 45° angle test paddle.

9.1.1.6 Effect of velocity/temperature regime on erosion:

Since the gas was convectively heated, the maximum specimen temperature could only be achieved by using the maximum gas velocity available. Since the latter increases with gas temperature, the room temperature and high temperature test conditions also differed in terms of particle velocities achieved. Figure 154 shows the effect of temperature/velocity testing regime on the erosion rate of bulk YPSZ, RT33 and the APS TBC using alumina grit. It can be seen that the high temperature test conditions are significantly more severe and especially so for bulk YPSZ.

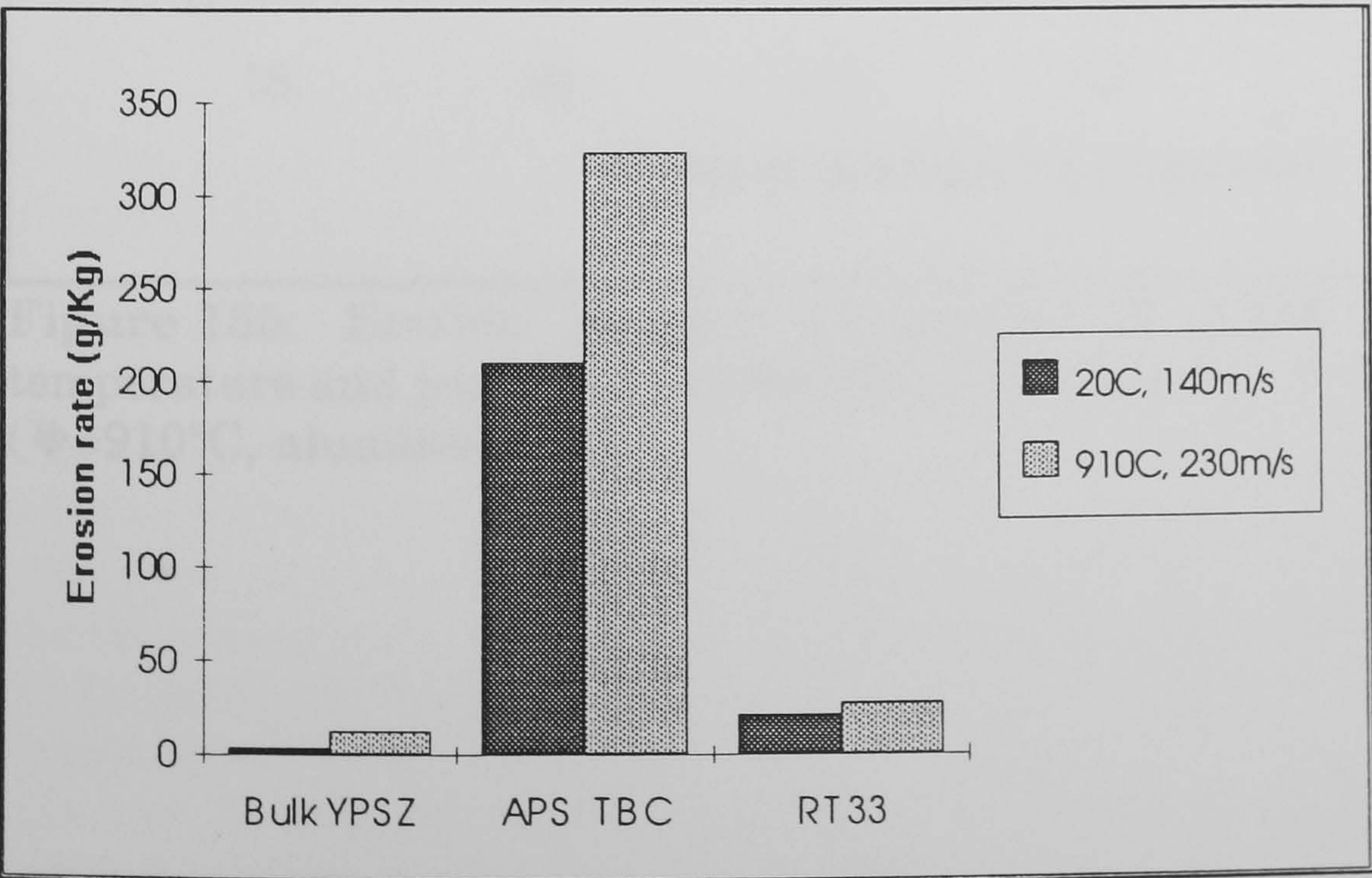


Figure 154: Effect of temperature/particle velocity regime on erosion rate using alumina grit ('batch 2' RT33).

9.1.1.7 The effect of attack angle on the high temperature erosion of RT33:

Figure 155 shows that the erosion angular dependence of the EB-PVD coating is a function of both temperature and particle type. A 'ductile-like' response was obtained at 910°C with silica beads contrasting with the 'brittle-like' response at room temperature. With angular alumina particles, the erosion at 910°C is more severe at 90° than at 30°, again a brittle type of response.

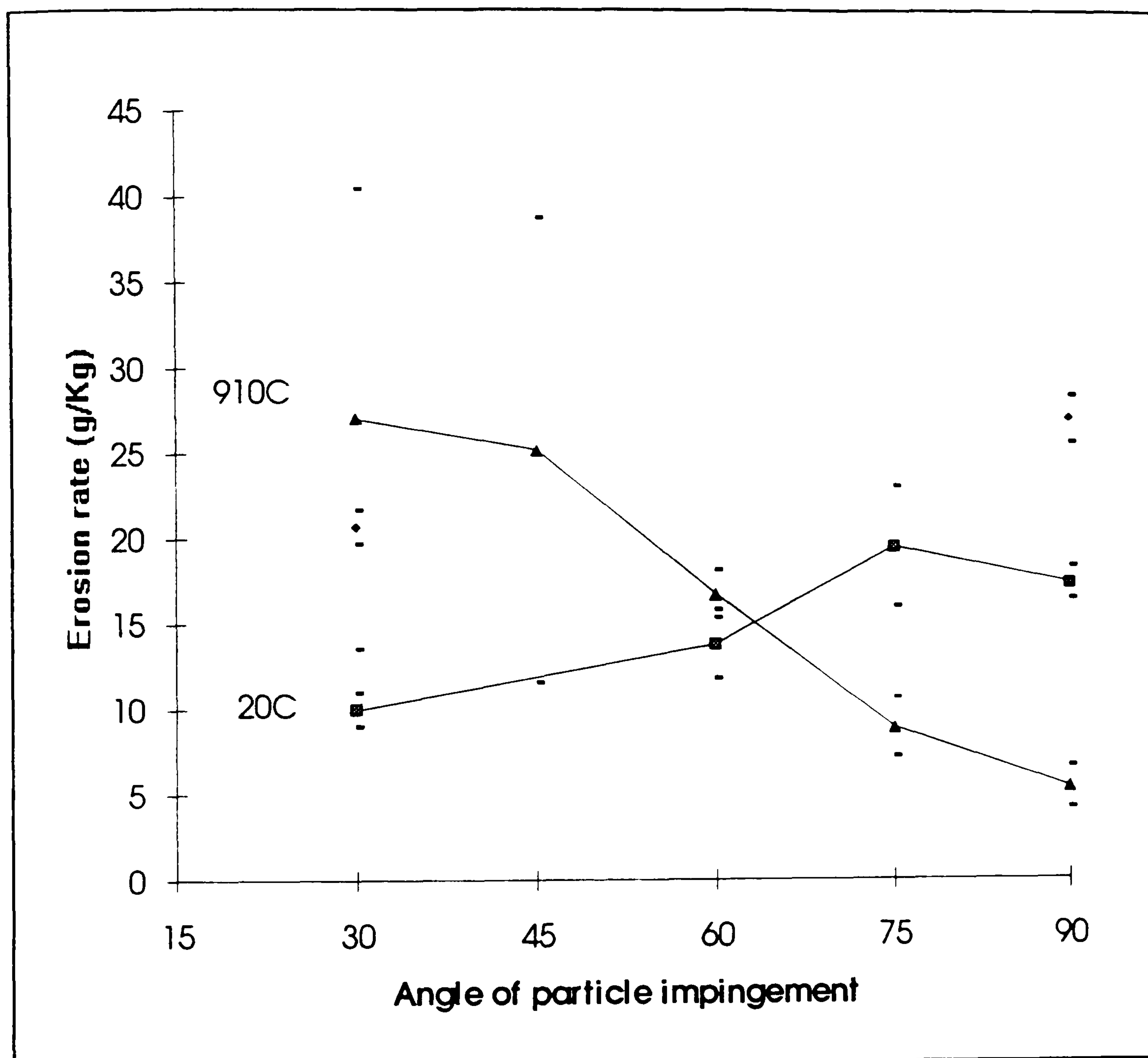


Figure 155: Erosion angular dependence of RT33 as a function of temperature and particle type (■=20°C, silica beads), (▲=910°C, silica beads), (◆=910°C, alumina grit).

9.1.2 Description of erosion damage

9.1.2.1 Bulk YPSZ:

No conclusive erosion damage could be identified on the surface of the bulk YPSZ impacted with silica beads (see Figure 156). This accounts for the fact that no weight loss could be measured. When impacted with alumina grit, the bulk ceramic behaves in a ductile manner (Figure 157). No signs of brittle fracture were found on the erosion scar. In the high temperature test, the erosion mode was found to be predominantly ductile with some signs of brittle fracture.

9.1.2.2 EB-PVD TBC

The erosion behaviour of the EB-PVD ceramic was found to be brittle at room temperature irrespective of the type of particle. The columns fracture in the coating plane to a depth of several tens of microns. The columnar structure is still recognisable from the surface micrographs. Some particle embedment could be observed with the alumina grit (Figure 158, Figure 159).

At high temperature, the brittle fracture of the column tops is replaced by a surface featuring extensive cutting and smearing (Figure 160). The columnar structure is hardly identifiable from the coating surface. The cross-section micrographs reveal typically 5 micron thick spalls (Figure 161). As these spalls are loose on the surface, they are lifted off upon shrinking of the impregnating resin during the preparation of the microsections. In the coating depth, fracturing of the columns identical to that described at room temperature is also present. The damage morphology with silica particles features some plastic deformation of the column tops similar to that with alumina grit with the exception of the cutting grooves and particle embedment (Figure 162). Smearing of the surface by the silica particles was found instead, the density of silica coverage increasing towards normal angles of impingement (Figure 163). Some brittle fracture of the columns can also be observed from the surface.

9.1.2.3 APS TBC

The erosion behaviour of the plasma sprayed ceramic was found to be purely brittle irrespective of the particle type and test temperature. The layering of the splats in the as-received condition is still identifiable after erosion from the as-eroded surface (Figure 164, Figure 165). The individual splats appear fragmented while their surface remains intact. This is consistent with the splats being removed at the original splat boundaries. No obvious erosion damage is present in the remaining coating material (Figure 166). The coating surface in the as-eroded condition is overall much rougher than for the EB-PVD TBC.

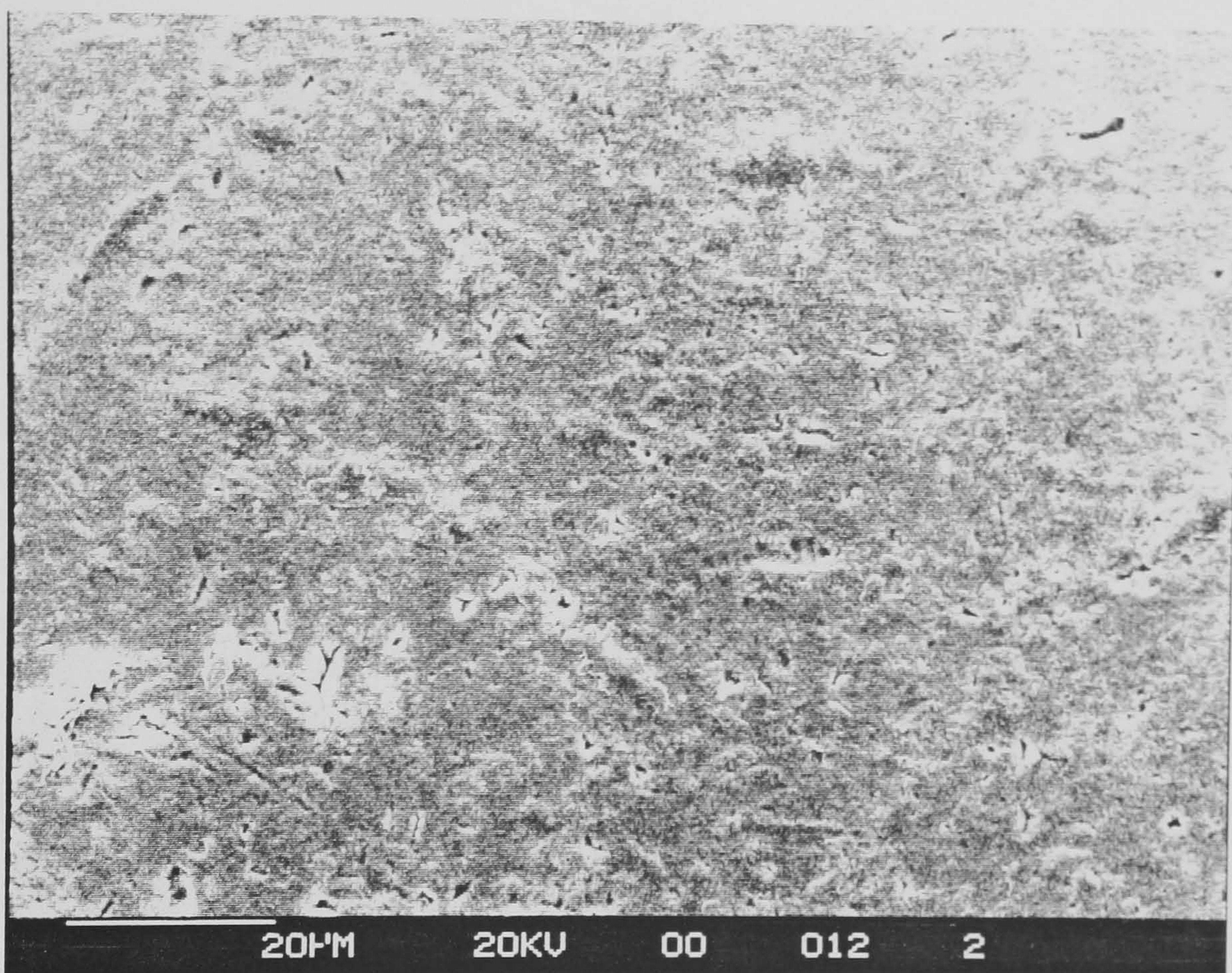


Figure 156: Surface of bulk YPSZ after room temperature erosion test with silica beads at 90° impingement angle (Secondary electron micrograph).

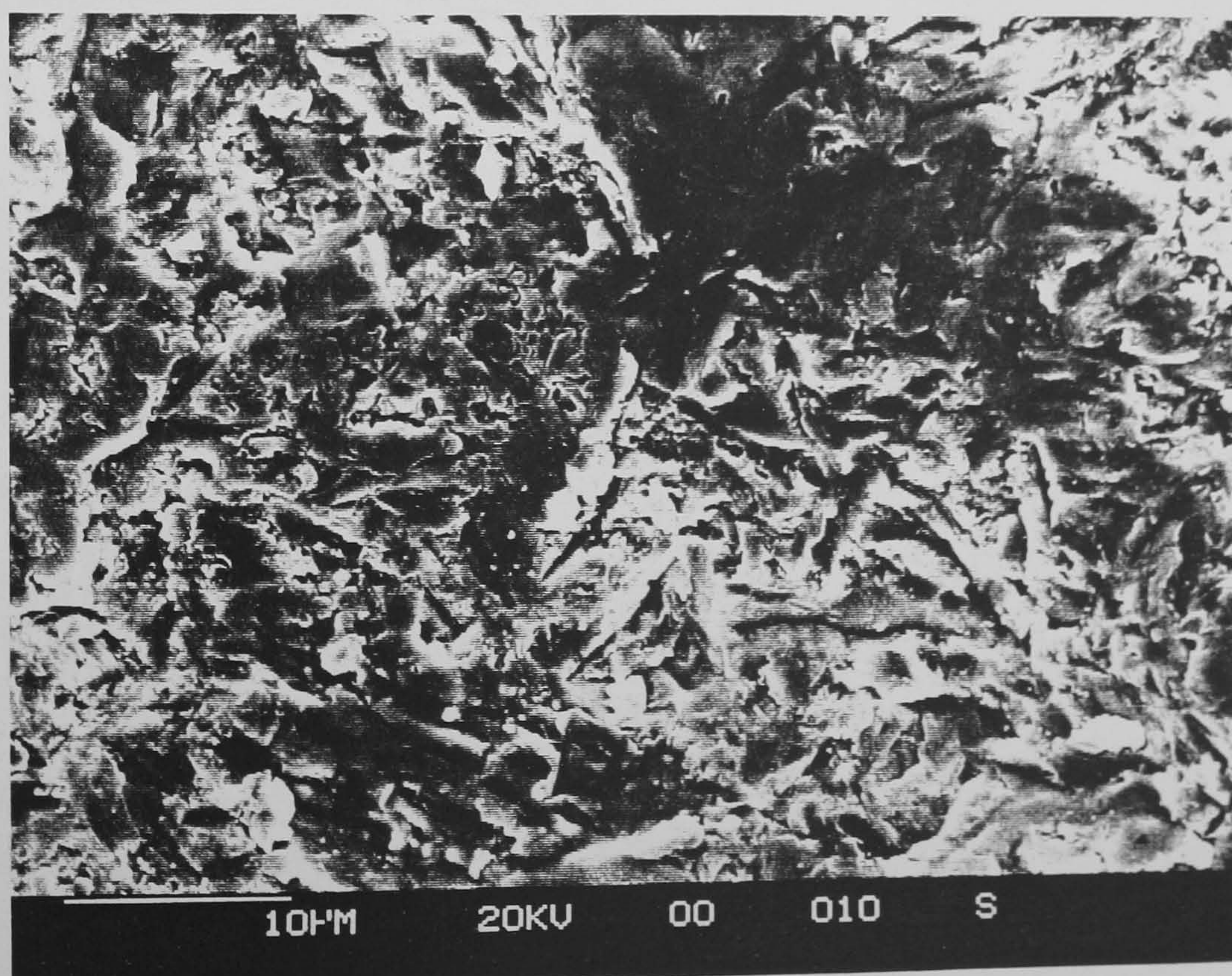


Figure 157: Surface of bulk YPSZ eroded at room temperature with alumina grit at 90° impingement angle (Secondary electron micrograph).

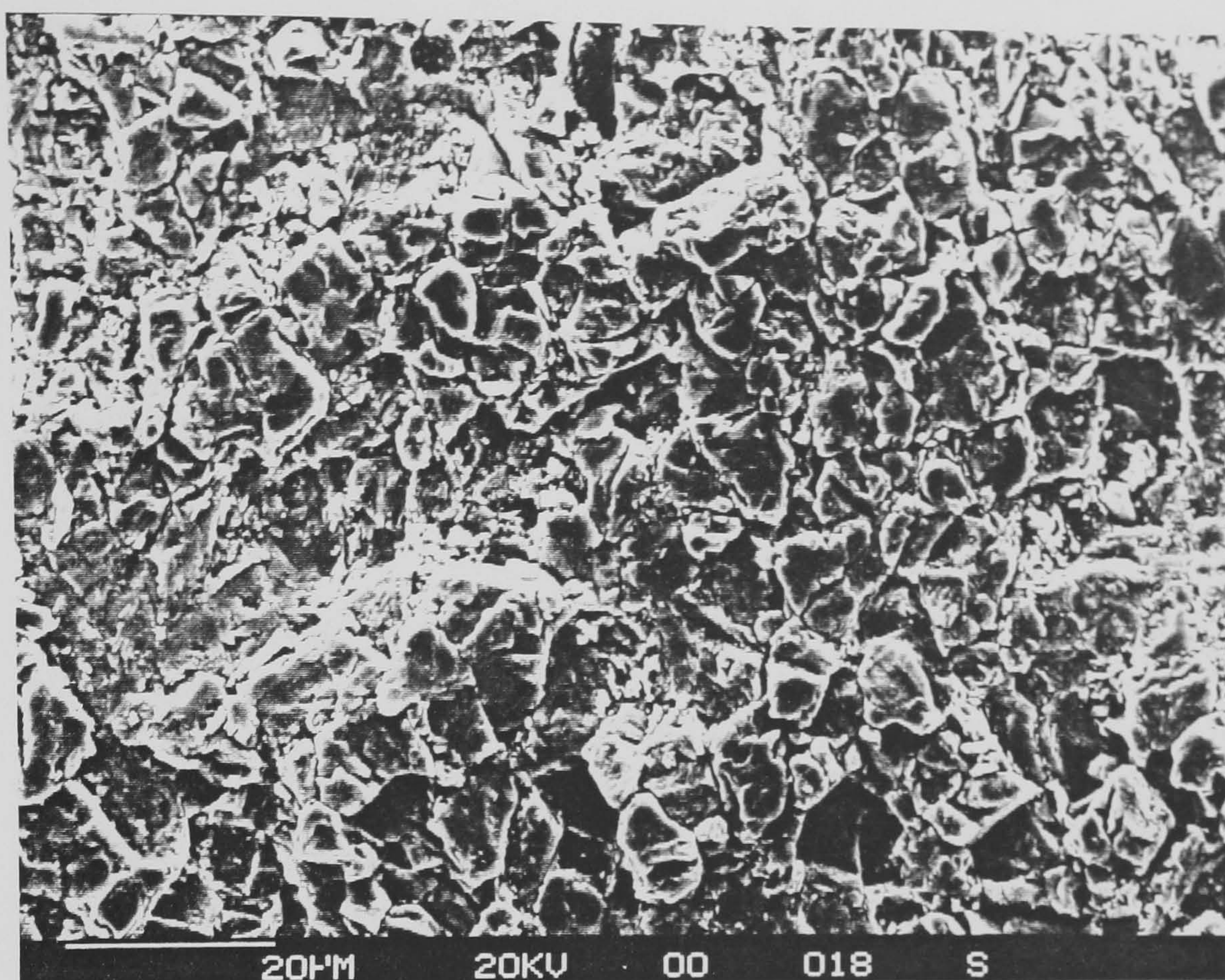


Figure 158: Surface of the EB-PVD coating eroded at room temperature with alumina grit at 90° impingement angle (Secondary electron micrograph).

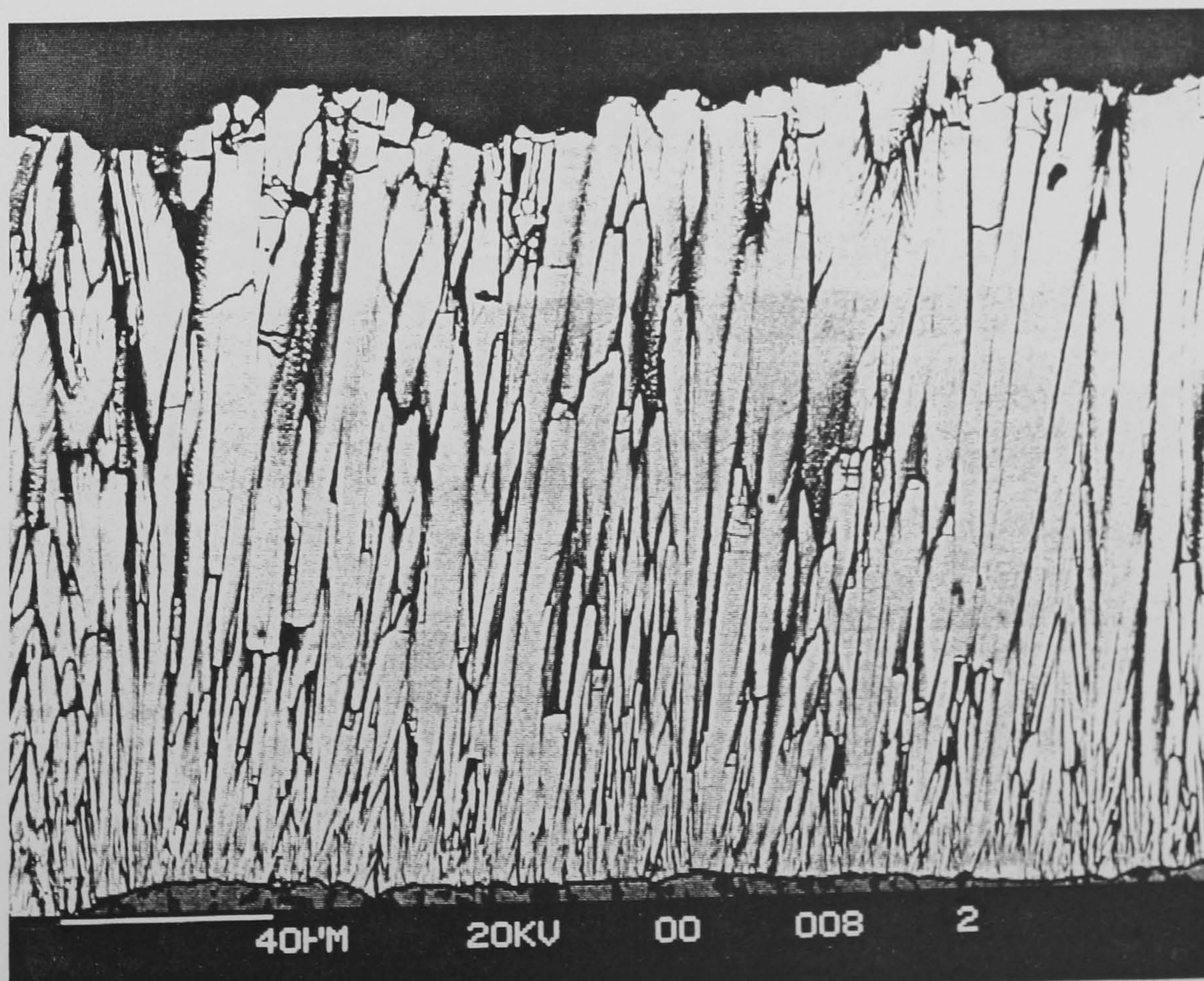


Figure 159: Cross-section of the EB-PVD coating eroded at room temperature with alumina grit at 90° impingement angle (Back-scattered electron micrograph).

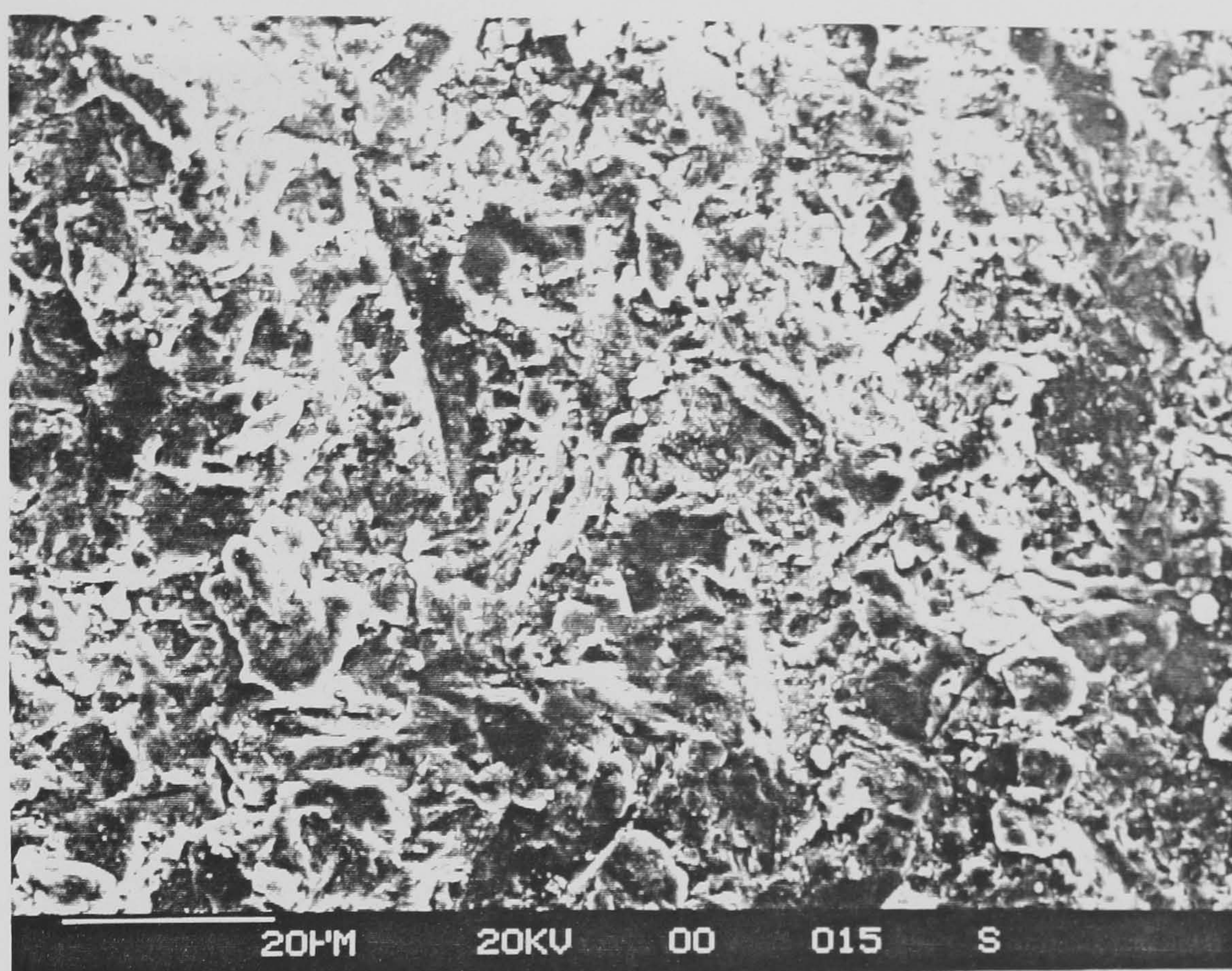


Figure 160: Surface of the EB-PVD coating eroded at 910°C with alumina grit at 90° impingement angle (Secondary electron micrograph).

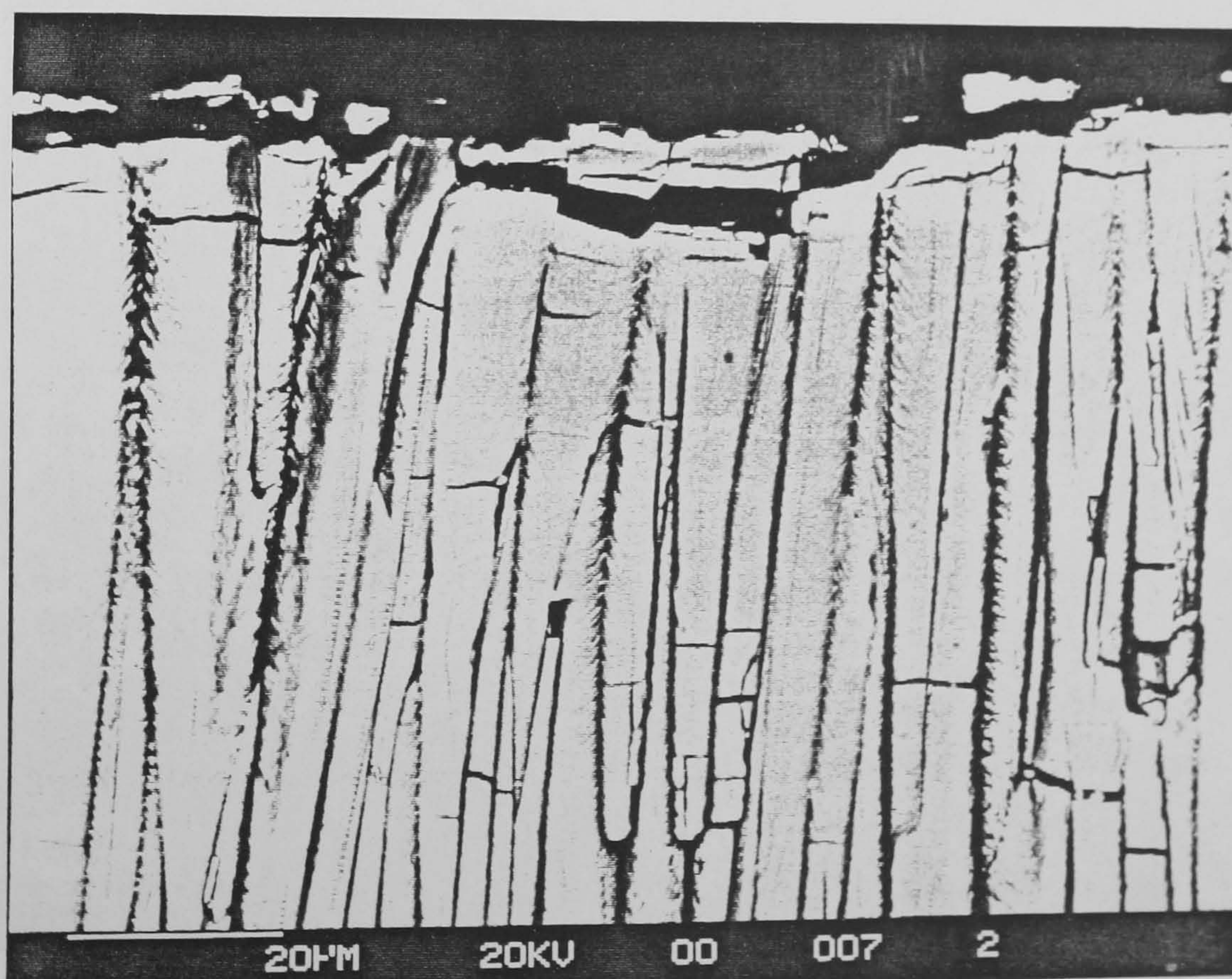


Figure 161: Cross-section of the EB-PVD coating eroded at 910°C with alumina grit at 90° impingement angle (Back-scattered electron micrograph).

