

CRANFIELD UNIVERSITY



**SCHOOL OF INDUSTRIAL AND
MANUFACTURING SCIENCE**

PhD Thesis

Academic Year 1999

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REACTIVE PLASMA SPRAYING

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ABSTRACT

Reactive Plasma Spraying (RPS) with a hydrocarbon gas has been studied as a method to improve the mechanical properties of a commercially available 80:20 nickel-chromium alloy, and subsequently as a method to reduce the oxygen content of sprayed MCrAlY coatings. A conventional d.c. plasma torch has been modified by attaching a conical graphite tube (reactor) onto the end of the gun. The powder is then sprayed through the reactor with injected reactive hydrocarbon gas. The reactor shrouds the plasma flame from the external atmosphere and contains the desirable inner atmosphere necessary for RPS. When spraying using a reactor and reactive gas the plasma environment is changed significantly. Work has been carried out to establish the effect various spray parameters have on the final coating such that new parameters can be selected which maximise the coatings quality and performance

Reactively sprayed 80:20 Ni/Cr coatings have been produced with an in-situ carbide reinforcing phase, leading to greatly improved wear properties compared with conventionally sprayed coatings. Reactively sprayed MCrAlY coatings have been deposited with an order of magnitude reduction in oxide levels, leading to considerably fewer line defects such as oxide stringers and delaminations.

An attempt has been made with the aid of computational fluid dynamics software, to model phenomenon occurring inside the reactor section as a method to appraise reactor design and suggest further design improvements.

ACKNOWLEDGEMENTS

Firstly, I would like to acknowledge the financial support from BOC Gases, and in particular to Dr. G. Creffield and M. Cole for their continued support for this project.

Secondly, I would like to express my profound gratitude to my supervisors Prof. D. Stephenson and Prof. J.R. Nicholls for their suggestions and support throughout my studies at Cranfield University.

Thirdly, I would like to show my appreciation to A. Dyer, C. Matthews, T. Pryor and J. Hedge, technicians whose assistance has proved invaluable.

And Finally, Elspeth, thank you not only for the help you have provided in compiling this thesis, but essentially, for the support and belief you have shown in me over the last four years.

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1.0 INTRODUCTION

With the evolution of 'Advanced Materials'; such as intermetallic compounds, engineering ceramics, reinforced metals (MMC's), reinforced ceramics (CMC's) and reinforced intermetallics (IMC's) production proves a major problem. These fibre or particulate reinforced metal or ceramic matrices are being proposed for use in many varied applications, from structural components to corrosion and wear resistant coatings, however, their commercial introduction has been limited by the lack of economical processing methods. Therefore, materials processes which can economically produce these types of materials are constantly being sought. Research is now finding that chemical synthesis routes for the production of these materials are more promising than some more conventional techniques. Reactive plasma spraying (RPS), a rapid particulate consolidation, high temperature technique with an inherent ability for chemical synthesis is one such candidate for the production of these materials.

Plasma spray coating, and to a lesser degree forming, has for many years been practised and shown to be a practical and economical method for depositing 'difficult' materials, including intermetallics, ceramics and composites. Conventional atmospheric plasma spraying (APS) uses an electric arc discharge produced by a generator to heat up the working gases, which expand to form a plasma jet. The plasma jet heats up small volumes of material, usually powder particles ($< 100 \mu\text{m}$), and accelerates them as droplets or heated particles towards a substrate. On impact with

the substrate, the particles are plastically deformed and rapidly solidified to form an ideally dense deposit.

The introduction of the plasma spraying technique into environmentally controlled chambers in the early 1970's was a leading reason for the advancement from being strictly a coating to a forming technology. More recently, controlled environment plasma spraying, modified for reactive plasma spraying, has been developed to combine both controlled dissociations and reactions in the plasma jets in order to create, in-situ, new materials or phases in the deposited materials. Moreover, reactive plasma spray forming is now an emerging processing method for the production of many advanced materials. The process is a modification of more conventional plasma spraying with the addition of injected 'reactive' species into the particle and/or hot gas streams. The reactive species may be gases, liquids or mixtures of reactant solids which upon contact with the high temperature plasma jet, decompose to produce highly reactive or ionic species. These species can then combine with the other heated materials in the plasma jet to form new compounds.

2.0 LITERATURE REVIEW

2.1 Thermal Spraying

The origin of thermal spraying dates back to the early 1900's. The invention of a metallising process by Schoop^[1] is generally accepted as the date of the technologies birth. Since then, there have been many developments that encompass new technology leading to a wide range of different techniques, some of which will be discussed later.

With most spraying techniques the gases, combustion gases or plasma are the sources of the thermal and kinetic energy, heating the particles and propelling them towards a substrate. Only in Laser spraying is the energy of photons emitted by a laser used to heat and melt the particles.

The principle of thermal spraying is to produce a deposit, usually a coating, on a substrate by rapidly heating the spraying material and directing it towards the substrate, where it impacts or splats, to form an ideally dense deposit.

2.2 Thermal Spraying Processes

Detailed below are some of the most common thermal spraying processes with an emphasis on plasma spraying, and its subsequent developments^[2].

2.2.1 Flame Spraying

In the flame spraying technique the chemical energy provided from combustion of fuel gas in oxygen is used to heat the spraying material. The spraying material may be in the form of powder, wires or rods. The flame temperature is typically 3000-3350 K with a velocity of 80-100 m/s. Flame sprayed coatings may have bond strengths as high as 70 MPa although 30 MPa is more typical. Porosity is usually of the order of 10 to 20 % and thicknesses are in the range 100-2500 μm .

2.2.2 Detonation Gun (D-gun™) Spraying

In the D-gun process oxygen and acetylene are fed into a water-cooled gun barrel together with an amount of powder. The gas is ignited with a spark plug producing a detonation wave that accelerates the powder along the barrel towards a substrate. Repeating this cycle produces a coating, typical frequencies are 1 - 15 Hz. In-between detonations the barrel is flushed with nitrogen. Figure 1, shows a sketch of the D-gun assembly.

A maximum detonation temperature occurs with 45 % acetylene at 4500 K. The detonation wave velocity is around 2900 m/s, giving a particle velocity of 750 m/s. An improved D-gun, called the Super D-gun, can

deliver particle velocities of 900 m/s. Bond strengths are typically 70-90 MPa with thicknesses around 300 μm .

2.2.3 High Velocity Oxy-Fuel (HVOF) Spraying

With the HVOF process, the fuel is burnt with oxygen at high pressures, which in turn generates a high velocity exhaust jet. Powder is injected axially into the jet with the aid of a carrier gas. Flame temperatures are typically 3000-3500 K with high jet velocities around 2000 m/s. Coating properties are such that bond strengths may be as high as 90 MPa with porosity's lower than 1 %. Typical thicknesses are in the range 100-300 μm . Figure 2, shows a typical HVOF spraying assembly.

Available now are commercial HVOF systems that use a liquid fuel, in many cases Kerosene and extremely high Oxygen flow-rates (typically 2000 scfm) giving very high particle velocities. On impact with the substrate particles experience considerable heating because of the change from kinetic to thermal energy and therefore do not always need to be sufficiently softened or melted during the spraying process. Liquid fuel HVOF systems are often used for spraying wear resistant cermet materials.

2.3 Plasma spraying

2.3.1 Atmospheric Plasma Spraying (APS)

The dc plasma gun shown in figure 3 consists of a circular anode, usually copper, and a cathode of thoriated tungsten. The electric arc discharge produced by a generator heats up the working gases, which expand to form a plasma jet.

The powder, which is suspended in a carrier gas, is injected into the plasma flame. The powder particles are melted and accelerated in the plasma flame and upon impact with the substrate form a coating. Bond strengths for ceramic materials are typically in the range 15-25 MPa, and for metallic alloys in excess of 70 MPa. Porosity is usually in the range 1-7%, but may be much higher. Coating thicknesses are typically 50-500 μm .

2.4 Vacuum Plasma Spraying (VPS)

In an effort to improve the properties of APS coatings, for often special applications, for example, electronic applications, a process was required which minimised undesirable reactions with the environment. Vacuum plasma spraying, sometimes called Low Pressure Plasma Spraying (LPPS) is such a process. A VPS installation is composed of a plasma torch (similar to the type used in APS) enclosed in a vacuum chamber. The chamber is initially evacuated to a pressure of 10^{-2} mbar and then back-filled with argon to around 40 mbar. Reducing the amount of oxygen in

the environment prevents oxidation of both particles and substrate. Consequently, excellent coatings result with superior densities and adhesion than those obtained through atmospheric plasma spraying. However, the requirement for a vacuum chamber means that the installation is fixed, is of high capital cost and must be automated. Furthermore, only small components can be coated and the higher heat input to the workpiece may cause some metallurgical or distortion problems.

2.5 Reactive Plasma Spraying (RPS)

Problems associated with vacuum plasma spraying, namely, high costs, workpiece dimensions and time have led in part to the development of reactive plasma spraying. The principle of RPS is to encourage reactions within the plasma under controlled conditions. The aim being to tailor compositions that would otherwise be difficult, if not impossible by other production routes. In the past, measures have been taken to reduce or eliminate reactions with the environment. In RPS, reactants are injected into, or downstream of, the plasma flame where they react in-flight with the powder being sprayed. Reactants may be any combination of solids, liquids, or gases. RPS is a recent development and success has been limited. Some of the materials that have been successfully synthesised by RPS or those which are currently being investigated will be dealt with in a later chapter (2.17 Materials processed by RPS).

A dc plasma jet has unique properties, such as a high-energy content and high velocity, and has been used successfully for melting and spraying.

Unfortunately the residence time of the injected particles is very small (~ 1 ms). For any reaction to occur in this time the reaction rates must be very high. Moreover, the steep temperature gradients in the plasma generally result in non-uniform heating and reactions. It is therefore necessary in RPS to use a reactor extension to increase the residence time of the particles in the plasma. The RPS system can be considered in terms of four zones as shown in figure 4.^[3]

Zone A: The injection zone. In zone A, it is crucial to inject reagents properly into the plasma without disruption, in competition with the high viscosity and magneto-hydrodynamic characteristics of the plasma.

Zone B: The heating and dissociation zone. In zone B, thermal and reaction histories, and trajectories must be effectively controlled and homogenised. These are intimately connected with the torch design and character of the generator.

Zone C: The reaction and quenching zone. In zone C, homogeneous and controlled reactions are essential. Especially, in the case of fine powder synthesis, nucleation and growth processes must be highly controlled by effective devices based solely on fluid dynamics not on electromagnetics as electrons can not be trapped by a magnetic field in a thermal plasma.

Zone D: The collection and deposition zone. In zone D, an efficient collection method is required which does not destroy the unique characteristics of the product. Temperature control of the substrate is also crucial to deposit high quality coatings.

2.6 Reactive Vacuum Plasma Spraying (RVPS)

This process is similar to vacuum plasma spraying and is sometimes called reactive low pressure plasma spraying (RLPPS)[4]. The only difference being the addition of reactive species. Figure 5, shows a simple reactive RLPPS system. Workers using this equipment have found that the following criteria yield the best results^[4]:

- Metal powders exhibit higher reaction rates if they have lower melting and vaporisation temperatures.
- The metal must have a high ΔH_f with the reacting species.
- The reaction will go to completion at a certain mole ratio
- Maximum reaction behaviour is expected at the stoichiometric reactant molar ratio's

It was also found that with increasing gas ratios the excess gas would have negative effects on plasma jet performance.

2.7 Spraying Parameters

The working parameters in plasma spraying are of paramount importance. Small changes will result in significantly different coatings. Furthermore, the intrinsic properties of the spraying material and the characteristics of the powder must be carefully controlled. Particle shape, size, densities, oxide content, all contribute to the quality of the end product. The melting and vaporisation temperatures of the coating material are important because they restrict the use of a material and dictate the spraying conditions. For example, the liquid vapour temperature range for pure alumina is narrow, and vaporisation may occur under conditions of superheating, and produce a 'sponge like' coating microstructure.

It is important that coating quality is consistent. Parameters for a particular material will vary, but the principles are the same. To achieve the best results the particles must melt in the plasma flame and remain molten until impact. Upon impact the particles will rapidly solidify and coalesce to form a dense deposit. Smaller particles with greater surface areas in contact with the hot plasma gases are more likely to melt completely. But, for the same reason are prone to in flight solidification. Care must also be taken to avoid excessive vaporisation, which is costly.

Because of very high jet velocities some very small particles cannot be injected into the centre of the plasma flame, and consequently may not be melted. RPS because of the need to manipulate plasma chemistry requires even closer control over the parameters.

2.8 Process parameters

2.8.1 Plasma Gases

The working gases are usually Argon or a mixture of Argon and Helium, Argon and Hydrogen or Argon and Nitrogen. Flow rates are typically in the range 40-50 litres per minute, and the velocity at the nozzle can reach several times the speed of sound.

The choice of working gas or gases is decided mostly by their ability to melt the sprayed particles. This ability is higher for molecular gases (especially H₂) due to their greater thermal conductivity, compared to monatomic gases. Conversely, monatomic gas jets reach a higher velocity. It is for this reason a mixture of molecular and monatomic gases are used to ensure particle melting and high velocities.

Argon-Helium gas mixtures have been compared with Argon-Hydrogen gas mixtures^[5]. Given that the jet velocity for the Ar-H₂ mixture is higher than that for the Ar-He mixture, it might be safe to assume that the Ar-H₂ system would give higher particle velocities. However, the viscosity for the Ar-He system is some 1.5 to 2.7 times higher than that for the Ar-H₂ mixture. The force F acting on a particle is related to the viscosity μ and relative velocity Δv as follows:

$$F \approx \mu \cdot \Delta v$$

$$[\text{Eqn. 2.1}]$$

Results have shown that particle velocities are higher for the Ar-He mixture which can only be explained in terms of viscosity.

2.8.2 Electric Power

The electric power (i.e. the arc current multiplied by arc voltage) is typically about 40 kW but can be as high as 100 kW. From a general point of view, the arc current has a strong effect on the velocity values. For a given spray torch design taking factors like nozzle diameter and total gas flow rate into account, the radial profile of the velocity axial component keeps an almost Gaussian shape whose maximum significantly increases with the arc current. It must be noted however, that this change in velocity becomes less pronounced for smaller nozzle diameters.

2.8.3 Powder Injection

A carrier gas, usually Argon, is used to support the powder. The powder can often be injected at different points within the plasma gun. This depends largely on the melting point of the spraying material. High melting point materials are injected internally and low melting point materials externally – these injection positions are indicated in figure 3. The carrier gas pressure has a significant effect on the resultant coating. The quality of a coating that has been produced by plasma spraying is highly dependent on the path and velocities of the particles being sprayed. Changing the flow rate of the carrier gas can have a strong effect on the trajectories and velocities of the particles

The carrier gas pressure must be high enough to direct the particles into the centre of the plasma flame, or insufficient particle melting will occur.

2.9 Additional Parameters for Reactive Plasma Spraying

Very little work has been done on investigating the effect of a reactor in RPS. Some work has been performed on the impact that a shielding nozzle has on a plasma torch^[6].

2.9.1 Effect of shielding nozzle

This work focused on the properties of the plasma jet, the effect of the shielding nozzle and the condition of the sprayed particles. The apparatus used is shown in figure 6.

When spraying in an open atmosphere it may be assumed that the surrounding cold air influences the plasma jet. Work has been undertaken by many researchers to establish the amount of air contamination in a plasma jet. Okada and Marcuo^[6] used a silica tube to sample gas at various points in the plasma flame; the results are presented in figure 7. When the shielding nozzle was not used, the proportion of argon in the plasma jet flame decreased rapidly as the distance from the torch exit increased. It was found that the argon content was no more than 10% 100 mm from the torch nozzle. These results indicate that the shielding nozzle has a very significant effect on controlling the gas composition in the plasma jet. As a result of air contamination differences in the temperature

distribution take place between the shielded plasma flame and the non-shielded flame.

At distances between 40 and 110 mm from the torch exit, the shielding nozzle dramatically effects the plasma and its temperature. The results are shown in figure 8. The measurements were made using WW-Re or PtPt-Rh thermocouples. This evidence strongly suggests that a higher temperature and more radial distribution can be achieved by using a shielding nozzle. The interaction between the plasma jet and cold air accounts for the difference.

If the plasma stream can be assumed as a one-dimensional, adiabatic and steady flow of perfect gas, the velocity U is evaluated from the equation below:

$$U = \left[\frac{2\gamma}{\gamma-1} \frac{P_o}{\rho_o} \left[1 - \left(\frac{P}{P_o} \right)^{\frac{\gamma-1}{\gamma}} \right] \right]^{1/2}$$

$$= \frac{A_o^2}{\gamma-1} \left[1 - \left(\frac{P}{P_o} \right)^{\frac{\gamma-1}{\gamma}} \right]^{1/2} \quad [\text{Eqn. 2.2}]$$

Where

γ = C_p/C_v Specific heat ratio of gas

P_o = Stagnation pressure

ρ_o = Stagnation density

P = Static pressure

A_o = Sound velocity = $(\gamma RT)^{1/2}$

When the plasma jet is ejected into the open atmosphere, the air content in the argon plasma is so increased that the value of γ and the density of gas must be corrected corresponding to the amount of air. The effective specific ratio, γ_{eff} , of the mixture is described as follows:

$$\gamma_{\text{eff}} = \frac{2.5 m RT + 3.5 n RT}{1.5 m RT + 2.5 n RT} = 1 + \frac{Z}{3 + 2 m} \quad [\text{Eqn. 2.3}]$$

Where:

R = universal gas constant

T = temperature ($^{\circ}\text{K}$)

m = fraction of argon in the plasma (%)

n = fraction of air in the plasma (%)

The pressures were measured with a water-cooled pitot tube. The findings were as follows:

- In an open atmosphere, the static pressure of the plasma flame was almost equal to the normal atmospheric pressure.
- When the shielding nozzle was used, the static pressure was measured through holes in the shielding nozzle and again was found to be nearly normal atmospheric pressure.
- With the shielding nozzle and substrate in place the pressure was found to increase by 10-30 mm Hg.

The plasma jet velocities were calculated using equation 2.2 with the measured temperatures and pressures. The results are shown in figure 9.

It can be seen that by using a shielding nozzle a higher plasma velocity is achieved. A higher plasma jet velocity will result in increased particle acceleration. This has an important effect in RPS because the particle residence time will be reduced.

In order to evaluate the effect of the shielding nozzle on the heat transfer characteristics of the system, calorimetric measurements were carried out. A portion of energy supplied is lost to the cooling water at the torch. The remaining energy is thus available for the plasma flame. The difference is the quantity of heat transferred to the substrate in both cases at various arc currents and stand off distances. These results conclude that the heat loss in the shielding nozzle configuration is considerably less than would be lost to the environment in the absence of a shielding nozzle.

The primary aim of the plasma jet is to heat and accelerate the particles towards the substrate. The temperature rise of the particle depends on the temperature gradient between the plasma flame and the particle in conjunction with the residence time. The residence time is highly dependent on velocity. Velocities of the powder were measured using a high-speed camera driven at a speed of 4000 frames per second.

The particle velocities were found to fluctuate but on average the particle velocity decreased with increasing particle diameter and decreasing plasma gas velocity. These findings have been confirmed by other workers^[7]. This increase in particle velocity is due to the velocity rise of the plasma flame by the application of a shielding nozzle, as discussed

before. The force F acting on a sphere in a viscous steady flow is given by:

$$F = m \frac{dU_s}{Dt} = \frac{1}{2} C_D \rho (U_p - U_s)^2 A \quad [\text{Eqn. 2.4}]$$

Where:

C_D = drag coefficient A = cross-sectional area of sphere

ρ = density of fluid m = mass of spherical particle

U_p = velocity of fluid t = time

U_s = velocity of sphere

In practise the temperature, density and velocity of the plasma flame vary according to the distance from the torch. Considering a particle travelling through a small length of plasma flame, Δl is given by:

$$\Delta U_s = \frac{\Delta l}{2 \cdot U_s m} \rho \cdot C_D (U_p - U_s)^2 A \quad [\text{Eqn. 2.5}]$$

The velocity can then be calculated by summing the ΔU_s along the flight direction. Figure 10, shows the results calculated for each size of particle of a Ni-Cr-B-Si alloy and a WC-Co alloy. The calculated velocities and experimentally determined velocities correlate well.

In considering the change of velocity, the particle is accelerated rapidly in the nozzle of the torch, and attains its maximum velocity at a distance of about 50 mm from the exit of the torch, where the velocities of the plasma gas and particles are approximately equal. The effect of the shielding

nozzle is higher than when injected into open air. A prolonged acceleration range may explain this.

Also mentioned earlier is the reduced residence time from the increased velocity, and the need to increase residence time for RPS applications. This raises the need to investigate how effectively the particles are being heated. According to Ranz & Marshall,^[8] the Nusselt number Nu , which is a non-dimensional parameter defining convective heat loss per unit area from a solid body, is given by the following formula and is valid for Reynolds numbers Re in the range $0 < Re < 200$:

$$Nu = \frac{\alpha D}{\lambda} = 2 + 0.6 Re^{1/2} Pr^{1/8} \quad [Eqn. 2.6]$$

Where

λ = thermal conductivity of fluid

α = convective heat transfer coefficient

D = diameter of particle

Pr = Prandtl number (0.67 for Argon)

If the average temperature of the plasma is assumed to be 12 000°K and that the velocity of a particle is small compared with 2×10^5 cm/sec of plasma, the heat transfer coefficient can be calculated. The heat transfer coefficient is found to decrease with increasing particle size.

Considering the heat transfer coefficient, flame temperature and residence time. The particle temperatures were estimated at each distance, figure

11. It may be concluded that for a Ni-Cr-B-Si alloy particle greater than 150 μm it is almost impossible to melt the particle within a distance of 100 mm. Under these spraying conditions, it is inappropriate to use a WC-Co powder larger than 70 μm or smaller than 40 μm because of incomplete heating and overheating respectively.

2.10 Plasma Chemistry^[9-11]

Electrons, largely produced from partial ionisation of the molecules and atoms in a plasma are the principal source for transferring electrical energy to the gas. Elastic electron-molecule collisions will result in an increase in the kinetic energy of the particles, while inelastic collisions generally result in the excitation, fragmentation or ionisation of the molecules. Possible plasma components that can take part in reactions are shown in figure 12. From these reactive species a complex plasma chemistry results. Also included in this chemistry are various mixtures of gaseous fragments including complex molecules, polar particles, electronegative molecules and even finely divided particles which may act as catalysts, as reinforcing agents or embedments for stress reduction in the final product. Many parallel and sequential processes may take place. These may be ionic in nature or primarily radical-orientated, and may differ in the order of sequential processes. Rates for the various processes can differ enormously, depending on plasma parameters and species reactivity. It is typical of the versatility of plasma processes that, for a given molecular feed, a process can proceed chiefly via ionic reactions with one set of parameters and chiefly by a free radical mechanism under a different set of parameters.

An important aspect of plasma reactions is that a variety of different sub-reactions may proceed at the same time, including ion-molecule, excited species-molecule, excited species-ion, ion-free radical, free radical-molecule, excited species-free radical, free radical-free radical etc. All these may change the overall rate of reaction, since each type of interaction responds to changing plasma conditions in a different way. Some of these

interactions create new chemical bonds and new molecules; others form secondary ions and secondary free radicals, or new excited species.

Researchers have discussed reaction mechanisms during RPS for the formation of reinforcing phases in composite materials, highlighting not only thermodynamics but also the importance of kinetic considerations.

Stable carbides, oxides, nitrides, silicides or even borides are candidates for possible reinforcing phases in many engineered composite materials. Their formation kinetics and their compatibility when formed from the matrix make them advantageous as reinforcements. In particular, the flexibility of refractory carbide/nitride formation can be demonstrated via a series of reactions, which are thermodynamically driven to produce stable carbides or nitrides. One process limitation however, is that although thermodynamic stability criteria may suggest the more stable phase, an intermediate less stable carbide or nitride may nucleate and kinetically grow at a faster rate. The reaction types that generate synthesised composites can be summarised as follows:

- Thermodynamically Stable Phase Formation
- Thermodynamically Unstable Phase Formation
- Thermodynamically Stable Intermediate Phase Formation
- Duplex Phase Formation

Some examples of the formation of carbides, nitrides, and mixed/graded refractory carbide/nitrides are presented later. The underlying reactions for in-situ formation can be applied to other systems, such as nickel, titanium,

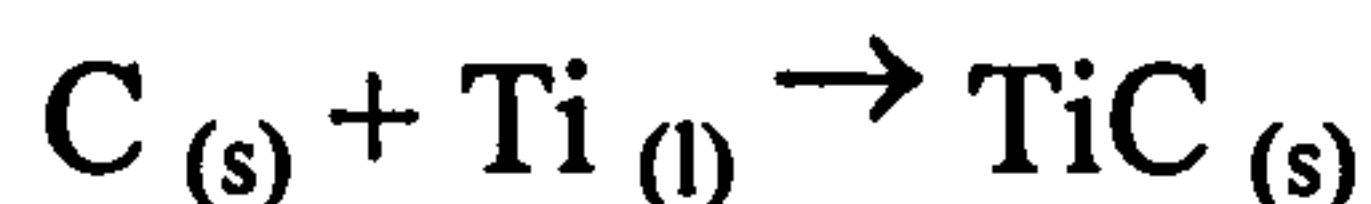
molybdenum, magnesium etc. In-situ processing can be used to form a variety of stable carbides and nitrides via matrix and gas chemistry choice. The formation of reinforced phases is illustrated in the following examples of partial reactions^[8]: which, it should be noted appear to contain a few errors. However, it was assumed accurate reproduction from the literature was more important.

Thermodynamically stable Carbide Formation

(i) Gas decomposition:



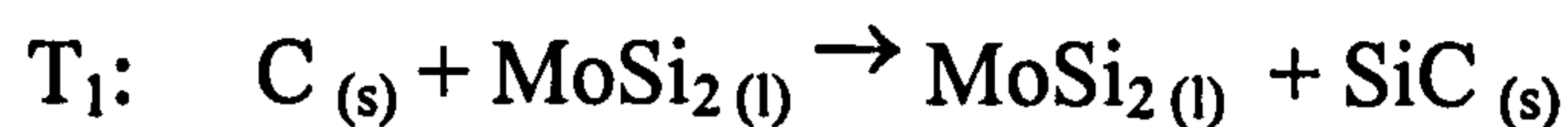
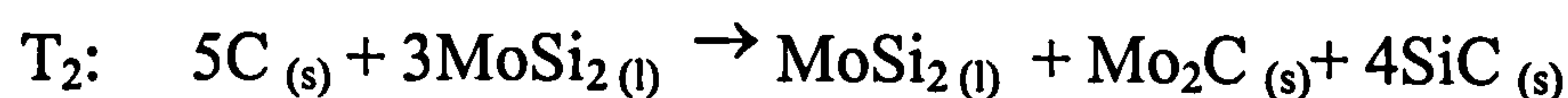
(ii) Carbon reaction and carbide formation:



Since TiC is thermodynamically stable, the predicted TiC formation occurs.

Thermodynamically unstable Carbide Formation

In the presence of two competing reactions, the choice of process temperature can significantly affect selectivity. In cases of MoSi₂ melts, active C[•] will form both SiC and Mo₂C. One can show that the predominant reaction is a function of temperature:



Although Mo₂C is an unstable carbide in the presence of Si, it is a stable product when at temperature T₂.

Duplex Reinforcement Formation

A third approach considers the nitriding reaction for the generation of two nitride phases:



and

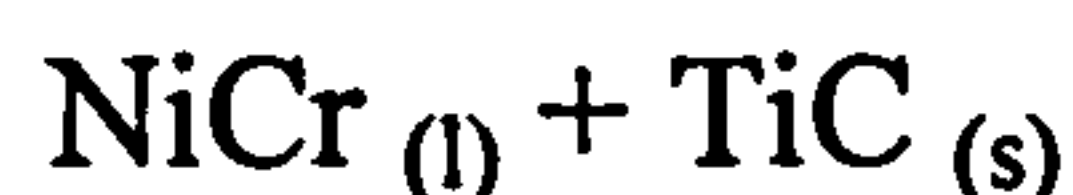
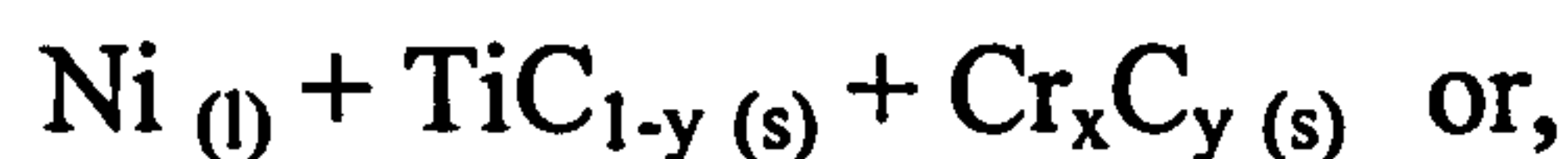


Although TiN is more stable than AlN, both are sufficiently stable to produce an aluminium matrix reinforced with both AlN and TiN. Via a modification of the alloy melt chemistry, the combination of two carbides may form independently or a mixed solid solution can result:

(i) Carbon decomposition:



(ii) Alternative reaction paths:

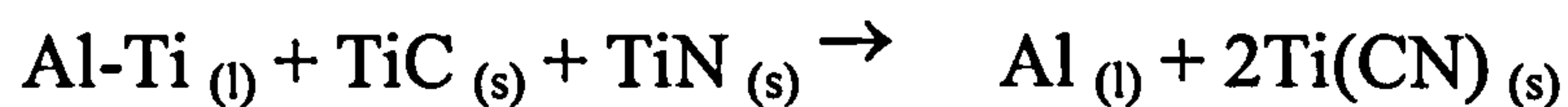
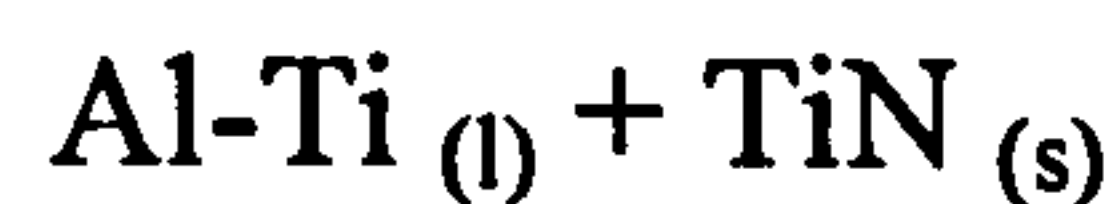


Carbonitride reinforcement formation may also be produced via gas chemistry control to produce a mixed carbide/nitride phase with the following reactions:

(i) Gas decomposition:



(ii) Nitrogen and Carbon reactions:



The degree of conversion of a particle's surface to a new compound depends on the reactive gas concentration as well as the residence time between the heated particles and the dissociated reactive gases, i.e. factors influencing the reaction kinetics, as discussed above.

2.11 Plasma-Particle Interactions

Understanding the behaviour of a particle and the interactions between a particle and the plasma surrounding it is important to the development and optimisation of the plasma spray coating process^[7,12,13].

The plasma flow field in an APS system can be characterised in terms of temperature, velocity, enthalpy and specie concentration.

In order to measure flame characteristics several techniques may be employed. Temperatures in the plasma are too high for the application of traditional techniques such as thermocouples and uncooled pitot tubes, and often are not high enough for the application of emission spectroscopy techniques. Methods to measure flame temperatures include most commonly the enthalpy probe, which is considered to be a reliable diagnostic tool in the range from 2000 to 14000 K. Other methods include laser-induced fluorescence and laser scattering.

Plasma velocity and often particle velocity are measured using laser Doppler velocimetry which assumes that very small and light particles have a velocity equal to that of the flame. This technique does not make it possible to follow the history of an individual particle. The photographic streak method uses a rapid camera to follow flame disturbances from one flame to the next. A spectral method based on the Doppler shift of the lines emitted by the flame is sometimes also used. These techniques although useful are unable to determine the temperature at the flame cone

because the luminosities of the particles used for the measurements are less than that of the plasma flame.

Mass spectrometry is the most commonly used method to measure the changing gas compositions in a plasma jet. Samples are taken at various points in the flame and analysed. Particle characterisation requires the in-flight size, velocity and temperature measurement of individual particles.

The easiest way to measure the degree of particle melting is to spray into water. If the particles are molten at impact, they become spherical.

Counting the percentage of spherical particles in order to assess the level of optimisation of the parameters can perform a crude quantitative analysis.

Serious measurements must be made using optical technology. The one colour pyrometer technique uses a photomultiplier, which has been calibrated using a tungsten ribbon lamp. A chopper and pinhole are used to simulate a particle of known diameter moving at a known velocity. More accurate is the two-colour pyrometry method^[14]. In this technique an optical signal from a small volume of flame is focused on the entrance of two monochromators and is later transformed by photomultipliers into a voltage. The ratio of voltages collected from the photomultipliers enables the particle temperature to be determined as described below. A blackbody at the temperature T , emits density of power (W/m^3) at the wavelength λ described, in the range of temperatures of interest, by the Wien relationship:

$$I_{(\lambda,T)} = 2\pi hc^2 \lambda^{-5} \cdot \exp(-hc/\lambda KT) \quad [\text{Eqn. 2.7}]$$

Where

K = Boltzman constant

h = Planck constant

c = Velocity of light

The ratio of powers emitted by a greybody (the body having an emission coefficient independent of the wavelength) is the same as for the blackbody and can be found from the following relationship:

$$T = A / \ln(RB) \quad [\text{Eqn. 2.8}]$$

Where:

A is the constant depending on the wavelength

B is the constant depending on the wavelength and the set up used.

The calibration procedure is similar to that used for one-colour pyrometry. Uncertainties arise from errors in the calibration coefficients, the greybody assumption, and the random fluctuations in the ratio of signal voltages.

As mentioned earlier the LDV technique is often used to measure particle velocities. It is the common practice now, and systems have been developed to simultaneously measure particle size, velocity and temperature.

The plasma-particle interaction in subsonic Argon-Helium thermal plasma jets has been investigated for a Nickel-Aluminium powder^[12]. Most of the techniques mentioned earlier have been employed in characterising the plasma flame and sprayed particles. The aim of this study was to investigate the complex interaction between the gas and particle flow fields.

The plasma torch (Miller SG-100) geometry and general particle flow field characteristics are shown in figure 13, the operating parameters were as follows:

Arc current:	800 A
Total power output:	28 kW
Arc gas flow rate:	2830 litres/hr Ar
Aux gas flow rate:	1330 litres/hr He
Carrier gas flow rate:	368 litres/hr Ar
Particle size:	50 to 125 μM

The particle injection velocity was measured at 15 m/s transverse to the plasma axial direction. This gives rise to the plasma spray geometry shown in figure 13. At an axial location 5 mm from the face of the torch and on its geometric centre the gas temperature was measured at around 12700 K. This temperature drops to only 2000 K at 5 mm radial location. Figure 15, shows a contour plot of gas axial velocity with again the highest particle number density indicated by the dashed line. The average particle velocities ranged from 180 m/s on the torch centreline to 80m/s on the outside of the jet. The gas composition is shown in figure 16.

In order to assess the impact that the plasma has on the particles it was necessary to follow the median trajectory. Because of the plasma geometry the majority of the particles flew through the plasma jet to the exit at the opposite side of the gas flow field.

The temperature map (figure 14) has shown that most of the particles have not passed through the hottest part of the flame. For instance, a particle travelling along the centre line would not see a temperature below 3000 K until the 55 mm axial position. However, a particle following the median trajectory would experience temperatures below 3000 K at the 20 mm axial position. Importantly, this implies that a particle following the median trajectory will impart heat back to the gas sooner than if it followed the centre line of the plasma. Figure 17 confirms this, where the average plasma temperature is plotted along the median particle trajectory. The slight downward trend of average particle temperature is consistent with the trend of lower gas temperatures as one moves outward both axially and radially.

Given that particles travel along the median trajectory they are only accelerated by the plasma in the first 60 mm. The cross over point for the particles and gas axial velocities along the median trajectory is shown in figure 18. This implies that past this crossover point, (where the particles have a higher velocity than the gas which is transporting them) the particles will be retarded by the surrounding gas.

Probably the most important point in the particle trajectory is at the stand-off distance (the point where the substrate would be placed). This

distance is a crucial parameter in all thermal spraying techniques. For the system considered, that distance was 6.35 cm. The radial distributions of average particle and gas temperature and velocity at the stand-off distance are shown in figures 19 and 20 respectively. Particles on the centre line are generally hotter because they have been exposed to higher temperatures and are smaller than those on the outside of the plasma jet.

2.12 Particle-substrate interactions

The way in which plasma sprayed particles deform on impact is very complex, and is dependant on several factors. Described below is a very simple account of what happens, and why it is important.

Coatings are built up from single particles that splat onto the substrate or previously deposited particles. In the plasma spray process, metal or alloy powders are fed into a high temperature plasma flame where they are rapidly fully or partially melted and accelerated toward a substrate. The impinging and deformation process of a heated particle can be divided into four categories.^[15]

- (i) A molten viscous particle impacts and spreads as a thin disk.
- (ii) A molten viscous particle impacts and splashes with some part of the particle remaining on the substrate.
- (iii) A plastic particle impacts and is deformed plastically.
- (iv) An elastic particle impacts and bounces off the substrate.

When viscous particles deposit on a substrate or previously deposited layer they deform to lamellae and rapidly solidify to give columnar or fine-grained equiaxed crystals. The first particles that land will determine the coating's adhesion properties. These adhesive properties can also be strongly influenced by pre-sprayed surface treatments.

The solid particles will bounce off the substrate or adhere weakly with the rest of the coating, reducing its mechanical properties. It is for this reason that spraying parameters must be chosen which ensure nearly all the particles are molten prior to impact.

Many workers^[16,17] have investigated and tried to model the phenomena at impact which determine the crystal structure, crystal sizes, porosity formation and formation of microcracks.

2.13 Rapid Solidification

Plasma spraying is a rapid solidification technique^[18]. The sprayed powder particles experience very rapid cooling rates upon impact with the substrate. Rapid solidification is a relatively recent development which can be attributed to reports by Pol Duwez in 1960^[19]. In these reports it was written that a two-phase mixture of equilibrium phases in a eutectic alloy could be replaced by an extended solid solution, a new crystalline phase, or, most remarkably, by a non-crystalline phase (i.e. a glass) simply by quenching with enough rapidity from the liquid state. Considerable research has subsequently been carried out into rapid solidification, particularly into metallic glasses, which are the only new class of material to emerge in

recent times. Rapid solidification has the following characteristics compared with conventional solidification of relatively heavy sections.

1. Large departures from equilibrium constitution resulting in substantial extensions of solid solubility and formation of new equilibrium crystalline phases and metallic glasses.
2. More uniform and size-refined solidification microstructure largely eliminating detrimental effects of segregation obtained in thick sections and exhibiting more consistent responses to heat treatment and working, with enhanced durability in service, at the least, and rendering previously non-workable (casting-only) alloys ductile, and even superplastic, at the most.
3. Elimination of redundant working and finishing operations involved in ingot processing, by solidifying or consolidating to dimensions nearer to or identical with those actually required.

Rapid solidification may be achieved by subjecting the molten metal to high cooling rates (e.g. $10^2 - 10^{10}$ K/s). In order for these cooling rates to be achieved, a good contact between the melt and a highly efficient heat sink is required. This condition imposes a limitation on the thickness of the melt such that very high cooling rates can be achieved (e.g. 10 mm for 10^2 K/s, 0.1 mm for 10^6 K/s and 1 μm for 10^{10} K/s).

2.14 Coating characterisation

2.14.1 Microstructure

Plasma spraying allows the production of many different types of coatings, including a range of metals, intermetallics, ceramics and their composites. As mentioned earlier, some compositions would be difficult, if not impossible to produce by other production methods.

Optical and electron, microscopy are often the first stage of analysis. Plasma sprayed coatings are typically in the range 50-500 μm thick and are well within the resolution of a good optical microscope. Electron microscopy will give a more detailed picture if a specific characteristic needs to be investigated. Many electron microscopes have further analytical techniques built in, for example, energy dispersive x-ray (EDX) analysis.

Microscopy will give information on:

- fraction and size of voids in the coating
- fraction and size of unmelted particles in the coating
- deformation of the substrate near the coating
- distribution of phases in the coating
- presence of particles that have reacted in the flame in the coating
- presence of solid inclusions in the coatings.

Before microscopic examination the specimens, usually in cross-section must be metallographically prepared. This is not normally a problem, but care must sometimes be taken to avoid damage caused by the preparation. This damage may take the form of void smearing or void pull-out. Furthermore, some weakly adhered coatings may be removed during cutting, grinding and polishing.

Microstructural features can give a good indication as to the effectiveness of the spraying parameters that have been selected.

2.14.2 Mechanical properties

The majority of thermally sprayed coating applications are related to wear resistance. Wear tests are fairly complicated and may take a long time involving many parameters and variations. These parameters can be divided up as follows:^[20]

- Input parameters, e.g. load, temperature, velocity, time.
- Process parameters, e.g. materials, lubricant, environment, geometry, surface preparation, operational procedure.
- Output parameters, e.g. friction, noise, vibration, wear.

On the other hand, the hardness or microhardness are relatively easy to measure but problems arise when this material specific property is used to predict wear or other aspects of coating behaviour. The overriding aim of a mechanical test is to simulate as closely as possible the conditions in service.

Microhardness tests are simple to carry out and require the same preparation required for optical microscopy. The most common microhardness test is the Vickers microhardness test. The indenter used is a pyramidal diamond and the average of the indentation diagonals is used to obtain the Vickers microhardness.

The greater the load used, the larger the indent. The size of indent used to measure the hardness should be as large as possible, but care must be taken to avoid regions near the edges of the coating. A typical microhardness indent is shown in figure 21.

Coating adhesion is another important mechanical property. Coating pull-off tensile tests are common in determining the adhesion strength. However, this is a destructive test, and research is now focusing on a non-destructive testing using ultra-sound.^[21]

2.14.3 Sliding Wear

Sliding wear is concerned with the wear that occurs when two solid surfaces pass over each other^[22]. In most practical applications sliding surfaces are lubricated in some way, and the wear that occurs is then termed lubricated wear. Although, in some engineering applications and in many laboratory investigations surfaces slide in air without a lubricant. The resulting wear is termed dry sliding wear, although it usually takes place in ambient conditions of appreciable humidity.

The frictional properties of materials in contact, and the wear that results from such contact, are of considerable importance in most engineering applications.

There are principally two main types of wear regime:

1. Adhesive wear
2. Abrasive wear

2.14.3.1 Adhesive wear

The term adhesive wear is commonly used but can be slightly misleading. Adhesion plays an important role in sliding wear, but is only one of several physical and chemical processes that may be involved. Other terms such as *scuffing* and *galling* are also used frequently when referring to severe sliding wear. Scuffing is often used to refer to localised surface damage resulting from local solid state welding between the sliding surfaces. The term is frequently used when describing the breakdown of lubrication, usually at high speeds. Galling represents a more severe form of scuffing, due to local welding, and is associated with gross surface damage. The word often refers to damage resulting from unlubricated sliding at low speeds, characterised by severely roughened surfaces and transfer or displacement of large fragments of material. Galling may occur in nominally lubricated systems when the lubricant film breaks down, and can be followed by seizure of the surfaces and consequent gross failure of the sliding system.

Laboratory investigations of wear are usually carried out either to examine the mechanisms by which wear occurs, or to simulate practical applications and provide useful design data on wear rates and coefficients of friction. For both purposes, control and measurement of all the variables which may influence wear are very important. Wear rate and friction are often critically dependant on the sliding conditions and apparently minor changes in conditions may lead to radical changes in the dominant mechanism and associated rate of wear.

Several methods of friction and wear testing have emerged which may be divided into two categories; those where the sliding surfaces are symmetrically disposed and the wear rates of the two material surfaces should be approximately the same; and more commonly where the system is inherently asymmetric, in which the two sliding bodies, even of the same material, will almost certainly experience different rates of wear. Two of the most common asymmetric rigs are the 'pin on disk' and 'block on ring' test, the geometries for which may be seen in figures 22 and 23 respectively. In these cases the contact may initially be over an extended nominal contact area (conformal) or only at a point on a line (counterformal). Schematic examples of conformal and counterformal geometries may be seen in figure 24. In asymmetric arrangements one component of the mating pair, commonly the pin or block is referred to as the specimen, and the other body, the disk or ring, is referred to as the counterface. The dimensions for specimens in laboratory wear testing usually lie in the range from millimetres to tens of millimetres, while the counterface dimensions are typically several tens of millimetres. The variables that affect friction and wear, and which must therefore be

controlled in wear testing, range from the most obvious such as speed and load to the less obvious, such as specimen size and orientation.

Wear is usually measured either by removing the specimen at intervals and weighing or dimensional measurement, or by continuously measuring its position with an electrical or mechanical transducer and deducing the wear from its change in dimensions. Ideally the frictional force is measured continuously throughout a test. This is usually done by measuring the tangential force on the specimen, or the torque on a rotating counterface. A continuous friction record not only provides numerical values for the coefficient of friction (μ), but also allows changes in sliding behaviour to be observed. These changes often report changes in surface nature or topography, or in the mechanism of wear. Running-in, for example, can be explored in this way, as can the breakdown of protective oxide or lubricant.

Wear under sliding conditions depends on the distance slid, but also to some extent on both the sliding velocity and the duration of the test, independently. The sliding velocity affects the rate of frictional energy dissipation, and therefore the temperature at the interface. It certainly cannot be assumed that one wear test performed at twice the speed and half the time of another will produce the same result, because sudden changes in wear mechanism or rate may occur when the sliding speed is altered.

Apart from the major variables of normal load, contact area, sliding speed and testing time, several other factors must also be considered and

monitored in wear testing. The testing temperature is important through its influence on the mechanical properties of the materials and on thermally activated chemical processes, although these may often be dominated by frictionally generated temperature rises. In lubricated systems it will also be important through its effect on lubricant viscosity. Atmospheric composition is extremely important; reactive components such as water vapour and oxygen strongly influence wear rates and mechanisms in all classes of material.

2.14.3.2 Abrasive wear

In abrasive wear, material is removed or displaced from a surface by hard particles, or sometimes by hard protuberances on a counterface, forced against and sliding along the surface. Common terms applied with abrasive wear include *two-body abrasive wear* and *three-body abrasive wear* are shown in figure 25. Two-body wear is caused by hard protuberances on the counterface while in three-body wear hard particles are free to roll and slide between the two surfaces. Wear rates due to three-body abrasion are generally lower than those due to two-body abrasion, although the severity of material removal in the two cases differ only in relative importance rather than in nature. Other terms used include *high-stress* and *low-stress* abrasion. With high stress abrasion the crushing strength of the abrasive particles is exceeded, such that they are broken up during the wear process, while in low stress abrasion this is not the case.

The hardness of the particles involved in abrasion has a very significant influence on wear rate. Particles with lower hardness than that of the surface cause much less wear than harder particles. For particles significantly harder than the surface, then the exact value of their hardness is much less significant. The wear rate becomes much more sensitive to the ratio of abrasive hardness H_a to the surface hardness H_s when H_a/H_s is less than ~ 1 . For a spherical particle pressed against a flat surface, the maximum contact pressure is about 0.8 times the indentation hardness of the particle material. Therefore for a sphere of hardness H_a to cause plastic indentation in a surface of hardness H_s , H_s must be less than 0.8 H_a ; that is if $H_a/H_s > 1.25$. Abrasion under conditions where $H_a/H_s < 1.2$ is sometimes termed *soft abrasion*, in contrast to *hard abrasion* when $H_a/H_s > 1.2$.

Wear rates depend strongly on the shapes of the particles, with angular particles causing greater wear than rounded ones. Angularity is difficult to define for a three dimensional particle and is seldom measured quantitatively. Differences in particle shape may result in differences in wear rate by a factor of ten or more.

The sizes of particles cover a wide range. Those responsible for most abrasive wear are between 5 and 500 μm in size, while gouging may involve hard objects some tens or even hundreds of millimetres across. Wear rates for particles smaller than 100 μm drop substantially with decreasing particle size. Similar behaviour is seen for quite different particle materials and different metals. The behaviour is thought to reflect a true size effect in the strength of the metal itself, which is also found in

indentation and scratching experiments. The flow stress of a very small volume of material is higher than that of a larger volume, perhaps because of the difficulty in nucleating or moving dislocations in a small volume. This increase in local flow stress as the scale of the deformation is diminished leads to reduction in wear rates by plastic processes, and hence to the observed particle size effect.

2.14.3.3 Wear resistance in thermally sprayed coatings

The effect of Microstructure on the wear behaviour of Thermal Spray Coatings has been investigated^[23] because thermally sprayed coatings are being considered as an alternative to the use of cast iron liners in aluminium engine blocks. Researchers developed a bench wear test in which parts of real components are tested such that the geometry, metallurgy and representative surface finishes of the engine could be preserved and evaluated.

The authors found ‘splat delamination’, a common wear mechanism in thermal spray coatings, where the coating breaks along splat boundaries to be the dominant wear mechanism. The authors report that most cracks initiate at the coating surface but argue that cracks may well form below the surface. The cracks then propagate easily along the boundaries until the splat is no longer attached and falls away. A schematic diagram of the splat delamination wear mechanism may be seen in figure 26. The intersplat boundaries are the weakest part of the coating, and it has been suggested that the intersplat cohesive strength is only 0.1 - 0.2 that of the bulk material^[24]. The authors continue that splat orientation and waviness

are important. If the splat is relatively flat with the boundary mostly parallel then delamination would be easy. However, if the splats are wavy with interfaces at some angle to the surface, it is much harder for the splat to delaminate. Figure 27 illustrates this idea schematically. It therefore follows that the wavier the splat, the harder for the crack to propagate along the boundary (crack path tortuosity), since the plane of maximum stress and the plane of the splat interface will only coincide part of the time.

When looking at the effect of oxides in thermal spray coatings it might be expected that the oxides would behave similarly to silicon particles in a 390-aluminium alloy by protruding from the surface and bearing the load. However, there was no evidence of this occurring in the thermally sprayed coatings and that in fact oxides would crack and fall out more easily. However, coatings with higher oxide levels were found in general to be more wear resistant and the authors speculate that oxides often make a positive contribution towards wear resistance and should not always be incidental or even detrimental.

Porosity in thermally sprayed coatings was found to be of considerable importance. Large pores are detrimental to wear since 'coating collapse' often occurs around pores.

With a pore close to the surface, there is not enough material behind the splat to support it and cracking of the splat becomes easier. Additionally, since there is less material to support the splat and to propagate through the crack then has to progress a shorter distance.

Resolidified or unmelted particles were not found to have a significant effect on wear resistance.

2.15 Variations in coating properties across a spray pattern

Thermally sprayed coatings have very different properties to most other engineering materials^[25]. These properties depend on the size and types of flaws found in the coating, as well as the properties of the deposited particles. Many flaws are created when particles escape the optimum part of the flame and are thus processed inadequately. Other flaws come from the original powder in the form of impurities or poorly sized particles.

The authors propose that in order to optimise the bulk properties of the coating it is necessary to identify the worst flaws, their distribution in the coating and their causes. Their approach involves examining the variation in particle properties within a spray pattern and comparing them to the properties of a spray profile whereupon it should be possible to link spray parameters, which affect particle properties, to coating properties. A summary of the work is presented below.

A Monte Carlo simulation was used to create a database of particles based on measured, average particle properties within the flame. The database was used to produce maps of particles of a specified type within the spray pattern. These maps were then related to measurements of coating properties. Novel measurement techniques were developed to enable highly localised measurements, for example, a foil peel test and

microstructure damage test. Microstructural analysis was used to characterise the state of particles arriving at the coating.

The Monte Carlo simulation was used to simulate a set of torch passes that follow the same path. This was based on the assumption that a flaw produced in an initial pass would be locked in by subsequent passes. The model simulated a spray pattern by introducing random fluctuations in a particle property about certain property distributions. The simulation outputs were then compared to profiles of samples made the same way. Comparisons were then made between model predictions and measured results and between different local measurement techniques. When the model parameters had been matched with the profiles, it was assumed that coating properties could be predicted with a reasonable confidence. The sample geometry shown in figure 28, was used as a direct comparison between model and process. The flow chart for the Monte Carlo coating simulation logic is shown in figure 29.

The peel test that was developed is shown in figure 30. The test comprises the following parts:

- (i) A coating deposition on a grit blasted metal foil that has been soldered to a copper block. The copper block serves as mechanical support and heat sink.
- (ii) After deposition the block, foil and coating are glued to a stiff aluminium plate and the copper block is removed.
- (iii) The foil is peeled from the coating.

The method causes a crack to propagate precisely along the coating-substrate interface, in a stable movement. The movement of the crack is controlled by the peeling speed. The result is a plot of instantaneous adhesion, in terms of peel force per unit width, versus location in the coating. With metal foils the effects of plastic work must be subtracted from the peel force for a true adhesion measurement.

The coating peel off tests for a Cr_2O_3 sprayed deposit with radial and axial powder feed are shown in figure 31, respectively. The zero position indicates the centreline of the torch.

With radial injection, figure 31, the bond strength dropped to zero where the slowest and coldest particles arrived. This indicates that although the particles did stick to the substrate, the bond was extremely weak.

The highest bond strength occurred at a position offset from the torch centreline; lack of symmetry is characteristic of radial feed torches. The slight rise in adhesion toward the end of the deposit is put down to adhesion between the foil and resin used. This occurs in a region where the coating is so thin that the resin can penetrate it and bond to the foil substrate. It was proposed that the properties of these poorly sprayed outside areas are locked into the coating by subsequent passes and remain as flaws in the coating.

When particles were axially injected (figure 31) the above effects were not observed to anywhere near the same extent. This is probably due to the fact that in an axial torch all particles are heated by the central position at the flame and thus start out with higher temperatures.

The authors stressed that these tests could not be directly compared because of different spraying parameters, namely, different stand-off distances and varying foil thicknesses.

The surface of each profile was scanned with a needle type profilometer. This provided a record of the profile across its width. The deposition rate across its width can then be calculated. If coupled with direct measurement of the mass flux in the plasma flame, a local deposition efficiency could be calculated. The results for radial and axial feed are shown in figure 32.

Both profiles are symmetric about their centreline and the shape is that of Gaussian distribution. From each profile the roughness was also calculated. The method of roughness calculation tended to emphasise large-scale features and was only slightly affected by the fine structure of the surface. The two cases examined have very different results. The axial feed torch showed a relatively constant roughness across its profile due to a more consistent processing of particles. The radial feed profile was rough on the sides and smooth in the centre. It was suggested that surface agglomeration of partially melted particles might be a cause of porosity. This would occur because agglomerations might partially cover areas of coating, shielding them from subsequent particles.

A third test was used to measure the variation in coating cohesion. In this test porosity was measured in certain areas. The section was then subjected to a “damage polish”. This consisted of a 30 second polish with 1 μm diamond grit on a flat iron plateau followed by a 20 second polish

with 1 μm diamond on a napped cloth wheel. The plateau and the cloth was used to pullout the broken or loosely adherent particles. This would increase the apparent porosity by pulling out particles from the coating and enlarging existing pores. The effect of a damage polish is shown in figure 33. It is believed that the change in porosity is a measure of coating cohesion. The variation in porosity across each profile is shown in figure 34. The difficulty in polishing each sample exactly the same way causes difficulties in ensuring that each test is repeatable. The observed change gives qualitative appraisal of cohesion but a more reliable damage method would be required for quantitative analysis.

2.16 Functionally Gradient Coatings

It is hoped a future will lie in RPS for the production of Functionally Gradient Coatings. This will enable coatings of graded composition and structure to be produced.

A Functionally Gradient Material (FGM) is a composite of at least two constituents that smoothly transitions from 100 % of constituent A to > 0 % of constituent B through controlled gradients. A functional gradient may be several lamellae or it may be a continuous change in composition'.

Researchers have produced a functionally gradient coatings,^[26] consisting of four components; Copper, Tungsten, Boron and Boron Nitride^[27]. The coating produced is for use in high heat flux applications. A gradient material can be used to optimise the design of high heat flux component. Advantages of incorporating a FGM include:

- Minimises a difference in thermal expansion between different materials, which reduces thermal stresses.
- Eliminates complex bonding and fabrication problems.
- Eliminates the reduction in heat flow through dissimilar material bond joints.
- Non-destructive examination by techniques such as ultrasonic inspection of bond joints is made simpler with the continuous gradient structure.
- Optimises design by placing the best materials in the best locations.
- Can be made to near net shape.

The objective of this project was to produce a material for applications in fusion reactors as a plasma-facing component. Some material properties required for this application are; low plasma poisoning potential (low atomic number), good high temperature mechanical properties and a high thermal conductivity. Only a brief summary is presented here.

The main obstacle faced in the production of functionally gradient structures was choosing a plasma spray gun anode/nozzle, which could spray all powders consecutively. Once the parameters were optimised by spraying separately onto steel coupons, a continuous gradient structure was deposited by varying the powder feed and carrier gas flow rates. After a copper, tungsten, boron gradient structure was deposited three methods were tried for the in-situ nitriding of the boron surface, shown below:

- VPS of boron with nitrogen plasma.
- VPS of boron with an Ar/H₂ Plasma with N₂ powder carrier gas.
- VPS of 50% B/50%BN agglomerated powder with N₂ powder carrier gas.

The authors found the third method to be the most effective for nitriding the boron surface. Figure 35 shows a cross-section of the Copper/Tungsten/Boron/Boron Nitride functionally gradient specimen.

2.17 Materials Processed by RPS

Reactive plasma spraying has been studied by many investigators with the aim of producing new materials or existing materials by another route either as compounds or composites. The literature contains details of several materials that have been successfully processed to varying degrees. These may be classified in terms of product morphology:

- Coatings
- Powders
- Bulk Materials

or in terms of material type:

- Metals
- Intermetallics
- Ceramics
- Composites (metal and ceramic matrix)

The RPS process is ideally suited to producing composite structures and indeed the majority of publications concentrate in this area.

Reactive plasma spraying can be defined as the plasma spraying of materials with the intentional introduction of reactive agents into the particle/gas streams. Agents include liquids, gases or mixtures of 'reactant' solids, which when in contact with the high temperature plasma jet decompose to form highly reactive or ionic species which combine and form new compounds on the surface of the particle.

Investigations into the production of composites and intermetallics have shown that new phases can be produced with the degree of their formation depending on the starting materials, introduction point and the atmosphere into which they are introduced.

Depending on the residence time and particle quenching phenomenon, the products which form vary. A 'plasma reactor' is used to promote interaction between the reacting species and the contained, desired atmosphere. On impact with a substrate or other target surface the particles 'splat' and flatten. The impact causes the reactively formed new compound shell to fracture and disperse. Figure 36 shows a schematic illustration of the formation of Ti/TiC composite deposits plasma sprayed with reactive gases. This section reviews some of the coatings or deposits that have been produced by RPS.

2.17.1 Metals

RPS has been the subject of many researches. However, as mentioned earlier the majority of this work has focused on the in-situ formation of nitrides, carbides and cermets by reaction between the spraying powder and atmospheric gases.

However RPS has been used to improve the properties of conventional metallic coatings. Oki *et al*^[28] have successfully applied RPS to improve the corrosion and wear resistance of stainless steel coatings. Their study aimed to increase the nitrogen content of the stainless steel coatings by using nitrogen gas when spraying. In this case nitrogen is contained in the

coating in solution as an austenite stabiliser instead of a compound former as described above. Alloying of stainless steel with nitrogen is known to improve corrosion resistance as well as stabilise austenite phases. In their study the formation of coatings with high nitrogen content is achieved without loss of nitrogen from the feedstock materials. Moreover by selection of the optimum spray conditions, nitrogen enrichment could be achieved. High manganese and high nitrogen stainless steel powder (DIN P-900) was used as the feedstock material. The powder was spherical gas atomised at 10 to 60 μm diameter containing 18%Cr, 19%Mn and 0.39%N. Plasma spraying was performed in a low pressure plasma spraying apparatus. Nitrogen was used as a plasma gas, powder carrier gas as well as atmospheric gas. The experimentation was carried out according to the conditions shown in table 1.

Table 1: Experimental Conditions

<u>Spraying Conditions</u>				
Plasma Gas	Ar + H ₂		Ar + N ₂	
Power Input	600-700 Amps / 65-75 Volts / 45 kW			
Powder Feed Gas	Argon			
Chamber Pressure /kPa	15	30	60	100
Spray Distance /mm	270	215	180	120

The plasma gas was Ar + H₂ or Ar + N₂ and the powder carrier gas Ar or N₂, the chamber pressure was 15 kPa, 30 kPa, 60 kPa and 100 kPa. The authors found it difficult to keep a constant relation between plasma current and voltage, because they were dependent on the type of plasma and atmospheric gas. Therefore, to maintain the plasma output at a

constant value of 45KW, the plasma current and voltage was controlled in the range 600 - 700A and 65 to 75V. The spray distance was optimised for the chamber pressure in a range of 270 to 120 mm. The coatings produced were dense and found to consist of Ferrite (α) and austenite (γ). The manganese content in the sprayed coatings was lower than the feedstock material (19 %Mn), being in the range 10-12%. The manganese content was found to be 13 to 15% in γ and 0 to 4% in α . However, while the manganese content is substantially independent of the spraying conditions, the ratio of γ to α phases was found to vary widely with spray parameters. The γ to α ratio is thought to affect the mechanical and chemical properties of the final coating. Therefore the volume fraction of γ phase in the coatings was measured to evaluate the effect of various spraying parameters. X-ray diffractometry was applied for quantitative measurement of the γ volume fraction, which was obtained using the following equation:

$$V_{f\gamma} = 1 / (1 + K (I_{\alpha} / I_{\gamma})) \quad [\text{Eqn. 2.9}]$$

Where:

$V_{f\gamma}$ = Volume fraction of γ phase

I_{α} & I_{γ} = Diffraction intensities of α and γ phase

F = Constant

The measurement of volume fraction by this technique was found to correspond well with other measurements taken by image analysis of optical micrographs.

The effect chamber pressure had on microstructure formation can be seen in figure 37 where the volume fraction of the γ phase and hardness values for Ar + N₂ and Ar + H₂ plasma gases are shown for various chamber pressures. The volume fraction of γ phase and the hardness of the coatings were not so affected by chamber pressure when using Ar + N₂ as plasma gases. The Volume fraction of γ and therefore hardness increased with chamber pressure up to 30kPa and then fell off. No definite reason was used to explain this phenomenon. Further experimentation was then carried out to determine the effect of other parameters. The results and parameters may be seen in figure 38. The results showed that the volume fraction of the γ phase decreased when spraying with Ar + H₂ plasma gases but stayed at almost the same level when using Ar + N₂ plasma gases. This despite the fact that the manganese, which is used as an γ stabilising element, decreases during spraying. This result suggests that the composition of plasma gas has the largest effect on the nitrogen content in the final coating, the pressure and composition of the atmospheric gas have smaller effects. This suggests, say the author that nitrogen enrichment can be achieved during RPS and that this enrichment occurs in the plasma jet.

2.17.2 Intermetallics

Much interest has been devoted to the production of in-situ intermetallics in particular titanium-aluminides. Titanium aluminides are expected to find a wide range of applications particularly in the aerospace industry, but are expensive to manufacture and their properties can be easily

compromised by contaminants such as oxygen. Ti and Al forms TiAl_3 , a high melting point reinforcing intermetallic, when it exceeds solid solubility (1 wt %). These alloys provide high temperature stability due to the slow diffusion of Ti in Al, with minimal increase in density.

A Reactive spray Forming (REFORM) process for the production of titanium aluminide intermetallics has been demonstrated with limited success^[29]. To manufacture the intermetallic by RPS, Al-30% Mg powder was sprayed with TiCl_4 as the reactive gas. Initial results were disappointing with samples showing undesirable porosity, lack of homogeneity and unwanted microstructures. A schematic diagram of the equipment used may be seen in figure 39. The D.C. torch was of a tubular type specifically developed for this application. Typical operating voltages for argon and 10% H_2 in argon plasma gases were 110V and 160V respectively. The current was varied between 200 and 350 amps. The product was collected either on a hot graphite sleeve surrounding the reaction zone or on a relatively cold crucible directly below the reaction zone.

As mentioned earlier there were two product collection sites: the sleeve and the crucible. Some of the powders reacted in flight and were deposited onto the hot graphite sleeve. While on the sleeve they remained hot near 1800 K as evident by the presence of molten regions of TiAl , and could continue to react until the deposition of the next droplet. Reactions could therefore occur both in flight and on the collector. By comparison the crucible was cold (around 1000 K as evident by the partial melting of

pure aluminium) and outside the hot reaction zone. Products collected on the crucible indicated only in flight reactions.

The product collected in the crucible was a composite of either TiAl or TiAl_3 intermetallics and an aluminium matrix containing around 3% Ti. The total titanium content varied between 15 and 45wt%. The sleeve product was either a composite or a pure intermetallic and contained between 25 and 85 wt % Ti.

The samples were analysed for both chlorine and oxygen content. The chlorine content of the solid deposits was measured at 30-90 ppm. However, some chlorides were deposited on the surface of the samples at the end of the run, when the surfaces cooled to temperatures below the boiling point of the chlorides in the surrounding environment. Surface contamination resulted in increasing the overall chloride content of the powders to levels reaching 300 ppm.

The oxygen level of the products varied from a low of 200 ppm to a high of 3000 ppm. The differences in oxygen content may have resulted from contamination at the end of the run, when for safety reasons, air was introduced into the reactor prior to opening. However, the powder used to reduce the TiCl_4 contained up to 1500 ppm of oxygen, and therefore the collected product frequently contained less oxygen than the starting material, suggesting that under carefully controlled conditions, low oxygen intermetallics can be produced.

This study proved that titanium aluminides could be produced in a d.c. plasma reactor, based on reactions between TiCl_4 and aluminium powders. The product composition varied from TiAl_3 in an aluminium matrix (15% total Ti content) to pure TiAl and Ti_3Al intermetallics (up to 85% total Ti content). The energy density of the plasma system and consequently the reaction zone was the most important variable in determining product composition. The Ti content could be increased by using an alloy of magnesium and aluminium as the reducing powder. The materials could be both synthesised and formed in a single unit operation if the collector temperature remained near the melting point of the intermetallic. Under such conditions about half the theoretically predicted conversion occurs in flight and the remaining on the hot substrate. Powders could also be produced on a cold crucible. The product contained relatively low levels of chlorine and oxygen. However, significant problems with homogeneity and porosity were observed.

More recently, the same author and other researchers collaborated to further investigate the synthesis of Al-Ti alloys by RPS^[30]. This more recent study had the following aims, to: (a) synthesise Al-Ti materials containing up to 10 wt % Ti, (b) understand the effect of the process parameters on the composition and microstructure of the product, and (c) evaluate the mechanical properties on a preliminary basis.

TiCl_4 was used as the source for Ti and either Al wire or Al powder was utilised as the sources of Al. Very few details are given with respect to the equipment used and there is no mention of whether spraying was performed in an inert environment or not. Liquid TiCl_4 was first

evaporated and then injected into the plasma region. Experiments were performed at a constant plasma power of 100kW. The reaction products were collected on a water cold substrate and neutralised with water prior to collection. The products were evaluated based on (a) Ti and Cl content, (b) distribution of Ti and (c) porosity.

The products were also crushed and subjected to Ti and Cl analysis using atomic absorption and ion chromatography analysis respectively. A Gaussian type of deposition was collected from the substrate as shown in figure 40.

The deposits were cut, mounted and polished and subjected to microstructural and microhardness analysis. Flat tensile samples were prepared by hot rolling the as-sprayed material at 400 °C followed by annealing. Hot isostatically pressed samples made from elemental powders were prepared similarly hot rolled and annealed. Both samples were tensile tested at a cross head speed of 1mm/min. The HIP'ed sample was used for comparison.

Results show that the material produced by RPS contained 2-25 wt% Ti depending on the experimental conditions. An example of the microstructures achieved may be seen in figure 41. The Al matrix contains a very fine TiAl_3 intermetallic phase. The average particle size for this phase is about 1 μm . The distribution of the intermetallic phase varied from particle to particle depending on their individual thermal histories in the plasma region. The authors found through microstructural analysis that each Al powder particle has a unique thermal history in the

plasma region resulting in a variation of Ti content from particle to particle. The variation in thermal history in the plasma region is a function of (a) particle size distribution, since smaller particles achieve a higher temperature (assuming the same trajectory) and (b) particle trajectory. This is inherent to most thermal plasma processes where sharp thermal and velocity gradients exist from the centre to the periphery of the plasma jet. The microstructural evolution of the Al powder particles through Al/TiCl₄ molar ration for individual particles varies from particle to particle. The latter results from difficulties injecting a gas into a plasma jet and de-mixing in thermal plasmas.

Through microstructural evolution the authors propose there are four possible thermal histories for the Al particles. A Ti-Al phase diagram is shown in figure 42. On the phase diagram three microstructural evolutions are indicated which correspond to three of the four thermal histories described below:

1. The Al particle may exceed its melting temperature ($>664^{\circ}\text{C}$) but it may have no accessible TiCl₄. Such a particle will deposit as pure Al. These particles form the matrix of the deposits
2. The particle may be heated slightly above 664°C and react with TiCl₄, forming a solid layer of TiAl₃ around the particle. The reaction then stops and the particle solidifies with a TiAl₃ shell and an Al core. The thermal history for this group of particles is represented by curve 1 in figure 42 and the microstructure as shown in figure 43
3. The particle may be heated well above 664°C , but below the liquidus temperature and react with TiCl₄ to form a solid layer of TiAl₃. This

limits further reaction between Al and TiCl_4 . With the particle still molten part of the TiAl_3 layer dissolves in the Al (molten core) to satisfy the phase equilibrium. Upon quenching the final microstructure as an Al- TiAl_3 composite inside a TiAl_3 shell. The thermal history for this group of particles is represented by curve 2 in figure 42 and the microstructure is shown in figure 44

4. The particle may be heated above the liquidus temperature of the alloy. While the reaction starts on the surface of the particle, the TiAl_3 does not form. Instead the Ti recovered from the TiCl_4 dissolved in the molten Al and the molten Al (containing Ti) is exposed to TiCl_4 . Eventually the Ti saturated molten Al quenches and the product consists of very fine dispersion of TiAl_3 in an Al matrix. The thermal history corresponding to this case is shown by curve 3 in figure 42 and the microstructure of the product is shown in figure 45.