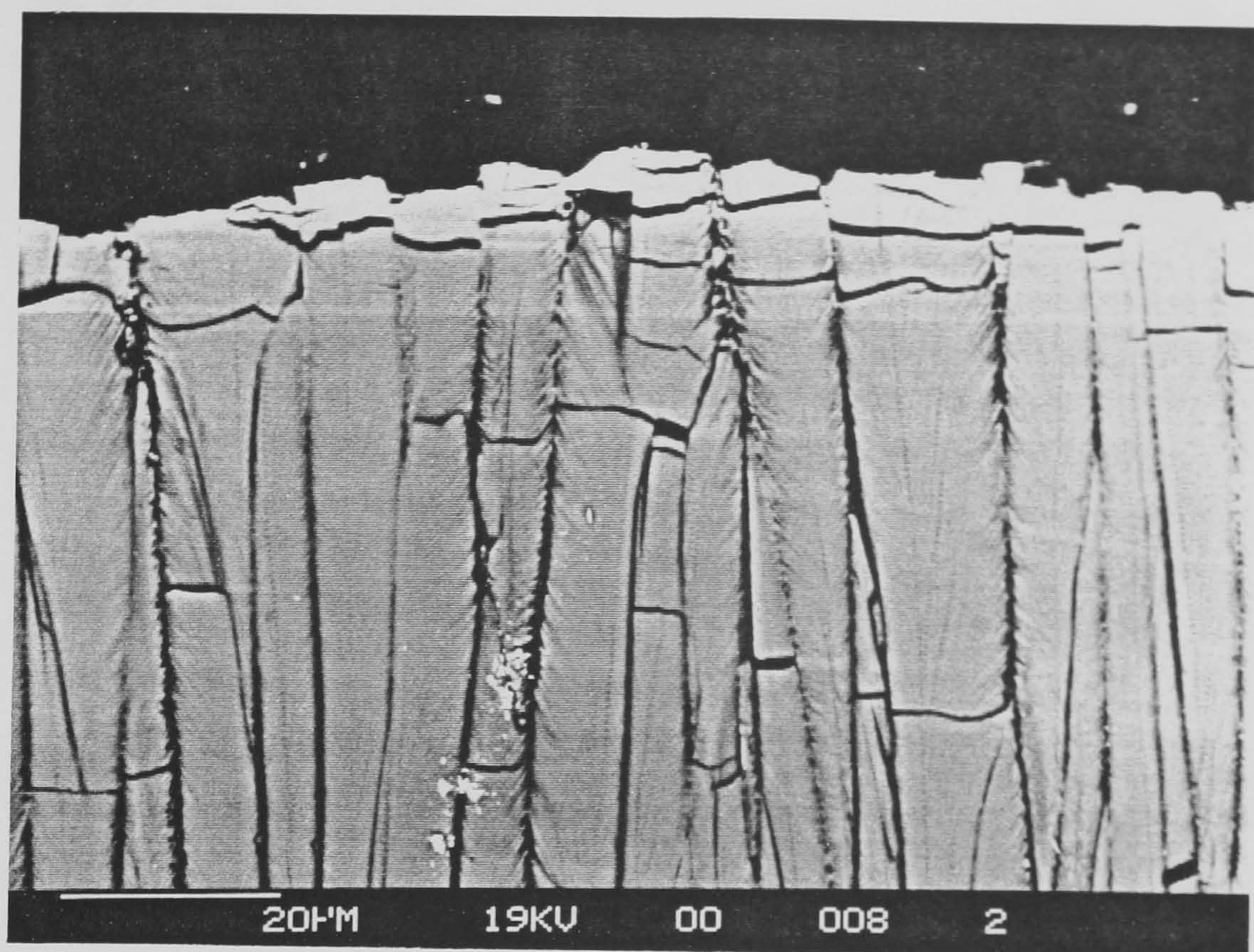


Figure 162: Cross-section of the EB-PVD coating eroded at 910°C with silica beads at 90° impingement angle (Back-scattered electron micrograph).

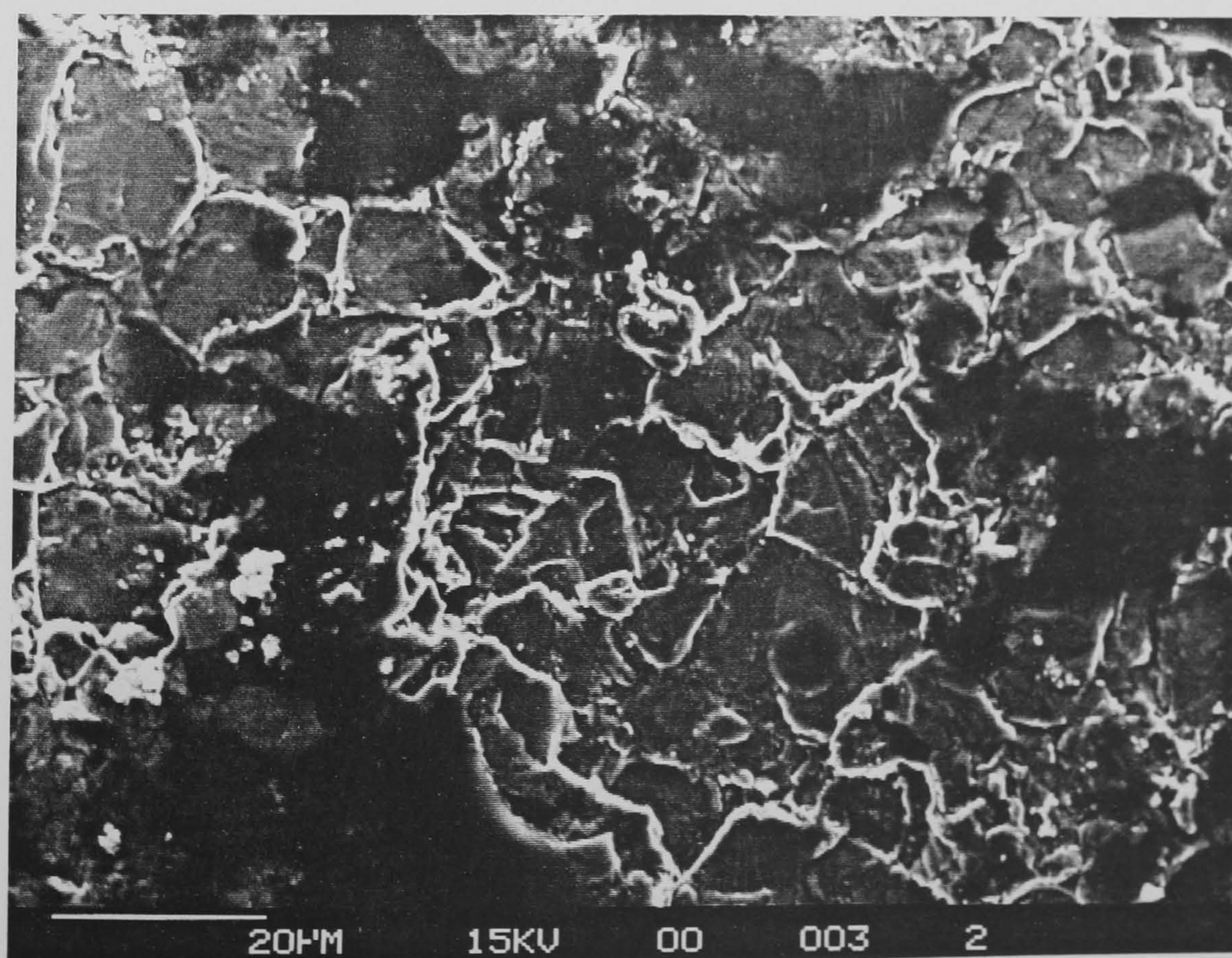


Figure 163: Surface of the EB-PVD coating eroded at 910°C with silica beads at 90° impingement angle showing smeared silica (Secondary electron micrograph).

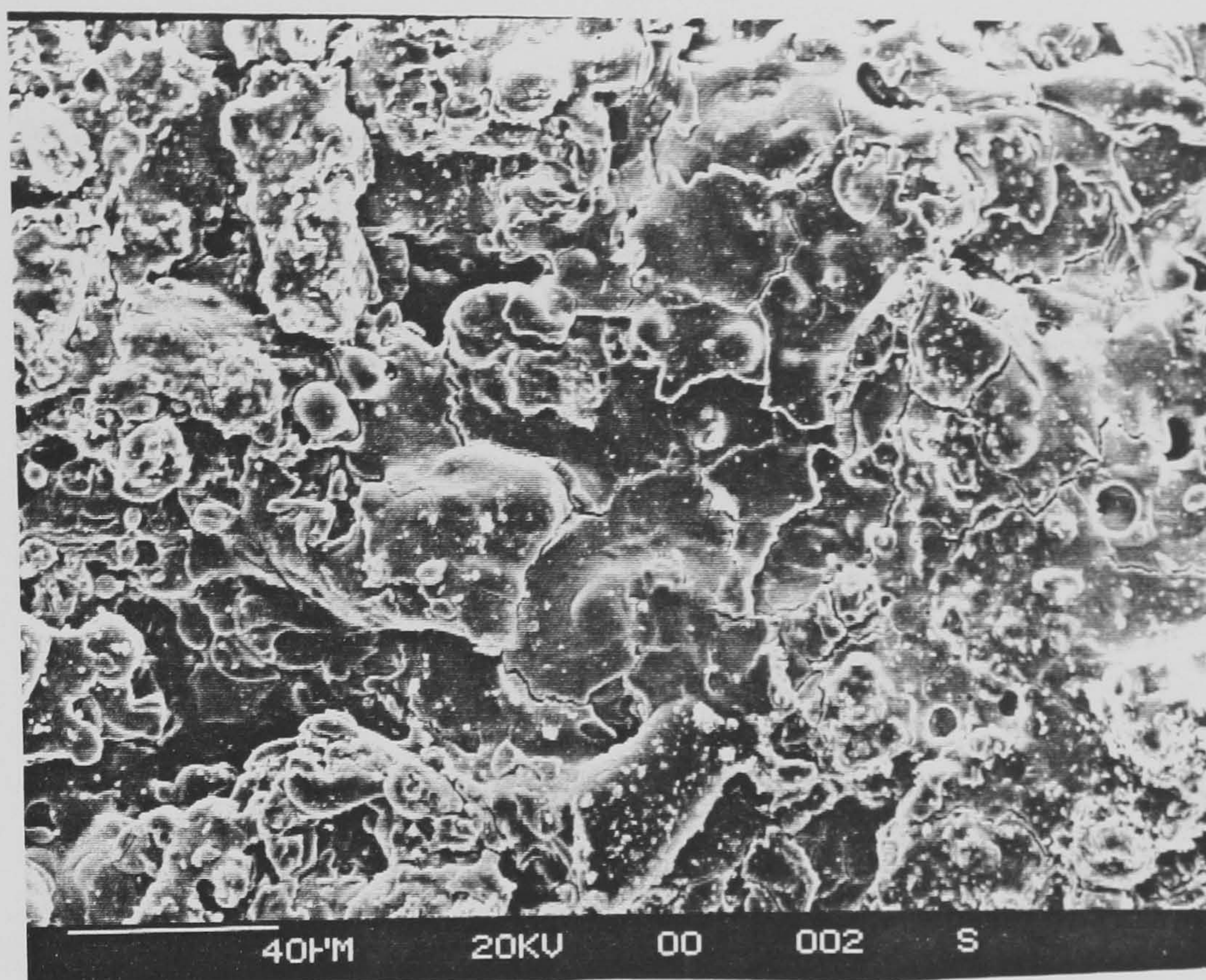


Figure 164: As-deposited surface of the APS thermal barrier coating (Secondary electron micrograph).

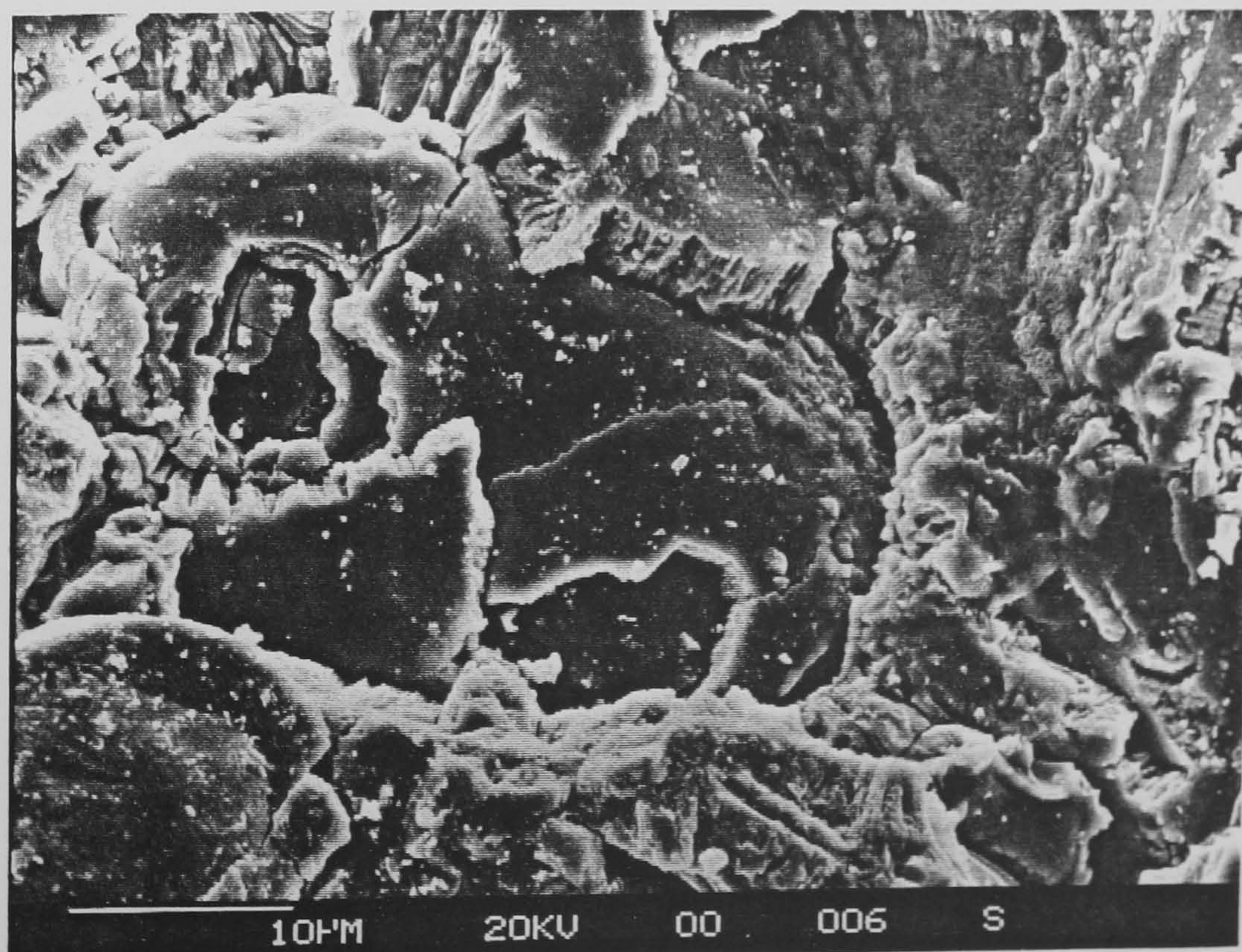


Figure 165: High magnification of the APS coating surface eroded at room temperature with alumina grit at 90° impingement angle (Secondary electron micrograph).

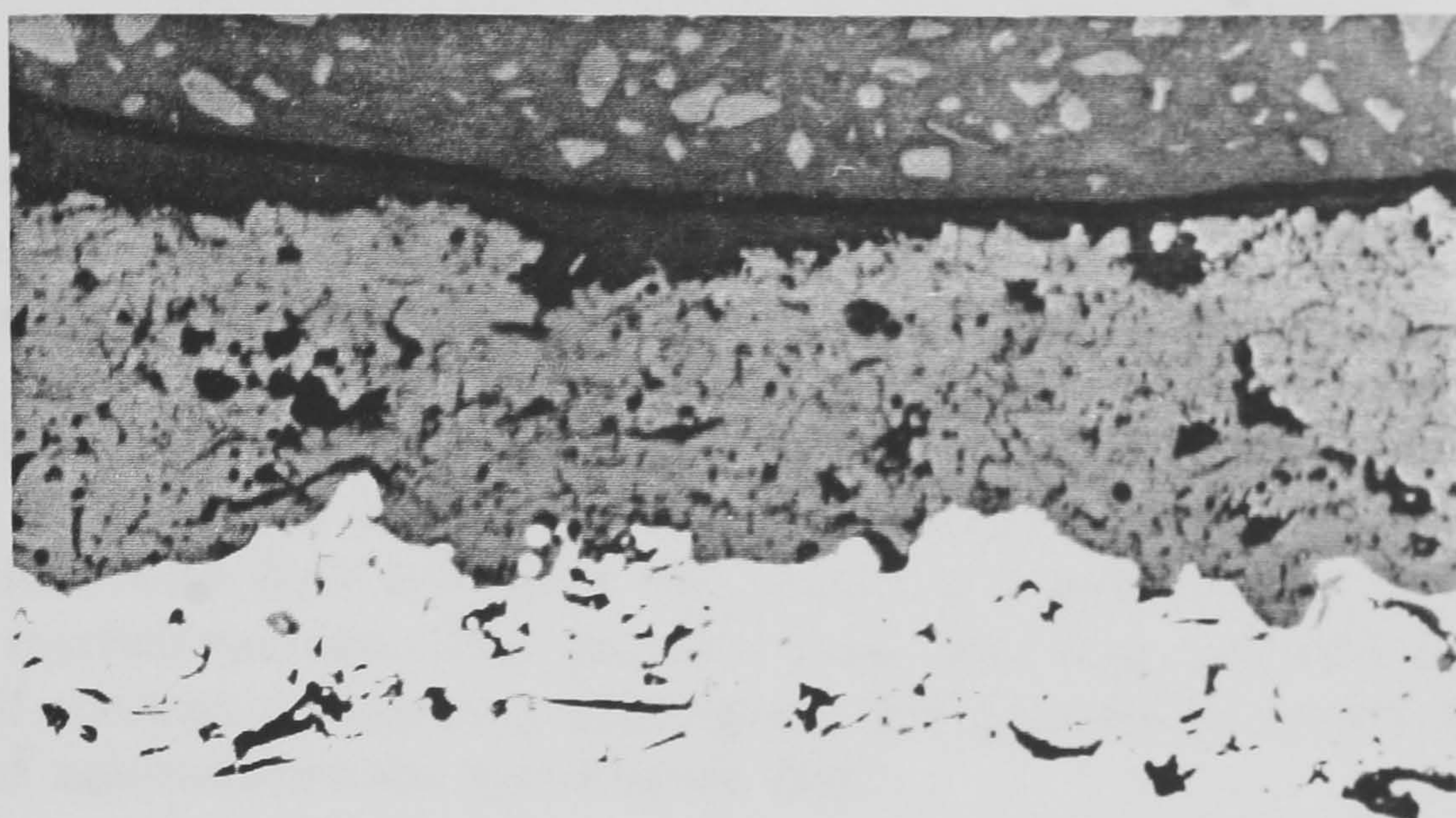


Figure 166: Cross-section of the APS coating eroded at room temperature with alumina grit at 90° impingement angle (Back-scattered electron micrograph).

9.2 DISCUSSION

9.2.1 The role of ceramic structure on erosion behaviour

The rate of material removal under erosive wear is determined by the magnitude of the stress at impact and the resilience of the material surface to erosion. Resilience to erosion means that the average material loss for a given impact stress is low.

Figure 151 is an explicit illustration of the role of microstructure on the resilience to erosion of a material. Nominally the same ceramic material can yield erosion rates that are up to two orders of magnitude apart, depending on their microstructure. The particle type also has an influence on the severity of erosion a material undergoes, the sensitivity to which is also a function of microstructure (see Figure 151).

9.2.1.1 The influence of particle properties on erosion.

In order to understand how the particle properties may affect the severity of erosion, it is worth examining their role on the impact stress since the magnitude of the latter partly determines the rate of material removal. As a particle impinges on and penetrates into the surface of a material, a stress develops. This stress may remain sufficiently low to only cause elastic deformation in which case the particle bounces off and leaves the surface undamaged. Alternatively, the stress generated may exceed the yield strength or fracture strength of the material causing plastic flow and/or cracking to occur.

The severity of a particle impact can be qualitatively assessed by considering the stress that would be attained if the system particle+surface remained elastic throughout. This can be done using Hertzian elastic analysis. The radius a of the contact area between a spherical indenter of radius r and a surface may be related to the applied load P through the Hertz equation¹⁵⁸:

$$a^3 = KPr \quad (86)$$

K is an elastic constant involving the Young's modulus E and Poisson's ratio ν of both the indenter (p) and the surface (s):

$$K = \frac{3}{4} \left(\frac{1 - \nu_p^2}{E_p} + \frac{1 - \nu_s^2}{E_s} \right) \quad (87)$$

The Hertzian analysis can be extended to impact conditions¹⁵⁹ so that the Hertz equation combined with the motion equation yields the force exerted by a spherical particle at the site of impact:

$$P = \left(\frac{5}{3}\pi\rho\right)^{\frac{3}{5}} K^{-\frac{2}{5}} (V_0^2 - V^2)^{\frac{3}{5}} r^2 \quad (88)$$

where V_0 and V are respectively the particle velocity just before impact and at a certain depth of penetration, ρ is the particle density and r its radius.

Hertzian theory predicts that a tensile stress will be induced in the surface plane at the contact radius a (Ref. 159):

$$\sigma_e = \frac{1-2\nu_s}{2\pi} \frac{P}{a^2} \quad (89)$$

This tensile stress is responsible for cracking in brittle materials (median and radial cracks). It can be expressed as a function of the particle parameters by combining equation (86) and (89):

$$\sigma_e = \frac{1-2\nu_s}{2\pi} \left(\frac{5}{3}\pi\rho\right)^{\frac{1}{5}} K^{-\frac{4}{5}} (V_0^2 - V^2)^{\frac{1}{5}} \quad (90)$$

The maximum elastic stress transmittable corresponds to $V=0$.

$$\sigma_{e,\max} = \frac{1-2\nu_s}{2\pi} \left(\frac{5}{3}\pi\rho\right)^{\frac{1}{5}} K^{-\frac{4}{5}} V_0^{\frac{2}{5}} \quad (91)$$

This maximum stress is rarely attained as in most situations it is accommodated by the onset of plastic flow and/or fracture. Although, the absolute value of the stress in equation (91) is unrealistic, it can still be contemplated as a measure of the impact severity that the material surface undergoes. Moreover, it highlights the relevant particle parameters that affect the severity of the impact. For a same particle velocity and size, it can be seen that heavy particles with a high elastic modulus are potentially more erosive than light and compliant particles. A remarkable feature of equation (91) is that the impact stress, as derived for a spherical particle, does not depend on the particle radius. This is because the impact load and the indentation area depend on the particle radius to the same extent.

Equation (91) as it stands does not account for the role of particle angularity on the impact severity. Sheldon and Finnie¹⁵⁹ adapted Hertzian theory to irregular shaped particles by defining an effective radius r' which is the radius of an equivalent spherical indenter. This radius is necessarily smaller than the radius r of the equivalent sphere of the same particle mass (see Figure 167).

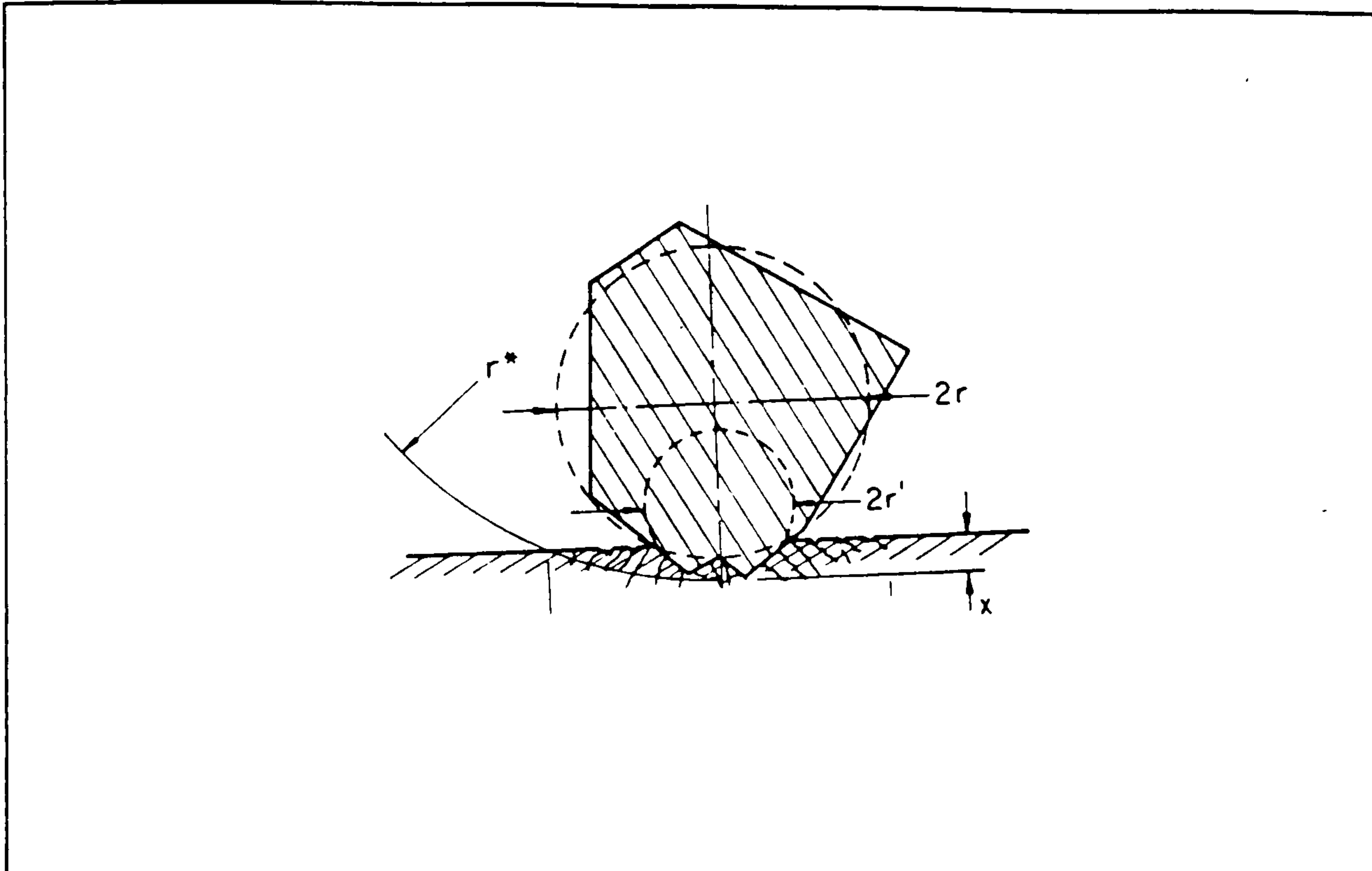


Figure 167: Effective indenting radius (r') and equivalent spherical volume radius (r) of an angular particle (Sheldon Finnie).

Using this approach, the maximum elastic stress transmittable by an angular particle can be calculated by combining equation (86) using r' with equation (89) using r :

$$\sigma_{e,angular} = \sigma_{e,spherical} \left(\frac{r}{r'} \right)^{\frac{3}{5}} \quad (92)$$

where $\sigma_{e,spherical}$ is the elastic stress derived for a spherical particle in equation (91).

Equation (92) therefore demonstrates that particle angularity enhances the impact severity. Moreover, this stress increases with particle size for a constant indenting radius r' . The effect of particle size on erosion is well documented^{30,160}. The severity of erosion was found to increase with particle size up to a point where it levels off. This levelling off does not show in equation (92).

From the above elastic analysis, four particle parameters influential to the severity of the impact have been identified. These are the elastic modulus, the density, the shape and the size of the particle. This analysis based on impact severity may not necessarily suffice to explain the dependence of erosion rate on particle properties. The type of particle may also affect the material resilience to erosion by influencing its failing mode. Particle hardness for instance is not relevant to the impact severity. It is however no less an important parameter as, after Tabor's criterion¹⁶¹, surface indentation may only occur with particles harder than the test material by over 20%. Particle shape also may influence the material failing mode, angular particles being more prone to induce plastic flow than spherical shaped particles¹⁶².

In the light of the above considerations, the properties of alumina and fused silica¹⁶³ relevant to either the impact severity or the material failing mode can be listed in order to qualitatively assess their relative erosiveness as particles (see Table XVII).

Table XVII: Properties influential to particle erosiveness.

	E(GPa)	Shape	ρ (g/cc)	size (μm)	Hardness (Kg/mm^2)	V_0 (m/s)
SiO ₂ / CaO (glass)	94	spherical	2.6	60	600 (¹⁶³)	170
Al ₂ O ₃	380 (¹⁶³)	angular	3.9 (¹⁶³)	100	1500 (¹⁶³)	140

Velocity, although not an intrinsic particle property was included in this table as it changed with the particle size.

From this table, it becomes evident that alumina grit is potentially a more erosive medium than silica beads and this concurs with the general observation in Figure 151. The velocities quoted in Table XVII are these that applied in the room temperature test. Although the silica beads are faster, their greater velocity over alumina is compensated by a lower density in the kinetic energy term of equation (91).

9.2.1.2 Ceramic structure and impact severity:

Although alumina is by enlarge a more aggressive erodent than silica, this is true to various degrees depending on the structure of the ceramic (see Figure 151). Clearly, the severity of impacts is not solely dictated by particle properties as the compliance of the target material also plays a role via the elastic constant K (see equation (87)). This constant may be termed 'compliance to impact' as it reflects on the capability of the system particle+material to cushion the impact for a given particle momentum. In the limit case where the target material has an elastic modulus much less than that of the particle, the latter becomes essentially irrelevant to the impact stress as:

$$K \propto \frac{3}{4} \frac{1 - \nu_s^2}{E_s} \quad (93)$$

As an indicator of how the erosion response may be affected by the combination of particle type with target material, the compliance term K can be calculated for each (target material, erodent) couple (see Table XVIII). The same Poisson's ratio of 0.22 for the target and particle materials was used in these calculations.

Table XVIII: K elastic constant at room temperature in GPa^{-1} using $\nu_p = \nu_s = 0.22$.

	Bulk (200GPa) ¹⁶⁶	APS (190GPa) ¹⁶⁶	EB-PVD (100GPa) ¹⁶⁶
Al ₂ O ₃ (390 GPa)	5.4x10 ⁻³	5.6x10 ⁻³	8.9x10 ⁻³
SiO ₂ (94 GPa)	11x10 ⁻³	11x10 ⁻³	14x10 ⁻³

It can be seen from this table that the EB-PVD ceramic has a compliance to impact that is significantly greater than that for the bulk and APS ceramics. This is due to its low surface modulus. Furthermore, its compliance to impact is less sensitive to the type of erodent than that of the APS and bulk zirconias. The compliance of the latter two is doubled when changing from alumina to silica whereas that of the EB-PVD ceramic is increased by some 65%. It may be added that the effective elastic modulus of the EB-PVD ceramic seen by a spherical particle might be higher than that seen by an angular particle. As with an angular indenter, the EB-PVD structure will be more inclined to accommodate the elastic stress by sideways displacement of the columns. This, to some extent will further reduce the change in K with

changing the particle type from the silica beads to the angular alumina particles.

9.2.1.3 Role of ceramic structure on resilience to erosion:

Having identified some of the parameters that affect the severity of the particle impacts, let us now examine how these impacts are dealt with by the ceramics.

Erosion of bulk YPSZ

No obvious erosion damage was found on the surface of the bulk YPSZ impacted by the silica beads (see Figure 156). This accounts for the fact that no weight loss could be measured. The tensile stress developing during impact did not exceed the fracture strength of the ceramic. The system may have behaved purely elastically or the glass beads may have shattered upon impact. In any case the ceramic was left undamaged. The angularity and hardness (1500Kg/mm^2) of the alumina grit relatively to that of the bulk YPSZ (1100Kg/mm^2) make possible the onset of plastic flow. The stress generated at impact is however insufficient to cause brittle fracture. The onset of brittle fracture in bulk ceramics require a certain depth of indentation^{159,162}. This requirement may not have been met at the particle velocities involved in the room temperature test (140m/s). At 230m/s particle velocity, some brittle fracture was found and this was in spite of the potentially enhanced plastic behaviour at 910°C.

Erosion of the EB-PVD TBC at room temperature

The apparent immunity of the bulk YPSZ to erosion damage with glass beads contrasts clearly with the brittleness exhibited by the EB-PVD ceramic structure. Extensive fragmentation of the column tops and lateral cracking in the coating depth can be observed (see Figure 158, Figure 159).

Generally, the brittle response to indentation of bulk materials features radial and median cracking orthogonally to the surface plane and lateral cracking underneath the indentation and parallel to the surface. It is the intersection of these crack planes under multiple particle impacts that cause the formation of loose ceramic debris and lead to erosion loss. The primary driver for the onset of radial and median cracking is the tensile stress (see equation (89)) developing at the periphery of the particle contact area.

Clearly, this tensile stress, used in classical Hertzian impact theory to model the erosion rate of brittle materials^{158,159,164} does not apply for EB-PVD ceramics. This is because the columns cannot transmit stress in tension since they are not bonded to each other. Therefore a more relevant stress criterion for EB-PVD ceramics is the elastic compressive stress exerted on the top of the columns during impact:

$$\sigma_{ex} = \frac{P}{\pi a^2} \quad (94)$$

This compressive stress is simply the impact force P divided by the projected indentation area. Cracking of the columns in the coating plane may occur upon relaxation of this compressive stress in the same way as lateral cracking in bulk ceramics is formed. Alternatively, the cracks may form as a result of column buckling generating a tensile stress at the inter-columnar boundary surface. Whatever the mechanism of this cracking, the important point is that the cracks are not continuous from one column to another. This is again a result of the lack of inter-columnar bonding which allow each individual column to act independently from its neighbours. Cracking therefore occurs at a height which is function of the applied stress and critical defect size in each column and is bound to the width of a column, the column boundaries acting as crack stoppers.

It is questionable how harmful the 'in-depth' fracturing of the columns can be to the coating integrity. The long column segments cannot be readily removed from the surface due to geometrical constraints. Their high aspect ratio and vertical stacking means that only pull out forces could extract them from the surface. Therefore, only surface column debris that are fractured at shallow enough depths to be removed upon impact recoil will contribute to material loss.

Schematically, the EB-PVD ceramic can be described in its eroded state as having a columnar structure where each column is made up of shorter columns stacked up one on top of the other (Figure 168).

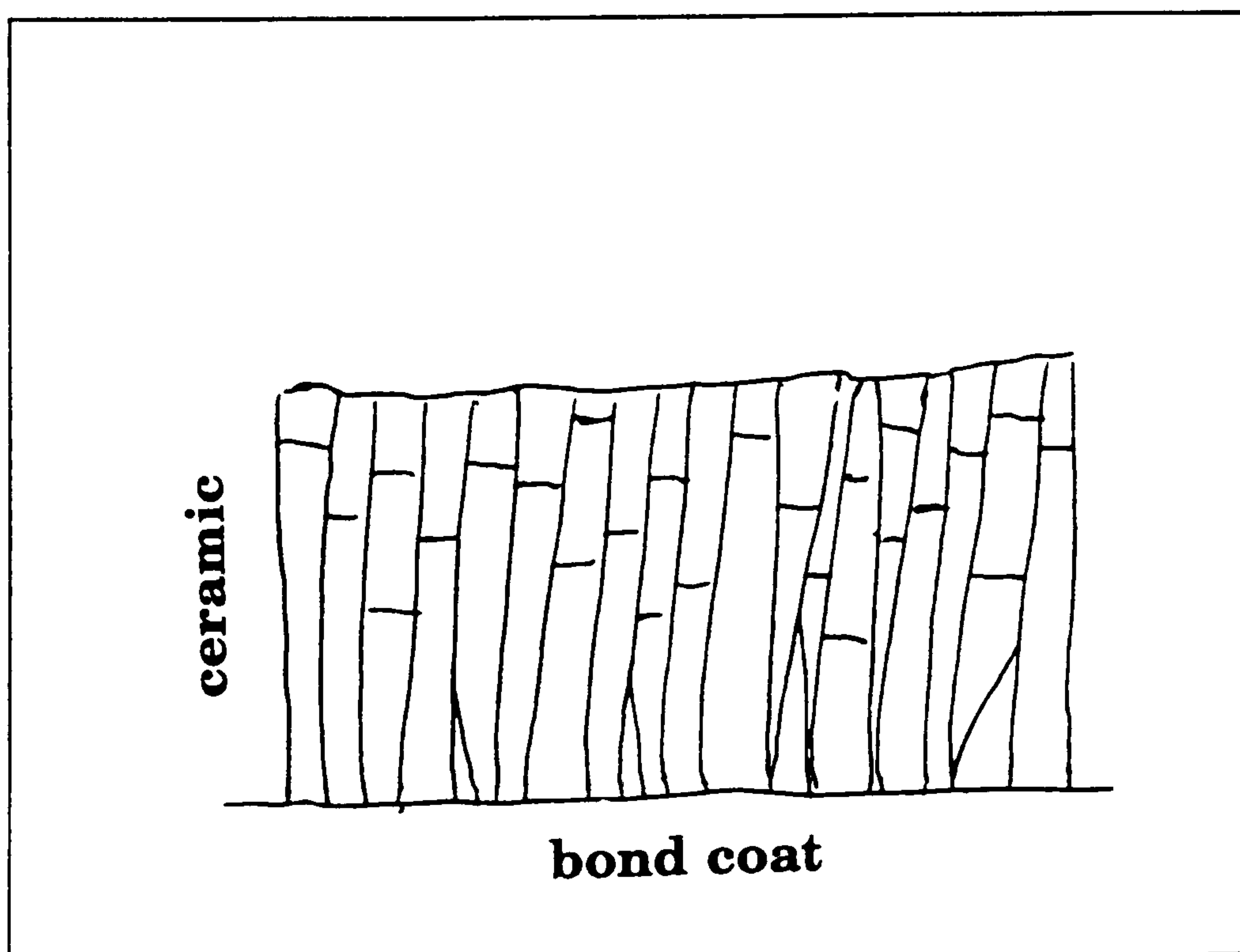


Figure 168: Schematic of the enhanced segmentation pattern of the EB-PVD coating after erosion.