Some chlorine was detected in the as-sprayed deposit (10.5 wt%). Energy dispersive spectroscopy analysis (EDS) performed on the polished samples revealed that chlorine was only present as a surface contaminant between particles. No chlorine was detected inside individual particles. The authors found that this chlorine could be removed to a concentration below 300 ppm by vacuum sublimation. Under a vacuum of 4×10^{-5} mbar and for a period of 1 hour at 300°C , an average of 6% weight loss was observed. This weight loss included moisture gained during the neutralisation of the deposit prior to removal from the substrate. No further improvement in dechlorination was achieved above 300°C . It was also observed that between 120 and 150°C maintaining a low pressure in the vacuum chamber was difficult indicating that most of the volatile

species (including moisture and aluminium chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$)) were removed in this temperature range.

The tensile test results for both the RPS sample and the HIP'ed sample are shown in table 2.

Table 2: Tensile properties of Al-Ti Alloys

Material	Tensile Strength (MPa)	Yield Strength (MPa)	Elongation in 25mm (%)
HIP'ed	175	119	6
RPS	106	101	1

The HIP'ed material demonstrates better mechanical properties than the RPS material which the author attributes to a non-uniform microstructure and the presence of porosity and chlorine. However, they believe that the optimisation of spraying parameters followed by proper degassing and consolidation by mechanical working would provide superior mechanical properties to those of conventional Al-base alloys. The reactively produced materials contained a variety of microstructures with a wide range of Ti contents. The hardness of these microstructures was measured as a function of TiAl_3 content. The microhardness was found to increase exponentially with TiAl_3 content and not linearly as would be expected from the rule of mixtures. It is believed this deviation can be explained by (a) non-uniform distribution of TiAl_3 phase in the Al matrix and (b) the fact that the microhardness test does not satisfy the equal stress and strain conditions for the deformation of two phase aggregates. The authors conclude that Al-Ti alloys can be produced through RPS using Al and TiCl_4 as raw materials and that the microstructures of individual particles are governed by their thermal histories. Additionally chlorine

contamination may be effectively removed through vacuum sublimation at 300°C and 10^{-4} mbar.

In summary RPS provides an alternative route away from powder metallurgy technologies for the production of dispersion hardened alloys. The two papers detailed in this section which have dealt with the production of Al-Ti alloys have demonstrated the feasibility of production by this route but also the need for optimisation of process parameters. Moreover, a thorough understanding of the environment in which the desired reactions are to take place is paramount.

2.17.3 Carbides

Carbides are a common reinforcement phase in metals. They are particularly attractive due to their high strength, stiffness and hardness which make them suitable reinforcements for the improvement of specific properties such as stiffness and strength or the enhancement of wear resistance^[10,31]. These materials with carbides in the form of whiskers, monofilaments, fibres and particulates are being developed and commercialised. Metal carbides, especially Ti, Cr, Mo and W, are particularly important due to their very high hardnesses. Excellent high temperature strength and modulus make them useful as reinforcing phases in high temperature structural materials. Many binary carbides have microhardness values between 2000 and 3000 Kg / mm² and lie between the hardness values and moduli of alumina and diamond.

Research has demonstrated^[32,33] that reactive plasma spraying has been applied to form carbides in the liquid or the liquid/solid state, i.e. between the alloy liquidus and solidus temperature and that they could be suitable for producing powders, ribbons, surface layer modification or the formation of graded structures. It may also be attractive to produce powders with large surface areas or as very fine submicron powders.

Dispersions of TiC have been produced when spraying Ti with propylene reactive gas using the reactive spray forming equipment shown in figure 46. To limit side reactions that may occur during conventional air plasma spraying, all deposits were produced under low pressure, inert gas (Ar/He) conditions. The reactor was ~ 25 mm in diameter and 150 mm long with a parallel flow 'shroud' gas along the inside wall of the reactor tube. Substrates were uncooled and substrate temperatures nominally exceeded >800 °C. Metallographic examination of the titanium deposits showed that the titanium deposits sprayed with argon had high densities and no oxides. However, when deposited with the hydrocarbon gases, up to 30 vol % TiC phases were formed in the Ti matrix. Reacted TiC phases varied in morphology, size (1 to 20 µm) and distribution. A laminated structure was produced which had an increased concentration of TiC phases at interlayers between the successive layers built up during the spray process. Deposited titanium hardness values increased from 200 to over 800 H_{v(300)} using either methane or propylene as the reactive gas, demonstrating that the reinforcement of titanium alloys by reactive plasma spraying is possible. Higher substrate temperatures ~ 800°C were found to enhance carbide formation.

Changes in C:H bonding (single CH₄, double C₃H₆ and triple C₂H₂) were also tried but showed a weak correlation to the hardness / carbide content of the titanium deposits^[31]. Investigations showed that environmental pressures when spraying had the strongest influence on deposit hardness and carbide content, indicating that the chemical reaction kinetics are better with the improved heat and mass transfer which occurs at higher spraying pressures of >300 mbar. The stoichiometry of the carbides was not directly determined, but gas analysis and XRD together confirmed that TiC of varying stoichiometry was formed.

A wide range of metallic matrices with reinforcing carbides can be formed. Table 3 below shows some of the matrix systems and carbides that have been deposited by reactive plasma spraying.

Table 3: Examples of Deposited Matrix/Carbide Systems

Matrix	Reactive Gas(es)	Carbide(s)
Ti	CH ₄ , C ₃ H ₆ , C ₃ H ₈ , C ₂ H ₂	TiC, Ti _x C _(1-x)
W	CH ₄ , C ₃ H ₆ ,	W ₂ C, WC
Mo	CH ₄ ,	MO ₂ C
NiCr/Ti	CH ₄ , C ₃ H ₆ ,	Cr _x C _y , TiC, Ti _x C _(1-x)
FeCrAlY	CH ₄ , C ₃ H ₆ ,	Cr _x C _y , Fe _x C _y

It can be seen that the process is highly flexible, provided that stable carbides are produced. The percentage of reinforcement, the structural homogeneity, and the compositional homogeneity, however, have been found to vary depending on deposit conditions.

2.17.4 Nitrides

Nitrides of transition metals have good wear resistance and corrosion resistance because of their high hardnesses and chemical stability^[26,34]. Chromium nitride coatings can be deposited by ion plating, however slow deposition rates and thin final coatings make them unsuitable for severe wear resistant applications. Chromium nitride in-situ composite coatings have been synthesised by reactive low-pressure direct current (dc) plasma spraying^[26]. They were synthesised by RPS using elemental chromium powder as a spray material and nitrogen plasma gas in a low pressure nitrogen atmosphere. A transferred arc between the gun electrode and substrate was used to enhance the nitriding reaction. The sprayed coatings were found to consist of chromium, Cr₂N and CrN which had a compositional gradient from the substrate to the surface.

A schematic diagram of the apparatus used is shown in figure 47 and the standard parameters used are shown in the table 4

Table 4:Standard spray parameters used in RLPSS

Parameter	Value
Plasma gas flow, m ³ /s	Nitrogen: 0.89 x 10 ⁻³
Plasma current, A	500
Plasma voltage, V	46 – 51
Powder feed rate, g/s	0.08 – 0.11
Chamber pressure, kPa	3.1
Spray distance, mm	300
Transferred arc current, A	0 - 38

The authors not only deposited composite coatings but also collected sprayed droplets. The droplets were collected by installing a fixed slit with a 10 mm circular hole and a moving graphite shutter of 46 mm

diameter between the spray gun and substrate. The flattened particles were collected on the substrate by opening the shutter for 93 ms. No rise in substrate temperature, which was measured by inserting a thermocouple into the substrate, was noted during this sampling period. Although the maximum substrate temperature significantly effects the formation of nitrides, a fundamental question is whether or not the nitriding reaction takes place in flight and/or on the substrate surface. Figure 48 shows x-ray mappings of deposited droplets for chromium $K\alpha$ and nitrogen $K\alpha$ and the existence of nitrogen on the droplet can clearly be seen, however there were no chromium-nitride diffraction peaks on an XRD pattern taken with copper $K\alpha$ radiation of the same deposited droplets. The authors remark that the nitriding reaction does not occur at the particle surface while in flight for 2 ms, and that nitrogen seems only to be absorbed onto the droplet surface. Moreover, since the nitriding reaction does not occur at room temperature then it must take place on the deposited chromium droplets at the substrate in the spray process because of exposure to nitrogen in the atmosphere at high temperatures.

In order to increase the level of nitride formation a transformed arc was used to increase the heat input into the substrate. Without a transferred arc the substrate temperature reached 1280 K and with the arc temperatures of more than 1400 K were achieved. Figure 49 and 50 show XRD patterns for coatings deposited with transferred arc current = 25A and without a transferred arc. The volume fraction of CrN in the coating deposited with a transferred arc is 0.71 compared to 0.36 for a coating deposited without a transferred arc. It was found that the nitrogen content at the coating surface increases with a transferred arc current up to 25A because of the

increase in volume fraction of CrN. The authors suggest that the nitriding reaction of chromium occurs as follows:



with reaction [1] proceeding first, then CrN forms at higher substrate temperatures. If the substrate temperature becomes too high with transferred arc currents above 30A a decrease in nitrogen content occurs. It is suggested this happens because CrN decomposes to Cr₂N (reverse of equation 2) above 1323 K, although substrate temperatures above 1300 K are necessary to produce coatings with higher volume fractions of CrN. The maximum nitrogen content was obtained with a transferred arc current of 25A because of the balance between the formation and the decomposition of CrN based on reaction dynamics.

Figure 51 shows electron probe microanalysis results demonstrating the composition gradient across the coating section for a coating without a transformed arc. It can be seen that the nitrogen k α intensity is weak close to the interface but at around 80 μ m becomes much stronger and Cr₂N is believed to be the dominant phase. Figure 52 shows results for a coating deposited with a transferred arc current of 25A. In this case un-reacted chromium is limited to 25 μ m from the coating interface. The nitrogen k α intensity becomes strong at about 30 μ m from the coating surface where

CrN has been shown to be the dominant phase hence the chromium nitride in-situ composite coating have a composition gradient.

The hardness of the coating was found to depend on the volume fraction of Cr_2N , and it increases to 1300 H_v at a Cr_2N volume fraction of 0.98. Wear tests carried out demonstrated excellent wear resistance.

RPS has been used with some success to produce silicon nitride by spraying silicon powders in a controlled nitrogen atmosphere^[34]. Direct thermal spraying of silicon nitride powders is prevented by its decomposition before melting. Si_3N_4 is however an important material for high temperature applications with resistance towards wear and corrosion.

2.17.5 Silicides

Silicides, particularly MoSi_2 , have good oxidation resistance and a relatively high specific strength up to temperatures exceeding 1000°C , making them suitable candidates for high temperature applications in furnaces or even engines^[35]. However a major limitation with MoSi_2 is its low ductility, sensitivity to SiO_2 formation during processing and poor creep properties. Reactive plasma spraying therefore provides a possible synthesis route for the production of MoSi_2 with reinforcing phases to strengthen and consolidate the material while limiting other negative aspects.

Pure Mo powders ($5\text{-}45\ \mu\text{m}$) have been injected into a plasma jet in the presence of disilane (Si_2H_6) gas. The aim being to produce MoSi_2 which contained a low volume fraction of Mo thereby improving the MoSi_2 ductility. A lamellar structure was produced consisting of Mo, Mo_3Si_5 and MoSi_2 . The volume fraction of silicides was low ($< 20\%$) however this value could be increased by reducing the powder particle size and increasing the particle residence time.

In other work a combination of Si_2H_6 and CH_4 were used as reactive gases. The aim being to simultaneously produce both silicides and carbides. SiC dispersed within MoSi_2 has been shown to increase the silicide creep strength and reduce ‘pest’ effects while also increasing toughness. Preliminary results showed that although a porous deposit was formed, SiC phases had formed in combination with MoSi_2 , demonstrating the potential for this technique.

2.17.6 Other Reactive Plasma Spray Synthesis

Reactive plasma spraying and its development has not been confined to the production of hard reinforcing phases in either metallic or ceramic matrices. Other material classes have been deposited with varying degrees of success. High T_c Superconducting oxide films are being investigated^[36,37] as a potential candidate for reactive plasma spraying. Diamond films have also been deposited^[38-41] by RPS with both D.C. and R.F. plasmas jets. The generation of CH_3 radicals along with ionic hydrogen, typical under many plasma jet conditions, can form diamond.

In producing these advanced materials, reactive plasma spraying further demonstrates its flexibility and its unique ability to synthesise a wide range of structures and compositions.

2.18 MCrAlY Coatings

2.18.1 Introduction

The demand for higher energy efficiencies from aerospace and other gas turbines has led to closer internal tolerances, higher rotational velocities and higher turbine inlet temperatures^[42]. Higher firing temperatures are required to improve engine efficiency which exacerbates corrosion problems. Turbine entry temperatures and the temperature capabilities of high temperature alloys have increased by about 745 °K and 440 °K, respectively, over the last four decades. The difference between the metal and gas temperatures has been successfully dealt with by internal cooling systems. The third and fourth generation Ni base single crystal alloys offer a temperature advantage of around 384 °K compared to conventionally cast IN-738, which is commonly used as a blading material for land based engines^[43]. Today, however, advanced directionally solidified (DS) and single crystal (SC) alloys are operating near their strength limits and alloy development has reached a point of diminishing returns. Improved coatings are therefore necessary to realise the full potential of new DS and SC alloys.

Different running environments for turbines and turbomachinery components produce different surface orientated problems^[44]. A summary of the relative problems (expressed by: S=Severe, M=Moderate and L=Light) encountered in the hot sections of various turbines may be seen in table 5 below.

Table 5: Comparison of surface-oriented problems in various industries

Industry	Oxidation	Hot Corrosion	Inter-diffusion	Thermal fatigue
Aircraft	S	M	S	S
Utility	M	S	M	L
Marine	M	S	L	M
Diesel	L	S	L	M

In a general way, hot corrosion is more severe for utility and marine engines than for aircraft engines. The primary cause for this increase in severity lie in the increased level of air-borne contaminants, for example salt and/or fuel-borne impurities such as sulphur, vanadium. The use of relatively pure aviation fuel generally makes oxidation a life-limiting phenomenon in the hot section of aerospace engines, although severe hot corrosion occurs under certain conditions involving increased levels of salt ingestion with high fractions of time near marine or related environments. The situation is different in power generation combustion turbines. Fuels with high sulphur and vanadium impurities bring about hot-corrosion, which significantly reduce the life of coated hot-section components under appropriate operating conditions^[45]. It must be noted however that salts of some kind (e.g., Na) must also be present to form the deposits necessary for hot-corrosion to occur.

Invariably, it is the functional life of the coating that determines the refurbishment and functional life of a component, and not the loss of high-temperature mechanical strength of the substrate. Coating development has lagged behind alloy development, and a major thrust in the aerospace-engine and power-generation industries is the development of advanced coatings to meet the challenges of designing more efficient engines with greater fuel economy and thus lower electrical energy costs.

Coatings have been utilised since the 1950's to compensate for the turbine alloys' lack of environmental protection. These coatings belong to either of two categories: diffusion coatings or MCrAlY overlay coatings. MCrAlY development work began in 1965 with the first application beginning around 1969.

The following sections describe forms of coating degradation and for simplicities sake oxidation of metals will be described separately from that of corrosion, although oxidation is considered a form of corrosion.

2.18.2 Oxidation

High-temperature oxidation is a major concern in today's high firing temperature gas turbines^[46]. At temperatures above 870 °C, relatively rapid oxidation can occur unless there is a barrier to oxygen diffusion on the surface of the part. Some superalloys form their own protective dense coatings, adherent aluminium oxide (Al_2O_3) scales during the early stages of oxidation if the alloys aluminium content is high enough. However, many currently used high strength alloys do not form sufficiently protective scales, because their chemical compositions have been optimised for high temperature strength and metallurgical stability rather than for oxidation/corrosion resistance.

Unlike aircraft gas turbine engine components which require very high temperature protection for short periods of time, industrial applications require coatings that sustain constant elevated temperatures for economically acceptable times between refurbishment intervals. This is

more easily met by thermally sprayed MCrAlY coatings by increasing the coating thickness in those circumstances where the weight gain would not be a severe penalty, which is not easily performed by other coating processes. The superiority of thermally sprayed MCrAlY coatings over other types is illustrated in table 6.

Table 6: Oxidation Resistance of Coatings on a Nickel-Base Superalloy

Coating	Coating life at 2075°F, hours*
Aluminide	100
Pt-Al	250
NiCoCrAlY	>1000

*Mach 1.0 gas velocity, air, cycled once per hour, life determined by visual and metallographic assessment of coating penetration.

The oxidation of MCrAlY coatings depends upon selective oxidation of elements such as aluminium, chromium or silicon. As oxidation is continued diffusion processes begin to exert effects. The nature of these effects is dependant upon the concentrations of the constituent elements and the diffusional parameters at the operating temperature. Generally, when the concentrations of chromium and aluminium are low, continuous layers of neither Cr₂O₃ nor Al₂O₃ can be developed, and a continuous scale of predominantly NiO is formed above a subscale zone of Cr₂O₃ and Al₂O₃ particles. At higher chromium or aluminium concentrations continuous layers of Cr₂O₃ or Al₂O₃ can be formed.

Oxide scales of Al₂O₃ are more effective means for developing oxidation resistance than either Cr₂O₃ or SiO₂. While selective oxidation of elements play a critical role in the development of alloy oxidation resistance, an equally important factor is the adhesion of the oxide scales

to the alloy substrates and it is necessary to use techniques to optimise oxide scale adhesion. Most recently it has been proposed^[47] that sulphur present in the alloy at low concentrations, segregates to and weakens the oxide scale-metal interface, thereby promoting oxide scale exfoliation. It has been suggested that the role of yttrium is to immobilise the sulphur through the formation of stable yttrium sulphide.

NiCoCrAlY type compositions are the most widely used overlay coatings for oxidation protection in aircraft engines. As a NiCoCrAlY coating oxidises, grains of the aluminium rich β (NiAl) phase gradually convert to islands of γ' (Ni₃Al); eventually only the less resistant γ (Ni-Al) matrix phase remains. At relatively low metal temperatures overlay coating compositions remain more or less independent of substrate composition. At higher temperatures diffusion rates become significant and the oxidation resistance can be significantly affected by substrate composition, just as are the diffusion aluminides.

In addition to superior oxidation resistance, a major advantage of MCrAlY coatings over diffusion aluminides for high temperature applications is a higher melting point that is essentially independent of substrate influence. Melting does not occur in the interdiffusion zone at temperatures significantly lower than the melting point of the bulk overlay composition. Compared to incipient melting points of 1121-1204 °C for most diffusion aluminides, overlay coatings have survived exposures of 1288 °C with no evidence of melting.

MCrAlY overlay coating development has largely focused on elemental additions that improve oxidation resistance. NiCoCrAlY coatings containing silicon, tantalum, and/or hafnium, for example, has exhibited improved oxidation resistance, though ductility may be reduced.

2.18.3 Hot Corrosion

In hot corrosion, metals and alloys are subject to much more severe attack and therefore degradation than is found with gaseous oxidation. Salts of some kind (e.g. Na) must be present to form the deposits (liquid) necessary for sulphur related hot corrosion to occur. At elevated temperatures substantial amounts of sulphide phases can be formed beneath the molten deposit. Such a condition was observed during some of the earlier investigation on hot corrosion of alloys in gas turbines; hence hot corrosion was believed to proceed as a result of the oxidation of sulphides and was called sulphidation. It is important to note that while some hot corrosion can proceed via a mechanism called sulphidation, not all corrosion proceeds in this manner.

Because of its high thermodynamic stability, Na_2SO_4 is found to be the dominant component of salt deposits. During the combustion of certain low grade fossil fuels, vanadium compounds such as NaVO_3 and V_2O_5 may also be deposited in the salt film. The mechanisms of hot corrosion have been extensively studied^[44,48-51], but no generalised definition of a single hot corrosion mechanism exists, as yet. Those processes by which the reaction product barrier becomes non-protective due to the formation of species that are soluble in the liquid deposit have been called “fluxing” reactions.

There are two types of fluxing reaction, basic and acidic. Both basic and acidic fluxing can occur depending on the sulphur content of the fuel and temperature. Type I corrosion may occur via basic fluxing (high oxide ion content of the Na_2SO_4) and Type II by acidic fluxing (high SO_3 content of the Na_2SO_4). In a very general way, increasing the chromium content of coatings (24-40% for Type II and 15-20% for Type I) increases resistance to both types of hot corrosion. In the Na_2SO_4 system, acidic oxides of Mo, W and V derived from base alloys can accelerate Type II acidic corrosion. Silicon is particularly good in the case of Type II hot corrosion (acidic fluxing) but above 800 °C, it tends to diffuse rapidly into the substrate and may form low melting phases or brittle intermetallic compounds.

3.0 EXPERIMENTAL METHODS

3.1 Plasma Spraying

Plasma spraying was performed at the BOC group thermal spray facility in Morden, London. The spraying apparatus used was a Praxair thermal spray systems (formerly Miller Thermal, Inc.) model sg-100 plasma gun. Many of the parameters important in thermal spraying have been dealt with and their importance discussed in earlier chapters. Briefly described here are the parameters specific to the operation of the plasma gun.

The gun's power is 40 kW and the variable used for different gun operations is electric current. The primary arc gas used was argon and the auxiliary gas was either helium or hydrogen. The powder carrier gas was also argon.

In order for different materials with different melting points, densities and thermal conductivities to be sprayed, changes in the above parameters alone would not be sufficient to achieve the best deposit efficiencies and coatings possible. The manufacturers therefore produce several anode / cathode configurations with various gas mixing units to alter the dynamics of the plasma produced and also the angle at which the powder is injected into the plasma jet. The manufacturers diagrams for these configurations may be seen in appendix A. The manufacturer thereby recommends a particular configuration for a particular powder.

Throughout this work essentially three gun set-ups were used, shown in table 7 below.

Table 1: Summary of gun parameters and settings

Set -up	Anode	Cathode	Gas Injector	Arc Current / Amps	Arc Gas Pressure	Auxillary Gas Pressure	Powder Gas Pressure	Powder Feed Rate / g min ⁻¹
1	145	129	113	800	50 P.s.i.	100 P.s.i.	40 P.s.i.	60
2	355	112	113	900	50 P.s.i.	100 P.s.i.	50 P.s.i.	60
3	355	112	113	550	50 P.s.i.	None	50 P.s.i.	40

In order to avoid repetition and improve the clarity of experimental tables in later sections, a set-up number (corresponding to one of the gun configurations shown above) will be given for each experimental programme. Any changes will be stated separately. The corresponding flow-rates for the pressure settings shown in table 7 may be seen in table 8 below:

Table 2: Working Gas Flow-rates

Arc Gas		Auxiliary Gas		Powder Gas	
Pressure	Flow-rate	Pressure	Flow-rate	Pressure	Flow-rate
/P.S.i.	/l min ⁻¹	/P.S.i.	/l min ⁻¹	/P.S.i.	/l min ⁻¹
Ar 50	36	He 100	26.5	Ar 40	5.2
		H ₂ 100	24.5	Ar 50	6.6

3.2 Reactive Plasma Spraying

Reactive plasma spraying was performed by bolting a gas injector unit onto the front of the plasma gun. The gas injector was manufactured from 316 Stainless Steel and the reactive gas was injected from three directions into

the plasma jet. The three injection points were slightly offset to promote gas mixing inside the reactor section. A technical drawing of the gas mixing unit may be seen in figure 53. The reactor section was secured onto the front of the gas injection unit with on early reactors three stainless steel bolts and on later reactors six stainless steel bolts. Also on later reactors a gasket cut from graphite paper was used to improve the seal between the reactor and gas injection unit. The reactor sections were manufactured from Commercial Standard graphite and were designed to be consumable. A reactor would be replaced when degradation of the reactor had occurred such that the wall thickness became less than approx. 2-3 mm. Three reactor lengths were used; 10, 15 and 20 cm from the flange on the reactor. Substrates were placed 2.5 cm from the end of the reactor such that the overall stand-off distance when using a 15 cm reactor would be 18.5 cm (includes flange and gas injector dimensions) from the substrate to the front plate of the plasma gun. A technical drawing of a 15 cm reactor may be seen in figure 54. A photograph of the reactor, gas injector unit and gun when assembled may be seen in figure 55, and a photograph of the assembly just after spraying may be seen in figure 56.

Reactive gas flow-rates were measured using a variable area flow-meter. For safety reasons an appropriate flashback arrestor was used with any flammable gas and to avoid surges in gas flow when opening and closing the gas supply a needle valve was also fitted.

3.3 Apparatus Set-up and coating procedure

A schematic diagram of the equipment used and how it is connected to produce a typical thermal spray assembly is shown in figure 57. A coating is produced by moving a manipulator arm supporting the plasma gun in a horizontal direction against a rotating table, shown schematically in figure 58. The substrates are attached to the rotating table with magnetic stubs or clamps. The surface speed (the speed at which the sample passes the gun) at 40 rpm is approximately 1200 mm s^{-1} . The vertical transverse speed was set to 250 mm s^{-1} . Coatings were produced by performing between eight and twelve passes.

3.4 Substrate Preparation

Prior to spraying, substrates had their edges ground away and were grit blasted with $60 \text{ }\mu\text{m}$ alumina grit at an angle of approximately 45° . Any alumina residue was blown away with compressed air and the substrate washed with acetone.

3.5 Substrates

Several different types of substrates were used depending on the type of investigation to be carried out on the coating. The majority of spraying was performed onto $50 \times 50 \times 5 \text{ mm}$ mild steel coupons. These coupons were sufficient for conventional metallurgical processing, S.E.M. and X-ray analysis.

For the purposes of coating analysis and T.E.M. sample preparation thin 0.7 mm mild steel plate, which was not grit-blasted, was used as the substrate material. After spraying the coating could simply be removed by peeling away the substrate.

Pin on disk wear pins were produced by spraying onto 40 x 50 x 25 mm mild steel blocks. 10 mm diameter pins were Electro-discharge machined from the block and machined to the correct length (10 mm) for the test.

For discontinuous oxidation testing on MCrAlY coatings, a Nimonic 263 substrate (approximately 3 mm thickness) was used. Coatings for these tests were sprayed on both sides of the substrate to leave as little substrate material as possible exposed to air during the test. Prior to weighing, samples underwent a stringent cleaning process to remove any oil and grease. The bulk of the oil and grease was removed by an initial rinse with Volasil 344 solvent. 15 to 20 minutes of ultrasonic cleaning in firstly clean Volasil 344, and then, clean isopropyl alcohol (IPA) followed. To minimise the level of contamination between baths, samples were rinsed in clean Volasil 344 and then clean IPA. Following the IPA bath the samples were rinsed with clean IPA, and then clean Analar IPA, prior to vapour degreasing. Vapour degreasing was performed in a Soxhlet reflux condensing column with clean Analar IPA.

3.6 Metallurgical Preparation

Coated substrates were cut and mounted in conductive Bakelite. Standard metallographic techniques were adopted for grinding and polishing, namely SiC paper (120 grit followed by 220 grit followed by 1200 grit) and diamond cloth (6 μ m followed by 1 μ m) to produce a 1 μ m polished surface suitable for optical, S.E.M. and microhardness measurements.

3.7 Materials

Two powder alloys were used. The powders were stored in a heated cabinet to prevent moisture affecting the powders flow characteristics. The powder hopper also heated the powder for the same reason.

The first an 80:20 Nickel Chrome supplied by William Rowland Limited^[52] the U.K. and Benelux agent for Praxair Thermal Spray Products. Two powder size ranges were used: AI-1015 is a gas atomised spherical powder with the following powder size range -125 + 45 μ m, and AI-1017 is also a gas atomised spherical powder with a -90 + 10 μ m size range. Data sheets supplied by the manufacturer may be seen in appendix B.

The second alloy was a CoNiCrAlY with the following Composition: Co-32Ni-21Cr-8Al-0.5Y. The alloy is manufactured by Alloy Metals, Inc^[53] and is given an Amdry 995 designation number. Nominal powder compositions for the Amdry range including Amdry 995 may be seen in

appendix B. Two Amdry 995 powders were used which differ only in powder particle size range. The powder size ranges and designations were as follows: Amdry 995/47 = - 75 + 45 μm and Amdry 995/1 = -37 + 5 μm .

Elemental chromium powder (-200 mesh/99.0 % Cr) was supplied by Sigma-Aldrich Ltd^[54]. Blending was performed in a Turbular® T2C mixer for three hours.

3.8 Mechanical Property Determination

The coatings mechanical properties were measured by two methods. Firstly by Vickers Microhardness measurements and secondly by wear testing. Wear testing was performed on a pin on disk machine with continuous data logging via a personal computer.

3.8.1 Microhardness Testing

A Vickers microhardness value is derived by producing an indent in the coating with a pyramid shaped diamond for a given load. The distances between the two opposite edges of the indentation are averaged and a value obtained by referring to tables. Testing procedures for all microhardness measurements were as follows:

Load	1000g
Time in load	15 seconds

Seven tests were carried out per coating, the highest and lowest value were excluded and a final value obtained by taking an average of the remaining five. Where a poor indent was produced, for instance where delamination of coated layers occurred, no measurements were taken.

3.8.2 Wear Testing

A schematic diagram of a pin on disk test may be seen in figure 22. Both the coefficient of friction and dimensional change were measured and recorded every second. Prior to testing both sample pins and disks were ultrasonically cleaned in acetone and IPA to remove any oil or grease that might affect the wear process. Pins were tested in the as-sprayed condition. A martensitic 440C (Fe-18% Cr-1% Si-1% Mn-0.7% Mo-1.2% C) heat treated disk was the counterface material.

Before the test is commenced a disk calibration is performed where four hundred measurements are taken during a 720° rotation of the disk. From this, an indication of the contact between the pin and disk can be realised. From experience where the difference between the highest and lowest reading is <0.06 a good contact exists and the load is distributed evenly over the pin. An example of a disk calibration plot may be seen in figure 59.

3.9 Surface and Subsurface Characterisation

Analytical equipment employed for surface and subsurface characterisation was as follows.

S.E.M.	CAMBRIDGE INSTRUMENTS 250 Mk III Stereoscan with LINK EDX analyser ABT-55 Stereoscan Microscope
T.E.M.	PHILIPS CM20 Scanning Transmission Electron Microscope with EDAX 9800 analyser
X.R.D.	PHILIPS PW1720 X-ray diffractometer

Compositional analysis, performed by Incotest^[55], was carried out on the following machines.

Element	Equipment
Chromium	Inductively Coupled Plasma OE
Nickel	Inductively Coupled Plasma OE
Oxygen	LECO TC436AR Analyser
Carbon	LECO CS244 Analyser

3.10 Electrolytic Etching

An etch for attacking carbides in nickel-chromium alloys was found in the literature^[56]. Metallographic etching was carried out by making a solution from:

100 ml Distilled water

10 g Potassium cyanide

Samples were electrolytically etched (6 V d.c. – platinum cathode) for three minutes.

Note – Poisons protocols need to be strictly observed.

3.11 Computational Fluid Dynamics

Computer modelling was performed on Digital Equipment Corporation (DEC) Alpha station computers (255 MHz) with DEC UNIX for the Operating System. PreBFC by Fluent, Inc was the Grid Generation Software used. Fluent and Rampant software, both by Fluent Inc, were the applications used.

4.0 RESULTS AND DISCUSSION

Reactive plasma spraying (RPS) has been studied by many investigators as a method to create new materials, either as compounds or composites, utilising the high temperature plasma chemistry available in plasma jets. Other investigators have shown reactive plasma spraying to be an alternative production route for existing materials.

Reactive plasma spraying may be defined as the plasma spraying of materials with the intentional introduction of 'reactive' species into the particle/gas stream. Species include liquids, gases, or mixtures of 'reactant solids', which when in contact with the high temperature plasma jet decompose to form highly reactive or ionic species which combine and form new compounds.

Investigations into the production of carbides, silicides or intermetallics have found that new phases can be produced with the degree of their formation depending on; the starting species, their introduction point and the atmosphere into which they are introduced.

The design of the reactor section was therefore paramount. The development of reactors will be discussed in a later chapter (Chapter 5.0 Reactor Development). This chapter will concentrate on how the reactors themselves performed and not necessarily on the resulting coatings. Changes to reactor design will be presented in chronological order detailing what changes were made and why. Further discussion on reactor

design will also be found in section 5.1 Computational Fluid dynamics, where from a modelling stand-point reactor design will be discussed.

The results and discussion section has been divided into subsections allowing each experimental study to be discussed individually, to aid greater understanding of the work as a whole.

However, the bulk of the thesis concentrates on two main strands. Firstly, modifications to a coatings microstructure and/or mechanical properties by the addition of phases or elements, and secondly, modifications to a coatings microstructure and/or mechanical properties by the removal of phases or elements. The work concerned with the addition of phases or elements to a coating microstructure has been the objective of the investigation on the 80:20 nickel chromium alloy. The overall objective being to improve the coatings mechanical properties.

However, while reactively spraying the nickel chrome alloy a reduction in the oxygen (oxide) content of the coating was observed. This finding led to the second strand of the thesis where the removal of phases or elements became the primary objective. The alloy selected for this work was an MCrAlY. MCrAlY alloys are predominately used for their oxidation and corrosion resistant properties. For this reason, changes in mechanical properties were not investigated for the MCrAlY alloy. Oxidation testing was however performed to determine whether reactively spraying the MCrAlY alloy detrimentally affected the coatings oxidation resistant properties.

It should also be noted that changes to parameters were usually only adopted where an increase in mechanical properties was observed.

Vickers microhardness measurements on the coating cross-section, was the most commonly used method to determine mechanical properties, largely because of the correlation between hardness and wear resistance, and the repeatability and simplicity of the hardness test. As large a load as possible was used (typically 1000g), thereby producing a large indentation, such that as many of the coatings features could be included in the test. Although attention was paid to avoid edges and therefore edge effects.

However, before any reactive spraying was investigated an optimisation programme was performed. The optimisation programme looked at four parameters (spray distance, powder feed rate, arc current and auxiliary gas pressure) at two levels in terms of hardness.

4.1 Optimisation Programme

4.1.1 Introduction

The spray optimisation programme looked at the following changes in parameters:

- Spray Distance From: 75 mm To: 100 mm
- Feed Rate From: 4.1 RPM To: 3.7 RPM
- Arc Current From: 800 Amps To: 600 Amps
- Aux Gas Pressure From: 100 Psi To: 50 Psi

4.1.2 Results

Table 9 shows the experimental programme and hardness results. Experiment 2 represents the manufacturers recommended parameters.

Table 9: Optimisation Programme Summary and Hardness Results

Experiment	Stand-Off Distance \\ mm	Hopper Speed \\ RPM	Arc Current \\ amps	Auxiliary Gas Pressure \\ Psi	Microhardness \\ Hv @1000 g
1	75	3.7	800	100	194
2	75	4.1	800	100	188
3	75	3.7	600	100	154
4	75	3.7	800	50	184
5	75	3.7	600	50	167
6	75	4.1	600	100	177
7	75	4.1	800	50	169
8	75	4.1	600	50	144
9	100	3.7	800	100	170
10	100	4.1	800	100	187
11	100	3.7	600	100	162
12	100	3.7	800	50	194
13	100	3.7	600	50	191
14	100	4.1	600	100	173
15	100	4.1	800	50	187
16	100	4.1	600	50	189

The aim of the optimisation programme was to look at these parameters and by statistical analysis reveal which changes in parameters and interactions between parameters have the most significant effect on coating hardness.

The analysis of variance (ANOVA) results may be seen in table 10.

Table 10: Analysis of Variance Results

ANOVA Analysis					
Main Effects					
		Sum Sq.	D.F.	Mean Sq.	F. Ratio
A	Spray Distance	1702.013	1	1702.013	13.75
B	Feed Rate	2.112	1	2.112	0.017
C	Arc Current	3962.112	1	3962.112	32.009
D	Aux Gas Pressure	103.513	1	103.513	0.836
Interactions					
A x B		465.612	1	465.612	3.762
A x C		1402.813	1	1402.813	11.333
A x D		4515.012	1	4515.012	36.476
B x C		137.813	1	137.813	1.113
B x D		2656.513	1	2656.513	21.461
C x D		308.112	1	308.112	2.489
Other Interactions		1419.063	5	283.813	2.293
Residual Errors		7922	64		
Totals		24596.69	79		

4.1.3 Discussion

From table 10 the larger the F ratio for a factor or interaction between factors then the more significant that parameter is in terms of hardness.

It can be seen that both Spray distance and Arc current have a significant effect on the hardness (Chance of error $\ll 1\%$). Arc current is most significant. The changes in parameters for both the powder feed rate and auxiliary gas pressure had very little effect at all on coating hardness. It should be noted that when changing from one parameter setting to the other, a highly significant parameter, for instance arc current, would represent the highest reduction in hardness, when changed.

With respect to interactions; Spray distance and Arc current, Spray distance and Auxiliary gas pressure and Feed rate and Auxiliary gas pressure have significant effects on hardness (chance of error $< 1\%$). The most important interaction occurs between Spray distance and Arc current. Tertiary interactions are not even significant at the 5% level.

Little difference in the microstructures could be seen for all sixteen experiments. Predicting coating mechanical properties from the sprayed microstructure is not feasible with any degree of accuracy. For instance, the microstructure for experiment one with the highest microhardness ($H_v=194$) is shown in figure 60, and that for experiment eight, with the lowest microhardness ($H_v=144$) is shown in figure 61. It appears that the microstructure for experiment one contains more Chromium Oxide from the number of stringers present. This oxide probably accounts for the increase in microhardness.

5.0 REACTOR DEVELOPMENT

The first reactor design, shown in figure 62, was manufactured from two 2 mm thick 310 stainless steel tubes, one of 20 mm internal diameter, the other 36 mm internal diameter, welded onto a circular stainless steel plate to produce a 140 mm long double walled reactor section. The aim was to cool the reactor by passing water between the two walls. However, when the reactor was connected to the gun it became immediately apparent that the 20 mm internal diameter was not sufficient and the high temperature plasma would melt the reactor.

This early reactor was modified by removing the internal tube and shortening the overall length by 80 mm. A diagram of the modified reactor may be seen in figure 63. Carbon dioxide was sprayed onto the walls of the reactor to provide cooling. This reactor was partially successful but could not spray at the parameters recommended by the manufacturer. In order for coatings to be produced the arc current settings had to be reduced from 800 amps to around 600 amps to allow enough spraying time to produce a coating before the reactor started to melt. Arc current has already been shown to be extremely significant in terms of coating hardness. The reactive gas was injected into the reactor from two opposite directions angled slightly downstream.

However, because it was imperative to be able to spray at the power settings recommended by the manufacturer, or higher, a new design was required. One of the major drawbacks for the stainless steel reactors was

the need for cooling. The carbon dioxide cooling was expensive and relatively inefficient. Water cooling would require a double skinned reactor, however this was difficult because of the way in which the reactor was secured to the plasma gun. The reactors were secured by using the same tapped holes that secure the plasma guns brass plate to the front of the gun. A double skinned reactor therefore has to have a narrower internal diameter to allow access to the securing screws and will therefore get much hotter. Moreover, because of the need to inject a reactive gas between the water-cooled walls a complex geometry would be required, which would be expensive to machine. Additionally, were the reactor to fail, repairs would be virtually impossible as would any changes to the design and there would also be serious safety concerns with respect to electric shock.

To solve these problems a new reactor was designed. Firstly, it was thought important to introduce the reactive species as upstream as possible. This was achieved by manufacturing a stainless steel reactive gas injection unit, which like the stainless steel reactors, was secured onto the gun with the tapped holes that support the plasma guns front plate. The guns high pressure water cooling system therefore also cools the gas injection unit. The reactive gases were injected through three holes 120° apart in the gas injector section at the torch exit. The injection direction was not into the centre of the plasma jet, but slightly offset by 3.5 mm to produce a swirling motion inside the reactor.

The main reactor section it was decided would be manufactured from graphite and would be consumable components. Graphite is cheap and

easy to machine. The reactor shape is divergent to allow for the non-axial powder stream direction.

The graphite reactor section was bolted onto the gas injector section with three screws. The gas injector section subsequently had an additional three holes tapped into it, such that the reactors were secured with six stainless steel screws and a gasket was made from graphite paper to ensure a good seal between the graphite reactor section and stainless steel gas injection unit. Three reactor lengths were produced (10, 15 and 20 cm). The ability to experiment easily with different reactor sections was a distinct advantage of this design. Furthermore, the reactors were capable of withstanding the high temperatures encountered during the plasma spraying process (sublimation of graphite ~ 3200 °C) and would sustain around 40 minutes of continuous spraying before replacement without the need for cooling.

When spraying without a reactive gas the carbon levels in the coating were found to increase very slightly when compared with a conventionally sprayed coating. This would indicate that the decomposition of the reactors slightly aids the reactive spraying process. A significant amount of reactor decomposition was found to occur on the outside of the reactor, which it is thought, reacted with air to form carbon dioxide when hot. An attempt to prevent this by painting the outside of the reactor with a thin layer of boron nitride was unsuccessful.

5.1 Computational Fluid Dynamics Modelling

5.1.1 Introduction

Computational Fluid Dynamics (CFD) modelling is a technique that has been used to develop an understanding of interactions between the gases and powder particles occurring inside the reactor section. The application software used initially was Fluent.

Before any calculations can be performed it is necessary to create a 'grid' which consists of many 'cells'. Each cell provides the basis of a calculation. The reactor geometry was entered into the computer in the following way. Firstly, points belonging to the reactor geometry are entered into the computer in two or three dimensional space. Curves are then created by joining points together. And finally, curves are joined together to create surfaces. Surfaces are only required for three dimensional problems. Once these stages have been performed a grid is then 'meshed' to fit the problem geometry, in this case the reactor section. Geometry and grid generation were achieved using preBFC, software designed for this purpose. The geometry and meshed grid are then imported into Fluent which is the application software that performs the CFD calculations.

Because of the visual nature of the results, discussion of the results will be included in the same text.

5.1.2 Results & Discussion

Initially, I hoped it would be possible to completely model the reactive plasma spraying process in three dimensions. However, once the geometry had been entered enormous problems were encountered at the grid meshing stage. As mentioned earlier, the three points where reactive gas are injected into the reactor are slightly of-set to produce a swirling motion inside the reactor section. Because of this complex geometry I was unable to satisfactorily mesh the grid to the geometry. Figure 64 shows a diagram of the 3D grid, and inset are the reactive gas injection areas which caused the meshing problems. Following this perhaps too ambitious start it was decided to model the problem in two dimensions, and swap to another CFD application package entitled Rampant, by the same manufacturers, and capable of importing geometry's and grids created in preBFC. Rampant is more suited to high velocity problems and can deal with compressible flows. However, because the problem is now two dimensional it would now not be possible to investigate the current reactor design, in particular the swirling gas motion. Nevertheless, CFD modelling may still provide important insight into factors important for good reactant mixing and therefore reactor design.

A simple 2D grid, shown in figure 65 containing 448 cells was generated and tested with air. The grid contains two inlets I_1 and I_2 (labelled) and one exit E_1 . I_1 is the larger of the inlets and is where the plasma gases would enter the reactor. I_2 is a smaller inlet and is where the reactive gas would be injected into the reactor, perpendicular to the plasma gas flow. At low air velocities there were no problems ($< 50 \text{ m s}^{-1}$). However, with

higher velocities the model would crash. This was thought to arise from the very steep velocity gradients associated with high velocity flows and relatively few cells with which to compensate. A new grid was subsequently generated, shown in figure 66 now containing 2626 cells, with the majority concentrated at the front end of the reactor. Higher air velocities could be achieved, up to 800 m s^{-1} at I_1 , which would be sufficient for modelling plasma velocities, however the model would again crash. This time problems were encountered near walls. Again, a new grid was designed shown in figure 67 containing 16912 cells and the wall treatment model was changed from a non-equilibrium wall function to a two layer zonal model. This model is more accurate, but takes considerably more time to complete calculations.

Moreover, the problem was initialised to zero. This means that the computer programme would start the flow at zero and work up to pre-entered values for pressure and velocity. By doing this the model was less likely to encounter terminal errors caused from the very steep temperature and velocity profiles. Unfortunately, considerably more time is required to reach a solution. For example, with each iteration taking approximately 20 seconds, and approximately 50000 iterations required to reach a solution, around twelve days of continuous processing are required.

This model worked well and was capable of dealing with large temperature and velocity gradients. Changes were made to the grid, such as incorporating tubes into the inlets thereby improving the plasma jet profile. Figure 68 shows the final geometry and grid design. Figures 69 to 71 show the area close to the reactive gas injection area in increasing

magnification to give the reader an indication of the number of cells and where there the greatest cell density occurs.

Demixing, a diffusion driven process of the component gases, namely Argon and Helium, was assumed not to occur. Demixing in free-burning arcs has been investigated^[57,58] and shown to be of significant importance in terms of arc composition. Demixing is a process driven by the differences in the diffusion velocities of the species that are present in the arc. It occurs in the presence of temperature and pressure gradients, or of certain external forces such as electric fields. For example, since the degree of disassociation and ionisation of a gas depends on the temperature, a temperature gradient can give rise to gradients in the mole fractions of the individual species present. These mole fraction gradients in turn drive diffusion until the sum of the forces, including those due to mole fraction gradients, frictional forces, thermal diffusion forces, and external forces, on the species is zero. However, it has also been shown that demixing has little effect on the arcs temperature and axial velocity for argon-helium plasmas and it is from these findings that the assumption that demixing does not occur is based

Transport coefficients such as viscosity for Argon-Helium plasma gas mixtures were not calculated by the CFD package but were instead entered manually from more accurate data sort in the literature^[59]. Velocity and temperature profiles were available in the literature^[12] for a Praxair thermal spray systems sg-100 plasma gun and were used as a method to examine the integrity and accuracy of the model.

Other material constants on argon, helium and methane not available in the literature were taken from values found in Rampants material database. Although methane would disassociate when injected into the plasma region this reaction was not entered into the model for reasons of simplicity.

Summaries of the boundary conditions, models and material properties may be seen in appendix C. The reactor material chosen was aluminium because graphite was not available in the database. However, melting was not allowed and this was therefore not a problem.

Table 11 provides a summary of the output corresponding to a particular figure.

Table 11: Summary of the output and corresponding to a figure

Summary	Figure
Contours of Velocity Magnitude	72
Contours of Static Temperature	73
Contours of Concentration of Ar	74
Contours of Concentration of CH ₄	75
Contours of Turbulent Kinetic Energy	76

Contours of Velocity magnitude, figure 72, show the high velocity region of the plasma to be around 845 m s^{-1} which fits well with the experimentally determined values found in the literature^[12] as do the contours for static temperature, shown in figure 73.

Contours of concentration of argon may be seen in figure 74. As would be expected, high concentrations of argon are present at inlet I_1 but there is also a high concentration of argon throughout the reactor section, resulting in a near inert atmosphere for the majority of sprayed powder particles. Initially it would appear from figure 75 that methane when injected towards the plasma jet is simply deflected away. However, from figure 76 a significant increase in turbulent kinetic energy is observed when moving away from inlet I_1 . As the high velocity plasma jet exits the anode nozzle into a stagnant environment, a laminar shear layer develops at the outer edge of the jet^[60]. The large velocity difference causes rolling up of the shear layer flow around the nozzle exit into a ring type vortex which is then pulled downstream by the flow, thereby allowing the process to repeat itself again at the nozzle exit. Adjacent vortex rings at the outer edge of the jet tend to coalesce, forming larger vortices, perturbations to these vortices then lead to instabilities growing around the entire ring. The distorted vortex rings then start entangling themselves with adjacent rings, finally resulting in total breakdown of the vortex structure into large-scale eddies and the onset of turbulent flow. A schematic diagram showing the formation of vortices and eventual onset of turbulent flow may be seen in figure 77. This entanglement process of adjacent unstable vortices results in large-scale engulfment of the external environment and some entrainment also takes place during the roll-up process of the jet's shear layer. This qualitative account of turbulence development has been corroborated by shadowgraphs and spectroscopic techniques^[61], by conditional sampling experiments^[62], and by probe sampling of the plasma^[63].

The degree of turbulence not only dictates the quantity of cold gas in the external atmosphere entrained in the plasma but also the volume of useful plasma available which affects heat transfer rates to particles travelling through the jet.

It is proposed that the phenomenon described above are responsible for methane entering the core region of the plasma jet, albeit slightly downstream, and not by direct injection into the plasma jet. This might be expected given the vast differences in gas velocity between the plasma jet and injected reactive gas. One might therefore continue that changing the nozzle exit design to promote greater turbulent flow and the entrainment of the external atmosphere as method to improve reactive plasma spray synthesis. Although these changes would reduce the plasmas ability to melt and accelerate powder particles, higher power settings may be able to compensate.

6.0 REACTIVE PLASMA SPRAYING OF AN 80:20 NICKEL-CHROMIUM ALLOY

The addition of phases by RPS has been one of the two primary objectives of this project. It is this area of the thesis that has been studied in the most detail. This area is also the most prominent aim of RPS found in the literature and many authors have tried and in many cases succeeded to add phases to a coating by either reaction in-flight or at the substrate. The specific aim of this project was to improve the mechanical properties of a commercially available 80:20 Nickel Chrome alloy by reacting the aforementioned alloy powder with a dissociated hydrocarbon gas, using a novel type of reactor, and therefore modify the coating chemistry in-flight.

Once this objective had been achieved it would then become necessary to develop an understanding of the phenomenon taking place and how these changes had occurred and what parameters are important in controlling RPS. The first obvious parameters that warrant investigation are the following:

- The effect of reactor and reactor length
- The effect of the reactive gas

Other factors that have been found to affect either coating properties and/or the microstructures of reactively sprayed coatings will be detailed later, these include:

- The effect of powder particle size
- Using different reactive gases
- Using hydrogen auxiliary gas
- The addition of elemental chromium

Changes in the coating microstructure and / or coating chemistry will be detailed in a later chapter (Chapter 7.0 Coating Modification). In this chapter, results from analytical work; such as X-ray analysis, scanning electron microscopy and transmission electron microscopy will be discussed.

Changes in mechanical properties were first measured in terms of coating hardness, because in general it can be assumed that harder coatings are more wear resistant, and wear resistance is one of the dominant material properties required for this alloy and other similar alloys. Due to the importance of wear resistance a later chapter (Chapter 8.0 Wear Properties) will discuss wear results in detail.

Reactive plasma spraying may be described as a function of two effects. Firstly, the effect of the reactor alone, shrouding and secondly, the combined effect of shrouding and the introduction of an injected reactive species, usually a gas.

6.1 Shrouding

6.1.1 Introduction

As mentioned earlier, RPS requires the use of a reactor, certainly with this alloy system. The function of the reactor is to not only separate the undesirable external atmosphere from the plasma flame, but also to contain the desirable inner atmosphere allowing in-flight interactions between the sprayed powder particles and the inner atmosphere. In this section the affect shrouding alone has on the sprayed coating will be investigated

6.1.2 Results

Table 12 shows the influence of graphite reactors (shrouds) of three different lengths (10,15 & 20 cm) compared to the a conventional APS coating.

Table 12: Effect of various Graphite Reactors compared with a conventional APS coating

Reactor Length / cm	Conditions ①	Hardness / H _v
-	Al-1015 / Manufactures recommended parameters (APS)	181 ± 10
10	Al-1015 / No reactive gas	205 ± 20
15	Al-1015 / No reactive gas	191 ± 20
20	Al-1015 / No reactive gas	180 ± 20

6.1.3 Discussion

From the literature^[6], shrouding has been found to be of great importance in the way a plasma flame is affected and hence on the corresponding coatings produced. Some of the findings are summarised below:

1. When shrouded the plasma jet has a higher overall temperature and greater radial temperatures were achieved.
2. When a shroud was not used, the proportion of Argon in the plasma jet was found to decrease rapidly as the distance from the torch exit increased. It was found that the argon content was no more than 10 %, 100 mm from the torch exit in the absence of a shroud, and near 60 % at the same axial distance for a shrouded flame. Air contamination produces large differences in the temperature distribution observed between the shrouded and non-shrouded flame.
3. The shroud has little effect on the plasma flame pressure, which is around atmospheric pressure.
4. It was also observed that a shroud delivers higher particle velocities, from higher plasma jet velocities. However, this would lead to a drop in particle residence time.
5. In terms of heat transfer, the authors found that considerably less energy was lost to the shroud than would be lost to the air in the absence of the shroud.

Initially, it can be seen that a 10 cm reactor alone produces a reasonable increase in coating hardness. As the reactor length increases above 10 cm a decrease in hardness is observed. With the 20 cm reactor the hardness

level has returned to that of the conventional APS coating. The fall in hardness values with increasing reactor length is thought to arise from longer spray distances that would result in lower particle velocities and temperatures on impact with the substrate. Figure 78 shows four optical micrographs of the corresponding coatings labelled such that they can be compared with each other. The microstructures seen are typical of a plasma sprayed coating containing reasonable amounts of porosity and oxide stringers or delaminations. However it must be noted that coatings produced using a reactor contain visibly lower quantities of oxide stringers or delaminations. It is important to note that coatings produced with a shroud containing less oxide stringers might be expected to show lower hardness values because of the reduction in hard oxide phases. However, this was not the case and so any increase in hardness is more than likely due to the deposition of denser coatings. These findings would appear to agree with the findings mentioned earlier in the literature, firstly less oxygen in the plasma jet would result in fewer oxide stringers, and secondly, more melting of the particles and higher particle velocities would lead to a denser coating with lower levels of porosity and delaminations.

In summary, increases in coating hardness are probably due to denser coatings being produced when shrouded. The denser coatings result from increased particle heating and higher particle velocities at a given distance when the shroud is present. However, as the reactor length increases to around 20 cm, the shroud is no longer able to compensate for the increased spray distance and the coating hardness falls.

6.2 Injection of Reactive Gas

6.2.1 Introduction

Once the effect from the shroud has been established any contribution from the reactive gas may be observed. The influence of different reactive gases such as acetylene or methane will be discussed in a later section (6.3 Using different Reactive Gases). It has been shown in 6.1 that using the shroud alone has produced reasonable improvements in the final coatings. However the aim of the project is to promote interactions between the sprayed powder particles and a reactive gas. The reactor is simply a tool to assist this objective.

6.2.2 Results

Table 13 similar to table 12 shows the contribution from injected methane reactive gas at a flowrate of 24 l / min on deposited coatings in terms of hardness for three (10,15 & 20 cm) reactor lengths. The hardness values for ‘shrouded coatings’ without an injected reactive gas are also shown for the purpose of comparison along with the value for a conventional APS coating.

Table 13: Effect of Reactive gas on hardness

Reactor Length	Conditions ①	Hardness / H_v
-	AI-1015 / Manufactures recommended parameters (APS)	181 ± 10
10	AI-1015 / Methane reactive gas (24 l min^{-1})	231 ± 18
10	AI-1015 / No reactive gas	205 ± 20
15	AI-1015 / Methane reactive gas (24 l min^{-1})	323 ± 30
15	AI-1015 / No reactive gas	191 ± 20
20	AI-1015 / Methane reactive gas (24 l min^{-1})	325 ± 25
20	AI-1015 / No reactive gas	180 ± 20

6.2.3 Discussion

The first important point to note is the difference in hardness values for the deposited coatings using the 10 cm reactor. The value for the coating produced with a reactive gas is higher than that for the coating produced without a reactive gas. This result demonstrates that injecting methane gas into the shroud produces a further increase in coating hardness.

More interestingly, when using a 15 cm reactor, a dramatic increase in hardness is observed between the coating deposited with an injected reactive gas and the one without. Compared to the conventional APS coating an increase in hardness of 78.5 % is observed when a 15 cm reactor and reactive gas are used and an increase of just 5.5 % when the reactor alone is used. This would suggest that the injection of a reactive gas has a significant hardening effect on the final coating independent of the shrouding effect alone. Furthermore, a reactor length greater than 10 cm is required to allow enough residence time for interaction between the

sprayed powder particles and injected reactive gas to interact to produce the most significant increase in coating hardness. With the 20 cm reactor the hardness level is similar to that of the coating produced with the 15 cm reactor. However with the 20 cm reactor a visible drop in deposition efficiency occurs and so the majority of work has been carried out using a 15 cm reactor. The drop in deposition efficiency is thought to result from lower particle velocities, lower particle temperatures and lower particle flux at the increased spray distance.

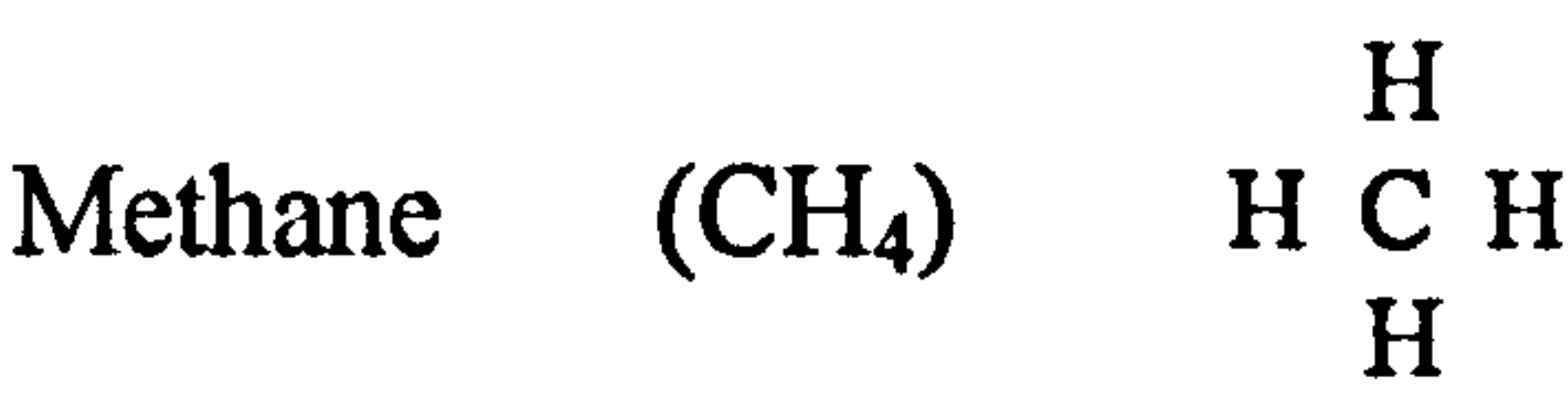
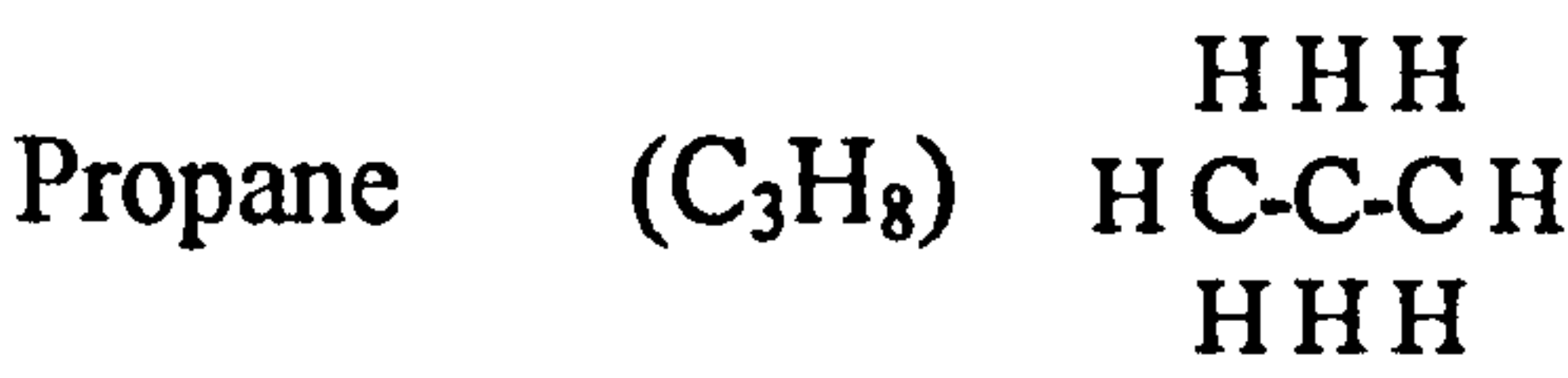
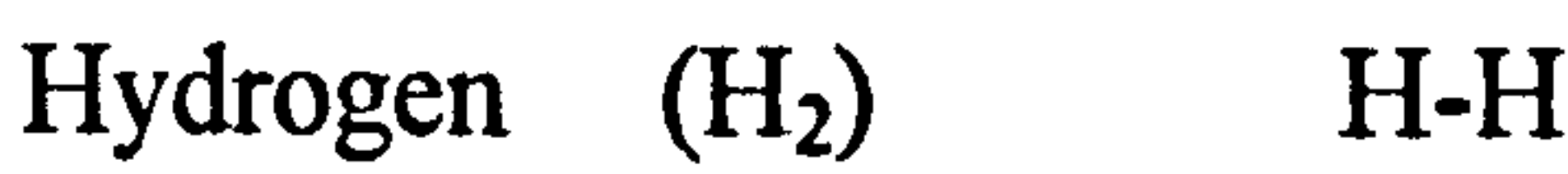
Figure 79 shows three optical micrographs, for comparative purposes, of a conventional APS coating, a coating produced with a 15 cm shroud only and a coating produced using both a 15 cm shroud and injected reactive gas. Figure 79 clearly shows the effect the shroud alone has on the resultant microstructure, namely a reduction in the level of oxide stringers or delaminations, and secondly, the further reduction in the amount of these features when a reactive gas is used in conjunction with the shroud.

However it is clear that there appears to be no evidence of carbides in the microstructure. It was hoped initially that carbon would react with the chromium in the Nickel-Chrome powder to produce an in-situ, hard, evenly dispersed chromium carbide phase. Although this does not appear to be the case, it is possible that carbides might have been produced but their size may be so small so as to be undetectable to both optical and scanning electron microscopes. Nevertheless, very significant increases in hardness have been achieved for the reactively sprayed coatings and the mechanisms thought to be responsible will be discussed in a later chapter (Chapter 7.0 Coating Modification).

6.3 Using different Reactive Gases

6.3.1 Introduction

The following reactive gases have been examined. Hydrogen was examined to see what effect it would have in reducing oxide levels.



6.3.2 Results

Methane was found to be the most effective reactive gas delivering slightly higher hardness results than acetylene. When sprayed at a flow-rate of 24 l min⁻¹ acetylene and methane produce similar results. Figures 80 and 81 show optical micrographs of the coating microstructures produced with the two reactive gases respectively. Both coatings exhibit similar hardness values; 345 ± 13 for acetylene and 361 ± 16 for methane. Propane has not

been examined with the latest parameters or reactor geometries. In addition methane became the preferred choice of reactive gas because much longer spray times were possible without interruption, particularly when compared with acetylene. When injected into the plasma, acetylene produced visibly more carbon soot than methane, which would deposit around the gas injection orifices and thereby cause an interruption to spraying while the deposit was cleaned off. A photograph of the deposit may be seen in figure 82. When spraying at higher flow-rates, such as 24 l min⁻¹ this soot would build up to a level where the injection orifices would become partially blocked and possible disruption to the plasma flame might occur. The level of soot build up with methane was negligible even with a flow-rate of 24 l min⁻¹.

Figures 83 and 84 show optical micrographs of the microstructures produced for coatings deposited with acetylene and hydrogen respectively. These coatings were produced with an earlier stainless steel type reactor that could not withstand the higher gun power parameters recommended by the manufacturer and are therefore less dense than coatings produced with later graphite reactors. It is however clear that the coating produced with acetylene reactive gas is denser and contains fewer oxide stringers compared to the coating deposited with hydrogen as a reactive gas

6.3.3 Discussion

All three hydrocarbon gases were effective in increasing coating hardnesses and also in reducing the level of oxide stringers or delaminations found in the deposited coatings.

Methane was found to be the most effective reactive gas delivering the highest coating hardness results followed by acetylene. Although propane has also been shown to increase coating hardness and reduce the amount of oxide found in the deposited coating, an experiment has not been performed which compares all three gases directly. Acetylene shows great promise as a reactive gas if the injection problems could be overcome, perhaps by altering the way in which the reactive gas is injected into the plasma jet, because acetylene has a distinct advantage by having the highest carbon to hydrogen ratio.

Hydrogen was not found to be an effective reactive gas when compared with a hydrocarbon gas in terms of reducing the oxide levels in deposited coatings.

6.4 Effect of Reactive Gas Flow-rate

6.4.1 Introduction

The effect reactive gas flow-rate has on the final coating hardness has been superficially investigated for acetylene.

6.4.2 Results

The change in coating hardness through RPS was found to be dependant on the flow rate of injected reactive gas. Table 14 shows the effect changes in acetylene flow-rate have on coating hardness. The four results shown have all been produced using a 15 cm graphite reactor, however, some of the coatings were sprayed with slightly different spraying parameters and this should be borne in mind when making a direct comparison.

Table 14: Effect of reactive gas flow rate on coating hardness

Powder	Gun Set-up	Arc Current	Carrier Gas Pressure /Psi	Acetylene Reactive gas flow-rate	Hardness
AI-1015	①	800	40	3 l min ⁻¹	214 ± 10
AI-1015	①	800	40	9 min ⁻¹	238 ± 14
AI-1017	②	900	50	15 min ⁻¹	330 ± 18
AI-1017	②	900	50	24 min ⁻¹	345 ± 13

6.4.3 Discussion

From table 14 it can be seen that higher reactive gas flow-rates lead to harder coatings within the range shown. This relationship has not been investigated thoroughly because the experimental work was aimed at

trying to inject as much reactive gas as possible into the reactor without causing the blockage problems described earlier when spraying with acetylene reactive gas.

6.5 Reduction in particle size

6.5.1 Introduction

Interaction between the powder particles and reactive inner atmosphere would from intuition be strongly dependant on the available surface area of the powder particles. Another powder (AI-1017) with a finer mean powder size and therefore greater surface area was sprayed under the same conditions to determine whether further increases in coating properties could be achieved.

Table 15 shows the powder size distributions for the two powder sizes used.

Table 15: Powder sizes for Plasmalloy AI-1015 and AI-1017

Powder Designation	Size Distribution
AI 1015	-125 + 45 microns
AI-1017	-90 + 10 microns

6.5.2 Results

Table 16 shows the results from the powder size experiments expressed in terms of hardness for the two powder size ranges. Conventional APS coatings, shrouded only coatings and reactively sprayed coatings (24 l min⁻¹ methane reactive gas) were sprayed with both powders.

Table 16: Effect of powder size on coating hardness

Powder	Conditions ①	Hardness /H_v
AI-1015	Conventional (APS)	181 ± 10
AI-1017	Conventional (APS)	224 ± 15
AI-1015	15 cm Reactor (Shrouded only)	191 ± 20
AI-1017	15 cm Reactor (Shrouded only)	213 ± 15
AI-1015	15 cm Reactor/24 l min ⁻¹ CH ₄ (RPS)	323 ± 30
AI-1017	15 cm Reactor/24 l min ⁻¹ CH ₄ (RPS)	451 ± 28

6.5.3 Discussion

Table 16 shows the effect of powder size on coating hardness. It can be seen that a marginal increase in hardness is observed for the finer powder. This is thought to result from a higher level of hard oxide phases formed in the coating when spraying in air due to the greater surface area of the powder, or possibly, the smaller particles lead to a higher final coating density.

When shrouded only, the larger powder size shows a slight increase in hardness and the finer powder size shows a slight decrease in hardness compared to the conventional APS coatings. This is thought to occur because the smaller particles will decelerate more rapidly, because they have less momentum than the larger ones, and therefore due to the greater stand-off distance when spraying with a shroud will have less velocity at impact and form a less dense coating. The slight increase in coating hardness for the larger particles is most probably due to the shrouding effect detailed earlier, whereby the shroud causes increased particle melting and higher jet velocities.

Most interesting is the massive increase in hardness values when a reactive gas is used. For the finer powder size an increase of 101 % is observed between the reactively sprayed coating and the conventional APS coating. For the larger particle size the increase is 72 %. Both these results testify once again that injecting reactive gas into the plasma flame significantly enhances coating properties. When the jump in hardness is compared between the reactively sprayed and shrouded only coatings thereby effectively measuring the correlation between powder size and reactive gas directly an increase of 113 % is observed for the finer powder and 69 % for the larger powder. These results confirm the hypothesis that by increasing the available surface area of the powder a greater amount of interaction between the powder and plasma flame can be achieved. In short, smaller powder particles are more susceptible to processing by reactive plasma spraying than larger ones.

6.6 Addition of Elemental Chromium

6.6.1 Introduction

In order to try and promote further interactions between the plasma flame and powder particles, elemental chromium powder was blended with the powder alloy. The aim was to allow this ‘free’ chromium to react with the dissociated carbon from the reactive gas. Reactively sprayed coatings were produced with the nickel-chrome powder on its own, and for powder blends containing 10 and 20 % elemental chromium. Both 15 and 20 cm graphite reactors were used.

6.6.2 Results

Table 17 shows the hardness results for the coatings produced.

Table 17: Addition of elemental chromium

Alloy Composition	Gun Set-up	Reactor length / cm	Reactive Gas /Flow-rate	Hardness /H _v
Al-1015	①	15	CH ₄ / 24 l min ⁻¹	323 ± 30
		20	CH ₄ / 24 l min ⁻¹	325 ± 27
Al-1015 + 10 wt % Cr	①	15	CH ₄ / 24 l min ⁻¹	284 ± 16
		20	CH ₄ / 24 l min ⁻¹	291 ± 13
Al-1015 + 20 wt % Cr	①	15	CH ₄ / 24 l min ⁻¹	320 ± 30
		20	CH ₄ / 24 l min ⁻¹	301 ± 33

From table 17 it can be seen that the addition of elemental chromium has not improved coating hardness values for any of the reactively sprayed coatings. However, some much harder regions were found, (705 H_v)

which are believed to be large chromium particles that were not fully melted. Figure 85 shows a region of coating microstructure and corresponding hardness indents (labelled) for the poorly melted chromium powder particle, and the rest of the coating (290 H_v). It should be noted that these much harder regions have not been included in the overall hardness value.

Figure 86 shows an optical micrograph of a reactively sprayed coating using a 15 cm graphite reactor with 20 wt % added chromium. There is a definite change in contrast between the chromium rich regions and the rest of the coating.

6.6.3 Discussion

As mentioned in the introduction, the objective behind this work was to promote reactions between the ‘free’ chromium and the injected hydrocarbon gas. These interactions would hopefully lead to the formation of Cr_xC_y in-flight. At the time this work was done it was not known that carbides were already being produced in-situ because they had not been detected yet. Furthermore, since the addition of elemental chromium had not yielded an increase in the hardness of the bulk coating, other than regions resulting from poorly melted particles, this line of work was not pursued further. However, it is recognised now that the addition of free elements, such as chromium or titanium, may yield a promising avenue for reactive spray applications in the future and this topic will be referred to in the suggested further work chapter later on.

6.7 Hydrogen Auxillary Gas

6.7.1 Introduction

The choice of working gas is usually decided by the gas mixtures ability to melt the sprayed powder particles. For the purposes of RPS lower particle velocities obtained from an argon-hydrogen mixture may be desirable because this would yield a longer residence time. Furthermore, the hydrogen may aid the removal of unwanted oxide phases.

6.7.2 Results

Table 18 shows the experimental conditions and hardness results for coatings deposited with argon-helium and argon-hydrogen gas mixtures for shrouded and reactively sprayed coatings.

Table 18: Effect of Auxillary Hydrogen Gas in terms of coating Hardness

Aux Gas / Pressure (Psi)	Arc Gas / Pressure (Psi)	Reactor	Reactive Gas / Flow-rate	Hardness / H _v
Helium / 100	Argon / 50	15 cm	No	182 ± 10
Hydrogen / 100	Argon / 50	15 cm	No	188 ± 13
Helium / 100	Argon / 50	15 cm	CH ₄ / 24 l min ⁻¹	361 ± 26
Hydrogen / 100	Argon / 50	15 cm	CH ₄ / 24 l min ⁻¹	293 ± 18

When shrouded only the hardness results are similar for both gas mixtures. Optical micrographs of the microstructures for the shrouded only coatings deposited with an argon-helium mixture may be seen in figure 87 and the argon-hydrogen mixture in figure 88. It can be seen that the coating

sprayed with the hydrogen mixture contains visibly more delaminations than the helium mixture produced, and is therefore a less dense coating. This trend is also observed for the reactively sprayed coatings. Optical micrographs of the microstructures may be seen for the reactively sprayed coatings produced with the helium mixture in figure 89 and hydrogen mixture in figure 90.

6.7.3 Discussion

Argon-Helium gas mixtures have been compared with argon-hydrogen gas mixtures^[5]. Molecular gases (especially H₂) have been found to impart more enthalpy to the plasma flame and also deliver higher jet velocities. It might be safe to assume that this would result in increased particle melting and higher particle velocities. However, although the former is certainly true, when compared with argon-helium gas mixtures lower particle velocities are observed using argon-hydrogen mixtures. The reason being the higher viscosity of the argon-helium system which imparts more acceleration to the particles, and although the jet velocity is lower the particle velocities are higher.

The results from coatings deposited with argon-hydrogen gas mixtures would indicate lower particle velocities on impact with the substrate, which is in keeping with the findings in the literature. Accordingly the helium mixture delivered higher hardness values than the hydrogen mixture. Helium is therefore the preferred auxiliary gas even though shorter residence times are likely.

7.0 COATING MODIFICATION

7.1 Introduction

This chapter will look at previous results and by various investigative techniques endeavour to explain them in relation to changes in the coating composition and microstructure. The techniques that have been employed include the following:

- Compositional Analysis
- X-Ray diffraction analysis
- Scanning Electron Microscopy (SEM)
- Transmission Electron Microscopy (TEM)
- Electron Diffraction
- Energy Dispersive X-ray analysis (EDX)

7.2 Results and Discussion

Each technique and the results produced will be discussed with respect to changes in structure and/or composition, alteration to coating, mechanical properties and performance.

7.2.1 Compositional Analysis

Some selected specimens were sent away to Incotest^[55] for detailed compositional analysis to primarily detect the levels of nickel, chromium,

oxygen and most importantly carbon. Details of the equipment used may be seen in Chapter 3.0 Experimental Methods. Table 19 shows the results of the analysis. All of the coatings were deposited with a 15 cm graphite reactor. The powders were as-received.

Table 19: Coating composition results

Conditions ③	% C	% Cr	% Ni	% O
Coating: AI-1017, Methane 24 l min ⁻¹	1.33	18.2	74.5	0.14
Coating: AI-1017, No Methane	0.047	18.2	76.0	1.40
Coating: AI-1015, Methane 24 l min ⁻¹	1.26	18.0	76.3	0.10
Coating: AI-1015, No Methane	0.12	18.0	77.4	0.50
Powder: AI-1015 Powder	0.008	19.6	78.3	0.075
Powder: AI-1017 Powder	0.031	19.2	78.5	0.049

From table 19 the carbon content can clearly be seen to have increased significantly for the reactively sprayed coatings. The reactively sprayed coating produced using the finer powder size (AI-1017) which contains 1.33 wt % C compared with 0.047 wt % for the shrouded only coating and 0.031 wt % for the as-received powder. This increase, in excess of an order of magnitude demonstrates that the carbon content of the coating can be significantly increased by reactive plasma spraying.

For the coarser powder (AI-1015) the same trend is observed but to a slightly lesser extent. The reactively sprayed coating contains 1.26 wt % compared with 0.12 wt % for the shrouded only coating and 0.031 wt % for the as-received powder. These results correlate well with what would be expected due to the lower surface area available for interactions to

occur between the molten powder particles and the reactive inner environment.

It should also be noted that a corresponding decrease in oxygen is observed between the reactively sprayed and shrouded only coatings. For the finer powder the drop in oxygen an exact order of magnitude change falls from 1.4 wt % for the shrouded only coating to 0.14 wt % for the reactively sprayed coating, and for the coarser powder a corresponding drop from 0.50 wt % to 0.10 wt % is observed. These findings compare well with the considerably lower levels of oxygen stringers seen in the reactively sprayed coating microstructures (For example, figures 80 and 81, reactively sprayed coatings with acetylene and methane respectively).

This finding is important, because it means that RPS offers a method by which coatings can be deposited (with modified APS equipment) that contain considerably lower oxide levels. This is usually only possible by spraying in a vacuum or inert environment. MCrAlYs are a series of alloys that have been developed for oxidation resistance, and therefore the lower the oxygen content of the coating prior to service, the longer the service life is. It is hoped that reactive plasma spraying may yield an alternative method for the deposition of MCrAlY alloys with low oxygen contents without the need for more expensive low pressure plasma spraying (LPPS) apparatus, the method by which these alloys are commonly applied now. The above finding and other factors such as oxidation resistance will be dealt with in chapter 9.0 Reactive Plasma Spraying of an MCrAlY alloy.

The increase in carbon content between the as-received powder and the shrouded only coatings is thought to derive from degradation of the

graphite reactors while spraying. The graphite reactors which are designed to be a consumable, seem to be helping with the central objective.

So far it has been established that harder more dense coatings have been produced by reactive plasma spraying compared with a conventional atmospheric plasma sprayed coating. Furthermore, it has been established that the reactively sprayed coatings contain increased levels of carbon and lower levels of oxygen from the compositional analysis above (Table 19). However, micrographs of the coatings do not reveal this carbon to be present in the microstructure, certainly not in the form of carbides unless they are so fine that detection proves impossible by optical and scanning electron microscopy.

7.2.2. Electrolytic Etching

Electrolytic etching (see experimental methods) was performed on a reactively sprayed coating, shrouded only coating and conventionally sprayed (APS) coating, for pre and post heat treated specimens. No carbide phases were revealed in either the shrouded only or conventionally sprayed specimens, before or after heat treatment – as would be expected. The pre-heat treated reactively sprayed specimen was vigorously attacked by the etch indicating large scale carbide formation. Figure 91 shows an optical micrograph of the coating post etching. The etch has attacked a large area of the coating. Some areas of the coating were attacked more than others, for instance those shown in figure 92. The etched microstructure consists of two main regions. The first region consists of microstructure that has not been attacked by the etch and therefore does

not contain carbides. These regions would result from powder particles that have not reacted in-flight. This may be because no interaction between the powder particles and reactive medium has taken place for certain particle trajectories, or possibly, because of insufficient reaction time.. The second region, which has been vigorously attacked by the etch, indicates a significant level of carbide phases within the matrix. An SEM micrograph of the etched specimen may be seen in figure 93.

An optical micrograph of the post-heat treated reactively sprayed specimen may be seen in figure 94. An evenly dispersed carbide phase can clearly be seen to have been attacked by the etch. Figure 95 an SEM micrograph shows the attacked regions more clearly.

The reactively sprayed sample was subsequently re-polished and microhardness measurements taken with a 10 g load. Two distinct sets of values were recorded, one set gave values believed to originate from splats not rich in carbide phases with a value of $546 \pm 50 H_v$, the second set of values were much higher at $1160 \pm 100 H_v$ and are believed to originate from splats which are rich in carbide phases. Microhardness measurements carried out on the heat-treated specimen showed a uniform Microhardness value of $454 \pm 29 H_v$. The microstructure for the coating shown in figures 94 and 95 (post heat-treated specimen) would be expected to be very hard and the drop is thought to occur due to over-ageing.

7.2.3 X-ray Analysis

X-ray analysis has been employed to investigate whether any phase changes occurred within the coating. X-ray plots for a conventional APS coating, a shrouded only coating, a reactively sprayed coating and the as received powder may be seen in figures 96 to 99. All the traces show the same peaks with similar relative intensities, allowing for some shift. Table 20 shows the diffraction angles, d-spacings and relative intensities produced from the x-ray diffraction analysis.

Table 20: X-ray Diffraction Results

Sample	Peak N°	Angle / 2θ	d-spacing / Å	Rel. Intensity
Powder (Al-1017)	1	50.74	2.088	100
	2	59.54	1.802	46
	3	90.05	1.264	30
APS Coating	1	51.75	2.050	100
	2	60.53	1.775	42
	3	90.82	1.256	24
Shrouded only coating	1	51.73	2.050	100
	2	60.58	1.773	41
	3	90.89	1.255	25
RPS Coating	1	51.31	2.066	100
	2	60.07	1.787	47
	3	90.23	1.262	15

It can clearly be seen that no new peaks have been found, and from this one might conclude (a) that no carbides or other phases have been synthesised during reactive spraying, or (b) that any phases that have been created are below the detectable limit of the equipment used.

However, by plotting $\sin \theta / \lambda$ against $B \cos. \theta / \lambda$ where B is the full width half maximum (FWHM) of a diffraction peak, θ is half the scanning

angle 2θ and λ is the wavelength of the radiation used a Hall-Williamson plot is produced. The gradient of the line produced is an indication of the level of strain present in the crystal lattice by measuring peak broadening and peak shift. A Hall-Williamson plot for a reactively sprayed coating, a shrouded only coating and the as-received powder may be seen in figure 100. Hall-Williamson plots have proved a very successful method for analysing deposited coatings. The plot shows three lines; one for the powder and the other two for the coatings. The powder line has the lowest gradient which would be expected as there are no other elements present to distort the lattice parameters. The line for the shrouded only coating has the next lowest gradient and the reactively sprayed coating has the highest gradient. It is proposed that these changes in gradient and therefore distortions to the lattice are caused by a very fine dispersion of carbide precipitates or by carbon in solution within the crystal lattice. It has already been shown that the reactively sprayed coatings contain more carbon from the compositional analysis results described earlier.

A second Hall-Williamson plot for the reactively sprayed and shrouded only coatings both before and after heat-treatment at 700 °C for 30 minutes together with the curve from the as-received powder may be seen in figure 101. After heat treatment both the reactively sprayed and shrouded only coatings show relaxation in their crystal lattices by a reduction in the gradients of their respective lines to a point above the as-received powder. This would indicate that whatever was causing distortion or pinning within the crystal lattices is no longer doing so and may well be accounted for by changes in residual stress. However there is still no evidence of other phases in the x-ray plots from which the Hall-

Williamson plot is derived. This would simply indicate that any phase created is present in quantities below the detectable limit of the x-ray diffraction equipment. X-ray analysis has therefore not proved successful in identifying the carbide phase found by electrolytic etching.

7.2.3 Scanning Electron Microscopy (SEM) / Energy dispersive x-ray analysis (EDX)

SEM examination of the deposited coatings, with greater resolution than an optical microscope, did not reveal the presence of carbides in the coating microstructures of the reactively sprayed coatings. Following from earlier findings, reactively sprayed coatings that were subsequently heat treated (700 °C for 30 minutes) did show evidence of precipitate formation. Figure 102 shows an S.E.M. micrograph of an RPS coating prior to heat treatment. Figures 103 and 104 show S.E.M. micrographs at the same magnification for a reactively sprayed and shrouded only coating post heat treatment (700°C, 30 minutes, air cooled). Note the presence now of what appear to be precipitates (400 nm in size) in the reactively sprayed coating. These features may be seen in the shrouded only-heat treated coating but in visibly smaller quantities. Energy dispersive x-ray (EDX) analysis of these darker precipitate areas showed them to be richer in chromium than adjacent lighter areas. The EDX plot for the darker precipitate areas may be seen in figure 105 and an adjacent area in figure 106. The EDX system is unable to detect carbon unless it is present in large quantities, 5-6 wt. %. Therefore, although likely it can not be concluded that the dark areas of interest are chromium carbide precipitates.

7.2.4 Transmission Electron Microscopy (TEM) / EDX / Electron Diffraction

T.E.M. examination for both the reactively sprayed and shrouded only coatings showed grain sizes to vary significantly in size. The majority of grains were fine (~ 0.1 to $0.4\ \mu\text{m}$) and equiaxed in morphology. Other grains were found that were much larger ($\sim 1\ \mu\text{m}$) and tended to be less equiaxed in nature. Figure 107 shows the fine grain structure for a reactively sprayed sample typical of most of the coating. Fine equiaxed grains are a typical characteristic of a rapidly solidified microstructure. For comparative purposes a micrograph of a shrouded only sample may be seen in figure 108. It should be noted that there is no evidence of precipitate formation. Some grains like those shown in figure 109, for a reactively sprayed sample, contained what appear to be a significant proportion of finely dispersed precipitates. On tilting the stage many of the 'dark areas' were found to be dislocations, however, many remained stationary and are probably precipitates of a second phase, approximately 5-15 nm in size. Both EDX analysis and calculations from a selected area diffraction pattern were inconclusive, revealing only the nickel-chrome matrix.

If these precipitates were chromium carbides detection would prove difficult, because the most intense diffraction peaks for the nickel-chrome matrix and the carbides occur at very similar d-spacings. Table 21 shows the most intense d-spacings for XRD analysis of a sprayed coating, results from a selected area diffraction pattern and d-spacing data for three

chromium carbide compositions. The wavelength for the electron diffraction pattern was calculated from an aluminium standard.

Table 21: d-spacings for a sprayed coating, electron diffraction results and chromium-carbides

XRD: Coating d Å / Int	Electron diffraction d Å / Int	Cr ₂₃ C ₆ d Å / Int	Cr ₇ C ₃ d Å / Int	Cr ₃ C ₂ d Å / Int
2.05 / 100	2.04 / 100	2.0520 / 100	2.0489 / 100	2.3063 / 100
1.77 / 42	1.72 / 50	2.176 / 24	2.1231 / 46	2.2409 / 60
1.25 / 24	1.22 / 20	2.383 / 23	2.2969 / 33	1.8691 / 49

The small differences between the electron diffraction results and the XRD results can be accounted for by differences in residual stress.

The carbon wt % at which the carbides form for equilibrium compositions are as follows: Cr₂₃C₆ (5.5 - 5.8 wt %), Cr₇C₃ (~ 9 wt %) and Cr₃C₂ (~ 13 wt %). The Cr-C phase diagram may be seen in figure 110. Given that compositional analysis has found the Carbon wt % of a reactively sprayed coating to be around 1.4 wt %, carbides that may have formed must have done so because of departures from equilibrium constitution due to rapid solidification. Furthermore, any carbides that may have formed are more likely to be Cr₂₃C₆ or possibly Cr₇C₃ in composition. In essence probably only the most intense peak belonging to the carbide phase would be perceptible in the electron diffraction pattern, which as table 21 shows, would interfere with the main peak for the nickel-chrome matrix. The reasons for this being firstly, the much lower concentration of any carbide phase compared with the matrix, and secondly, the low intensities of the secondary diffraction peaks for the carbide phases.

Vacuum heat treatment of the reactively sprayed sample for between 30 minutes and one hour at 700 °C did show enhanced precipitate formation. However, definitive analysis of the precipitates was not achievable and therefore neither was their composition. Some of the precipitates showed evidence of preferred orientation, like those in figure 111, others did not, like those in figure 112. The precipitates which in all likelihood are chromium carbides were between 10 and 60 nm in size. Vacuum heat treatment of the shrouded only coating showed very little evidence of precipitate formation. A micrograph of the shrouded only sample post heat treatment may be seen in figure 113. As would be expected there is no evidence of precipitate formation.

One further reason why T.E.M. analysis might have been unable to definitively identify the precipitates could be because of the sample preparation method. The T.E.M. samples were ion-beam milled and harder regions of the microstructure (those containing carbides) would experience a lower sputtering rate than softer regions of the coating (those not containing carbides) and are therefore less likely to be milled to a point where the electron beam can pass through the sample. Due to time constraints further T.E.M. examination and sample preparation by other methods was not possible.

8.0 WEAR PROPERTIES

8.1 Introduction

Non-lubricated wear tests were performed on conventionally sprayed, shrouded only and reactively sprayed coatings. The objective was to see how the different coatings wear properties compared and whether the increases in hardness for reactively sprayed coatings would translate into superior wear properties.

8.2 Results

Typical wear graphs and coefficient of friction graphs may be seen for the conventionally sprayed coating in figure 114, shrouded only coating in figure 115 and reactively sprayed coating in figure 116. The spread on the data points (red) arises from a minute vertical oscillation between the rotating disk and transducer. A line (black) is produced by employing a moving average.

Table 22 shows a summary of the wear test conditions and resulting wear coefficients. Hardness values for the coatings before testing are also displayed.

Appendix D details a simple theory of sliding wear and the derivation of the Archard wear equation

Table 22: Pin on Disk Wear Results

Coating	Reactor	H _v	Summary	Coefficient of Friction (μ) Initial / Steady State	Wear Coefficient k /m ³ N ⁻¹ m ⁻¹
Conventional APS	-	224	Non-lubricated	0.8 / 0.65	4.72 E ⁻¹⁴
Shrouded only	15	192	Test velocity 1 m/s	0.7 / 0.6	11.5 E ⁻¹⁴
Shrouded only	20	177	Load 20 N		12.7 E ⁻¹⁴
Reactively sprayed RPS	15	370	Temperature - Ambient	0.85 / 0.65	3.01 E ⁻¹⁴
Reactively sprayed RPS	20	404	440C SS Disk		2.51 E ⁻¹⁴

Optical micrographs of the wear pins in cross-section parallel to the sliding direction may be seen in figure 117 for the conventionally sprayed coating, figure 118 for the shrouded only coating (15 cm reactor) and figure 119 for the reactively sprayed coating (15 cm reactor

Figure 120 shows a photograph of a wear disk and pins after testing for the reactively sprayed (inner track) and shrouded only (outer track) coating.

8.3 Discussion of Wear Results

The results will firstly be discussed for each coating type and a further discussion will focus on differences between the coatings.

8.3.1 Conventionally Sprayed APS coating

From figure 114 during the first 30 metres of the test the coefficient of friction rises rapidly from around 0.2 to 0.8. In this period due to the as-sprayed condition of the pin and therefore rough surface finish, asperity junctions are being formed. This condition is common to all the coatings but is most severe for this coating and a significant amount of wear occurs.

During the next 70 metres the coefficient of friction falls to approximately 0.65 where it remains stable for the remainder of the test and a steady wear rate is achieved. From figure 117, a micrograph of the coating post testing in cross-section parallel to the sliding direction, a surface layer has been formed and severe plastic deformation near the surface is evident.

The structure is very similar to reported work on the wear behaviour of reactive hot pressed nickel aluminides^[64] (Ni-40% Al) in which a three zone structure has been described. Zone 1 consists of the bulk material that is unaffected by the test. Zone 2 shows a highly plastically deformed region with the plastic shear strain increasing towards the wear surface. And Zone 3 is a combination of ultra-fine grains (submicron) and a thin film. The film was found to contain a mixture of bulk material, material transferred from the counterface and oxides. A schematic of the subsurface zones may be seen in figure 121.

Returning to the APS coating, microhardness measurements taken in the zone 3 region were found to be around 1350 H_v (25 g load, 15 sec load

time) and in the plastically deformed zone 2 region around 430 H_v. The zone 3 layer was found to vary in thickness between 6 and 16 µm. Measurements taken in the bulk coating were around 320 H_v at this lower test load and should be compared with a value of 224 H_v for earlier tests carried out with a 1000 g load. Visual inspection of both pin and disk after testing showed very little formation of oxide debris. S.E.M. examination of the pin in cross-section, shown in figure 122, found the highly deformed surface layer by EDX analysis to contain iron, nickel and chromium. Further investigation showed a fine dividing layer. Analysis on the left side (toward the wear surface) found high levels of iron, whereas the right side (toward the bulk coating) found no iron present. This would indicate transfer of material from the pin to the disk which has subsequently returned.

8.3.2 Reactively Sprayed Coating

From figure 116 during the first 30 metres of the test the coefficient of friction rises from around 0.3-0.75. Again in this period due to the as-sprayed condition of the pin and therefore rough surface finish, asperity junctions are being formed. Then from 30 metres to approximately 140 metres the coefficient of friction increases further from 0.75 to 0.85. The level of friction then falls to around 0.65 and fluctuates between 0.6 and 0.75 for the remainder of the test. From the wear graph in figure 116 a significant period of wear occurs in the first 80 meters whereafter the wear rate falls and steady state appears to be reached. Except for some 'blips' that correspond to reductions in friction. Significant levels of black debris

were observed on both the pin and disk (later found to be FeO) after this test.

The data suggests that during the initial stages of the test corresponding to the high levels of friction, temperatures in excess of 570 °C were achieved and FeO was formed. The FeO acts as a lubricant and caused a corresponding drop in friction and therefore a drop in wear rate. The blips may be explained by a build up of debris which then falls away.

An optical micrograph of the pin in cross-section post wear test may be seen in figure 119. Unlike the the APS pin there is no evidence of the zonal structure described earlier, namely the surface layer (Zone 3) and/or yielding of the coating beneath the wear surface (Zone 2).

The surface of the pin appears smooth with the exception of areas of the coating that have been pulled out. A higher magnification S.E.M. micrograph figure 123 shows a section of pulled out coating containing some debris. The debris was found to contain nickel, chromium and iron. Figure 124, another S.E.M. micrograph shows a splat in the process of delaminating. From these factors it appears there is considerably less ductility in the RPS coating and that wear is taking place by splat delamination. However, from figure 120, a photograph of the wear disk and pins after the test, (RPS sample: inner track) two distinct regions on the track can be seen. In the centre of the RPS wear track (inner track) is a region similar to that for the shrouded only test (outer track) and on the inner and outer edges of the RPS track a 'polished' region can be seen. S.E.M. and EDX analysis of the disk found the polished region to have no nickel on the surface, whereas the central region did. S.E.M. micrographs

for the polished region may be seen in figure 125, and the central dull area in figure 126.

In summary, it would now appear that perhaps two wear mechanisms are occurring. Firstly, an oxidative mild wear type regime responsible for the polished areas on the disk and the large scale formation of FeO lubricating debris, and secondly, a general metallic adhesive mechanism where material is transferred from the pin to the disk creating a surface composite layer on the disk. Because no surface layer was found on the pin, the coating material found on the disk may have originated from splats that have delaminated and subsequently been compressed to form a composite surface layer on the disk. The mechanism by which composite wear debris may form has been described in the literature^[64], a schematic diagram of the process may be seen in figure 127. However, it is believed that the improved wear resistance for RPS coatings occurs because of the formation of substantial quantities of lubricating oxide debris over the majority of the pin. The relatively high coefficient of friction might remain because sections of the pin are undergoing an adhesive type regime. From the electrolytic etching findings a substantial quantity of the coating is comprised of regions rich in a carbide phases. However, regions were found that contained less carbide phases, it may be these regions that are responsible for the more severe wear mechanism. In which case improved optimisation to the spraying process, such that a more uniform dispersion of the carbide phases exist, would suggest even more superior wear properties are likely for reactively sprayed coatings.

8.3.3 Shrouded only coating

From figure 115 the same initial increase in the coefficient of friction from around 0.1 to 0.7 during the first 30 metres is observed. The value then falls to around 0.6, increasing slightly and then remains at around 0.65 for the remainder of the test. Unlike the APS and RPS coatings very little change on the wear graph occurs until 150 metres have past. The wear rate then increases slightly and steady state is achieved. These results are misleading because it would appear that the shrouded only coatings have the greatest wear resistance. However, the shrouded only pins showed the greatest weight change. It must be noted that the wear graph represents a change in dimensions. Disk weights were not recorded.

From figure 118, an optical micrograph of the coating post testing in cross-section parallel to the sliding direction, shows the formation of a surface layer and severe plastic deformation below the surface is evident. In many ways this coating is very similar to the APS coating as the same zonal structure was observed – described earlier. A hardness value taken in the zone 3 surface layer was found to be 1068 H_v (25g load, 15 sec load time) compared to a value of 1350 H_v (25g load, 15 sec load time) for the APS pin. One might expect excellent wear properties to result, however, it would appear the surface layer is not stable and continuously transfers to the disk. This would explain the small change in dimensions observed and also the large weight change for the pin. S.E.M. / EDX examination of the surface layer on the pin showed no iron to be present. An S.E.M. micrograph of the pin surface layer may be seen in figure 128.

An S.E.M. micrograph of the disk surface may be seen in figure 129. EDX analysis showed the protruding regions to contain large amounts of nickel and chromium, adjacent areas on the disk contained high levels of iron and chromium and lower levels of nickel. This would indicate transfer of material from the pin to the disk and the absence of iron on the pin surface would indicate that this deposited layer is not transferring back.

8.4 Final wear discussion

Returning to table 22 the order of increasing wear resistance from the wear coefficients is as follows; shrouded only, conventionally sprayed (APS) and reactively sprayed (RPS).

The shrouded only coating and atmospherically sprayed coating showed extensive levels of plastic deformation beneath the wear surface and the formation of a hard composite surface layer on the wear pin. Moreover, these coatings did not show significant formation of lubricating FeO debris. The reactively sprayed coating did however produce significant amounts of FeO, and plastic deformation of the wear pin surface and underlying region was not apparent. The differences between the wear mechanisms are thought to result from differences in coating hardness and ductility. It must also be noted that although the shrouded only coating contained fewer oxide stringers and delaminations than the conventionally sprayed APS coating, wear resistance was detrimentally affected. It is unclear why once a composite structure of iron, nickel and chromium and oxides has formed on the wear disk, why this layer does not transfer back

to the pin and if it does why it is not stable on the pin surface for the shrouded only coating. Possible explanations may include low inter-diffusion between the oxide and metal or glazing.

Given that the Iron content was the same for all the wear systems the increased hardness and reduced ductility for the reactively sprayed coating must have caused higher local temperatures during the wear test and therefore the formation of larger quantities of FeO. These findings indicate that unless the coatings ductility is reduced and hardness increased, the removal of oxide phases from the coating microstructure result in reduced wear performance.

In summary, RPS has proved a successful technique for improving the wear resistance of conventionally sprayed APS coatings. Furthermore, it is fair to say that the improvement is likely to be greater than the wear coefficients suggest. This is because the wear coefficients were calculated assuming maximum theoretical coating density, and since the RPS coatings have proved denser than the APS coatings the total volume loss of material would be lower. Moreover, because porosity (coating collapse) and oxide stringers (splat delamination) have been shown to be predominant mechanisms of failure in thermally sprayed coatings, the improvements in microstructure, such as the greatly reduced levels of oxide stringers and porosity, are indisputable evidence for the assertion that RPS improves wear resistance, in addition to the evidence for the formation of in-situ reinforcing phases.

9.0 REACTIVE PLASMA SPRAYING OF AN MCrAlY ALLOY

9.1 Introduction

Reactive plasma spraying offers advantages other than the addition of elements to sprayed coatings by in-flight reaction, namely the removal of unwanted phases by in-flight reaction. Certain materials are extremely susceptible to oxidation when sprayed and therefore have to be sprayed in expensive low-pressure or vacuum plasma spraying apparatus.

One example of this type of material are MCrAlY's. MCrAlY's are a range of alloys that have been developed for resistance to high temperature oxidation and sulphidation and are used in gas turbine engines. M can be Fe, Co, Ni or Ni-Co.

This work is concerned with depositing MCrAlY coatings with low oxide contents came about from earlier findings on 80:20 Ni/Cr powders showing lower oxide levels when reactively sprayed. MCrAlY coatings are often used as bond coats for Thermal Barrier coatings (TBC) in the aerospace industry in addition to their oxidation and corrosion resistant properties. Spraying of these alloys for such applications is frequently performed in Low Pressure Plasma Spraying (LPPS) equipment to minimise the level of oxide formation. Lower oxide levels in the deposited coating lead to longer service times because more of the aluminium and chromium is available to form protective oxide scales. It

was hoped that reactive plasma spraying in a reducing plasma stream would allow the deposition of MCrAlY alloys by Atmospheric Plasma spraying (APS) techniques while keeping the oxide level to a minimum, thereby offering a potentially more economically viable production route.

9.2 Results

Table 23 details the experimental parameters used. Because these powders are not usually sprayed using an APS system no recommended parameters exist. Initially, the parameters for the Ni-Cr powder (gun set-up 1) were adopted and subsequently some other lower power parameters were attempted (gun set-up 3).

Table 23: MCrAlY Spray Programme

Powder	Gun Set-up	Reactor	Reactive Gas / Flow-rate	Oxygen wt %	Carbon wt %
995/1	1	No	-	3.6	0.014
995/1	1	Yes / 15 cm	-	2.3	0.018
995/1	1	Yes / 15 cm	CH ₄ / 24 l min ⁻¹	0.35	0.34
995/47	1	No	-	2.2	0.021
995/47	1	Yes / 15 cm	-	1.5	0.034
995/47	1	Yes / 15 cm	CH ₄ / 24 l min ⁻¹	0.12	0.43
995/1	3	Yes / 15 cm	-	-	-
995/1	3	Yes / 15 cm	CH ₄ / 24 l min ⁻¹	-	-
995/1	3	Yes / 20 cm	-	-	-
995/1	3	Yes / 20 cm	CH ₄ / 24 l min ⁻¹	-	-

Table 23 also details coating analysis results performed on the deposited coatings to establish oxygen and carbon levels. Coating analysis was only performed on coatings produced using one of the gun (set-up 1)

conditions. The two powder size ranges were as follows; Amdry 995/1 - $37 + 5 \mu\text{m}$, and Amdry 995/47 - $75 + 45 \mu\text{m}$. Amdry 995 is a CoNiCrAlY alloy. For the powders composition please refer to the materials section in the Experimental Methods chapter.

Figure 130 shows optical micrographs of the two conventionally sprayed coatings employing gun set-up 1 parameters.

Optical micrographs comparing shrouded only and reactively sprayed coatings produced employing gun set-up ① parameters may be seen in figure 131 (smaller particle size range: Amdry 995/1) and figure 132 for the larger size range (Amdry 995/47).

Optical micrographs comparing shrouded only and reactively sprayed coatings produced employing gun set-up ③ parameters may be seen in figure 133 for the smaller particle size range: Amdry 995/1 and figure 134 shows micrographs adopting the same parameters except a 20 cm reactor was used. The gun set-up ③ parameters were not of sufficient energy to fully soften the larger particles and suitable coatings were not produced.

9.3 Discussion of Results

From the coating analysis results, RPS can clearly be shown to reduce the oxygen levels found in the deposited coating. For the larger powder cut a reduction from 2.2 wt % to 0.12 wt % oxygen was observed between the conventionally and reactively sprayed coatings. For the smaller powder cut a reduction from 3.6 wt % to 0.35 wt % oxygen was observed between

the conventionally and reactively sprayed coatings. In both cases an order of magnitude reduction has been recorded.

The shrouded only coatings as would be expected show slightly lower oxygen values and slightly higher carbon values. The increase in carbon is thought to originate from decomposition of the graphite reactors. It then follows that the reactive gas, in this case methane at a flow-rate of 24 l min⁻¹ is directly responsible for the large reduction in oxygen levels when coatings are reactively sprayed

Optical micrographs of the deposited coatings and the corresponding microstructures reveal the same trends. Figure 130 which compares the conventionally sprayed coatings for the two powder sizes clearly shows the coating produced with the smaller particle size to contain a larger proportion of oxide stringers. Figures 131 and 132 the first of the figures comparing the shrouded only and reactively sprayed coatings, again demonstrates that by using a reactive gas in addition to a shroud promotes a significant reduction in the proportion of oxide stringers observed in the deposited coating for both the smaller and larger powder size ranges respectively. Furthermore, the gun set-up ① parameters appear to produce reasonable coatings for both powder sizes. When using the gun-set-up ③ parameters and the smaller powder size a dramatic difference between the shrouded only and reactively sprayed coating is observed, figure 133. The same is true when using a 20 cm reactor, figure 134.

9.4 Discontinuous Oxidation Tests

9.4.1 Introduction

Discontinuous oxidation tests were performed on conventionally sprayed, shrouded only and reactively sprayed coatings. Coatings were sprayed onto both sides of a nimonic 263 substrate, leaving only the sides of the specimen uncoated. A section of uncoated substrate was included in the test as a control.

Samples were subjected to heating in air at 1100 °C for extended periods of time. The weight increase recorded was the result of oxidation. The samples were accurately weighed after 0,1,3 and 30 hours of exposure. A more detailed account of experimental procedures can be seen in the experimental methods chapter.

As with the 80:20 Ni/Cr alloy a significant corresponding increase in carbon is observed when reactively spraying. It should be noted that the objective of this work was not to investigate the oxidation properties of MCrAlY coatings, but to examine whether reactive spraying has a detrimental effect on MCrAlY oxidation properties.

9.4.2 Results

A graph of weight change per unit area plotted against time on log scales may be seen in figure 135. The graph shows the three lines for the coated specimens and one for the substrate control. It should be noted that the

lines for the specimens represent only the weight change of the MCrAlY coating. Weight changes due to oxidation of the exposed substrate have been deducted from the overall weight gain by knowing the exposed surface area, and the oxidation properties of the control substrate specimen.

9.4.3 Discussion

From figure 135, it can be seen that the MCrAlY coatings show a much lower weight change due to oxidation than the nimonic 263 substrate, which would be expected. If anything the reactively sprayed coating performs better than both the conventionally sprayed and shrouded only coating. However, it would not be sensible to make this conclusion from just this one test. What can be said though is that reactive spraying and particularly the addition of carbon to the coating does not appear to be detrimental to the oxidation properties of this MCrAlY coating.

Given that the recommended application temperature for this alloy^[65] is around 980 °C the reason for the high test temperature of 1100 °C was to reduce the test time.

10.0 SUMMARY DISCUSSION

10.1 80:20 Nickel / Chrome Alloy

Reactive plasma spraying has proved a very successful method for improving the mechanical properties of an 80:20 nickel-chromium alloy. Figure 136(a) and (b) shows two micrographs; one an APS coating sprayed using the manufacturers recommended parameters, and the second a reactively sprayed coating with the most optimised parameters to date. A summary of the changes in parameters, microstructures and mechanical properties are as follows:

<u>APS Coating</u>	CHANGE in <u>Parameters</u>	<u>RPS Coating</u>
No No AI-1015	15 cm Reactor Reactive Gas Powder	Yes Yes /24 l min ⁻¹ CH ₄ AI-1017
Figure 136a 10-20 % 5-10 %	<u>Microstructure</u> Delaminations / Stringers Porosity	Figure 136b < 1 % 1-2 %
181 H _v 4.72 E ⁻¹⁴	<u>Mechanical Properties</u> Hardness Wear Coefficient k /m ³ N ¹ m ⁻¹	452 H _v 2.51 E ⁻¹⁴

In summary, RPS offers the ability to make significant improvements to conventional APS coatings through interactions between the sprayed powder particles and a reactive gas in-flight. These interactions have led to the formation of in-situ carbides which act as a reinforcing phase within the nickel-chrome matrix. Regions rich in carbides were found to demonstrate very high hardness values ~1160 H_v. Unfortunately the

composition and volume fraction of the reinforcing phase has not been determined. Nevertheless, mechanical properties of RPS coatings have been shown to be far superior to those of a conventional APS coating. Microhardness values for the RPS coatings are more than double those of APS coatings leading to enhanced wear properties, the central objective of the project. In fact, the wear coefficient k , for the RPS coating is almost half that of the APS coating. Furthermore, it should be noted that the wear coefficients were calculated assuming a maximum coating density, and since the RPS coatings were denser than the APS coatings it is fair to conclude even greater wear resistance for RPS coatings.

Improvements to coating appearance and microstructure have been striking in the best RPS coatings; delaminations, oxide stringers and porosity have almost been eliminated leading to almost fully dense coatings. These findings suggest that reactive spraying and particularly using a reactor significantly improves the heating and melting of the powder particles, and perhaps is better able to compensate for variations in powder particle size distributions.

In order to promote interactions between the sprayed particles and injected reactive gas a reactor section was designed. The design after a few attempts proved very successful, largely because of the achievements mentioned above. Computational Fluid Dynamics (CFD) has been employed to further investigate mechanisms occurring inside the reactor. Although CFD modelling has only been attempted at a basic level, the method seems a promising way of further optimising the reactive spray process. So far CFD has established that the reactive gas is not being

injected directly into the central region of the plasma jet. Evidence suggests, from the increase in turbulent kinetic energy on the periphery of the plasma jet, and findings in the literature, that the areas around the plasma jet are through the formation of vortices, entrapped into the plasma stream, and that this is the method by which the reactive gas is interacting with the powder particles. If it assumed that the reactive gas is not approaching the central region of the plasma until 80 mm after the torch exit, and that particle velocities are around 100 m s^{-1} ^[12], then with a 10 cm reactor only 0.2 ms of reaction time is available. With a 15 cm reactor this reaction time increases to 0.7 ms, assuming a 100 ms^{-1} particle velocity. From the hardness measurements on reactively sprayed coatings using a 10 and 15 cm reactor the amount of time required for reactions to occur between the disassociated reactive gas and sprayed powder particles is likely to lie between 0.2 and 0.7 ms.

10.2 MCrAlY ALLOY

Reactive spraying of an MCrAlY alloy has shown that materials, which are particularly susceptible to oxidation in-flight, can be deposited with substantially lower oxide levels.

It was not possible to obtain a value for a low pressure plasma sprayed (LPPS) or vacuum plasma sprayed (VPS) MCrAlY bond coat with which to compare values.

Discontinuous oxidation tests showed that the reactive spraying process if anything enhanced the oxidation properties of the alloy. However, not

enough work has been carried out to conclude this. For instance it is reasonable to expect that since carbides were formed in an 80:20 nickel-chromium alloy, that carbides may well have been formed in the MCrAlY alloy, and the effect this would have, say on thermal cycling properties would need to be thoroughly investigated.

In summary, RPS may prove with further work and optimisation of parameters, a viable method for depositing these highly specific coatings with substantial economy savings, a patent is being applied for.

11.0 CONCLUSIONS

1. Arc Current has been found to be the most significant gun parameter in terms of deposited coating hardness followed by stand-off distance when compared with auxiliary gas pressure and powder feed rate.
2. The manufacturers recommended parameters are sufficient to fully melt the powder particles in the size range used.
3. Using a reactor section has been shown to promote interactions between the plasma gases, injected reactive gas and sprayed powder particles.
4. Reactive plasma spraying with a hydrocarbon reactive gas, such as methane, acetylene or propane increases the deposited coating hardness.
5. Reactively sprayed coatings demonstrate improved wear resistance compared with conventionally sprayed APS coatings
6. Reactively sprayed coatings have been deposited with an in-situ carbide phase through in-flight reaction. However, the volume fraction and composition of the carbides has not been determined.
7. Electrolytic etching with potassium cyanide has been an effective method to reveal carbides in nickel-chromium alloys.
8. Reactively sprayed coatings have been shown to contain considerably lower levels of oxide stringers and porosity than conventionally sprayed APS coatings.
9. MCrAlY coatings have been deposited with an order of magnitude reduction in oxide levels.

10. Smaller powder particles with a greater surface area are more susceptible to reactive plasma spraying.

11. Ar-He plasma gas mixtures compared with Ar-H₂ gas mixtures denser coatings.

12.0 SUGGESTED FURTHER WORK

1. Greater improvements in reactive plasma spraying synthesis may be possible by increasing the level of reactive species in the plasma jet. This could be achieved by developing hydrocarbon-auxiliary gas mixtures or making a hopper capable of using a hydrocarbon carrier gas.
2. Although attempted without much success, blending of powder stock suggests a promising avenue for reactive plasma spraying. In particular the addition of reactive metals, like titanium. Moreover, the ability to closely control powder stock and reactive species would lead to other advanced materials synthesis, for example the production of functionally gradient materials.
3. Reactive design is paramount to the reactive plasma spraying process. Computational fluid dynamics modelling has proved a reliable method to examine phenomenon occurring inside the reactor section, albeit in two dimensions. Optimisation of reactor geometry and process parameters may benefit greatly from a concerted effort in terms of time and expertise. In summary future reactive plasma spraying research may do well to start the investigation with Computational Fluid Dynamics modelling. Particularly because software is now as available that can process high speed flows and reacting species simultaneously.

4. Other mechanical properties such as bond strength require investigating. For the MCrAlY alloy, the oxidation resistance appears not to have been affected by reactive plasma spraying, however, other properties such as thermal cycling are also very important and need to be investigated.

REFERENCES

1. Schoop, M U., Grünling, W H. Das Schoopsche Metallspritzverfahren. Franckh Verlag, Stuttgart, Germany, 1917.
2. PAWLOWSKI, L. The Science and Engineering of Thermal Spray Coatings. Wiley, 1995.
3. Yoshida, T. **The future of thermal plasma processing.** *Mat. Trans. JIM.*, 31(1), 1990, 1-11.
4. Mutasim, Z Z., Smith, R W. **Reactive plasma spray forming.** IN: Proc. 4th Nat. Thermal Spray Conf., Pittsburg, 4 - 10 May 1991, PA, USA, 273-279.
5. Planche, M., Fauchais, P., Coudert, J F., Betoule, O., Valletoux, H. **Comparison of D.DC plasma jet velocity distributions for different plasma gas mixtures: Ar-H₂, Ar-He, Ar-He-H₂.** IN: Berndt, C C., Sampath, S. (ed), Proc. 7th Nat. Thermal Spray Conf., 20-24 June 1994, Boston, Massachusetts, 349-354.
6. Okada, M., Marcuo, H. **New plasma spraying and its application.** *British Welding Journal*, 15(8), 1993, 371-386.
7. Notomi, A., Nod, M., Takeda, Y., Mizuta, S. **Correlation between particle velocity and diameter in plasma spraying of Ni-Cr alloy.** IN: Proc. Int. Thermal Spray Conf. & Exposition, 28 May-5 June 1992, Orlando, Florida, 349-353
8. Ranz, W. E., Marshall, W. R. *Chem. Eng. Progr.*, 48, 1952, 141-146 and 173-180.
9. BOENIG, H V. Fundamentals Of Plasma Chemistry. Pen, USA: Technomic Publishing Co., 1998.

10. Smith, R W. **Reactive plasma spray forming for advanced materials synthesis.** *PMI*, 25(1), 1993, 9-16.
11. Stephenson, D J., Nicholls, J R. *Reactive Plasma Spraying, A review.* Cranfield University, Department of Advanced Materials, WA/263V, 1994
12. Swank, W D., Fincke, J R., Haggard, D C. **Plasma/Particle interaction in subsonic argon/helium thermal plasma jets.** IN: Proc. 1993 Nat. Thermal Spray Conf., 7-11 June 1993, Anaheim, CA. 25-30
13. Kramarsic, R C., Muehlberger, E. **Methods to improve melting of large particles in plasma stream.** IN: Proc. Int. Thermal Spray Conf. & Exposition, 28 May-5 June 1992, Orlando, Florida, 63-68
14. PAWLOWSKI, L. The Science and Engineering of Thermal Spray Coatings. Wiley, 1995, 68-107.
15. Fukanuma, H., Ohmori, A. **Behaviour of molten droplets impinging on flat surfaces.** IN: Berndt, C C., Sampath, S. (ed), Proc. 7th Nat. Thermal Spray Conf., 20-24 June, 1994, Boston, Massachusetts, 563-568.
16. Liu, H., Lavernia, E J., Rangel, R H., Muehlberger, E., Sickinger, A. **Deformation and interaction behaviour of molten droplets impinging on a flat substrate in plasma spray process.** IN: Proc. of the Nat. Thermal Spray Conf., 7-11 June, 1993, Anaheim, CA.
17. Solonenko, O P., Ushio, M., Ohmori, A. **Comprehensive investigation of 'metal drop-substrate' interaction.** IN: Proc. Nat. Thermal Spray Conf., 7-11 June, 1993, Anaheim, CA. 55-60
18. JONES, H. Rapid Solidification of Metals and Alloys. PubThe Institution of Metallurgists.

19. Duwez, P., Willens, R. H., Klement, W. *J. Appl. Phys.*, 31, 1960, 1136.
20. PAWLOWSKI, L. The Science and Engineering of Thermal Spray Coatings. Wiley, 1995.
21. Namba, Y., Nakazato, H., Honma, K. **An ultrasound method to study the adhesion of thermally sprayed coatings**. IN: Proc. Int. Thermal Spray Conf. & Exposition, 28 May-5 June, 1992, Orlando, Florida, 241-245.
22. HUTCHINGS, L. M. TRIBOLOGY-Friction and Wear of Engineering Materials. Edward Arnold, 1992.
23. Hartfield-Wünsch, S. E., Tung, S. C. **The effect of microstructure on the wear behavior of thermal spray coatings**. IN: Proc. 7th Nat. Thermal Spray Conf., 20-24 June, 1994, Boston, Massachusetts, 19-24.
24. FESSENDEN, K. S., Zurecki, Z., Slavin, T. P. Thermal Spray Coatings: Properties, Processes and Applications. Ohio: ASM Metals Park, 1991, 81.
25. Sexsmith, M., Troczynski, T. **The variations in coating properties across a spray pattern**. IN: Proc. 7th Nat. Thermal Spray Conf., 20-24 June, 1994, Boston, Massachusetts, 751-757.
26. Tsunekawa, Y., Okumiya, M., Kobayashi, T., Okuda, M., Fukumoto, M. **Chromium-Nitride in situ composites with a compositional gradient formed by reactive DC plasma spraying**. *Journal of Thermal Spray Technology*, 5(2), 1996, 139-144.
27. McKechnie, T. N., Richardson, E. H., Watson, R. D. **Continuous spray forming of functionally gradient materials**. IN: Proc. 8th

Nat. Thermal Spray Conf., 11-15 September, 1995, Houston, Texas, 737-742.

28. Oki, S., Gohda, S., Lugscheider, E., Jokiel, P., Smith, R W. **Reactive plasma spraying of high nitrogen stainless steel.** IN: Proc. Int. Thermal Spray Conf., May, 1995, Kobe, 561-564.
29. Tsantrizos, P G. **The reactive spray forming production of titanium aluminides in the tail flame of a D.C. plasma torch.** IN: Proc. Int. Thermal Spray Conf. & Exposition, 28 May-5 June, 1992, Orlando, Florida, USA, 195-198.
30. Entezarian, M., Shanker, K., Tsantrizos, P. G., Allaire, F., Immarigeon, J. P., Drew, R. A. L. **Reactive plasma spraying of Al-Ti alloys.** IN: Proc. 8th Nat. Spray Conf., 11-15 September, 1995, Houston, Texas, 749-754.
31. Smith, R W., Lugscheider, E., Jokiel, P., Mueller, U., Merz, J., Wilbert, M. **Synthesis of composite materials by reactive plasma Spray processing.** IN: Proc. 1993 Nat. Thermal Spray Conf., 7-11 June, 1993, Anaheim, CA, 439-444.
32. Pehlivan, N Y., Inal, O T. **Ion nitriding.** IN: Spalink, T. (ed), Proc. Int. Conf. on Ion Nitriding, ASM International, 1986, 179.
33. Inal, O T., Robino, C V. *Thin solid film*, 95, 1992, 195.
34. Eckardt, T., Malléner, W., Stöver, D. **Reactive plasma spraying in controlled nitrogen atmosphere.** Proc. 7th Nat. Thermal Spray Conf., 20-24 June, Boston, Massachusetts, 515-519.
35. Liang, X., Lavernia, E J., Wolfenstine, J., Sickinger, A. **Microstructure evolution during reactive plasma spraying of MoSi₂ with methane.** *Journal of Thermal Spray Technology*, 4(3), 1995, 252-260.

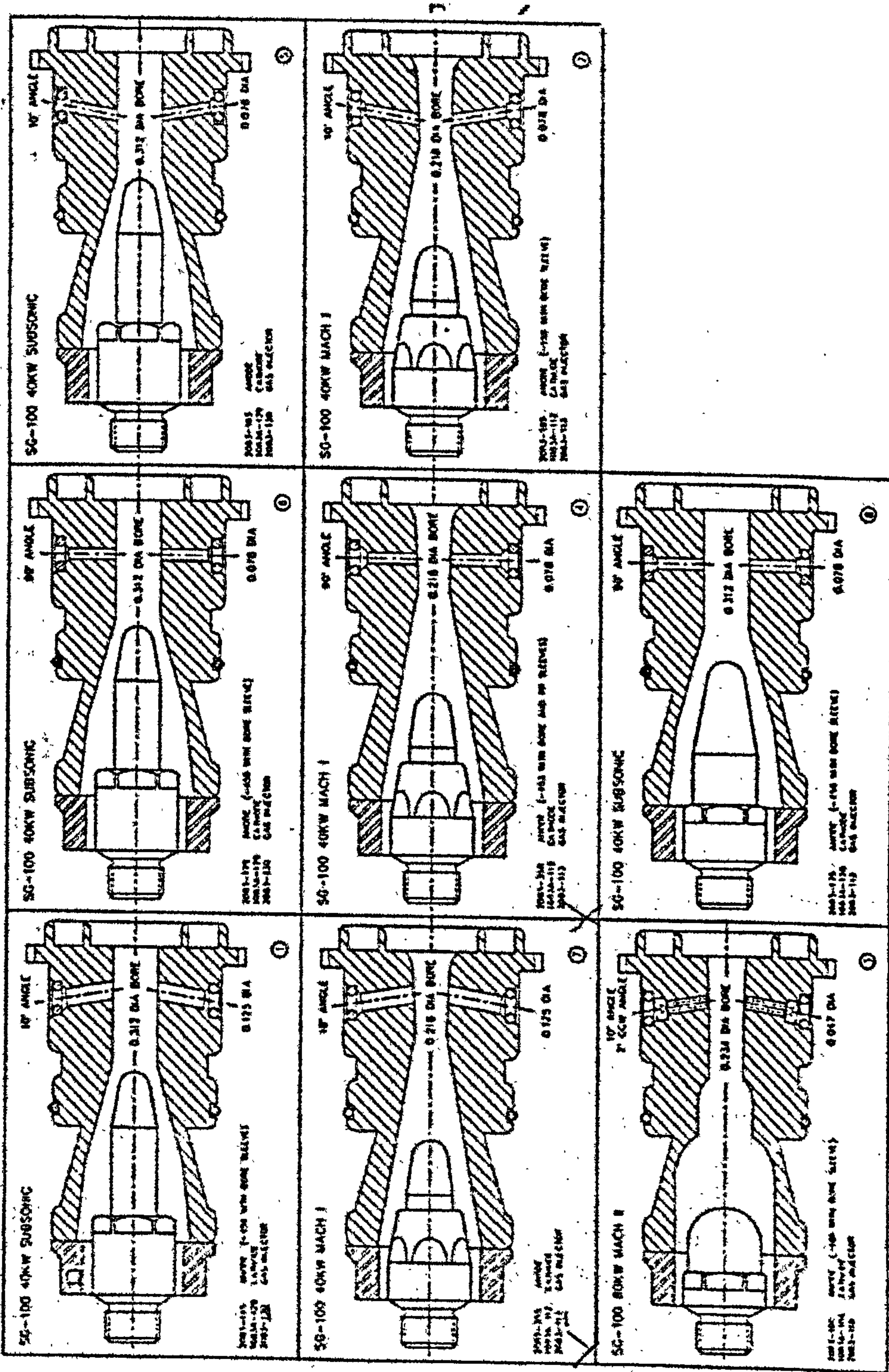
36. Arsenault, B., Champagne, D., Dupe, P. Lambert IN: Proc. 3rd Nat. Thermal Spray Conf., ASM International, 1990, Long Beach, USA,
37. ZHU, H., Lau, Y C., Pfender, E. Material Science & Engineering, Elsevier, A 139, 1991, 252.
38. Matsumoto, S., Kobayashi, T., Hino, M. IN: Proc. 8th Int. Symp. on Plasma Chemistry, 4, 1987, 2458.
39. Kobashi, K., Nishimura, K., Kawate, Y., Horiuchi, T. IN: Proc. 8th Int. Symp. on Plasma Chemistry, 4, 1987, 2475.
40. Muller, U., Lugscheider, E. IN: Proc. 3rd Int. Conf. on the New Diamond Science and Technology, September, 1992, Heidelberg, Germany, COMST.
41. Tsai, J., Nelson, W., Gerbereich, J., Herberlein, Pfender, E. IN: Proc. 3rd Int. Conf. on the New Diamond Science and Technology, September, 1992, Heidelberg, Germany, COMST
42. Sahoo, P., Goward, G W. **The suitability and application of MCrAlY coatings under various operating conditions.** IN: Proc. 8th Nat. Thermal Spray Conf., 11-15 September, 1995, Houston, Texas, 539-544
43. Bannister, R L., Cheruvu, N S., Little, D A., McQuiggan, G. **Development requirements for an advanced gas turbine System.** IN: The International Gas Turbine and Aeroengine Congress and Exposition, June 13-16, 1994, The Hague, Netherlands, Paper 94 GT-388.
44. Petit, F S., Goward, G W. **High temperature corrosion and use of coatings for protection.** Metallurgical Treatises, Tien, J K., Elliott, J F. (eds), 1983, 603-619.

45. Srinivasan, V. **High temperature corrosion and erosion in gas turbine engines, where do we stand?** *JOM*, December, 1994, 34.
46. Schilke, P W., Foster, A D., Pepe, J J., Beltran, A M. **Advanced materials propel progress in land-based gas turbines.** Adv. Mater. Proc, April, 1992, 22-30.
47. Tien, J K., Petit, F S. Met. Trans., 3, 1972, 1587-1599.
48. Luthra, K L., Electrochem, J.. Soc. 132, 1985, 1293.
49. Rapp, R A., Zhang, Y S., Hot corrosion of materials, fundamental studies. *JOM*, December, 1994, 47-55.
50. Bornstein, N S., DeCrescente, M A. Met. Trans, 2, 1971, 2875.
51. PETIT, F S., Giggins, C S. Hot corrosion in "superalloys" II. Sims, C T., Stoloff, N S., Hagel, W C. (eds), John Wiley & Sons, 1987, 327-358.
52. William Rowland Ltd. 9, Meadow St., Sheffield ,S3 7BL.
53. Alloy Metals Inc., 1972 Meijer Drive, PO Box 84310, Troy, Michigan, USA.
54. Sigma-Aldrich Company Ltd., Gillingham, Dorset, SP8 4XT.
55. IncoTest, Wiggan Works, Holmer Rd., Hereford, HR4 9SL, (NAMAS Testing Laboratory No. 0281)
56. PETZOW, Metallographic etching. Ohio: American Society for Metals, 1978, 78.
57. Murphy, A B. **The Influence of demixing on the properties of a free-burning arc.** *Appl. Phys. Lett.*, 69(3), 1996, 328-330.
58. Murphy, A B. **Demixing in free-burning arcs.** *Physical Review E*, 55(5), 1997, 1-22
59. Murphy, A B. **Transport coefficients of helium and argon-helium plasmas.** *IEEE Transactions on Plasma Science*, 1997

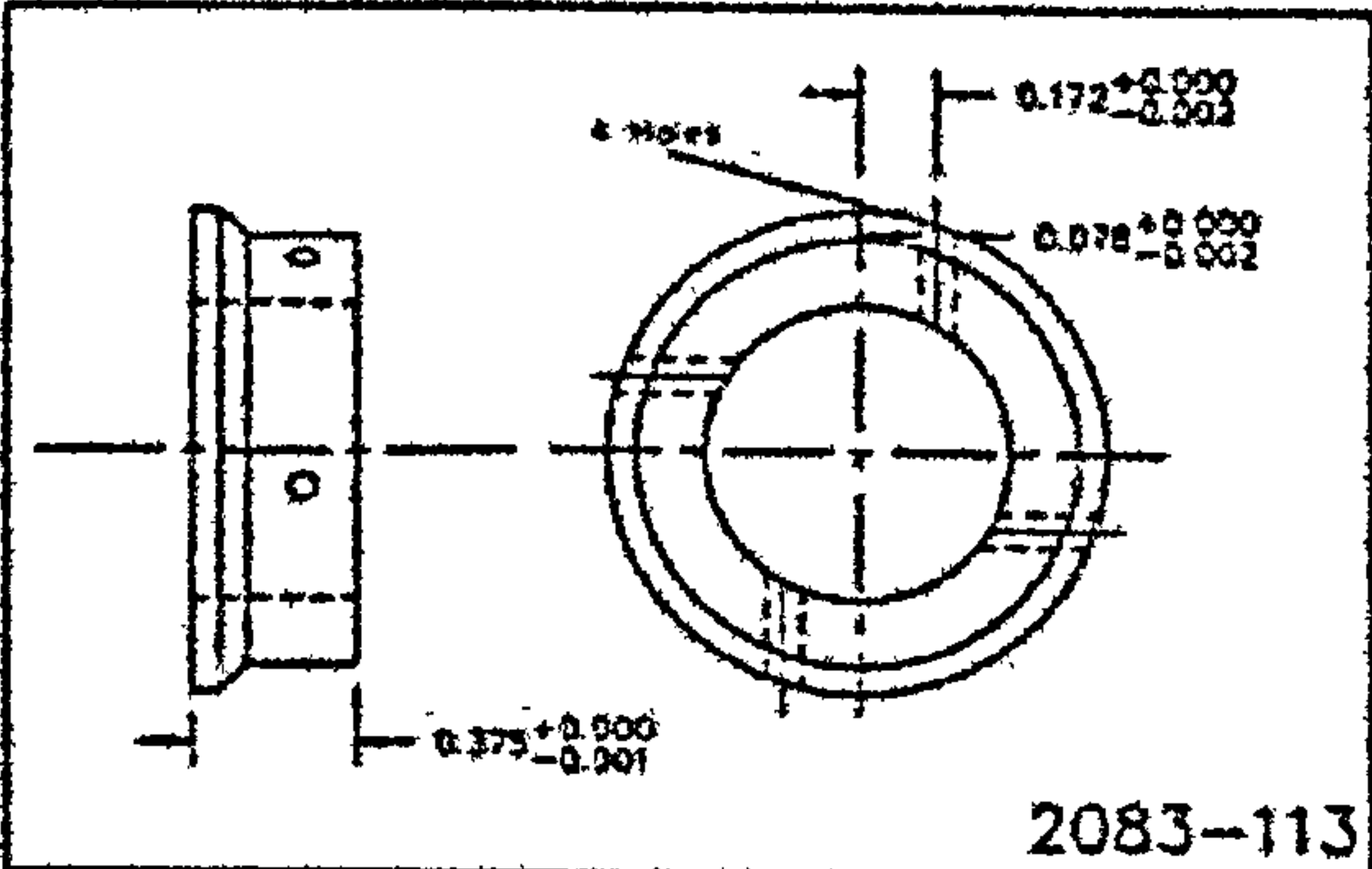
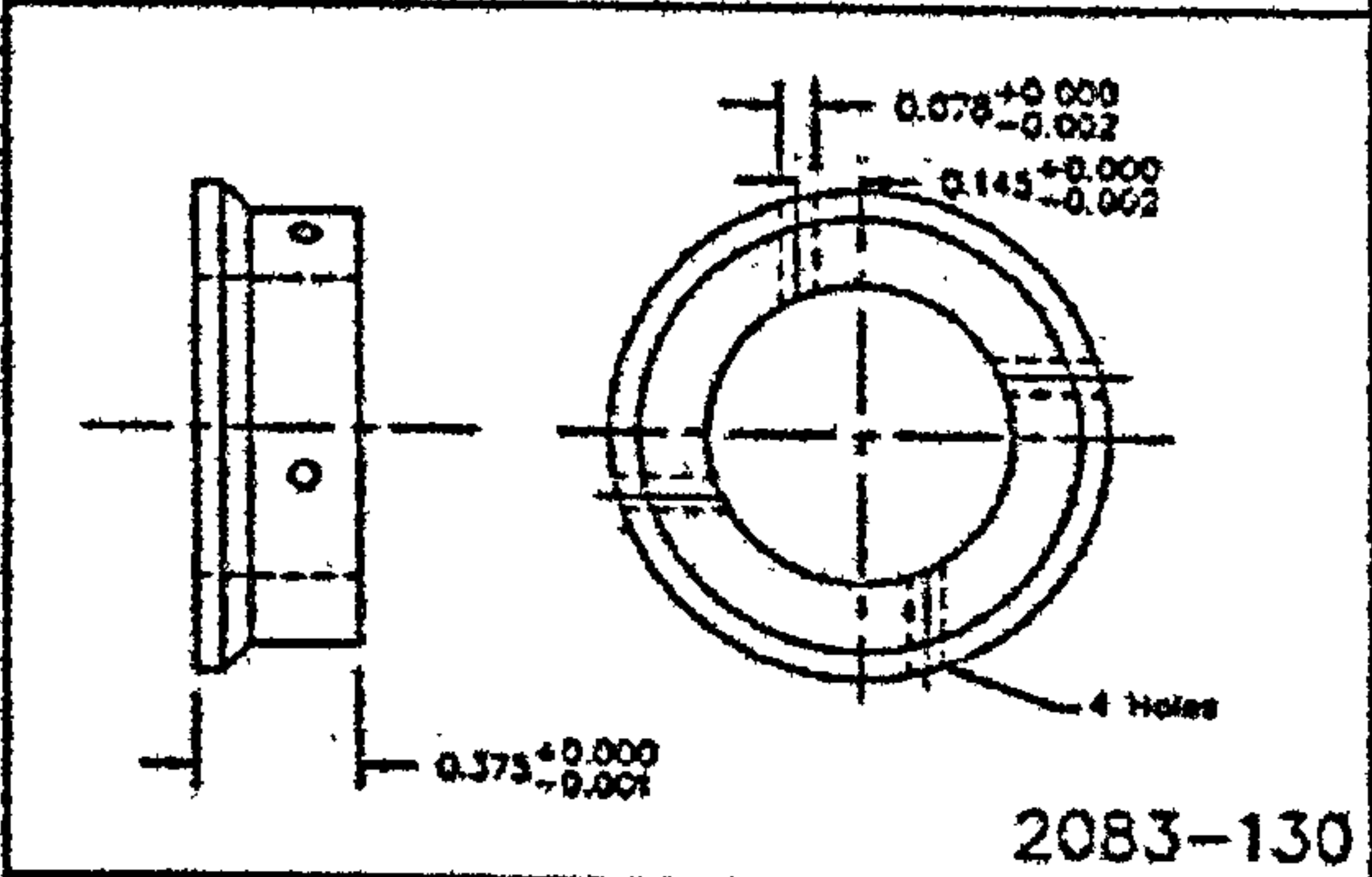
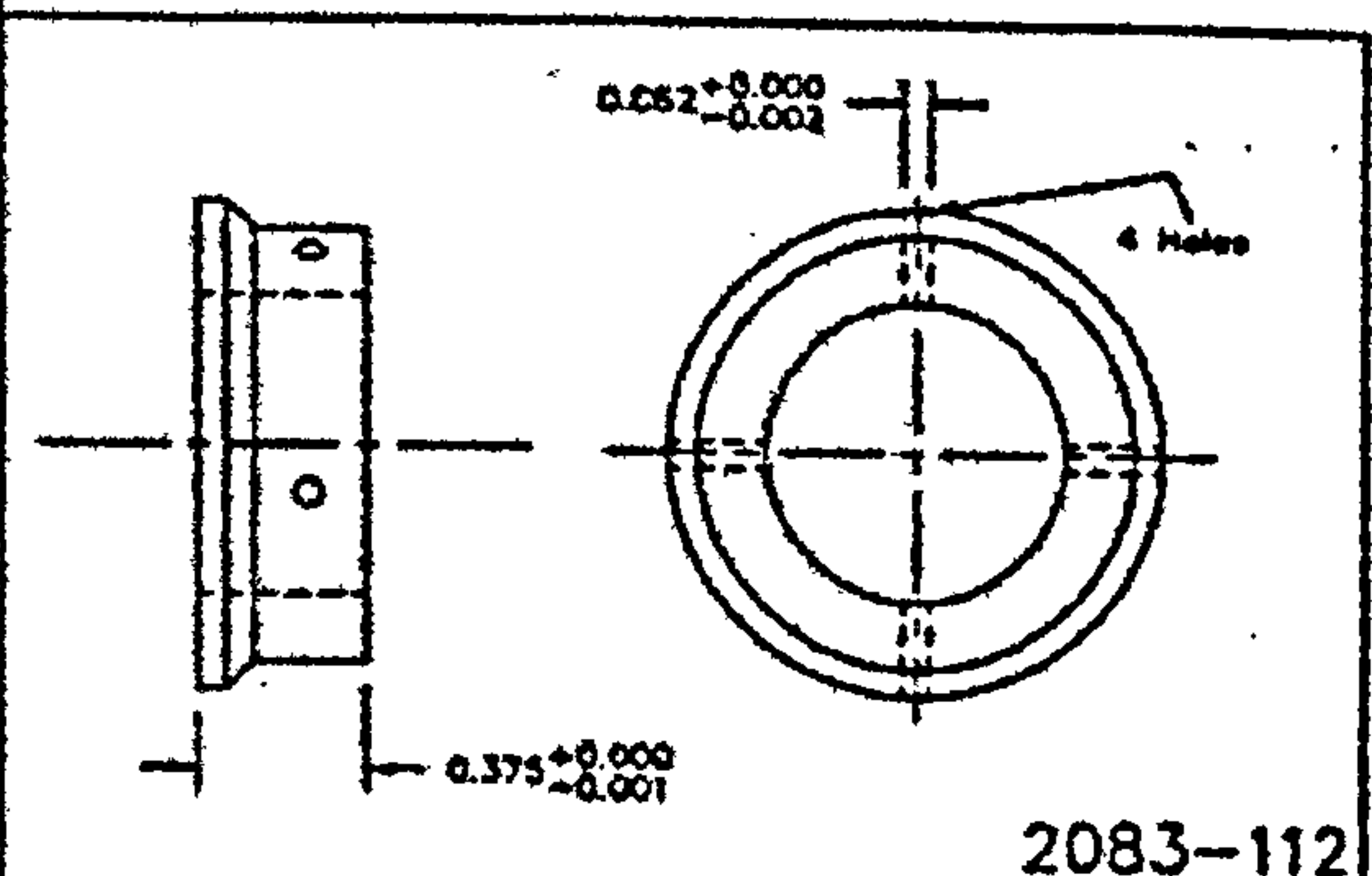
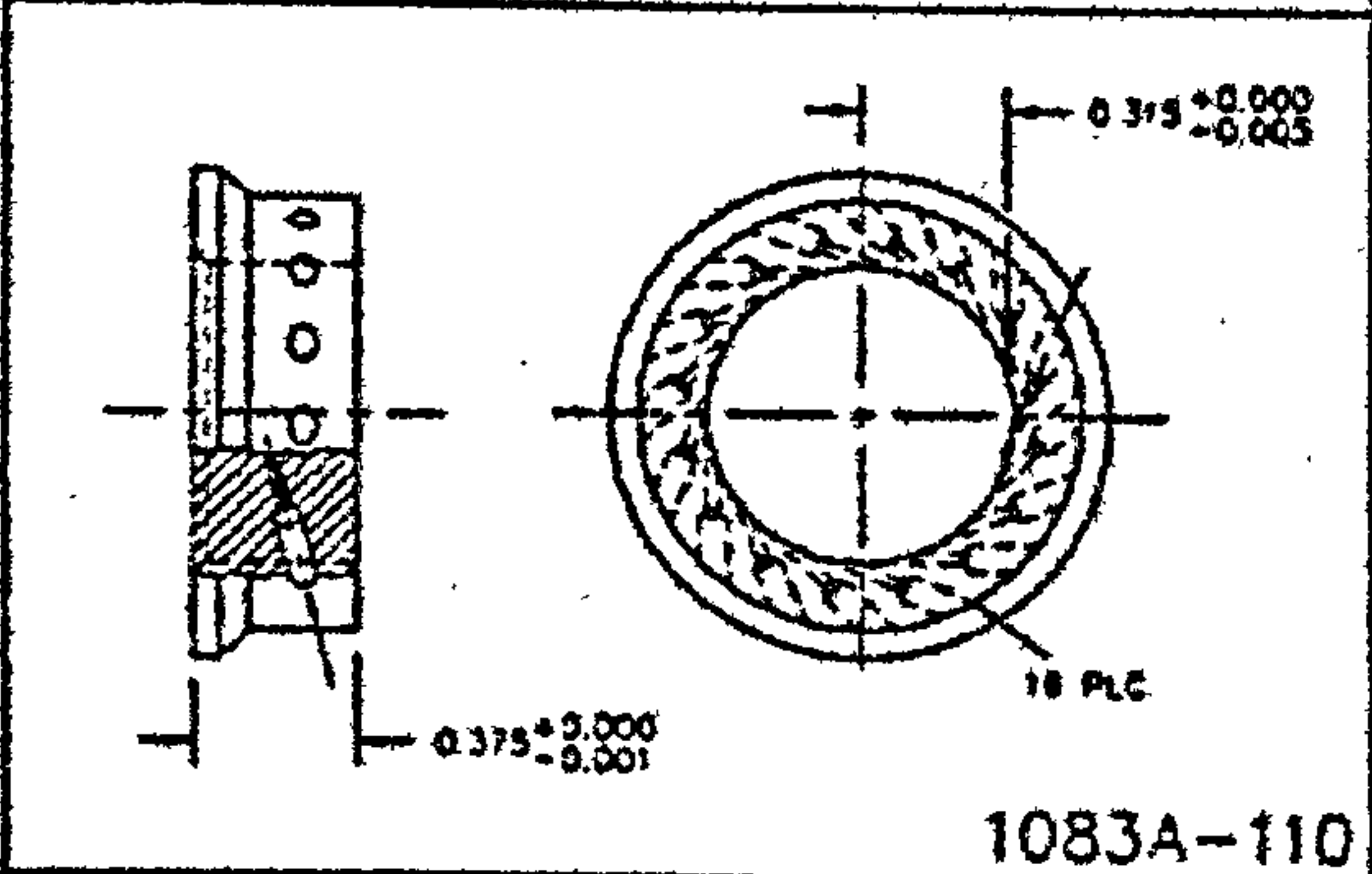
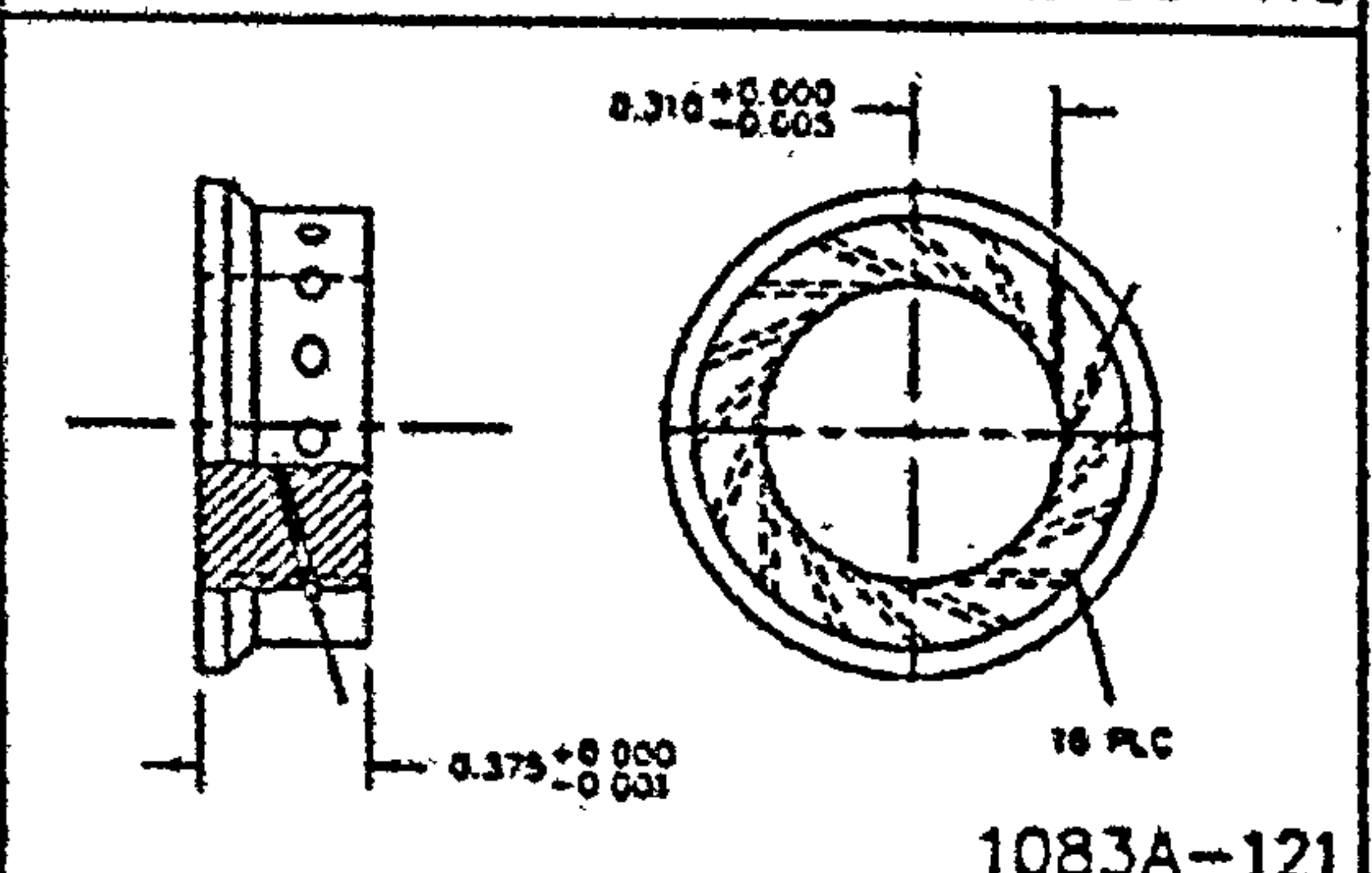
60. Pfender E., Chang C H. **Plasma spray jets and plasma-particulate interaction: modelling and experiments.** IN: Proc. 15th Int. Thermal Spray Conf., 25-29 May, 1998, Nice, France, 315-327.
61. Pfender, E., **Thin Solid Films.** 238, 1994, 228-241.
62. Pfender, E., Fincke J., Spores. R. **Plasma Chemistry. Plasma Process.**, 11(4), 1991, 529
63. Schefer, R W., Hartmann, V., Dibble, R W., **AIAA J.**, 25, 1318 (1997)
64. Jin J H., Stephenson, D J. **The sliding wear behaviour of reactively hot pressed nickel aluminides.** *WEAR* 217, 1998, 200-207.
65. Private communication: Sulzer Metco U.K. Ltd, Westmead, Farnborough, GU14 7LP.
66. Private communication: BOC Gases, 24 Deer Park Rd., Morden, London, SW9 3UF
67. GRAINGER, Stan. Engineering coatings – design and application. Cambridge: Abington Publishing, 1989.
68. Al-Sabouni, O., Stephenson, D J., Nicholls, J R., Creffield, G. **Reactive Plasma Spraying of a 80:20 Ni/Cr and MCrAlY Powders with Hydrocarbon Reactive Gases.** IN: Coddet, C. (ed), Proc. 15th Int. Thermal Spray Conf., 25-29 May, 1998, Nice, France, 1315-1320.