This enhanced segmentation can be expected to modify the coating mechanical response to impacts. The ceramic decohesion should improve its dampening capability by effectively increasing its compliance. The coating compliance being further enhanced, the elastic term K becomes even less dependent on the particle modulus (see equation (87) and (93)).

Erosion of the APS TBC

Figure 164 and Figure 165 are surface micrographs of the APS ceramic in the as-deposited and as-eroded states. The layering of the splats in the as-received condition can be seen in Figure 164. After erosion, the splats appear more fragmented but are still identifiable as their surface remains intact. It appears that the splat fragment by through-thickness cracking and break away to reveal the surface of the underlying splats (Figure 165).

The APS ceramic structure is in its own right a segmented ceramic. The difference with the EB-PVD ceramic is that the segments are plate-like (splats), laid down horizontally and inter-locked with each other¹⁰. The interlocking of the segments means that the ceramic behaves in a cohesive manner. Therefore, the stress state developing upon impact will resemble that in bulk ceramics. The tensile stress described in equation (89) may therefore develop and trigger radial and median cracking of the splat layers. The lateral cracks are provided by default in the form of splat boundaries. Unlike the fractured columns in the EB-PVD ceramic, the loose fragments formed during erosion of the APS ceramic have no geometrical constraints to limit their loss from the surface (Figure 169). Therefore impact damage is readily accompanied by material loss.

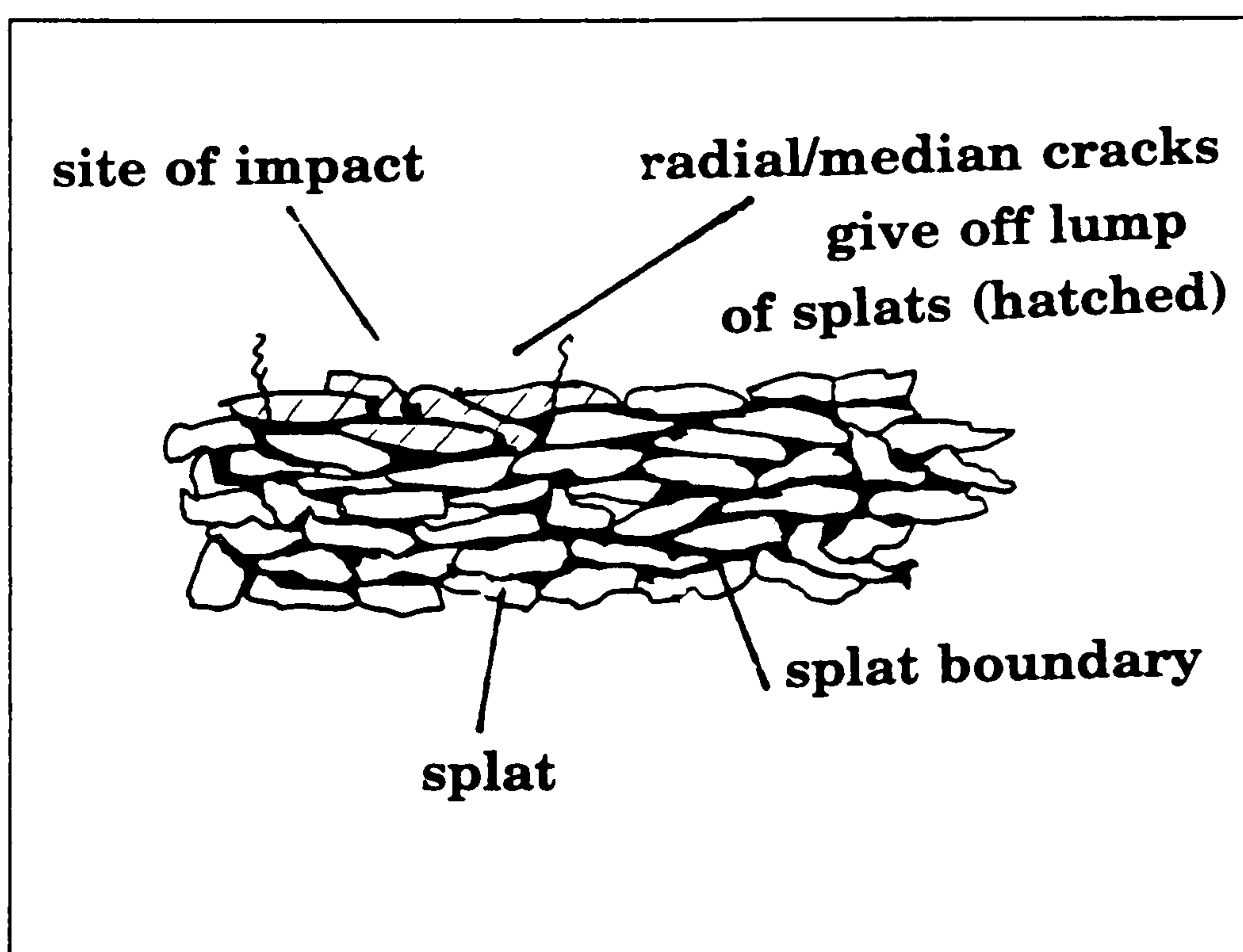


Figure 169: Schematic of the erosion process in the APS TBC.

It can be seen from Figure 166 that apart from the coating loss, the remaining material shows no sign of distress. This supports the argument that the erosion debris are efficiently removed. It also suggests that the elastic properties of the APS ceramic in the as-eroded state differ little from that in the as-deposited condition.

9.2.1.4 The effect of angle of particle impingement on erosion rate:

The erosion rate of both the APS and EB-PVD ceramics peak at normal angle of impingement (Figure 152). This is consistent with their brittle behaviour outlined above. In order to assess the relative dependence of erosion rate on angle of impingement between the two systems, the erosion rate data in Figure 152 was normalised and replotted as a function of angle (Figure 170). Relatively, the angular dependence of the erosion of the EB-PVD ceramic appears to be very similar to that of the APS ceramic, although the erosion rate of RT33 seems to be higher at glancing angles of particle impingement.

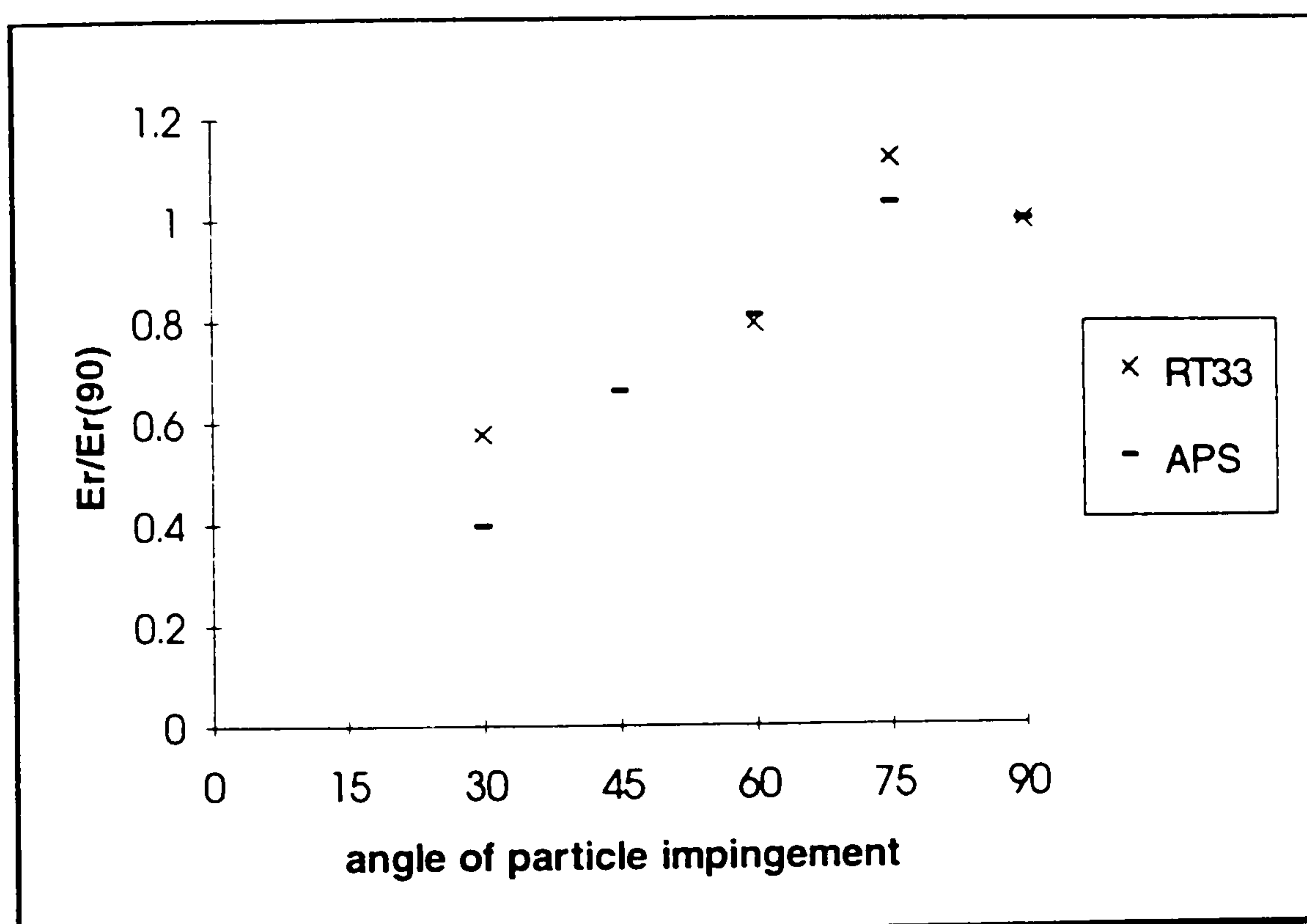


Figure 170: Normalised plot of Figure 152 (silica beads).

As the particle impinges at more glancing angles, the velocity component normal to the surface decreases. The velocity component parallel to the surface contributes to stressing the coating surface on impact via friction. The surface area of contact with the particle will be greater with the EB-PVD ceramic due to its low modulus and its low indentation resistance relatively to the APS ceramic. Based on this argument, the friction coefficient between the silica particle and the EB-PVD ceramic may be expected to be greater than with the APS structure, and this may account for the relative increase in erosion rate.

9.2.1.5 Summary comparison of erosion performance at room temperature:

The low erosion rate exhibited by the bulk YPSZ relatively to the APS and EB-PVD systems clearly demonstrates that ceramic segmentation, although necessary for thermal strain tolerance, compromises the resistance to foreign impact damage when compared to bulk YPSZ. The two coating systems behave distinctively different from the bulk YPSZ in that they exhibit brittle failure with silica beads as well as with angular alumina grit.

The segmentation pattern and elastic properties of the coatings are believed to be very influential to their erosion behaviour. The EB-PVD TBC is more erosion resistant than the APS TBC because it combines both a greater impact dampening capability and a greater impedance to the removal of surface debris. The former is due to a high compliance from the coating structural decohesion, which is further increased by the erosion damage. The latter is a result of the 'vertical' segmentation pattern of the EB-PVD as opposed to horizontal pattern for the APS system.

The coating systems behaving in a brittle manner, their erosion rate is highly dependent on the impact severity, of which the maximum transmittable stress is a measure (see equation (91)). This in turns depends on particle properties such as modulus and shape (see equation (87) and (92)). This makes alumina potentially a more erosive medium than silica beads. The erosion rate of the EB-PVD structure is however hardly affected by the particle type. This is believed to be due first to its low effective modulus overriding the contribution of that of the particle in the compliance to impact (K). Second, the potential increase in impact stress with particle angularity is compensated in the EB-PVD coating by a greater elastic compliance to indentation by an angular particle.

9.2.2 The role of temperature on the erosion of the EB-PVD TBC

9.2.2.1 High temperature erosion behaviour with alumina grit

Figure 154 compares the erosion rates of the three ceramic systems (EB-PVD, APS and bulk) obtained in the room temperature and the high temperature tests. The high temperature test conditions appear to be the more severe. The question must be addressed as to whether the increase in erosion rate is attributable to increased temperature or to greater particle velocities.

The effect of particle velocity on the erosion response of materials has been extensively studied. Erosion rate usually obeys a power law dependence on particle velocity. Data by Finnie¹⁵⁸ on a large range of ceramics including oxides yield velocity exponents between 2.5 and 4. As was pointed out in chapter 1, Toriz and Tabakoff²⁹ showed that the erosion rate of both the EB-PVD TBC and the APS TBC increased linearly with velocity in the range 0 to 305m/s at 538°C. The coatings used in their study were nominally identical to the ones tested in the present work. The EB-PVD system was purchased

from CR&T at Orangeburg (USA) and the APS system supplied by Rolls-Royce PLC at Derby (UK)²⁹. Using this data, it is possible to extrapolate what the room temperature erosion rate of the EB-PVD and APS TBC's would have been at a velocity of 230m/s.

The following assumptions were made in this extrapolation:

- the velocity exponent of 1 found for the APS and EB-PVD ceramics at 538°C with 40µm alumina grit is assumed valid at room temperature with 100µm grit.
- a velocity exponent of 2.5 is taken for the bulk YPSZ.
- the velocity threshold to cause erosion is taken as 0 for all systems.

Table XIX: Predicted relative increase in erosion rate at room temperature resulting from particle velocity change using the above assumptions.

	RT33	APS TBC	Bulk YPSZ
Er(230m/s)/Er(140m/s)	1.64	1.64	3.45

The figures in Table XIX must be compared with the increase in erosion rates obtained from the room temperature to the high temperature test conditions (see Table XX) .

Table XX: Actual ratios of 'high temperature test' to 'room temperature test' erosion rates.

	RT33	APS TBC	Bulk YPSZ
Er(HT)/Er(RT)	1.29	1.54	3.47

Using a none-zero velocity threshold in Table XIX would increase the predicted room temperature erosion rates even more. Therefore, it may confidently be concluded that temperature does not adversely affect the erosion resistance of YSZ ceramics. To the contrary, these figures would imply a reduction in erosion rate with temperature. Considering the errors in erosion rate measurements and velocity calculations, it cannot categorically be stated at this stage that this is the case.

Figure 160 and Figure 161 are surface and cross-section micrographs of the EB-PVD TBC tested at 910°C compared with that tested at room temperature. The brittle fracture of the column tops obtained at room temperature is replaced by a surface featuring extensive smearing and cutting. The columnar structure is hardly identifiable from the damage surface topography. The cross-section micrographs reveal typically 5 micron thick spalls. These spalls seem to form from the lateral cracking of plastically deformed column tops that have merged together. Brittle fracture of the columns in the coating depth identical to that described at room temperature is also present.

These observations show that the EB-PVD ceramic behaves differently at 910°C than at room temperature in that it undergoes some plastic deformation. Its erosion behaviour though cannot be described as that of a classical ductile material with the formation of extruded and forged platelets¹⁶⁵. Rather, material removal occurs by cracking underneath the plastically deformed surface region. This cracking probably is the result of lateral elastic mismatch during impact at the interface between the continuous surface layer and the bulk columnar ceramic. This mixed mode ductile/brittle behaviour mode will require more work to cause material removal than pure brittle failure as the energy delivered by the impacting particles can now be expended to some extent into plastic work. Moreover the compliance to impact of the EB-PVD ceramic is greater at elevated temperature, its Young's modulus being much lower than at room temperature (40 GPa at 900°C)¹⁶⁶. Therefore, based on the facts of plastic deformation of the coating surface and lower impact severity, the indication hinted by the figures in Table XIX and Table XX that erosion is lessened at elevated temperature is believed to be real.

9.2.2.2 High temperature erosion behaviour with silica beads

Having concluded that the erosion resistance of the EB-PVD system does not deteriorate at elevated temperature with alumina grit, the case is now re-examined with silica particles. Figure 155 compares the high temperature erosion rate data with that obtained at room temperature. This is striking in three respects.

Firstly, the overall magnitude of erosion rates obtained at 910°C and at room temperature is similar. This is in spite of the ostensibly more severe conditions in the high temperature test with particle velocities greater by

70%.

Secondly, the angular dependence of erosion rate resembles that from a ductile response i.e. an erosion peak is found in the region of 30° . This is in contrast with the results obtained with the angular alumina particles where erosion was found to be more severe at 90° than at 30° (see Figure 155).

Thirdly, the erosion rate data contains considerable scatter at glancing angles of particle impingement.

9.2.2.2.1 Significance of silica deposition on erosion rate data

Silica particles are not generally used for high temperature erosion testing because they become soft at elevated temperature⁵. This was found to be a reality in the present work as seen from the smearing of the particles (see Figure 163). However, silica particles are very representative of the particulates that may be entrained into an engine in operation. The significance of silica deposition as a source of error in the erosion rate data must be addressed. In principle, the concurrent deposition of silica with ceramic erosion should yield underestimates of erosion rates. This is true provided that the amount of deposited silica increases with time and that the rate of deposition is significant comparatively to the erosion rate.

EDAX qualitative analysis of the surface area eroded at 90° impingement angle was used in order to assess whether the deposition of silica increased with test time. The idea was that a change in the relative surface coverage by the silica would be reflected in a change in the relative SiK α and ZrK α line intensities. No conclusive evidence of silica deposition increasing with test time was found using this method. Neither was it possible to find such evidence from SEM evaluation of the surface. This would therefore indicate that the amount of deposited silica reaches a steady state after a time less than the first test duration which was 1 minute at 0.55g/min.

Would the deposition of silica increase with time, one may attempt to evaluate its significance comparatively to the erosion rate. The total mass of deposited silica can be overestimated at 0.8mg assuming total coverage of the 90° erosion scar with a 4 μ m thick layer. Assuming that this mass was deposited at a steady rate for three minutes, the deposition rate would amount to 10% of the erosion rate quoted at 90° angle of impingement. As the amount of smeared silica is greatest at 90° impingement angle, 10% represents the uppermost error introduced by the deposition of silica for all angles.

9.2.2.2.2 Erosiveness of softened silica beads

Silica glass, with the composition of sand, has its softening point¹⁶⁷ at about 500°C . Given the gas temperature, the gas velocity and the particle transit time in the acceleration tube, it was estimated theoretically that the average

60 μ m particle would have its core and its outer surface respectively below and above the softening temperature (see Appendix 9). The silica particles used in the high temperature testing can therefore be seen as having a hard core ($T < 500^{\circ}\text{C}$) overlaid by a soft and pasty outer envelope ($T > 500^{\circ}\text{C}$).

The particles superficial softness is an obvious argument to account for why the erosion rate is halved at 910°C in spite of particle velocities at 300m/s compared to 170m/s in the room temperature test. It does not however procure a straight forward explanation for the fact that erosion increases with glancing angle of impingement (see Figure 155, Figure 171). If the 'ductile-like' angular dependence was attributable to the ceramic eroding via a ductile mechanism, then such a response would be expected to be enhanced with the hard angular alumina particles. The fact that erosion is more severe at 90° with the alumina grit than at 30° precludes such an hypothesis.

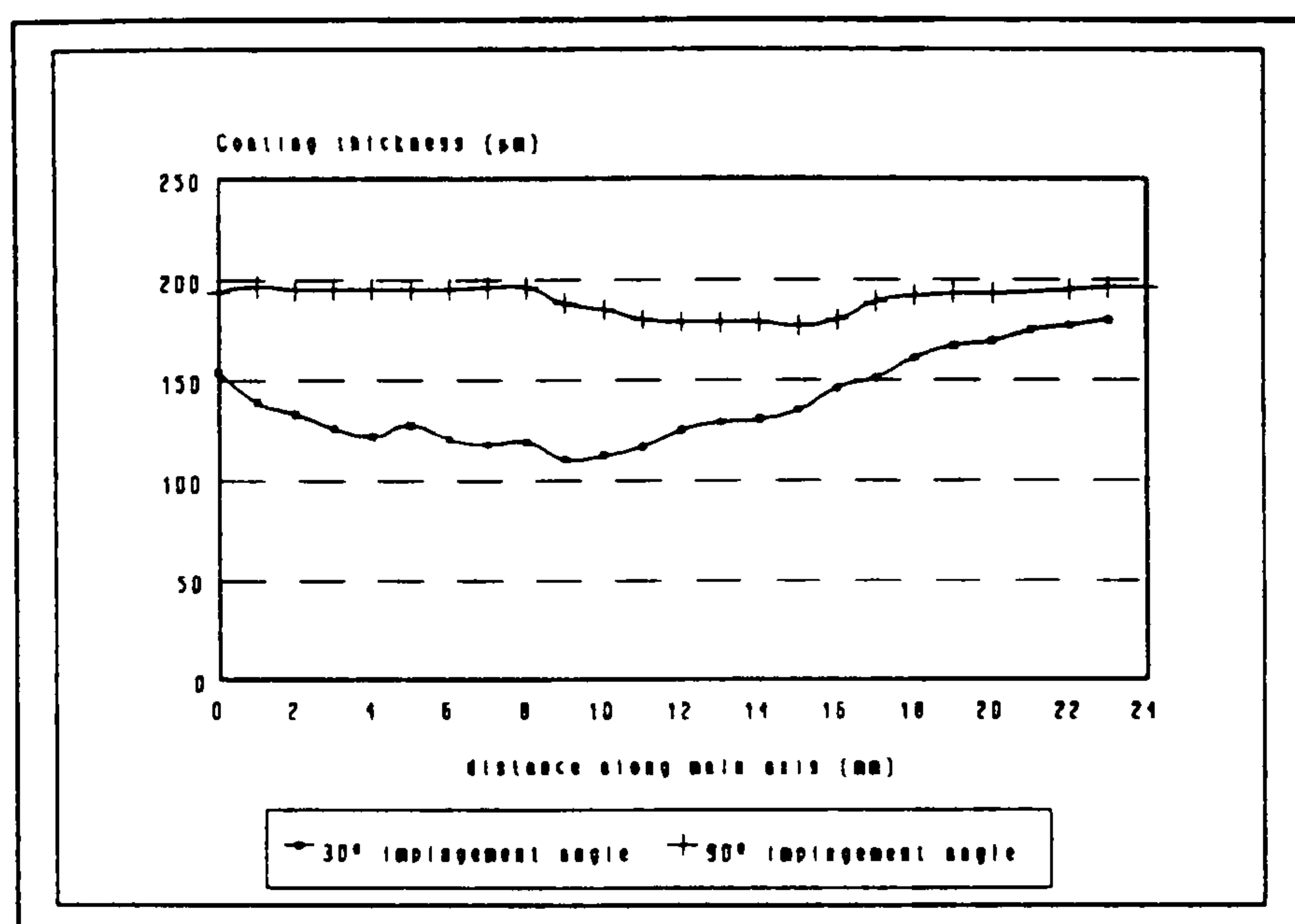


Figure 171: Depth profile of erosion scars obtained at 30° and 90° impingement angles after 0.55g particle loading of silica beads at 910°C .

Careful examination of the testpieces revealed that the erosion damage obtained at 30° angle of impingement appeared overall more brittle than that at 90° . This is because the plastically deformed surface region, characteristic of the high temperature erosion damage was sometimes missing (see Figure 172), following these 30° impacts. The removal of this surface damage region at 30° accounts for the high observed erosion rate at this angle.

With the alumina grit, smearing of the column tops was present both at 30° and 90° impingement angles. There is no obvious reason why the ceramic should behave in a more brittle manner at 30° than at 90° with the silica beads. It may therefore be argued that the plastically deformed surface region did form at 30° but was removed during the erosion process. It was seen that with alumina grit, material removal occurred by the formation of spalls formed due to the lateral cracking below the plastically deformed surface (see 9.2.2.1). It is believed that with the silica beads, the removal of these spalls

is more efficient at glancing than at normal angles of impingement.

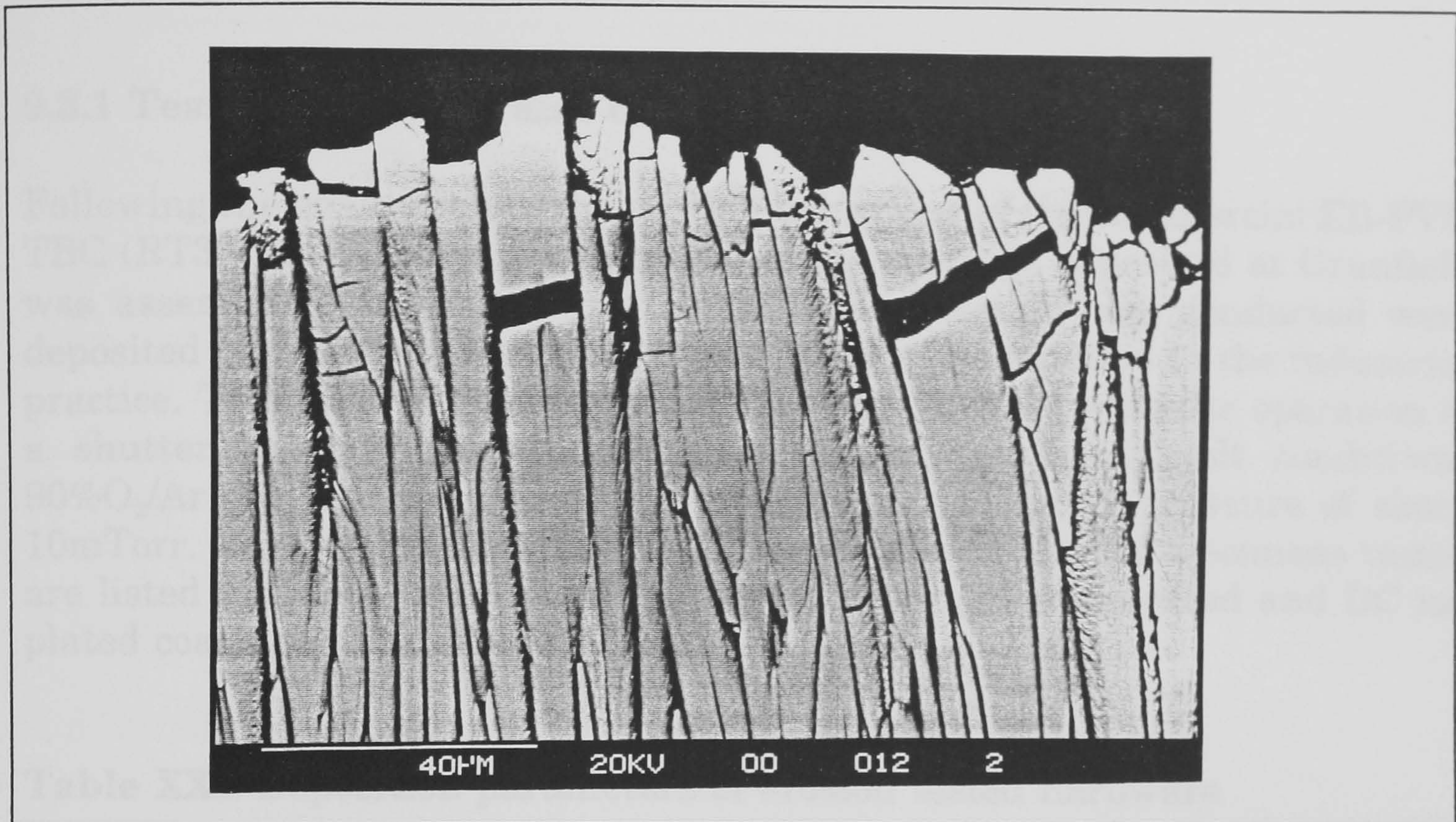


Figure 172: Cross section of the EB-PVD TBC eroded at 910°C with silica beads at 30° angle of impingement (Back-scattered electron micrograph).

Due to their pastiness, the beads will transmit a shear stress as well as a normal stress upon impact and peel off the spalls from the surface before bouncing off (this is illustrated schematically in Figure 173). Therefore, the erosive nature of the silica beads at low angles lies not only in their ability to create surface debris but also in their effectiveness to remove these debris. At glancing angles, the pasty particles 'clean' the coating surface of the loose ceramic debris thus exposing ever fresh ceramic material to further erosion damage. At 90° impingement, the ceramic debris are not so readily removed from the surface and contribute with the deposited silica to dampening of the particle impacts.

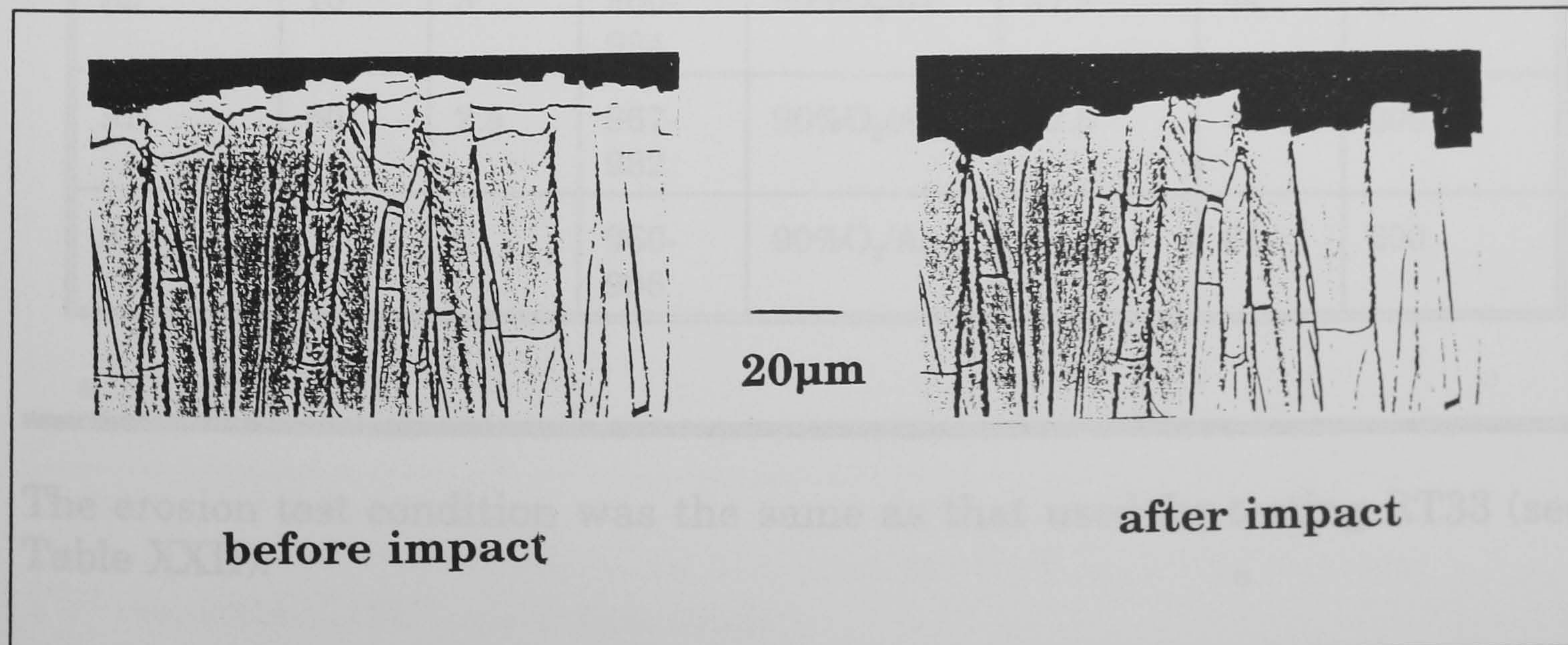


Figure 173: Erosiveness of pasty silica particles at glancing angles of impingement.

9.3 HIGH TEMPERATURE EROSION BEHAVIOUR OF DEVELOPMENT EB-PVD TBC'S

9.3.1 Tested hardware and erosion test conditions

Following the evaluation of the erosion behaviour of the commercial EB-PVD TBC (RT33), the erosion performance of the coatings deposited at Cranfield was assessed. The systems on which erosion testing was conducted were deposited under conditions aimed to be as close as possible to the industrial practice. This involved the use of the vacuum furnace with the operation of a shutter so that deposition started under stabilised melt conditions. 90%O₂/Ar gas was bled inside the furnace at a chamber pressure of about 10mTorr. The designation and deposition details of the six specimens tested are listed in Table XXI. Both high temperature gas evaporated and DC ion plated coatings were evaluated.

Table XXI: Deposition parameters of erosion tested hardware

Designation	Run time	Bias (kV)	T(°C)	Gas	I(mA) at 1000°C	Gun %	thick (µm)
K	30	2.5	1000-1009	Ar	14	41	40
N	26	0	1000-1024	90%O ₂ /Ar	0	47	44
AG	10	3	966-997	90%O ₂ /Ar	45	43	60
AH	10	1.75	960-997	90%O ₂ /Ar	21.75	48	45
AJ	10	3	960-994	90%O ₂ /Ar	37.5	44	40
AN	60	2.5	967-982	90%O ₂ /Ar	22.5	47	200
AO	70	0	960-996	90%O ₂ /Ar	0	64	200

The erosion test condition was the same as that used for testing RT33 (see Table XXII).

Table XXII: Erosion test conditions of Cranfield systems

Particle type	Al ₂ O ₃ (100μm)
Specimen temperature:	910°C
Angle of particle impingement	90°,30°
Particle velocity	230m/s

9.3.2 Results

9.3.2.1 Erosion rate data

Overall, the Cranfield coatings were found to erode at a lower rate than the commercial datum 'RT33' by a factor of 2 to 3 irrespective of the ion plating regime (see Figure 153, Figure 174 and Figure 175).

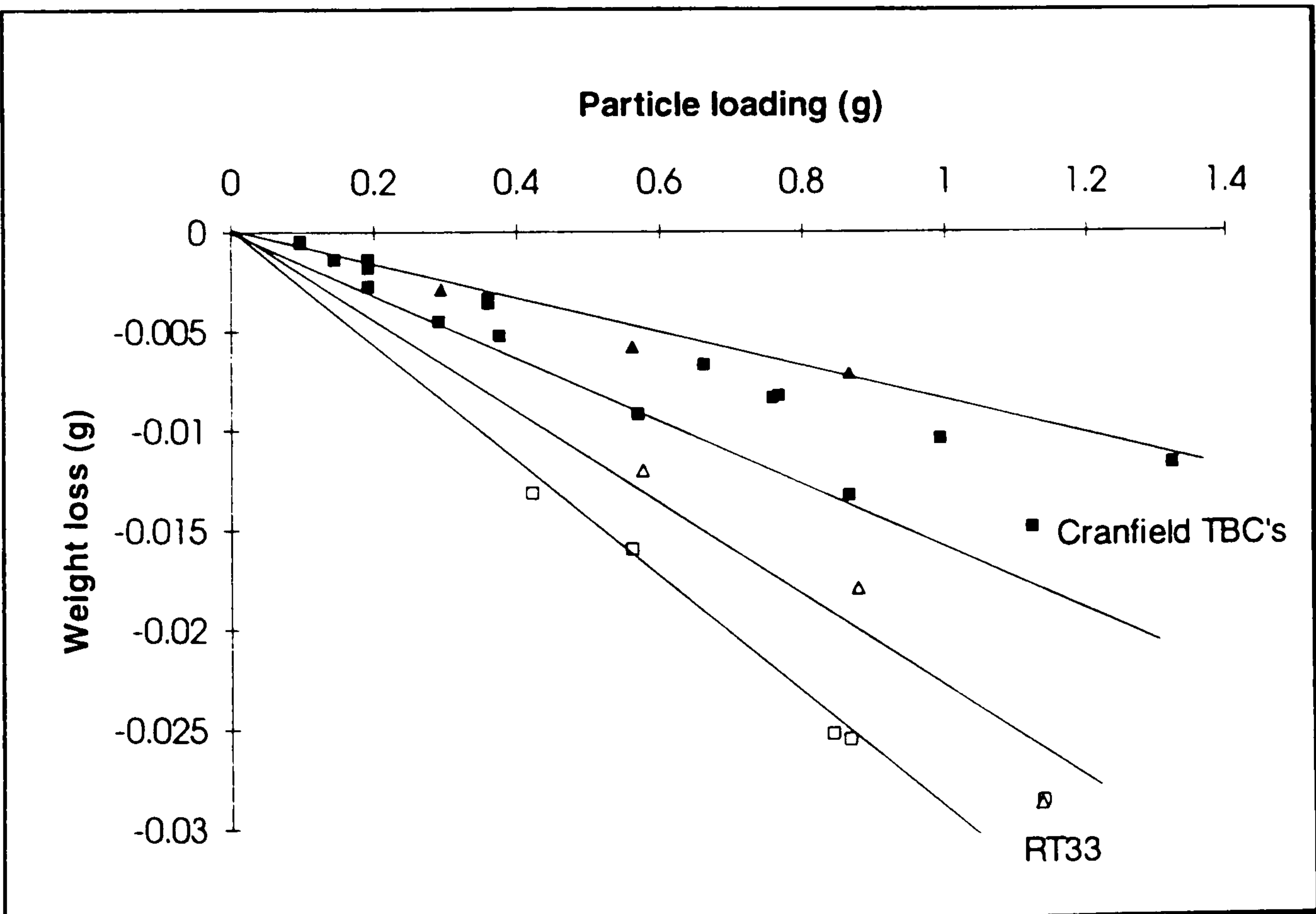


Figure 174: Comparison of erosion weight loss versus particle loading between the datum RT33 and the Cranfield high temperature YSZ deposits (□:90°, Δ:30° test angle).

For all coatings evaluated at both 90° and 30° angles of particle impingement, the erosion rate was found to be the greater under normal impact conditions

(see Figure 175).

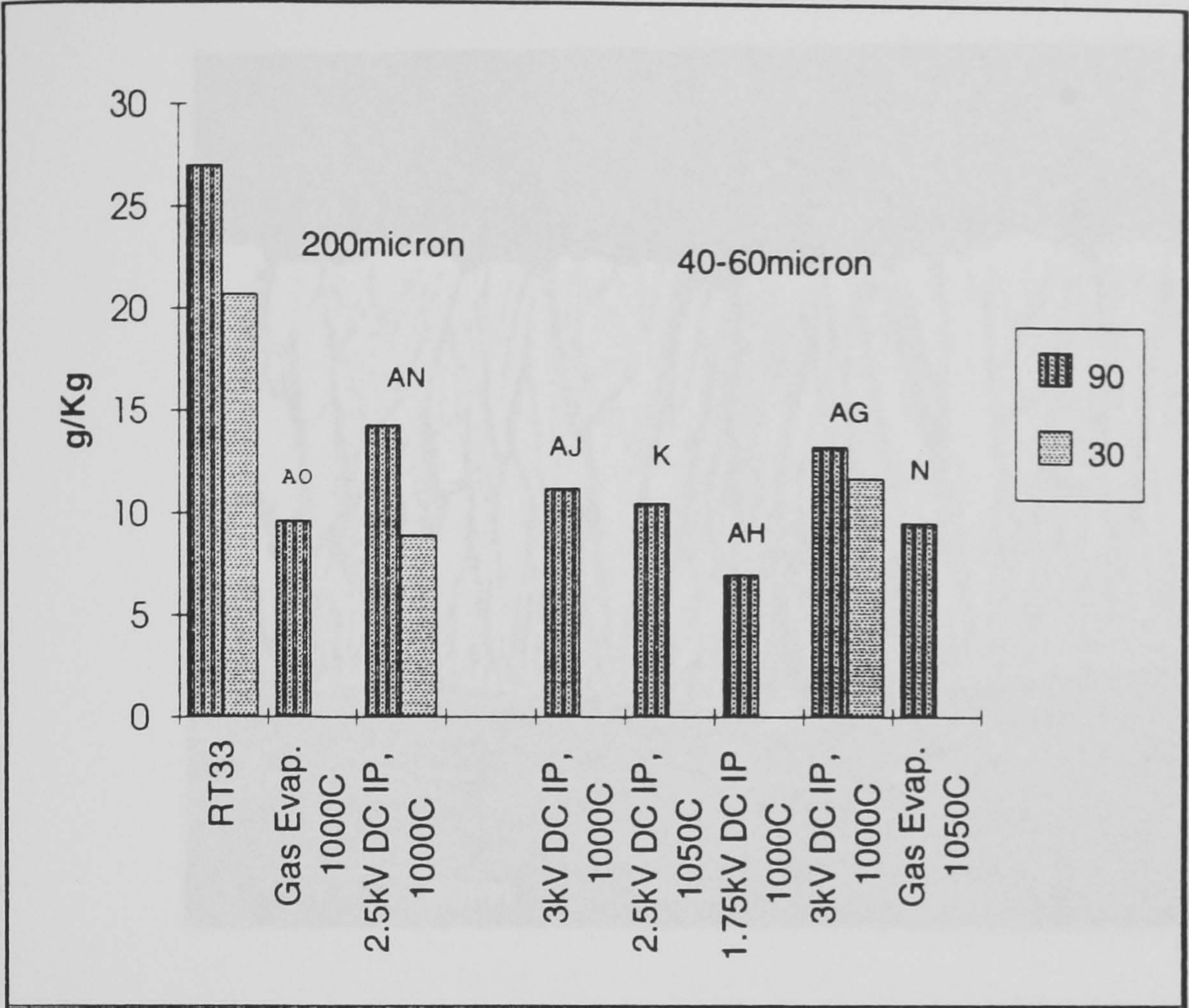


Figure 175: Erosion rate of Cranfield coatings as a function of coating thickness and deposition parameters.

The variations in erosion rate amongst the Cranfield coatings could not be related to the controllable deposition parameters within the working process window.

9.3.2.2 Description of erosion damage morphology:

The erosion behaviour of the high temperature EB-PVD TBC's was markedly different from that of RT33. The thin coatings (45-60 microns) underwent plastic deformation that extended deep into the coating bulk (see Figure 176 to Figure 180). The original columnar/fibrous morphology became less distinctive as a result of coating compaction (see Figure 177, Figure 178 and Figure 180). Lateral cracks were nucleated in the densified region typically 5 to 10 micron below the coating surface giving off large lumps of coating material (see Figure 177 and Figure 178). The extensive plastic deformation and the formation of voluminous coating debris resulted in a rougher as-eroded surface topography. Comparatively, the thicker coatings showed relatively little distress in that both plastic deformation and lateral cracking were confined in the near-surface region (see Figure 181).

Figure 177: Cross-section of sputtered Al₂O₃/SiC coating showing lateral cracks and debris (scattered electron micrograph).

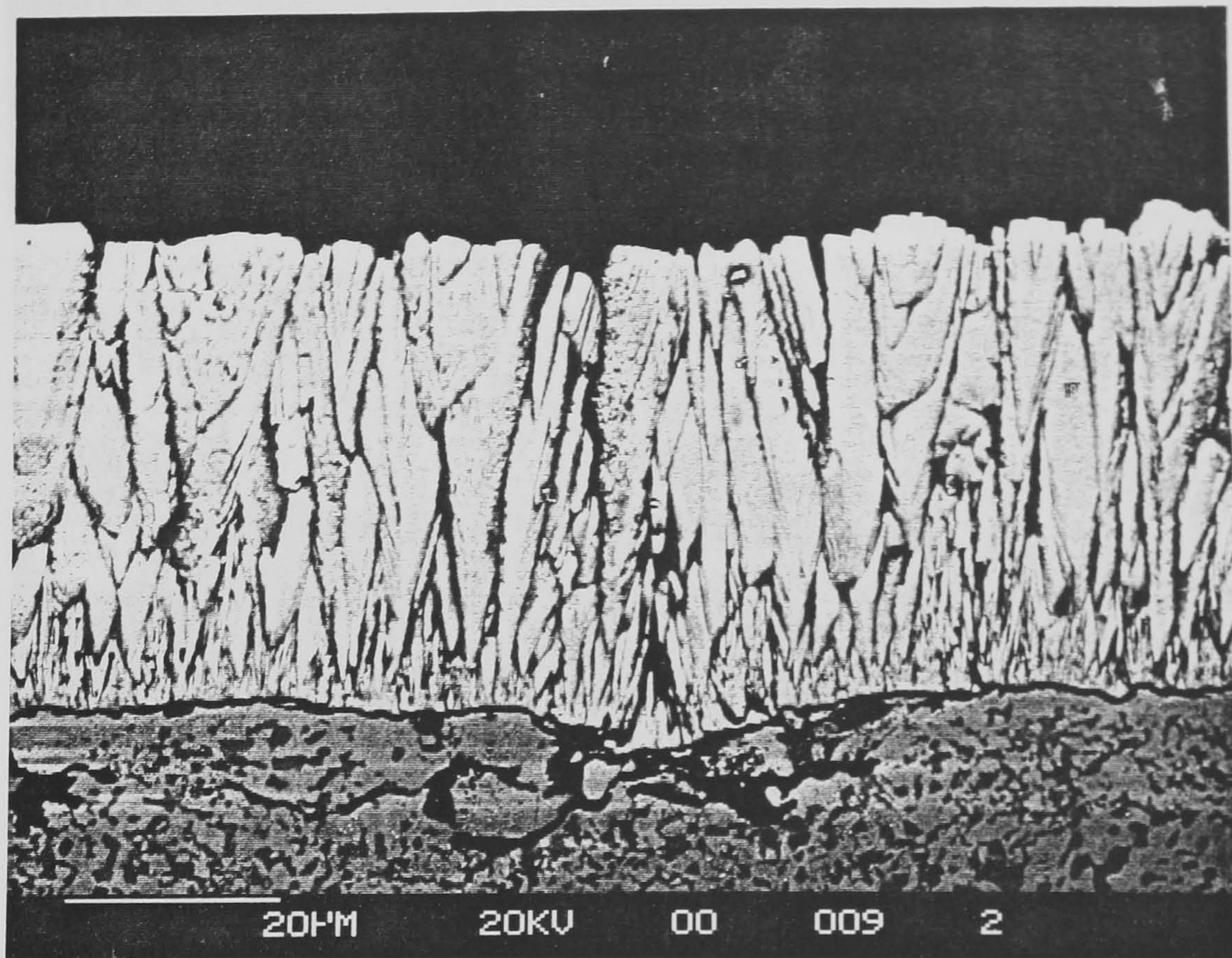


Figure 176: Cross-section of as-deposited AH coating (<111> textured) (Back-scattered electron micrograph).

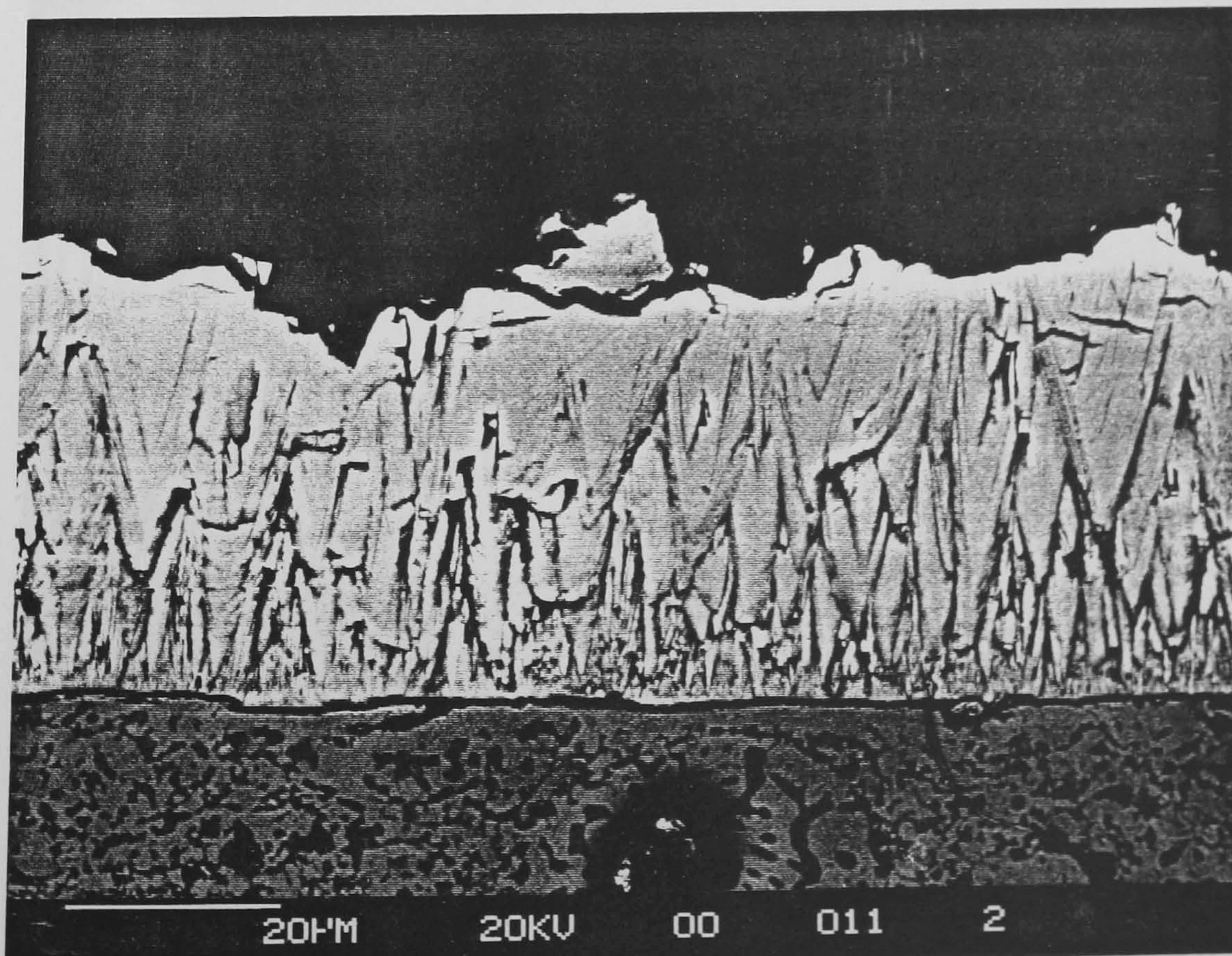


Figure 177: Cross-section of as-eroded AH coating (<111> textured) (Back-scattered electron micrograph).

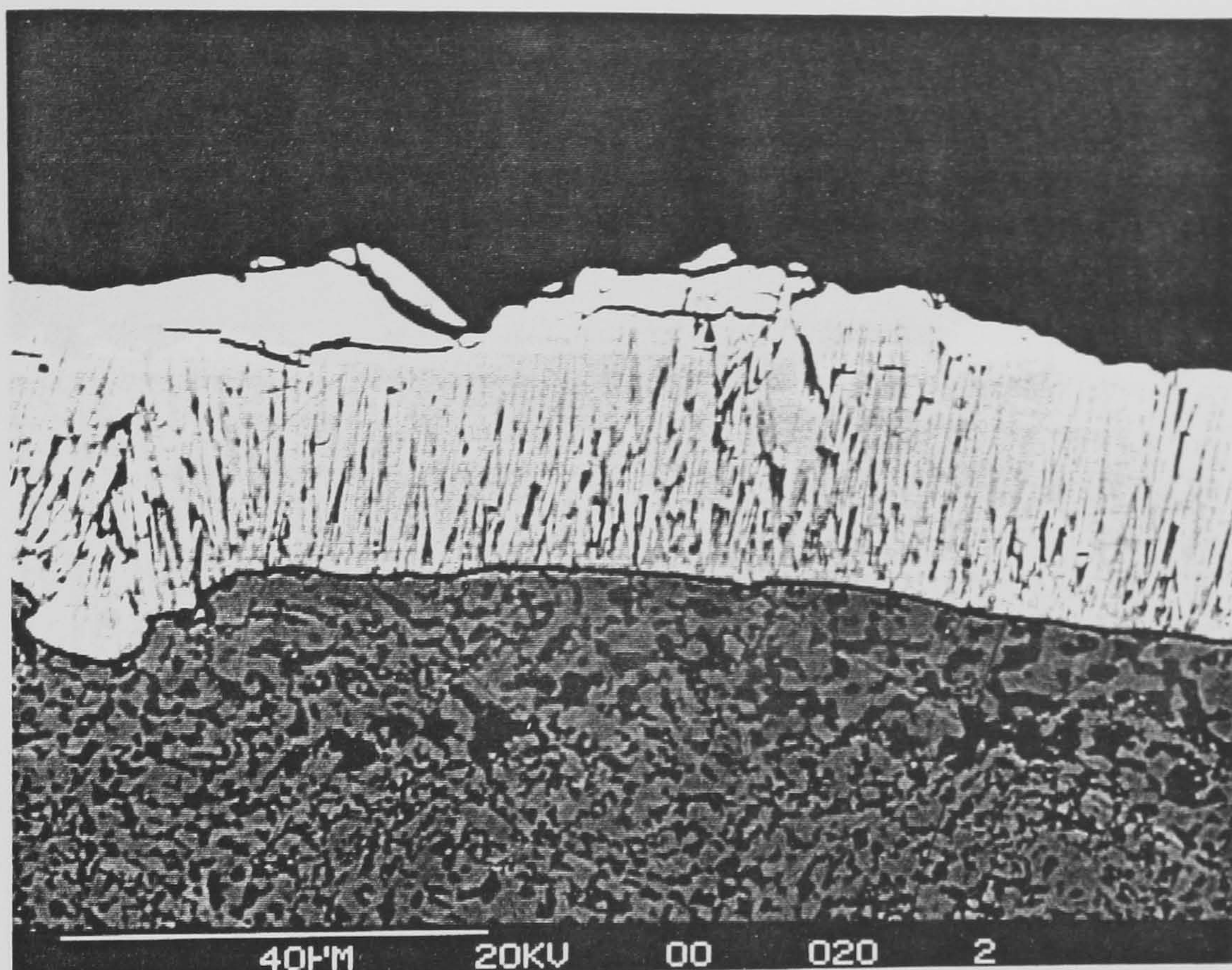


Figure 178: Cross-section of as-eroded K coating ($\langle 111 \rangle$ textured) (Back-scattered electron micrograph).

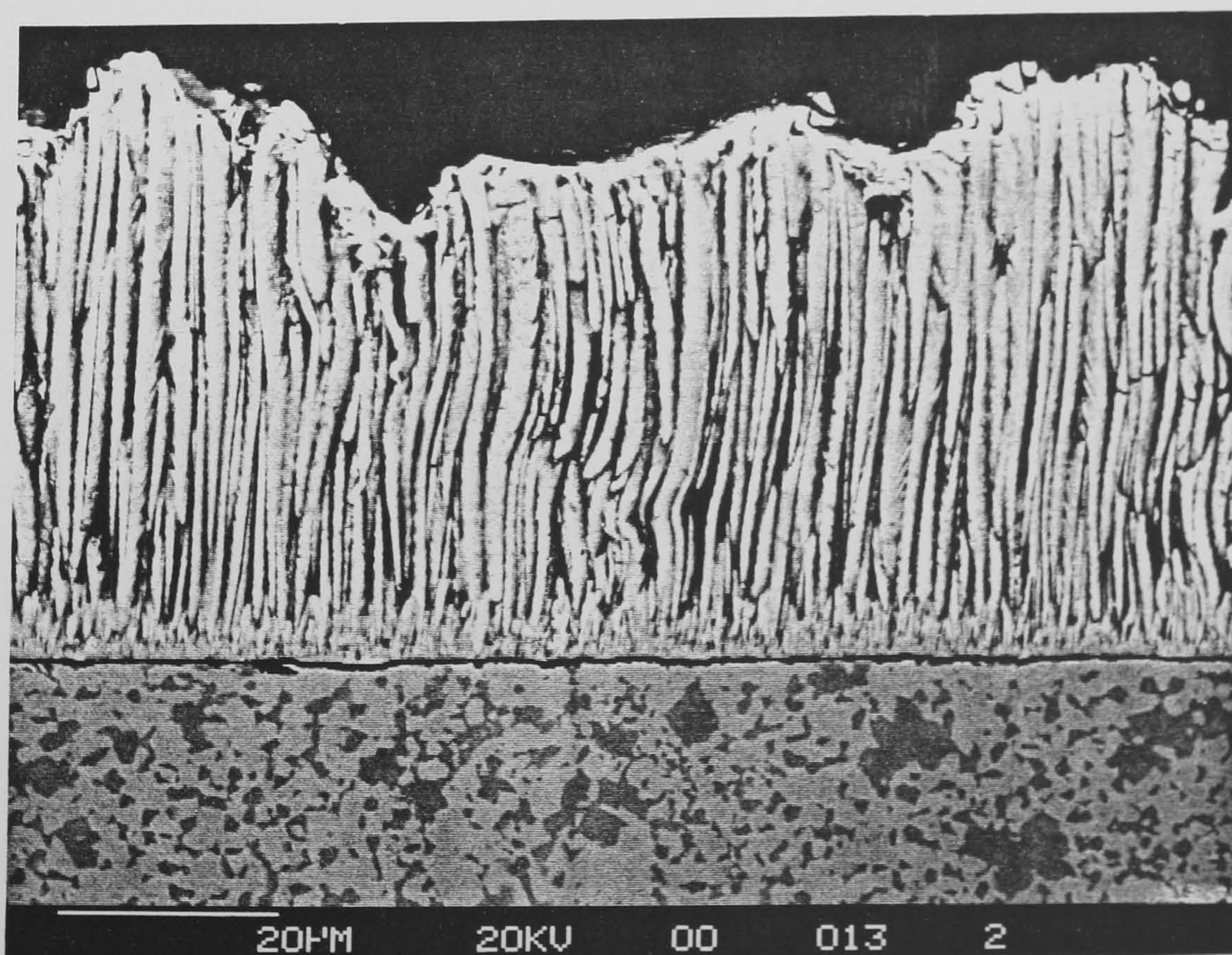


Figure 179: Cross-section of as-eroded AG coating ($\langle 111 \rangle$ textured) (Back-scattered electron micrograph).

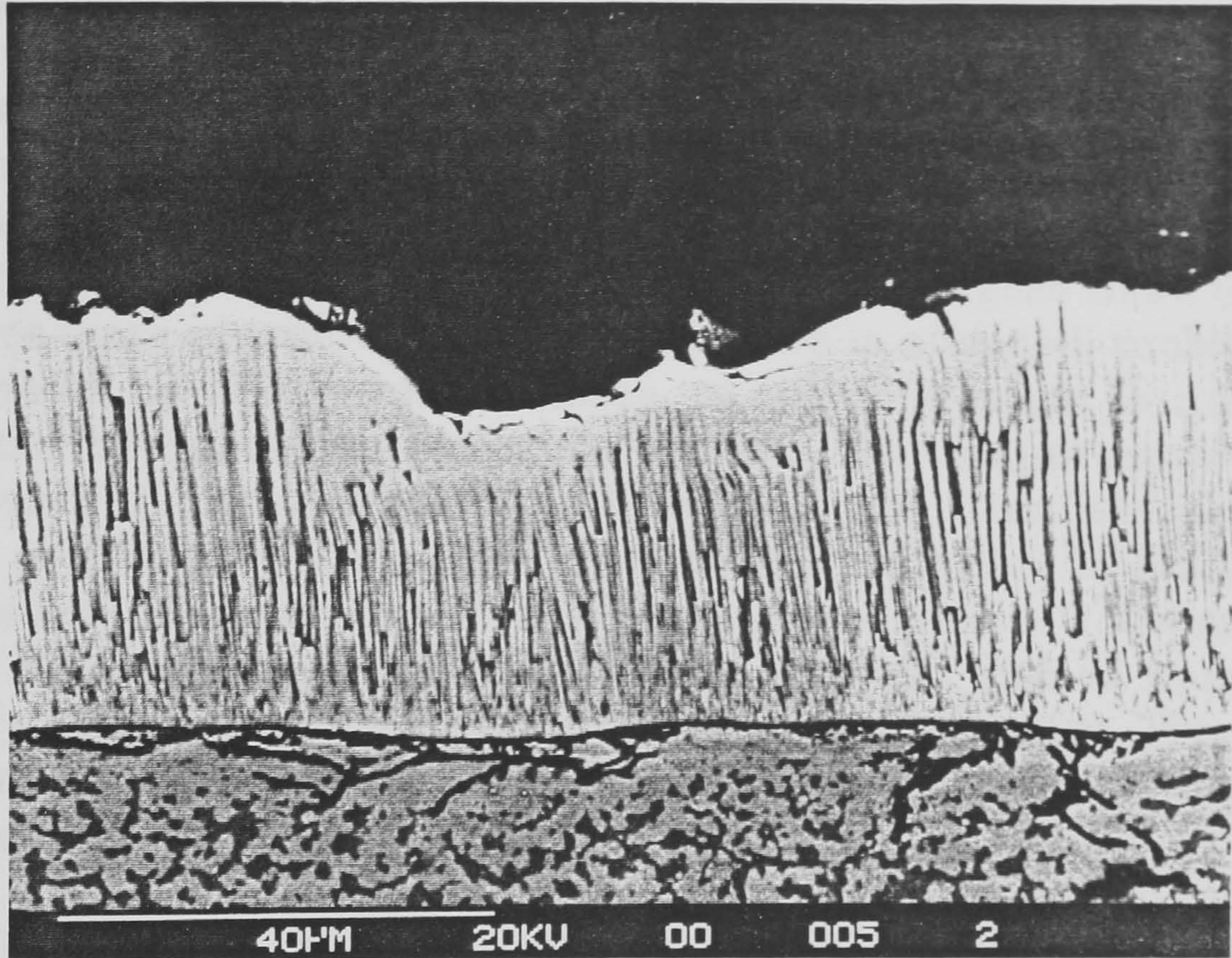


Figure 180: Cross-section of as-eroded AJ coating (<100> textured) (Back-scattered electron micrograph).

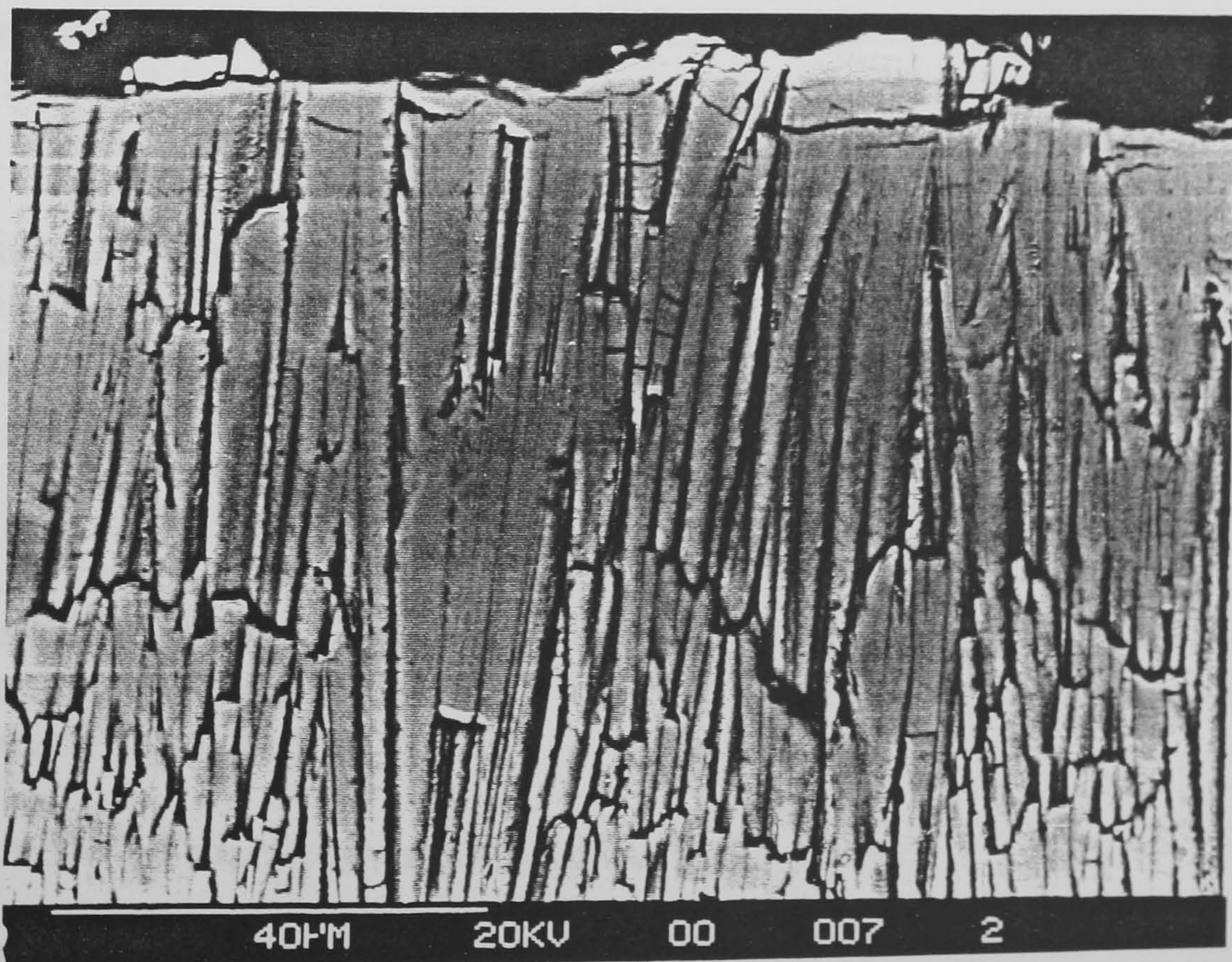


Figure 181: Cross-section of as-eroded AN coating (<100> textured) (Back-scattered electron micrograph).

9.4 DISCUSSION

9.4.1 Assessment of erosion performance

The plastic behaviour of the thin Cranfield deposits accounts for their low erosion rate relative to that of RT33 since the energy delivered by the impacting particles is expended into plastic deformation which is not readily accompanied by material loss. As the coating undergoes more densification and stores more plastic work, a critical stress is attained, probably assisted by the build up of residual stresses, at which a crack is nucleated and propagated by subsequent particle impacts. The requirement for storing plastic work to cause material loss renders the Cranfield deposits more resilient to erosion. This behaviour contrasts with that of RT33, for which plastic deformation was found to be limited to a depth of a few microns, with material loss occurring from the formation of spalls formed from the lateral cracking underneath the plastically deformed surface region. This process was also accompanied with the fracturing of the columns to a depth of several tens of microns (see Figure 161).

Erosion rate is not the sole criterion to rank the erosion performance of TBC's. As it was emphasized in chapter 1, it is of paramount importance for aerodynamics considerations that an acceptable surface finish of the TBC be retained after erosion damage. In this respect, the commercial coating is found to outperform the Cranfield deposits for which the degree of plastic deformation, although responsible for enhanced erosion resistance, may be potentially detrimental to their function as TBC's because of the associated coating compaction and surface roughening. The good surface finish retention observed in RT33 is inherent to its erosion process occurring via the removal of shallow surface debris resulting from the lateral cracking underneath the plastically deformed surface region. In the Cranfield deposits, the densification associated with the plastic deformation is a pre-requisite for the attainment of a stress sufficient to cause fracture. Because densification extends deep into the coating and is accompanied with the loss of the columnar morphology, the lateral cracks responsible for material loss are nucleated further away from the surface and can propagate farther in the coating plane than is possible with RT33. This is the consequence of the resorption in the thin Cranfield deposits of the columnar boundaries that are potential crack-stoppers. This leads to the formation of voluminous irregular-shaped coating debris which, after removal, could leave behind a rough as-eroded surface topography.

9.4.2 The role of surface indentation resistance

The erosion rate of the deposits were plotted against their surface indentation resistance (see Figure 182). It must be emphasized that the indentation resistance data quoted is that measured at room temperature. This limits somehow the pertinence of such a plot given that the erosion rate relates to that for a test specimen surface temperature of 910°C and that it was shown

by Twigg and Page¹⁶⁸ that the 'hardness' of a commercial EB-PVD TBC dropped to a third of its room temperature value at about 677°C. Moreover, previous investigators¹⁶⁹ have expressed the importance of considering dynamic values e.g. dynamic hardness as opposed to static hardness for impact conditions. Bearing in mind these strong limitations, it is not unreasonable to assume that the ranking of the specimens tested in this work on their dynamic hardness at 910°C bears some comparison with their ranking on room temperature static values given that the same ceramic material is being considered and that the indentation resistance is believed to be primarily dependent on coating density, as discussed in chapter 8. Thus, should there be a correlation between the dynamic surface indentation resistance of the deposits at 910°C and their erosion rate, such a correlation would be reflected when considering room temperature static values of surface indentation resistance.

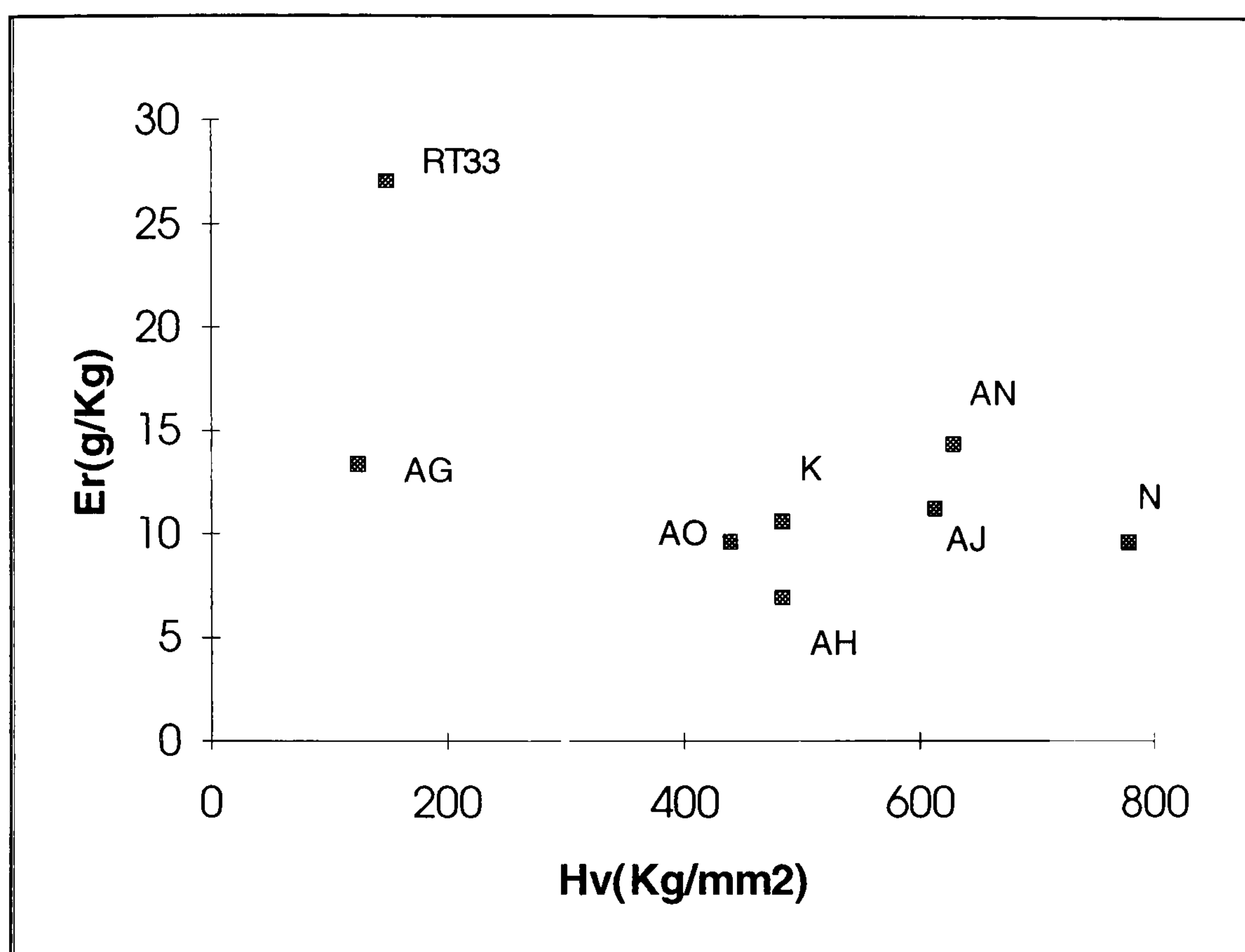


Figure 182: Plot of erosion rate at 90° impingement angle and 910°C versus Vickers surface indentation resistance at room temperature.