APPENDIX A

Anode-Cathode configurations



Gas mixing units



APPENDIX B

80:20 Nickel-Chrome Alloys

AI-1015

DESCRIPTION	AI-1015 IS A GAS ATOMISED, NICKELCHROME FOR FLAME SPRAY AND PLASMA SPRAY APPLICATIONS. THE PARTICLE SHAPE IS SPHERICAL	
APPLICATION	DENSE COATING RESISTS OXIDATION AND CORROSION RESISTS HEAT AND SCALING OF STEELS GOOD MACHINABILITY DIMENSIONAL RESTORATION EXCELLENT BOND PROPERTIES AND DENSITY	
SPECIFICATIONS	PWA 1315 GE B50TF40 CLASS A MSRR 9507/8 BMS 10-67 TYPE 6 MIL-P-83348 COMP. B TYPE I CL. 2 MIL-P-85856/8 UNS NO6003	
CHEMISTRY	C	.25 MAX
	Mn	2.5 MAX
	Si	1.5 MAX
	Fe	1.00 MAX
	Cr	18-21
	Ni	76-80

AI-1017

DESCRIPTION AI-1015 IS A GAS ATOMISED, NICKELCHROME FOR FLAME SPRAY AND PLASMA SPRAY APPLICATIONS. THE PARTICLE SHAPE IS SPHERICAL

APPLICATION DENSE, CLEAN BRIGHT COATINGS
GOOD FOR HOT ATMOSPHERES TO 1800 °F
RESISTS OXIDATION AND CORROSION GASES
GOOD FOR DIMENSIONAL RESTORATION
EXCELLENT BOND PROPERTIES AND DENSITY

SPECIFICATIONS PWA 1317
GE B50TF40 CLASS B
MIL-P-83348 COMP. B TYPE I CL. 1
MIL-P-85856/7
UNS NO6003

CHEMISTRY

C	.25 MAX
Mn	2.5 MAX
Si	1.5 MAX
Fe	1.00 MAX
Cr	18-21
Ni	76-80

MCrAlY Alloys

AMDRY MCRAlY	NOMINAL POWDER COMPOSITION						
	Ni	Co	Fe	Cr	Al	Ti	Y
961	Rem			17	8		0.5
962	Rem			22	10		1.0
963	Rem			23	8		0.5
964	Rem			31	11		0.8
970			Rem	24	8		0.5
995	32	Rem		21	8		0.5
996	10	Rem		25	7	5	0.6
S57	10	Rem		25	3	5	0.6
997	Rem	23		20	8.5	4	0.8

TABLE I

APPENDIX C

FLUENT

Version: 2d, coupled exp, spe3, rngke (2d, coupled explicit, 3 species, RNG k-epsilon)
Release: 5.0.2
Title:

Models

Model	Settings
Space	2D
Time	Steady
Viscous	RNG k-epsilon turbulence model
Wall Treatment	Non-Equilibrium Wall Functions
RNG Differential Viscosity Model	Disabled
RNG Swirl Dominated Flow Option	Disabled
Heat Transfer	Enabled
Melting-Freezing	Disabled
Radiation	None
Species Transport	Non-Reacting (3 species)
Coupled Dispersed Phase	Disabled
Pollutants	Disabled
Soot	Disabled

Boundary Conditions

Zones

name	id	type
fluid-1	1	fluid
fluid-2	2	fluid
interior-1	4	interior
interior-2	5	interior
wall-1	6	wall
pressure-outlet-1	7	pressure-outlet
interior-8	8	interior
pressure-inlet-2	9	pressure-inlet
pressure-inlet-1	10	pressure-inlet
wall-1:003	3	wall

Boundary Conditions

fluid-1

Condition	Value
Material Name	mixture-template
Specify source terms?	no
Source Terms	()
Motion Type	0
X-Velocity Of Zone	0
Y-Velocity Of Zone	0
Rotation speed	0
X-Origin of Rotation-Axis	0
Y-Origin of Rotation-Axis	0
Laminar zone?	no
Porous zone?	no

X-Component of Direction-1 Vector	1
Y-Component of Direction-1 Vector	0
Direction-1 Viscous Resistance	0
Direction-2 Viscous Resistance	0
Direction-3 Viscous Resistance	0
Direction-1 Inertial Resistance	0
Direction-2 Inertial Resistance	0
Direction-3 Inertial Resistance	0
C0 Coefficient for Power-Law	0
C1 Coefficient for Power-Law	0
Porosity	1
Solid Material Name	aluminum

fluid-2

Condition	Value
-----	-----
Material Name	mixture-template
Specify source terms?	no
Source Terms	()
Motion Type	0
X-Velocity Of Zone	0
Y-Velocity Of Zone	0
Rotation speed	0
X-Origin of Rotation-Axis	0
Y-Origin of Rotation-Axis	0
Laminar zone?	no
Porous zone?	no
X-Component of Direction-1 Vector	1
Y-Component of Direction-1 Vector	0
Direction-1 Viscous Resistance	0
Direction-2 Viscous Resistance	0
Direction-3 Viscous Resistance	0
Direction-1 Inertial Resistance	0
Direction-2 Inertial Resistance	0
Direction-3 Inertial Resistance	0
C0 Coefficient for Power-Law	0
C1 Coefficient for Power-Law	0
Porosity	1
Solid Material Name	aluminum

interior-1

Condition	Value
-----	-----

interior-2

Condition	Value
-----	-----

wall-1

Condition	Value
-----	-----
Wall Thickness	0
Heat Generation Rate	0
Material Name	aluminum
Thermal BC Type	1
Temperature	300
Heat Flux	0
Convective Heat Transfer Coefficient	0
Free Stream Temperature	0

Apply a velocity to this wall?	no
Define wall motion relative to adjacent cell zone?	yes
Apply a rotational velocity to this wall?	no
Velocity Magnitude	0
X-Component of Wall Translation	1
Y-Component of Wall Translation	0
External Emissivity	1
External Radiation Temperature	300
Wall Roughness Height	0
Wall Roughness Constant	0.5
Discrete Phase BC Type	2
Normal	
((polynomial angle 1))	
Tangent	
((polynomial angle 1))	
Impact Angle Function	
((polynomial angle 1))	(0)
(((constant . 0) (profile)))	
Rotation Speed	0
X-Position of Rotation-Axis Origin	0
Y-Position of Rotation-Axis Origin	0
Specify shear stress?	no
X-component of shear stress	0
Y-component of shear stress	0
Swirl component of shear stress	0

pressure-outlet-1

Condition	Value
Gauge Pressure	101325
Backflow Total Temperature	300
Turbulence Specification Method	1
Backflow Turb. Kinetic Energy	1
Backflow Turb. Dissipation Rate	1
Backflow Turbulence intensity	0.0099999998
Backflow Turbulence Length Scale	0.01
Backflow Turbulent Viscosity Ratio	10
Backflow Hydraulic Diameter	1
Backflow	(((constant . 0.67)
(profile)) ((constant . 0.33) (profile)))	
Discrete Phase BC Type	4

interior-8

Condition	Value

pressure-inlet-2

Condition	Value
Gauge Total Pressure	101326
Supersonic/Initial Gauge Pressure	101325
Total Temperature	300
Direction Specification Method	0
X-Component of Flow Direction	0
Y-Component of Flow Direction	-1
X-Component of Axis Direction	1
Y-Component of Axis Direction	0
Z-Component of Axis Direction	0

X-Coordinate of Axis Origin	0
Y-Coordinate of Axis Origin	0
Z-Coordinate of Axis Origin	0
Turbulence Specification Method	1
Turb. Kinetic Energy	1
Turb. Dissipation Rate	1
Turbulence intensity	0.0099999998
Turbulence Length Scale	0.01
Turbulent Viscosity Ratio	10
Hydraulic Diameter	1
	((constant . 0)
(profile)) ((constant . 0) (profile))	
Discrete Phase BC Type	4

pressure-inlet-1

Condition	Value
Gauge Total Pressure	106500
Supersonic/Initial Gauge Pressure	101325
Total Temperature	7700
Direction Specification Method	0
X-Component of Flow Direction	1
Y-Component of Flow Direction	0
X-Component of Axis Direction	1
Y-Component of Axis Direction	0
Z-Component of Axis Direction	0
X-Coordinate of Axis Origin	0
Y-Coordinate of Axis Origin	0
Z-Coordinate of Axis Origin	0
Turbulence Specification Method	1
Turb. Kinetic Energy	1
Turb. Dissipation Rate	1
Turbulence intensity	0.0099999998
Turbulence Length Scale	0.01
Turbulent Viscosity Ratio	10
Hydraulic Diameter	1
	((constant . 0.67)
(profile)) ((constant . 0.33) (profile))	
Discrete Phase BC Type	4

wall-1:003

Condition	Value
Wall Thickness	0
Heat Generation Rate	0
Material Name	
aluminum	
Thermal BC Type	1
Temperature	300
Heat Flux	0
Convective Heat Transfer Coefficient	0
Free Stream Temperature	0
Apply a velocity to this wall?	no
Define wall motion relative to adjacent cell zone?	yes
Apply a rotational velocity to this wall?	no
Velocity Magnitude	0
X-Component of Wall Translation	1
Y-Component of Wall Translation	0
External Emissivity	1
External Radiation Temperature	300
Wall Roughness Height	0

Wall Roughness Constant	0.5
Discrete Phase BC Type	2
Normal	
((polynomial angle 1))	
Tangent	
((polynomial angle 1))	
Impact Angle Function	
((polynomial angle 1))	(0)
(((constant . 0) (profile)))	
Rotation Speed	0
X-Position of Rotation-Axis Origin	0
Y-Position of Rotation-Axis Origin	0
Specify shear stress?	no
X-component of shear stress	0
Y-component of shear stress	0
Swirl component of shear stress	0

APPENDIX D

Simple theory of sliding wear: The Archard Wear Equation

When two surfaces in contact slide over each other, one or both of the surfaces will suffer wear. A simple theoretical analysis of this type of wear due originally to Holm and Archard, is given here. By virtue of its simplicity, it highlights the main variables which influence sliding wear, by means of the wear coefficient K , which is valuable and widely used. The model was originally derived for metals but some insight into wear in other material classes can also be gained.

The starting point for the model is the assumption that contact between the two surfaces will occur where asperities touch, and the true area of contact will be equal to the sum of the individual asperity contact areas. This area will be closely proportional to the normal load, and it can be assumed that under most conditions, for metals at least, the local deformation of the asperities will be plastic. Figure 137 shows a schematic diagram of the evolution of a single contact between two asperities as they pass over each other, the asperities are assumed to be circular in plan view with a radius a . Where the two asperities completely cover each other (fig. 137(c)) the normal load supported, δW , will be given by:

$$\delta W = P \pi a^2 \quad [\text{Eqn. D.1}]$$

where P is the yield pressure for the plastically deforming asperity (P will be approximately equal to the materials indentation hardness). As sliding proceeds, the two surfaces become displaced and the load originally born

by the asperity will be transferred to other asperity junctions. Continuous sliding leads to the continuous formation and destruction of individual asperity junctions. Wear is associated with the detachment of fragments of material from the asperities, and the volume of each wear fragment will depend on the size of asperity junction from which it originated. It is assumed that the volume of material removed by wear, δV , will be proportional to the cube of the contact dimension a . If the detached fragment is assumed to be hemispherical in shape then:

$$\delta V = 2\pi a^3/3 \quad [\text{Eqn. D.2}]$$

However, not all asperity contacts will give rise to wear particles. Let it be assumed that a proportion κ does so. Therefore, the average volume of material δQ worn away per unit sliding distance due to sliding of one pair of asperities over a distance $2a$ is given by:

$$\delta Q = \kappa \delta V / 2a = \kappa \pi a^2 / 3 \quad [\text{Eqn. D.3}]$$

The overall wear rate Q arising from all the asperity contacts is the sum of the contributions over the whole real area of contact:

$$Q = \sum \delta Q = \kappa / 3 \sum \pi a^2 \quad [\text{Eqn. D.4}]$$

The total normal load W is given by:

$$W = \sum \delta W = P \sum \pi a^2 \quad [\text{Eqn. D.5}]$$

and hence

$$Q = \kappa W / 3P \quad [\text{Eqn. D.6}]$$

For the purposes of convenience the factor of $1/3$ is combined into the constant of proportionality, by putting $K = \kappa/3$ and to also assume that P (yield pressure) is equal to H (indentation hardness). The equation can then be re-written:

$$Q = KW / H \quad [\text{Eqn. D.7}]$$

This equation, relating the volume worn per unit sliding distance, Q , to the macroscopic quantities W , the normal load, and H , the hardness of the softer surface, is often called the *Archard wear equation*. The constant K , usually termed the wear coefficient or sometimes the coefficient of wear, is dimensionless and always less than unity.

However, for engineering applications the quantity K/H is often more useful. This is given the symbol k and called the dimensional wear coefficient. k is usually quoted in units of $\text{mm}^3 (\text{Nm})^{-1}$, and represents the volume of material removed by wear (in mm^3), per unit distance slid (in metres), per unit normal load on the contact (in newtons).

APPENDIX E

DESIGN FOR THERMALLY SPRAYED COATINGS^[2,67]

Component Shape

Consideration must be given to the shape of the component to be sprayed. The surfaces to be coated must be accessible to the spray gun chosen for the process and the component must provide adequate routes for dispersion of the hot spray gases and overspray. Additionally, it must be possible to direct the spray at 90° to the surface, although sometimes this can be reduced to an angle of 45° at the expense of increased overspray and some loss of adhesion to the substrate.

Recessed areas of any type may produce a problem with depth/width ratio, especially if there is no through passage to provide adequate ventilation for gas and overspray. Attachments or modifications are available for some spraying processes that permit spraying inside recesses.

If the recess performs no practical function it may be easier to seal it off with a welded-in plug which after grinding flush leaves a smooth, clean, external surface to be sprayed.

Surface Profile Details

Fabrications

Thermal spraying yields considerably better results when spraying is performed onto smooth (macro-scale) surfaces with very few discontinuities. For instance, unsealed surfaces and joints can harbour dirt and moisture which can give rise to local defects in the sprayed coating and sites of premature failure

Precision Components

If the whole surface is not to be covered then normal practice requires the sprayed deposit to finish flush with the parent material of the workpiece. This involves the creation of a recess to accommodate the required finish thickness of the deposit and the provision of a finishing allowance on adjacent areas. Bearing in mind the low heat input of most thermal spraying processes and the low risk of distortion, this finishing allowance can normally be quite small, typically $<0.5\text{mm}$ per face. The important feature of the recess is that it should be provided with the edges chamfered full depth at an included angle with the base of the recess not more than 45° although a lesser angle would be better.

When coatings reach a corner on the component the corner should be provided with a radius or chamfer. A heavy local build up of deposit must be avoided as this encourages additional stress and a possible risk of the coating lifting. In general sharp edges should be avoided.

Deposit Thickness

Factors to be considered when using different deposit thickness' vary for new and reclamation work. For new work it is best to apply the minimum amount of deposit necessary bearing in mind any regrinding work that might have been done before recoating. For repair work, thicker deposits may be necessary. Excessive wear can often be made good by spraying a first coating of a separate material and then finishing with a top coating - this is because soft materials applied by low energy processes can be applied in thicker coatings having lower residual stress than hard materials, particularly if applied by high energy techniques.

Coating Production

Surface Preparation

Surface preparation is critical for thermal spraying in order to achieve high and consistent bond strength between the coating and substrate. The following operations are typical.

- Degreasing
- Masking prior to surface roughening
- Surface roughening
- Masking prior to thermal spraying

Degreasing can be performed using common organic solvents e.g. methyl alcohol, acetone or sometimes vapour degreasing - especially for larger pieces.

Masking prior to roughening is generally performed using masks different to those used during thermal spraying. Typical masks used include cloths, rubber or plastics.

The roughness of a sample is usually described by the parameter Ra (sometimes called AA or CLA) and is defined as:

$$Ra = \frac{\int_0^1 |y| dx}{1} \quad \text{[Eqn. E.1]}$$

In some applications it is important to know the values of the greatest irregularities on the surface, where this is the case the parameter $R_{\max}$ is used.

There are several methods to roughen the surface of the material to be sprayed, these include macro-roughening, chemical etching and grit blasting. Grit blasting is by far the most common technique.

Grit Blasting

The grits mostly used are:

- Metal Grits e.g. steel or cast-iron
- Spherical metal grit (shot), as above but spherical in shape
- Ceramic grit e.g. silica, alumina (electro-corund) or silicon carbide.

The size of the grit used depends on the thickness of the sprayed piece (finer grit is required if the piece is thin) and on the desired roughness of the sprayed coating (finer grit results in a finer surface after blasting). Furthermore smaller sized particles permit blasting of a larger area per hour, larger particles provide more rapid removal of material and as mentioned earlier give a rougher surface finish.

Silica sand is usually used as a fine grit for the smoothest finishes, alumina grit is used as a coarse grit. Another important point is the size of the grit gradually decreases in size with prolonged use, the grit must be frequently changed depending on the pressure of the blast and the hardness of the blast piece. The action of abrasive blasting significantly increases the surface area of the workpiece and in its clean and abraded state it is very active and oxidises readily, it should therefore be sprayed as soon as possible after the blasting operation and never handled directly by the fingers, to prevent transfer of dirt and grease to the surface. Any contamination can impair adhesion of the coating. The abraded area should always extend beyond the area to be coated to prevent the risk of overspray lifting and the bond failure propagating beneath the coated area.

Abrasive blasting can lead to distortion of thin components and a reduction in grit size, impact velocity may not always overcome this. Some materials are so hard that grit blasting may not roughen the substrate surface sufficiently to allow good coating deposition, under these circumstances a preliminary layer of a bond coat may be applied.

Bond coats have several functions, two examples, allowing coatings with very different coefficients of thermal expansion from their substrates to be used in conjunction, or to act as a barrier from oxidation and corrosion at elevated temperatures. Bond coatings will be described in more detail later on. Furthermore a bond coat can be used to overcome the problems described in the above paragraph.

Nickel-Aluminium is used for a large number of applications as it has better high temperature properties and low dependence on operator technique. Substrate materials include most steels (even nitriding steels, although nitrided and carburised surfaces are best removed before spraying), nickel, nickel-chrome alloys, magnesium, aluminium and titanium. Coating thickness' are generally specified at 75-125µm. It is sometimes necessary to preheat the workpiece to around 90°C for best results.

Molybdenum is widely used as a bond coat on all common steels, chrome-nickel alloys, cast steels, magnesium, most aluminium steels, monel, nickel and cast iron but does not bond well to copper, brass, bronze, chrome plate, nitrided surfaces or electroless nickel. Coating thickness' are typically in the range of 30-80µm. The work must be preheated to a surface temperature of around 90°C to avoid condensation, and further heating to 175°-260°C improves the bond. In general, the substrate should be as rough as is possible this is achieved using as coarse a grit as possible and blasting at an angle of 90° to the substrate. Blasting for longer times does not necessarily lead to rougher surfaces.

Masking Prior to Spraying

With thermal spraying processes, the use of a mask prevents deposition on undesired surfaces. The mask should be positioned above the surface to be sprayed, if placed directly on the surface the coating will link the job and the mask, removal is then likely to damage the coating. Masks are generally made from metallic or glass fibre tapes which are supported rigidly to prevent the force of the spray from dislodging them. There are commercially available liquid compounds, e.g. Metco Anti Bond TM which prevent the adhesion of hot particles during spraying. Holes and slots in the sprayed piece can be protected with Teflon or metal inserts.

Post Spray Treatments

The as-sprayed coatings are seldom ready for use. In most practical applications they have to be ground and polished to get the required surface finish. Heat treatment is sometimes necessary to change the coatings phase composition, to decrease porosity or to improve another coatings property. Impregnation or sealing is sometimes necessary for electrical applications or to prevent fluid penetrating the coating which may accelerate corrosion or even reach the substrate where corrosion would cause the coating to lift.

Heat Treatment

Furnace treatment is the most common heat treatment applied to sprayed coatings. Laser treatment and HIPing are less frequent but are used in specialised applications.

Furnace Treatment (Metals and Alloys)

The furnace treatment of metal and alloy coatings may be applied to enhance the adhesion of the coatings to the substrate e.g. bond coatings on turbine blades, or to decrease the electrical resistivity of conductor coatings by high temperature reduction in hydrogen.

Furnace Treatment (Oxide Ceramics)

Oxide ceramics usually have a rather small thermal expansion coefficient (TEC), which is why any high temperature treatment of such coatings deposited on metallic substrates is impossible due to TEC mismatch. Care is also required with respect to high temperature phase transformations. For example, thermally sprayed Al_2O_3 is composed casually of γ -phase which transforms to α -phase above 1270K. Since this transformation is associated with density change (γ -phase has a density of 3.67g/cm^3 , α -phase of 3.98g/cm^3) the coating, after high temperature furnace treatment, is more porous than the as-sprayed one. Furnace treatment is also applied to the manufacture of thermally sprayed free-standing bodies.

Intermetallic or ceramic powders produced by techniques such as RPS have the potential for ultrafine structure due to high cooling rates during processing. Very fine powders i.e. sub-micron powders, are likely to exhibit relatively homogenous compositions and structures which should ultimately result in improved properties in the final product. Consolidation techniques must be adopted which aim to produce materials with theoretical densities, maintain homogenous microstructure and limit grain growth.

Laser Processing

Surfacing can be carried out using a laser which supplies enough energy in the form of a beam of radiation to melt or modify a coating on the surface of a parent metal. The use of lasers to modify surface coatings has been studied for various plasma sprayed materials including cermets and ceramics. Typically 1-5KW CO₂ lasers have been used to enhance densification and/or improve adhesion. Local surface and melting of deposits may also modify the local structure and properties. For example, lasers have been used for the surface modification of Zirconia. Zirconia coatings are widely used for thermal protection of high temperature components. Such coatings provide better thermal barrier properties and strain tolerance if they contain porosity. Unfortunately this means that such coatings are permeable to the atmosphere and the attendant oxidation and corrosion problems.

Heat treatment procedures following RPS have been particularly suited to intermetallic formation. The short reaction times available during

processing may result in mixed intermetallic phases and perhaps unreacted material.

Hot Isostatic Pressing (HIP)

HIPing consists of the simultaneous application of high pressure, up to 3000MPa, and high temperature, up to 2300K. The treated component is classed in the vessel and the operating pressure (using Argon as a working gas) is then applied with the help of compressors. The final pressure is obtained with the expansion of the hot gas. HIPing can only be applied to smaller sprayed components. The main requirement is to achieve the optimum level of consolidation at minimum temperature in order to maintain fine structure. To this end the use of pressure assisted techniques have become very important, where higher pressures can be used to off-set reduced processing temperatures. HIPing has been used for several years to upgrade the properties of plasma sprayed coatings.

Coatings produced by thermal spraying techniques often contain small amounts of porosity which can be detrimental to the coatings mechanical strength, corrosion resistance and adhesion. A post-sprayed HIP cycle can remove unwanted porosity leaving a fully dense and homogenous structure, for example, WC-Co coatings are usually deposited using thermal spraying techniques due to the high melting point of WC. Maximum wear resistance is achieved when the cobalt content is kept to a minimum, typically around 10%, but this can result in high porosity and poor bonding.

Impregnation

Impregnation is used mainly to seal the interconnected porosity in thermally sprayed coatings. The liquid sealer penetrates by capillary action into the pores and then solidifies. The sealers may be of inorganic or organic origin. Inorganic sealers include silicon oxide or chromium oxide and in some cases copper. Organic sealers designed especially for thermally sprayed coatings are commercially available e.g. MetcosealTM. There are a number of resins such as epoxy, silicone or phenol which may be applied to the sprayed coating depending on the application. The sealers are low viscosity fluids containing an inert resin binder in a solvent. Silicon resins are available for service up to 500°C.

Finishing

Finishing, the final stage in the production of thermally sprayed coatings, is required to deliver the specified tolerated dimensions and roughness. Grinding is used to achieve the desired dimension and polishing or lapping to get the required roughness.

Grinding

Diamond or cubic boron nitride (CBN) wheels are generally used to grind ceramic coatings, metallic coatings or very hard coatings, for instance those with a high tungsten carbide content. Metallic coatings can be ground with silicon carbide wheels. Grinding wheels for sprayed coatings should be relatively coarse grained, of open structure and low

bond strength. Wet grinding is preferable to dry grinding in order to avoid glazing and excessive wheel vibration. The coating should ideally be sealed to ensure a better and cleaner initial ground finish. The sealer should be applied before grinding to prevent debris from the grinding operation entering the pores of the coating, a smoother finish also facilitates cleaning. Removal of all debris may be a critical factor in the life of a bearing used with a metal sprayed shaft.

Polishing and Lapping

Polishing is usually carried out using the same machines as for grinding but with finer abrasive materials. Careful control of the polishing parameters achieves surfaces of Ra less than 0.2 μ m (Chromium oxide coatings). Further improvement in roughness can be achieved by lapping. Lapping is a process in which the abrasiveness (e.g. Diamond or Alumina) are used in an oil or grease mixture. Lapping is recommended if the vibrations in the grinding/polishing machine leave traces in the finished surface.

FIGURES

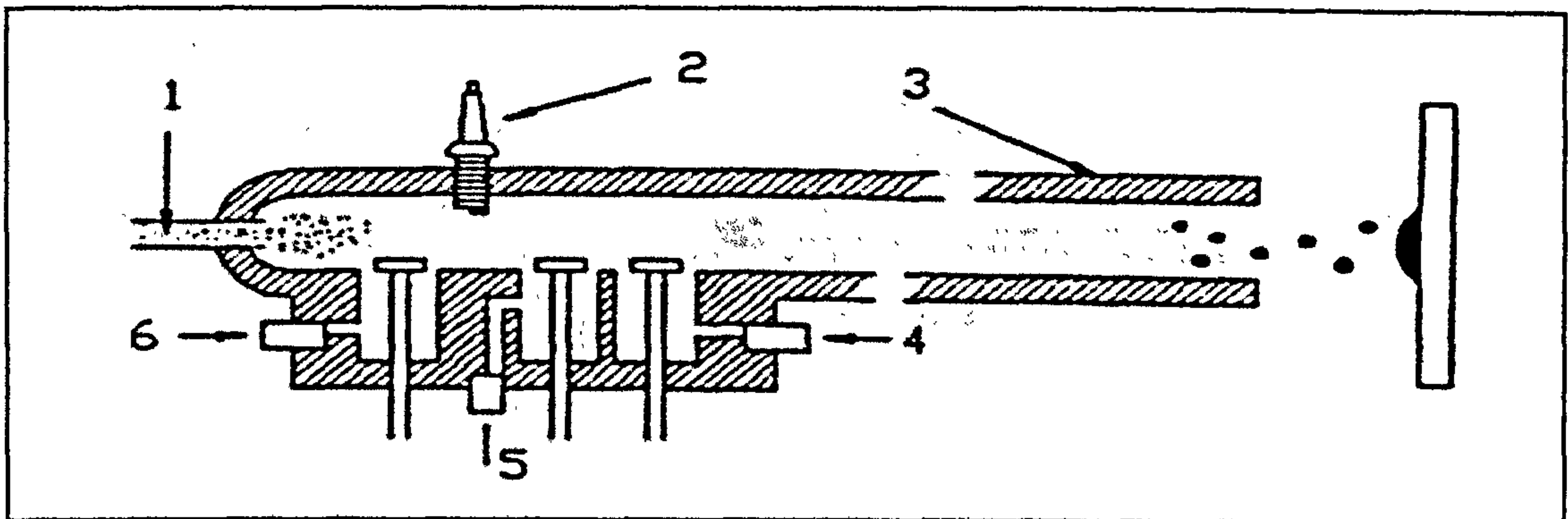


Figure 1 - D-Gun assembly^[2]

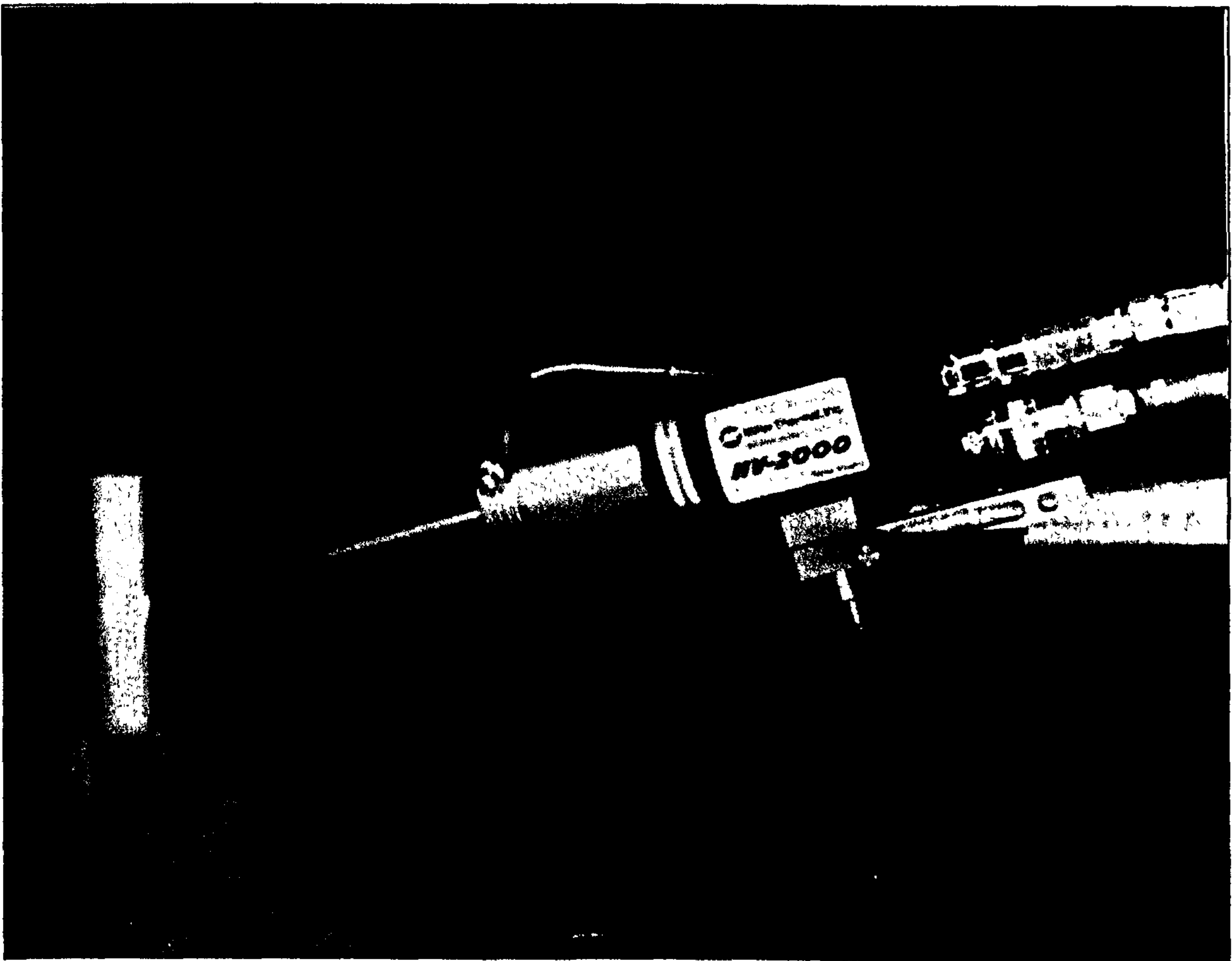


Figure 2 - HVOF Gun^[2]

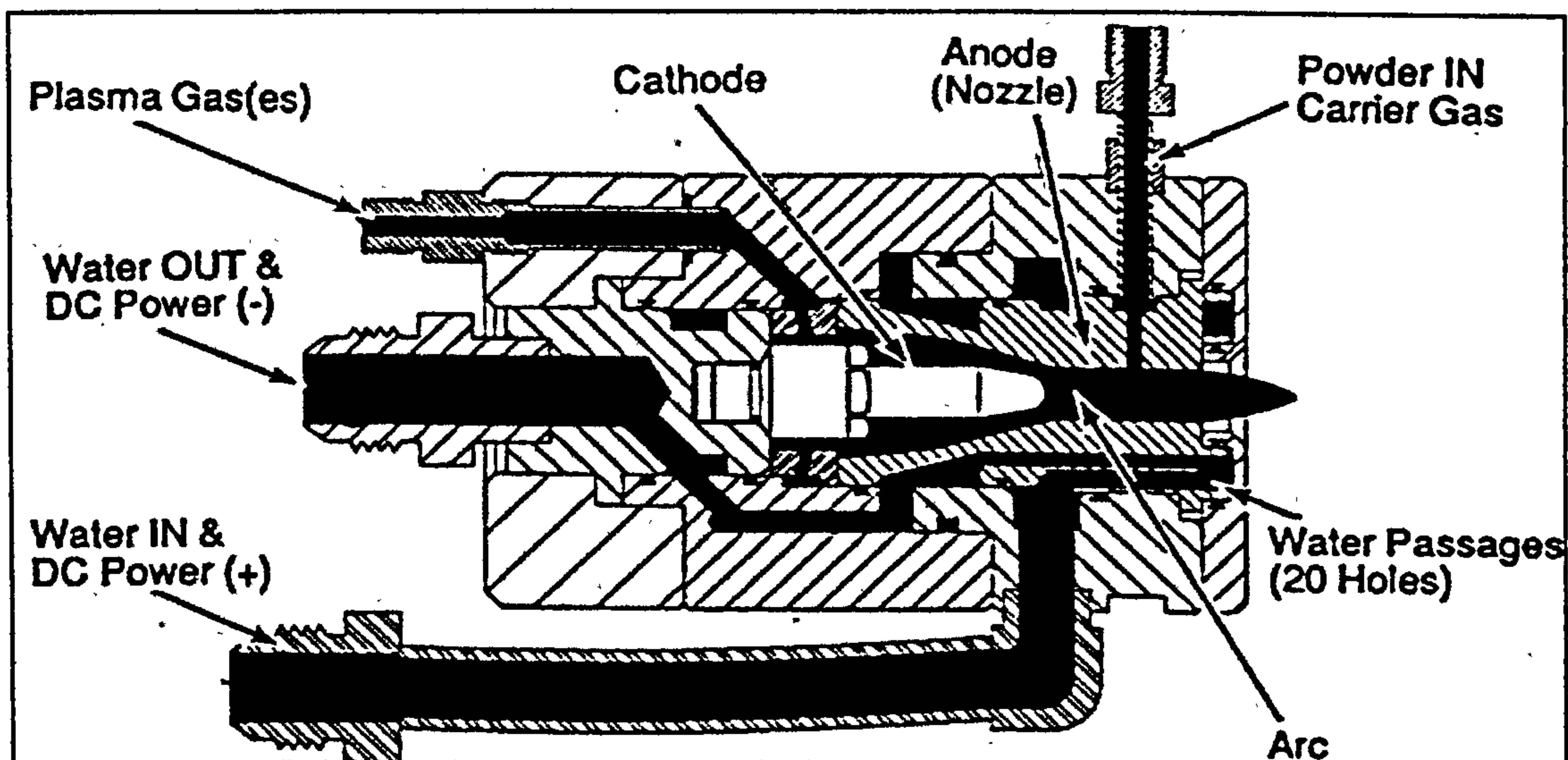


Figure 3 - Praxair Thermal Spray systems model SG-100 Plasma torch^[66]

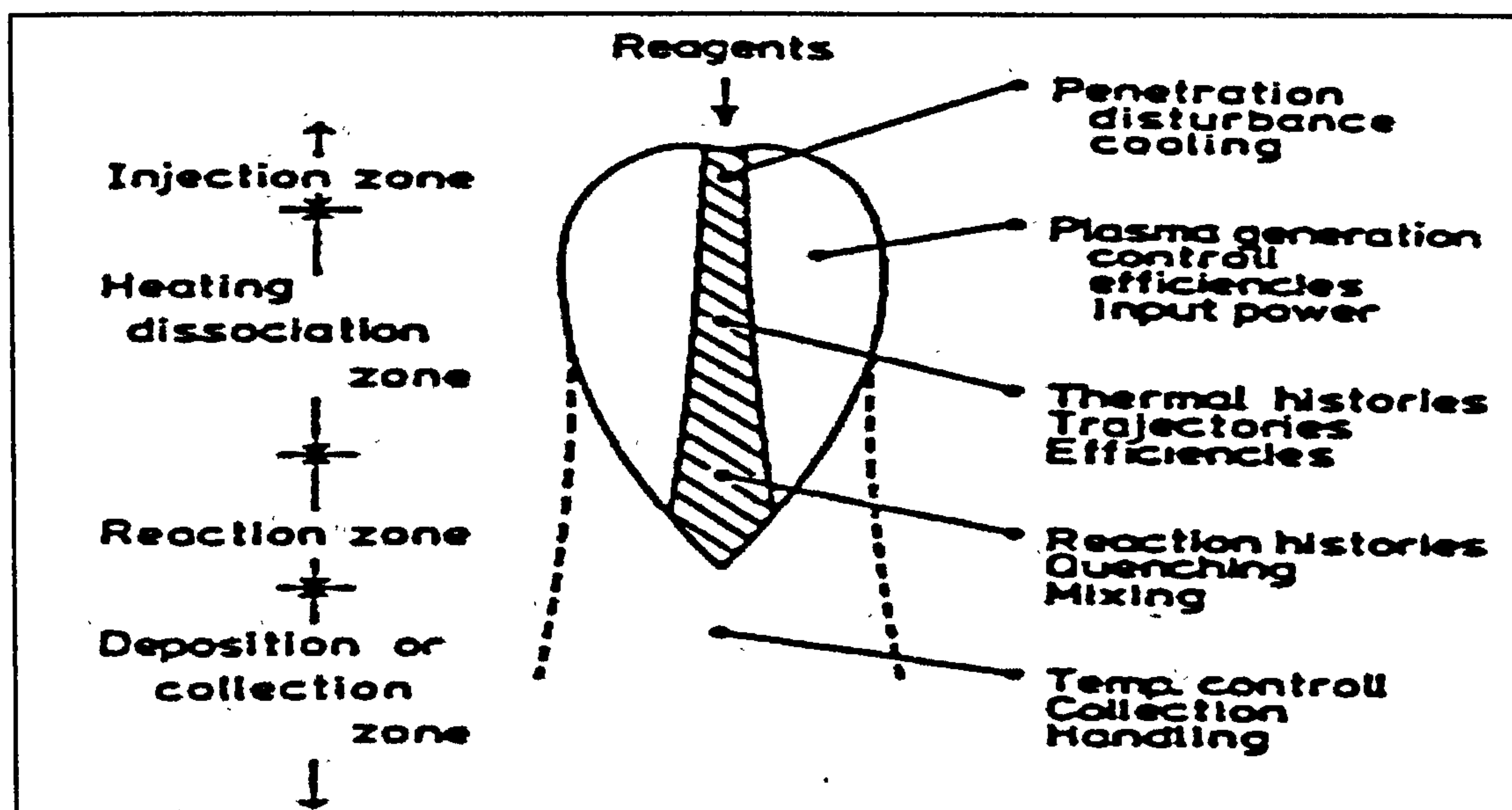


Figure 4 - The four important zones which make up an RPS system^[3]

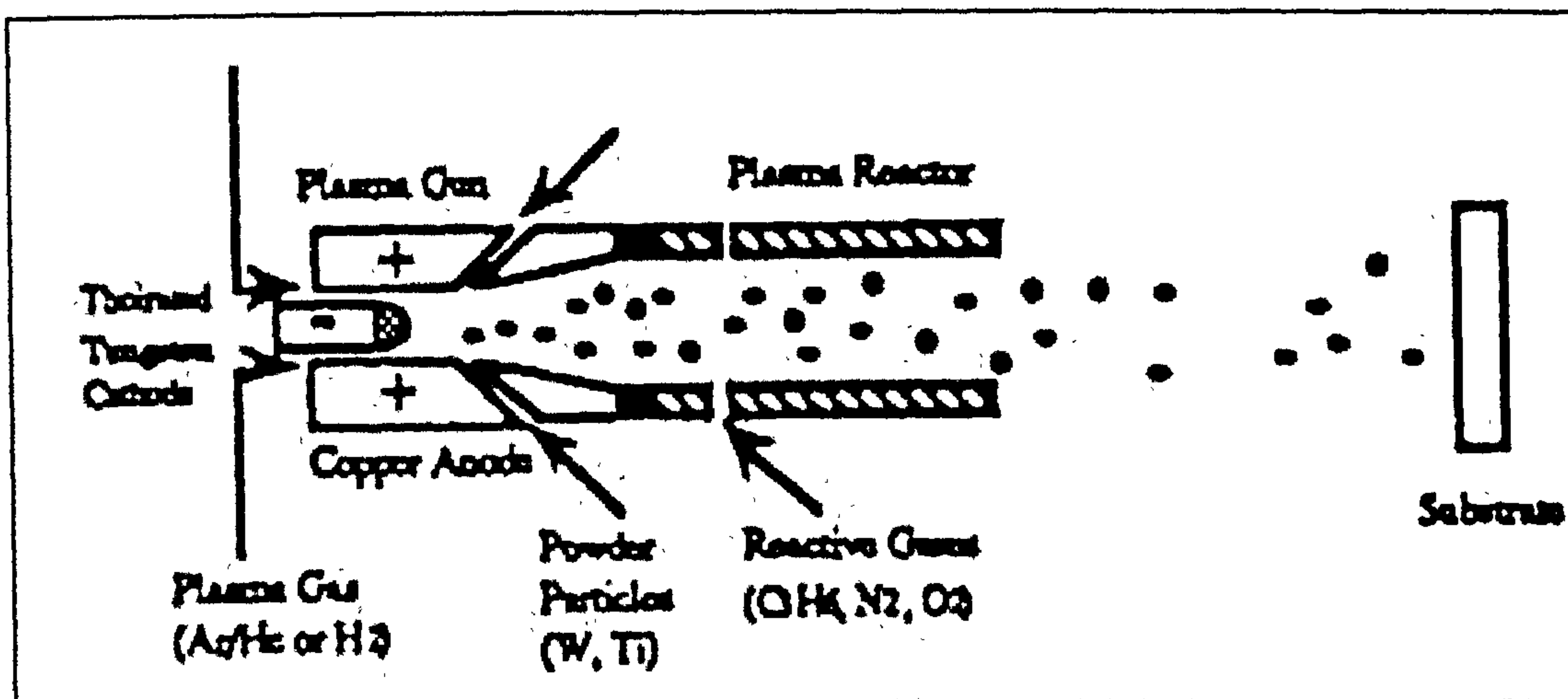


Figure 5 - Schematic of a Plasma Reactor connected to a DC Gun^[4]

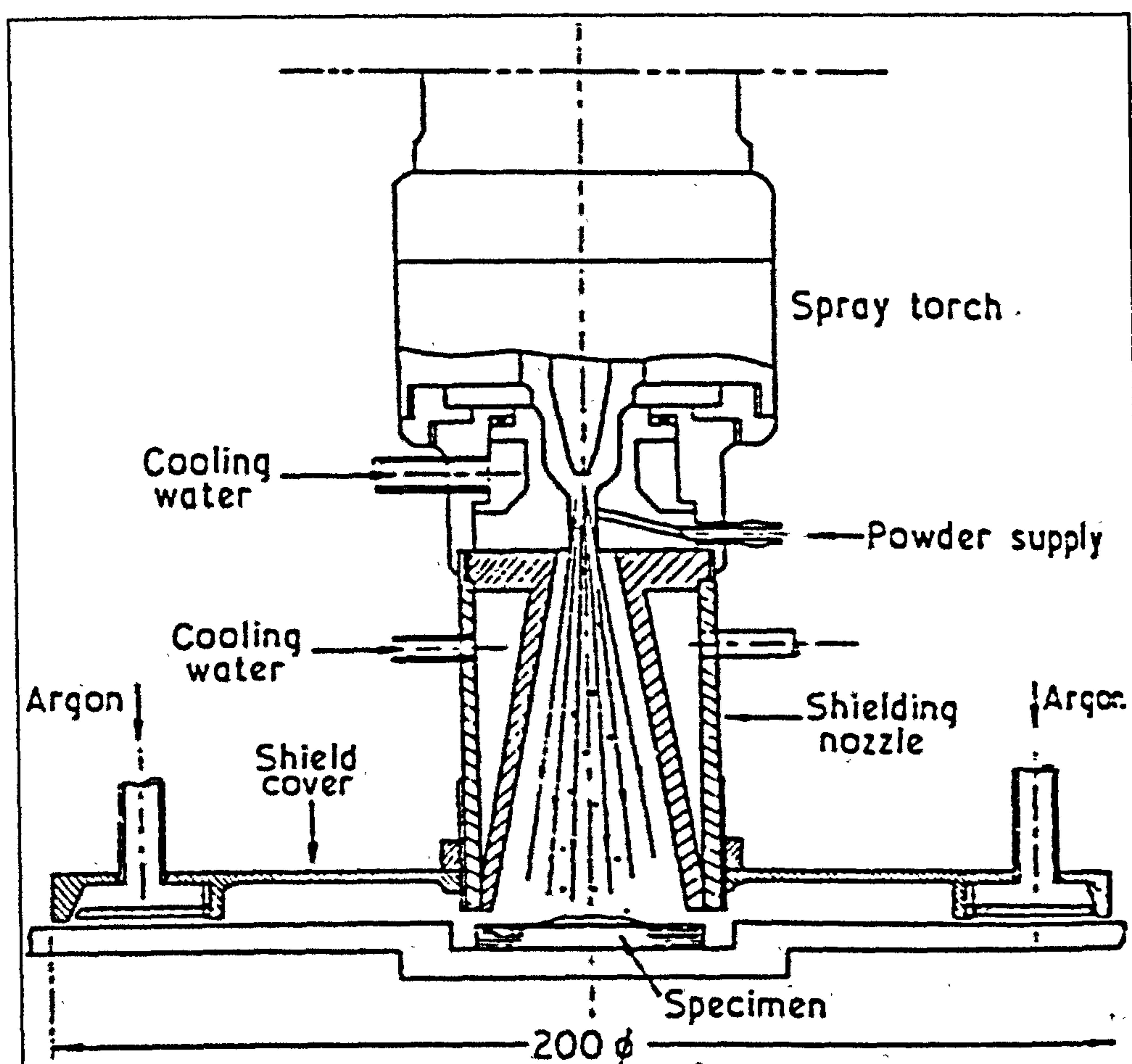


Figure 6 - Shielding nozzle used by Okada and Maruo^[6]

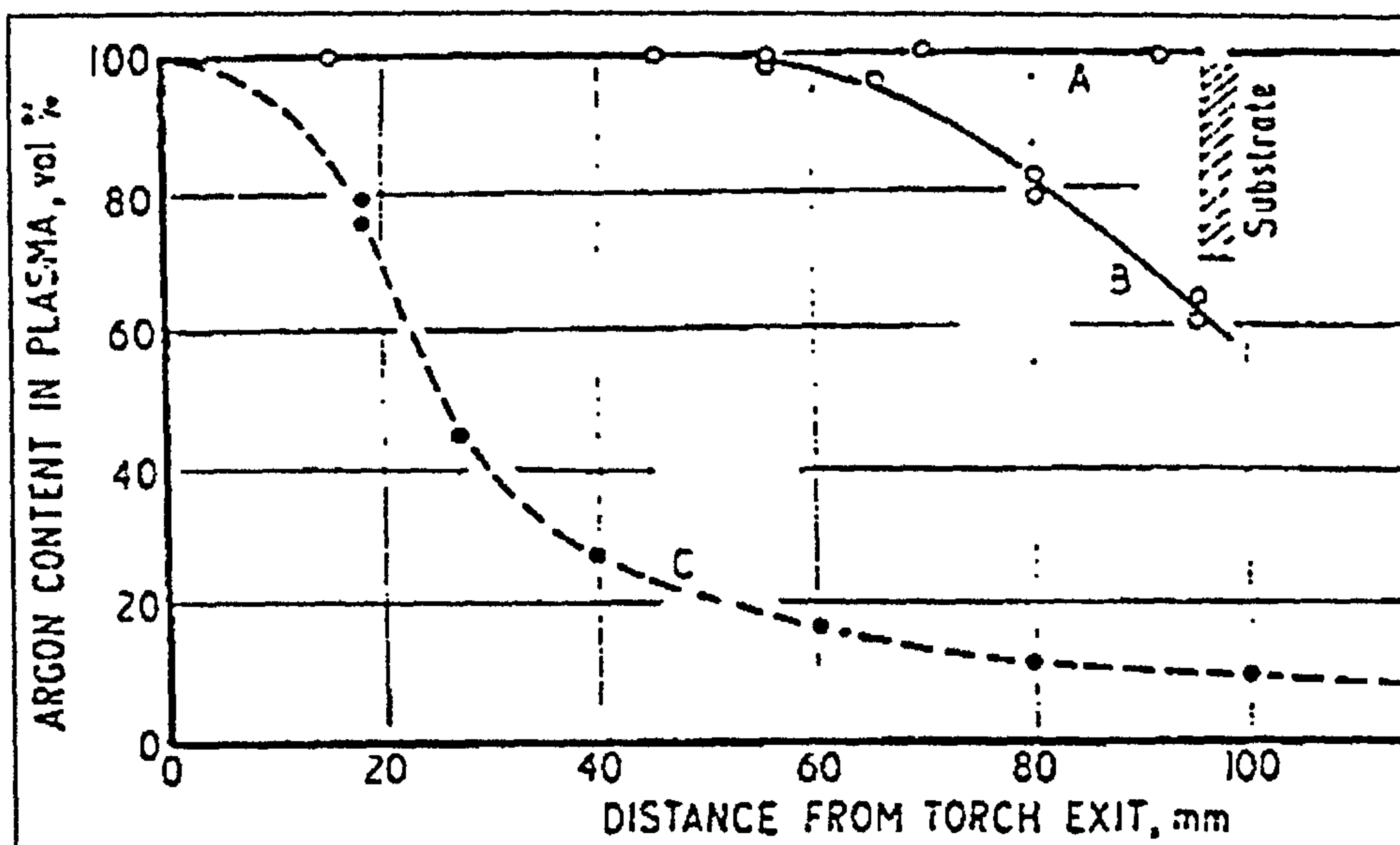


Figure 7 - Experimental results of gas analysis of plasma flame. A- result when substrate is placed in front of shielding nozzle; B - shielded plasma flame in absence of substrate; C - argon in non-shielded plasma flame^[6]

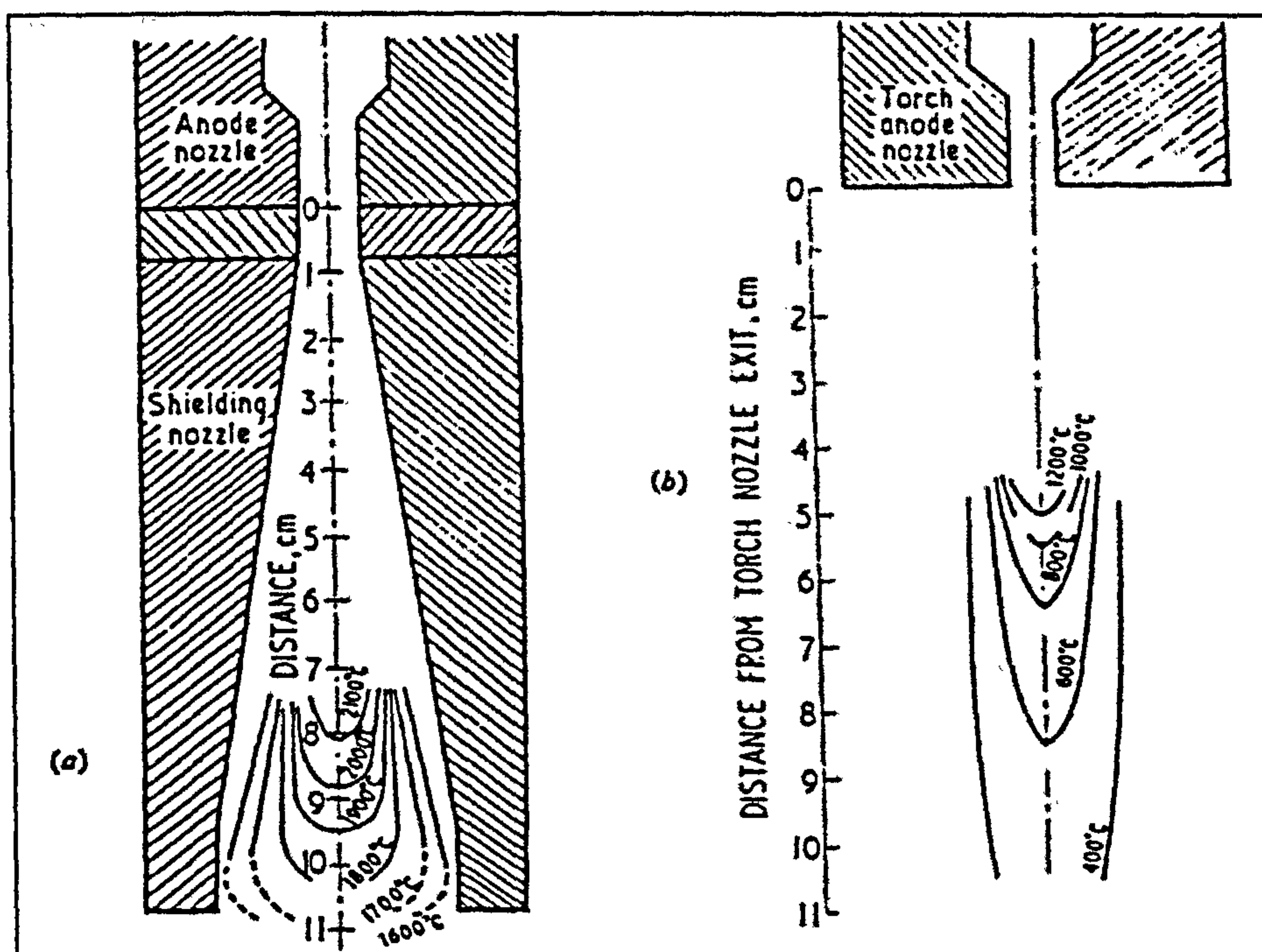


Figure 8 - Temperature distributions of (a) shielded plasma flame; (b) non-shielded flame. Arc current 400 A, Ar gas flow 60 l/min^[6]

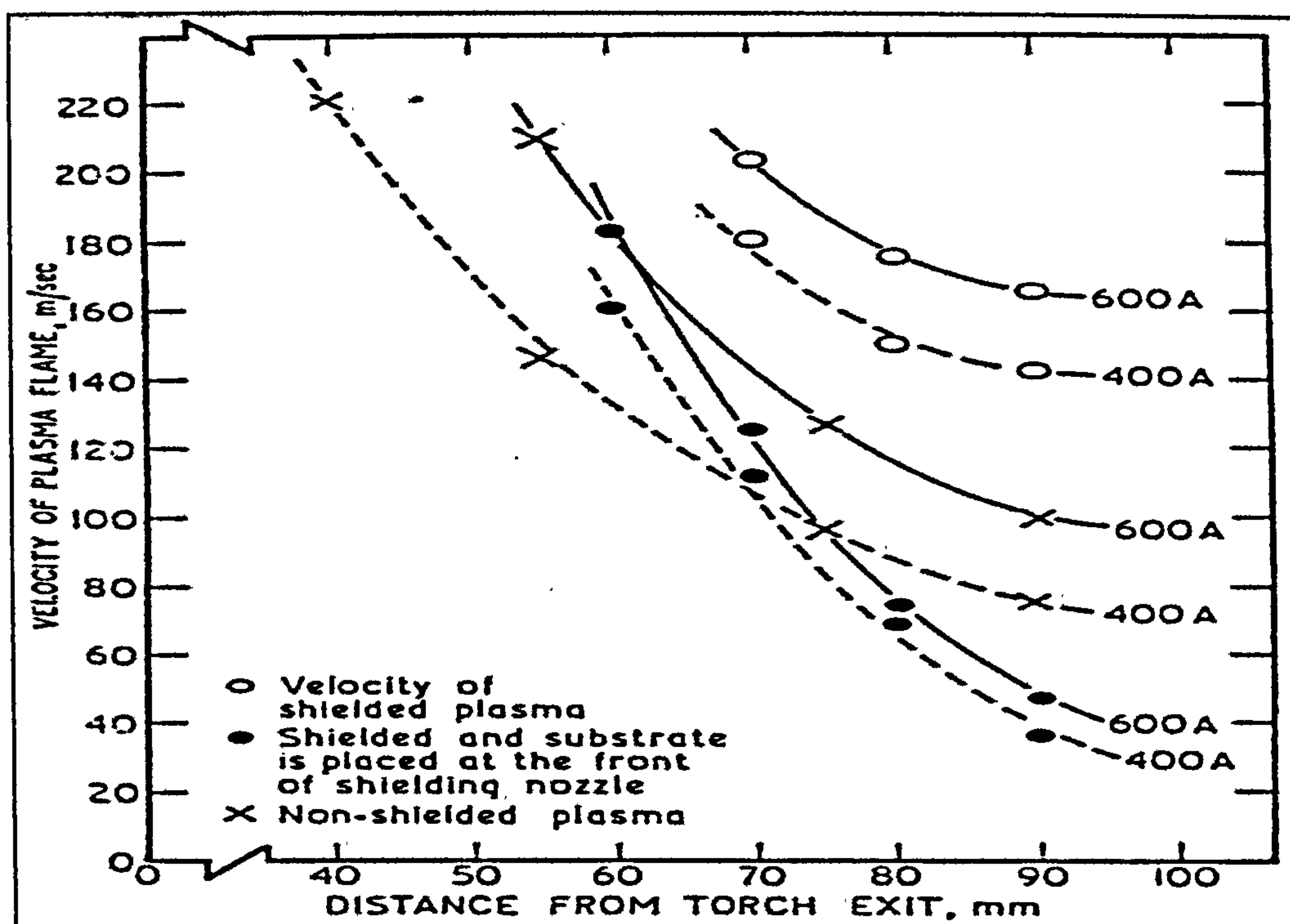


Figure 9 - Plasma velocities of shielded plasma and non-shielded plasma, calculated from temperature and pressure measurements. Ar gas flow 60 l/min^[6]

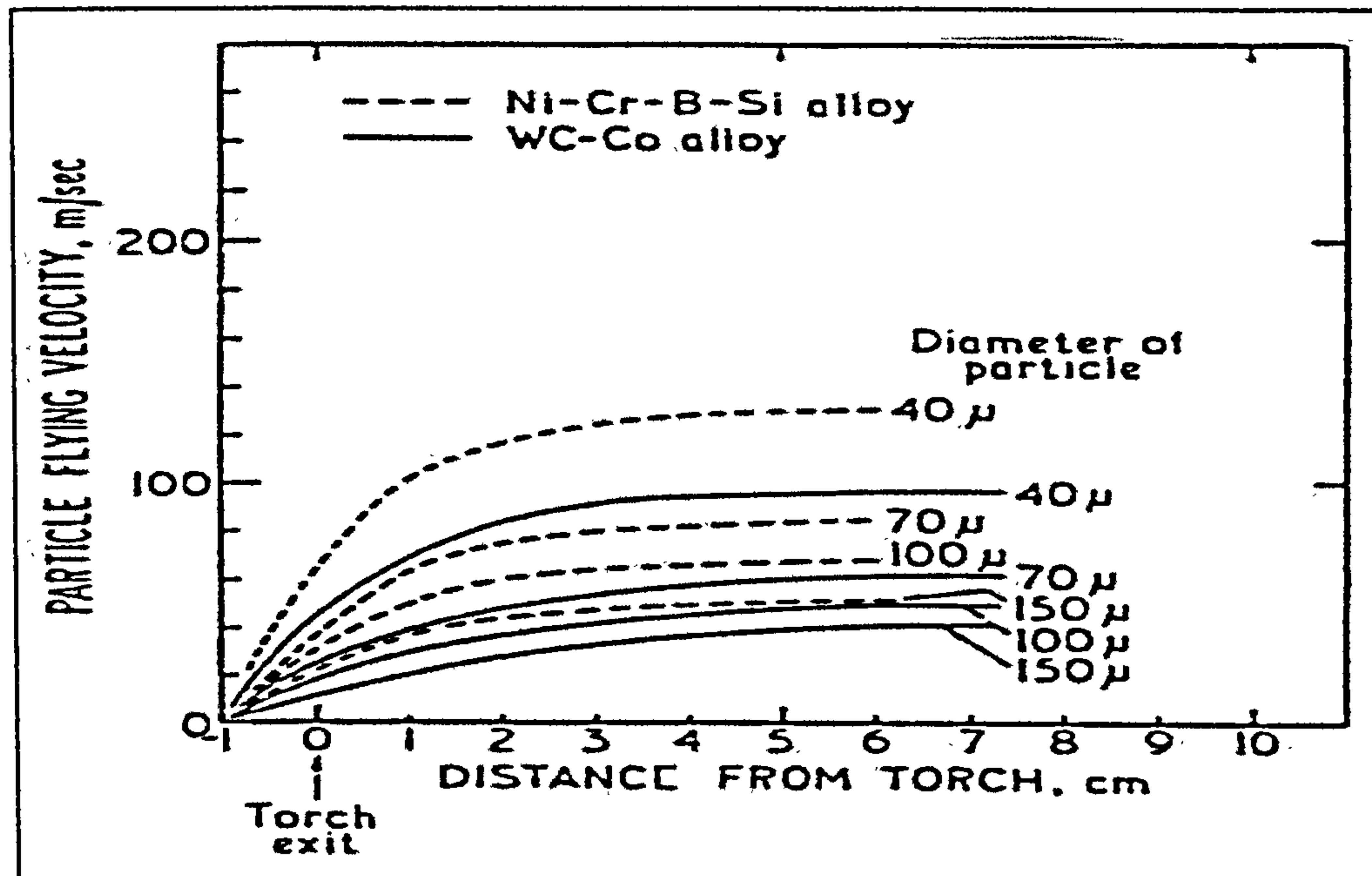


Figure 10 - Acceleration of various sizes of particle in the plasma jet flame, calculated theoretically. Flight velocity of Ni-Cr-B-Si alloy powder was estimated for the plasma flame, 500 A, 60 l/min; and WC-Co powder for the plasma flame, 1000 A, 50 l/min^[6]

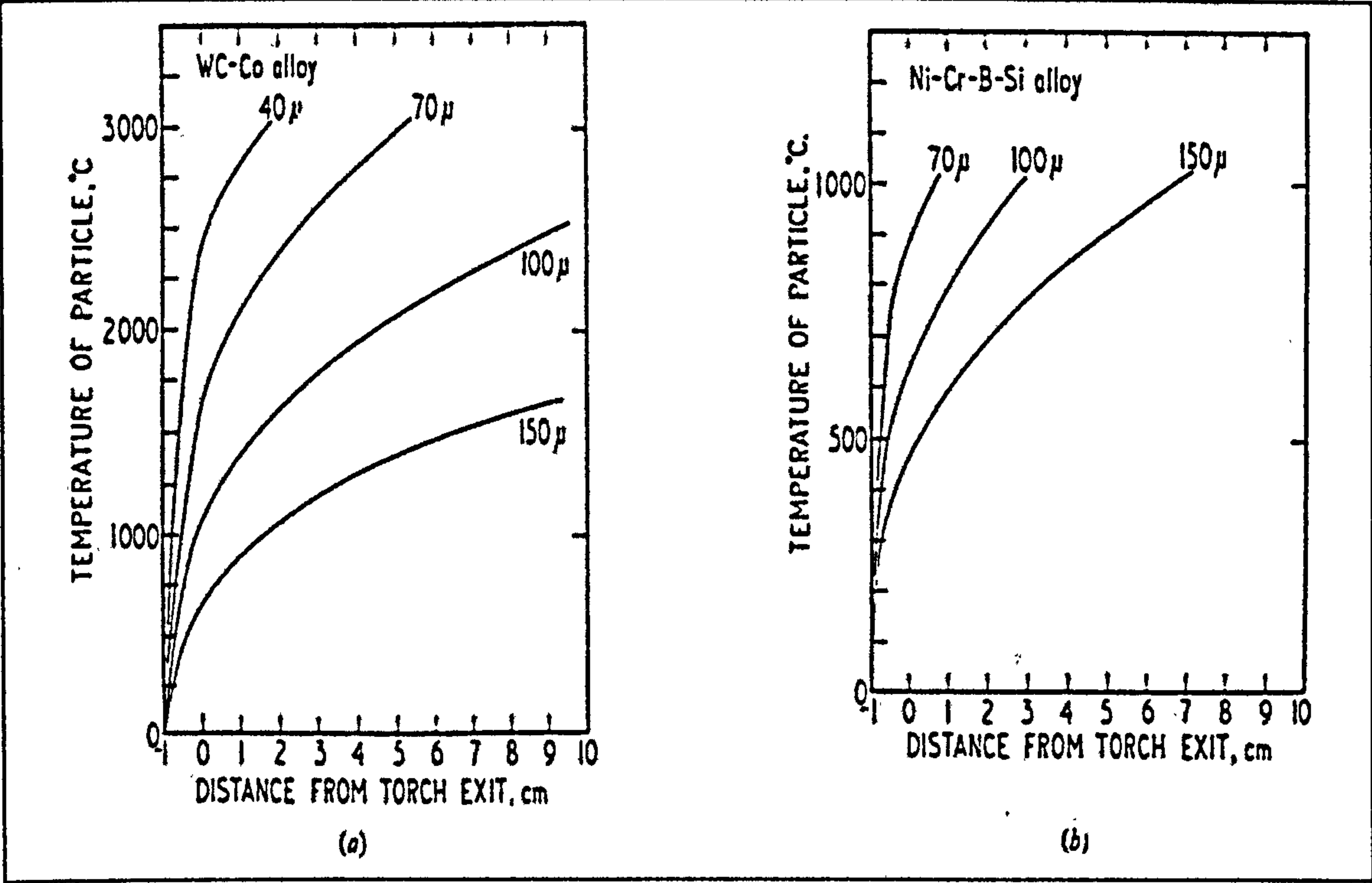


Figure 11 - Estimated temperature rise of spraying materials in shielded plasma spraying: (a) temperature of each size of Ni-Cr-B-Si alloy particle in the plasma flame, 500 A, 60 l/min: (b) WC-Co particles in plasma flame, 1000 A, 50 l/min^[6]

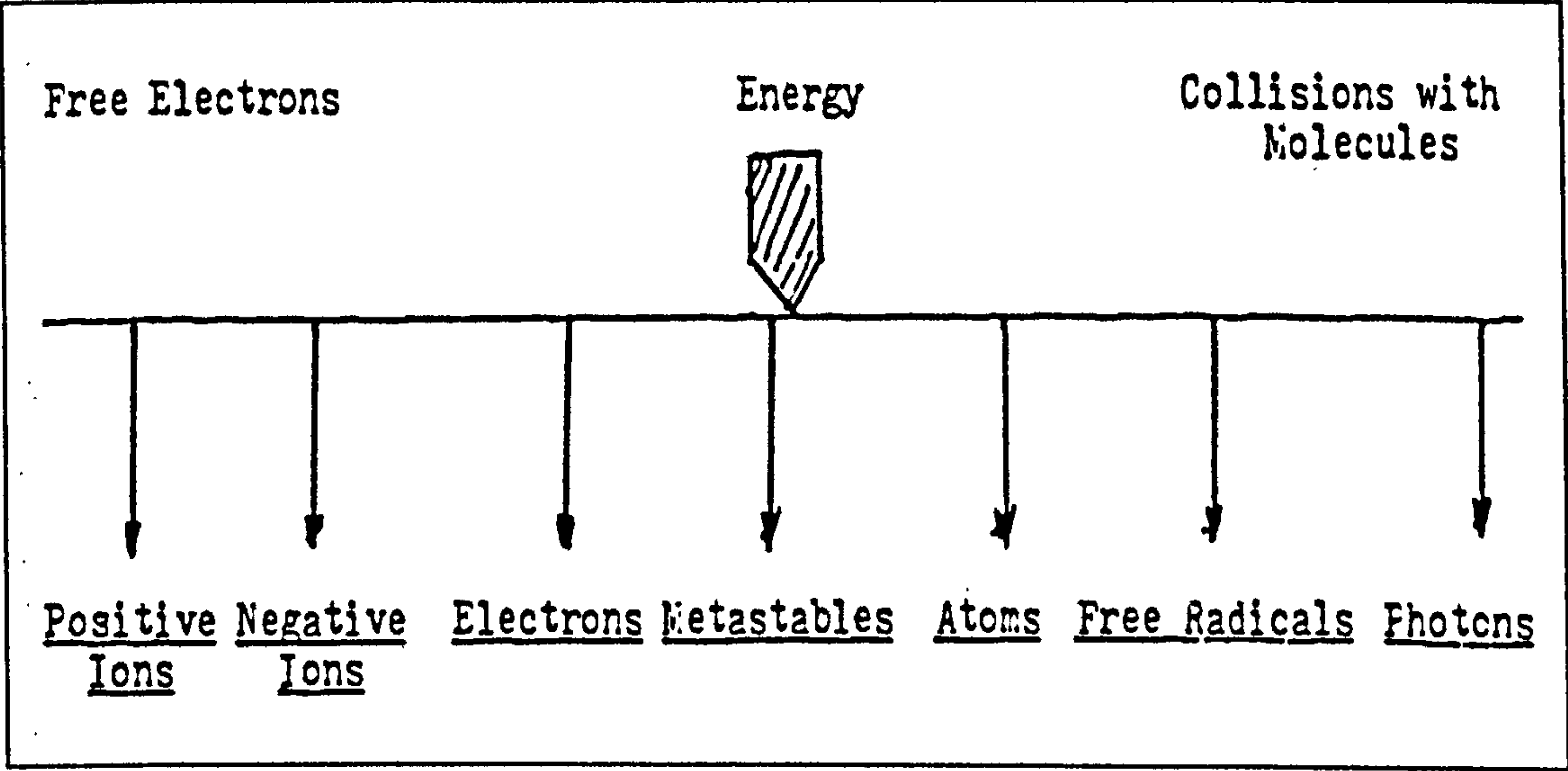
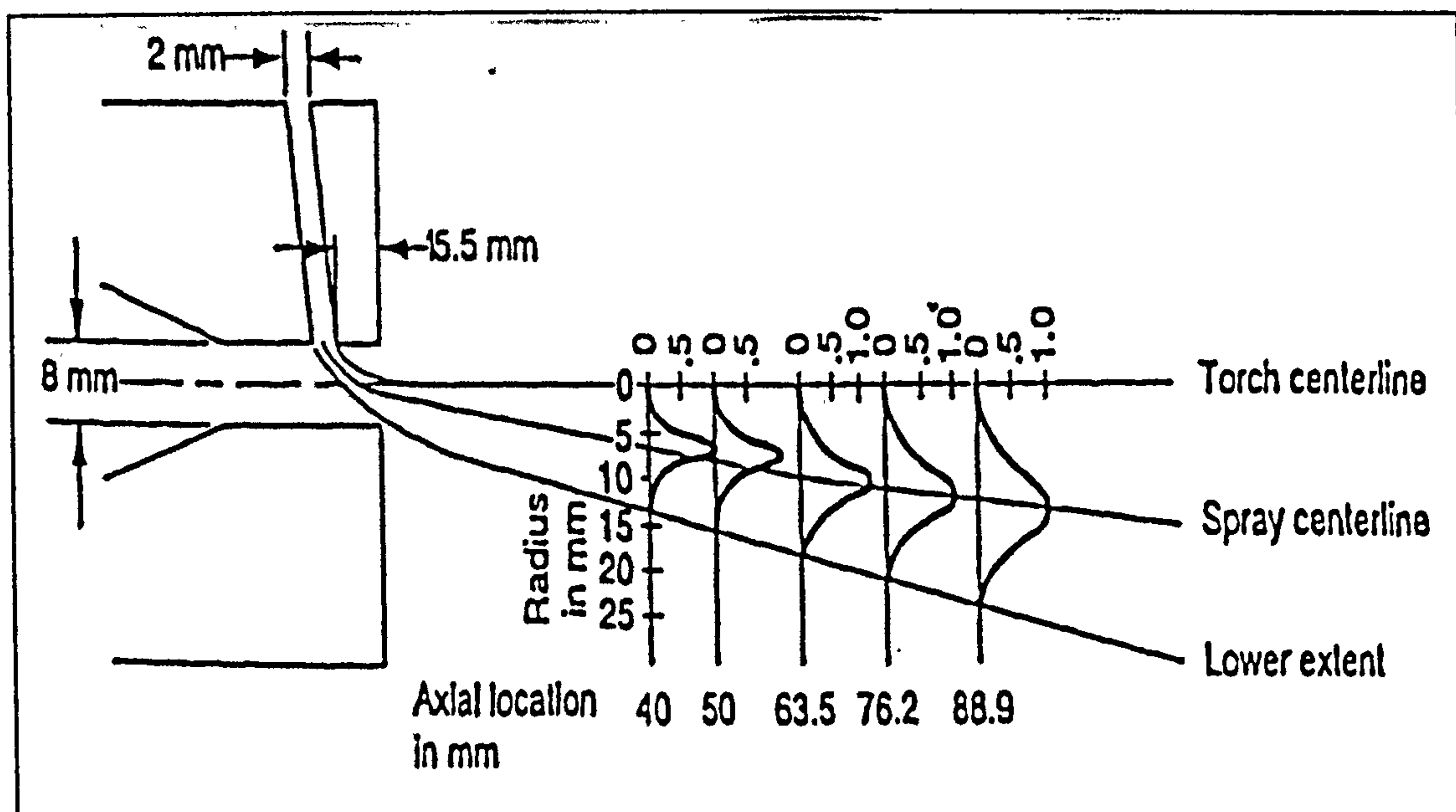
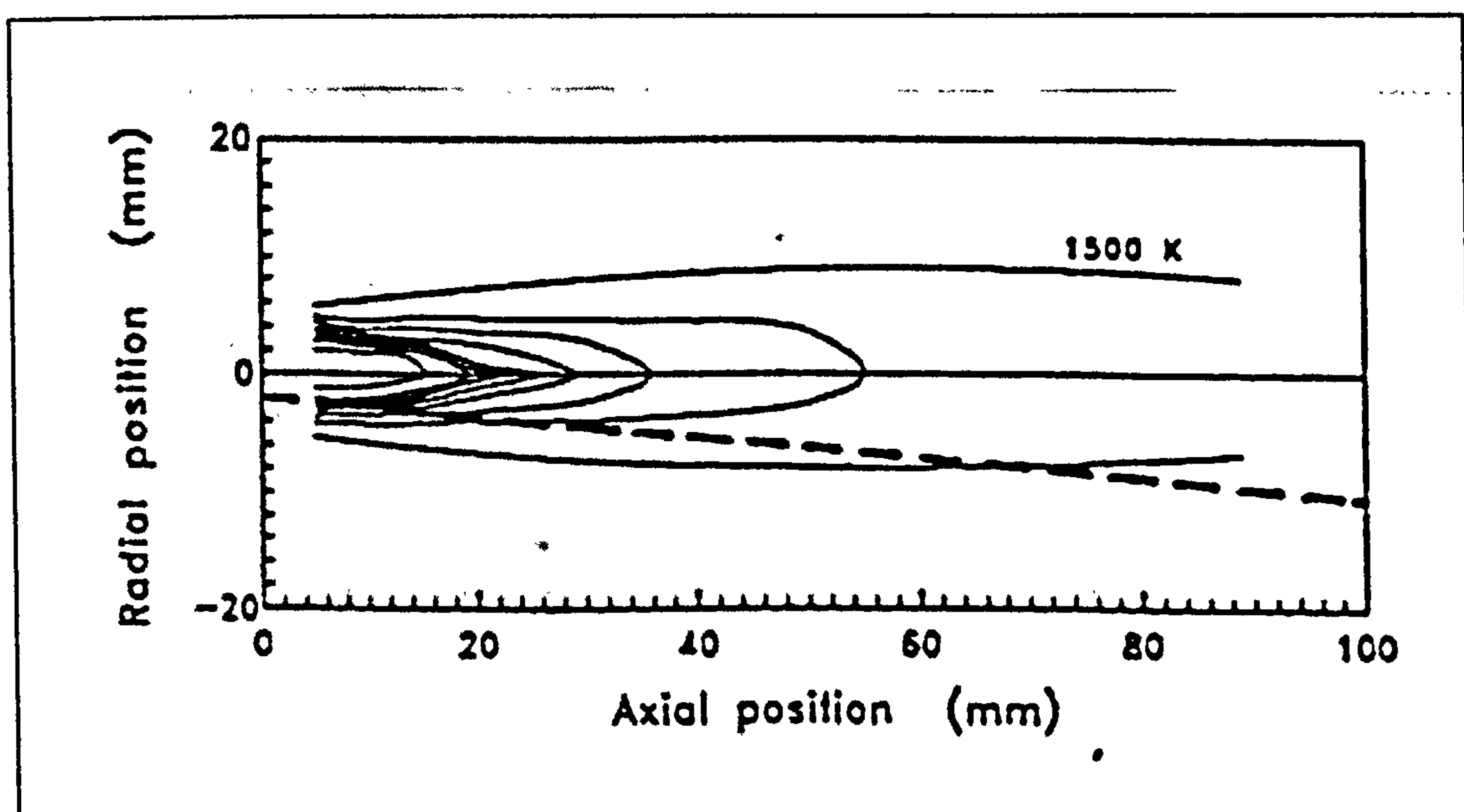


Figure 12 - Possible plasma components which can take part in reactions^[9]



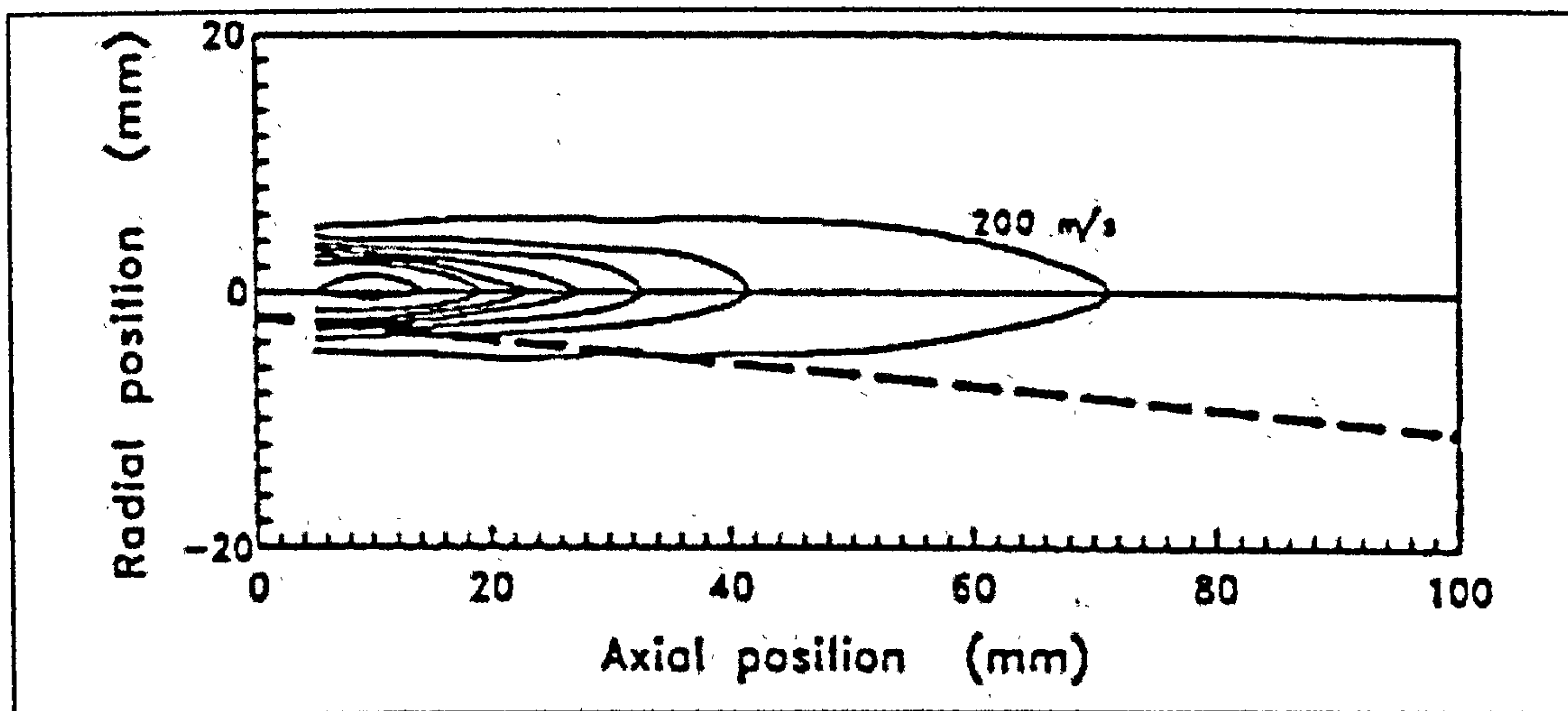


Figure 15 - Contour plot of gas axial velocity with the highest particle density shown by the dashed line.
Contours are in increments of 200 m/s^[12]

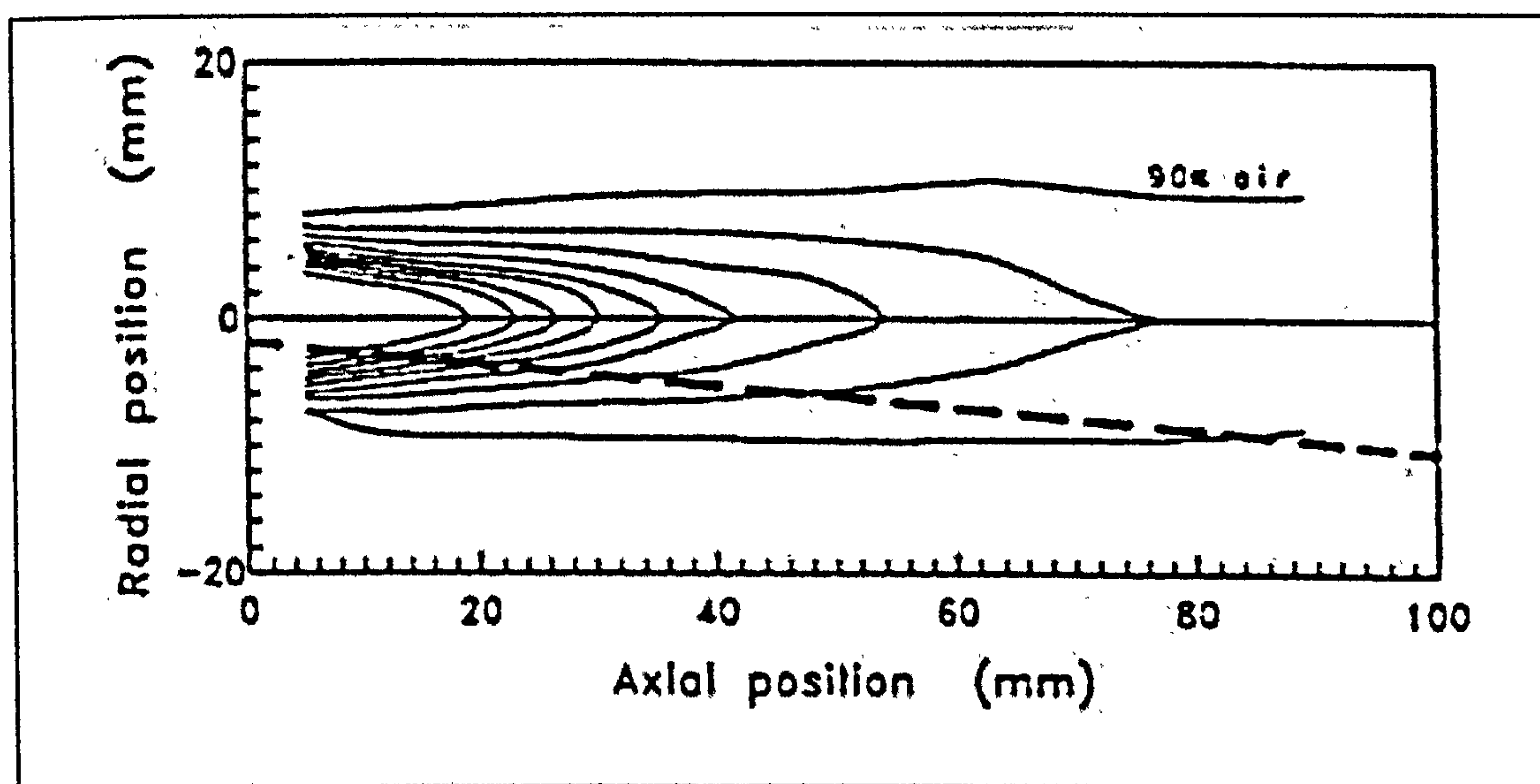


Figure 16 - Contour plot of air concentration with the highest particle number density shown by the dashed line.
Contours are in increments of 10 %^[12]

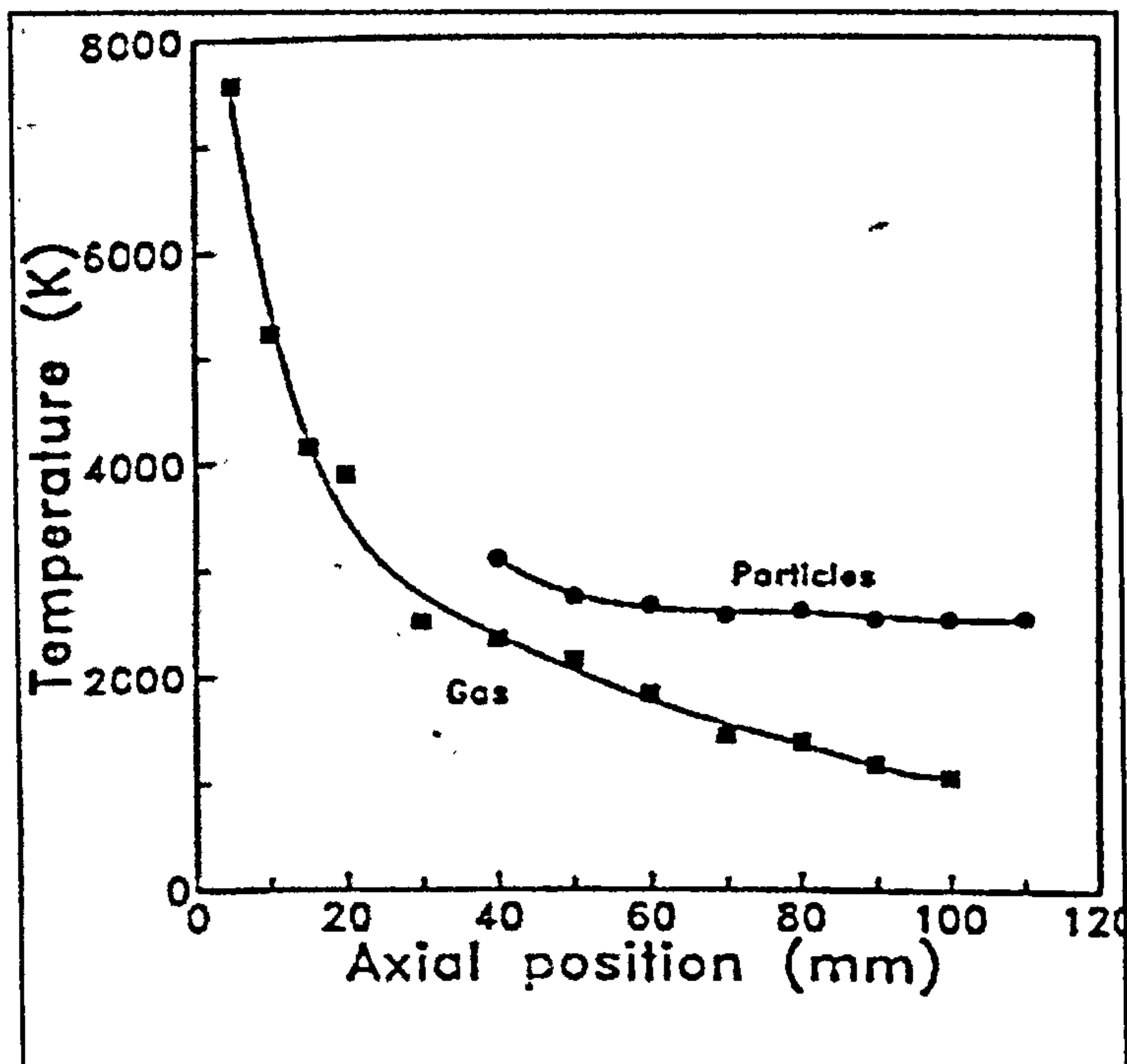


Figure 17 - Gas and particle temperatures on the median trajectories^[12]

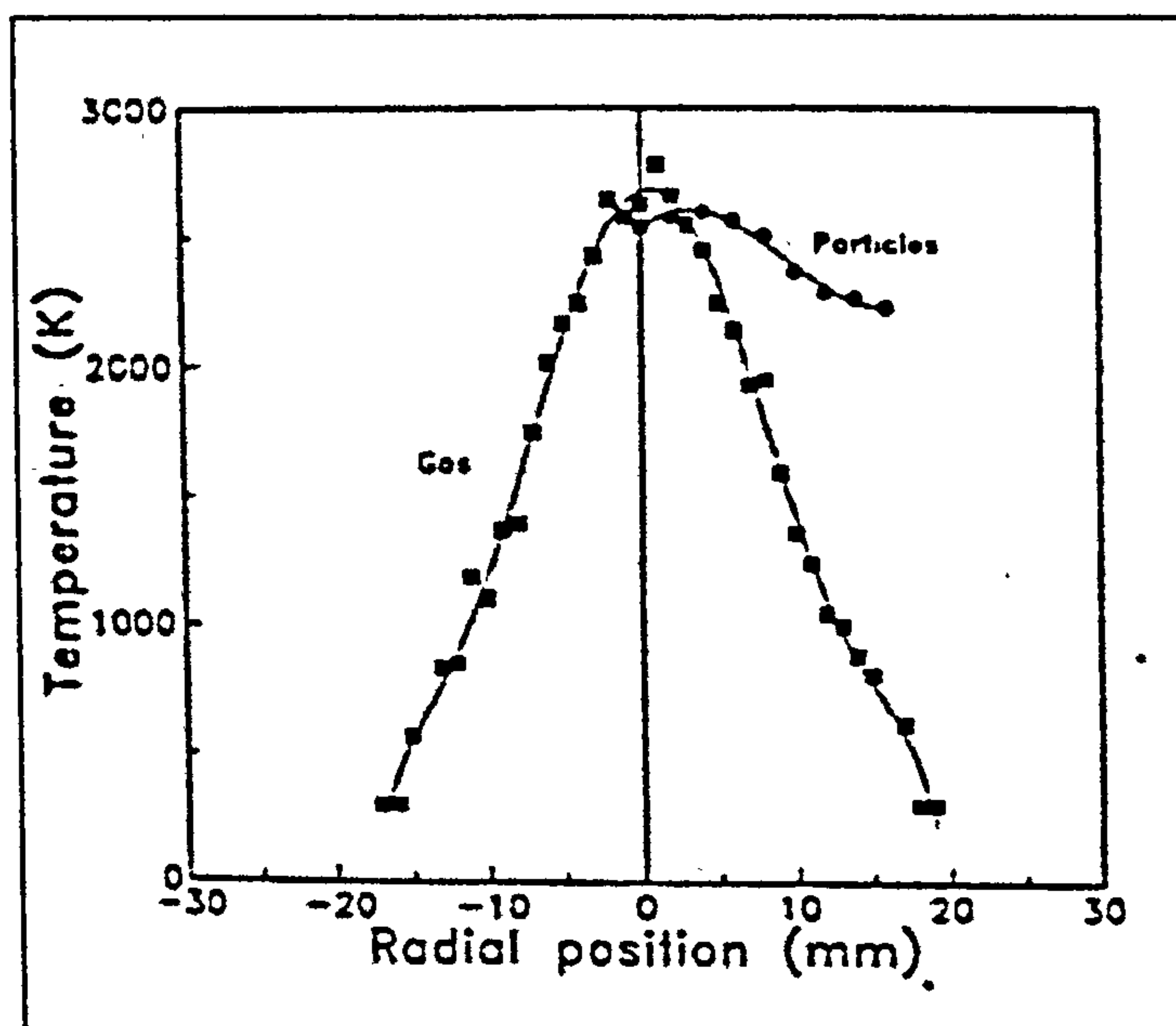


Figure 18 - Radial distribution of particle and gas temperature at the 63.5 mm axial position^[12]

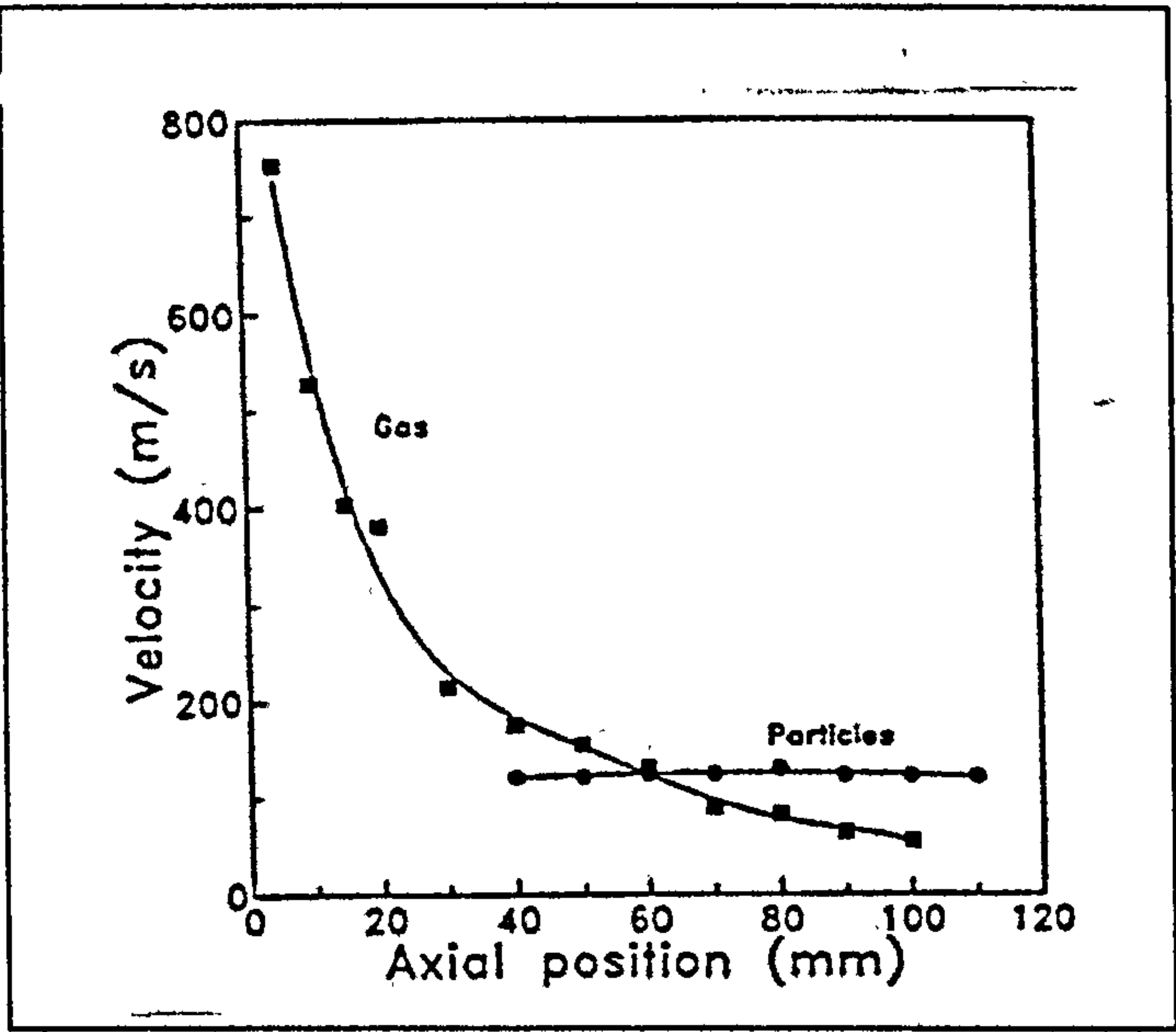


Figure 19 - Axial velocity of gas and particles along the particle trajectory centreline^[12]

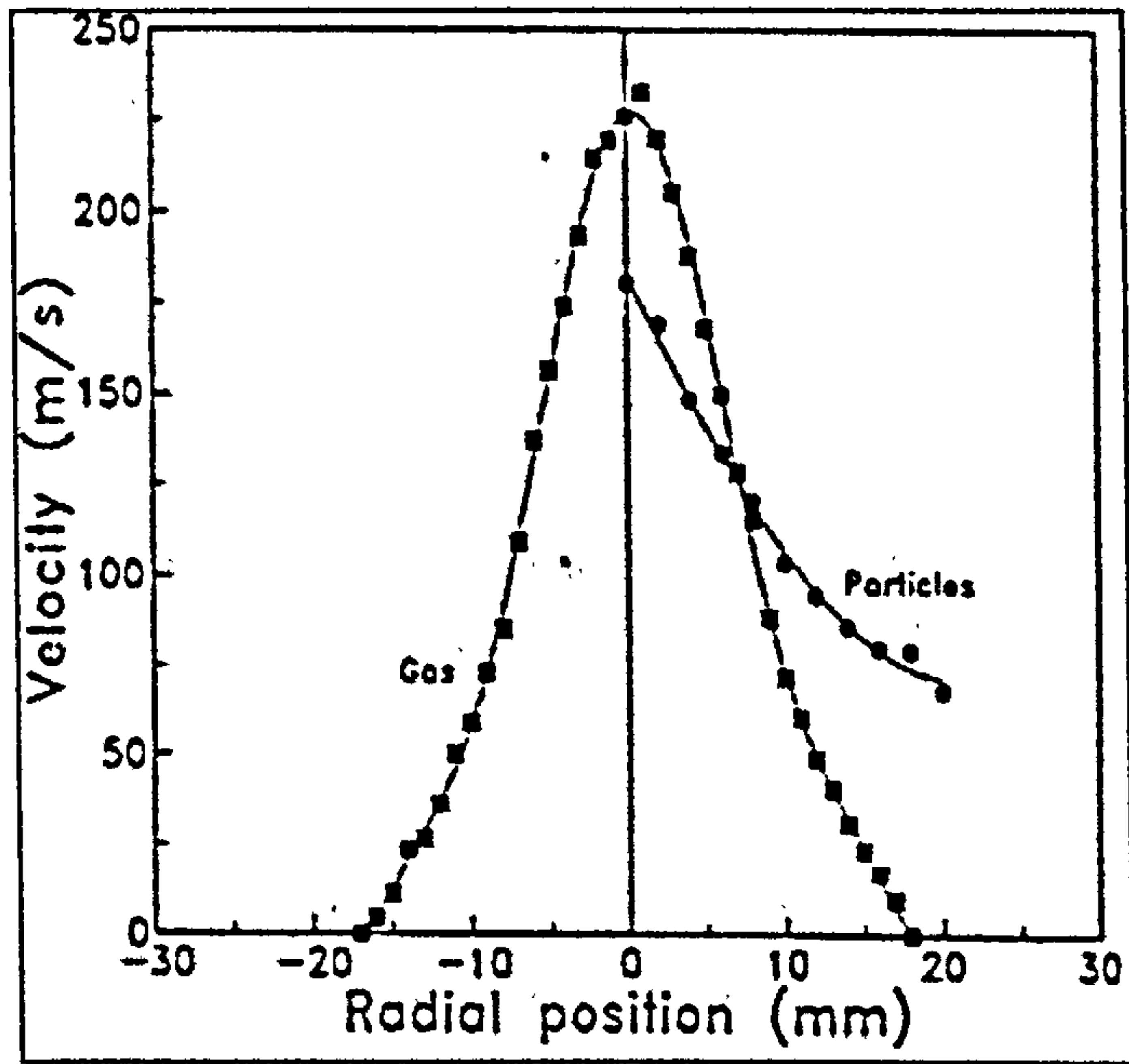


Figure 20 - Radial distribution of average particle and gas axial position^[12]

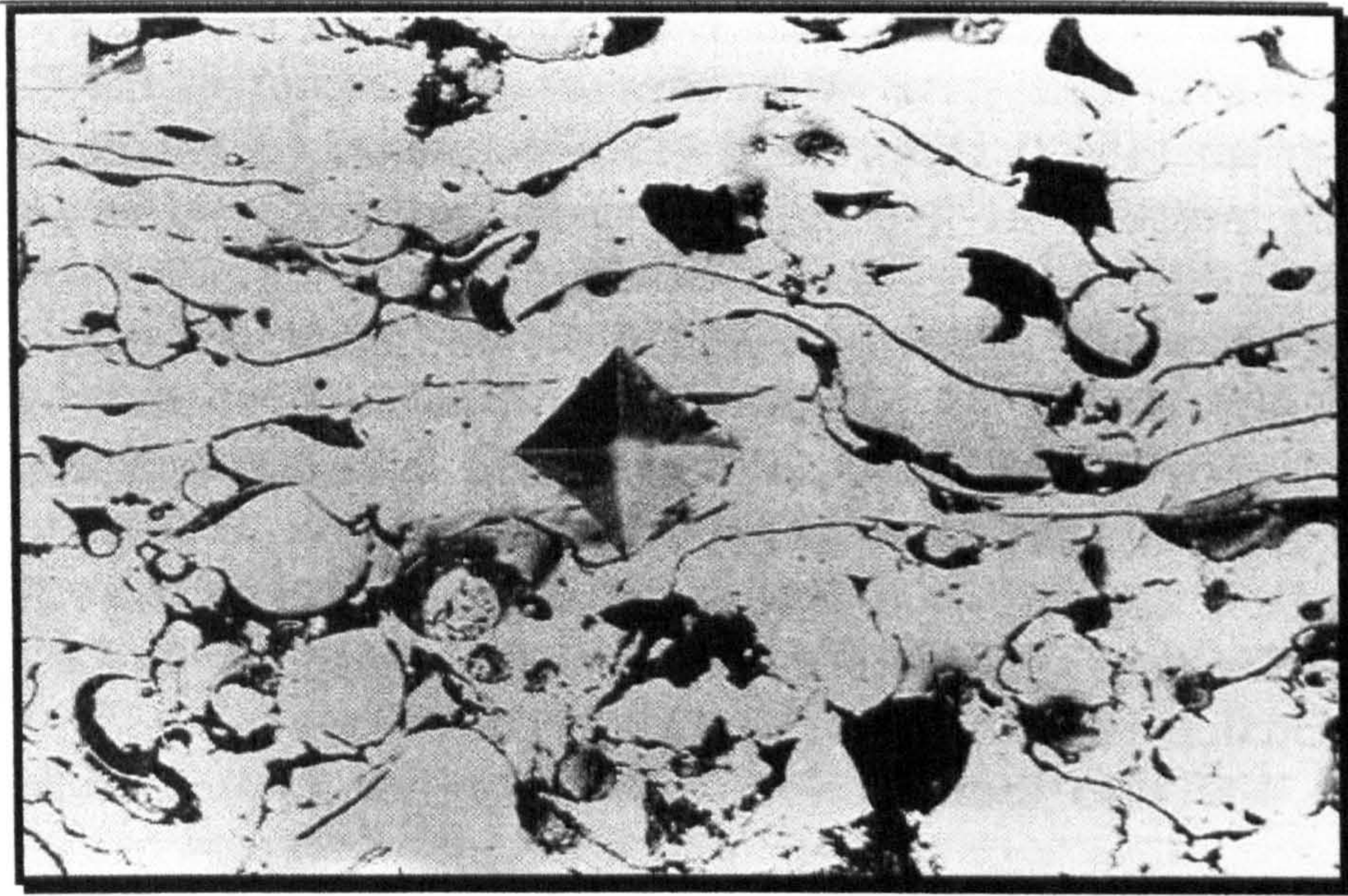


Figure 21 - A typical microhardness indentation^[2]

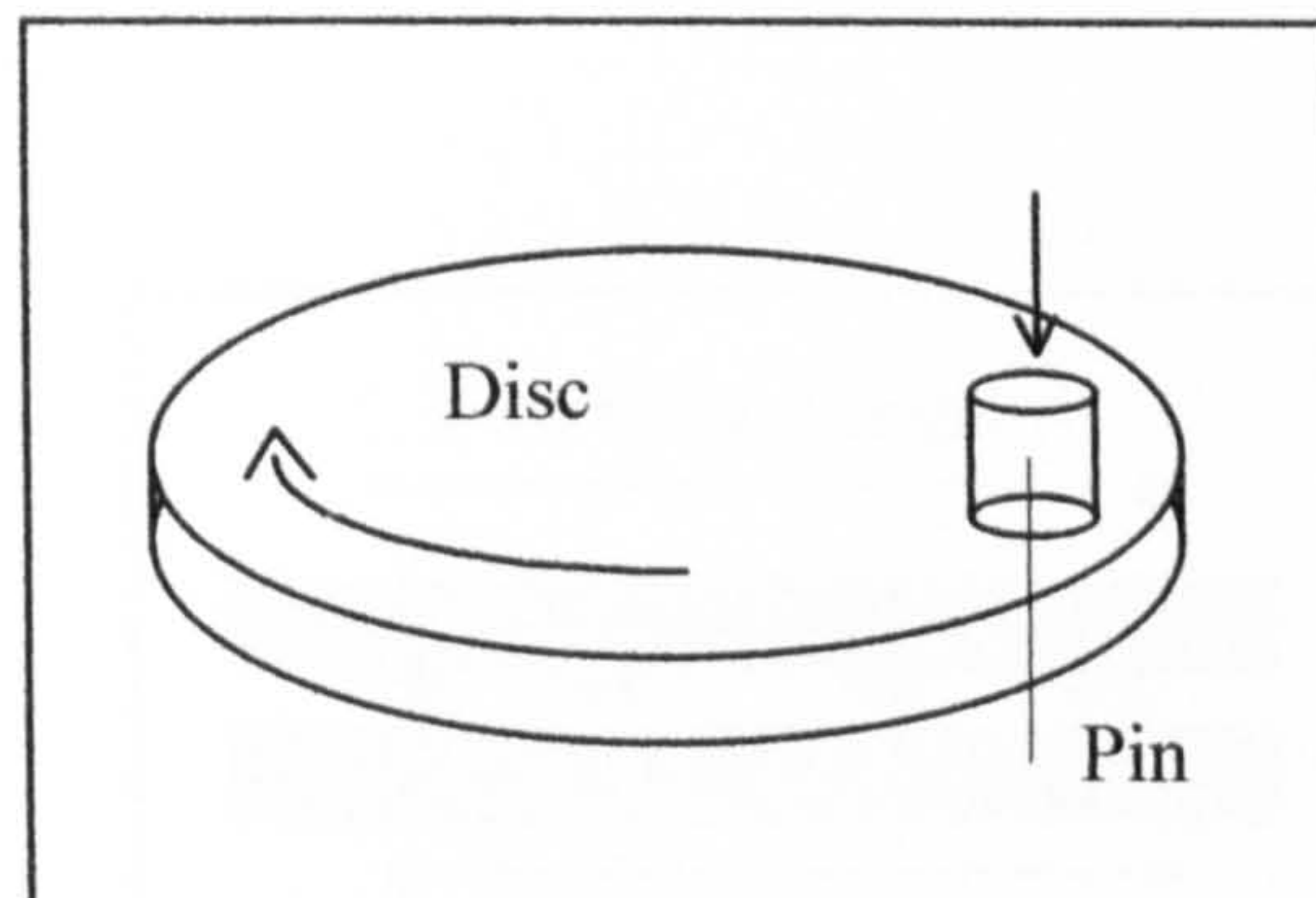


Figure 22 - Schematic of a 'pin on disc' wear test

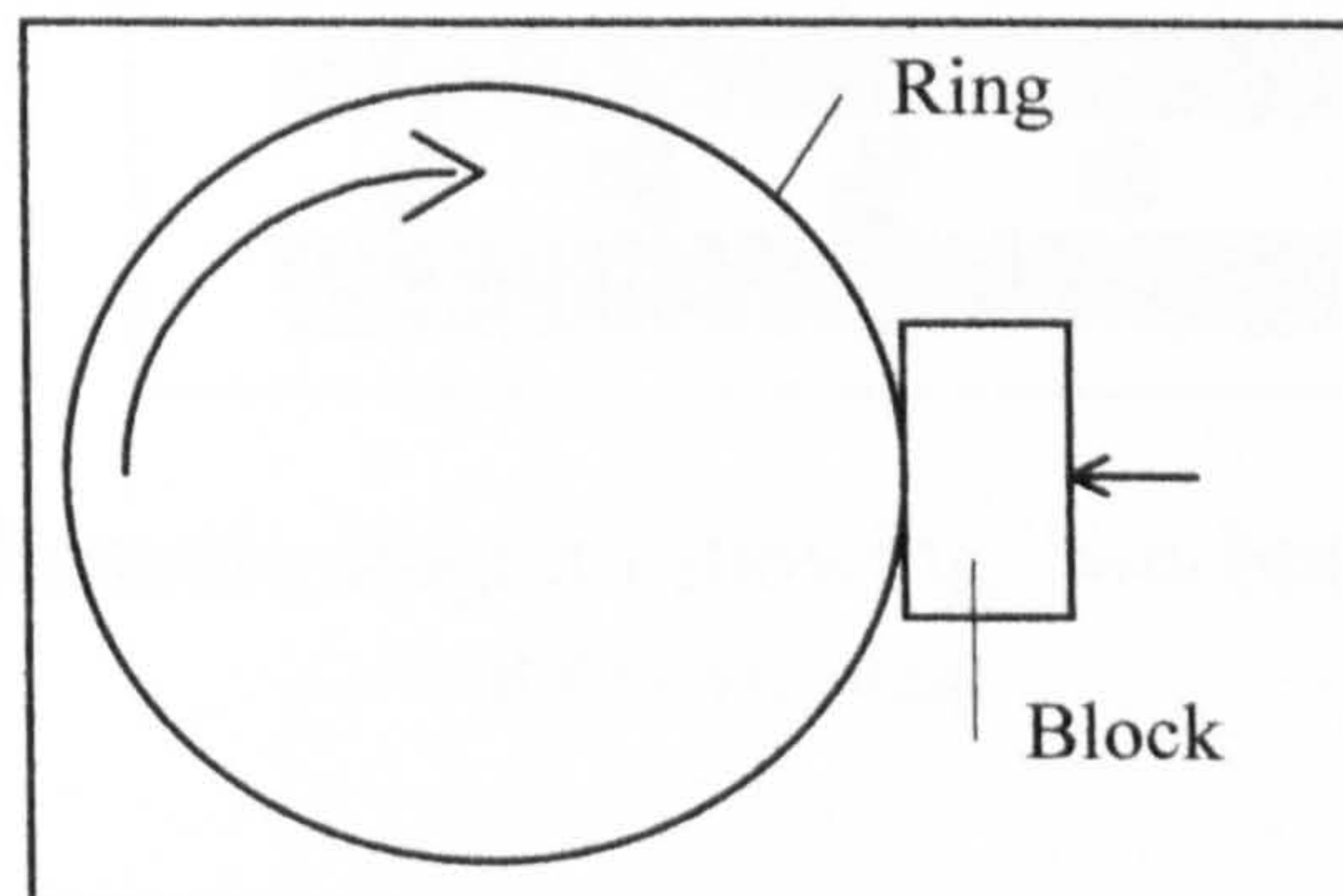


Figure 23 - Schematic of a 'block on ring' wear test

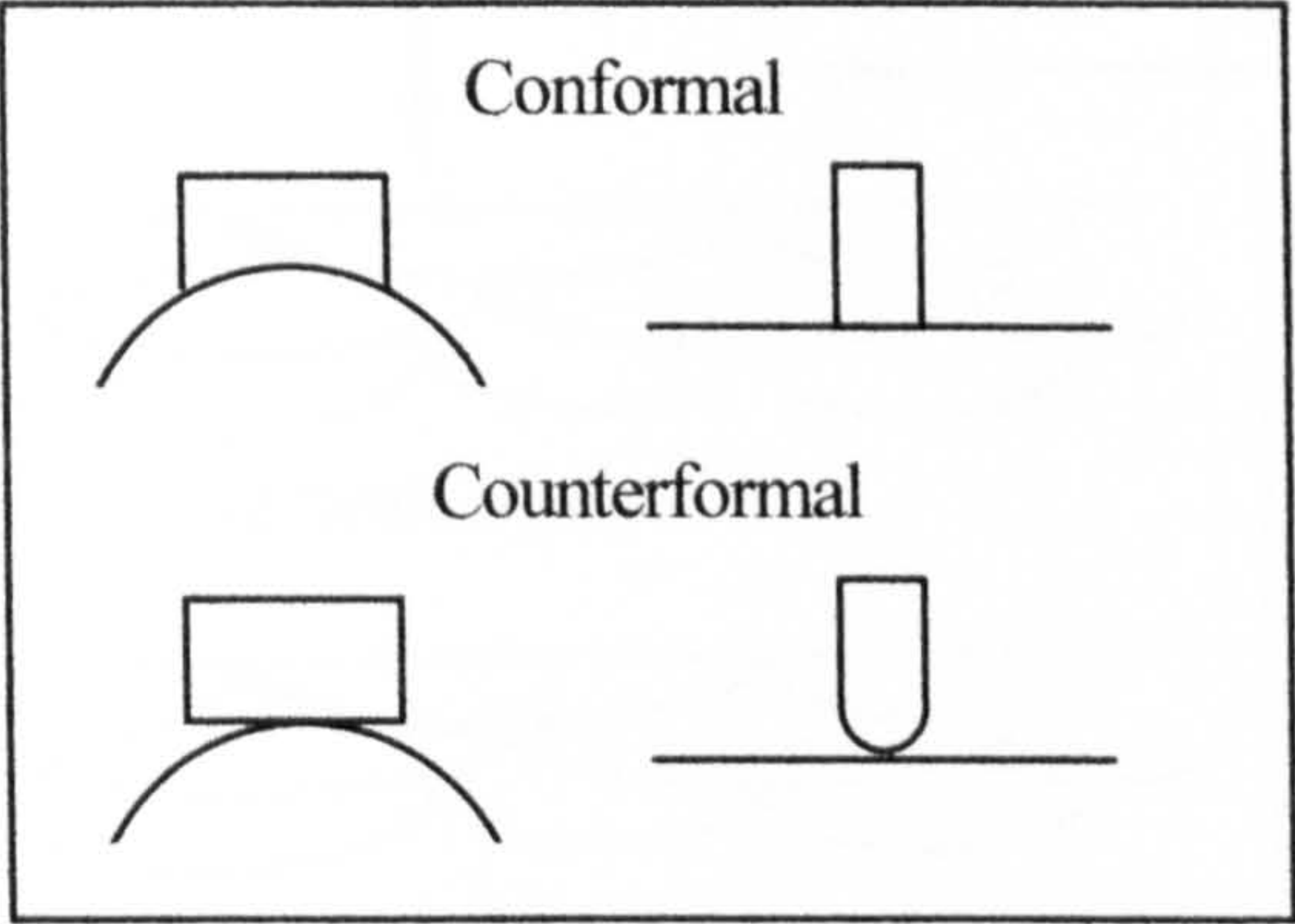


Figure 24 - Schematic diagram showing conformal and counterformal geometry's

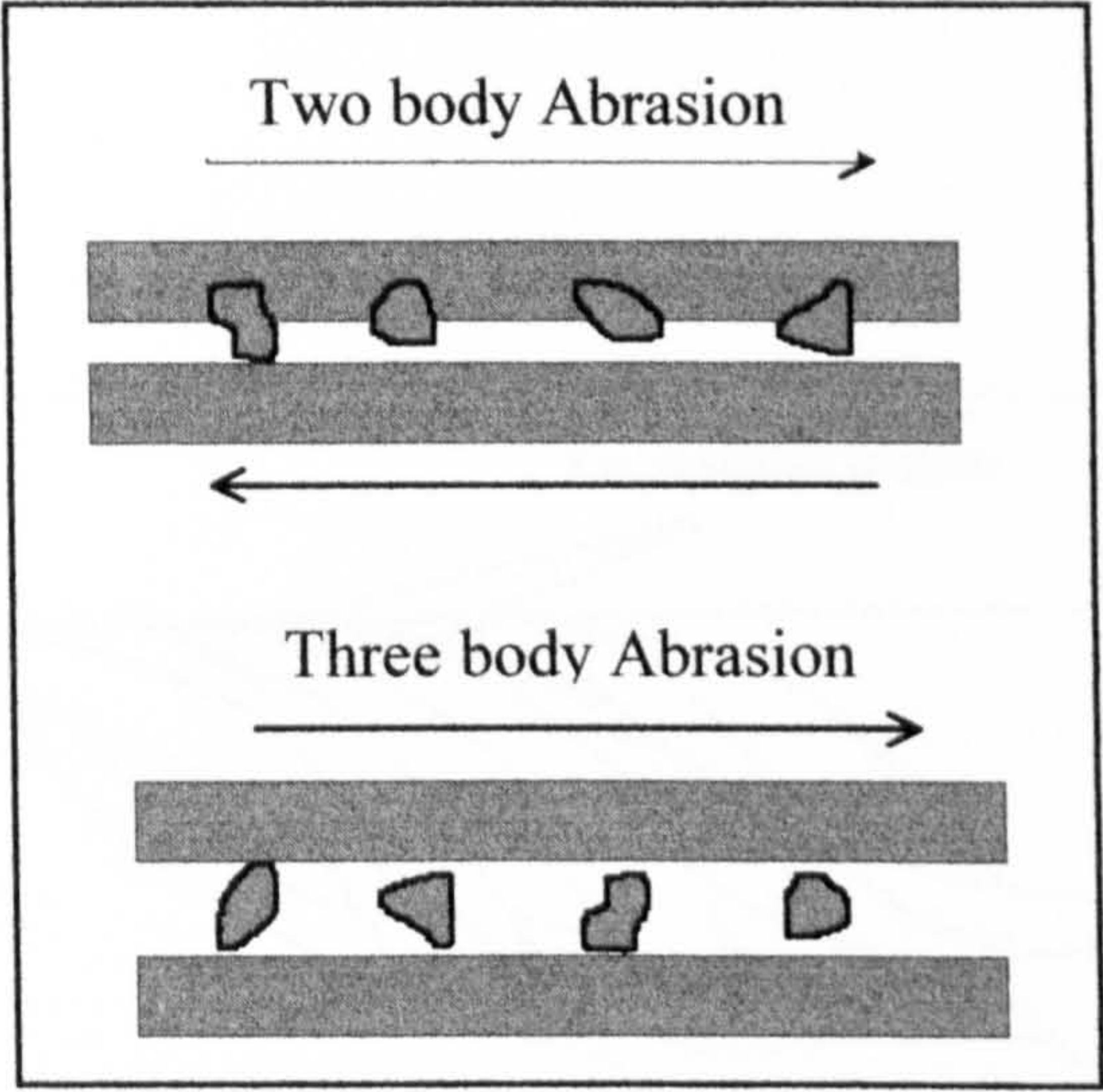


Figure 25 - Schematic diagram showing two-body and three-body abrasive wear

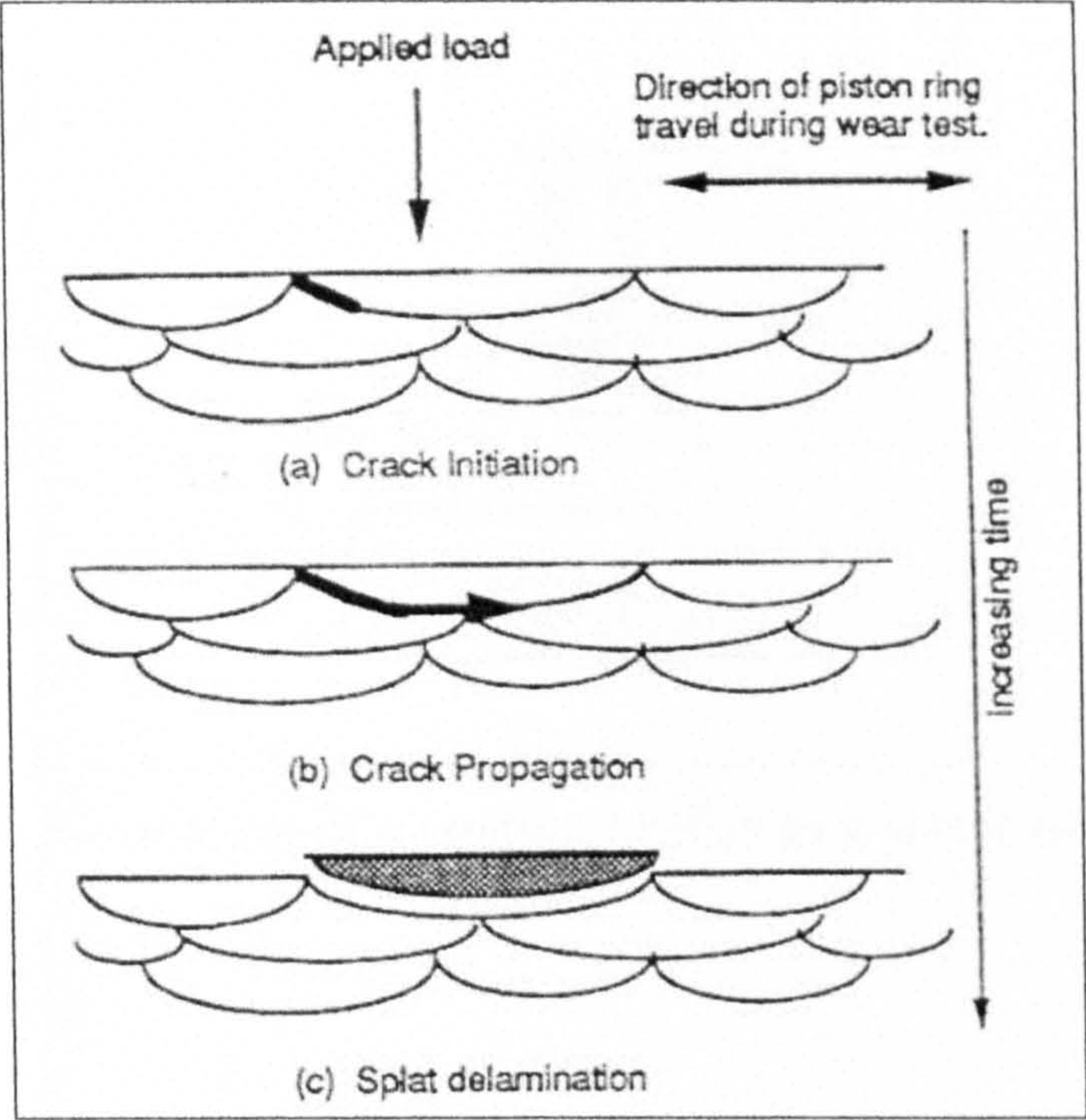


Figure 26 - Schematic subsurface cracking wear mechanism. The crack initiates in (a), propagation in (b), and the splat finally falls out in (c).^[23]

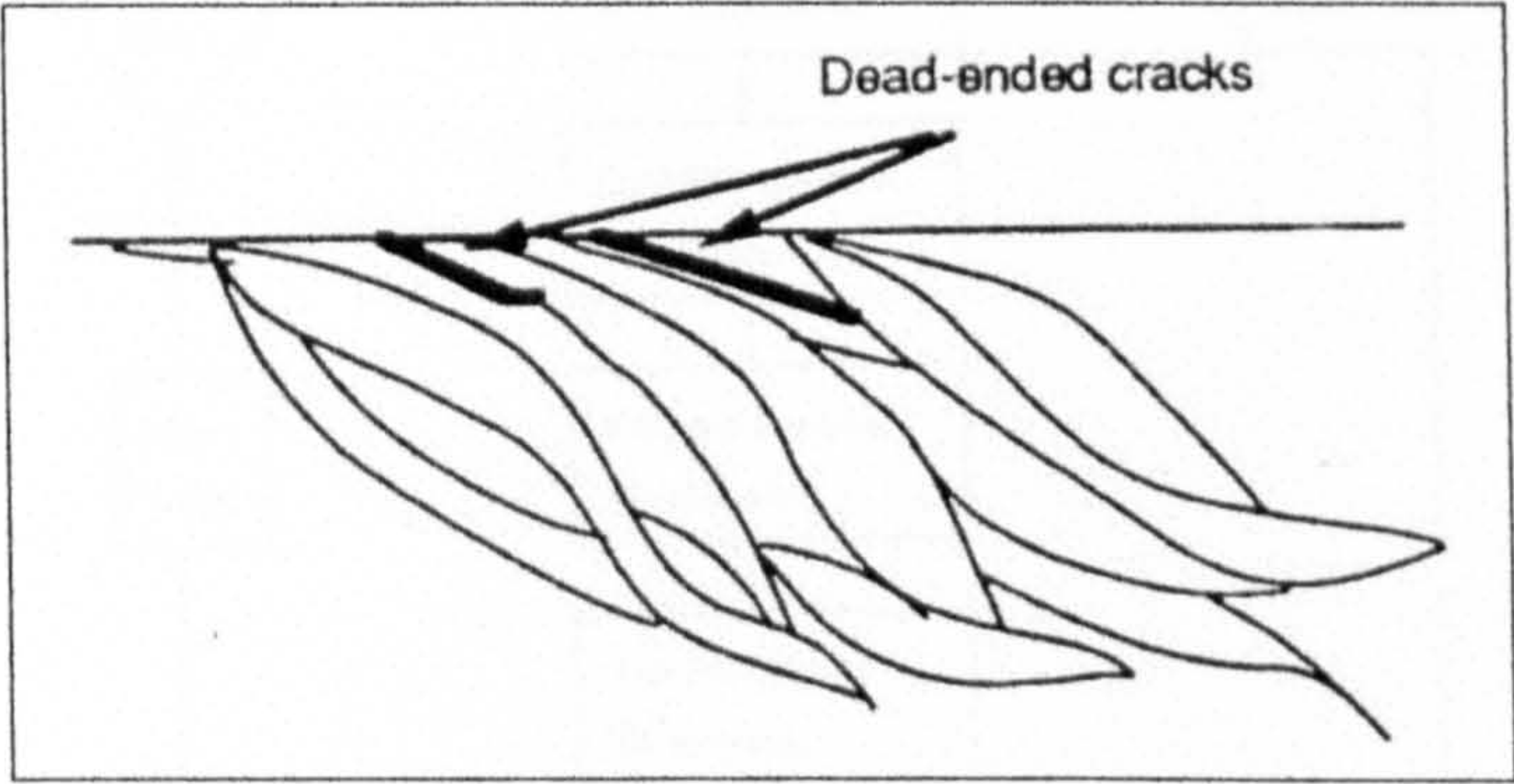


Figure 27 - Schematic depiction of crack propagation and "dead-ending" of cracks in a thermal spray coating with irregular, wavy splats. The wavy splats provide crack path tortuosity.^[23]

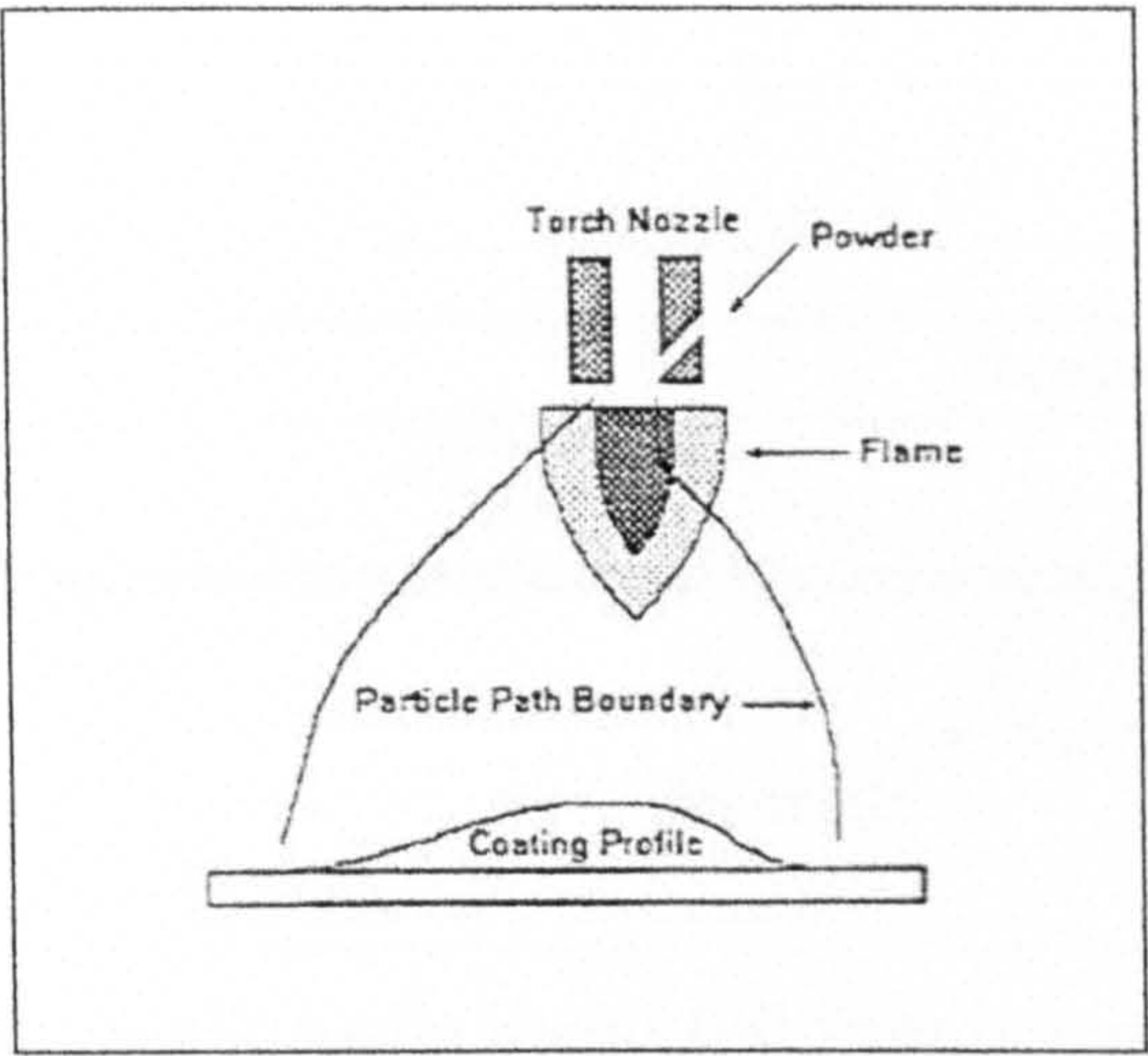


Figure 28 - The formation of a coating profile as a series of unidirectional passes^[25]

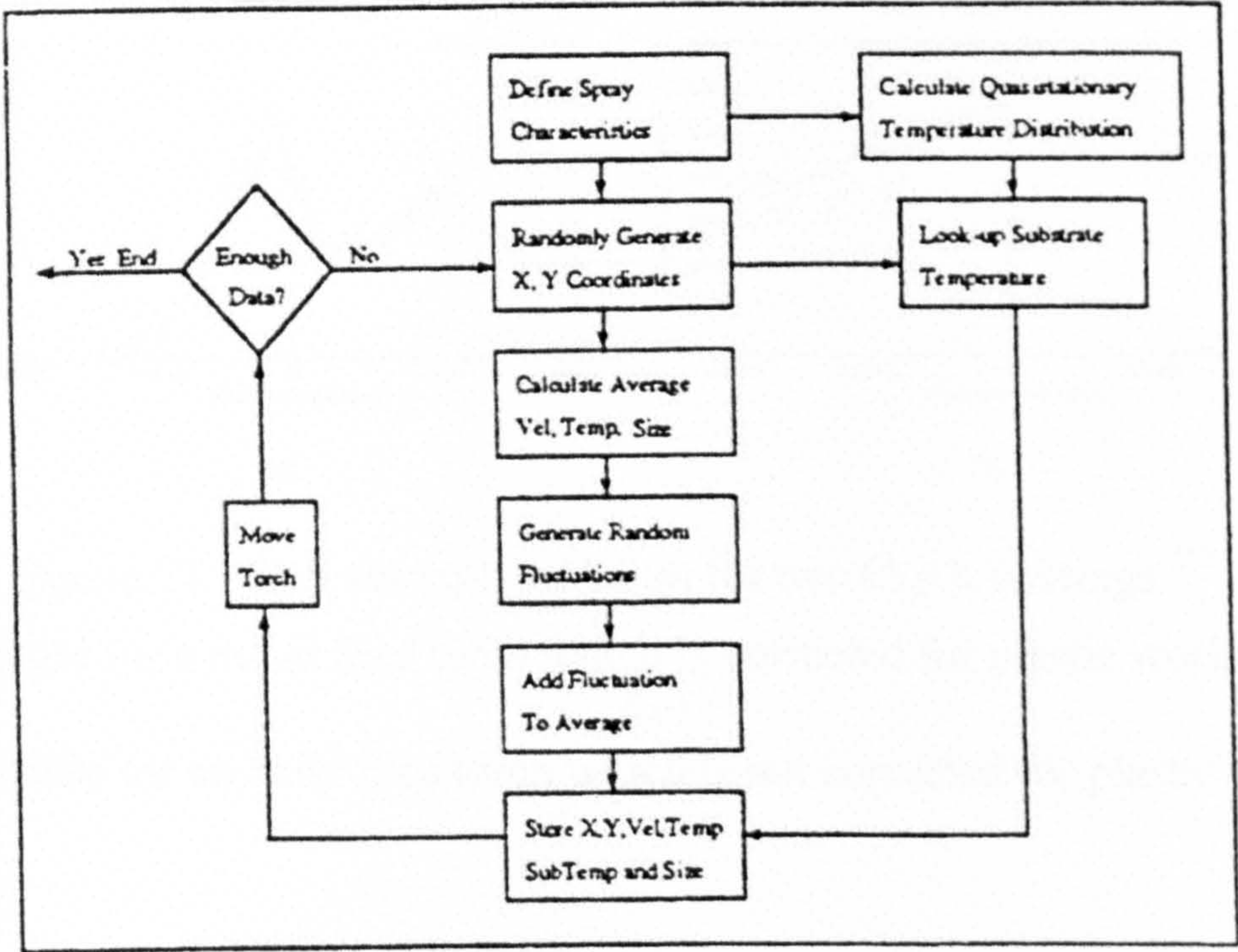


Figure 29 - Flow chart of Monte Carlo coating simulation logic^[25]

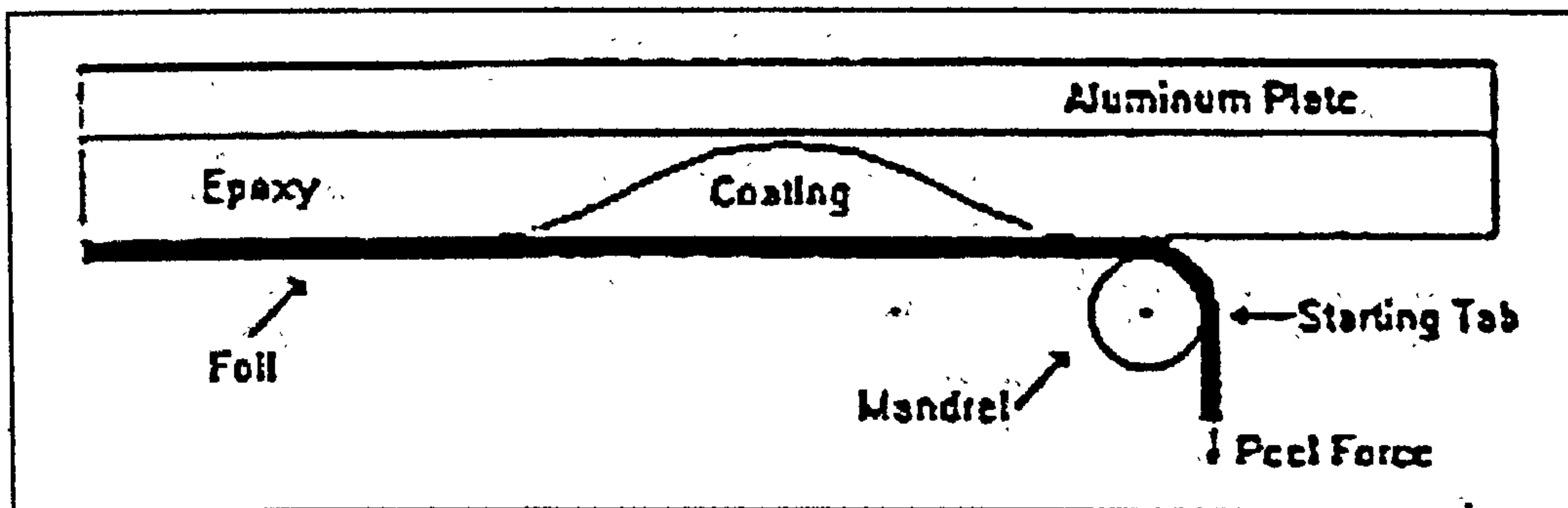


Figure 30 - The peeling of a metal foil from a coating profile^[25]

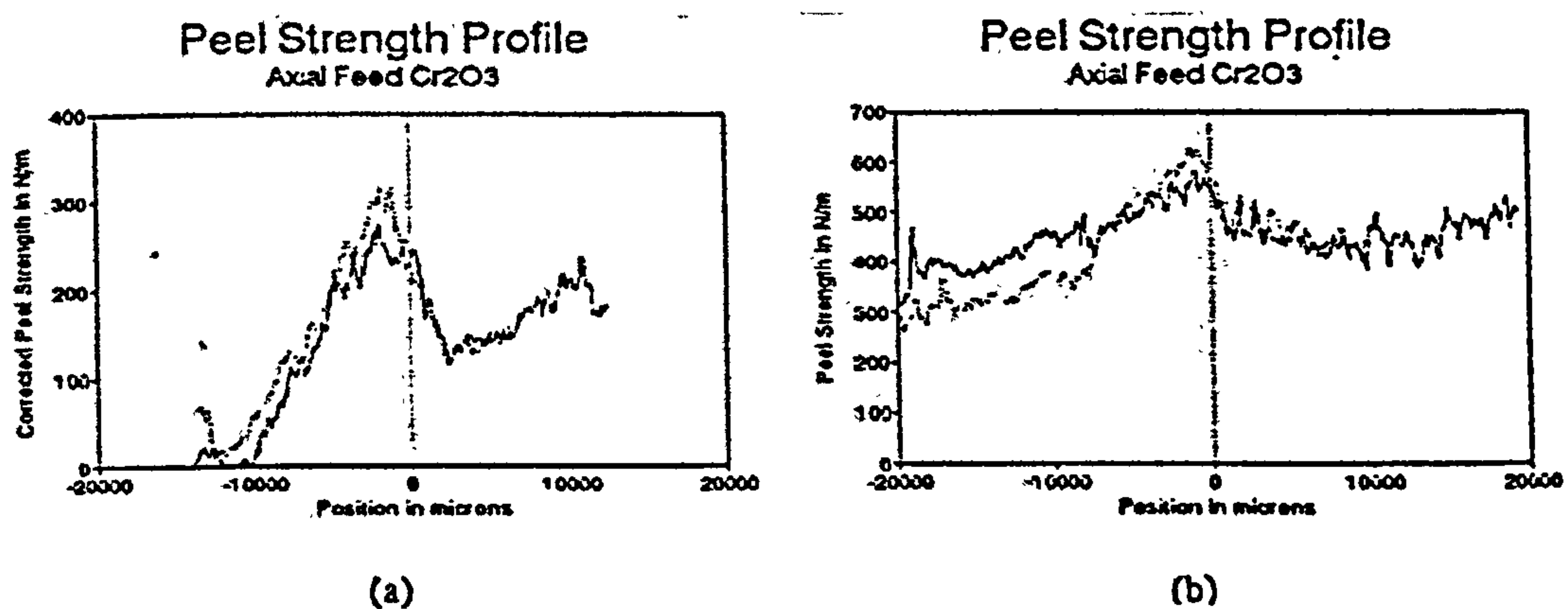


Figure 31 - Peel strength variation for two Cr_2O_3 coatings.^[25]

(a) Profile for a radial feed torch which is corrected for plastic work in the foil

(b) Profile for an axial feed torch which is not corrected for plastic work.