Figure 182 suggests that indentation resistance does not emerge as a strongly influential parameter to erosion resistance at 90° angle of impingement. This does not disagree with the theoretical models of the erosive wear of brittle materials that were developed by Evans et al¹⁷¹ and Wiederhorn and Lawn¹⁷⁰ assuming an elastic-plastic behaviour. Despite important differences in modelling the impact event¹⁶⁹, both these models predict a weak dependence of erosion rate (Er) on surface hardness (H) but a high dependence on the fracture toughness (K_c):

$$Er \propto \frac{1}{K_c^m H^n}$$

with

	m	n
Evans et al ¹⁷¹	1.3	0.25
Wiederhorn and Lawn ¹⁷⁰	1.3	-0.11

These theoretical models not only corroborate the lack of dependence between the indentation resistance and erosion rate in Figure 182, within the limitations highlighted above, but also point to the importance of considering the coating's fracture toughness K_{IC} . This aspect will be discussed later in the discussion.

Although surface indentation resistance does not appear to significantly affect erosion at normal angles of impingement, it is believed that its role may become important at glancing angle of particle impingement. This is because a wear mechanism closer to hard abrasion is expected at glancing angle of impingement and that the volume of material that can be removed on average per ploughing event increases with the depth of penetration of the particle (see Figure 184). At a given particle velocity and oblique angle of impingement, the depth of penetration will increase with decreasing surface indentation resistance of the target material. Thus, one would expect erosion rates at glancing angles of impingement to increase with decreasing surface indentation resistance. In order to verify this hypothesis, the ratio of glancing (30°) to normal (90°) angle erosion rate was plotted as a function of the room temperature static surface indentation resistance (see Figure 183).

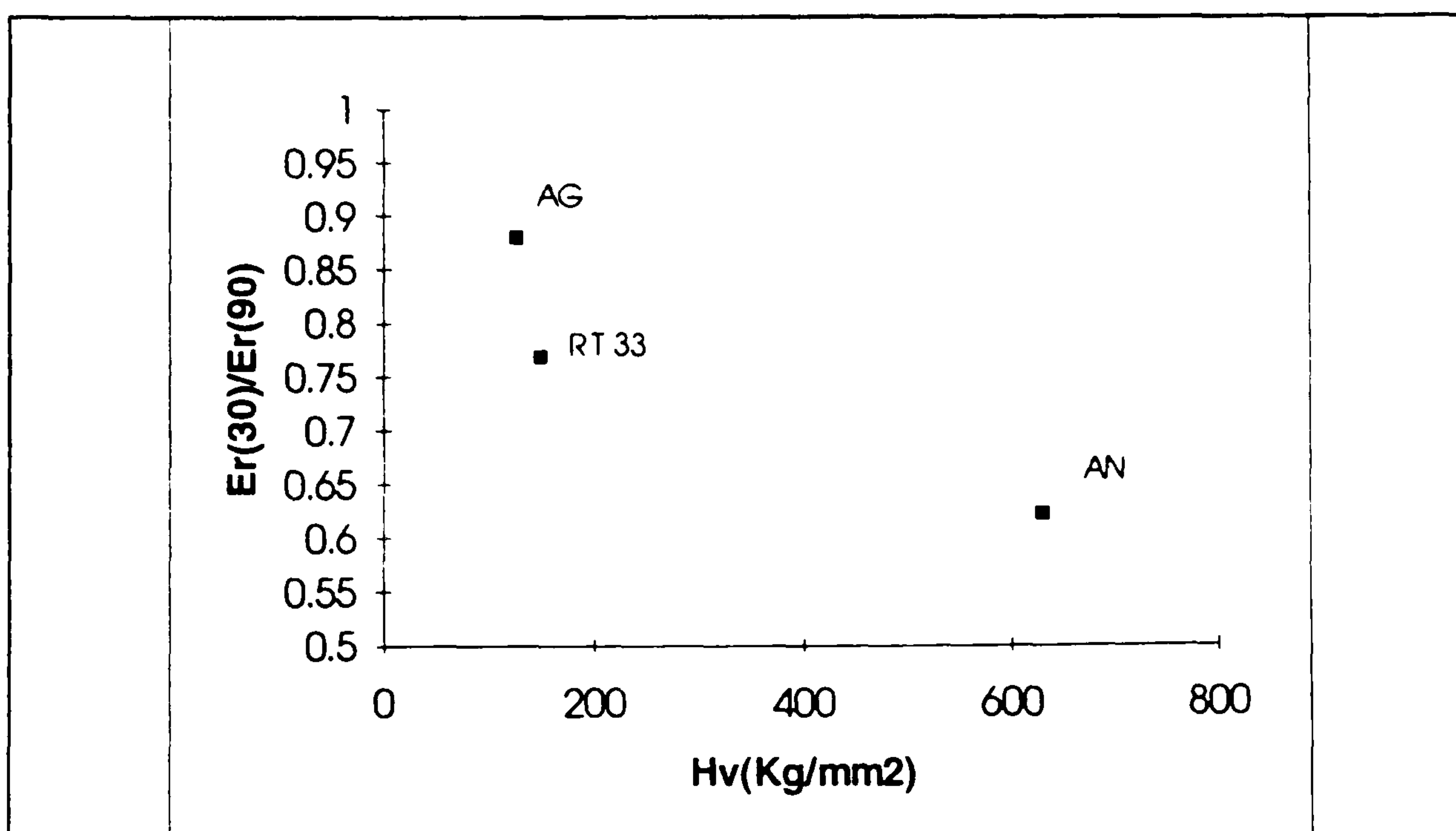


Figure 183: Ratio of glancing to normal attack angle erosion rate as a function of room temperature surface indentation resistance.

This plot gives some substance to the above argument but there is still obviously a need to generate more data points to confirm the trend.

It could be first expected that an enhanced surface indentation resistance would be beneficial for an acceptable surface finish retention, on the basis that the surface impressions from the particle impacts would be less deep. This logic is however offset by the fact that surface roughening comes about also from the removal of bulky irregular shaped coating debris and, as such, does not relate directly to surface indentation resistance (see for example Figure 177 and Figure 178).

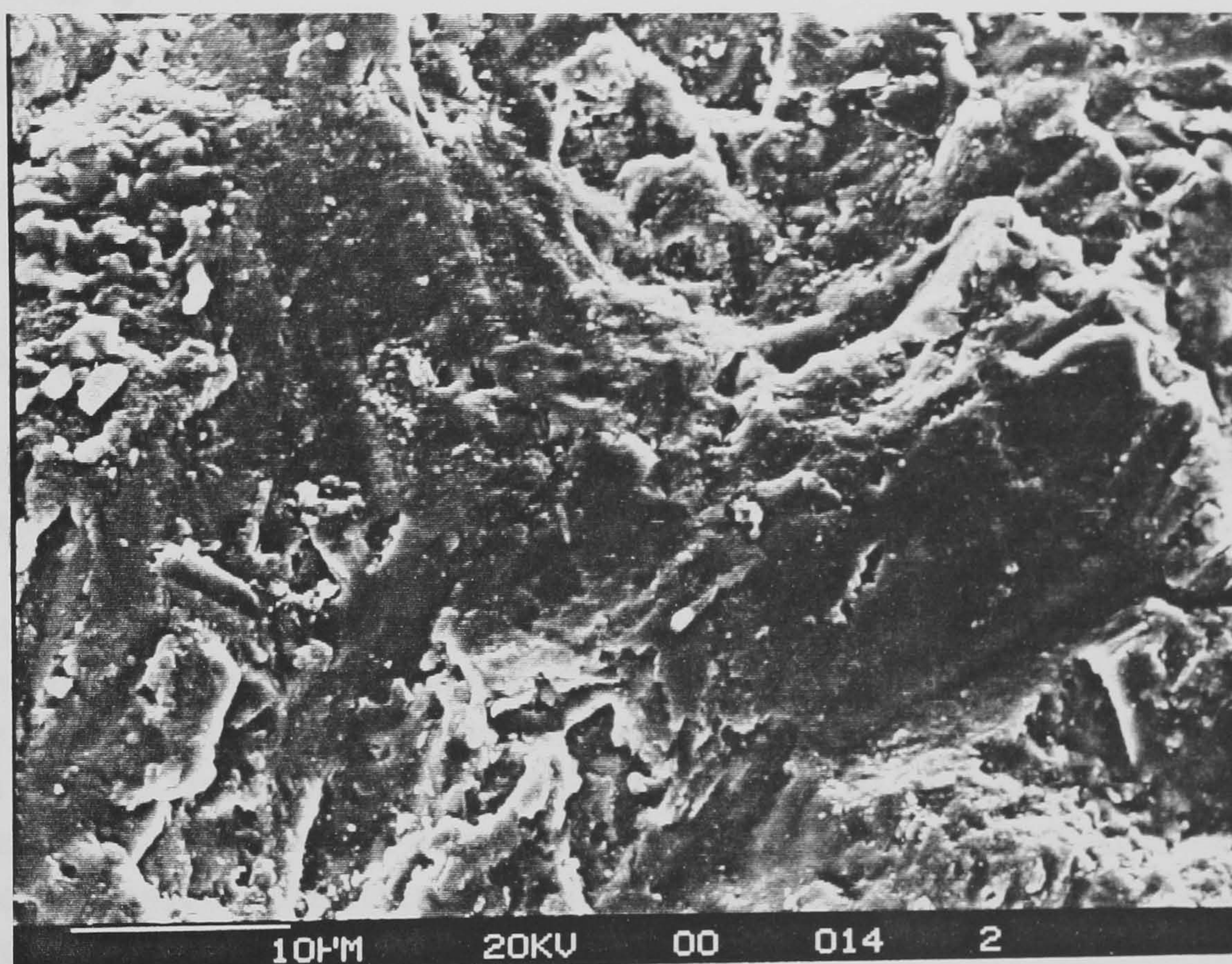


Figure 184: Surface topography of 2.5kV DC IP YSZ coating (AN, 630 Kg/mm²) showing ploughing as eroded at 30° angle of particle impingement.

9.4.3 Structural parameters influencing the coating response to particle impacts

Having described the erosion mechanisms of the Cranfield deposits, it is now attempted to give an account as to why their response to particle impacts at high temperature is so dramatically different from that of RT33. The following terminology will be used in this discussion:

σ_i : maximum transmitted impact stress

σ_p : stress required to cause plastic flow

σ_f : stress required to cause fracture

σ_y : uniaxial yield strength of a single elementary crystallite

The subscript Cran and RT33 refer respectively to the Cranfield coating systems and the commercial TBC datum.

The ductile or brittle behaviour of a coating subjected to particulate erosion is dictated by the magnitude of the stress that develops upon impact (σ_i) and on whether this stress exceeds the flow stress (σ_p) or the fracture stress (σ_f) or both. The observation of the erosion damage morphology in RT33 suggests that the impact stress exceeds both the yield point and fracture strength in this coating:

$$\sigma_{i,RT33} > \sigma_{f,RT33} \quad \text{and} \quad \sigma_{i,RT33} > \sigma_{p,RT33}$$

This contrasts with the Cranfield deposits for which the impact stress can be accommodated by plastic flow only,

$$\sigma_{f,Cran} > \sigma_{i,Cran} > \sigma_{p,Cran}$$

until enough plastic work is stored to nucleate a crack propagated by subsequent particle impacts.

The propensity of an EB-PVD deposit to undergo plastic deformation or brittle fracture depends on the relative stress level requirements for plastic flow or fracture of its structural elements (columns, intra-columnar crystallites). In order to assess the brittle or ductile behaviour of this material, as-subjected to a given impact stress at a certain temperature, an approach was chosen to separately consider the structural factors affecting the fracture stress and the flow stress of the coating structural elements.

9.4.3.1 Factors affecting the flow stress

The stress required to cause coating plastic flow will depend partly on the intrinsic material properties affecting the ductility of the ceramic crystallites, as characterized by their yield strength σ_y . Diffusional creep processes are ignored here, as these are not believed to be of importance in accounting for the difference in erosion damage morphology observed between the Cranfield deposits and RT33, given the high strain rates involved in the erosion process.

Lattice structure and yield strength:

The yield strength of a crystal depends on the number of slip planes available for dislocation glide, on the number of dislocations present in the lattice, and on the ease of dislocation motion for a given slip system. For a given YSZ material, the yield strength may vary with structural defects such as

inclusions, interstitials and on the dislocation density and the presence of dislocation sources. These structural defects, if significant, should in principle be reflected in X-Ray Diffraction line broadening. However, it was seen in chapter 8 that, given the error in the lattice strain measurements, there was no conclusive evidence of differing lattice imperfections between the commercial system RT33 and the Cranfield deposits. Given the analytical tools available in the present work, it cannot be concluded that there exists a difference in yield strength due to lattice imperfections between these two families of coatings.

Crystallite size:

Classically, the yield strength of a crystallite should increase with decreasing size by virtue of dislocations piling up at the crystallite boundaries thus generating a stress field increasingly hampering the glide of following dislocations. Alternatively, a fine crystallite size in the sub-micron range, typical of that in PVD condensates, could encourage plastic flow of the ceramic columns via superplasticity (crystallite boundary sliding). Although superplasticity may not be very likely in bulk ceramics at the elevated strain rates involved during impact conditions, the situation might differ in the EB-PVD YSZ deposits for which the strength of the inter-crystallite boundaries may be expected to be lowered due to the presence of coalesced porosity as discussed in chapter 8. The crystallite size of the high temperature deposits, as that of RT33, typically exceeded the XRD resolution limit ($>200\text{nm}$) and thus could not be differentiated. However, given that both families of coatings were deposited in the same temperature range and that the deposition temperature was found to be overriding in controlling the coating crystallite size (see chapter 8), there is no obvious reason to believe that the crystallite size should differ markedly between the two coating families. An argument based on crystallite size to account for the difference in erosion behaviour between RT33 and the Cranfield deposits is not therefore easily defensible.

Residual stresses

It has been evoked that compressive thermal and growth stresses could influence the flow stress in PVD coatings¹⁶⁸. This hypothesis does not appear to be very plausible in the present context given that no significant stresses were found within the deposits (see chapter 8).

Crystallographic texture:

Crystallographic texture potentially affects the crystallite yield strength as the slip systems for dislocation glide are anisotropic by definition, and thus these may or may not operate depending on the relative applied stress and slip directions. However, the extensive ductile behaviour in the Cranfield systems was equally exhibited by deposits having the $\langle 100 \rangle$ or $\langle 111 \rangle$ texture (see AJ and AH for example). This shows that crystallographic texture alone

cannot be accountable for the difference in plastic behaviour between RT33 and the Cranfield deposits.

In the light of the above considerations, there is no obvious argument based on the intrinsic material properties of the ceramic coatings to suggest differences in the plastic behaviour between RT33 and the Cranfield deposits. In other words, there is no indication that the uniaxial yield strength of RT33 material would be markedly different from that of a Cranfield deposit. This is not to say however that the stress required to cause plastic deformation is the same between these two systems, as argued below.

In order to proceed this discussion further, one must start to make assumptions on the nature of the loading to which the columns are subjected during particle impacts. It is believed that a fair representation is that when a particle impinges on the surface of an EB-PVD deposit at normal angle of impingement, some column buckling occurs subjecting one half of the column material to a tensile stress field and subjecting the other half to a compressive stress field, the two halves being separated by a neutral plane (see Figure 185). Possibly, the column may revert to a symmetrical stress state upon particle unloading (see Figure 187). When the ceramic column is loaded this way, the lateral near surface region suffers little lateral constraint from the ceramic and thus will be subjected to near plane stress conditions (no stress perpendicular to the column length). Further towards the column core, the lateral matrix constraint increases and a stress perpendicular to the column length develops accordingly giving rise to a triaxial stress state. In Figure 185, the shaded region corresponds to the volume of the ceramic subjected to plane strain conditions (no strain perpendicular to the column length) where the stress state is triaxial, whereas the white region is that subjected to plane stress conditions with a biaxial stress state. The transition from one region to the other was depicted as abrupt for the sake of simplicity but is gradual in reality.

The Von Mises's criterion for yield is that "the strain energy per unit volume used in changing the shape of the material reaches the value of energy used in changing the shape of the specimen in the simple tensile test up to the yield point"¹⁷² from which the following formula ensues:

$$(\sigma_1 - \sigma_2)^2 + (\sigma_1 - \sigma_3)^2 + (\sigma_2 - \sigma_3)^2 \geq 2\sigma_y^2 \quad (96)$$

where σ_1 , σ_2 and σ_3 are the principal stresses for the given applied stress state. The implication from equation (96) is that the magnitude of the stresses required to cause plastic deformation is greater than σ_y and increases the more the stress state becomes triaxial.

The triaxiality of the stress state in the shaded ceramic region means that the stress required to cause plastic deformation of the column core is greater than

that required to deform the surface region. As the column width is decreased the ceramic volume subjected to plane stress conditions decreases approximately linearly with column width d whereas the column volume region subjected to plain strain conditions decreases approximately with d square. In other words, the ceramic volume subjected to a triaxial stress state decreases more rapidly than the surface region volume as the column diameter is decreased (see Figure 186). Therefore, the stress requirement to cause plastic deformation of a column will be less the finer its width. Hence the proposition that the flow stress of an EB-PVD deposit increases with column size. This is consistent with the observation that RT33, with a mean column diameter of $13\mu\text{m}$, exhibits an erosion rate of 27g/kg compared to the Cranfield deposits, with mean column diameters in the 1 to $4\mu\text{m}$ range, exhibiting erosion rates in the 7 to 15g/kg range.

To summarise the above considerations, there is no ground to ascertain that there is a difference in the intrinsic ductility between RT33 and the Cranfield deposits, as characterized by their yield strength σ_y . However, it is believed that the coating morphology, as characterized by the mean column width influences strongly the impact stress requirement to cause plastic flow, i.e. the latter increases with increasing column width.

Having assessed the coating structural parameters influencing the coating flow stress (σ_p), the factors controlling the coating fracture stress (σ_f) are now examined.

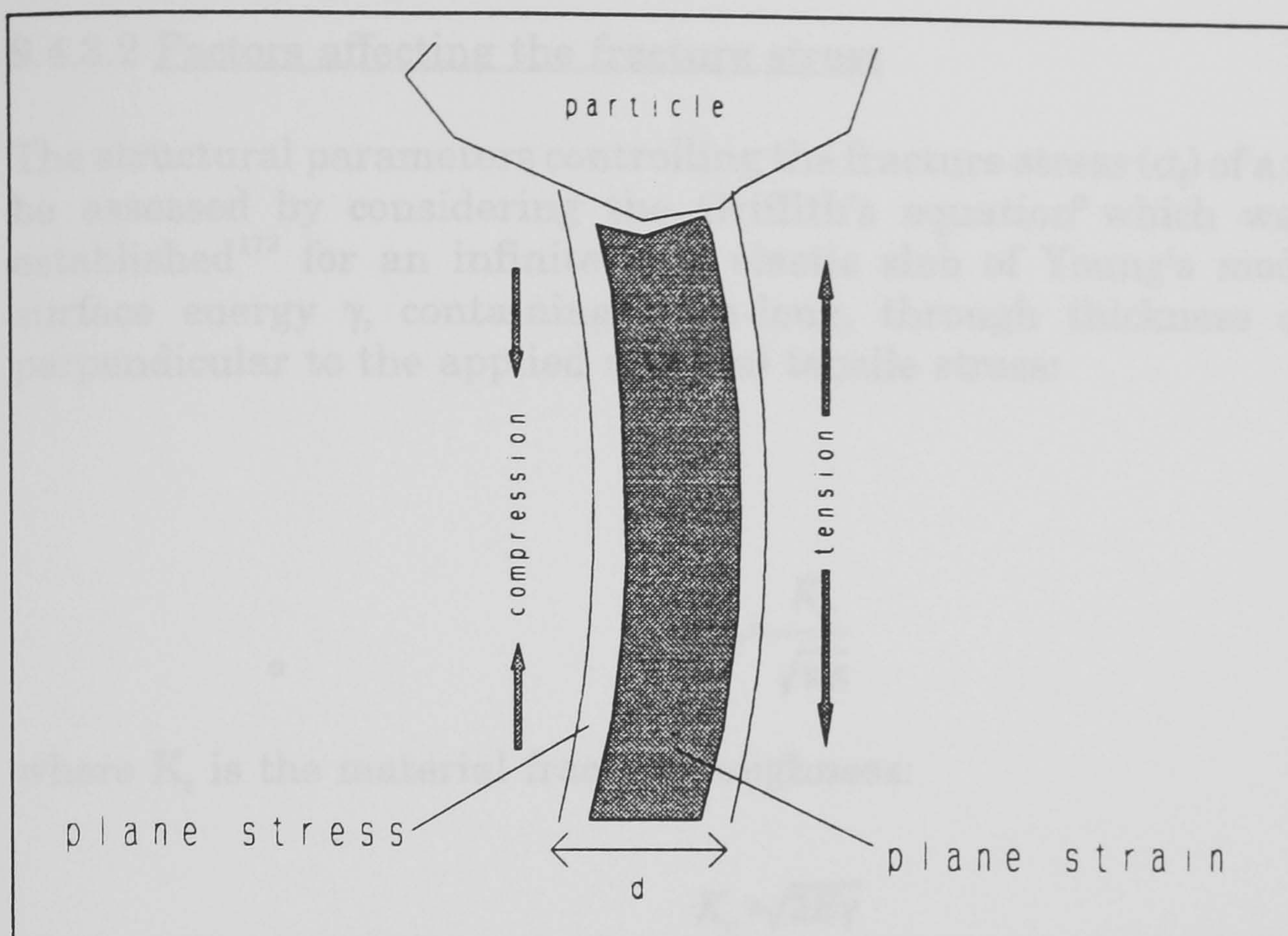


Figure 185: Column buckling on particle loading.

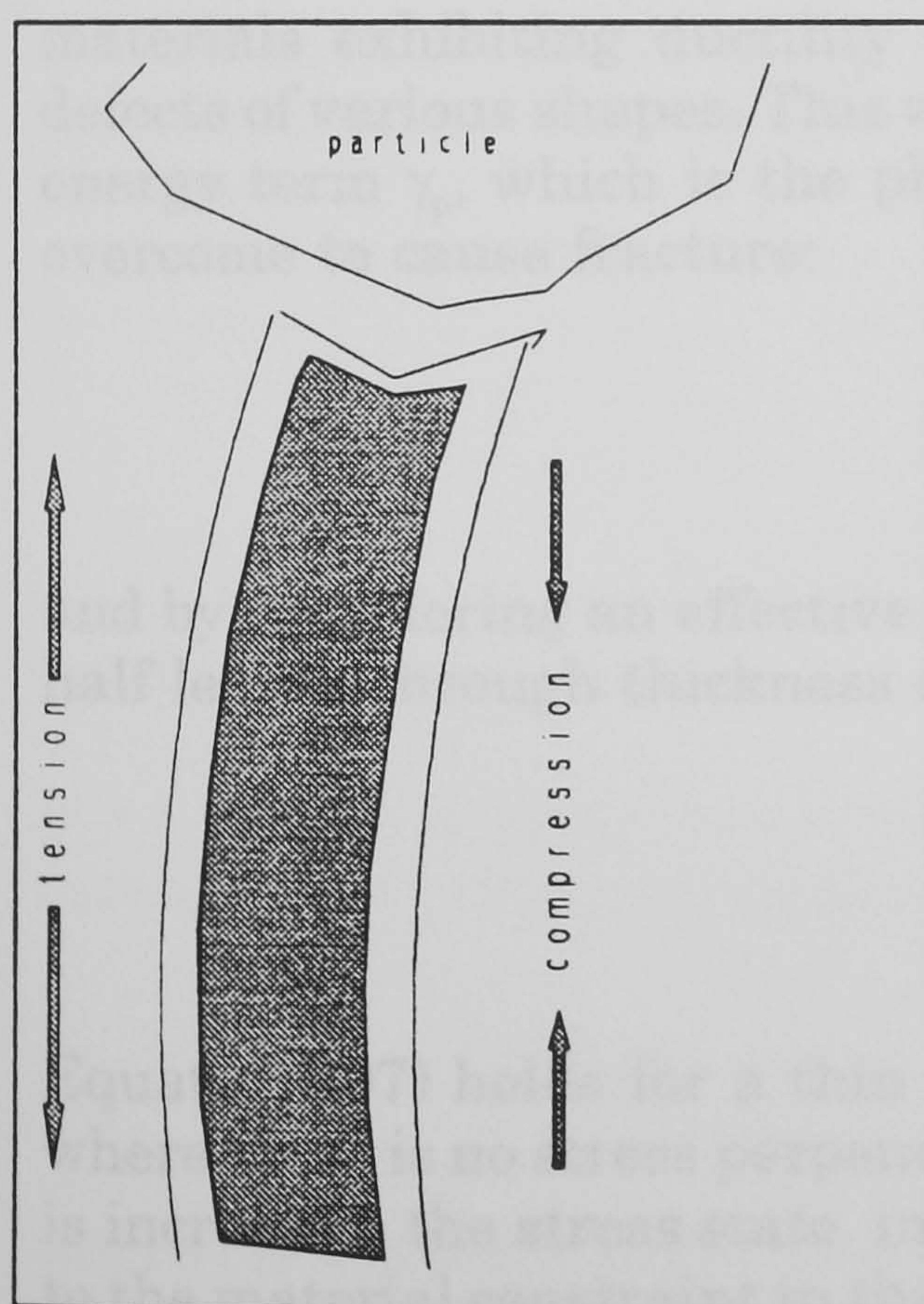


Figure 187: Elastic strain recovery during particle unloading.

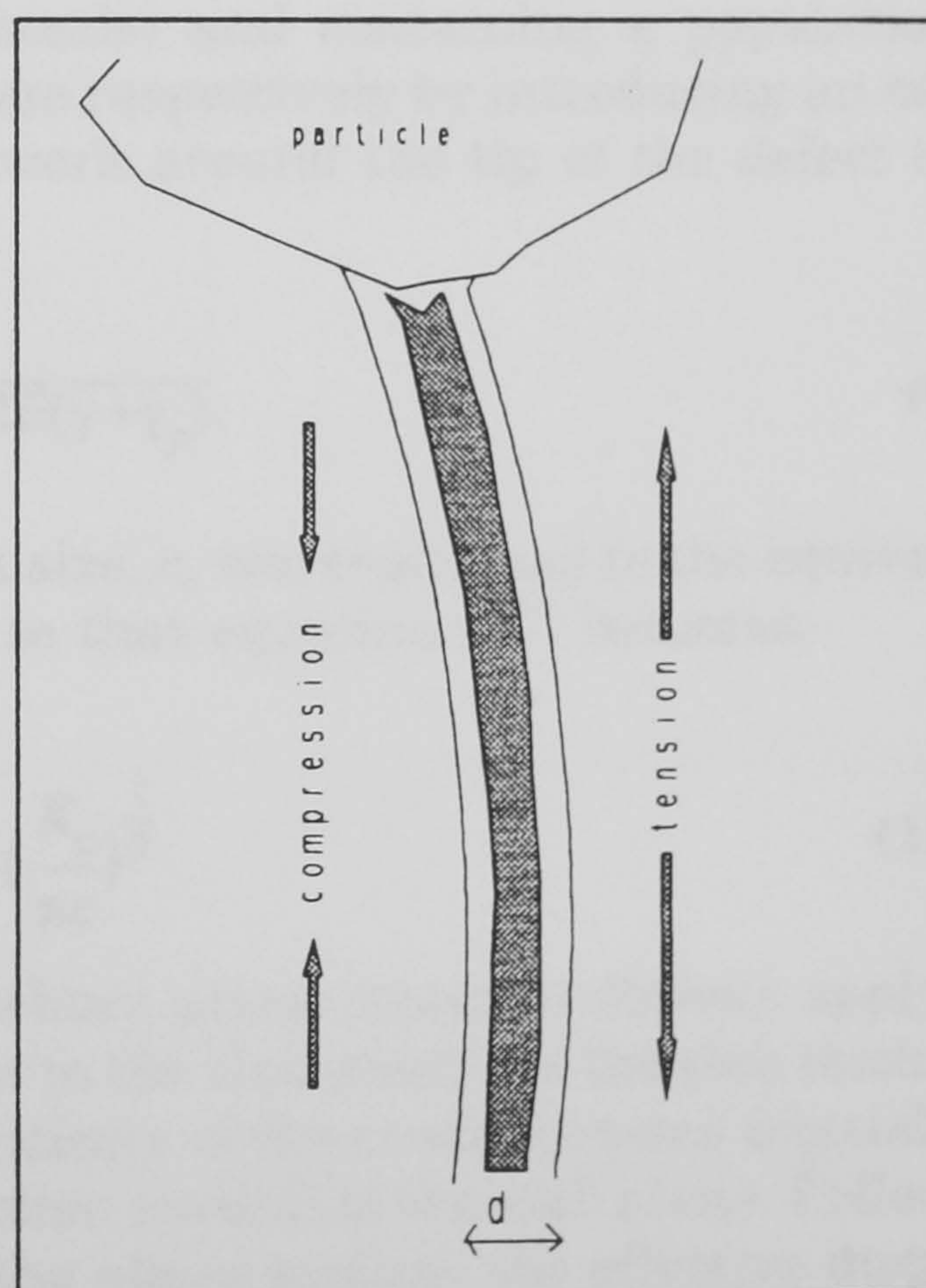


Figure 186: Buckling of finer column showing the reduction in the 'plane strain' ceramic volume relative to the 'plane stress' volume.

9.4.3.2 Factors affecting the fracture stress

The structural parameters controlling the fracture stress (σ_f) of a material can be assessed by considering the Griffith's equation which was originally established¹⁷³ for an infinite thin elastic slab of Young's modulus E and surface energy γ , containing a $2a$ -long, through thickness center crack perpendicular to the applied uniaxial tensile stress:

$$\sigma_f = \frac{K_c}{\sqrt{\pi a}} \quad (97)$$

where K_c is the material fracture toughness:

$$K_c = \sqrt{2E\gamma}$$

This equation has been subsequently adapted for predicting the fracture in materials exhibiting ductility (e.g. steels) and containing a population of defects of various shapes. This was done respectively by introducing an added energy term γ_p , which is the plastic work around the tip of the defect to be overcome to cause fracture:

$$K_c = \sqrt{2E(\gamma + \gamma_p)} \quad (99)$$

and by considering an effective defect size, c , corresponding to the equivalent half length through thickness crack so that equation (97) becomes:

$$\sigma_f = \left(\frac{K_c}{\pi c} \right)^{\frac{1}{2}} \quad (100)$$

Equation (97) holds for a thin slab where plane stress conditions apply i.e. where there is no stress perpendicular to the slab plane. As the slab thickness is increased, the stress state in the vicinity of the crack becomes triaxial due to the material constraint in the direction normal to the slab plane. Following the same argument as that used in the above section, the effective ductility γ_p at the crack tip will decrease as the stress state becomes more triaxial, so that according to equation (99), the fracture toughness decreases with slab thickness (see Figure 188).

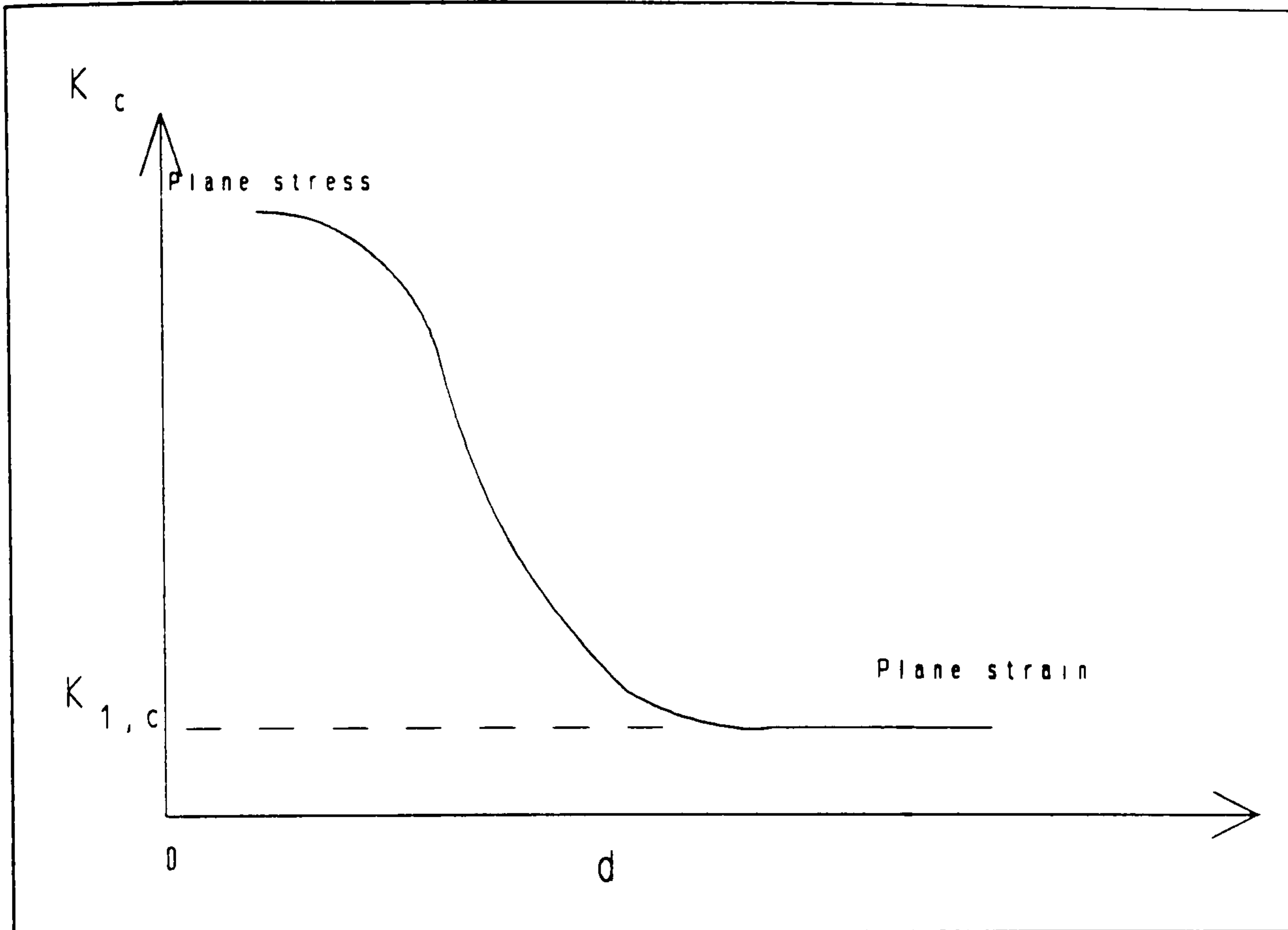


Figure 188: Variation of fracture toughness with thickness slab.

In the limiting case of plane strain conditions (no strain in the direction perpendicular to the applied stress and crack length plane equation (100) becomes:

$$\sigma_f = \left(\frac{K_{1c}}{\pi c(1-\nu^2)} \right)^{\frac{1}{2}} \quad (101)$$

where K_{1c} is the fracture toughness under plane strain conditions and ν is the material Poisson's ratio.