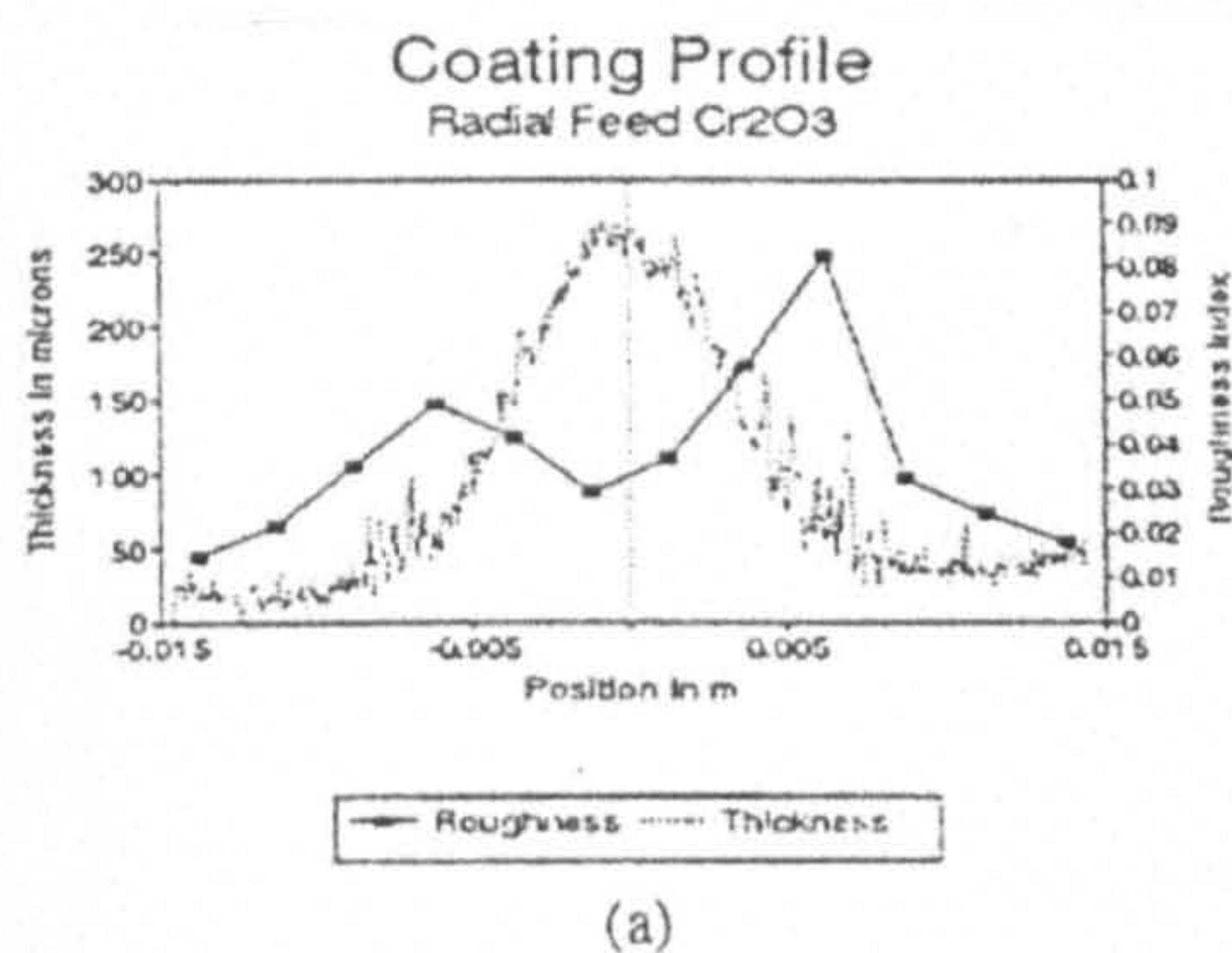
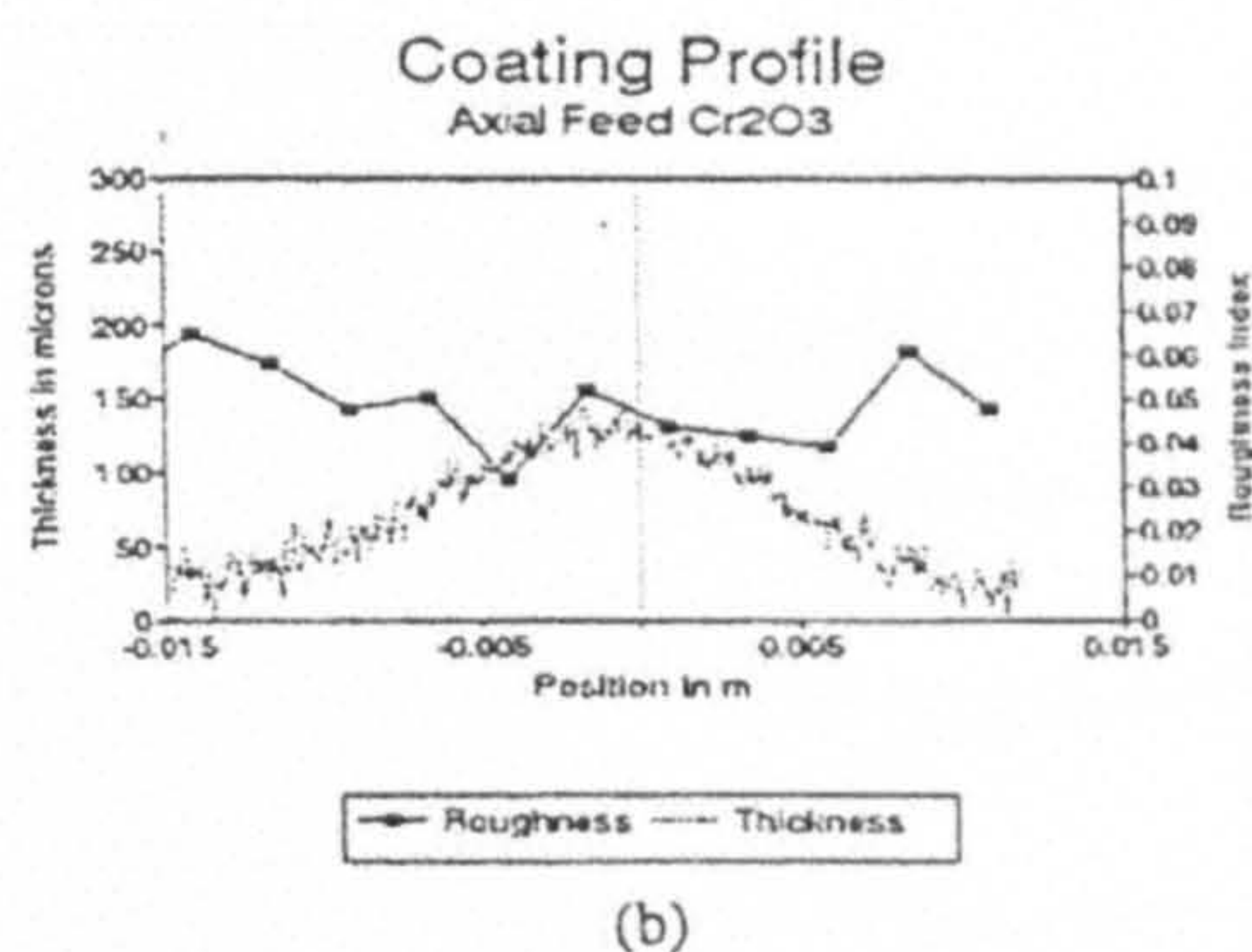


Figure 32 – Profiles of two Cr_2O_3 coatings showing the variation in R.M.S. roughness across the profile. The roughness is expressed as a fraction of the maximum profile thickness. ^[25]

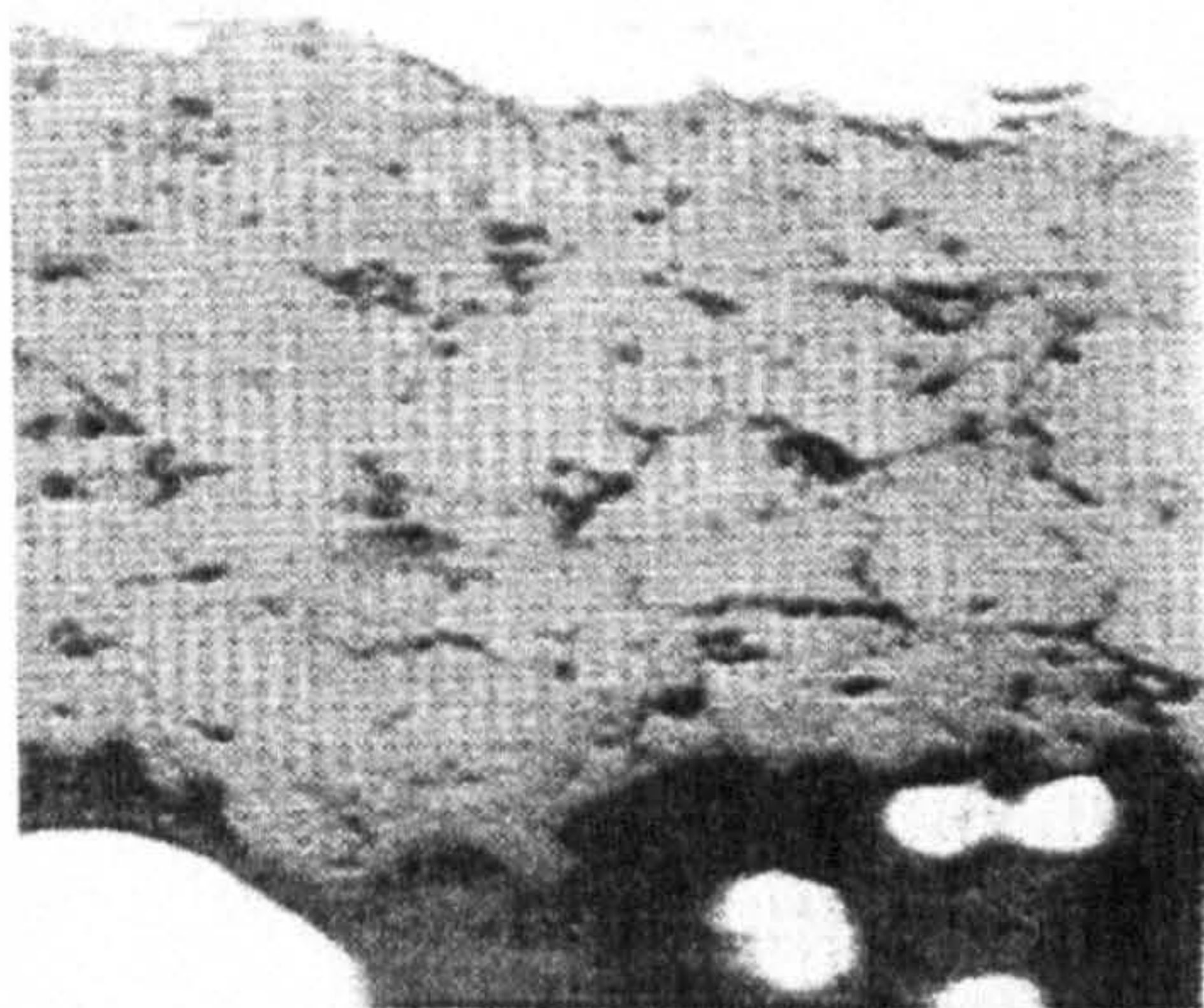
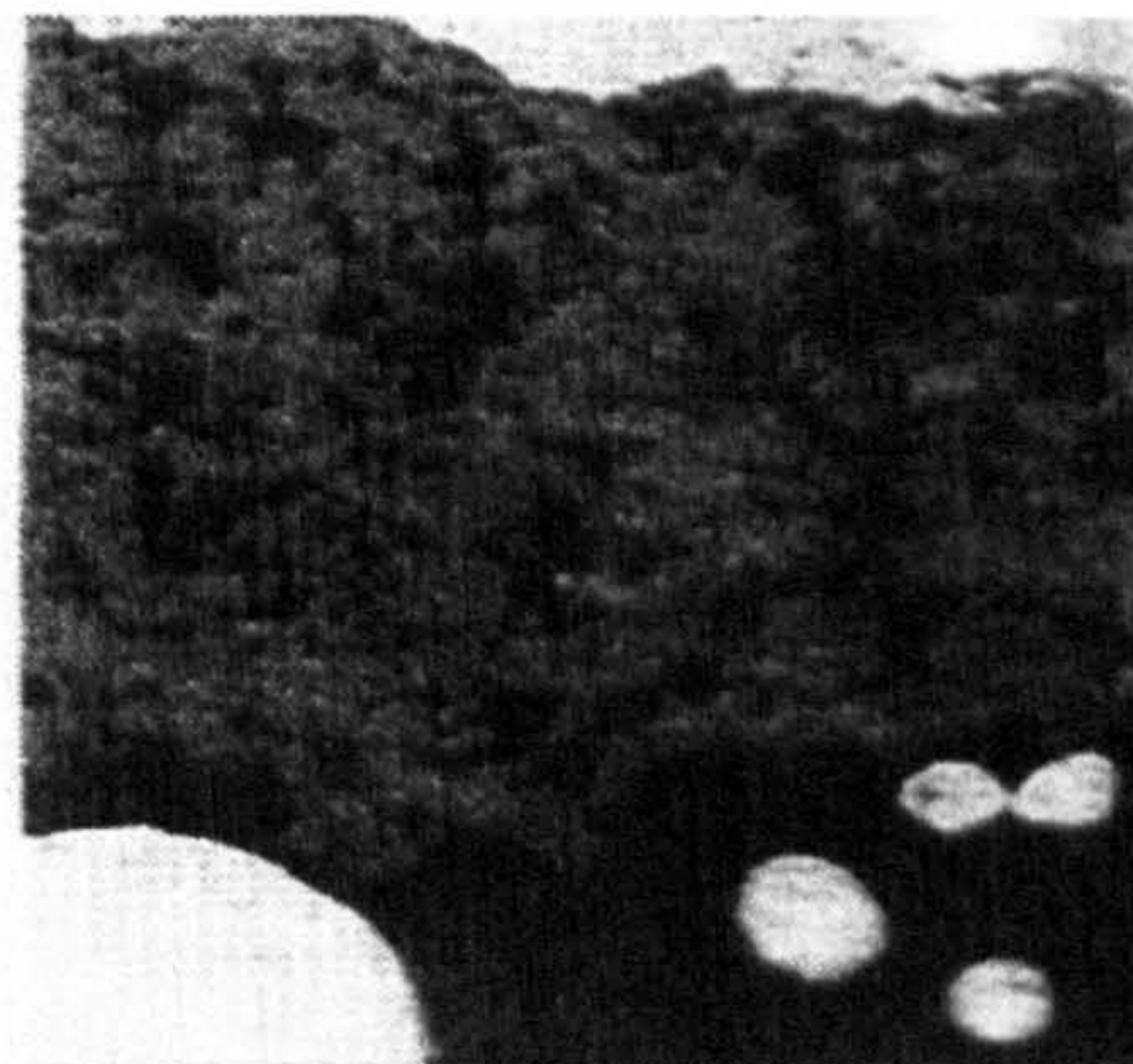


Figure 33 - Porosity of a Cr_2O_3 coating before and after a 'damage polish' ^[25]

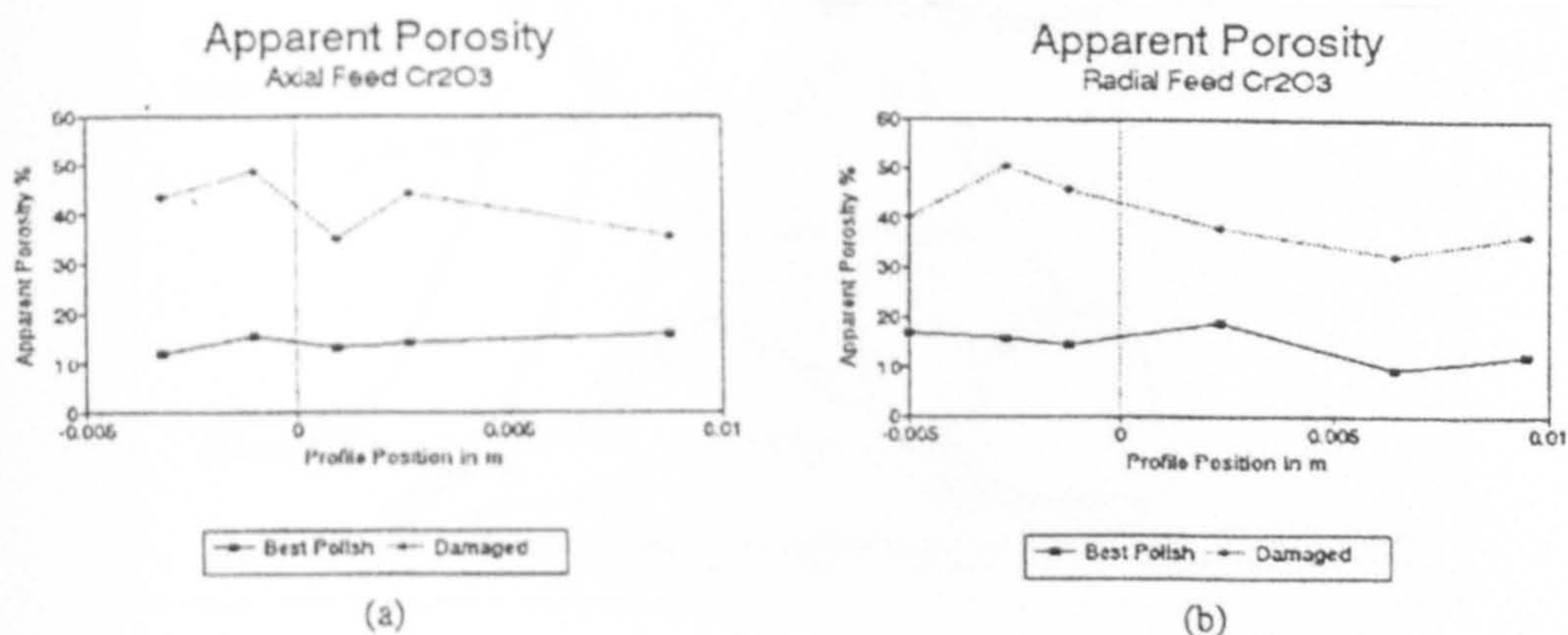


Figure 34 - The variation in porosity across two Cr₂O₃ coating profiles showing the effect of the 'damage polish': (a) Axial Feed (b) Radial Feed. Note that direct comparison between the two samples is not possible as the severity of the damage polish may have been different.^[25]

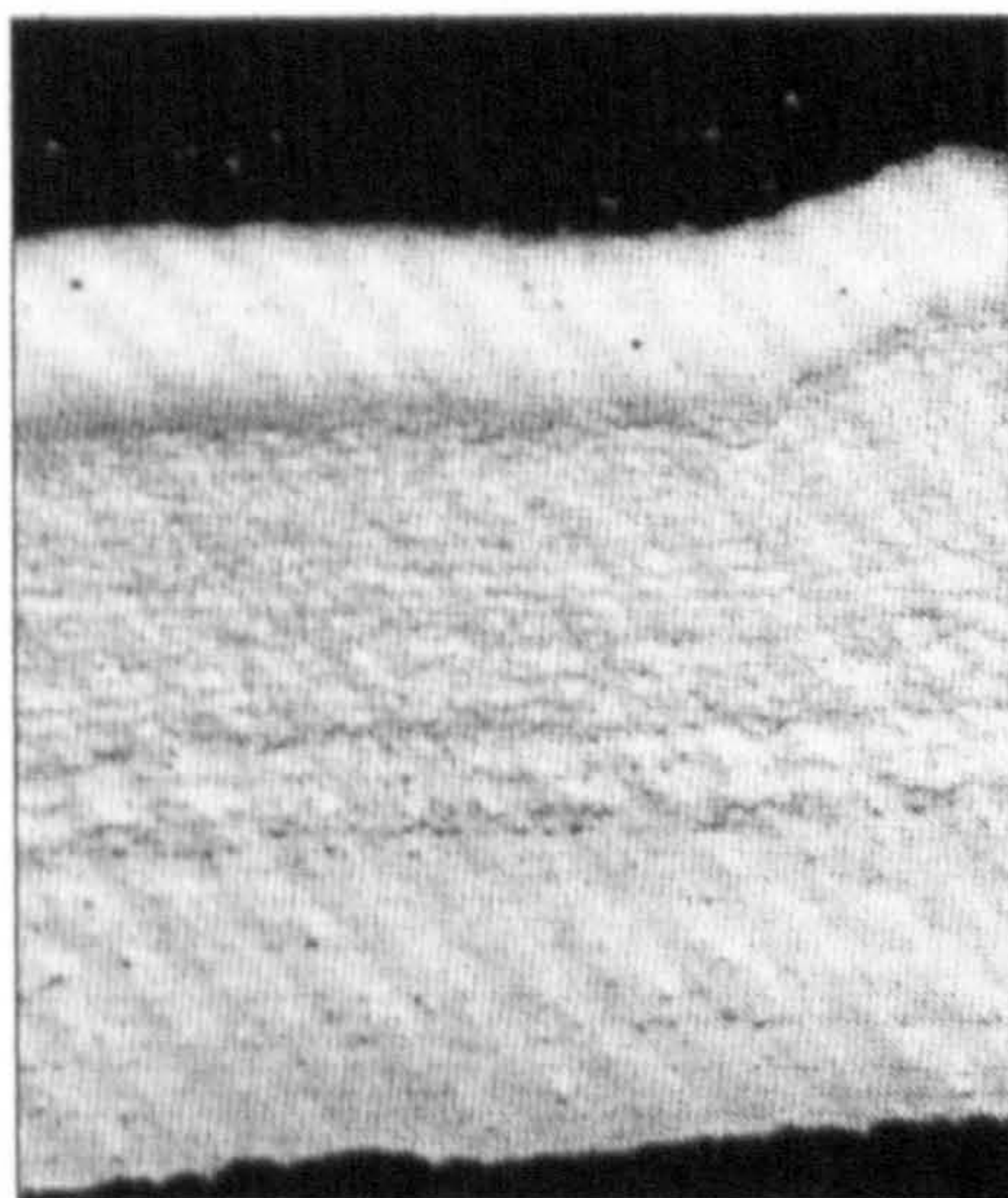


Figure 35 - Copper/Tungsten/Boron/Boron Nitride functionally gradient coating.^[27]

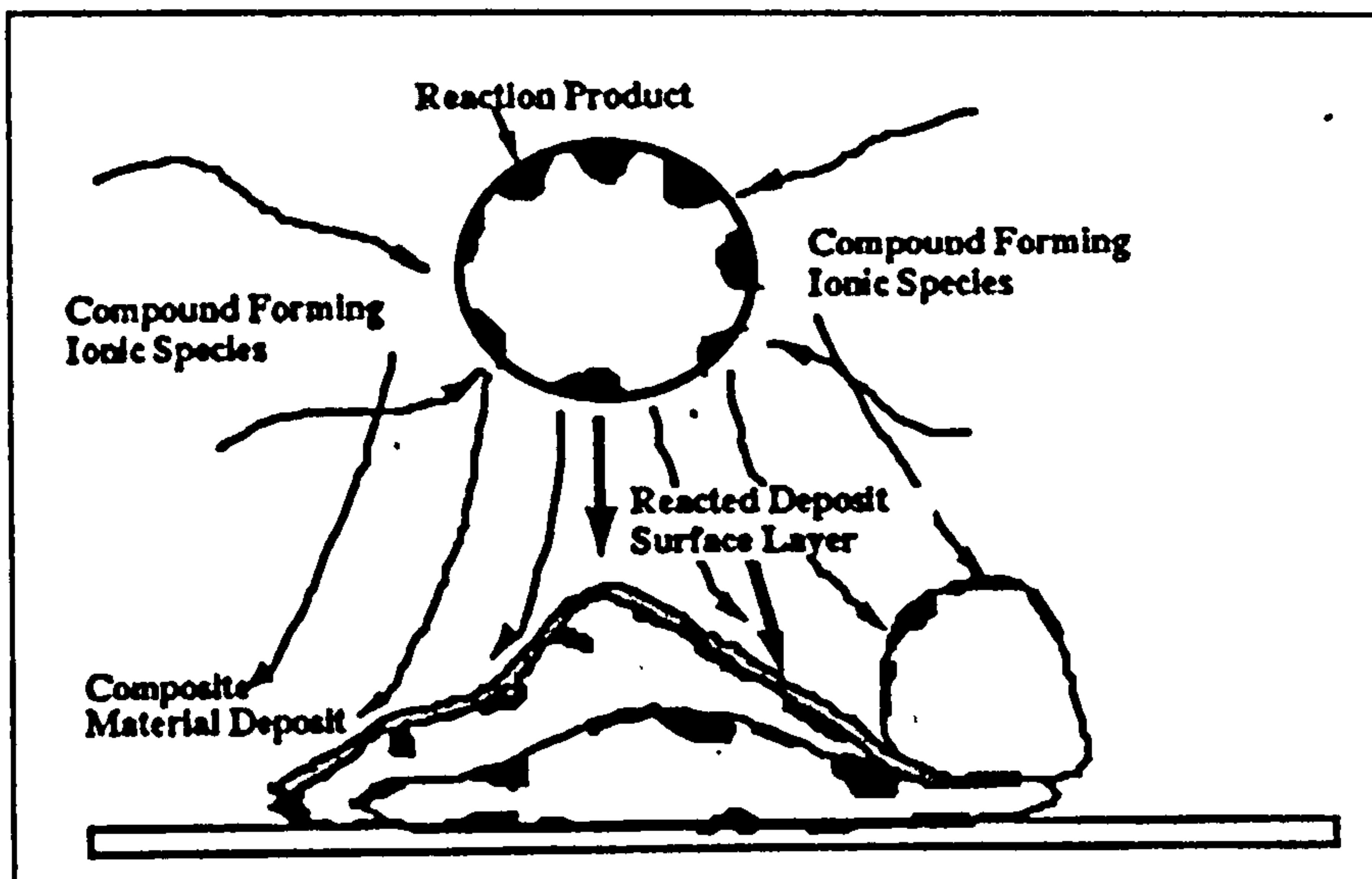


Figure 36 - Schematic illustration of the formation of TiC composite deposits plasma sprayed with reactive gases^[31]

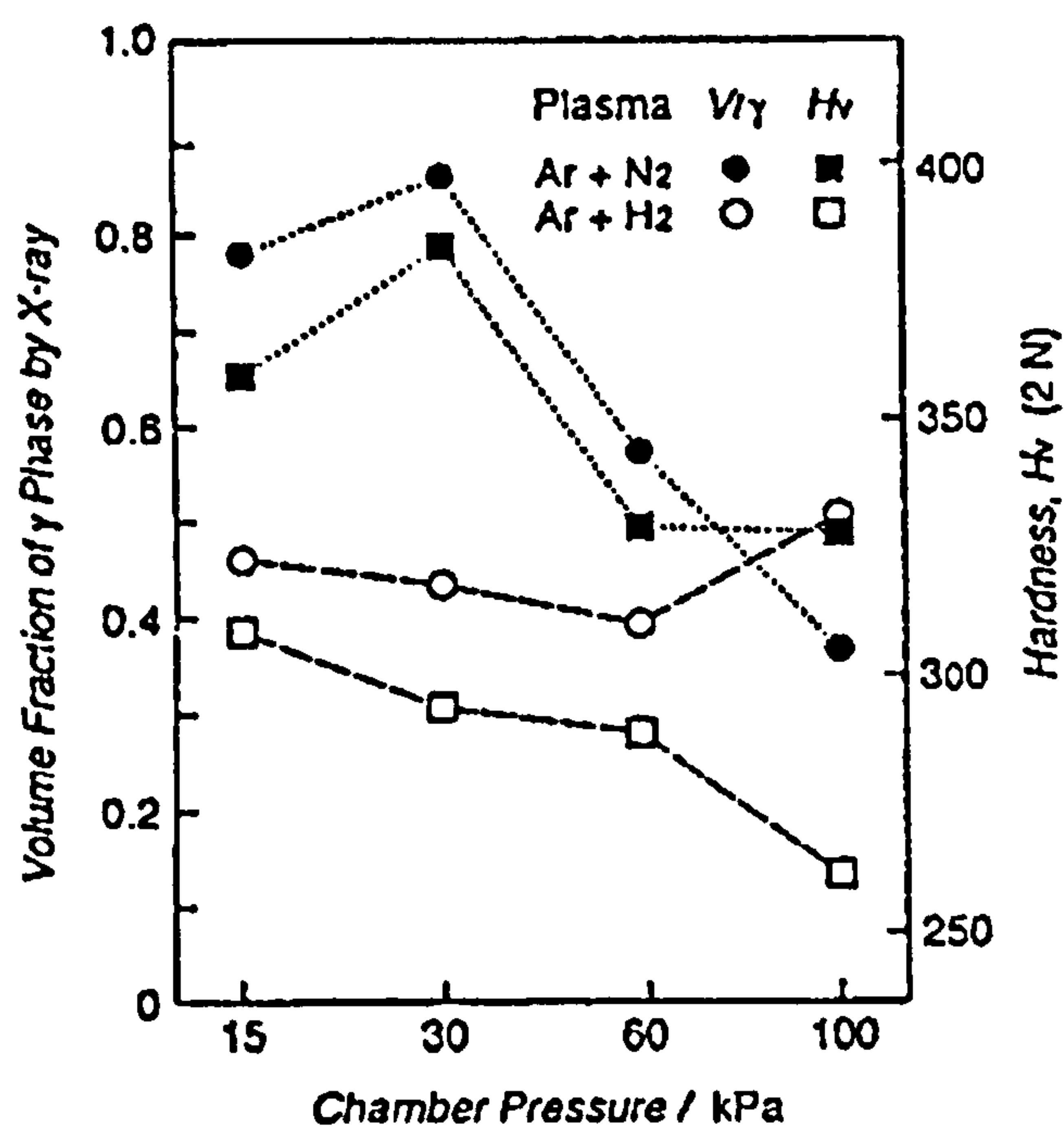


Figure 37 - Effect of chamber pressure on volume fraction of γ phase and hardness of coating^[28]

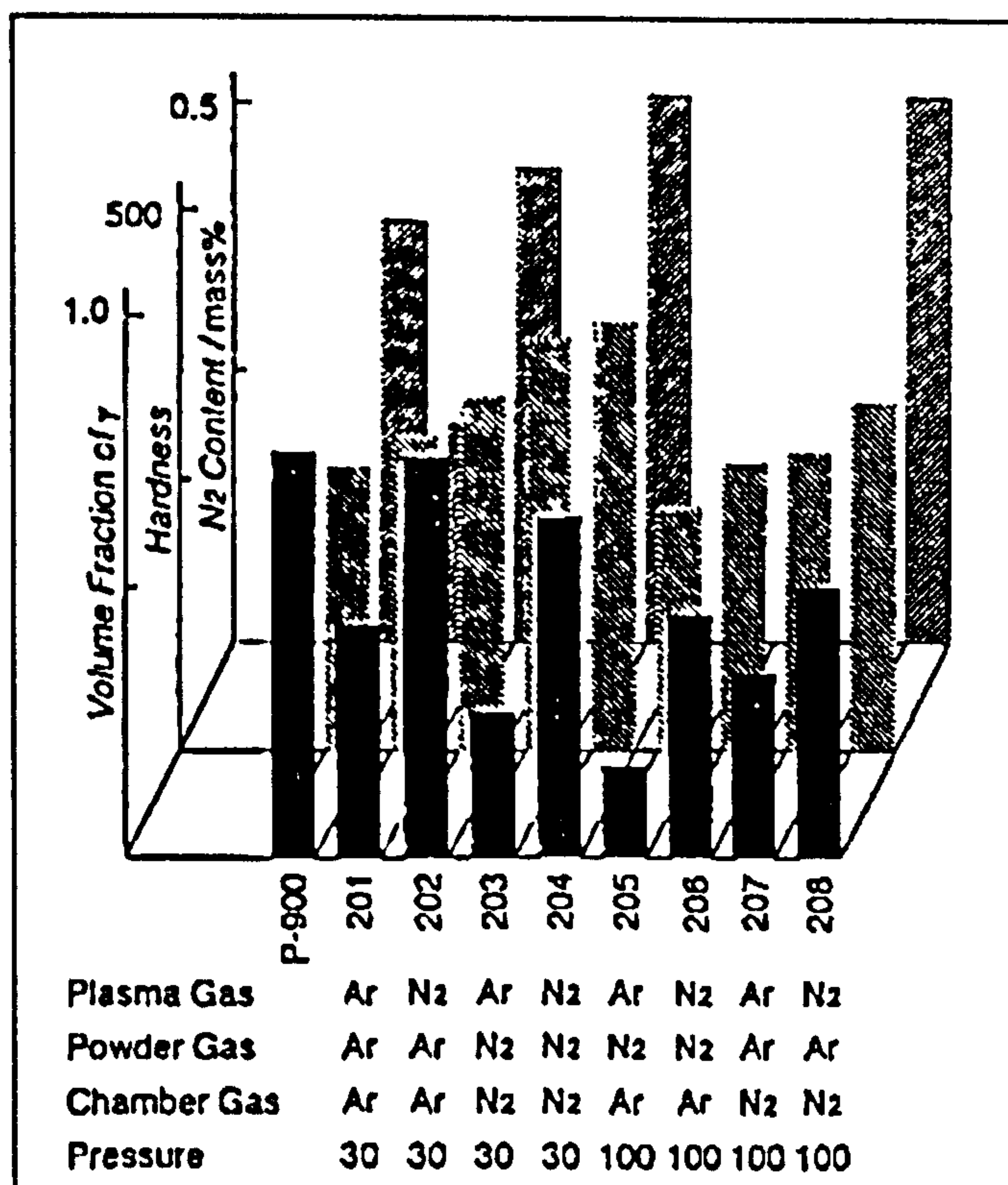


Figure 38 - Effect of spraying conditions on microstructures of coatings

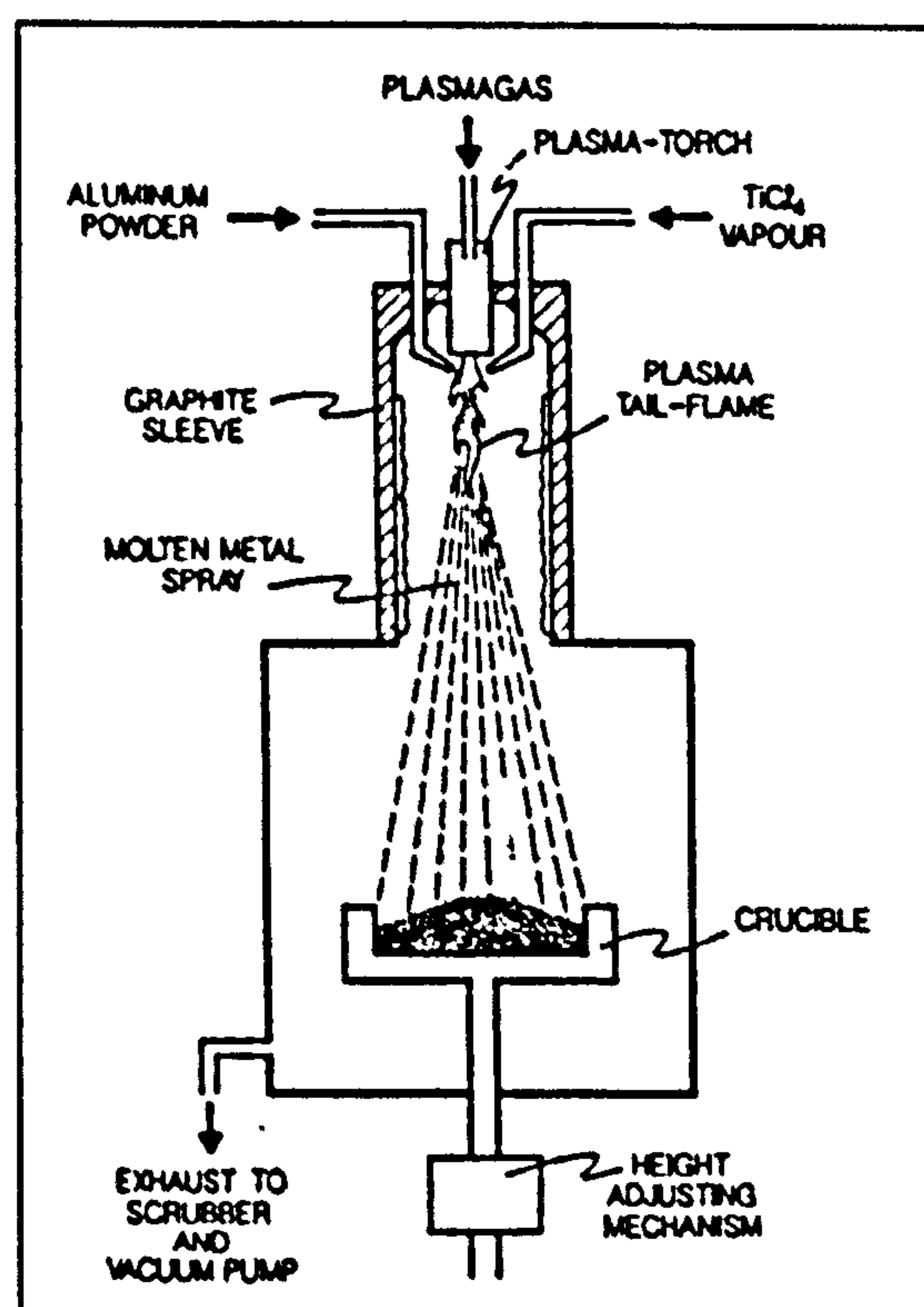


Figure 39 - Schematic of reactor^[29]

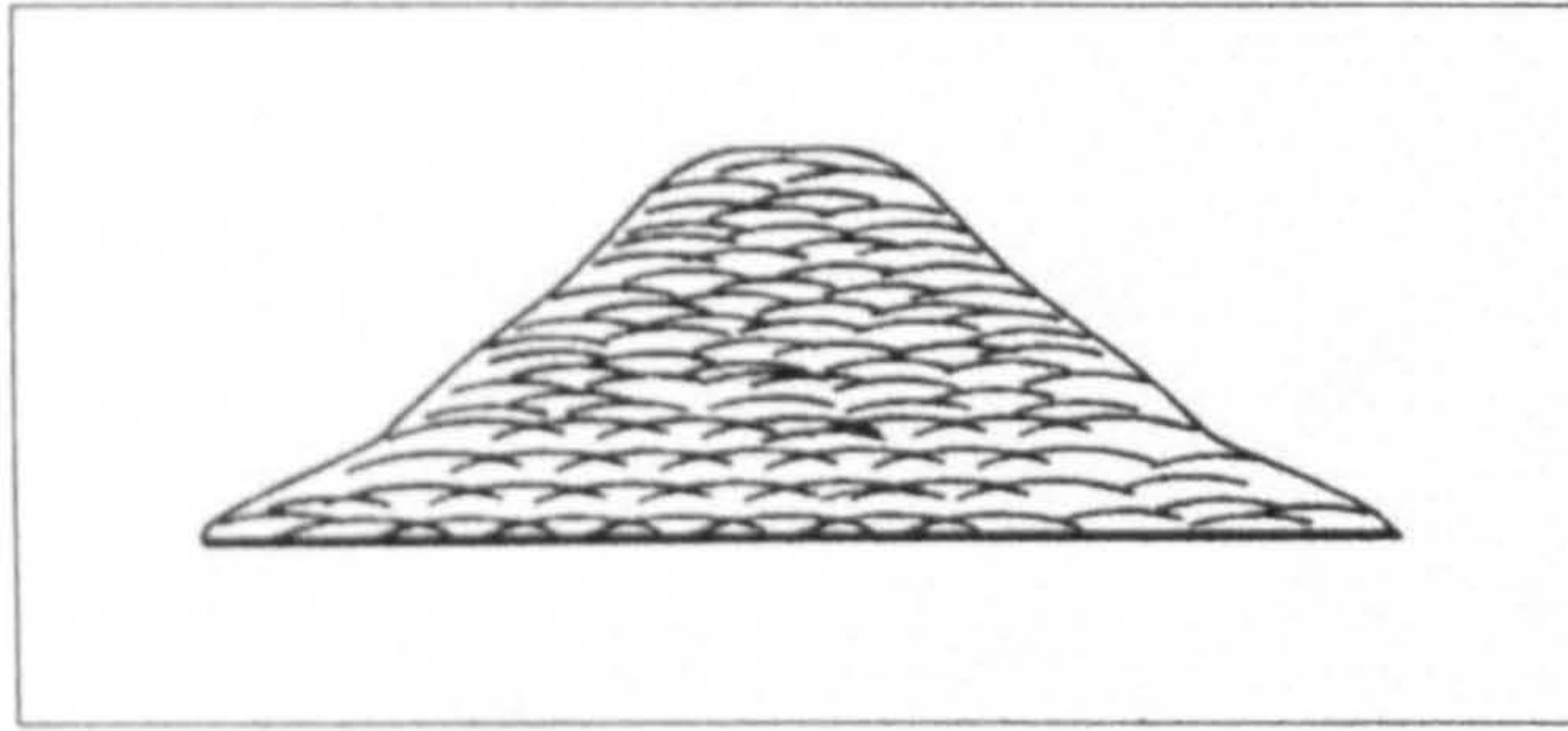


Figure 40 - Reactive plasma spray deposit^[30]

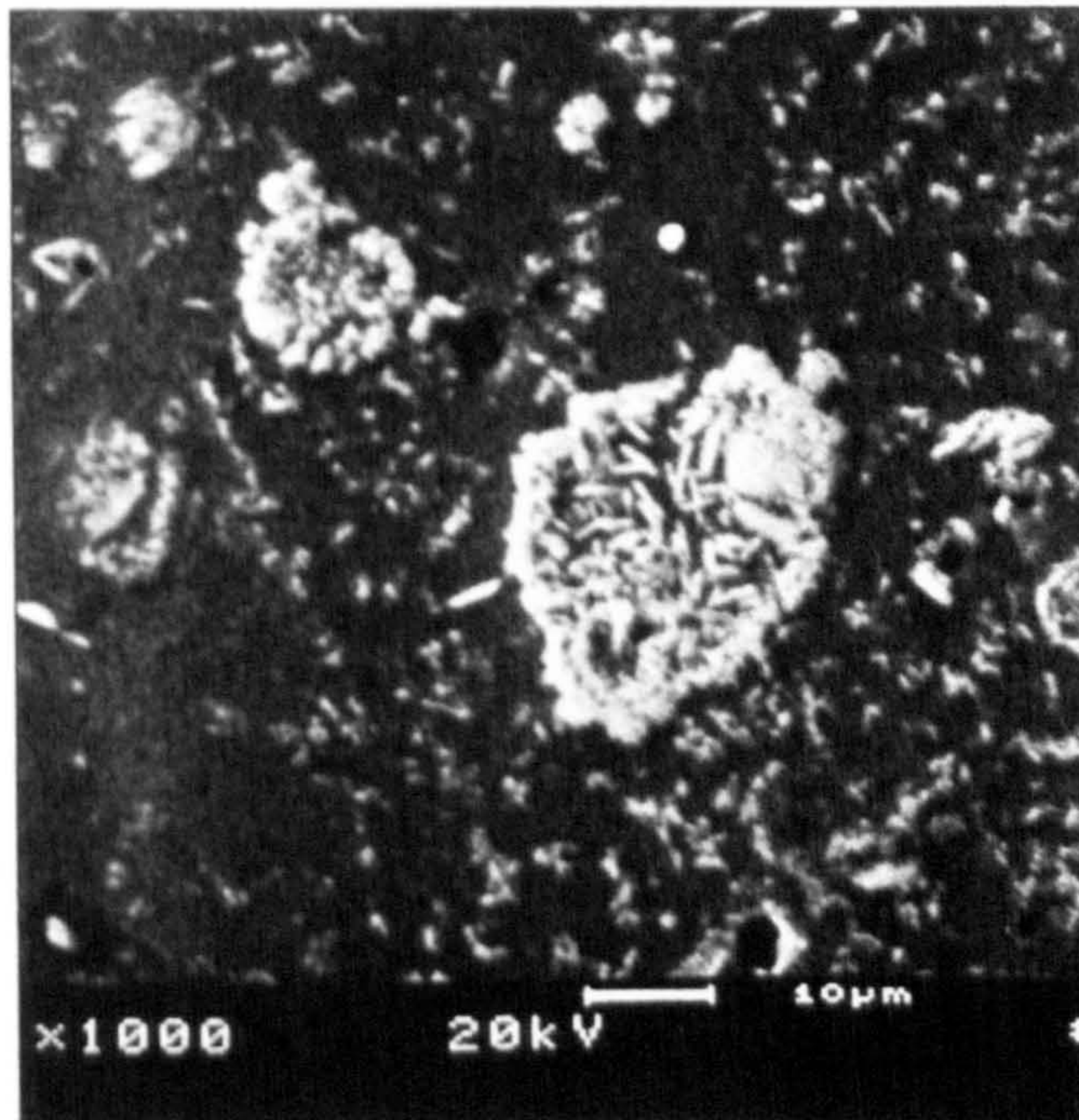


Figure 41 - Microstructure of Al-Ti alloys produced through reactive plasma process^[30]

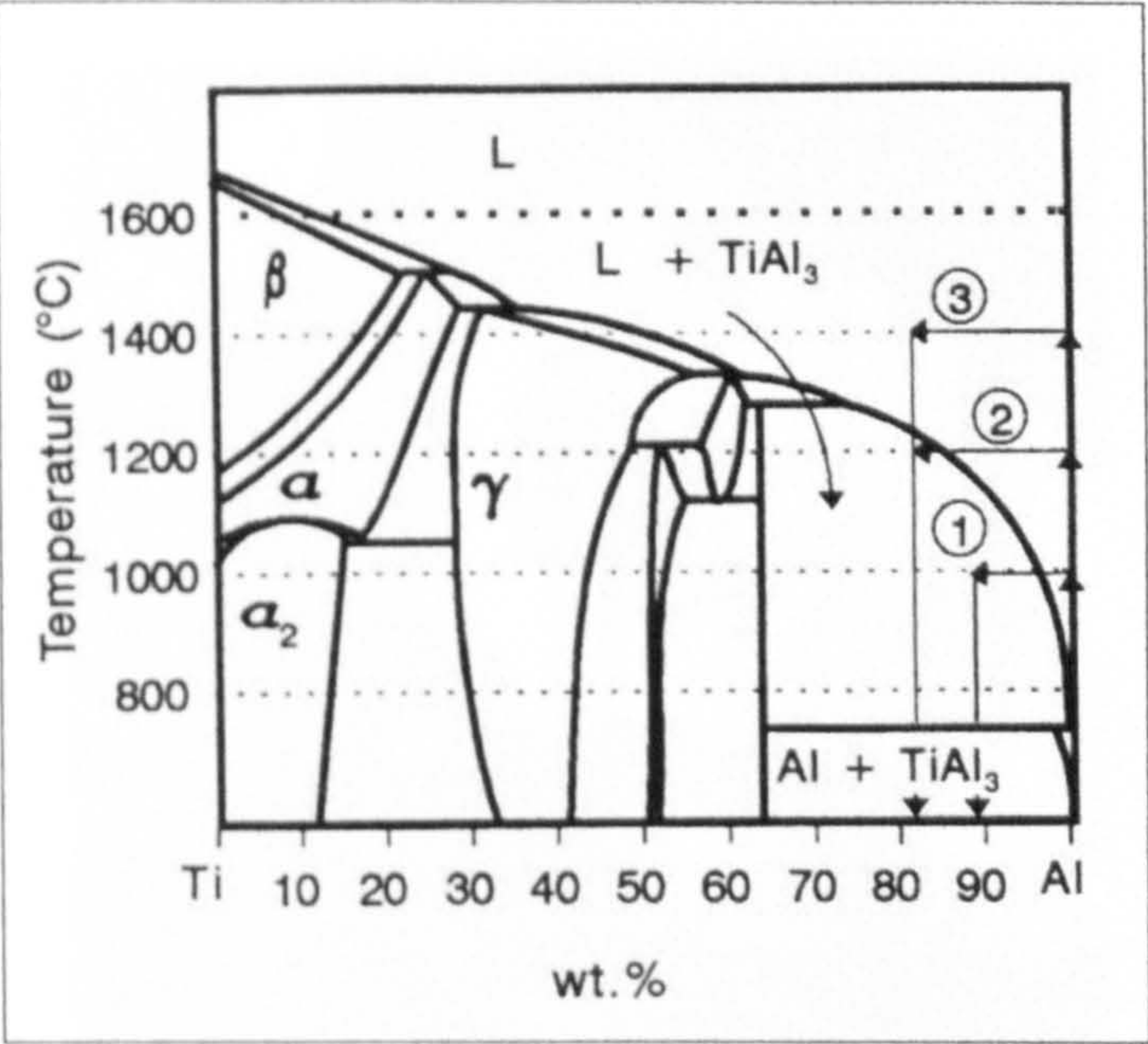


Figure 42 - Ti-Al phase diagram^[30]

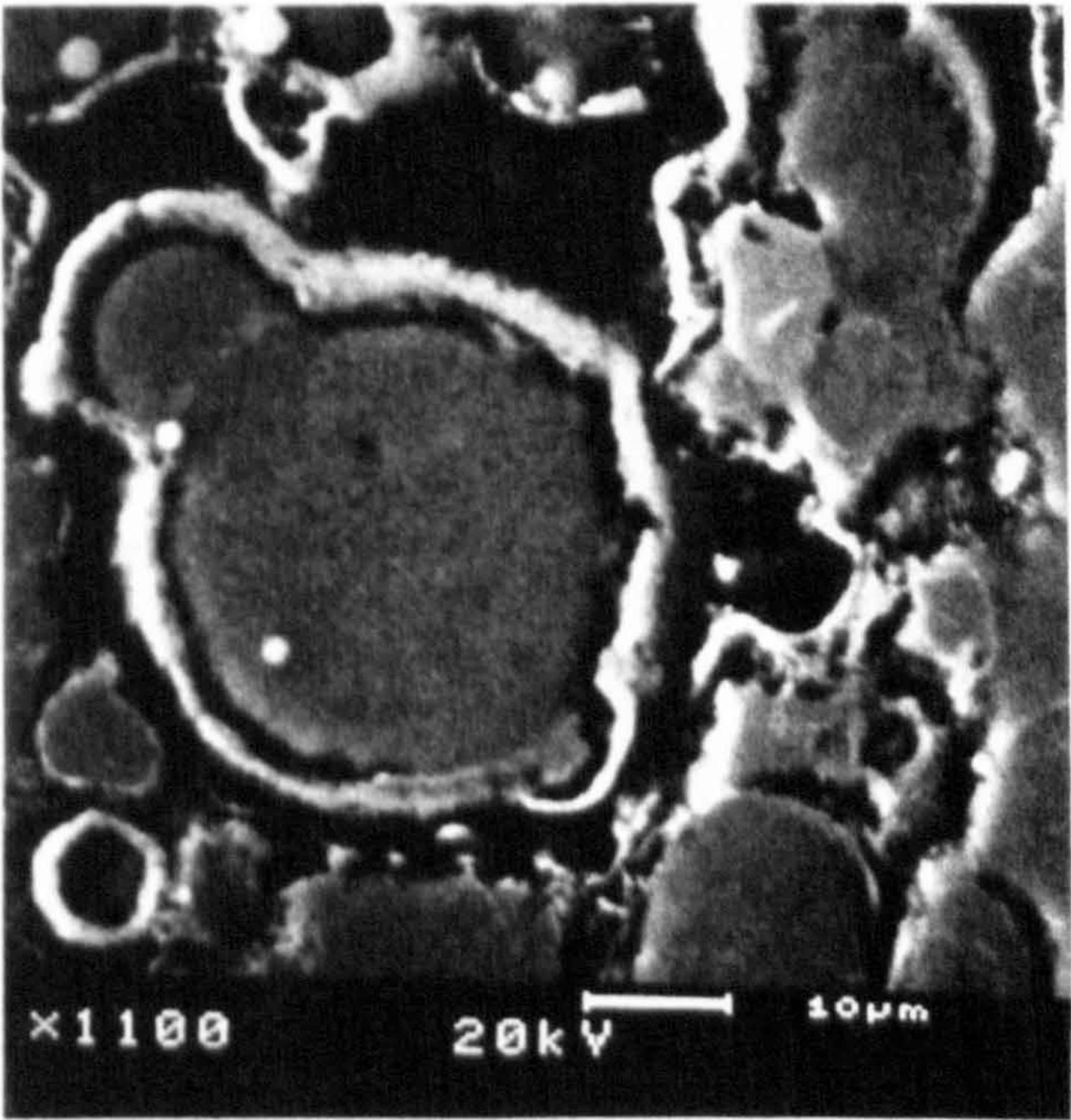


Figure 43 - Microstructure of Al-Ti alloys representing particle with a thermal history corresponding to curve 1 in figure 42^[30]

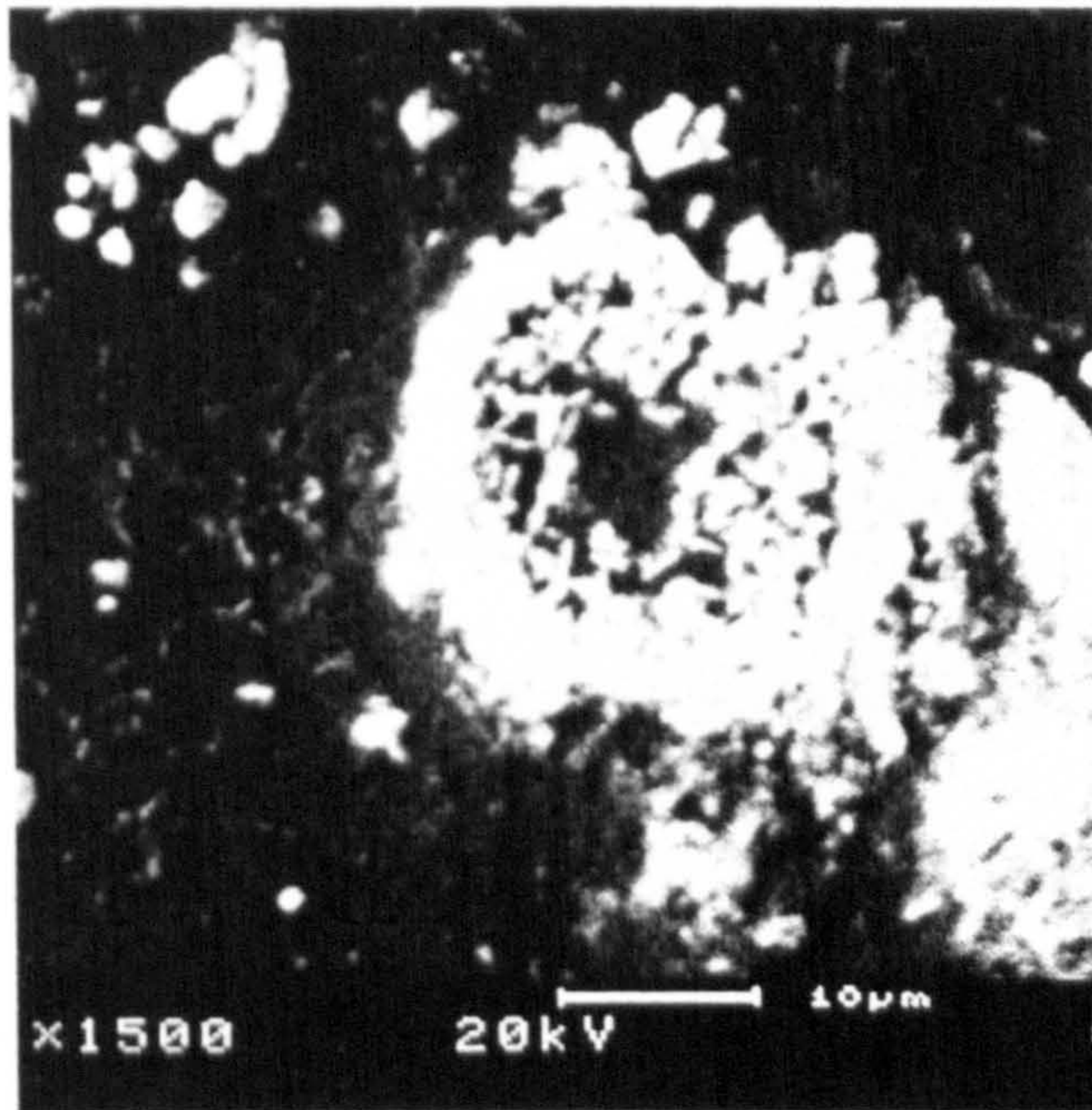


Figure 44 - Microstructure of Al-Ti alloys representing particles with a thermal history corresponding to curve 2 in figure 42^[30]

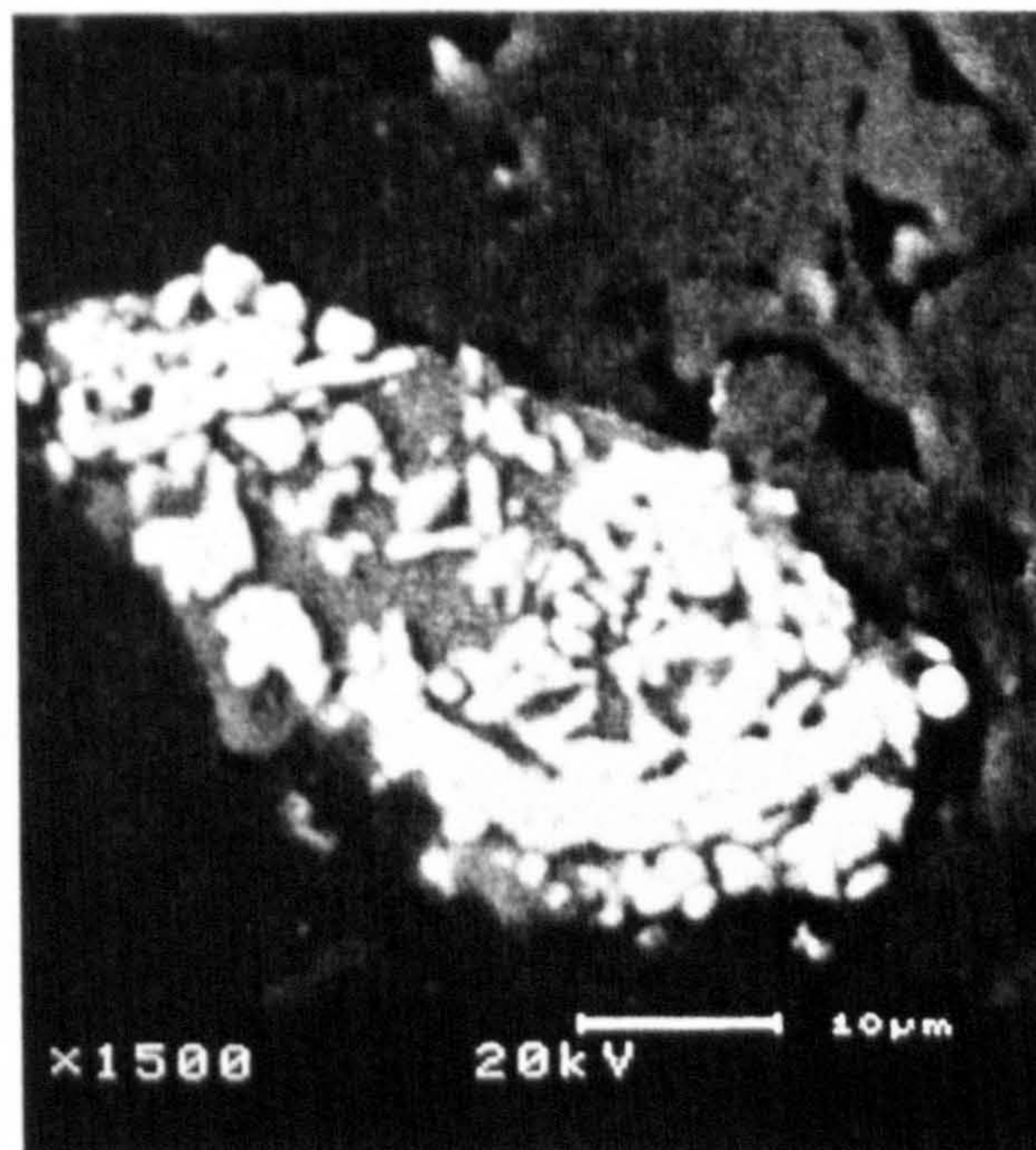


Figure 45 - Microstructure of Al-Ti alloys characterised by curve 3 in figure 42^[30]

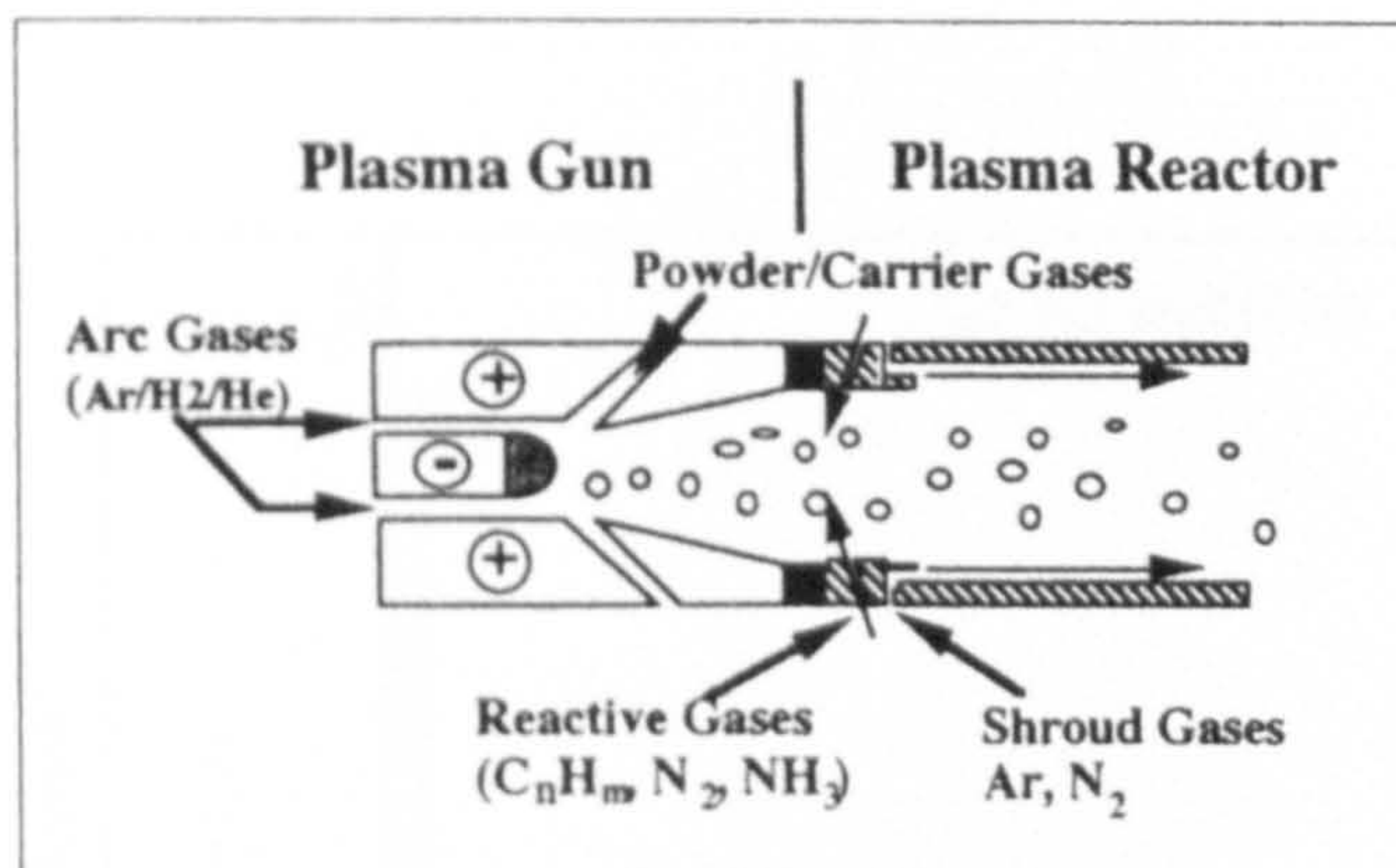


Figure 46 - Schematic diagram of D.C. reactive plasma spray forming apparatus^[10]