In a situation intermediate between the limiting plane stress and plain strain conditions, the fracture toughness may be written:

$$K_c = f(d)K_{1c}$$

where f is a dimensionless function asymptotically decreasing towards 1 with thickness d .

Equation (100) can then be written:

$$\sigma_f = \left(\frac{f(d)K_{1c}}{\pi c(1-\nu^2)} \right)^{\frac{1}{2}} \quad (103)$$

Equations (99) and (103) summarize the coating parameters controlling the fracture stress.

Clearly, it cannot be stated that the fracture toughness K_{Ic} of RT33 is less than that of the Cranfield deposits given that, as discussed in the previous section, there is no evidence of differing intrinsic ductility between these two systems and nor can it be proved that their lattice Young's modulus and surface energy in the vicinity of a defect are different. Crystal orientation could effect the resistance to fracture as cracks propagate along preferred crystallographic planes. In many crystalline materials, cleavage occurs along crystallographic planes of high atomic density¹⁷⁴ which is the (111) plane in the case of zirconia systems. As pointed out by Lelait, Alpérine and Diot⁸³, a crack propagating parallel to the coating plane is unlikely to meet easy cleavage planes in coating systems with the $\langle 100 \rangle$ texture, which is that of RT33. Therefore the $\langle 100 \rangle$ texture should enhance the resistance to fracture of RT33 relative to that of some of the Cranfield systems that exhibited the $\langle 111 \rangle$ texture. Still these did not undergo brittle fracture. The apparent more brittle behaviour of RT33 relative to that of the Cranfield deposits cannot therefore be argued on the grounds of a lower fracture toughness value K_{Ic} . However, the effective fracture toughness, as influenced by the column diameter (d) (see Figure 188), will be potentially greater in the Cranfield deposits than that in RT33 by virtue of their finer morphology.

The other critical parameter controlling the coating fracture stress is the presence of defects, as depicted in equation (103) via the defect size c . These defects act as stress concentrators i.e. stresses of magnitude much higher than that of the applied stress develop in the defect vicinity to cause fracture. This 'stress raising' effect is a sensitive function of the defect size and shape which addresses the necessity of defining the nature of these defects. In the light of the preceding chapter, these defects may consist of intra-columnar residual porosity as segregated at the inter-crystallites boundaries and/or as entrapped within the crystallites, resulting from the dynamic sintering growth process. The XRD line broadening evidence in chapter 8 does not support an hypothesis that there is a difference in the intra-crystallite porosity content between RT33 and the high temperature Cranfield deposits. It is more likely that the difference in the defect population between these two families of coatings resides in different amounts of entrapped inter-crystallite porosity, as that reported by independent investigators using TEM studies. This porosity, being coalesced at the boundaries of the diffracting domains (crystallites), is not detectable using XRD.

In their work on predicting the failure of oxide scales, Hancock and Nicholls¹⁷⁵ state that whatever the shape and distribution of the defects present in a scale, they can be combined using inter-active rules and treated as one composite defect equivalent to a 'through-thickness crack of half-length a '. If such an approach is extended to ceramic coatings, a greater content of residual porosity can be associated with a greater effective defect size (see a

in Figure 189). Therefore one should expect that the effective defect size c present in the coating increases with increasing column width, which is analogous to the Hall-Petch argument. Moreover, for a given column width, the effective defect size c will increase with increasing pore concentration. That is to say that for a given morphology, the effective defect size increases with increasing intra-columnar porosity.

In addition to residual intra-columnar pores acting as stress concentrators, one should evoke the potential role of adjacent crystallites at the column surface effectively forming a notch and favouring the initiation of a crack (see b in Figure 189 and example in Figure 161 and Figure 162).

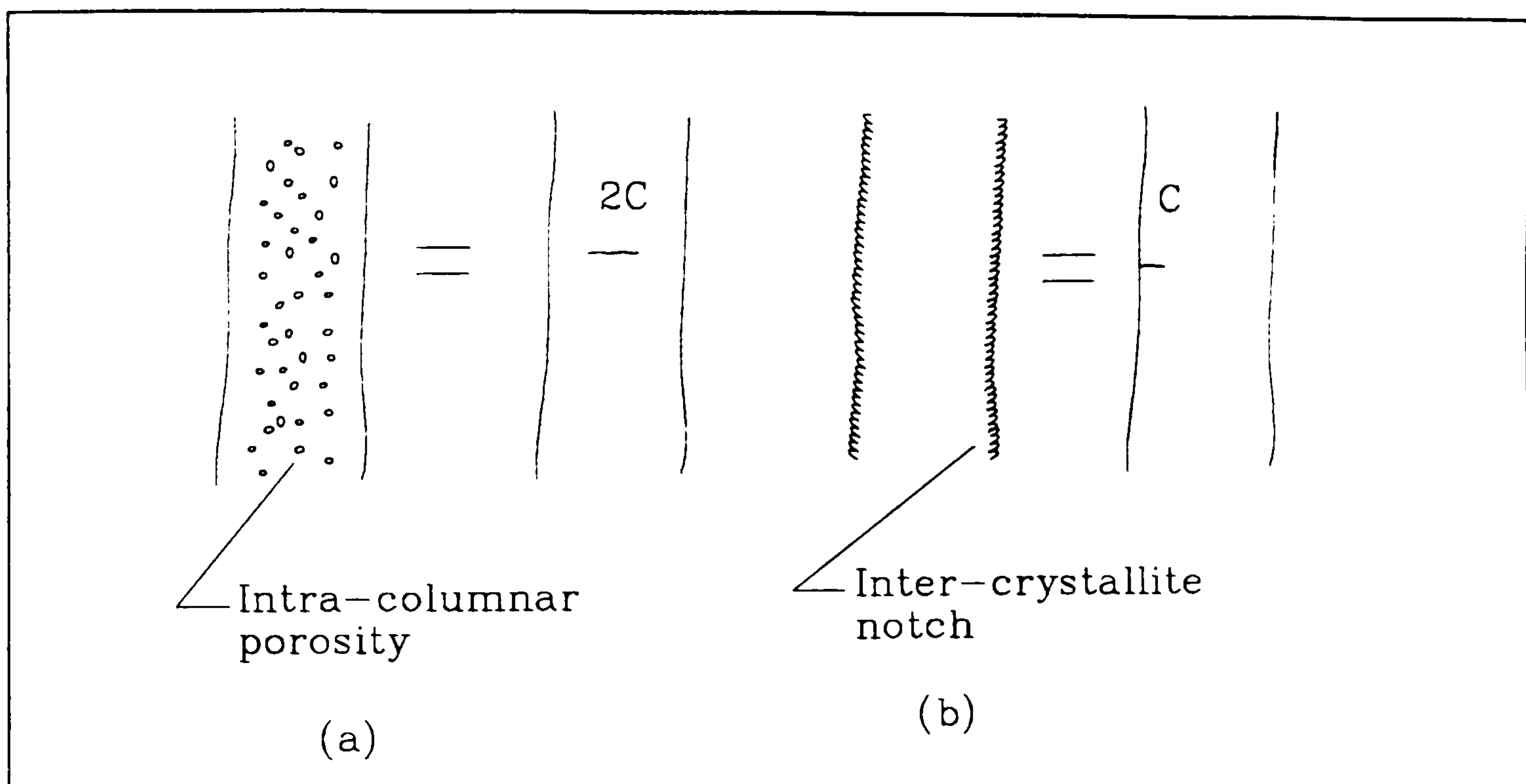


Figure 189: Schematic of critical defects responsible for the fracturing of columns during particle impacts.

9.4.3.3 Summary

It has been attempted to explain the difference in the response to high temperature erosion damage observed between RT33 and the Cranfield deposits. An approach was chosen to separately consider the coating structural factors affecting the relative stress level requirements to cause plastic deformation and fracture respectively. Some salient features have been identified as accountable for the difference in erosion behaviour between the two coating families. The coating morphology, in terms of column diameter, is believed to be of paramount importance in controlling the coating response to particle impacts. Increasing the column diameter is believed to encourage a brittle response of the coating to particle impacts by increasing the flow stress at the same time as decreasing the fracture stress requirement. The fracture stress is lowered with increasing column width because:

- the effective fracture toughness decreases with column width

- the effective defect size increases with column width
- the column defectiveness (pore concentration) is expected to increase with increasing column width. This ensues from the understanding of the dynamic sintering in the preceding chapter, thereby a finer column size will be more perfect, i.e. contain less porosity, by virtue of a high column surface-to-volume ratio favouring the evacuation of vacancies during coating growth.

Also, for a given column width, a brittle behaviour will be encouraged by the production of a high concentration of columnar defects, as those depicted in Figure 189, as dependent on the deposition process parameters. Although what controls the notch-type of defects is not actually understood in this work, the deposition parameters controlling the pore concentration have been identified in chapter 8. The basis for the claim of improved TBC erosion resistance in the GE patent¹⁵⁰ (see chapter 2) can now be understood in the light of the above considerations. The dense layers in the 'banded' ceramic structure recommended by this patent will require a greater impact stress to undergo fracturing as the lowered amount of porosity translates into a reduced effective defect size c .

Figure 190 summarises the effect of the structural factors that were identified as controlling the ductile/brittle response to high temperature particulate erosion. The shape of the temperature dependence for the flow stress and fracture stress is reproduced as represented by Hancock and Nicholls¹⁷⁵ for the failure of oxide scales involving creep mechanisms. In the context of erosion, the temperature dependence of the flow stress should follow more closely that of the material yield strength.

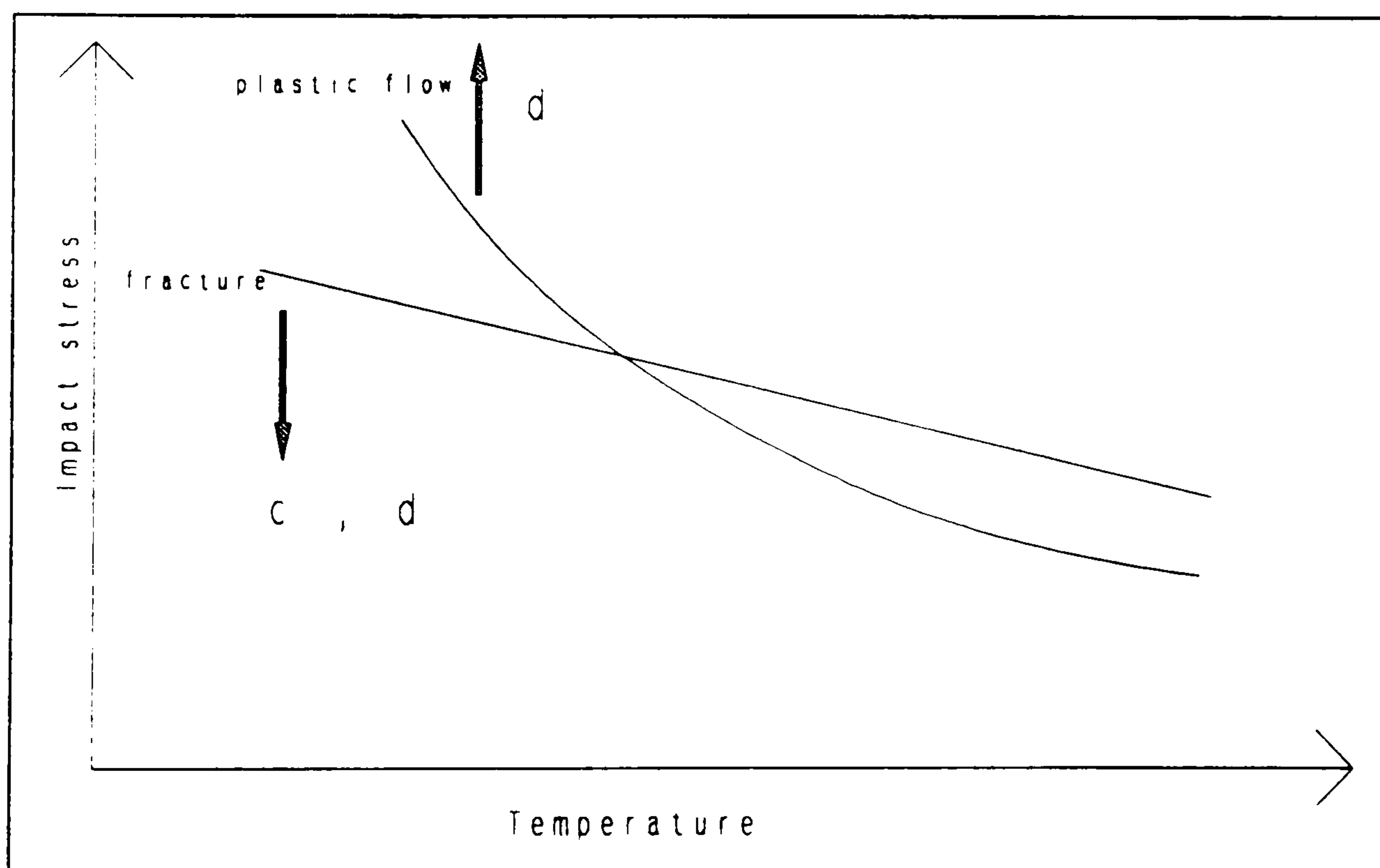


Figure 190: Dependence of the flow stress and fracture stress requirements on the diameter (d) and effective defect size (c) of the TBC columns.

The implications of Figure 190 is that there exists a transition temperature above which plastic deformation will occur prior to fracture. This transition temperature increases with increasing column width (d) and increasing inherent porosity (c).

Moreover, the question could be raised as to whether the ceramic undergoes work hardening as a result of the storage of plastic work, in which case the flow stress of the as-eroded ceramic should be considered as opposed to the as-deposited flow stress. Similarly, if the ceramic deforms as a result of crystallite sliding, the ensuing compaction would increase the flow stress requirement relative to that in the as-deposited state. It was observed that the extensive ductility during erosion damage seemed to be peculiar to the thin deposits. To account for this observation, one may evoke the fact that both the average mean crystallite size and column width affected by the stress state from particle impacts decrease nearer the interface with the substrate. The finer column size should ease plastic deformation as discussed above whilst a finer crystallite size would enhance inter-crystallite boundary sliding, if this deformation mechanism applied.

10

OUTLOOK AND RECOMMENDATIONS

In this work, it has been attempted to generate a sound understanding of some aspects of the relationship between the deposition process and the structure of EB-PVD YSZ thermal barrier coatings. In particular, the role of deposition temperature in simply thermal evaporated TBC's and the feasibility of using plasma assistance of the EB-PVD process to modify the ceramic structure have been investigated. The object of this chapter is to appraise how this understanding could be exploited in order to achieve improved TBC performance.

A prime objective of the R&D effort within Rolls-Royce is to achieve lowered thermal conductivity of EB-PVD TBC's to levels equivalent to that in thermal sprayed TBC's. To this effect, new explorable routes are proposed to achieve lowered thermal conductivity of EB-PVD TBC's, as identified from the findings in this work.

Some of the recurrent recommendations in the literature are that densification of the ceramic coat is desirable to achieve improved system durability in terms of resistance to erosion and molten salt damage (see chapter 2). This aspect will be discussed in the light of the erosion behaviour of EB-PVD TBC's characterised in chapter 9.

10.1 THE ROLE OF TEMPERATURE ON THE STRUCTURE OF EB-PVD TBC'S

It has been established that EB-PVD YSZ ceramics deposited at low temperature (up to 650°C) are not viable systems as thermal barrier coatings due to their lack of thermal stability. This was attributed to their massive porosity content (~50%) which causes the ceramic deposit to sinter when exposed to elevated temperatures. As evidenced from the comparison between SEM evaluation and density measurements, it was realised that the bulk of the coating voidage was distributed at the microscopic level. It was also demonstrated from careful isochronous anneal studies of the low temperature deposits that densification of the ceramic occurred via diffusion processes with activation energies as low as 1.0eV, which compares with activation energies for surface diffusion. This further demonstrated the atomistic distribution of the voidage both within the crystallites (X-ray diffracting domains), as evidenced from lattice strain measurements, and between the crystallites, as demonstrated by the abnormally low activation energies for grain boundary diffusion. These findings are in accordance with the idea

conveyed by Muller⁷⁷ that a PVD deposit grows as a porous atomic network.

The inherent defectiveness of thermally evaporated films deposited in the absence of thermal excitation is classically explained in the literature as the consequence of low kinetic energy of the arriving vapour atoms and atomic shadowing. The effect of electrostatic forces between condensed atoms and arriving atoms, promoting the formation of atomic agglomerates and micro-columnar porosity has also been proposed. All these factors are intrinsic to the thermal evaporation process and therefore equally apply to high temperatures of deposition. This train of thought formed the basis for the proposal of a coating growth model for the high rate deposition of ceramics, whereby diffusion processes occur concurrently to the adsorption of vapour atoms to overcome the spontaneous defectiveness of the atomic build up (see Figure 191).

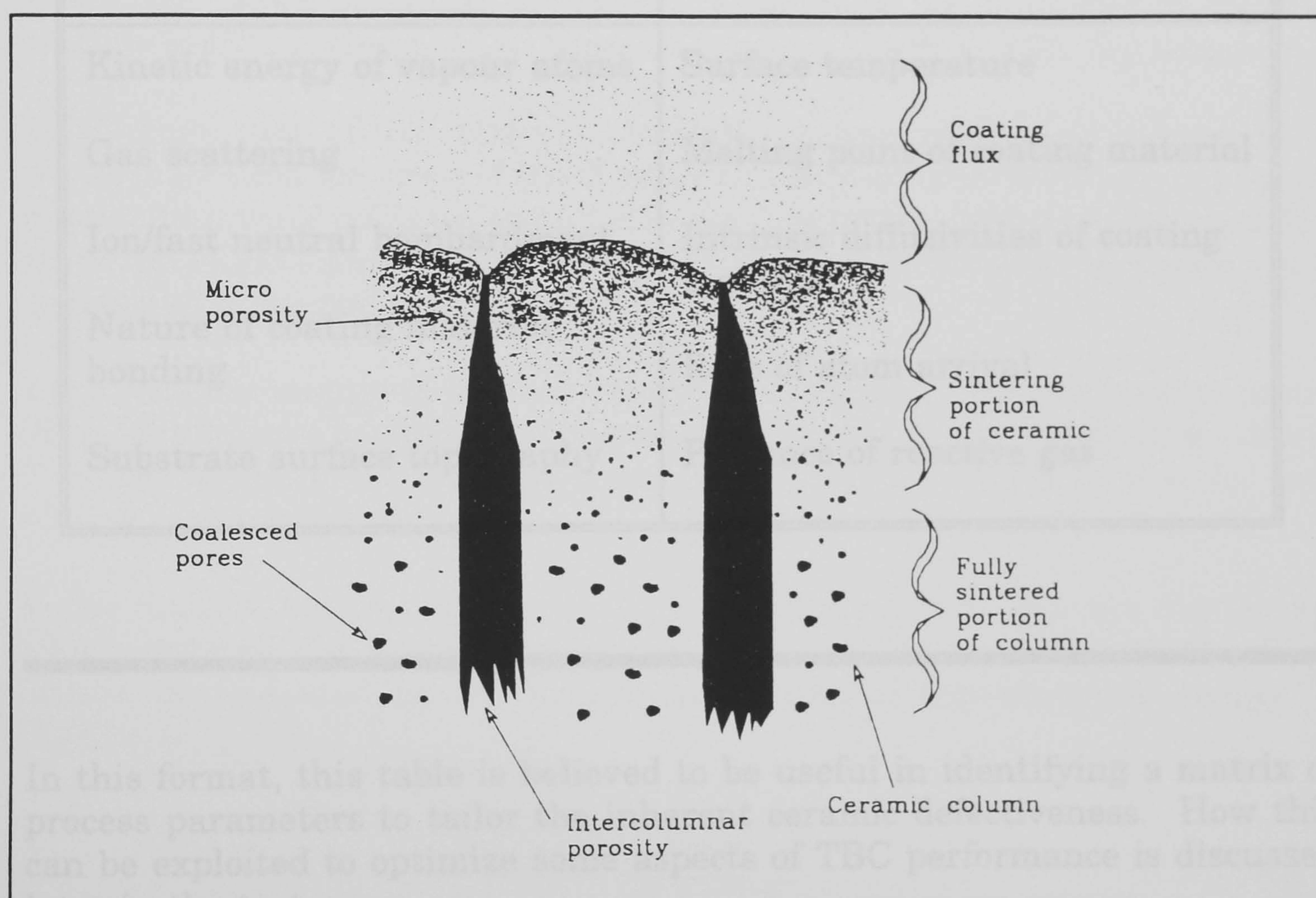


Figure 191: Schematic of dynamic sintering coating growth.

This model, termed 'dynamic sintering coating growth', was substantiated by the analogous effects on the ceramic structure of deposition temperature and post-deposition annealing of the low temperature deposits. This model can also account for the finely distributed porosity in high temperature EB-PVD TBC's observed by independent investigators using TEM techniques. Although, in its simplicity, this model does not fully explain the detailed morphological developments of EB-PVD TBC's deposited at high temperature, the concept it conveys allows to formulate predictions on the effect of other parameters on the defectiveness of the ceramic.

parameters on the defectiveness of the ceramic.

These parameters can be dissociated into those that affect the coating defectiveness in its 'green' state i.e. deposited without thermal excitation and those influencing the extent to which mass transport mechanisms can anneal out the spontaneous defectiveness of the freshly deposited atomic layers (see Table XXIV).

Table XXIV: Deposition parameters expected to affect the residual porosity in high temperature deposited EB-PVD ceramics.

'Green' state parameters	Mass transport parameters
Kinetic energy of vapour atoms	Surface temperature
Gas scattering	Melting point of coating material
Ion/fast neutral bombardment	Intrinsic diffusivities of coating material
Nature of coating material bonding	Rate of atom arrival
Substrate surface topography	Presence of reactive gas

In this format, this table is believed to be useful in identifying a matrix of process parameters to tailor the inherent ceramic defectiveness. How this can be exploited to optimize some aspects of TBC performance is discussed later in the text.

10.2 THE ROLE OF PLASMA ASSISTANCE

10.2.1 Parameters controlling the effectiveness of ion plating

RF ion plating at low deposition temperatures was found not to be a substitute for the high deposition temperatures required in the simple thermal evaporation process of EB-PVD TBC's. In other words, RF plasma assistance offered no tangible improvements in the thermal stability of the low temperature ceramic deposits. The low temperature RF ion plated TBC's

were found to undergo sintering densification when exposed in thermal fatigue tests, similar to that undergone by the low temperature gas evaporated systems. This is because ion bombardment, although leading to some coating densification, failed to overcome the bulk of the porosity content inherent to the low temperature deposits. In turn, the atomistic porosity is believed to be responsible for the lack of inducement of structural defects such as interstitials and associated stresses, as the energy requirement for the creation of interstitials (25eV)¹⁷⁶ is much higher than that required for the in-filling of vacancies (of the order of 5eV, as-indicated by the activation energy for lattice diffusion). Therefore, the energy transmitted (E_t) to the film lattice from the bombardment by ions and fast neutrals is preferentially expended in filling the microscopic voidage, which is believed to be a pre-requisite stage to the inducement of ion-bombardment structural damage.

There are three potential arguments thought to be accountable for the relative ineffectiveness of ion bombardment in EB-PVD YSZ deposition:

1-the magnitude of the inherent atomistic voidage in the low temperature deposits reduces the scope of the bombarding ion/neutrals for producing long-range and inward collision cascades in the film lattice. This is to say that the efficiency of ion bombardment in causing lattice densification decreases with decreasing atom packing density.

2-the incident energy of ion/fast neutral bombardment per condensing atom (E) is insufficient, especially when compared to that in bias sputtering, where E is greater by more than an order of magnitude relative to that for ion plating (see chapter 8).

3- the masses, between gas atom (m_g) and lattice cation (m_l), are dissimilar which reduces the transmittable energy of ion bombardment to the film lattice, as indicated by the maximum fraction of transmittable energy¹⁷⁶ (E_t/E):

$$\frac{E_t}{E} = \frac{4m_g m_l}{(m_g + m_l)^2} \quad (104)$$

Considering that previous investigators¹⁷⁷ found that ion plating was effective for other deposit materials, such as TiN, with expected similar E values to that used in this work, it is perceived that the lack of effectiveness of ion plating with YSZ arises mainly from the inherent deposit microporosity, as deposited at low temperature, and from an inadequate Zr-to-Ar mass ratio.

10.2.2 Scope for improving the effectiveness of ion plating

Based on the above considerations, there exist potentially three different routes to improve the effectiveness of ion plating in EB-PVD YSZ: these are

increasing E , changing the working gas and increasing the deposit atom density. If the attempt of using ion plating to render low temperature deposited EB-PVD TBC's thermally stable was to be pursued, then the microporosity responsible for the ceramic to sinter would have to be resorbed by the sole effect of ion bombardment. Greater E values should be sought along with a working gas more appropriate to improve the transmitted bombardment energy to the film lattice. In principle, increasing the incident energy of bombardment per condensing atom (E) can be achieved either by increasing the power density of bombardment P_b , or decreasing the deposition rate J_v as

$$E = \frac{P_b}{J_{vap}} \quad (105)$$

Clearly, the latter option can be ruled out for obvious economics considerations of the industrial process. Therefore, increasing E relies on increasing the power density of ion bombardment (P_b).

10.2.2.1 Potential synergistic effects of deposition temperature and ion bombardment:

If the more realistic route of high deposition temperatures is chosen, the coating densification is provided by default by thermal excitation, which increases the scope for ion inducement of structural damage using heavier gas atoms and greater E values. The possibility has been evoked in chapter 8 that the freshly deposited atomic layers act as a buffer to the generation of ion-induced structural damage, as these contain a high level of microporosity. If there is such an effect, the thickness of this buffer layer should decrease with increasing deposition temperature, according to the coating growth model. However, too high deposition temperatures could anneal out the structural damage induceable by ion bombardment and thus there needs to be an intermediate temperature regime where structural damage can be produced to a significant level and be stable at the typical operating temperatures in the High Pressure Turbine sections. If one refers to the work after Cléry⁹⁴ on bias sputtered YSZ, it was found that the ion-induced atomic disorder, manifested by peak broadening, was unrecoverable upon annealing at temperatures up to 1350K. This allows one to think that there is scope to introduce significant and permanent structural damage using ion bombardment in EB-PVD TBC's over a certain a temperature/ion bombardment regime.

10.2.2.2 RF or DC biasing?

If ion plating is to be used in conjunction with high deposition temperatures, the alternative exists between using RF or DC biasing.

As experienced in this study, RF electric fields make even more acute the difficulty of designing HV electrical feed throughs with a dielectric strength capable of resisting the high temperature environment. Another difficulty associated with RF biasing was that the emitted radiation interfered with the control electronics of the evaporator, causing the abortion of numerous projected coating runs. The radiation from the RF field also interfered with the electrics of sensors, such as temperature and pressure monitors. These difficulties experienced with the laboratory coater can be expected to be manifold greater in an industrial plant, considering the high degree of sophistication expected. Moreover, capacitively coupled RF discharges suffer from the added constraint that no net current must flow to the cathode over the RF period. This makes them less flexible than their DC counterpart as this was thought to be a cause for their extinguishing in the presence of an added vapour ion flux (see chapter 7).

DC biasing is therefore a more recommendable approach to high temperature ion plating than RF biasing, for a ceramic that is an electrical conductor at temperature.

10.2.2.3 Increasing the power density of ion bombardment:

Increasing the power density of ion bombardment can be achieved by increasing the substrate bias voltage and current densities, either simultaneously or independently, in the presence of an external ionizing agent.

Increasing the substrate bias voltages, as a means of increasing both the energy and the flux densities of the bombarding species, is an option that is practically limited by the capability of the electrical insulation of the HV feedthrough to withstand the electric field in the high temperature environment. Therefore, a more recommendable approach would be to seek increased current densities. It was found that high temperature DC biasing was accompanied by thermionic electron emission from the cathode (substrates), and that these electrons, accelerated by the substrate bias voltage, provided further ionization (see chapter 7). Cathode thermionic emission offers extra flexibility as it permits the increase in current densities, at a set substrate bias, by increasing the cathode temperature. To this effect, it should be recalled that small changes in cathode temperature translates into dramatic increases in thermionic current:

$$\frac{I(T+\Delta T)}{I(T)} = \left(1 + \frac{\Delta T}{T}\right)^2 \exp \frac{\Phi \Delta T}{kT(T+\Delta T)}$$

where Φ , activation energy, is a function of the applied voltage and of the work function of zirconia for thermionic emission. Increasing the cathode temperature implies using higher deposition temperatures, which is

compatible with increasing the effectiveness of ion plating on the ceramic structure as discussed above.

An alternative approach to increasing the ion current densities, at a set bias voltage, would consist in increasing the gas density within the chamber. Such an approach was hindered in the present work due to the limitations imposed by the maximum operating pressures permissible for the 270° EB gun. Such limitations only exist to a lesser degree with Pierce guns which would make this approach more practical within an industrial coater.

One could have first expected that the gun electron beam would provide overriding ionization of the gas, considering the magnitude of the current involved (typically 0.6A) compared to tens of mA for the thermionic electrons from the substrates. If so, the ion current drawn by the substrates at a set electron beam current and accelerating voltage would have increased markedly with increasing the pressure (see Figure 74). This lower-than-expected enhancement from the gun electron beam can be explained considering that the electron beam traverses a region of the chamber where the gas is rarefied. This is because the gun assembly is housed in the lower chamber at a pressure of about 10^{-4} Torr and that the gas density in the vicinity of the evaporation source is lowered due to the very high temperature. This situation however would not be representative of that in the industrial coater, where:

- the path covered by the electron beam emitted from a Pierce gun is longer than that in the laboratory process

- the gas density in the chamber volume traversed by the electron beams may be potentially higher than that in the Cranfield reactor.

Therefore, it is expected that the discharge enhancement from the gun electron beams in an industrial coater will be more significant than that experienced using the laboratory facility in this study.

Finally, as ion recombination occurs predominantly at the wall surfaces, the plasma density is believed to increase with increasing plasma volume-to-surface ratio, for given ionizing conditions. Because of its greater dimensions, higher plasma densities should be expected in an industrial coater than in a laboratory facility for identical biasing conditions and gas density.

In the light of the above considerations, it may be concluded that any benefits attributable to ion bombardment obtained using the laboratory facility should be achievable more easily using an industrial facility.

10.2.2.4 Working gas substitute

Krypton (atomic mass=83.8), as a substitute to argon (atomic mass=39.9) or oxygen would offer the perfect match in terms of maximum fraction of

transmittable incident energy to the Zr (atomic mass=91.2g) cations (see equation (104) and Table XXV).

Table XXV: Maximum fraction of transmittable energy in the elastic collision between of a gas atom/ion and a lattice cation in zirconium.

	Ar (39.9)	O ₂ (32)	O (16)	Kr (83.8)
Zr(91.2)	0.85	0.77	0.50	0.998

Still, the economics of using Krypton would have to be looked into, with the possible option of gas recycling using a closed loop exhaust.

It is not known what fraction of the oxygen plasma is dissociated into atomic oxygen. Clearly, the relative proportions of atomic to molecular oxygen ions impinging on the substrates will influence the significance of ion bombardment. It is recognised that the low mass of the atomic oxygen ion species is partly responsible for the relative ineffectiveness of oxygen ion plating, then to compensate it is recommended that substitute working gases, such as Krypton, should be used as indicated in Table XXV. This however implies that the ceramic be deposited under oxygen deficient conditions, which would represent a significant departure from the current industrial practice. This addresses the need to better understand the role of oxygen partial pressure on the coating structure.

10.2.3 Effect of oxygen bleed

The bleed of oxygen in the vacuum furnace was introduced as a means to replicate the commercial deposition process. It was observed that the presence of a partial pressure of oxygen within the chamber had a marked influence on the deposit properties in many respects. As the programme did not concentrate specifically on understanding the effect of oxygen pressure on the structure of the EB-PVD TBC's, some of these experimental observations are at this stage not fully understood.

10.2.3.1 Phase composition:

Depositing the ceramic under oxygen deficient conditions lead to the formation of the monoclinic phase. It was found however that the monoclinic phase could be reverted back to the non-transformable tetragonal phase after ageing in air at 700°C. This phase transformation is believed to be the consequence of the resorption of the coating oxygen deficiency. This observation naturally raises the question as to whether the monoclinic-to-

tetragonal transformation undergone by the deposit is detrimental to its mechanical integrity. If not, then one should address the question of the necessity of evaporating zirconia in the presence of a partial pressure of oxygen, given that this is an added complication to the deposition process which could be avoided using a post-deposition ageing in air at low temperature. This is permissible because of the low activation energy for oxygen diffusion. This question is central to the adoption of a substitute working gas, such as Krypton, for enhancing the effectiveness of ion plating.

10.2.3.2 Texture:

The $\langle 111 \rangle$ coating texture was found to systematically be the prevailing crystal growth habit when depositing the ceramic in a pure argon environment. Textures such as the $\langle 100 \rangle$ or $\langle 001 \rangle$ were obtained for the first time when the bleed of oxygen during deposition was introduced. Coatings that were deposited in pure argon in the early stage of the deposition followed by the introduction of oxygen bleed still could exhibit textures such as the $\langle 100 \rangle$ or $\langle 001 \rangle$ that were never obtained when the depositions were fully carried out in pure argon. The latter observation suggests that the crystal growth habit can be disrupted *in vivo* by changing the rate of oxygen atom impingement of the growing coating crystallites as discussed in chapter 8.

10.2.3.3 Indentation resistance

There was also indication that the gas evaporated coatings deposited in 90%O₂/Ar had a surface indentation resistance greater than those deposited in pure argon. To account for such an effect one could evoke that the coating being deficient in oxygen is less dense than its stoichiometric counterpart and thus offers less resistance to indentation. Alternatively, the oxygen deficiency may have reduced the cation diffusivities during film growth and thus increase the residual porosity content, as would imply the logic of the coating growth model. This proposition however would disagree with Strangman²⁰ who associated the presence of a thin dense zirconia region adjacent to the interface with the bond coat with the initial deposition in oxygen deficient conditions. It is interesting to note that the same author reported that abnormally low oxygen bleed during deposition resulted in a zirconia microstructure that was too dense after exposure to an oxidising environment, an effect attributed to the ceramic expanding upon recovering stoichiometry. The observations after Strangman²⁰ are consistent with the apparent dependence, in this study, of indentation resistance on stoichiometry. However, further work is needed to ascertain the role of oxygen bleed on the structure of EB-PVD TBC's.

10.2.4 **Deposition temperature and gas density:**

In the light of the analysis in chapter 7, it was realised that the need for high temperatures of deposition in the manufacture of EB-PVD TBC's bore some major implications on the physics of the deposition process as a whole.

Probably one of the most significant observations regarding the physics of the deposition process was the importance to distinguish between gas density and chamber pressure. Chamber pressure is *a priori* uniform within the chamber volume, which makes it a practical parameter to monitor. Gas density however varies inversely with temperature for a given chamber pressure. Therefore, a distribution of temperature within the chamber volume will correspond to an associated distribution in gas density. This is a very important consideration to bear in mind given the positioning of the heat sources and heat sinks in a typical industrial PVD coater from which large temperature gradients across the chamber volume should be expected. Moreover, the average chamber temperature can be expected to increase with coating campaign time, as the rate of heat loss from the water cooled chamber walls and condensation hood potentially continuously decreases with the build up of ceramic condensate. At a set mass flow rate of gas and pumping speed, this potentially leads to a decrease in the mean gas density within the chamber. Gradients and fluctuations in gas density should be taken in earnest as these will change the gas scattering effects on the vapour flux pattern, in terms of vapour density, vapour atom kinetic energy and direction. This potentially leads to variations of coating structure within a batch of coatings and inconsistencies from one batch processed early to one batch processed late in a coating campaign cycle.