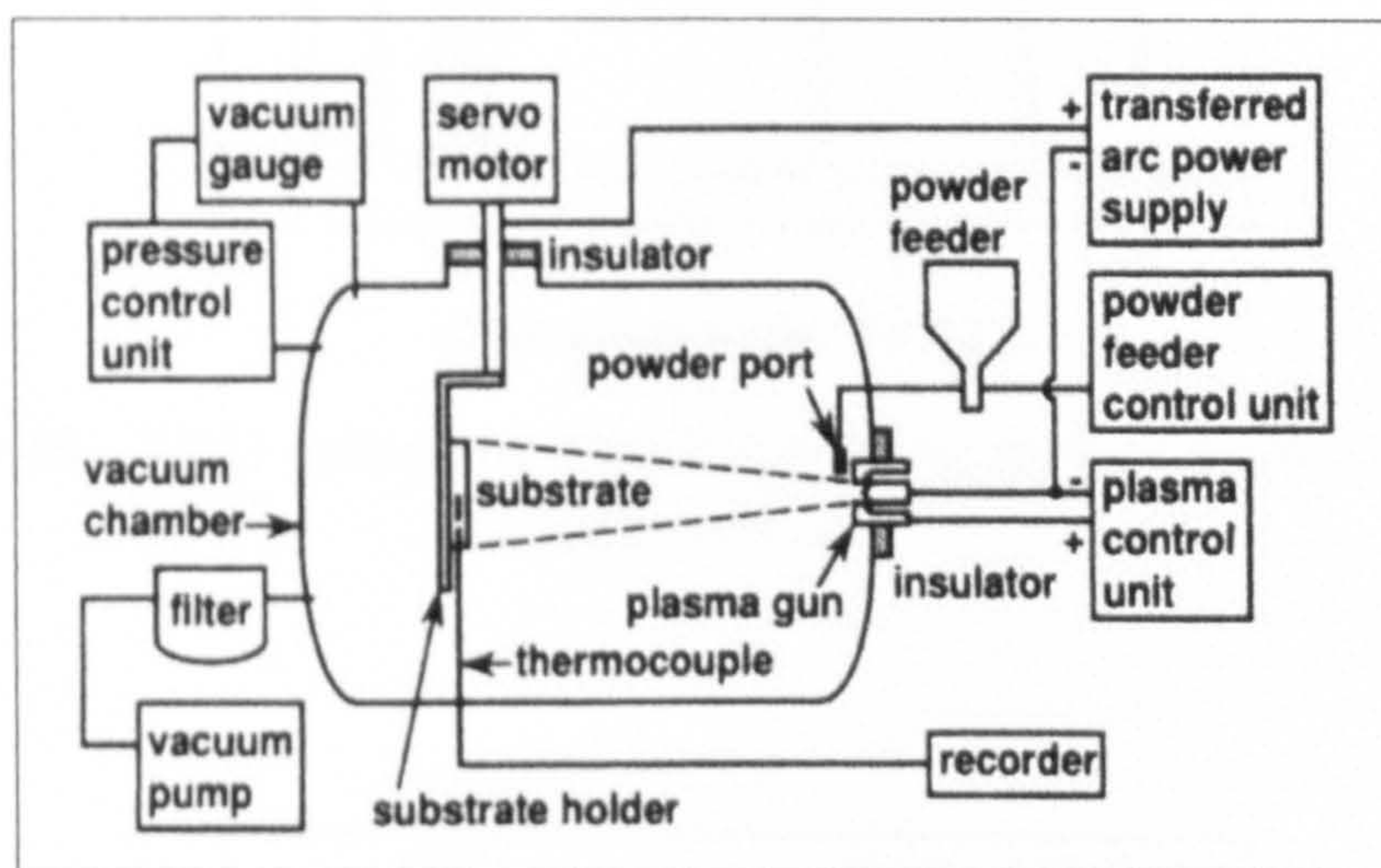


Figure 47 - Schematic of RLPSS system with a transferred arc current for the direct fabrication of chromium-nitride composites^[26]

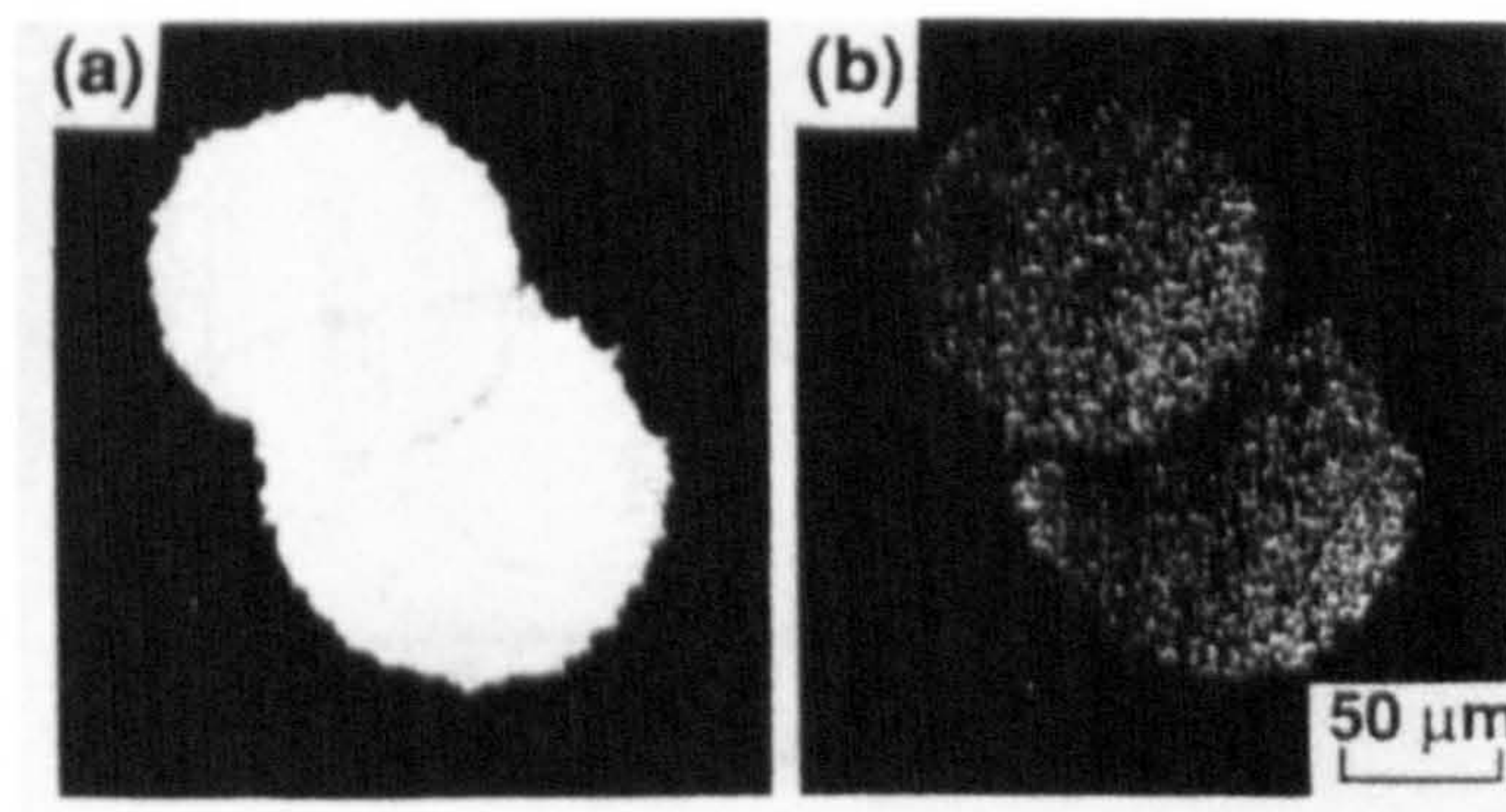


Figure 48 – Element mappings due to characteristic x-ray of impinged chromium droplets: ^[26]

(a) chromium $K\alpha$ image and (b) nitrogen $K\alpha$ image

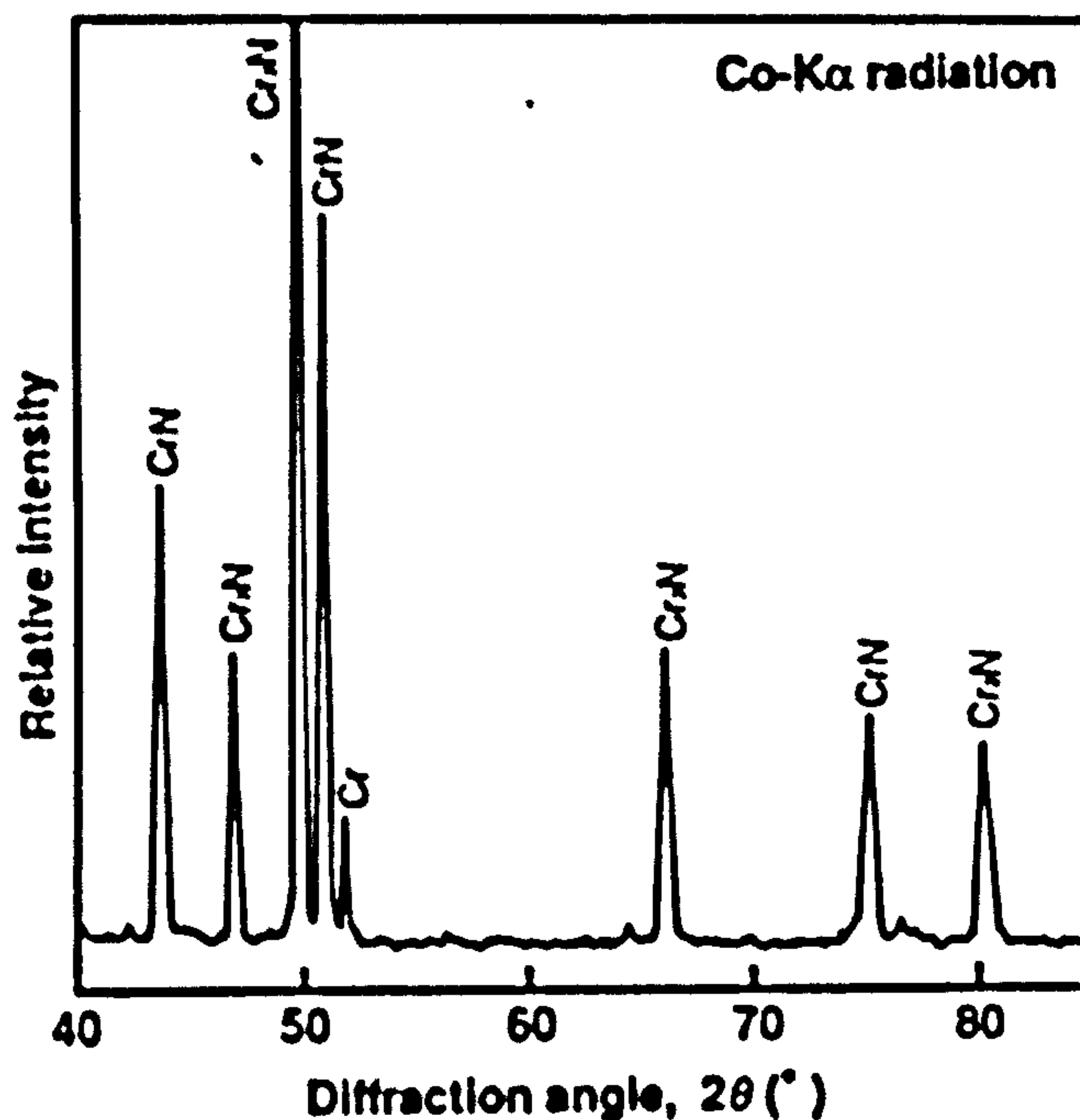


Figure 49 - XRD pattern of a typical coating surface sprayed without transferred arc^[26]

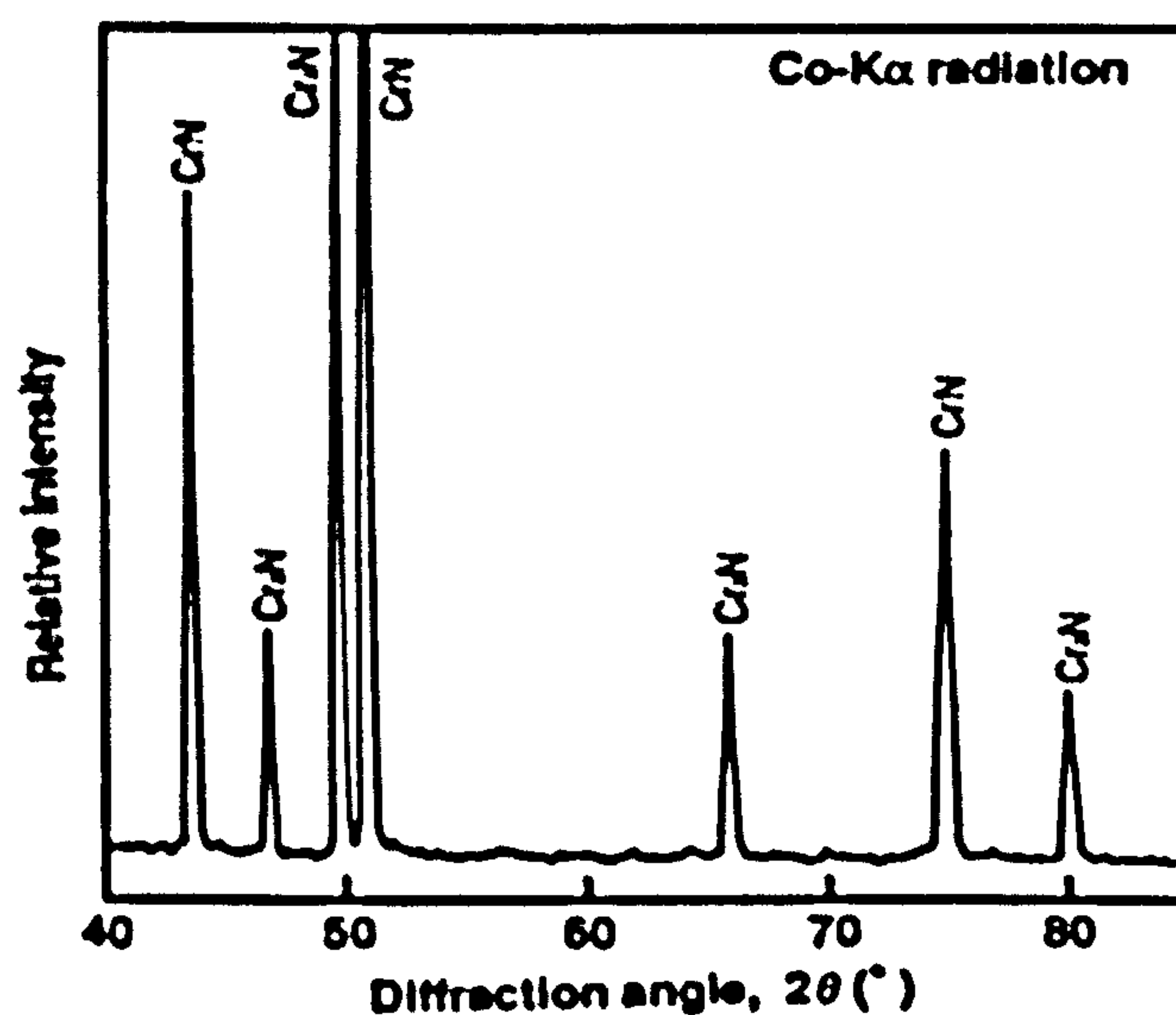


Figure 50 - XRD pattern of a typical coating surface sprayed with transferred arc current (I_t) of 25 A^[26]

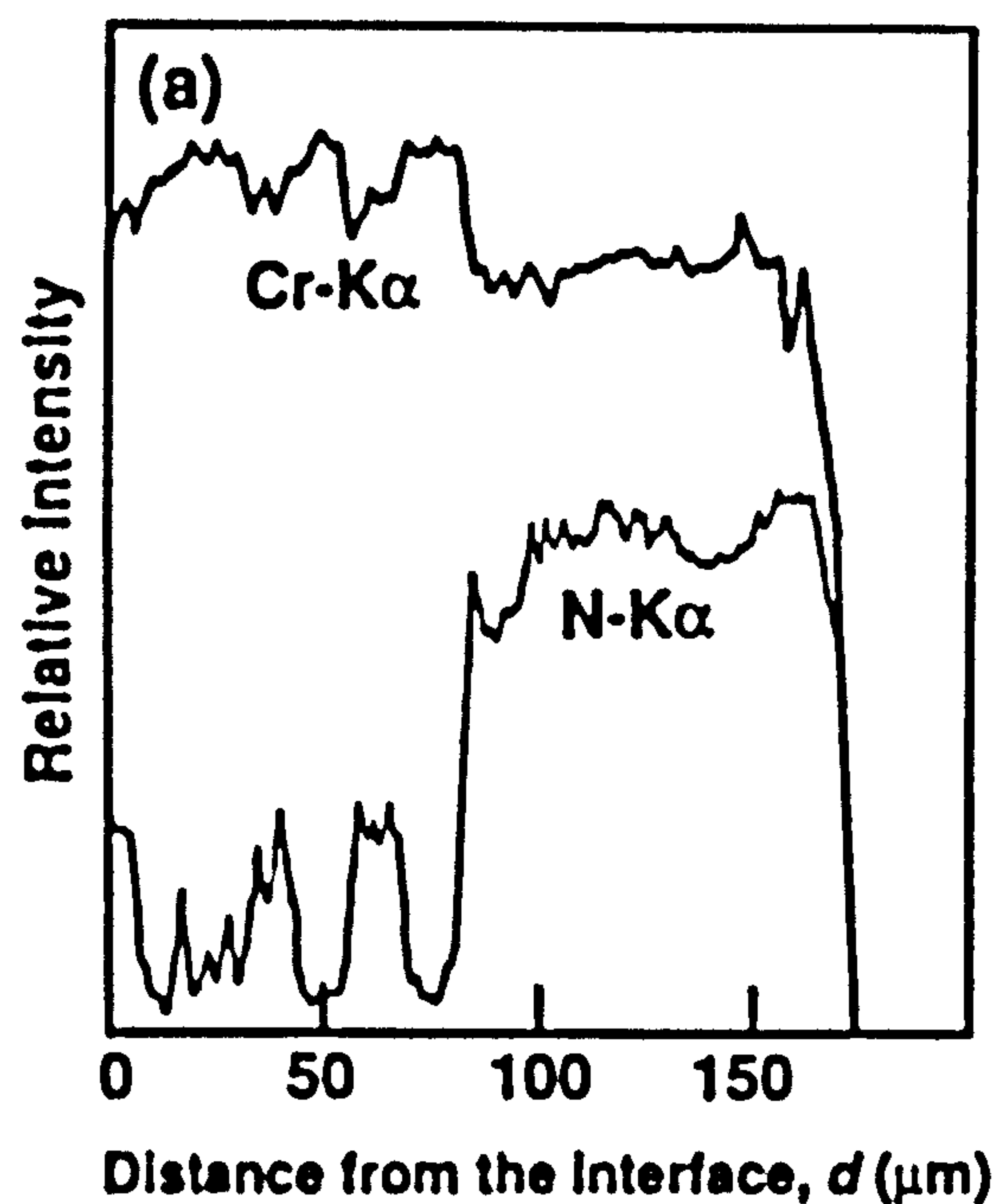


Figure 51 - Electron probe microanalysis results demonstrating the composition gradient across the coating section for a coating without a transferred arc^[26]

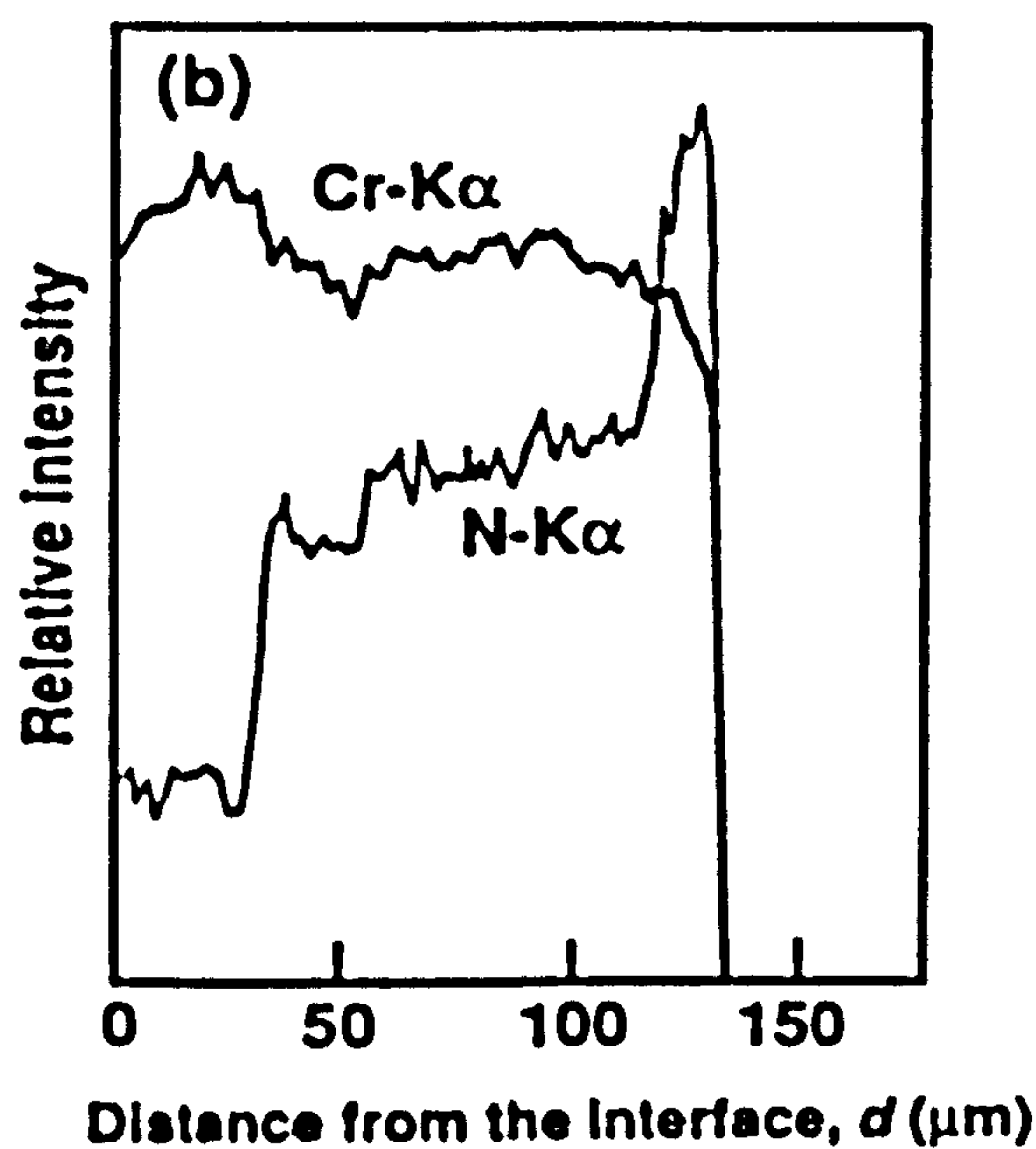


Figure 52 - Results for a coating deposited with a transferred arc current of 25 A^[26]