Moreover, gradients in gas density within the chamber are associated with gradients in gas atom impingement rate on the substrate, which, in the case of a reactive gas such as oxygen, may lead to variations in coating properties within a batch, such as stoichiometry, texture and crystallographic structure as discussed above. Sohn, Biederman and Sisson⁸² reported wide variations in the crystallographic texture of deposits within the PVD chamber, which could not be correlated to the controllable deposition parameters. In this study similarly, different crystal orientations have been found in deposits processed under nominally the same conditions in the same coating run, when using the vacuum furnace with the oxygen bleed. It is possible that an inhomogeneous distribution of oxygen gas density in the furnace enclosure played a part in this variation of texture.

Lastly, relative to the prospect of incorporating electrical biasing for ion plating, it is clear that variations in gas density would lead to variations in ion current densities impinging on the parts being coated.

Given these considerations, there is a strong requirement to ensure a uniform gas density surrounding the batch of parts to be coated (i.e. known temperature distribution and pressure), as variations in this process parameter potentially has repercussions on a number of other process conditions.

10.2.5 Kinetic energy of deposition:

It is thought that the effect of vapour atom kinetic energy should not be overlooked as a parameter controlling the structure of EB-PVD TBC's deposited at high temperature. If one refers to the sputtering of YSZ after Cléry⁹⁴, films with no measurable porosity were formed with deposition temperatures of 250°C and no substrate bias. At this temperature, this level of density achieved can only be attributed to the incident kinetic energy of the vapour atoms, which is typically a few eV. In other words, YSZ films with near bulk densities form with energies of a few eV per condensed atom. This is in sharp contrast with the situation in ion plating, where deposits with 50% density are formed in spite of incident energies of ion bombardment per condensing atom of 20eV. This comparison implies that the structure of YSZ PVD deposits is more sensitive to the kinetic energy of the condensing atoms than the incident Ar ion bombardment energy per condensing atom. Other investigators^{178,179} have reported the detrimental effect of gas scattering on the structure of evaporated films.

10.3 TBC PERFORMANCE

10.3.1 Thermal conductivity

10.3.1.1 Defective ceramic structures

Air plasma sprayed TBC's owe their superior thermal insulation capability to the shape and distribution of the porosity parallel to the coating plane. In contrast, the inter-columnar porosity in EB-PVD TBC's does not hinder the conduction of heat since this porosity is normal to the coating plane. Although it is believed that the bulk of the intra-columnar porosity in EB-PVD TBC's is segregated at the boundaries between the elementary crystallites, it is not unfair to propose that it can still contribute to reducing the ceramic thermal conductivity. If such a proposition was valid, the propensity of EB-PVD TBC's to grow with the entrapment of residual porosity within the columns could be used to advantage to enhance their thermal insulation capability.

One can think of many ways of increasing the intra-columnar porosity content of EB-PVD TBC's given the coating growth model proposed in this work. In the light of Table XXIV, an optimised combination of deposition conditions can be sought so as to maximise the residual porosity content within the TBC ceramic columns.

For example, modifying the ceramic composition in order to reduce the cation diffusivities is a possible approach. For example, evidence exist in the literature that increasing the yttria content decreases the cation diffusion rate. Therefore, EB-PVD YSZ systems with increased yttria concentration

would be expected to exhibit lowered thermal conductivity. This derivation can be tested using the output of the Brite Euram TBC programme¹⁸⁰ in which the thermal conductivity of both 8wt% and 20wt%Y₂O₃-ZrO₂ EB-PVD systems, deposited by DLR, was evaluated. In accordance with the expectation, the thermal conductivity of the latter was found to be lower than that of the former at all test temperatures (1.2W/m.K against 1.4W/m.K). Of course one should address the question as to whether this difference is significant or whether it reflects variations within the bounds of the coating process reproducibility. The potential however exists to select the nature and concentration of the stabilising oxide with the view to lower the cation diffusion of the zirconia so as to promote the formation of porosity. Also, increasing gas scattering as a means to reduce the kinetic energy of the vapour atoms could be a practical way of increasing the intra-columnar content. Above all, the deposition temperature is the most effective parameter controlling the porosity content in EB-PVD TBC's. An optimised approach could consist in combining a reduced deposition temperature (but still greater than T₁) with a zirconia system with reduced cation diffusivities. It must be pointed out that the minimum thermal conductivity achievable using this approach should be less than the thermal conductivity of the low temperature deposits in the as-annealed state (post-deposition sintered). It is therefore recommended to measure the latter as a means of assessing the scope for thermal insulation improvements using the above proposed approach.

10.3.1.2 Layered ceramic structures

It must be pointed out that ion plating is antagonist to the approach proposed above as, to the contrary, one of its effects is to promote ceramic densification. However, scope exists for using intermittent ion plating as a means of inserting structurally damaged ceramic layers (structure modulated ceramic structures). The concept of layered ceramic structure is a concept being pursued at General Electric¹⁵⁰.

It is proposed that the concept of interfacing the ceramic structure can be approached by pulsing oxygen within the deposition chamber. This follows from the experimental indication in this work that the ceramic crystal growth habit could be disrupted *in vivo* by changing the oxygen partial pressure. For instance it is believed that crystallographic textures such as the <100> can only be achieved with a sufficient oxygen atom impingement rate to allow for the formation of pure oxygen planes normal to the crystal growth direction. Disrupting the crystal growth habit by pulsing oxygen gas in the deposition chamber is therefore expected to induce coating renucleation.

Although the following idea may be considered amongst the most adventurous of those proposed in this document, it is wondered whether the brittle erosion behaviour of EB-PVD TBC's at room temperature and the damage morphology consisting of the lateral cracking of the columns could be beneficial in terms of their insulation capability. It is legitimate to think that the fractured columns are less prone to conduct heat than their intact

counterparts. Moreover it was concluded that the in-depth lateral cracking of EB-PVD TBC's was not detrimental to their erosion performance as the erosion rate of these systems is controlled by the rate of removal of shallow plastically deformed surface debris (see Figure 168 in chapter 9). If the ceramic decohesion, consisting of the stack up of elongated column segments does not compromise their resistance to other degradation modes, such as thermal cycling for example, then why not deliberately introduce this kind of structural damage in a controllable manner, using glass peening for example, as an attempt to improve their insulation capability.

10.3.2 Erosion performance

In this work, some understanding of the erosion behaviour of EB-PVD TBC's has been generated and some important structural parameters have been highlighted as controlling their erosion performance. It is now of interest to compare this understanding with the ideas that have been conveyed in the literature.

A recurrent proposition in the literature is that erosion resistance should be sought via ceramic densification (see chapter 2). In this work, no straight forward relationship was found between coating density and erosion rate given that systems with both high and low column packing density were found to erode at similar rate. The fact that the ability of EB-PVD TBC systems in resisting erosion loss was not directly related to their density was illustrated by the lack of correlation between the room temperature indentation resistance, believed to reflect coating density (see chapter 8), and the erosion rate at 910°C (see figure in chapter 9).

More pertinently, it is concluded in this work that the erosion performance of EB-PVD TBC's is controlled by the extent to which they can exhibit ductility. The more impact energy can be expended into plastic work, the more resilient to erosion the ceramic can be. Column diameter and the population of inherent defects are therefore believed to be crucial parameters to consider. Given this line of thought, one could believe that the proposal of improving the thermal insulation capability of EB-PVD TBC's by maximising their residual porosity content is in conflict with their resistance to erosion. This is true as far as erosion rate is concerned. However, it was pointed out that a good surface finish retention for EB-PVD TBC's results from a more brittle behaviour, and that too extensive a plastic behaviour may lead to surface roughening.

As reduction in thermal conductivity of EB-PVD TBC's is the prime aim of all the R&D efforts in ceramic structural developments, it should be sought even if it leads to a compromise in the coating erosion resistance, within acceptable limits.

CONCLUSIONS

The aim of this work was to generate a sound understanding of the role of deposition temperature and plasma assistance on the structure of EB-PVD ZrO_2 -8wt% Y_2O_3 ceramics and to appraise how this understanding could be exploited to achieve improved TBC performance. Increased awareness has been achieved regarding the physics of the deposition process, their influence on the structural properties of the deposit and the erosion behaviour of EB-PVD TBC's. New explorable approaches are formulated to increase the thermal insulation capability of EB-PVD TBC's.

The findings of this work can be summarised as follows:

Plasma physics:

1.

Simple mathematical modelling of DC gas discharges was carried out to estimate the ion current densities impinging on the substrates. As the substrate temperature is increased, the plasma sustaining mechanism shifts from secondary electron emission maintenance to thermionic electron emission maintenance. Thermionic emission at temperatures as low as 900°C is significant due to the enhancement from the electric field in the surface vicinity of the electrically biased substrates.

2.

It was demonstrated that increasing the temperature of the chamber environment resulted in a decrease in the chamber gas density and a resulting decrease in the ion current density drawn from DC substrate biasing.

3.

A semi-empirical methodology was developed to estimate the ion current density impinging on the substrates from low frequency RF gas discharges, using cathode heating considerations. The results from this analysis were consistent with the assumptions that the ions in transit in the plasma sheath respond to the instantaneous sheath field, and that the energy delivered by the ions is proportional to the square of the quadratic time averaged sheath voltage over the RF period (τ):

$$\langle V_{c,sheath} \rangle^2 = \left(\frac{1}{2} + \frac{a}{\pi} \right) (V_{DC}^2 + \frac{V_{RF}^2}{2}) - \sin(2a) \frac{V_{RF}^2}{4\pi} + \cos(a) \frac{2V_{DC}V_{RF}}{\pi} \quad (107)$$

with

$$\alpha = \arcsin\left(\frac{V_{DC}}{V_{RF}}\right) \quad (108)$$

where V_{RF} , V_{DC} and t are respectively the RF voltage, RF induced DC voltage on the driven electrode and time over which the potential of the driven electrode is negative relative to ground.

4.

E evaporation was found to interact with plasma assistance leading to an increase in the ion current density with DC ion plating and causing the RF plasma to extinguish. The extinguishing of the RF plasma is thought to originate from a combination of lowered gas density and the added vapour ion flux perturbing the net zero charge flow requirement on the cathode.

Structure of EB-PVD YSZ

5.

Low temperature gas evaporated YSZ deposits contain a massive content of microscopic voidage (~50%). This is responsible for their lack of thermal stability.

6.

A model for the post-deposition annealing behaviour of low temperature deposited YSZ has been developed. It highlights that sintering densification occurs with a low mass transport activation energy. This corroborated the atomistic distribution of the ceramic porosity referred to above.

7.

A 'dynamic sintering' coating growth model is proposed. This is based upon the parallels between the effects of post-deposition annealing and deposition temperature. This model was appraised against the Structure Zone Model after Movchan and Demchishin and other findings from independent investigators, and accounts for the observations in ZrO_2 deposition over a wide range of studies.

8.

Low temperature RF ion plating failed to overcome the effects of the bulk microporosity content in YSZ deposits. Some coating densification was observed. As such, RF ion plating in argon was found not to be a substitute for high deposition temperatures.

9.

High temperature ion plating of YSZ using RF and DC substrate biasing did not result in significant ion-induced structural damage of the ceramic ('ion-peening').

10.

No significant internal stresses were found in EB-PVD YSZ regardless of the ion plating and deposition temperature regime.

In light of conclusions 9 and 10, the scope for improving the effectiveness of ion plating in causing ion-induced structural damage was assessed, and recommendations formulated to this effect.

11.

Oxygen bleed during deposition was found to be very influential to the crystallographic structure of YSZ deposits. Oxygen deficient deposition conditions favour the formation of the monoclinic phase and the <111> texture at high deposition temperatures. The monoclinic phase can be converted back into tetragonal upon restoration of the coating stoichiometry.

TBC erosion performance

The erosion behaviour of commercial TBC's as-deposited by plasma spraying and electron beam physical vapour deposition was investigated. This involved upgrading the temperature and velocity capability of an existing erosion test facility, so as to evaluate the erosion performance of TBC's under conditions representative of the High Pressure Turbine environment. A specimen test temperature of 910°C was achieved with predicted particle velocities of 300m/s for 60µm particles. This represents a unique testing capability within Europe to date.

12.

Erosion follows a pure brittle behaviour for both the APS and EB-PVD TBC's at room temperature.

13.

Increasing the test temperature was found not to adversely affect the erosion rate of YSZ systems, but to the contrary, there is indication that erosion of EB-PVD TBC's is less severe, the higher the temperature. This is attributable

to the ability of the ceramic to absorb some of the energy from the particle impacts by undergoing plastic deformation. This behaviour was in contrast with that of the APS TBC's that exhibited a pure brittle behaviour even at 910°C.

14.

High temperature erosion with silica particles was found to be the most severe at glancing angles of impingement. This was attributed to the pastiness of these particles at high temperature, favouring the removal of ceramic surface debris.

15.

The erosion damage morphology of EB-PVD TBC's features both plastic deformation of the near surface region and fracturing of the columns to a depth of a few tens of microns. The erosion rate of the commercial EB-PVD TBC is controlled by the rate of removal of the shallow surface debris originating from the lateral cracking underneath or within the plastically surface deformed region.

16.

Common defects in EB-PVD deposits such as 'flakes' are readily removed upon particle impact leaving a pit down to the bond coat. These so formed holes are potential sites for localised corrosion attack which could compromise the integrity of the coated component. The significance of this problem must be addressed.

The high temperature erosion behaviour of the coating systems deposited at Cranfield was evaluated. From this study, two major coating structural parameters were identified as controlling the erosion performance of EB-PVD TBC's. These are respectively the coating morphology, in terms of column diameter, and the population of defects inherent to the ceramic columns.

17.

Coating hardness, as measured at room temperature, was not found to correlate with the erosion rate at 910°C.

18.

The residual porosity within the columns, originating from the dynamic sintering coating growth, and increased column diameter promote a brittle response to particle impacts.

FURTHER WORK

EB-PVD process

Further understanding of the EB-PVD process is required to improve coating reproducibility and optimize TBC performance. In particular further work is required to better understand the role of:

- substrate rotation

The work in this study was carried out on static substrates. Substrate rotation would be required to coat all round turbine components.

- oxygen bleed

In particular, this work should address the role of the tetragonal-to-monoclinic transformation in EB-PVD YSZ resulting from the restoration of stoichiometry using TEM techniques. The author is not aware of studies on the tetragonal-to-monoclinic transformation in EB-PVD systems.

- gas scattering

It is thought that the reduction of vapour atom kinetic energy from gas scattering plays a significant role in increasing the inherent microporosity of the deposit. This effect could be assessed by comparing the structure of EB-PVD YSZ as deposited in hard vacuum and as-deposited in a partial pressure of gettered argon, using both low and elevated deposition temperatures.

- vapour flux pattern

The major difficulty encountered in this work was to establish good evaporation conditions in a reproducible manner. This was found to have major repercussions on the reproducibility in coating morphology. This only emphasizes the importance of the vapour flux pattern (field of vapour atom density, velocity and direction) in controlling the deposit morphology. In order to better control the vapour flux pattern and understand its influence, in-depth theoretical studies should be undertaken using computer simulation, assessing the role of source geometry and evaporant material.

- deposition rate

The actual rate of deposition in the industrial process (3 μ m/min on rotated hardware) is higher than that used in this study (3 μ m/min on static substrates). This could be partly responsible for the difference in morphology (greater column diameter) and greater inherent porosity of the ceramic

columns. The importance of quoting deposition rates in mass per unit area per deposition time as a more relevant deposition rate parameter is indicated. This simply involves weighing the parts prior to and after deposition.

- Plasma assistance

Further work is required to understand the reason why the RF plasma extinguished with electron beam evaporation. To ascertain whether it is gas density related, one could attempt to re-establish the plasma by increasing the gas flow rate. To ascertain whether it is related to the zero net charge flow on the cathode, it could be attempted to remove the coupling capacitor. One of the consequence of removing the capacitor would be to eliminate the DC offset, thus lowering and increasing the amplitude of the cathode and anode sheath voltage respectively.

In order to improve the effectiveness of ion bombardment, it is recommended to carry out depositions at higher temperature. This would have the effect of increasing the ion current density by increasing the ionizing thermionic electron current as well as accelerating the densification of the film near surface atomic layers, so that structural damage can be induced.

In order to improve the effectiveness of ion bombardment, it is also recommended to substitute argon or oxygen for a heavier gas such as Krypton. The effect of ion mass on the effectiveness of ion plating could be investigated using both low temperature RF ion plating and high temperature DC ion plating.

Thermal insulation capability

Explore the potential of enhancing the thermal insulation capability of EB-PVD TBC's by maximizing their residual intra-columnar porosity content. As a first step, the thermal conductivity of the low temperature deposits in the as-annealed state (post-deposition sintered) could be measured. This should give a lower bound in thermal conductivity achievable using this approach. TEM should be used for characterising the residual porosity content.

Explore the potential of enhancing the thermal insulation capability of EB-PVD TBC's by oxygen bleed pulsing, as a means of interfacing the ceramic YSZ deposit.

Explore the potential of enhancing the thermal insulation capability of EB-PVD TBC's by mechanically introducing structural damage (room temperature peening?) in the form of fractured columns. As a first step, the thermal conductivity of EB-PVD YSZ ceramic deposited on a same substrate could be measured in the as-erosion tested state against the as-deposited state. If promising, the ceramic could be embrittled further by maximising its defectiveness as a means of enhancing the extent of column fracturing.

Erosion behaviour

To better understand the nature of the plastic deformation undergone by the EB-PVD TBC's under erosion damage, one could attempt to use X-Ray Diffraction or TEM techniques as a means of distinguishing between a dislocation glide or superplasticity mechanism for the ceramic deformation.

The significance of the potential localised corrosion attack, resulting from the formation of pits down to the bond coat after erosion removal of the coating's 'flakes', must be addressed.

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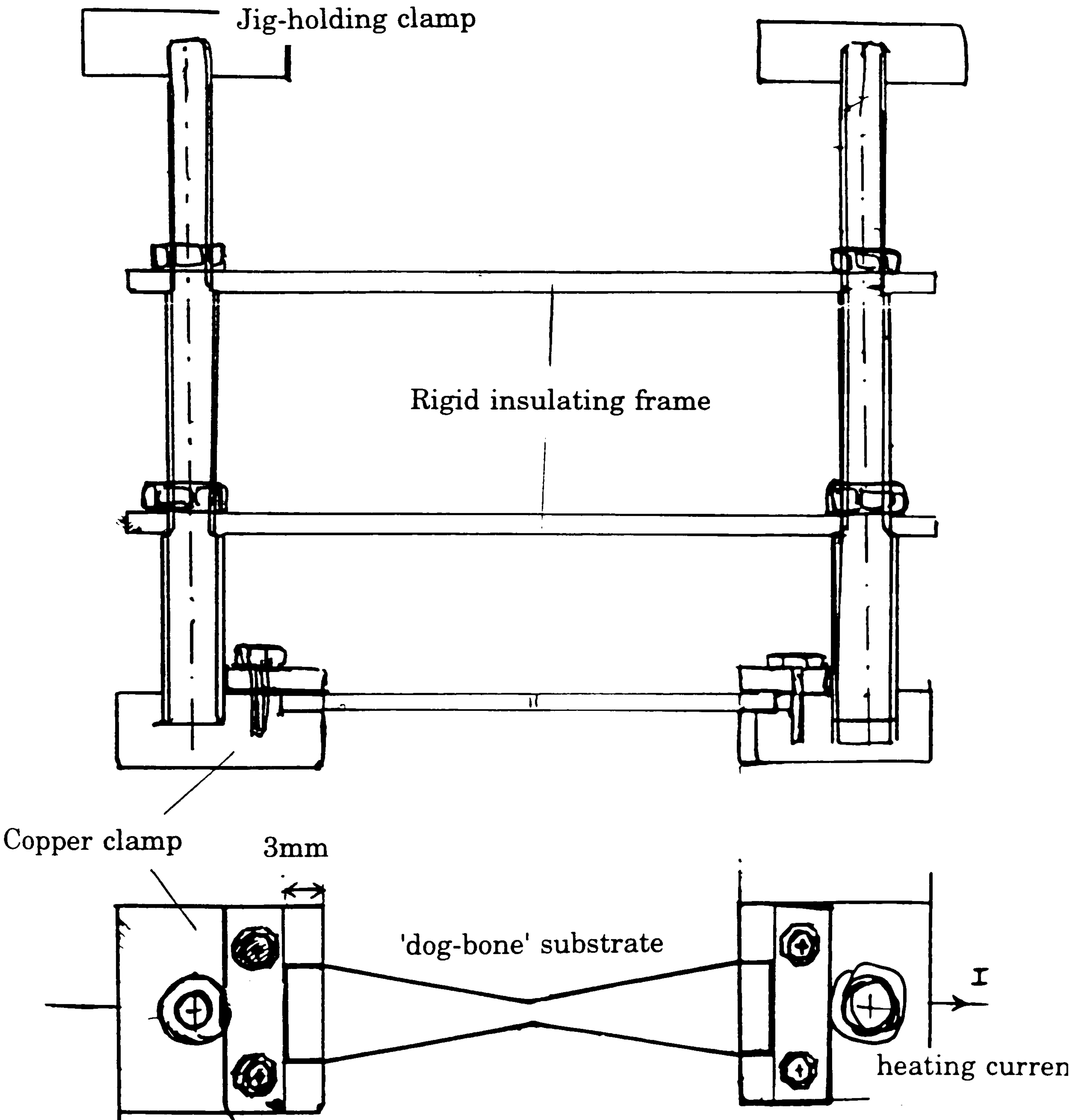
APPENDIX 1: CONVERSION TABLE OF YTTRIA CONCENTRATION IN ZIRCONIA.

Ref. G.Tremouilles 'Etude microstructurale d'interfaces céramique-métal'
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unknown variable

$\%$	X % mol in Y ₀ 1.5	Y % mol in Y ₂ O ₃	U % mass
X		$\frac{200 \cdot Y}{100 + Y}$	$\frac{100 \cdot U}{91,629 + 0,08371 \cdot U}$
Y	$\frac{100 \cdot X}{100 - X}$		$\frac{100 \cdot U}{183,258 - 0,83254 \cdot U}$
U	$\frac{100 \cdot X}{109,136 - 0,09136 \cdot X}$	$\frac{100 \cdot Y}{56,568 + 0,4543 \cdot Y}$	
V	$\frac{100 \cdot X}{92,831 + 0,0717 \cdot X}$	$\frac{100 \cdot Y}{46,4152 + 0,53585 \cdot Y}$	$\frac{100 \cdot U}{85,06 + 0,1494 \cdot U}$

APPENDIX 2: SCHEMATIC OF HOLDER JIG FOR THE RESISTIVE HEATING OF 'DOG-BONE' SUBSTRATES.



APPENDIX 3: PREPARATION PROCEDURE FOR EB-PVD TBC CROSS-SECTION EVALUATION

IMPREGNATION

1. Samples were pre-heated to 180°C for 30 minutes.
2. A8 resin was smeared over the coated surface.
3. Samples were cured at 180°C for 60 minutes.

MOUNTING

Triofix-2 mounting resin from Struers was used as per manufacturer's instructions.

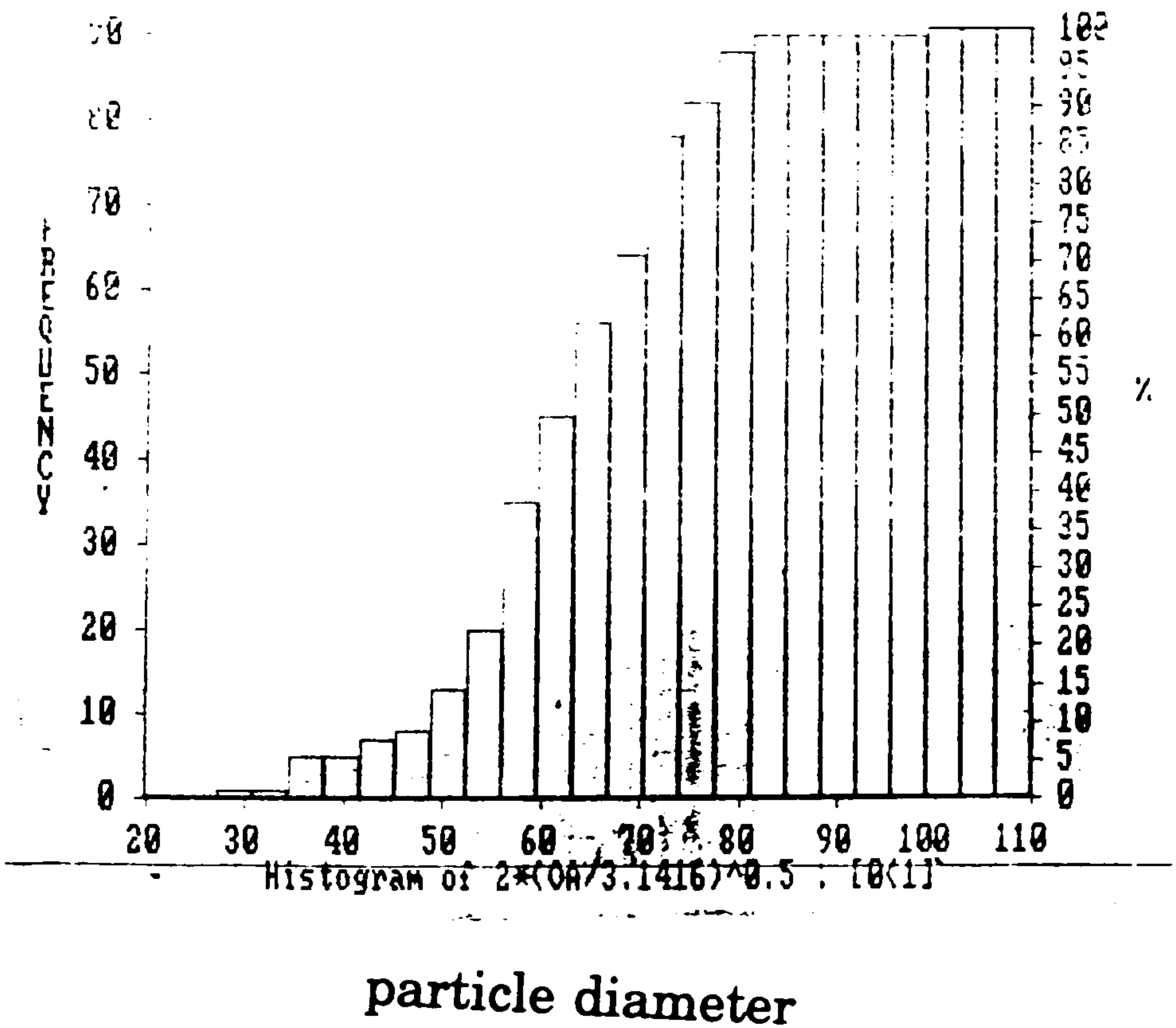
POLISHING

Surface	Abrasive	Force	Speed	time
Rotal	120 grit abrasive SiC	1 pound per specimen + 1.	250rpm	until flat
Rotal	220 grit abrasive SiC	1 pound per specimen + 1.	250rpm	1min
Rotal	1200 grit abrasive SiC	1 pound per specimen + 1.	250rpm	1min
I/S 1	6µm diamond	1 pound per specimen + 1.	150rpm	6 min
I/S 1	1µm diamond	1 pound per specimen + 1.	150rpm	30-60 seconds
DP Mol	0.06µm SiO ₂	1 pound per specimen + 1.	150rpm	30 seconds

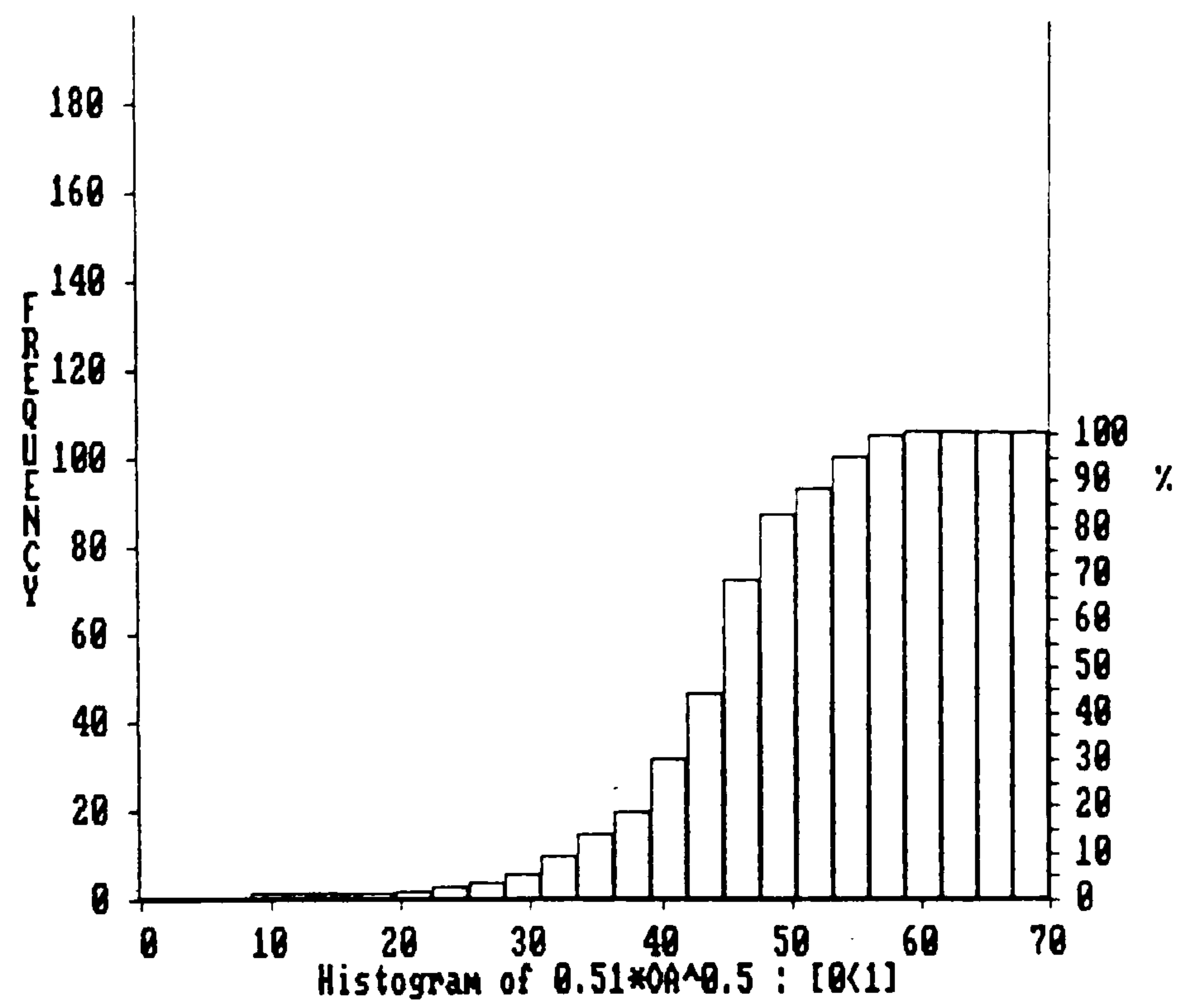
APPENDIX 4: SIZE DISTRIBUTION PLOTS AND STATISTICS OF PARTICLES USED FOR EROSION TESTING.

Particle diameter (µm)	Alumina grit (aspect ratio= 1)	Alumina grit (aspect ratio= 2)	Silica beads
Sample	over 109	over 109	over 189
minimum	20	18	18
maximum	136	122	104
median	102	92	60
25% quartile	92	82	59
75% quartile	106	98	27
mean	98	89	55
geometric mean	97	87	57
harmonic mean	93	83.8	55
Sample standard deviation	18	16	13

Silica beads:



alumina grit size distribution



particle radius

APPENDIX 5: METHODOLOGY FOR PREDICTING PARTICLE VELOCITY

The methodology used to calculate particle velocity comprises two steps. The first one is the choice of a simple flow model that describes satisfactorily the gas flow parameters (velocity, pressure, density) over the tube length travelled by the particles. The second is the derivation of particle velocity from the aerodynamic drag force which depends on the flow parameters inferred from the first step.

1 ESTIMATIONS OF GAS FLOW PARAMETERS

1.1 Assumptions

- The gas flow model was chosen mono-dimensional.

That is to say the gas parameters are described by the sole abscissa x (position on the tube). The implication is that variation of gas velocity with distance from the pipe wall (boundary layer) and velocity components normal to the main flow direction (turbulent flow) are ignored.

- The flow was assumed adiabatic.

This assumption is justified because:

- the gas used is not generating heat through a chemical reaction
- the tube is not heated externally
- the transit time of the gas in the tube is too short to allow for significant heat conduction losses of the gas.

To help the latter assumption hold true, the acceleration tube was wrapped with aluminium foiled 5cm thick mineral insulation material (Rockwool Fire Barrier).

- The friction losses were taken into account.

The significance of friction losses depends on the gas velocity, the surface finish of the tube wall and its aspect ratio. In the present instance, friction losses cannot be ignored seen the high gas velocities used and the high tube aspect ratio (length:635 mm, inner diameter:10 mm). If the flow were frictionless as well as adiabatic (isentropic), the gas velocity would not vary in the tube. Pressure measurements along the tube length contradict this hypothesis. It is therefore necessary to take into account the effect of friction.

The model that describes one-dimensional adiabatic flow with friction in a

constant area duct is called Fanno Line flow. Details can be found in the text book after James E.A. John¹³¹.

1.2 Features of Fanno flow theory

Fanno flow theory predicts that the Mach number either increases or decreases towards 1 depending on whether the flow is subsonic or supersonic respectively. For a given mass flow, the mach number cannot go passed 1. In the subsonic regime, if Mach 1 is already reached at the end of a duct, the addition of an additional length of duct would bring about a reduction in mass flow.

The flow parameters such as velocity, pressure and temperature are tabulated in a dimensionless form as V/V^* , P/P^* , T/T^* where $*$ is the Mach 1 reference point. These parameters can be related to the position in the tube via the dimensionless distance fL_{max}/d , where f is the friction coefficient, d the pipe inner diameter and L_{max} the distance from the point considered to the point at which Mach 1 would be reached. Figure 1 shows how the flow parameters vary with the position in the duct.

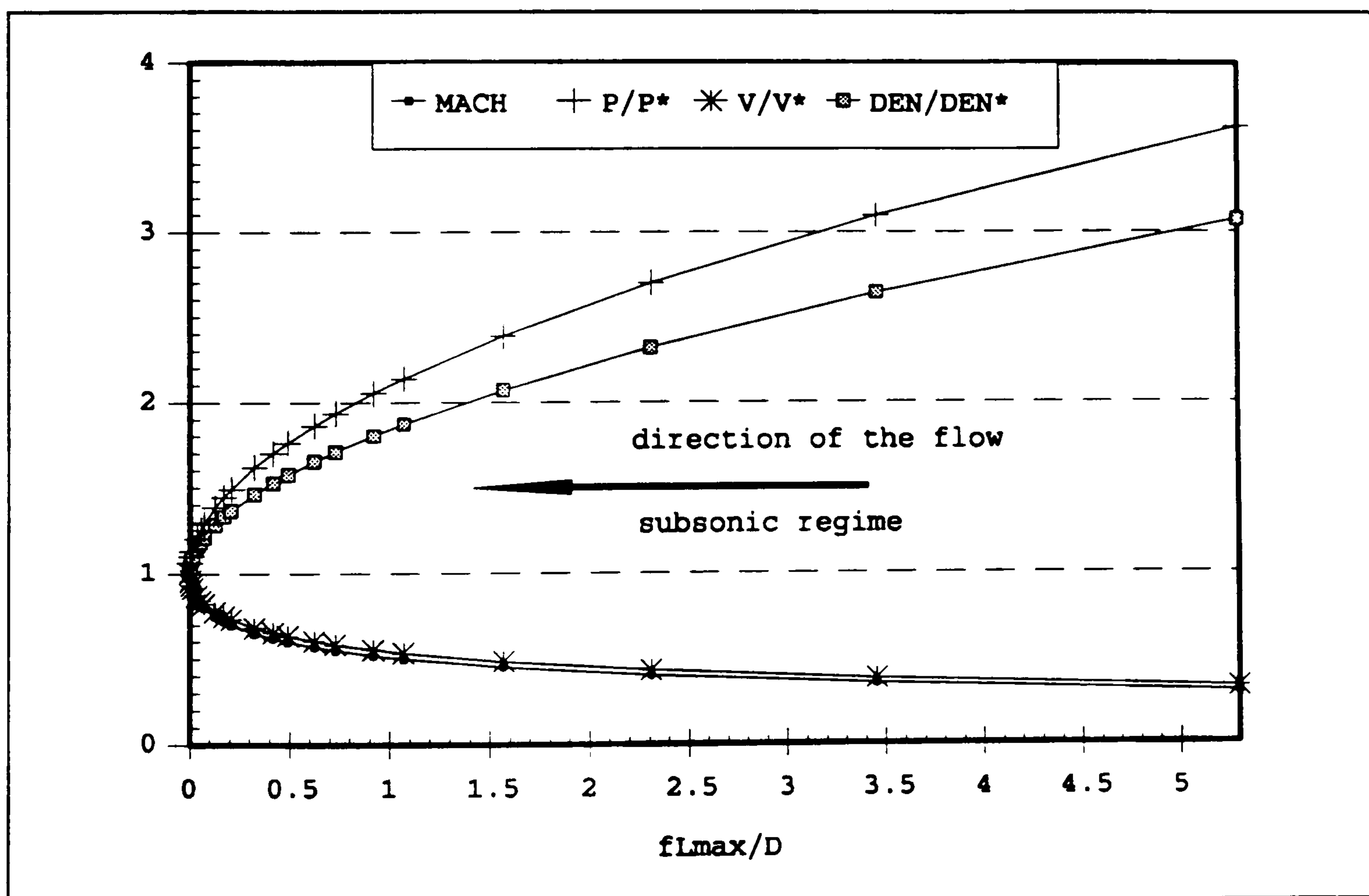


Figure 1: The dependence of gas flow parameters on position in the duct (Fanno flow theory)

The friction coefficient can be estimated from the Moody diagram (see Figure 2) as a function of the relative wall surface finish (center-line-average roughness over pipe inner diameter) and the flow Reynolds Number.

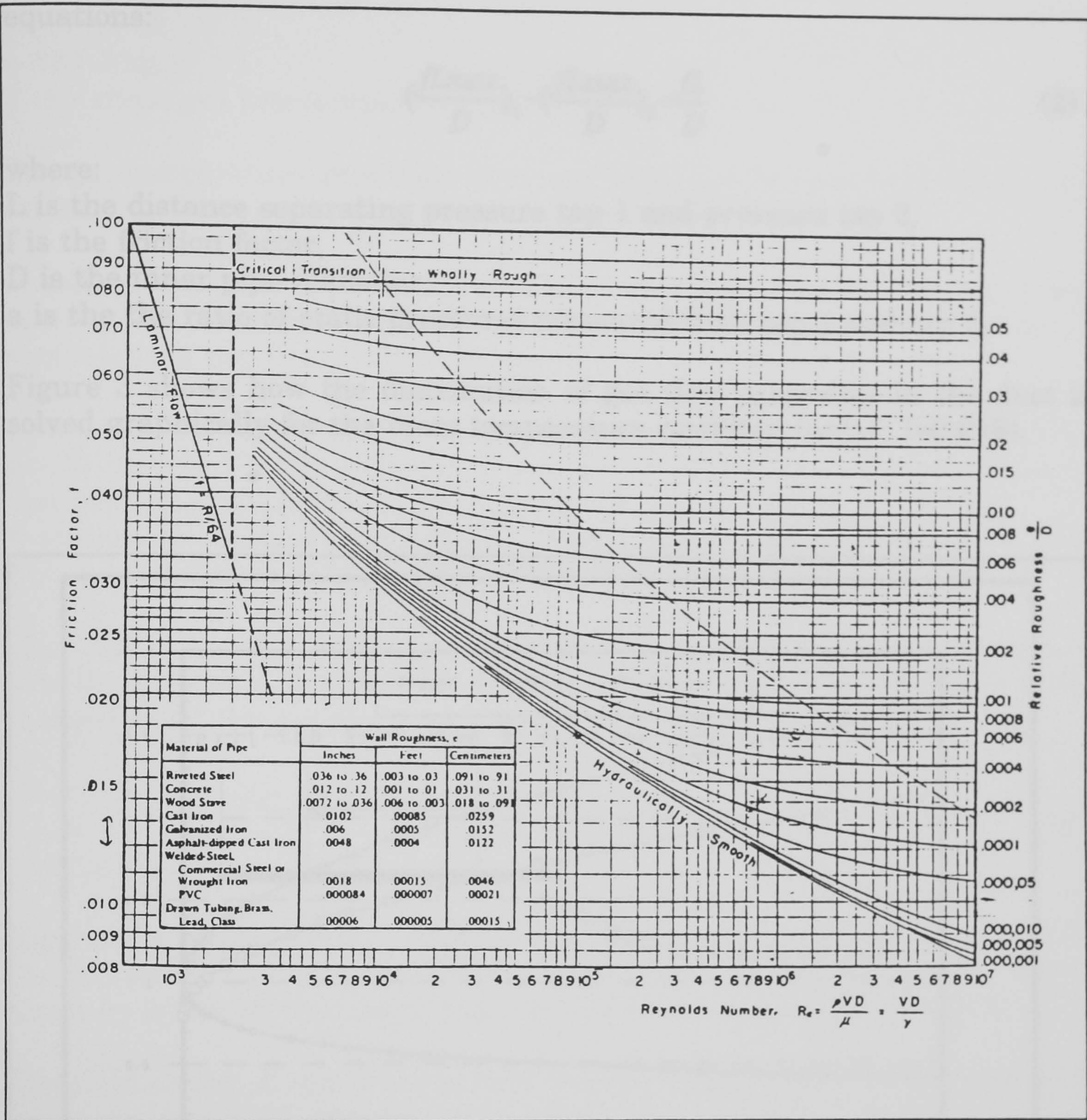


Figure 2: Moody diagram.

1.3 Methodology

Assuming that the assumption of Fanno flow regime is valid, then the distribution of gas properties inside the duct can be determined from the measurement of static pressure at two different points (1 and 2) and of temperature at one point.

1.3.1 Static pressure measurements

$$\frac{P_1}{P^*} \cdot \frac{P^*}{P_2} = a \tag{1}$$

The measurement of static pressure at two different points of the tube allows to determine the gas property profile. It suffices to solve the following set of

equations:

$$\left(\frac{fL_{max}}{D}\right)_1 - \left(\frac{fL_{max}}{D}\right)_2 = \frac{fL}{D} \quad (2)$$

where:

L is the distance separating pressure tap 1 and pressure tap 2,

f is the friction factor,

D is the inner pipe diameter,

a is the the ratio of static pressures measured from tap 1 and tap 2.

Figure 3 shows how the distribution of gas flow properties in the duct is solved graphically for the room temperature condition (a=0.8, f=0.016).

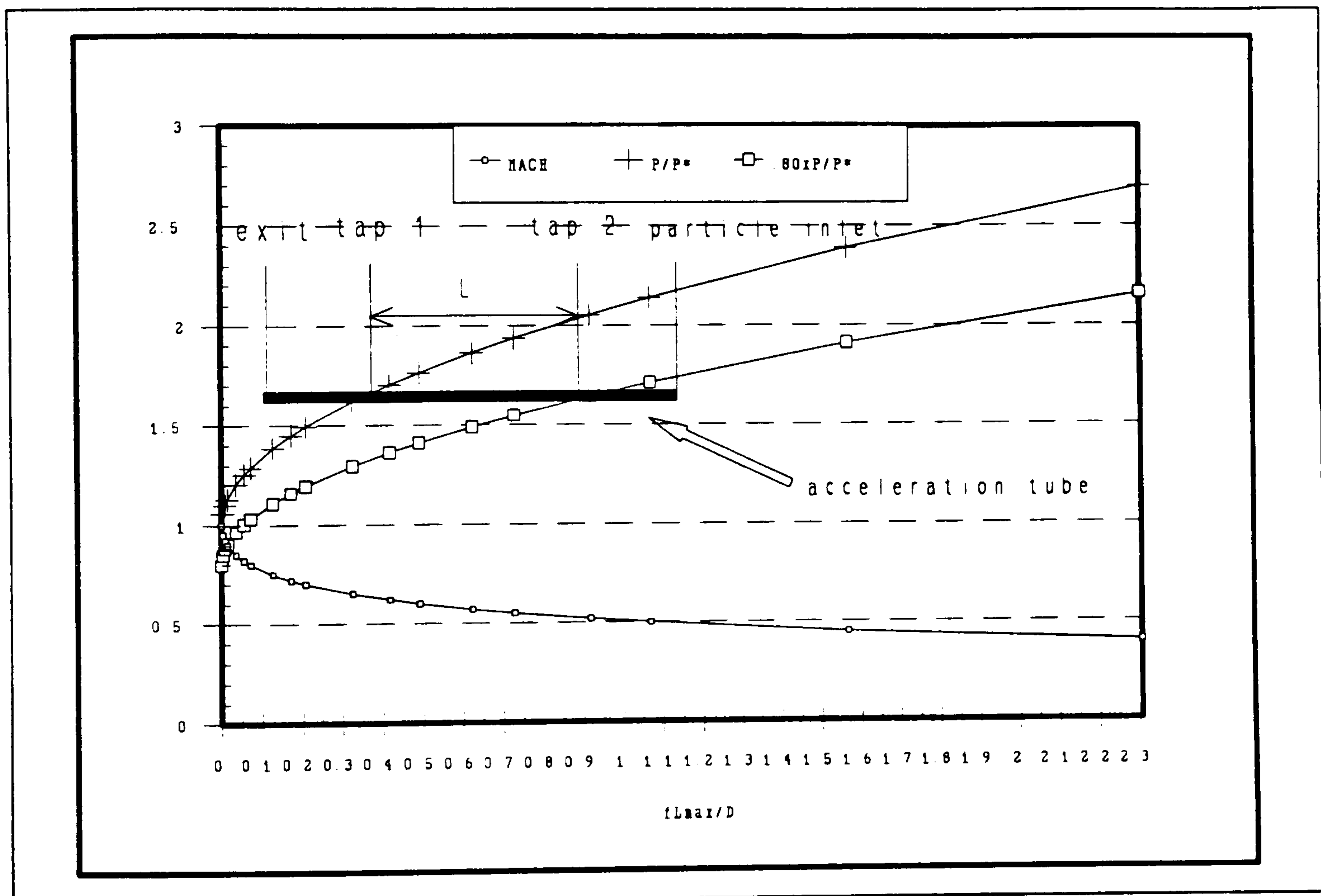


Figure 3: Graphical resolution of equation (1) and (2) in the room temperature test condition. a=0.8, L=38cm, f=0.016

1.3.2 Temperature measurement: what for and how

It can be seen that the Mach number varies from 0.5 near the particle inlet to 0.8 at the tube exit. The relationship between the gas velocity V and the Mach number M is:

$$V = M\sqrt{\gamma rT} \quad (3)$$

where:

$\gamma=1.4$ for air

$r=387 \text{ J/kg.K}$

T the static gas temperature in Kelvin.

The gas temperature must therefore be determined in order to 'quantify' the velocity distribution from the Mach number distribution.

It can be seen from Figure 1 that it is reasonable to assume that the gas velocity varies linearly with the Mach number. From equation (3), this is equivalent to say that the gas temperature is constant in the duct.

It is practically not possible to measure the static gas temperature as this would involve having a thermocouple junction at rest with the gas i.e. a thermocouple flying at a speed of several hundred meters per second!

A stationary thermocouple can only measure the total gas temperature T_t , from which the actual gas temperature can be derived.

The total temperature, also called stopping temperature, is the temperature that the gas would assume if its kinetic energy was fully converted into heat. It depends on the gas static temperature and Mach number as:

$$T_{tot} = T \left(1 + \frac{\gamma - 1}{2} M^2 \right) \quad (4)$$

Rigorously, a thermocouple junction does not probe the total temperature but the adiabatic wall temperature. The difference between the two, brought about by frictional heating of the gas, can be ignored in this instance.

The implication of the above is that the gas temperature can be estimated from the specimen temperature, which is a measure of the total gas temperature.

$$T = \frac{T_{spec}}{1 + \frac{\gamma - 1}{2} M_e^2} \quad (5)$$

where:

T_{spec} is the measured specimen temperature

M_e is the Mach number at the tube exit

2 DERIVATION OF PARTICLE VELOCITY

2.1 The aerodynamic drag

Particles that are entrained in a gas flow of velocity V_g are subjected to an aerodynamic drag force:

$$f = \frac{1}{2} \rho S C_d (V - V_p)^2 \quad (6)$$

where:

ρ is the gas density,

S is the cross-section area of the particle

C_d is the aerodynamic drag coefficient

V is the gas velocity

V_p is the particle velocity

The drag coefficient depends on the particle Reynolds number defined as:

$$R_e = \frac{\rho (V - V_p) d}{\mu} \quad (7)$$

where:

d is the particle diameter

μ is the gas viscosity

For a spherical particle,

$$C_d = 24 \cdot \frac{(1 + 0.197 R_e^{0.63} + 0.00026 R_e^{1.38})}{R_e} \quad (8)$$

The drag force is solely responsible for the change in particle momentum:

$$f = m_p \frac{dV_p}{dt} \quad (9)$$

where:

m_p is the particle mass,

V_p the particle velocity.

Since the flow is stationary:

$$\frac{dV_p}{dt} = \frac{dV_p}{dx} V_p \quad (10)$$

Combining equations (6), (9) and (10) yields:

$$\frac{V_p}{C_d (V - V_p)^2} dV_p = \frac{3\rho}{4\rho_p d} dx \quad (11)$$

Integrating equation (11) yields:

$$\int_0^{V_p} \frac{u du}{C_D(V-u)^2} = \frac{3}{4\rho_p d} \int_0^{L_t} \rho dx \quad (13)$$

where:

V_p is the particle velocity attained at the tube exit,
 L_t is the tube length over which the particles are accelerated.

2.2 Particle velocity calculation

The difficulty in solving equation (12) is that the gas flow properties such as velocity and density are not constant in the tube (see 1.2 and 1.3). To overcome this difficulty, the acceleration length over which particle velocity is calculated was split into two. The gas properties are averaged on each segment.

$$L_t = L_1 + L_2 \quad (14)$$

where:

L_1 is the distance from the particle inlet to the pressure tap 2 (43cm),
 L_2 is the distance from the pressure tap 2 to the tube exit (20.5cm).

This allows to integrate equation (11) over the particle travel length L_1 and L_2 where the gas properties are taken as average. The particle velocity at the tube exit is calculated in two steps through the calculation of an intermediate particle velocity V_1 .

$$\int_0^{V_1} \frac{v_p dv_p}{C_D(V-v_p)^2} = \frac{3\rho L_1}{4\rho_p d} \quad (15)$$

$$\int_{V_1}^{V_p} \frac{v_p dv_p}{C_D(V-v_p)^2} = \frac{3\rho L_2}{4\rho_p d} \quad (16)$$

A mathematical software was used to solve equations (15) and (16). The gas properties used in the calculations were derived from properties measured experimentally and tabulated data available in the literature.

Table I: Measurements of specimen temperature and static pressure at two different points of the acceleration tube.

Room temperature test measurements	
T _{spec} (K)	285
P ₁ (bar)	1.54
P ₂ (bar)	1.30
High temperature test measurements	
T _{spec} (K)	1193
P ₁ (bar)	1.7
P ₂ (bar)	2.2

Table II: Values of flow properties used in the calculation of particle velocity at room temperature.

x	L_1 0-----> 43cm	L_2 43---> 63.5cm	Source
mean pipe Re	2.10 ⁻⁵		equation 7, d=1cm
f	0.016		Moody's diagram
a	0.80		
Mach	0.55	0.7	Figure 3
T (K)	255	255	equation 5
V (m/s)	176	224	equation 3
P (bar)	1.42	1.21	inferred from pressure measurements and Figure 3
ρ (kg/m ³)	1.94	1.67	calculated from P and T assuming perfect gas
ν (Nm/s)	18x10 ⁻⁶	18x10 ⁻⁶	Tabulated data

Table III: Values of flow properties used in the calculation of particle velocity at high temperature.

x	L_1 0-----> 43cm	L_2 43---> 63.5cm	Source
mean pipe Re	5.10 ⁴		equation 7, d=1 cm
f	0.022		Moody's diagram
a	0.78		
Mach	0.52	0.7	Figure 3
T (K)	1057	1057	equation 5
V (m/s)	340	457	equation 3
P (bar)	1.95	1.41	inferred from pressure measurements and Figure 3
ρ (kg/m ³)	0.64	0.47	calculated from P and T assuming perfect gas
ν (Nm/s)	44x10 ⁻⁶	44x10 ⁻⁶	Tabulated data

Table IV: Predicted values of silica particle velocities in the room temperature condition.

Room Temperature test, Silica (2650kg/m ³)		
Particle size (μm)	V ₁ (m/s)	V _P (m/s)
20	176	207
40	155	185
60	142	170
80	133	159
100	124	150

Table V: Predicted values of alumina particle velocities in the room temperature condition.

Room temperature test, Alumina (ρ=3900Kg/m ³)		
Particle size (μm)	V ₁ (m/s)	V _P (m/s)
60	133	160
80	123	147
100	114	138
120	108	130
140	103	125

Table VI: Predicted values of silica particle velocities in the high temperature condition.

High temperature test, Silica ($\rho=2650\text{Kg/m}^3$)		
Particle size (μm)	V_1 (m/s)	V_P (m/s)
20	323	401
40	281	345
60	247	302
80	222	277
100	208	254

Table VII: Predicted values of alumina particle velocities in the high temperature condition.

High temperature test, Alumina ($\rho=3900\text{Kg/m}^3$)		
Particle size (μm)	V_1 (m/s)	V_P (m/s)
60	225	275
80	202	246
100	186	229
120	178	214
140	162	197

Note:

The drag coefficient defined in equation (8) is strictly valid for spherical particles. The same drag coefficient was applied to the alumina particles in the velocity calculations.

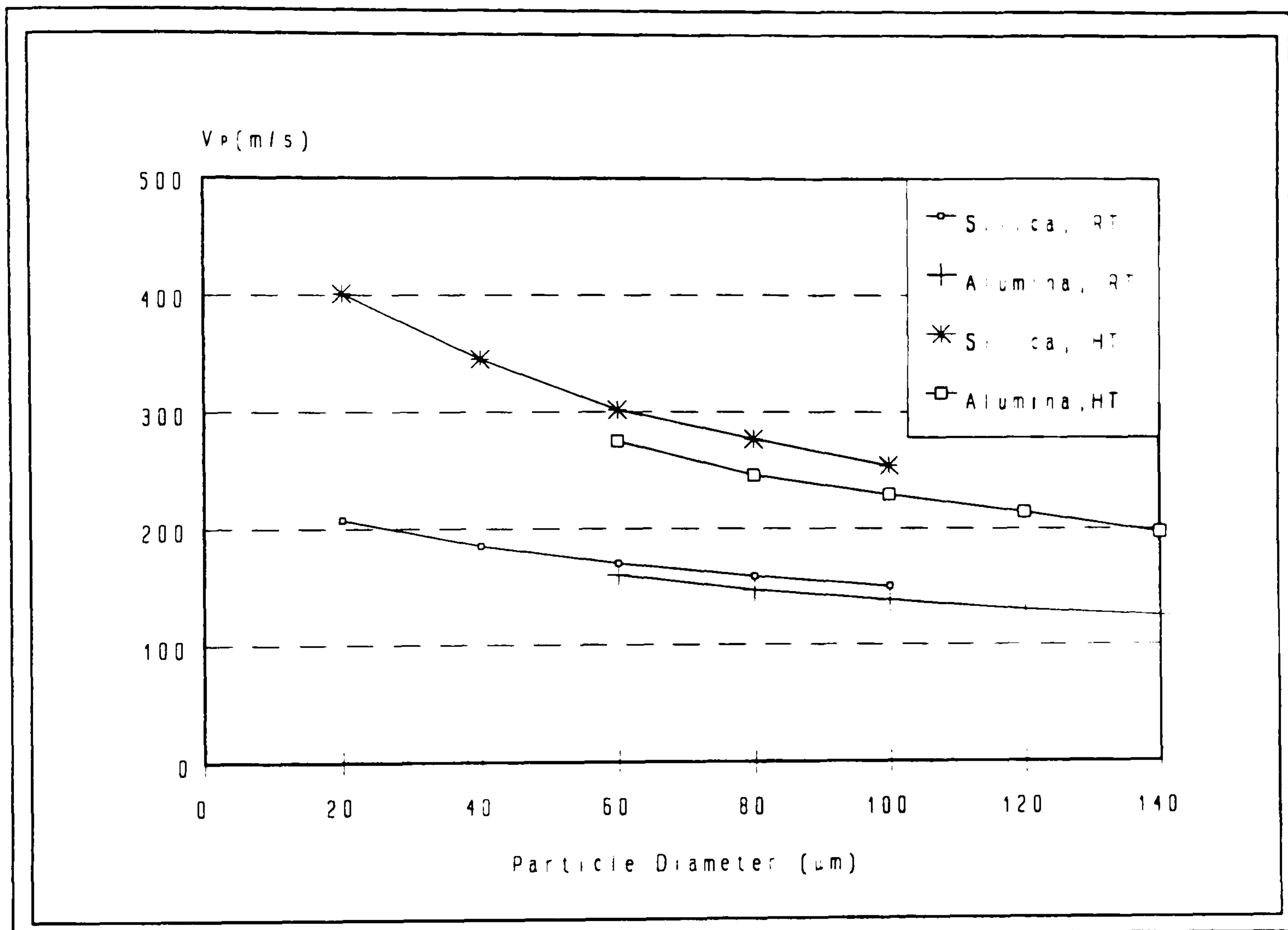


Figure 4: Predicted particle velocities attained at the tube exit in the room temperature (RT) and high temperature (HT) test conditions.

APPENDIX 6: CALCULATION OF THE QUADRATIC TIME AVERAGED SHEATH VOLTAGE

Since the plasma potential is negligible over t^- ,

$$\langle V_{c,sheath} \rangle^2 = \frac{1}{\tau} \int_{t^-} (V_{DC} - V_{RF} \sin(\omega t))^2 dt \quad (1)$$

which can be expanded into the sum of three terms:

$$\langle V_{c,sheath} \rangle^2 = \frac{t^-}{\tau} V_{DC}^2 + \frac{V_{RF}^2}{\tau} \int_{t^-} \sin^2(\omega t) dt - \frac{2V_{DC}V_{RF}}{\tau} \int_{t^-} \sin(\omega t) dt \quad (2)$$

Given that:

$$\sin^2(\omega t) = \frac{1}{2}(1 - \cos(2\omega t)) \quad (3)$$

equation (2) becomes:

$$\langle V_{c,sheath} \rangle^2 = \frac{t^-}{\tau} \left(V_{DC}^2 + \frac{V_{RF}^2}{2} \right) - \frac{V_{RF}^2}{2\tau} \int_{t^-} \cos(2\omega t) dt - \frac{2V_{DC}V_{RF}}{\tau} \int_{t^-} \sin(\omega t) dt \quad (4)$$

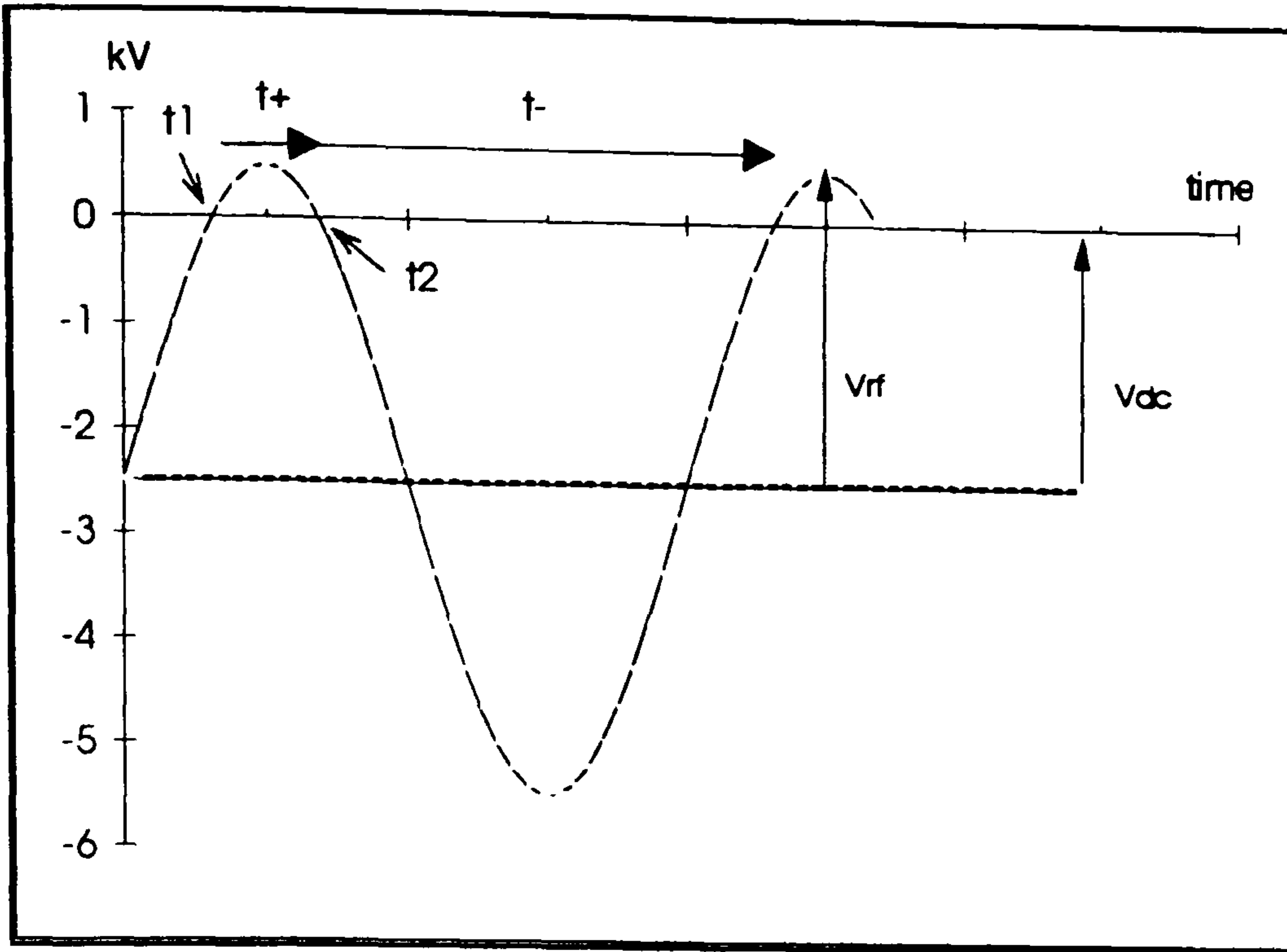
Since $t^- + t^+ = \tau$,

$$\int_{t^-} \sin(\omega t) dt = - \int_{t^+} \sin(\omega t) dt \quad (5)$$

and

$$\int_{t^-} \cos(2\omega t) dt = - \int_{t^+} \cos(2\omega t) dt \quad (6)$$

Moreover, $t^+ = t_2 - t_1$ where t_2 and t_1 are the roots of $V_{DC} - V_{RF} \sin(\omega t) = 0$ over $[0, \tau]$ (see figure below).



One has:

$$\omega t_1 = \arcsin\left(\frac{V_{DC}}{V_{RF}}\right) = a \quad (7)$$

and

$$\omega t_2 = \pi - \arcsin\left(\frac{V_{DC}}{V_{RF}}\right) \quad (8)$$

Hence

$$\frac{t^-}{\tau} = \frac{\tau - t^+}{\tau} = \frac{1}{2} + \frac{a}{\pi} \quad (9)$$

and equations(5) and (6) become (10) and (11) respectively:

$$\int_{t^-}^{t_2} \sin(\omega t) dt = - \int_{t_1}^{t_2} \sin(\omega t) dt = - \frac{2}{\omega} \cos(a) \quad (10)$$

$$\int_{t^-}^{t_2} \cos(2\omega t) dt = - \int_{t_1}^{t_2} \cos(2\omega t) dt = \frac{1}{\omega} \sin(2a) \quad (11)$$

Replacing (9), (10) and (11) into (4) yields:

$$\langle V_{c,sheath} \rangle^2 = \left(\frac{1}{2} + \frac{a}{\pi}\right) \left(V_{DC}^2 + \frac{V_{RF}^2}{2}\right) - \sin(2a) \frac{V_{RF}^2}{4\pi} + \cos(a) \frac{2V_{DC}V_{RF}}{\pi} \quad (12)$$

APPENDIX 7: COATING RUNS DETAILS AND X-RAY DIFFRACTION DATA.

Table I: Low temperature (300-400°C) runs in 100% argon, 22cm source-to-substrate distance, 800cm2 cathode plate area.

Run No	time	rfpower	Gun%	Temp(C)	thick (mic)	Phase	Texture
1	20	high	40%	300-400	60	cubic?	random
2	40	high	60%	300-400	250	cubic?	random
3	20	high+DCg	60%	300-400	40	cubic?	random
4	15	high	60%	300-400	140	cubic?	random
5	12	0	60%	300-400	95	cubic?	random

Table II: Low temperature (500-650C) runs in 100% argon, 15cm source-to-substrate distance, 800cm2 cathode plate area.

Run No	time(min)	rfpower	AREA	Gun%	Temp(C)	thick (mic)	Phase	Texture
3/11	40	high	800cm2	33%	500-650C	120	cubic?	<111>
3/13	40	0	800cm2	38%	500-650C	95	cubic?	<111>
3/105	82	high+0	100cm2	50%	500-750C	235	(tet)	<111>

Table III: Dog-bone substrate runs, 100% argon, 18cm source-to-substrate distance.

Run No	time	RFpower	AREA	Gun%	Temp(C)	thick (650C)	Phase	Texture
3/J1/1	35	0	small	30	700	130mic	(t)	<111>
3/J1/2	35	0	small	30				
3/J1/3	35	0	small	30	1000		(m)+(t)	<111>
3/M1/1	45	high	small	30	700	45mic	(t)	random
3/M1/2	45	high	small	30	900		(t)	random
3/M1/3	45	high	small	30	1000		(t)	random
3/10/1	20	high	large	30	760	97mic	(t)	<111>
3/10/2	20	high	large	30	900		(t)+(m)	<111>
3/10/3	20	high	large	30	1000		(m)+(t)	<111>
J1Y3	40	0 + high	large	30		49mic		

Table IV: Coating runs in vacuum furnace in 100%Ar gas.

Run No	time	I(mA)	kV	Gun%	Temp(C)	thick (mic)	Phase	Text
3/91	40	0	0	42	909-953	100	(tet)+(m)	<111>
3/16	34	0	0	42	841-947	40	(m)	<111>
3/60	36	0	0	60	890-985	53	(tet)+(m)	<111>
3/34	33	0	0	52	845-972	80	(m)+(tet)	<111>
3/104	36	0	0	56	834-1020	120	(tet)+(m)	<111>
J	135	0	0	53	865-937	120	(tet)+(m)	<111>
K	30	14	2.5	41	1009	40	(tet)+(m)	<111>
L	90	4-20	0.1-2.5	43	970-1030		(tet)	random

Table V: Coating runs in vacuum furnace in 90%O₂/Ar gas.

Run No	time	I(mA)	kV	Gun%	Temp(C)	thick (mic)	Phase	Texture
M	60	0	0	45	1004-1030	100	tet	<100>
N	26	0	0	47	1000-1024C	44	tet	<100>
AF	10	15	1	44	960-996	30	tet	<001>
AG	10	45	3	43	966-997	60	tet	<111>
AH	10	21.75	1.75	48	960-997	45	tet	<111>
AJ	10	37.5	3	44	960-994	40	tet	<100>
AN	60	22.5	2.5	42	967-982	200	tet	<100>
AO	70	0	0	42	960-978	200		
3/302	15	30	2.5	46	943-980	50	tet	<100>
3/300	20	0	0	64	960-996	80	tet	<100>/<111>

APPENDIX 8: EROSION RATE DATA

Steady-state erosion rate (mean) in g/kg.

SD: standard deviation.

Table I:Room temperature testing using silica beads.

Angle		30	45	60	75	90
RT33	mean	10	31.2	13.8	19.5	17.4
batch 1	sd	1	2.9	2	3.5	0.9
APS YSZ	mean	49.2	82.5	101	129	125
	sd	4.2	1.6	11	17	10
Bulk YSZ	mean					0

Table II: High temperature testing using silica beads.

	Angle	30	45	60	75	90
RT33	mean	27	25.2	16.7	8.9	5.4
batch 2	sd	13.4	13.6	1.4	1.7	1.2
APS YSZ	mean					540
	sd					

Table III: Room temperature testing using alumina grit.

	Angle	30	45	60	75	90
RT33	mean					21
batch 2	sd					1
RT33	mean					19
batch 1	sd					2.8
APS YSZ	mean					210
	sd					26
Bulk YSZ	mean					3.6
	sd					0.11

Table IV: High temperature testing using alumina grit.

	Angle	30	45	60	75	90
RT33	mean	0.0207				30
batch 2	sd	0.0001				5
RT33						27
batch 2						1.4
APS YSZ	mean					323
	sd					26
Bulk YSZ	mean					12.5
	sd					2

Table V: High temperature testing using alumina grit.

	angle	30	45	60	75	90
AG	mean	11.7				13.3
AO	mean					9.6
AN	mean	8.9				14.3
AJ	mean					11.2
K	mean					10.5
AH	mean					7
N						9.5

APPENDIX 9: CONVECTIVE HEATING OF A 60 μm PARTICLE.

The heat flux received by a particle from the hot gas is:

$$Q = hS(T_{gas} - T_p) \quad (1)$$

where T_p is the particle temperature (assumed uniform), S the particle surface area and h the heat transfer coefficient:

$$h = \frac{kN_u}{d}$$

where k is the gas thermal conductivity, N_u is the Nusselt number and d the particle diameter.

For a sphere, the following empirical law applies:

$$N_u = 0.37Re^{0.6}$$

for $17 < Re < 4 \times 10^4$ where Re is the Reynolds number:

$$Re = \frac{\rho(V_{gas} - V_p)d}{\mu}$$

where ρ and μ are the gas density and viscosity respectively.

The heat flux can be written:

$$Q = mc_p \frac{dT_p}{dt} \quad (5)$$

Combining (5) with (1), the average temperature increase attained by the particle at the exit of the acceleration tube is:

$$T_p - T_0 = (T_{gas} - T_0) \left(1 - \exp\left(-\frac{6h}{c_p \rho_p d} \Delta t\right) \right)$$

where Δt is the particle transit time, T_p is the average particle temperature

at the tube exit, T_0 is the particle temperature at the tube inlet, ρ_p is the particle density and c_p the particle specific heat capacity.

Calculation,

Assuming:

$V_{gas}(m/s)$	$V_p(m/s)$	$\mu(N/m.s)$	$k(W/mK)$	$d(m)$	$T_{gas}(K)$	$c_p(J/kgK)$	$\rho(kg/m^3)$
400	280	44×10^{-6}	0.06	60×10^{-6}	1060	1500	0.5

The following values are obtained:

$$Re=80$$

$$N_u=5.1$$

$$h=5000W/m^2K$$

$$\Delta t=2 \times 10^{-3}s$$

This yields a temperature increase of 470K (~500°C).

In effect, due to low thermal conductivity of silica, the particle skin temperature will be much higher than the core temperature thus limiting the the heat flux received. The skin temperature will exceed the silica softening point (500°C), whereas the particle core will be hard.