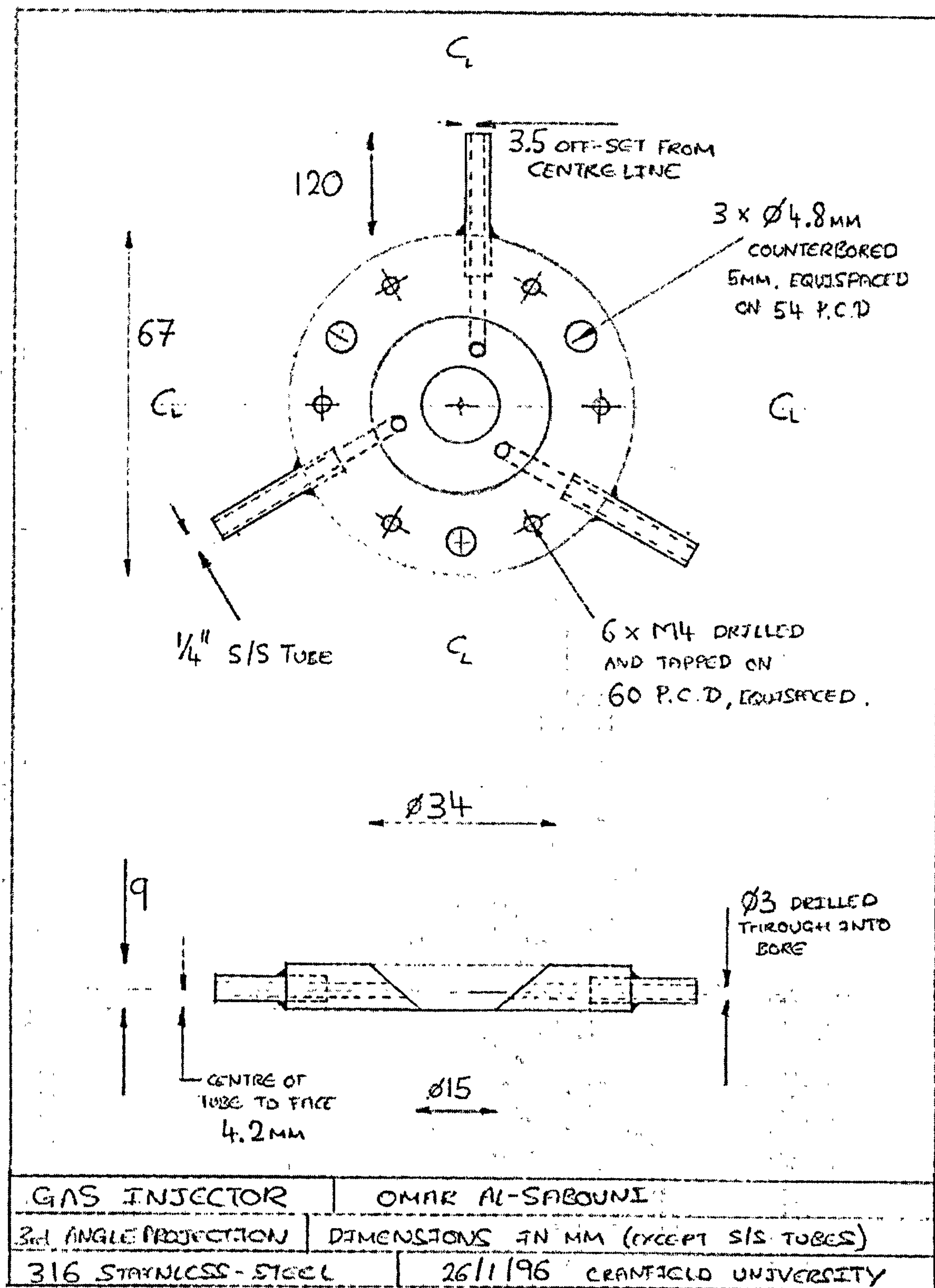


Figure 53 – Technical drawing of a gas mixing unit

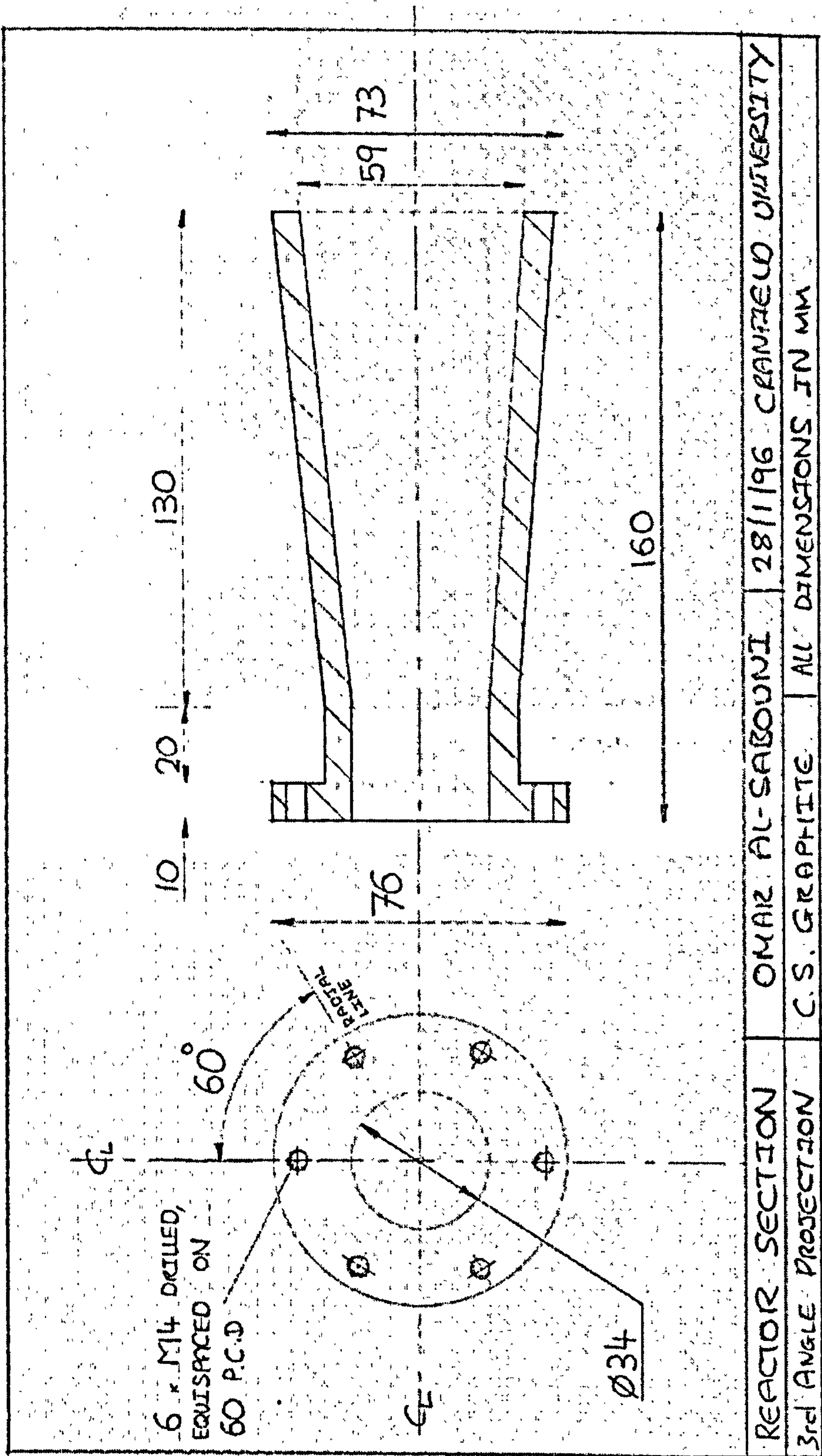


Figure 54 – Technical drawing of a 15 cm reactor

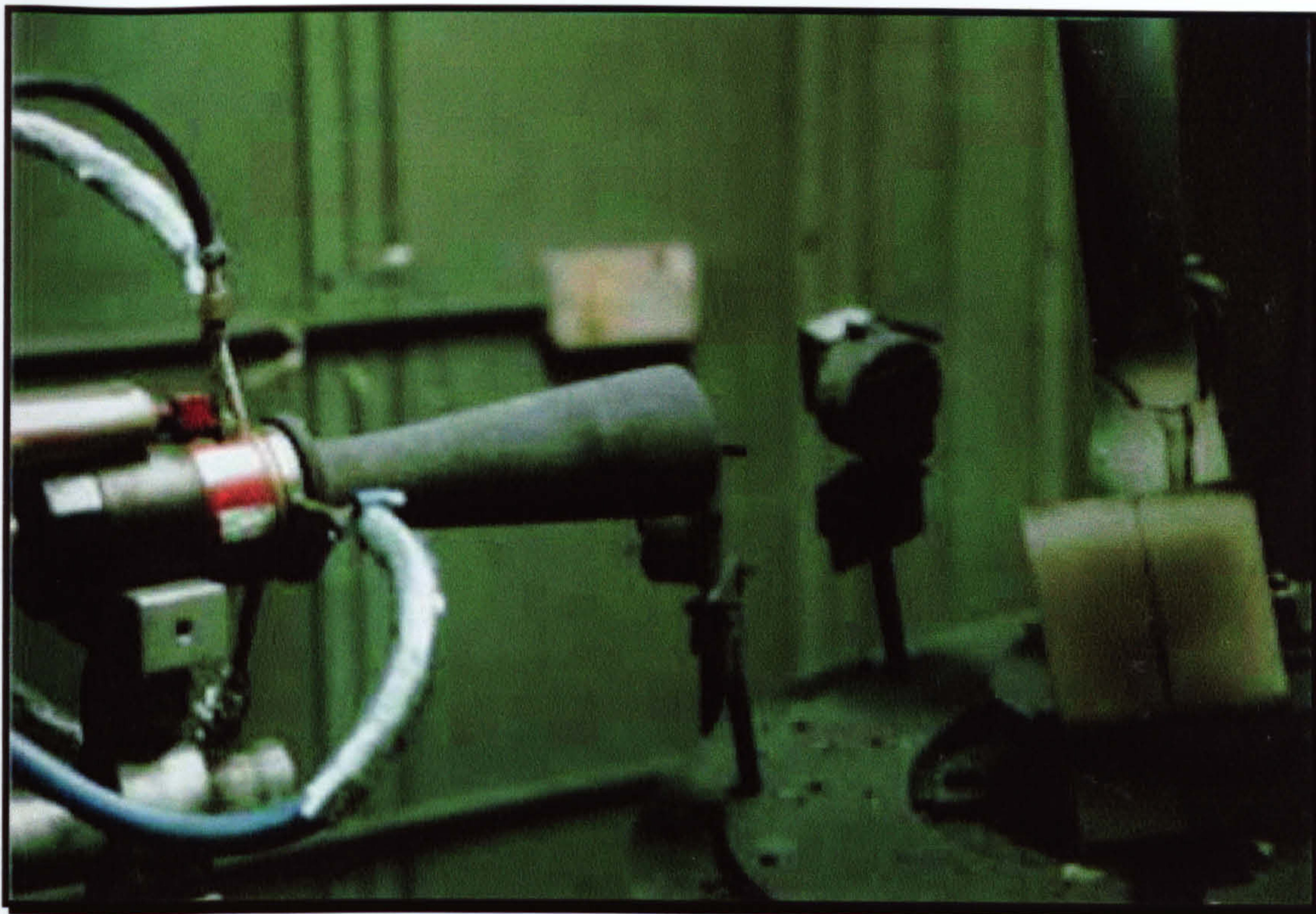


Figure 55 – Photograph of reactor, gas injector unit and gun when assembled

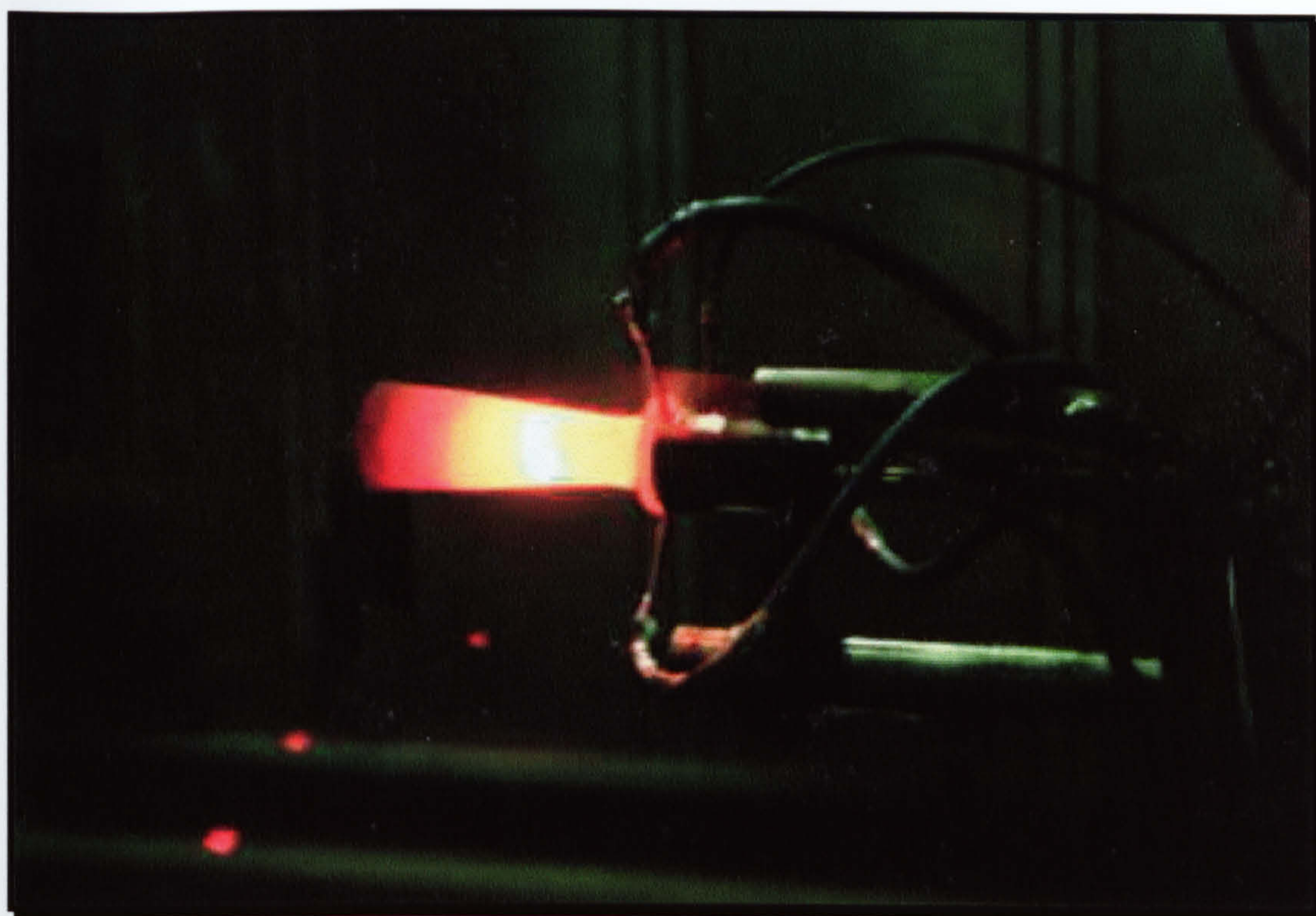


Figure 56 - Photograph of the assembly just after spraying

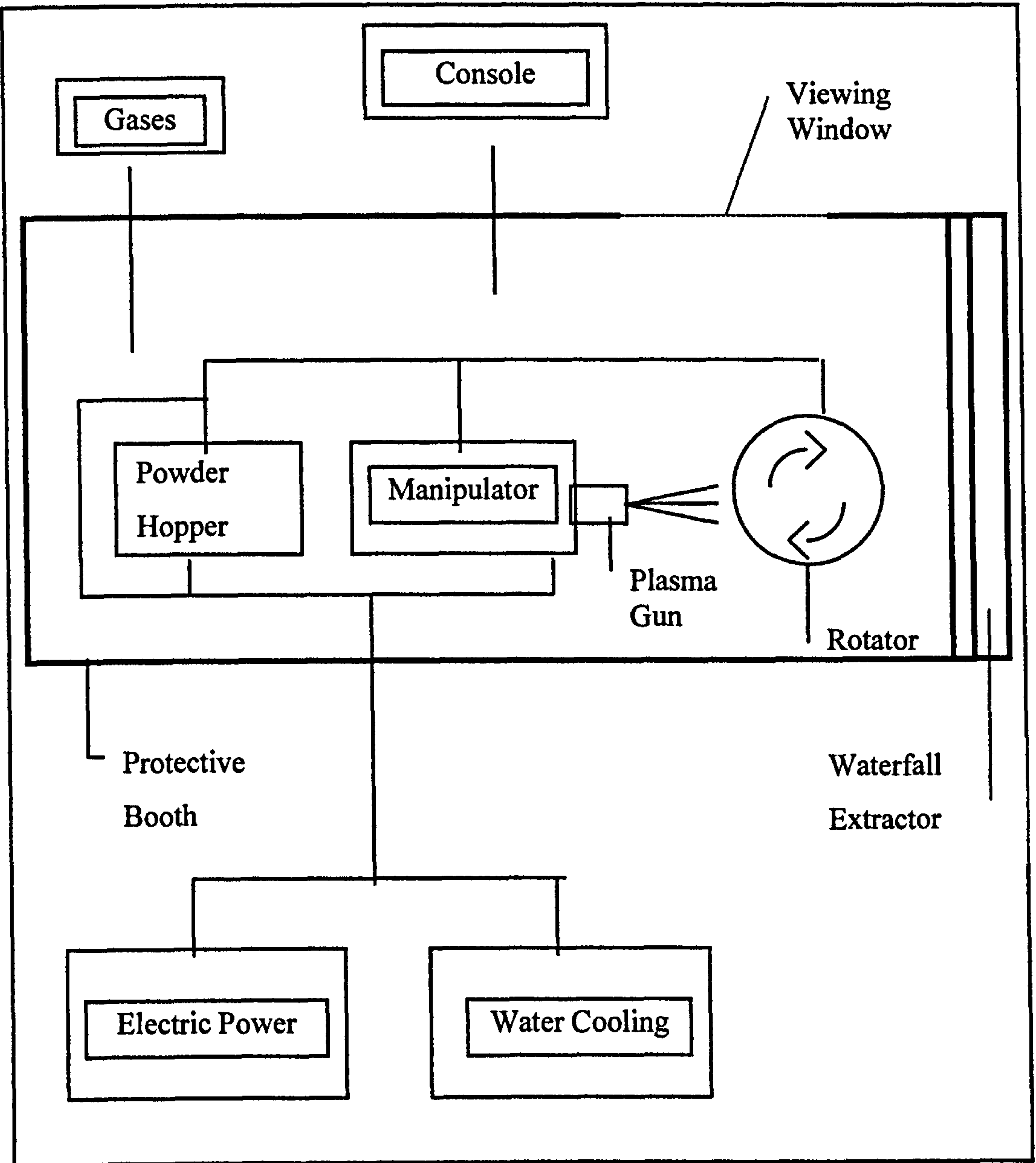


Figure 57 - A typical thermal spray assembly

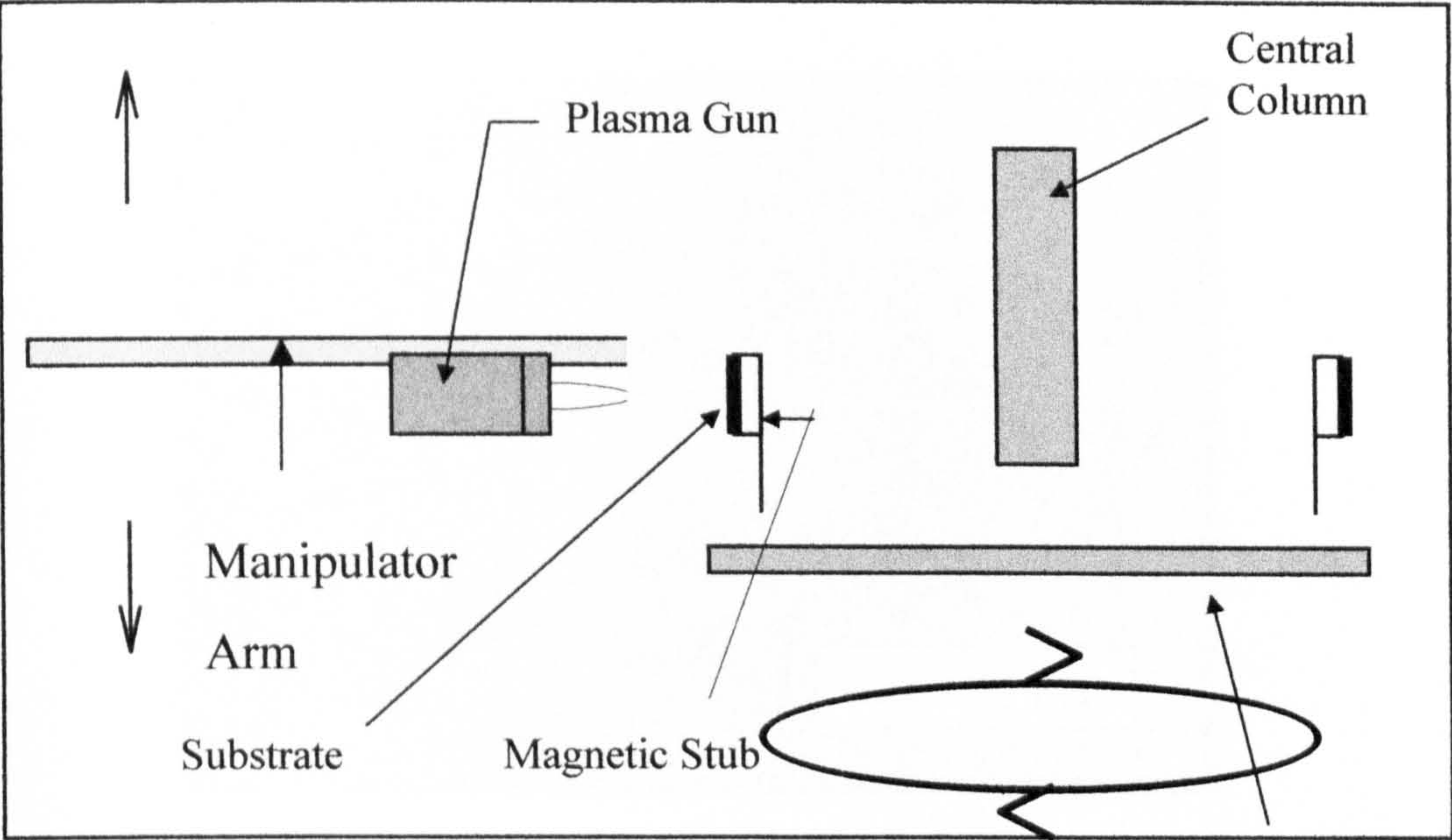


Figure 58 - Plasma Gun manipulator arm and Rotator set-up

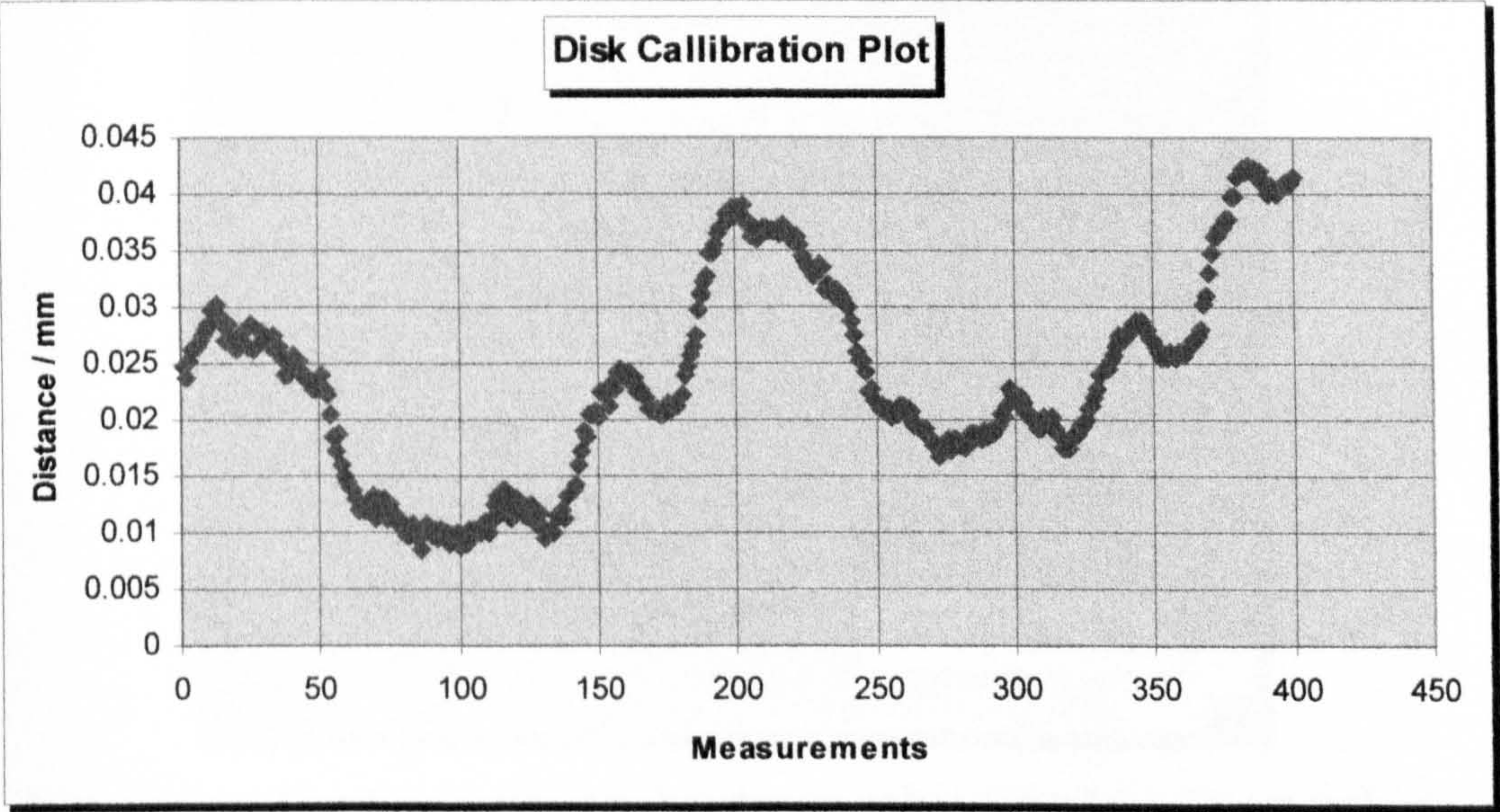


Figure 59 - Pin on Disk Test - Disk Calibration Plot

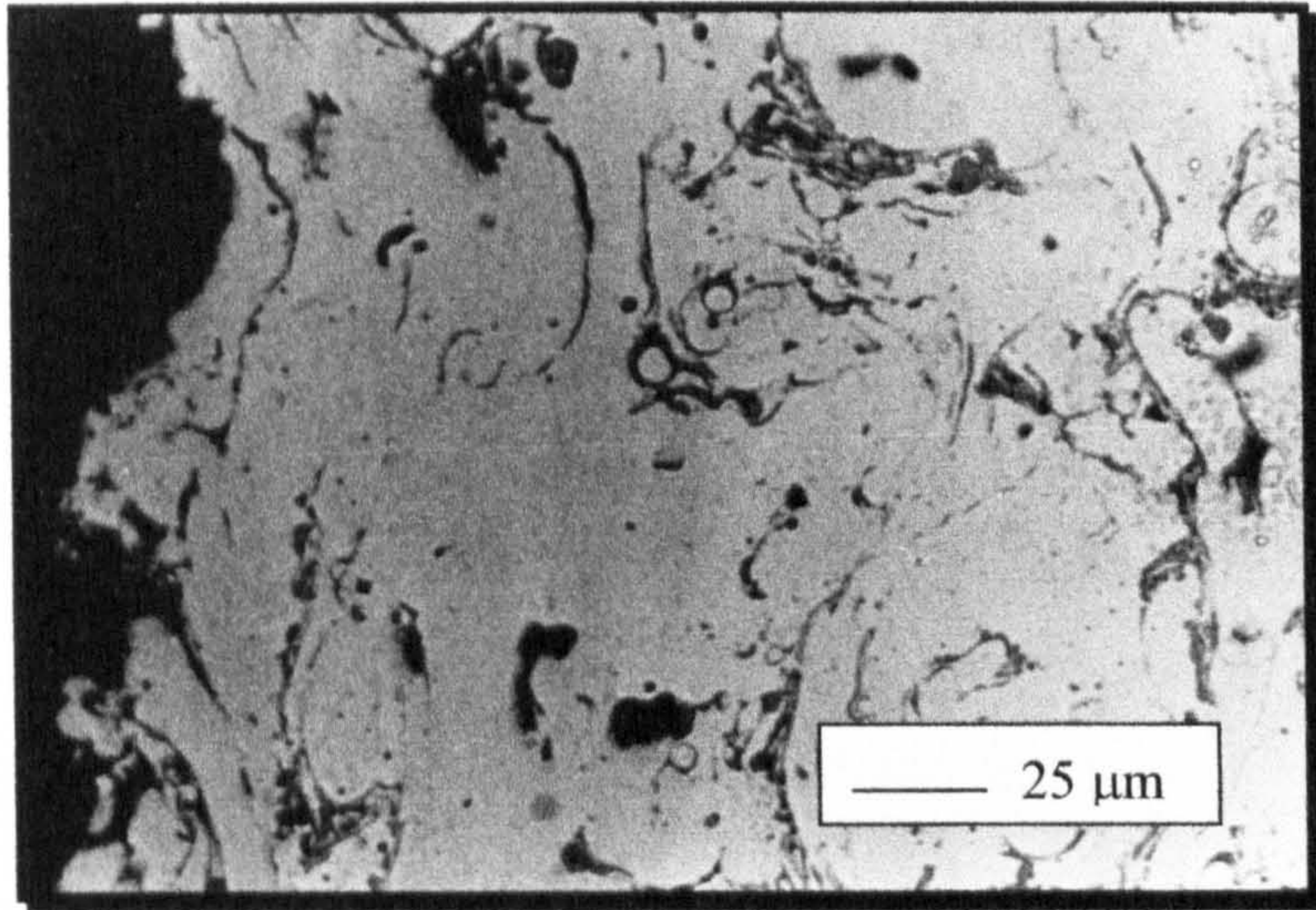


Figure 60 - Coating with high hardness value ($H_v=194.1$): unetched

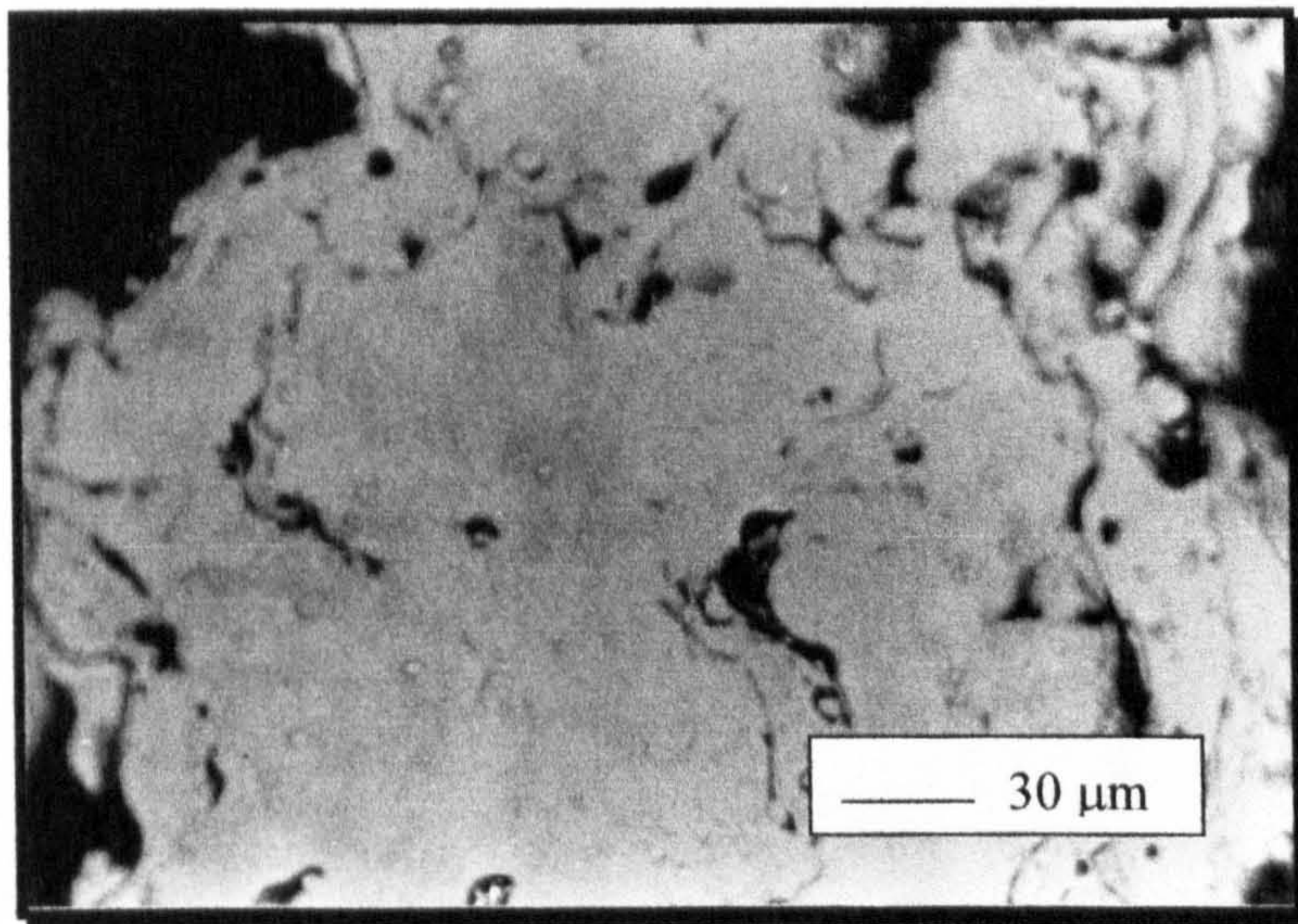


Figure 61 - Coating with low hardness value ($H_v=144.2$): unetched

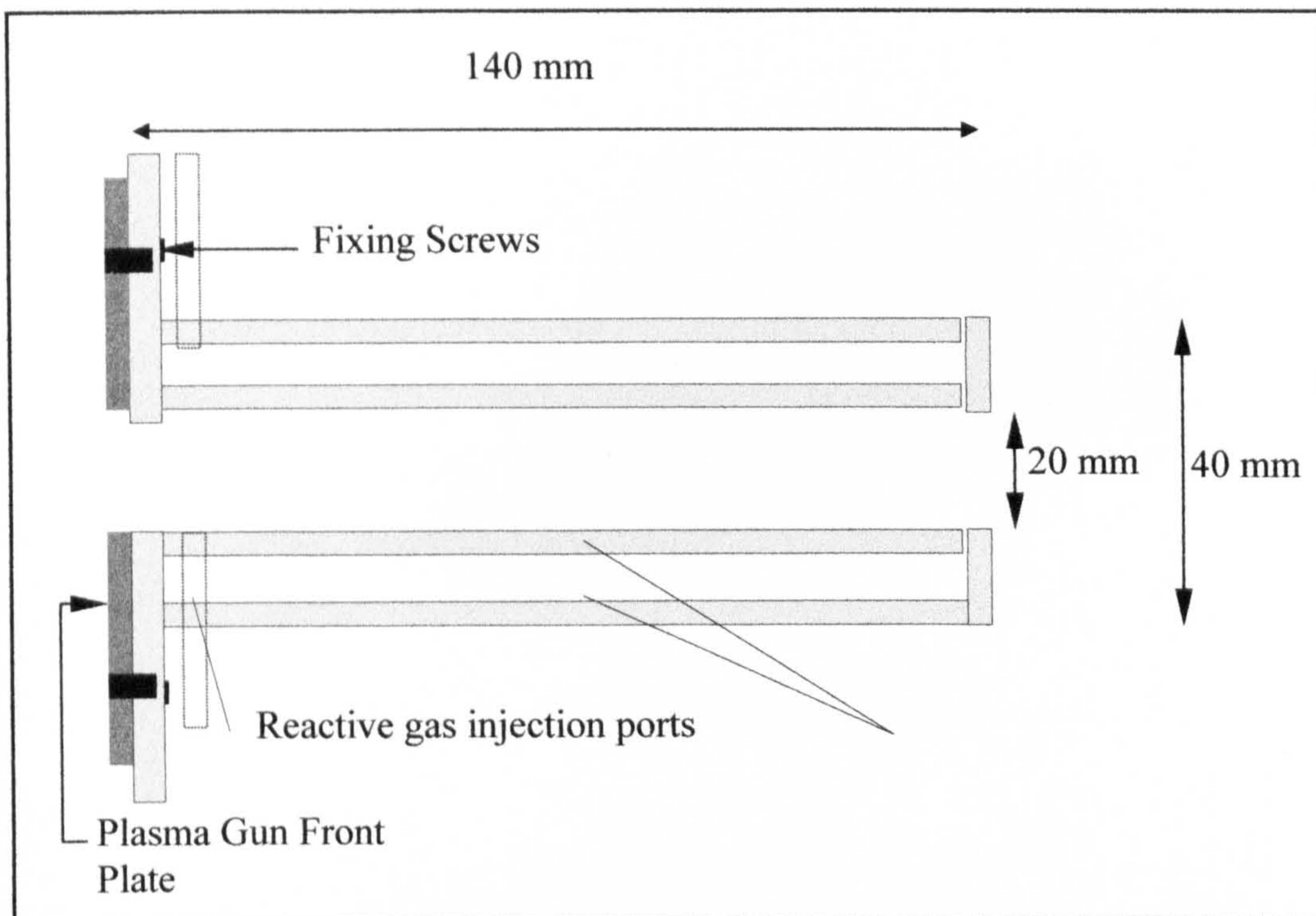


Figure 62 - First reactor design

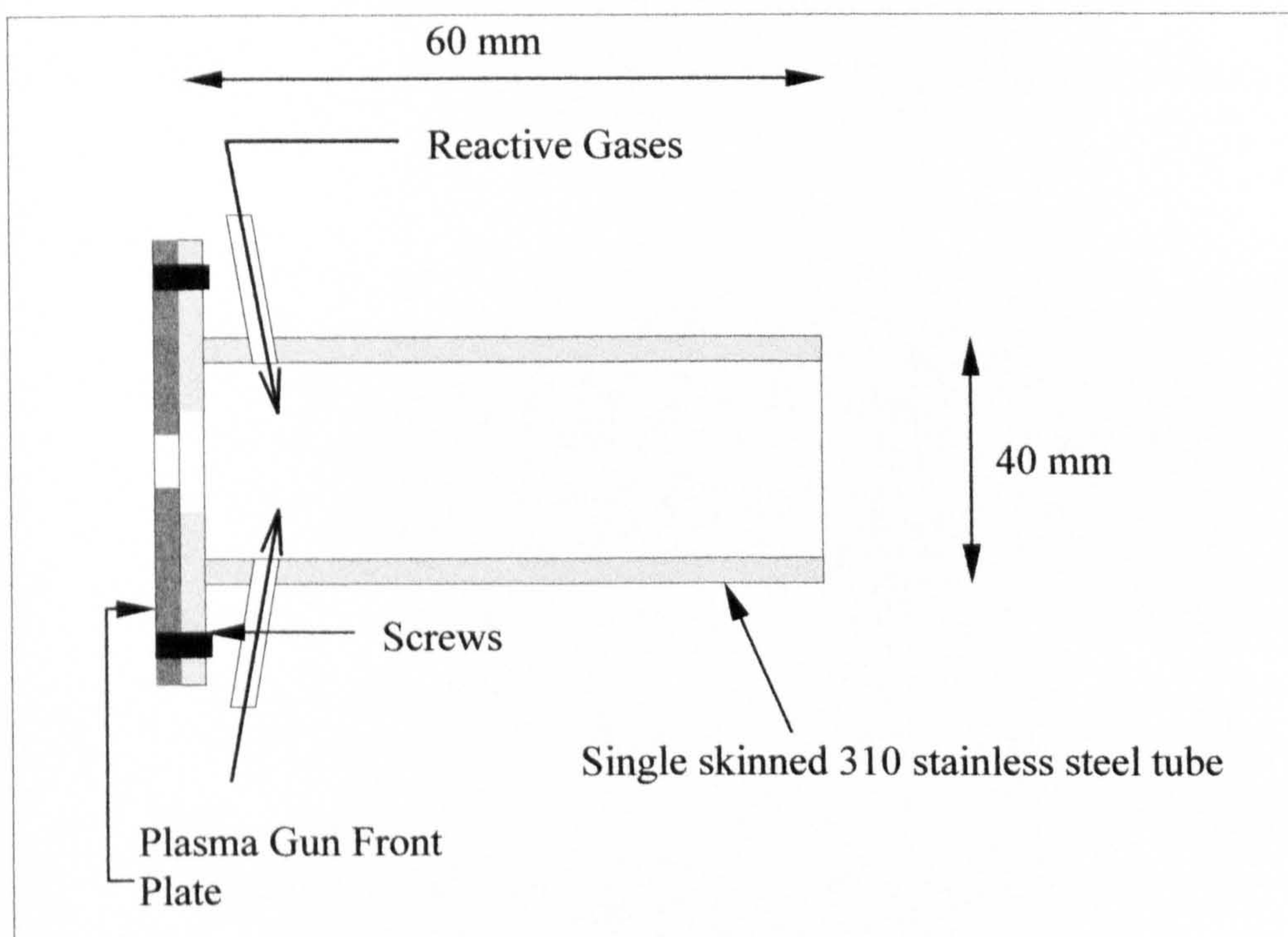


Figure 63 - Diagram of modified reactor

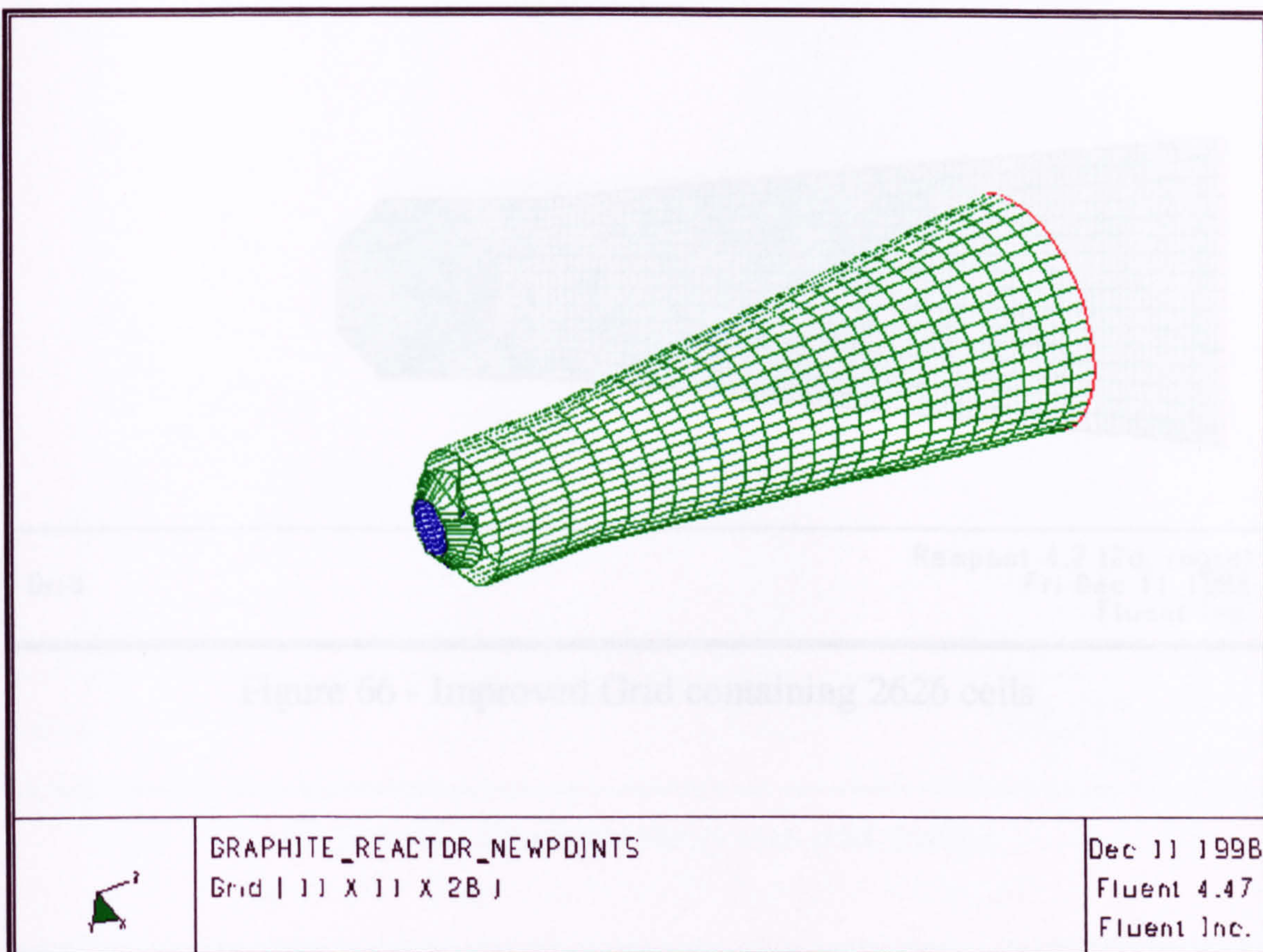


Figure 64- Diagram of 3D grid

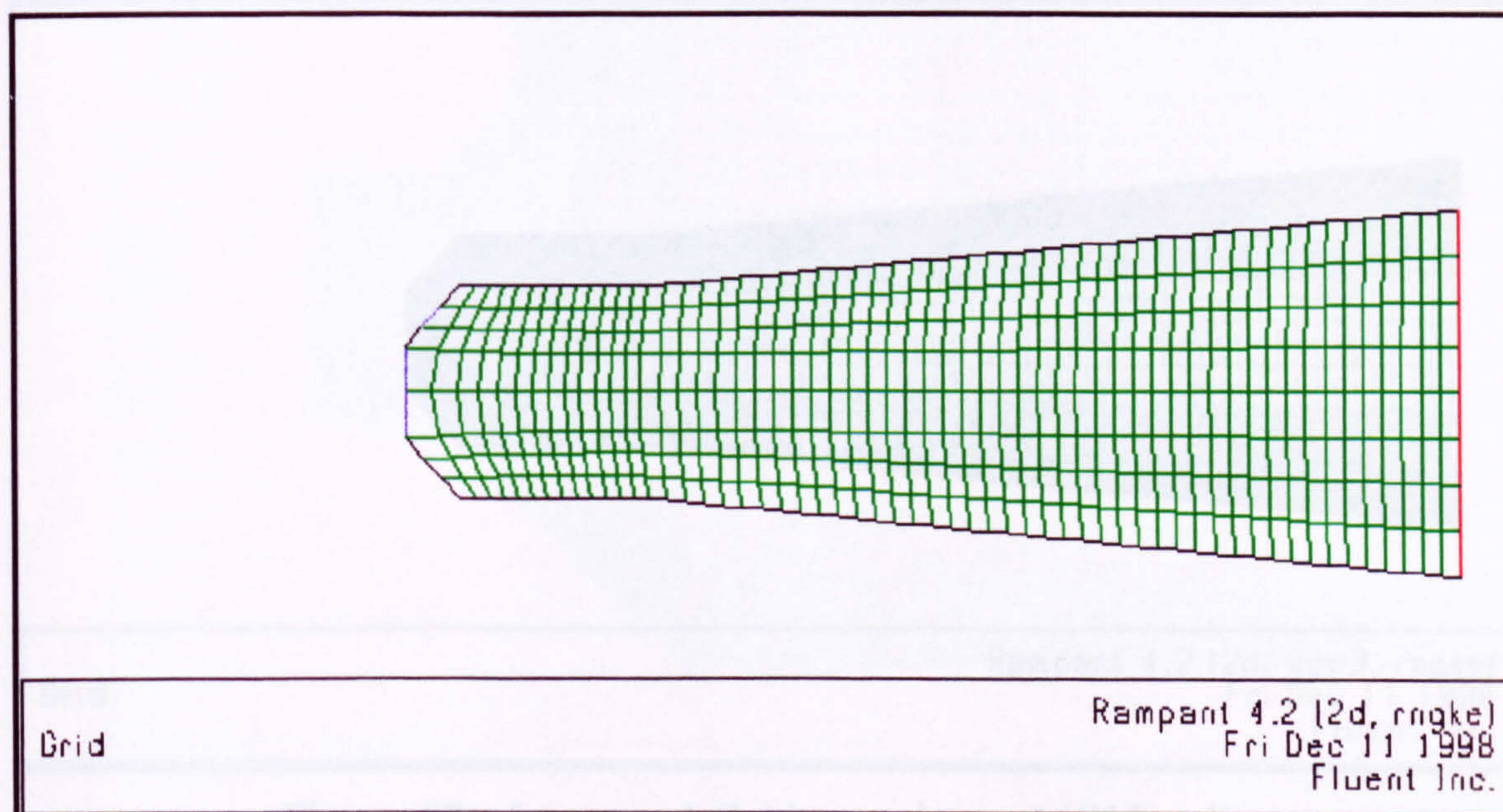


Figure 65 - Diagram of 2D grid

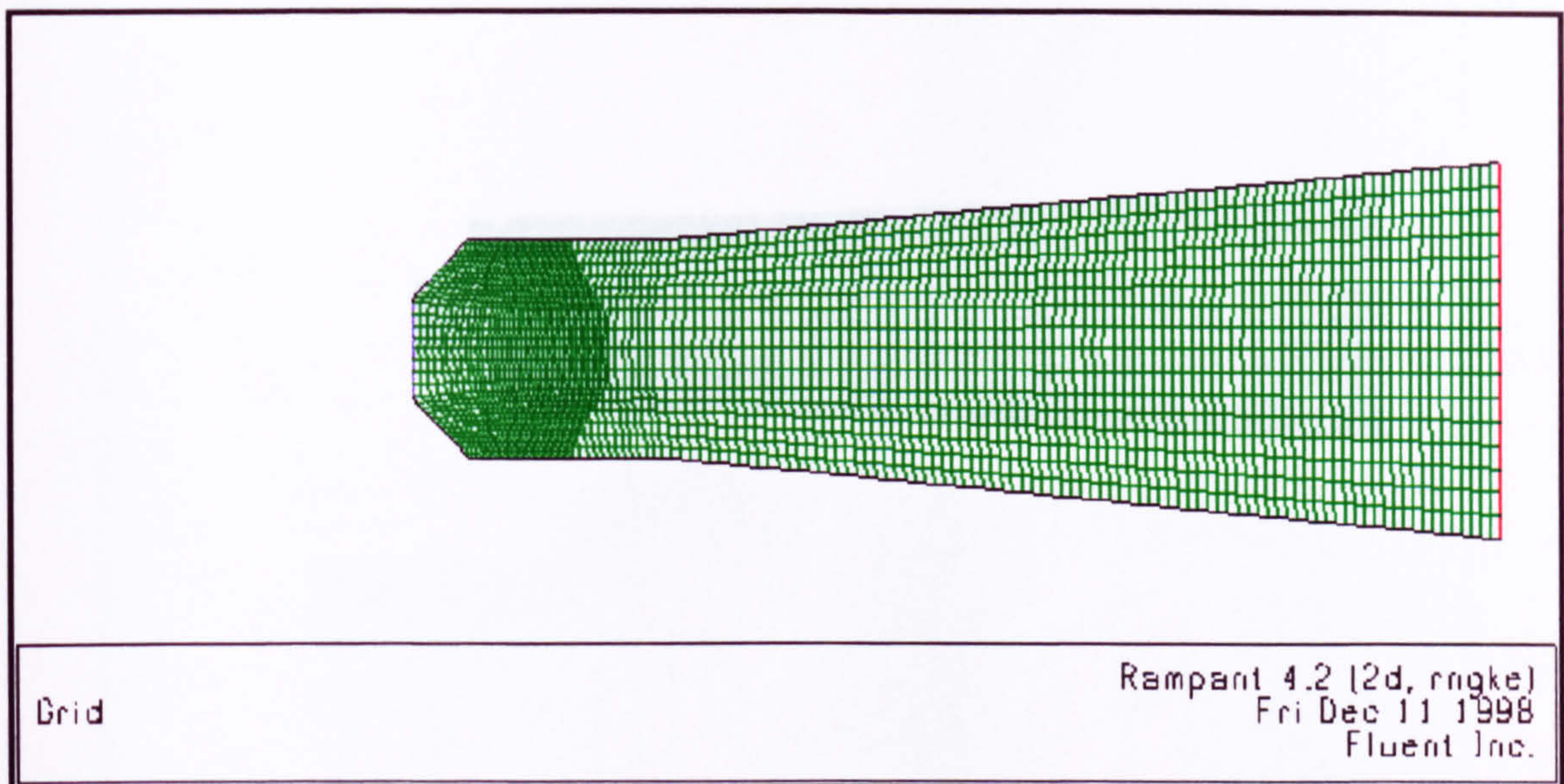


Figure 66 - Improved Grid containing 2626 cells

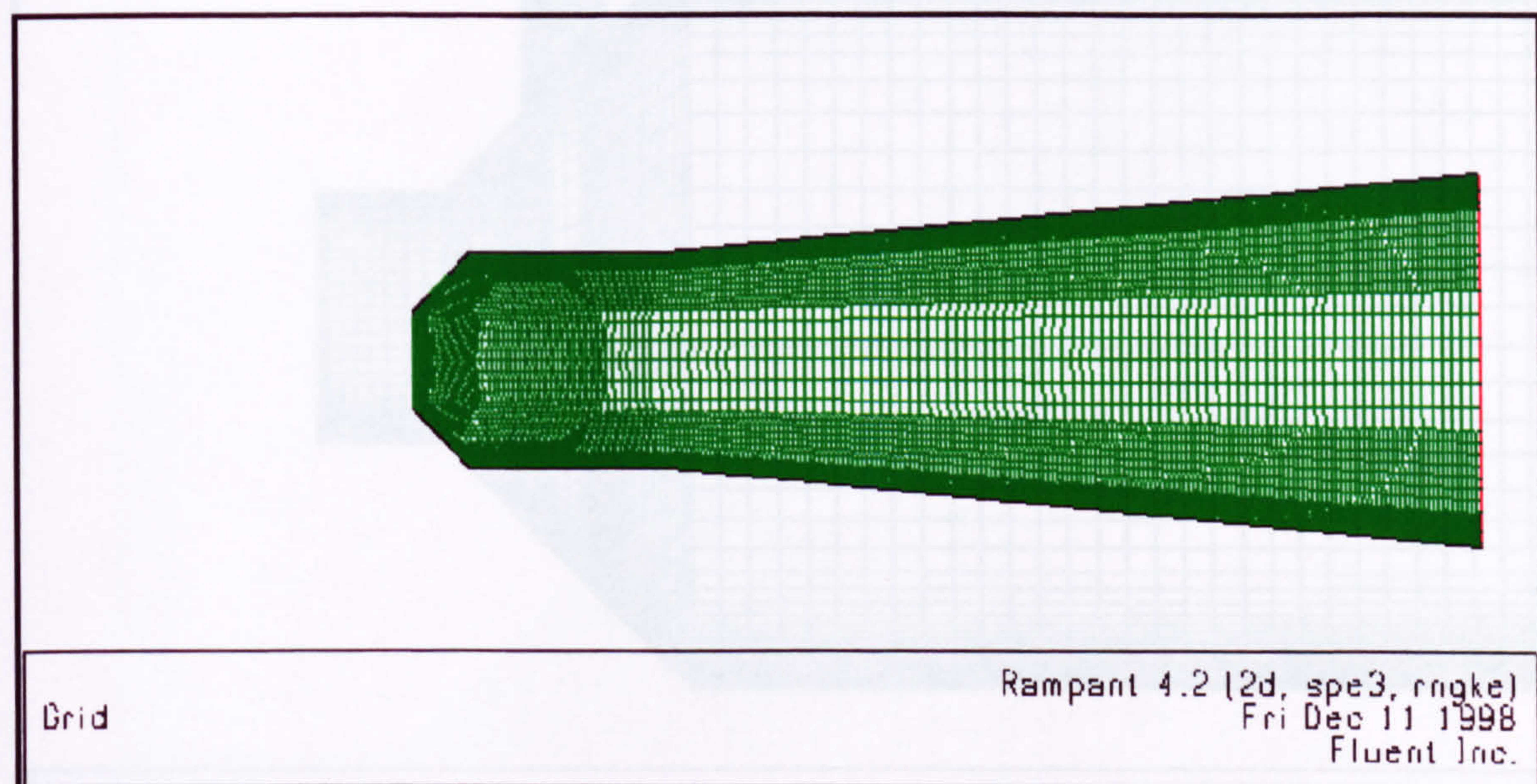


Figure 67 - Improved Grid containing 16912 cells

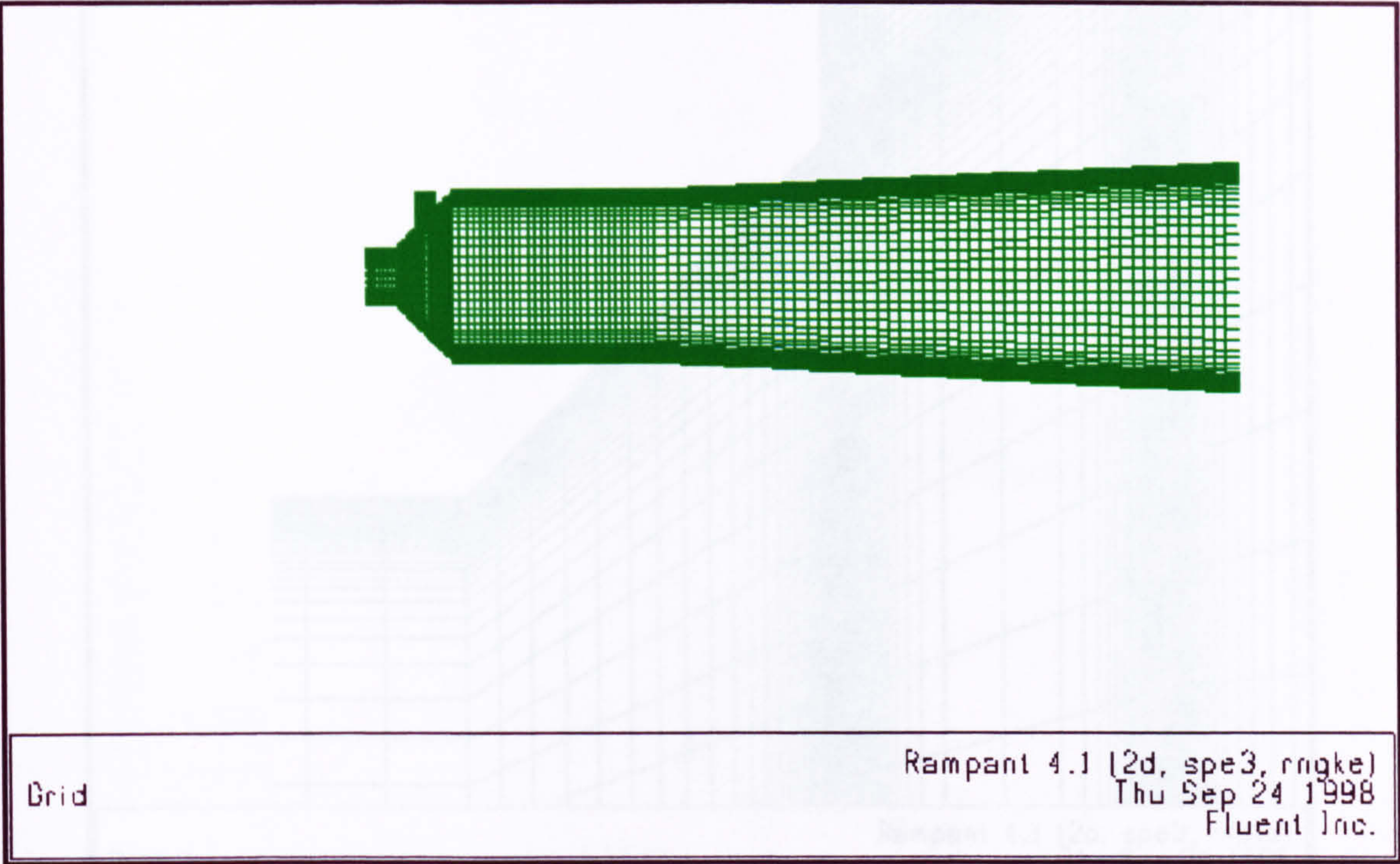


Figure 68 - Final geometry and grid design

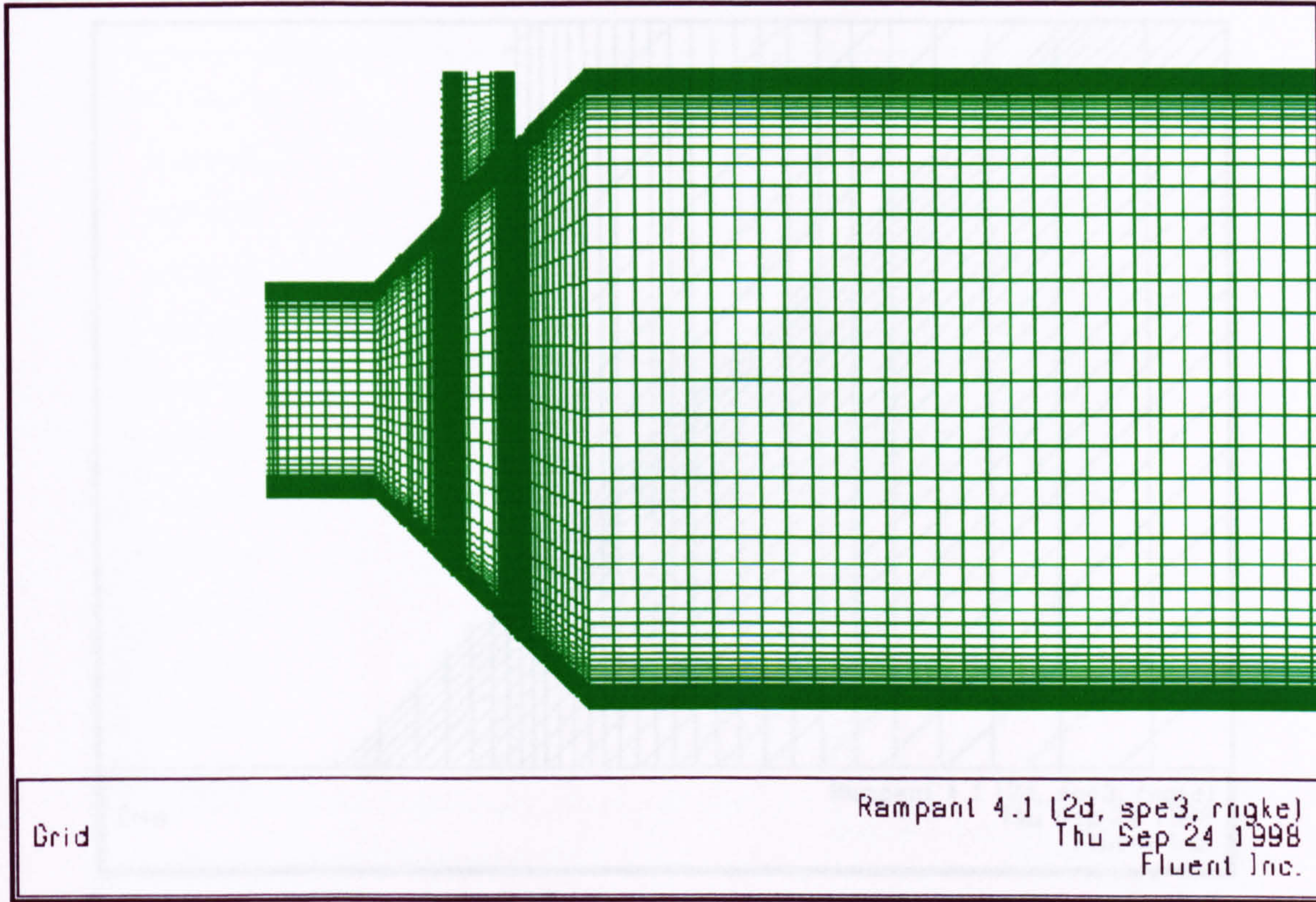


Figure 69 - Reactive gas injection area

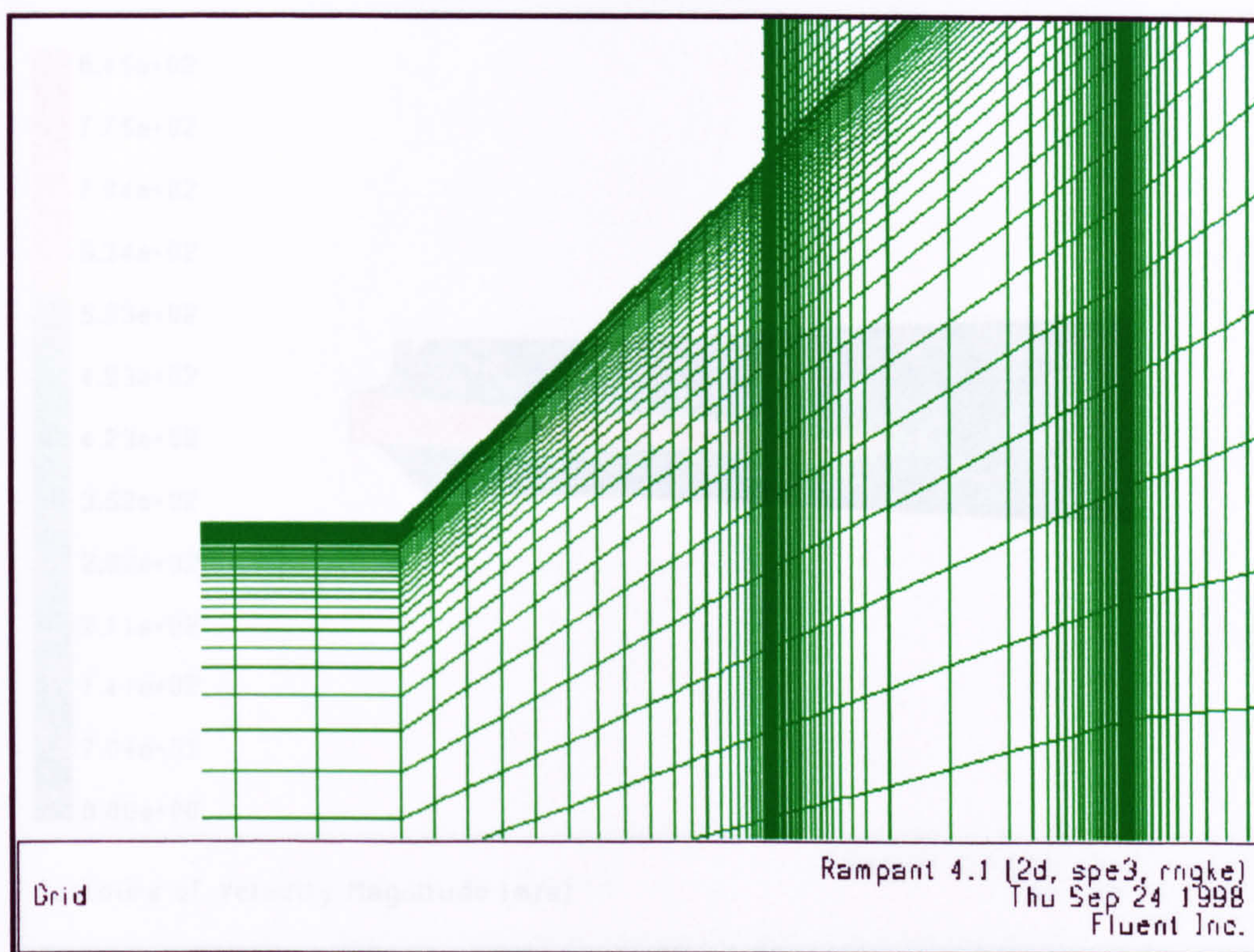


Figure 70 - Reactive gas injection area (enlarged)

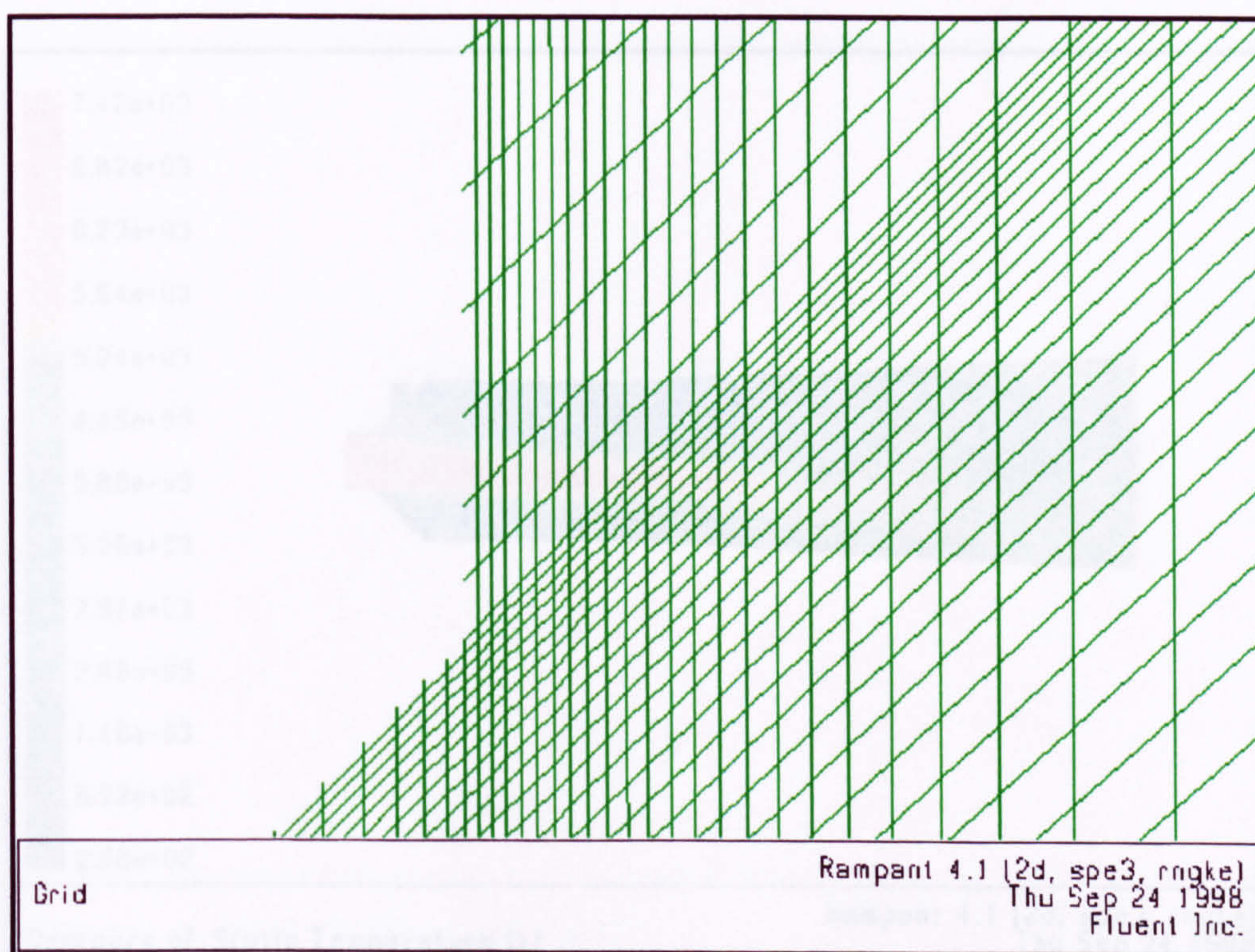


Figure 71 - Reactive gas injection area (further enlarged)

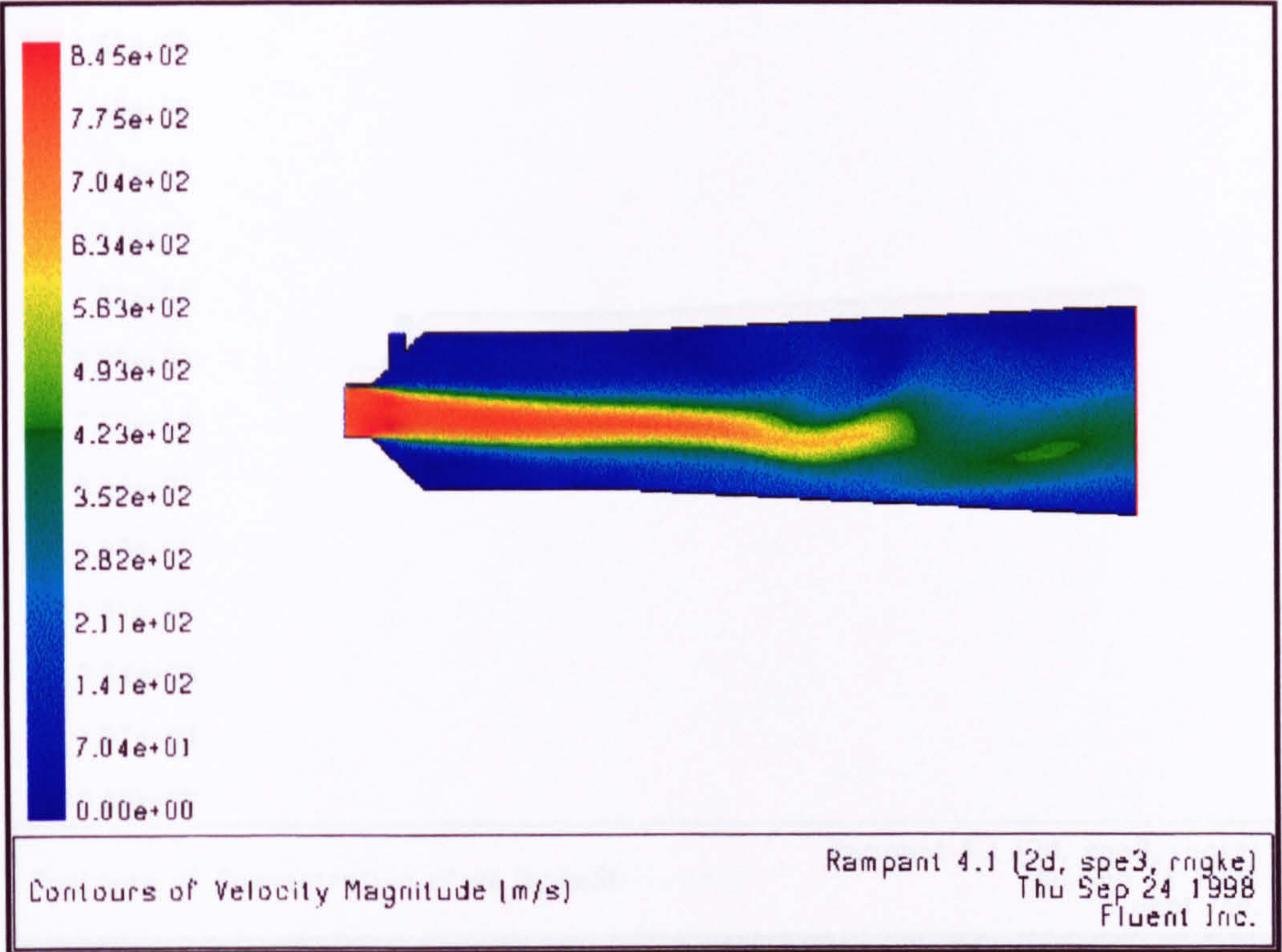


Figure 72 - Contours of velocity magnitude

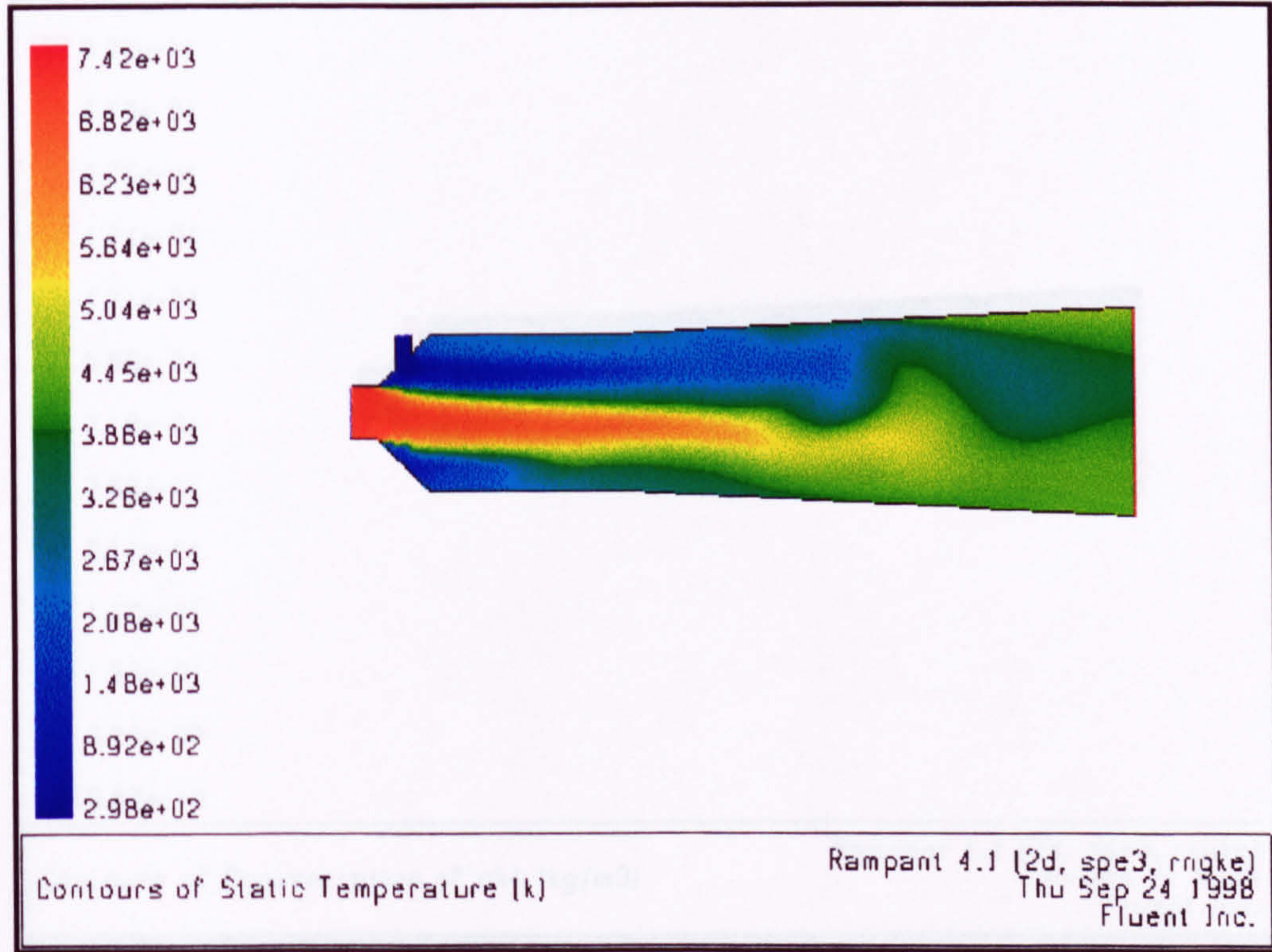


Figure 73 - Contours of static temperature

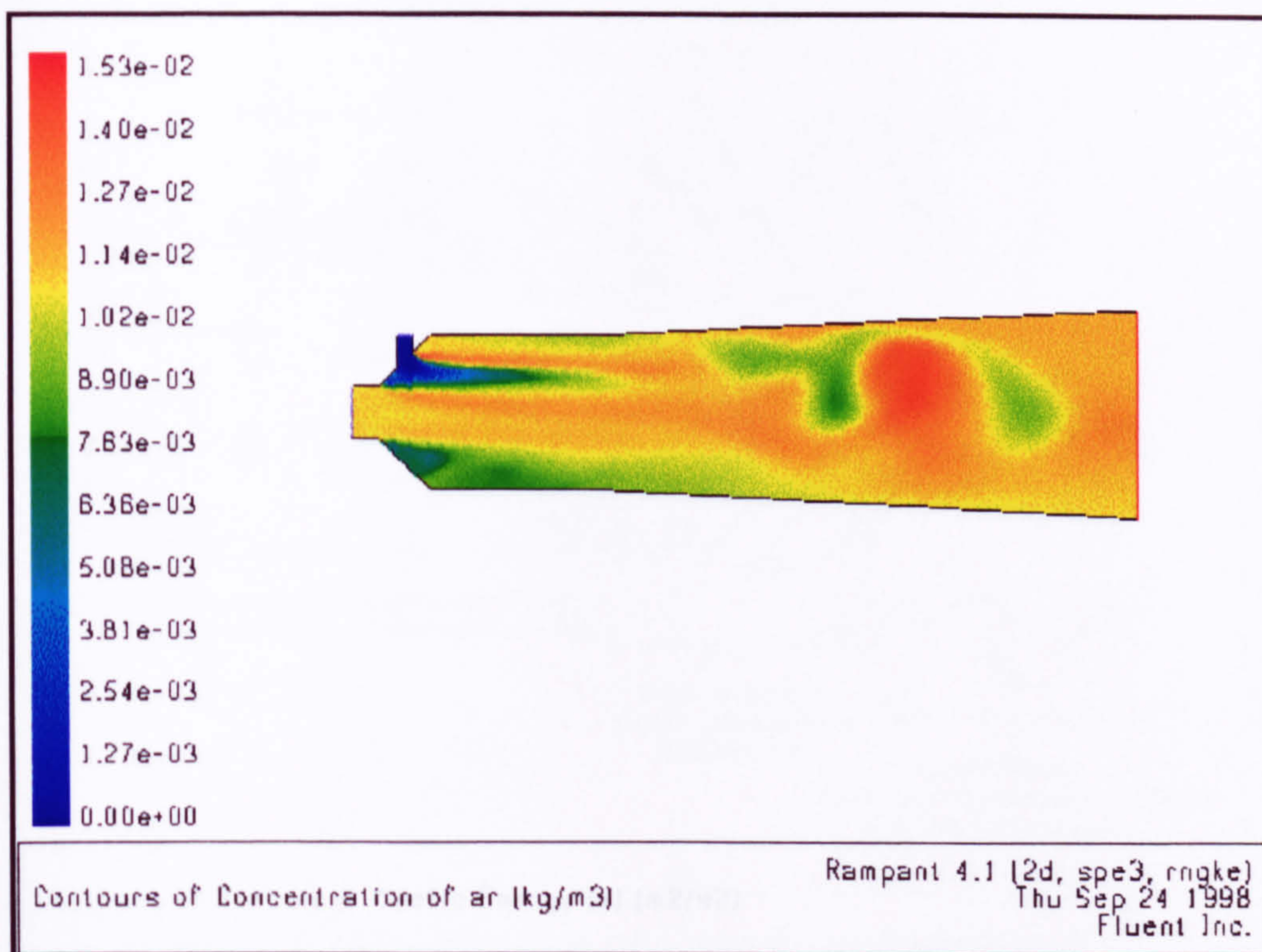


Figure 74 - Contours of concentration of Argon

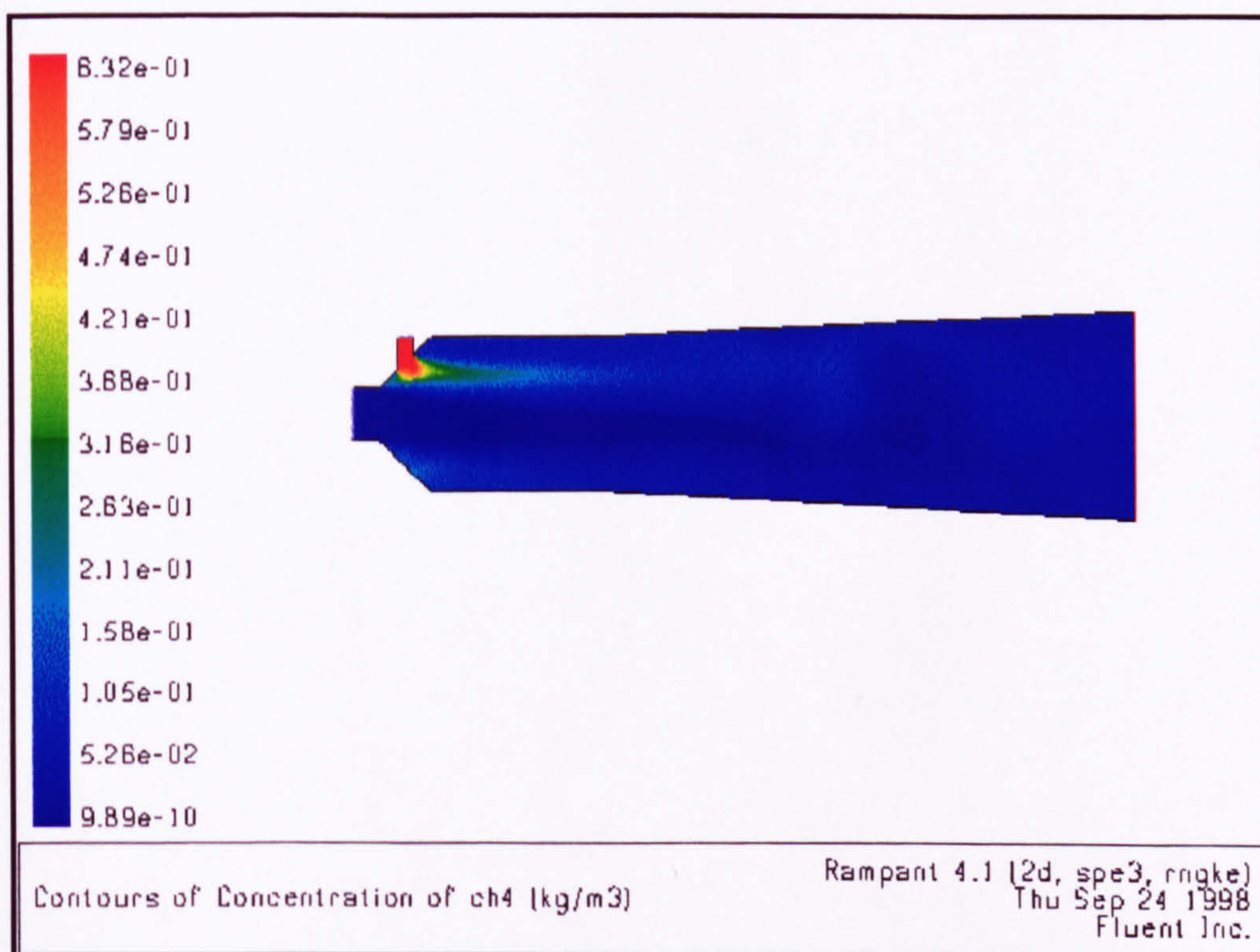


Figure 75 - Contours of concentration of CH₄

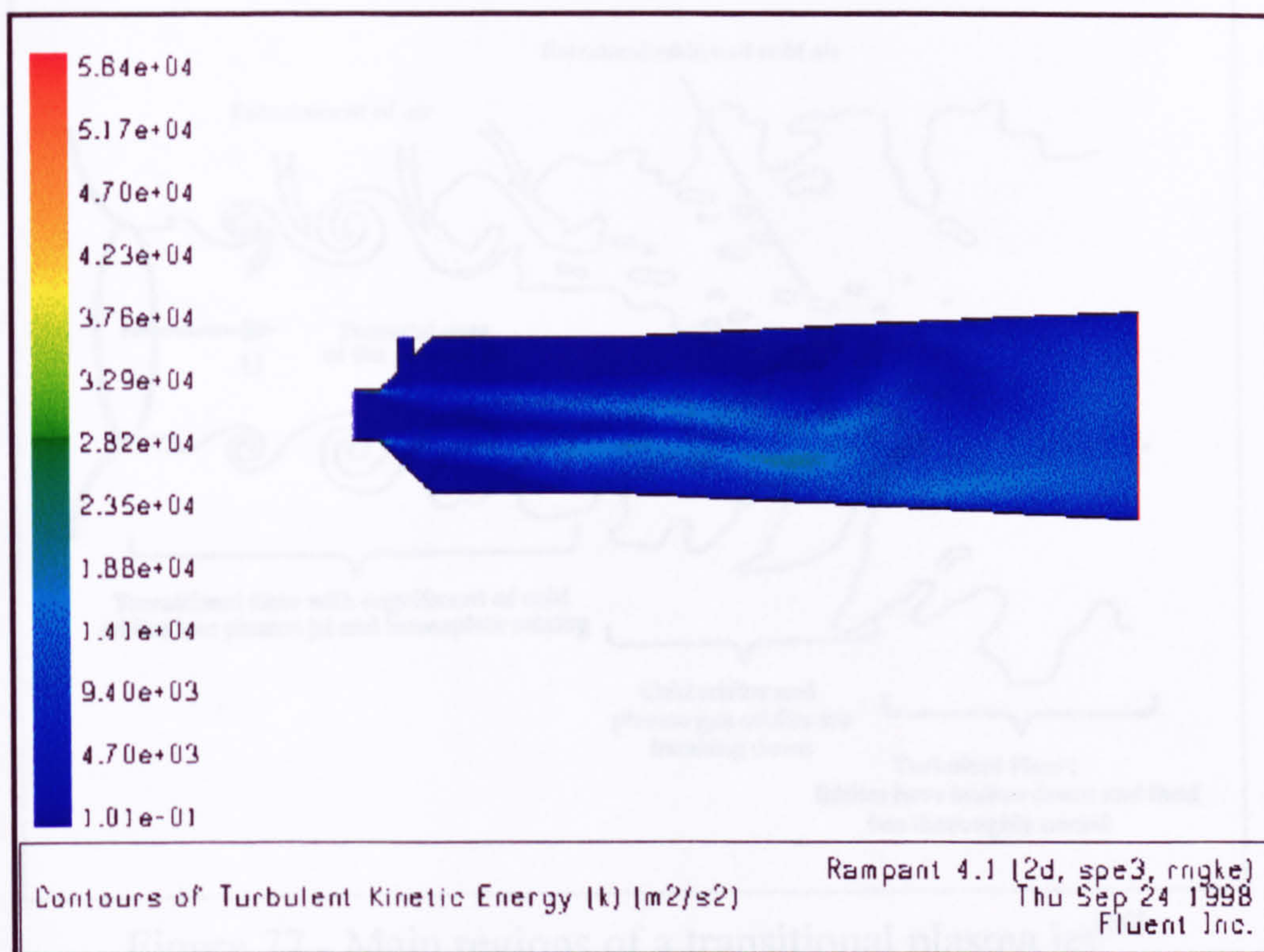


Figure 76 - Contours of Turbulent Kinetic Energy

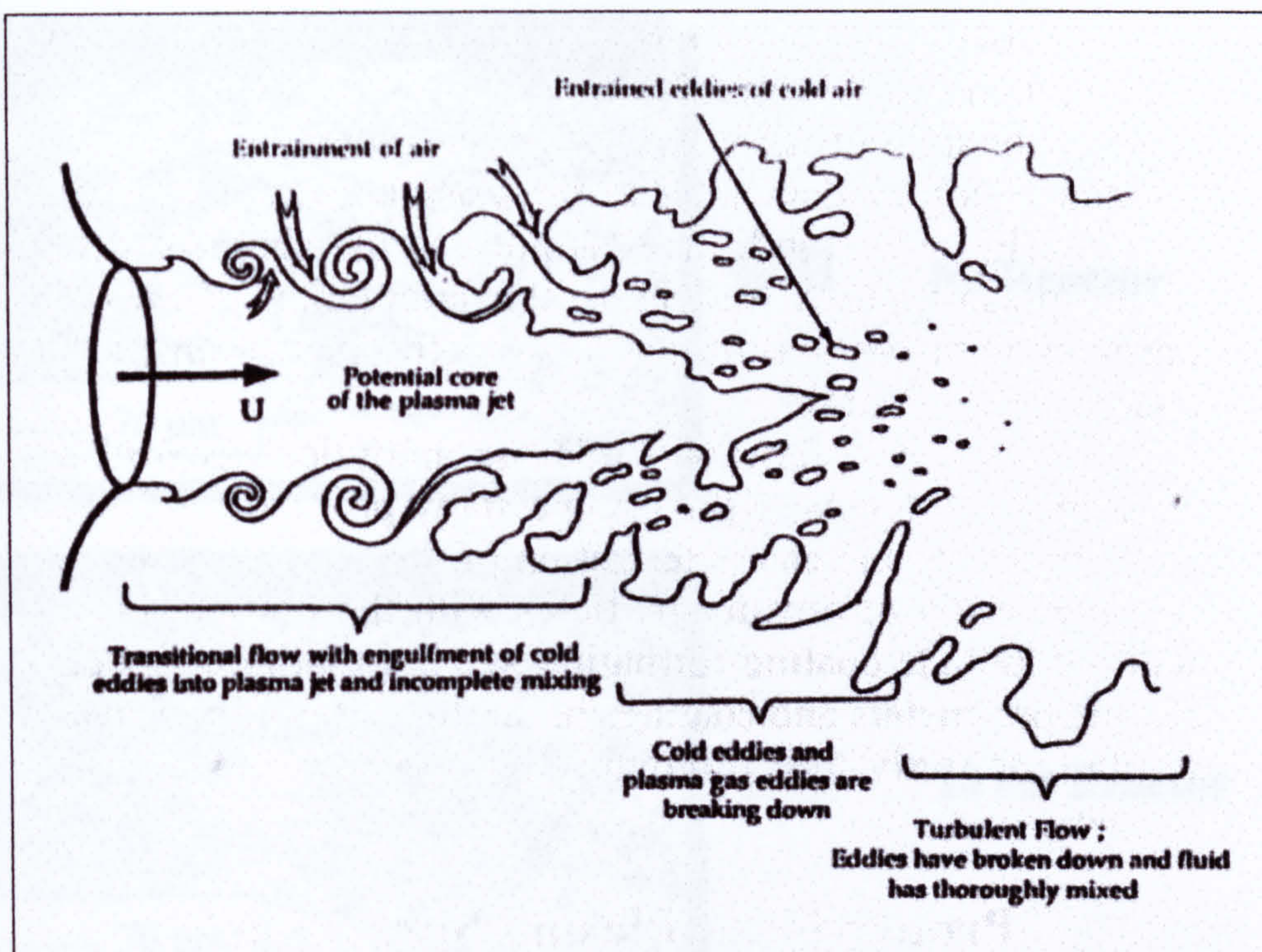
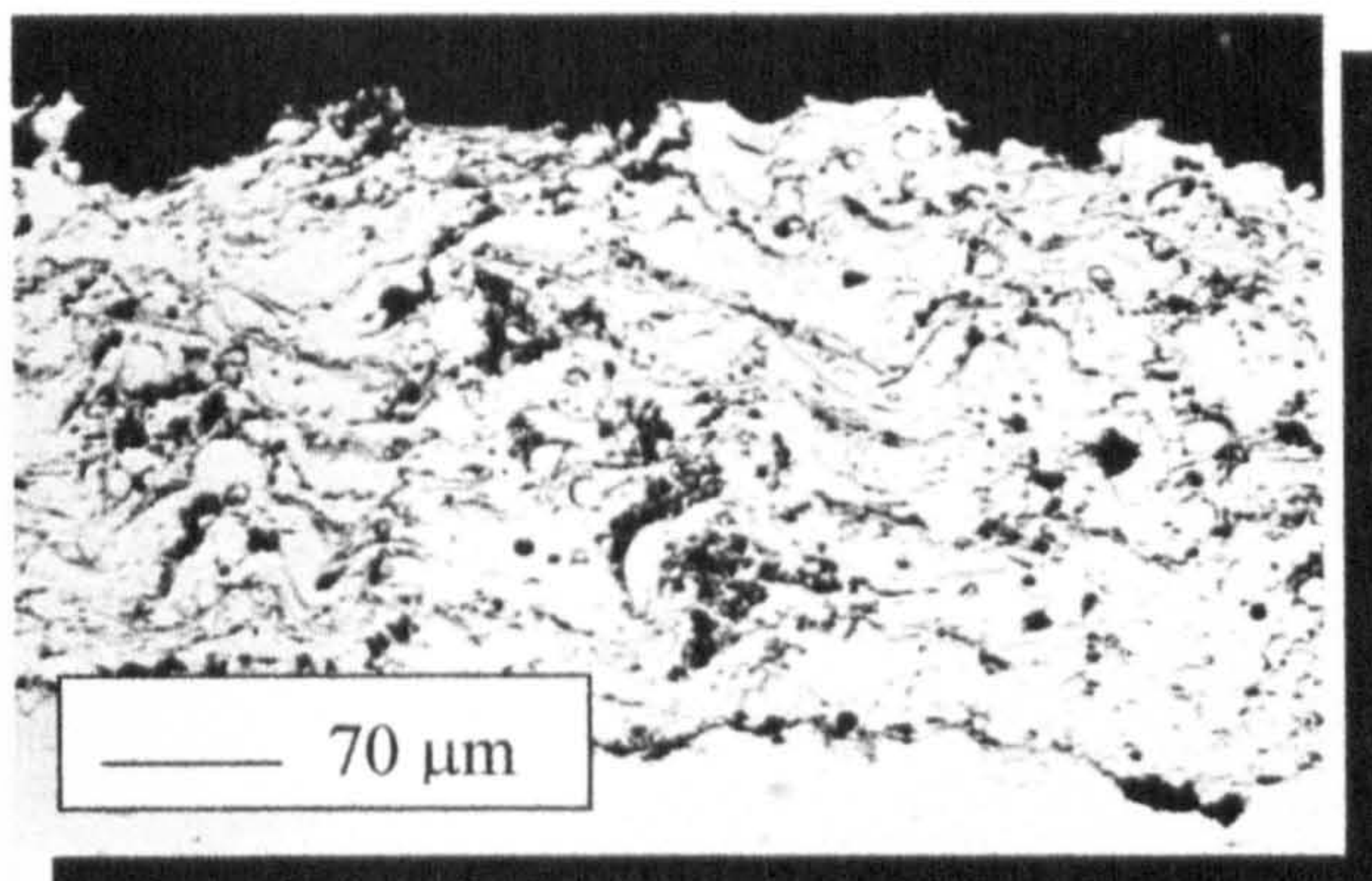
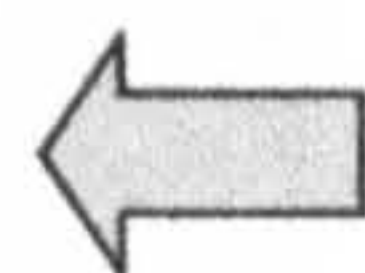
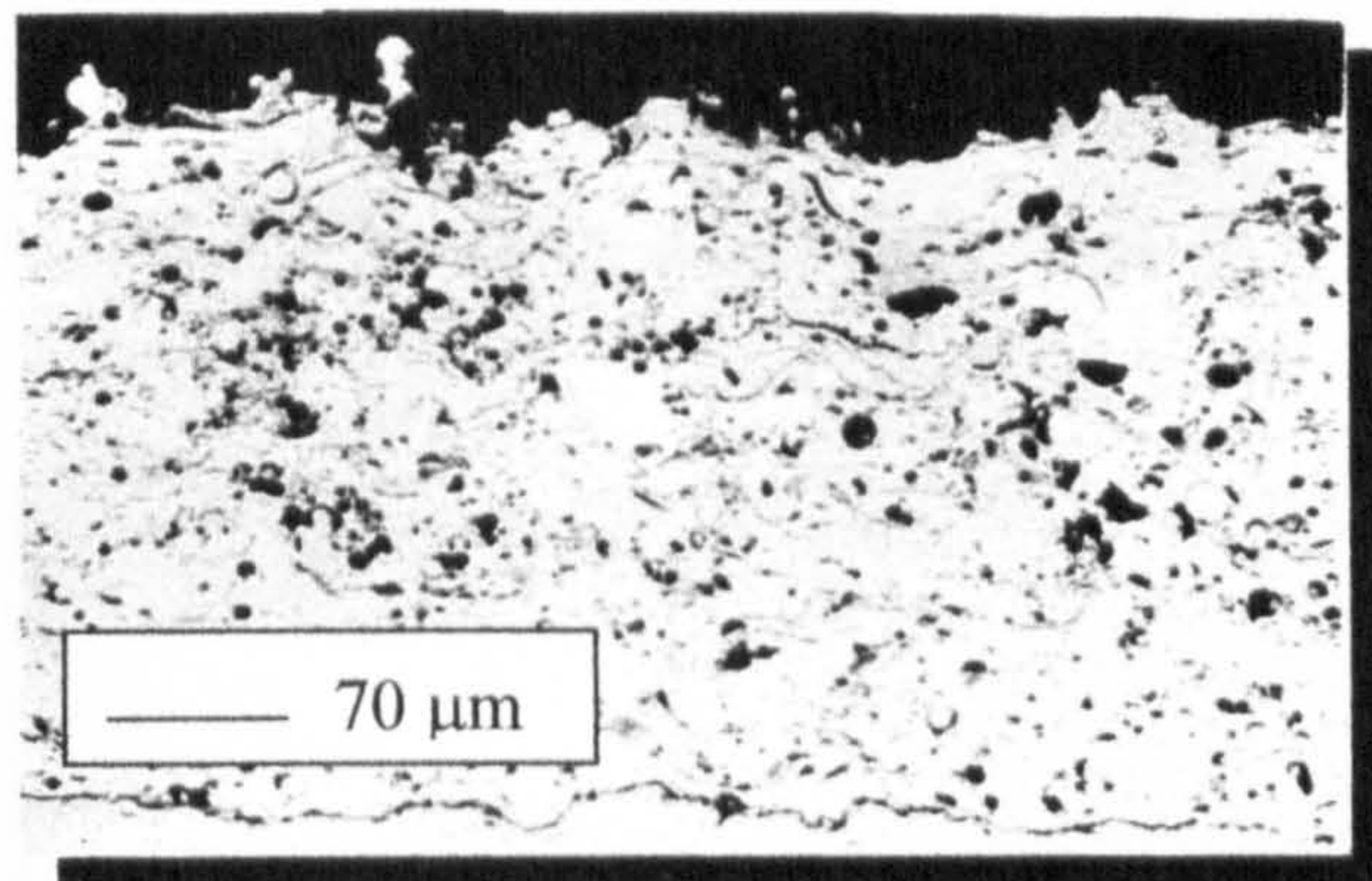
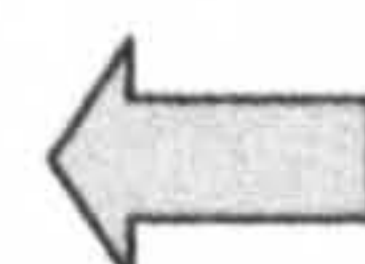


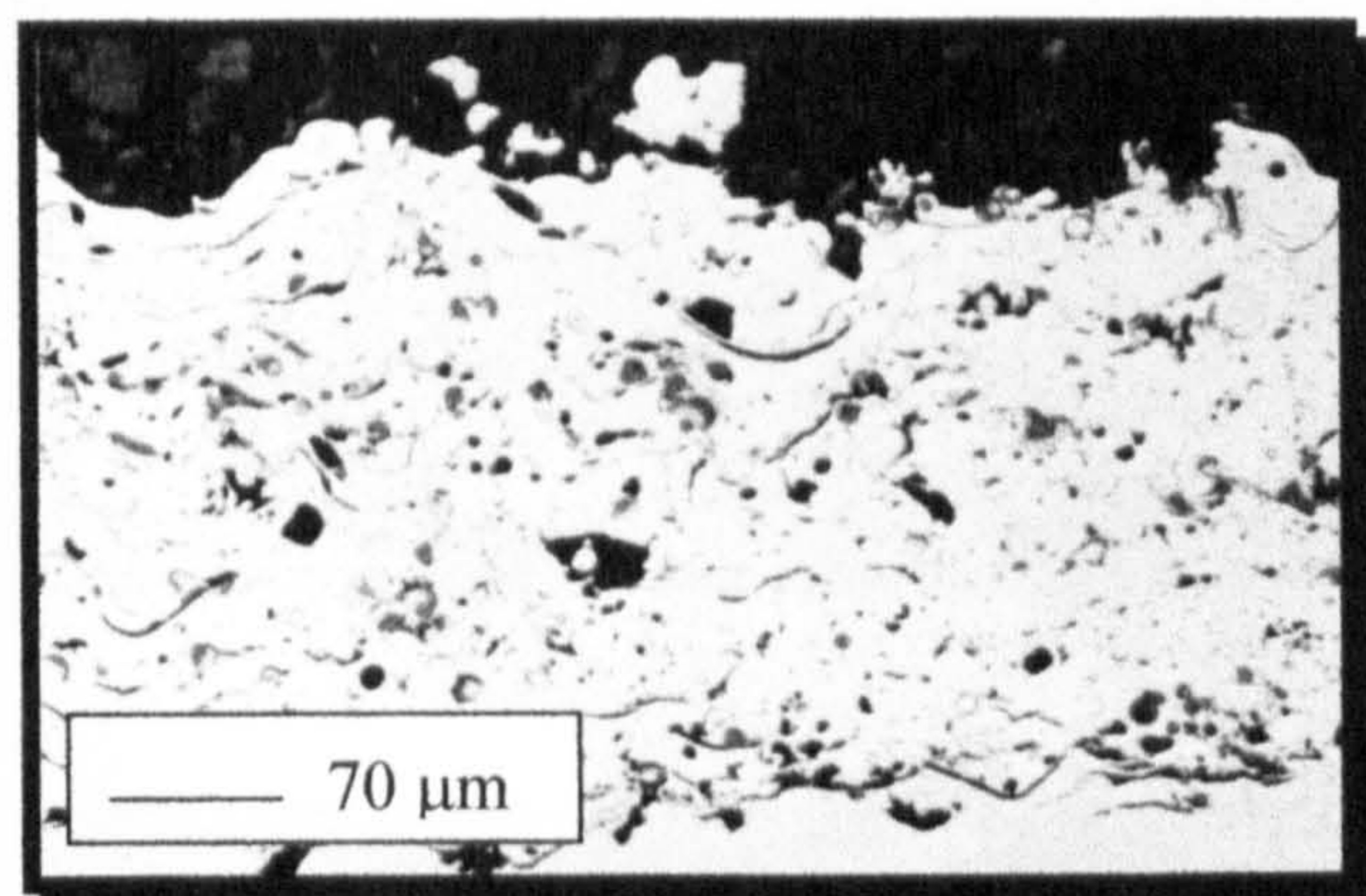
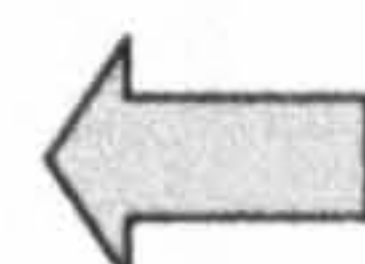
Figure 77 - Main regions of a transitional plasma jet^[60]



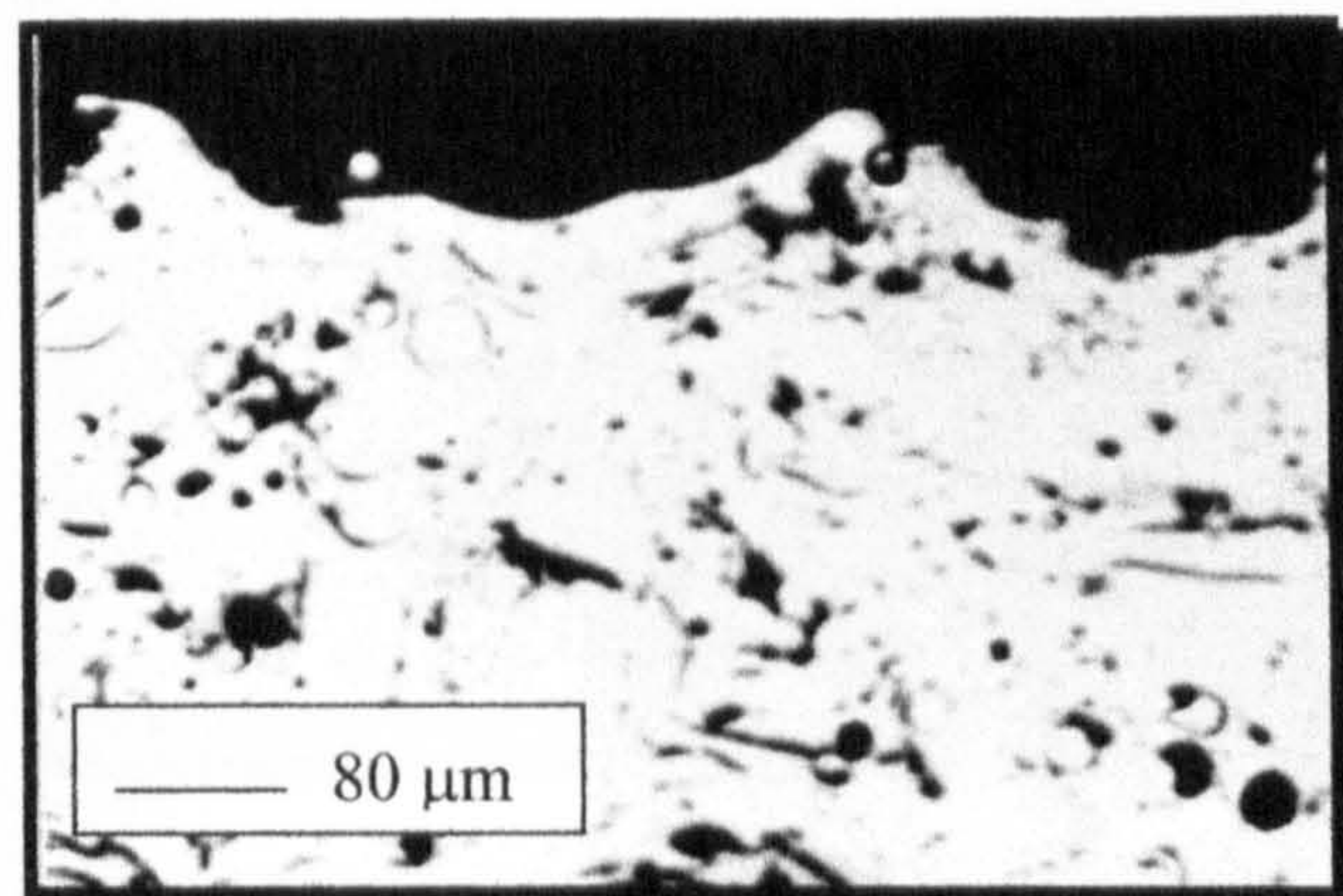
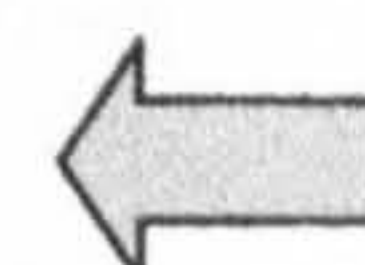
No Reactor



10 cm Reactor

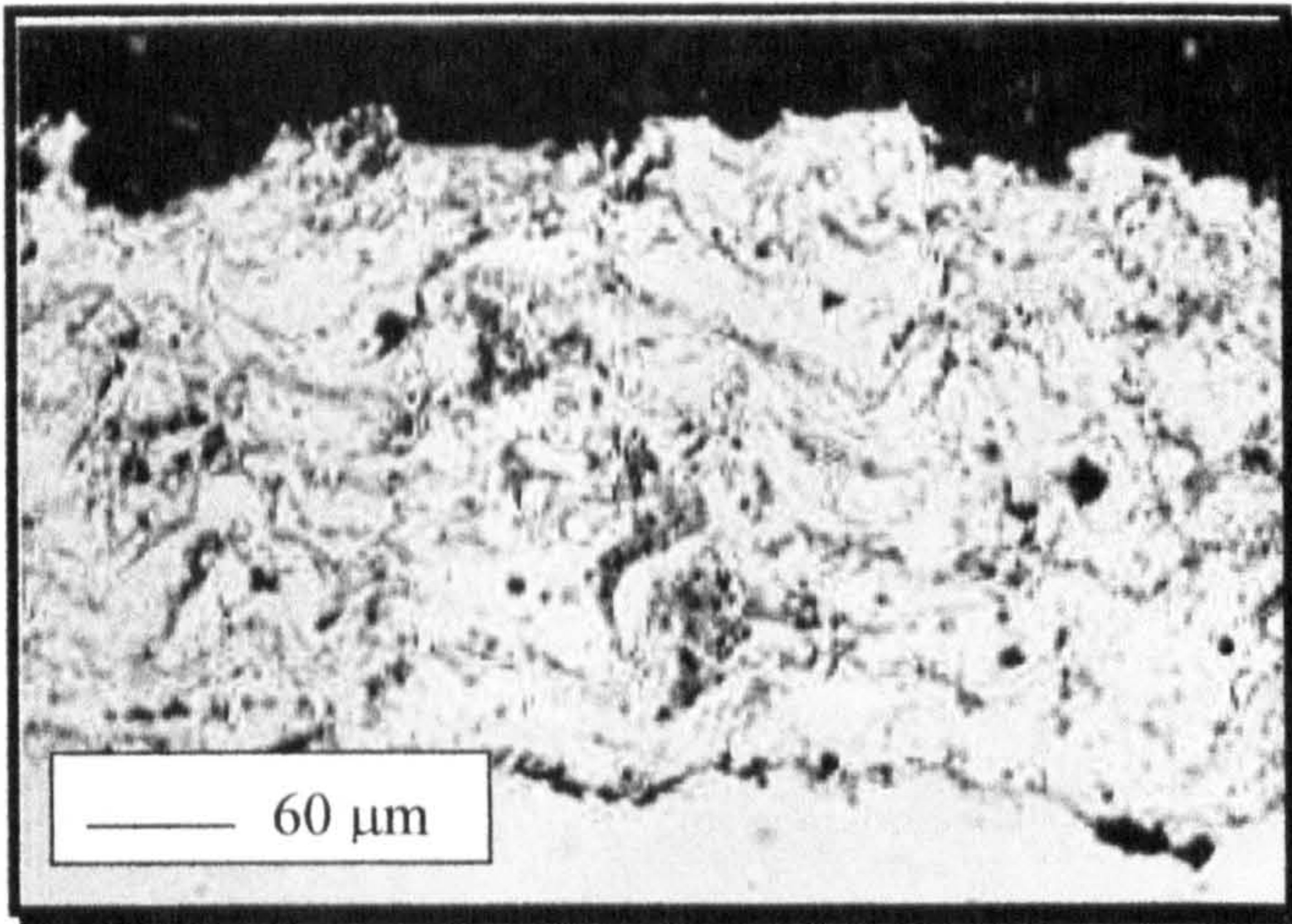
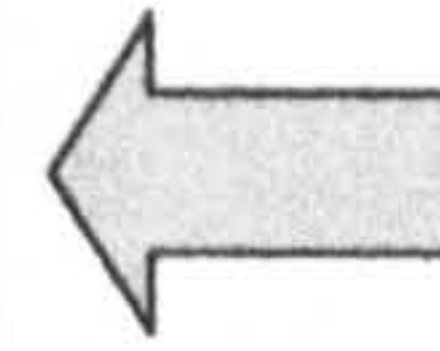


15 cm Reactor

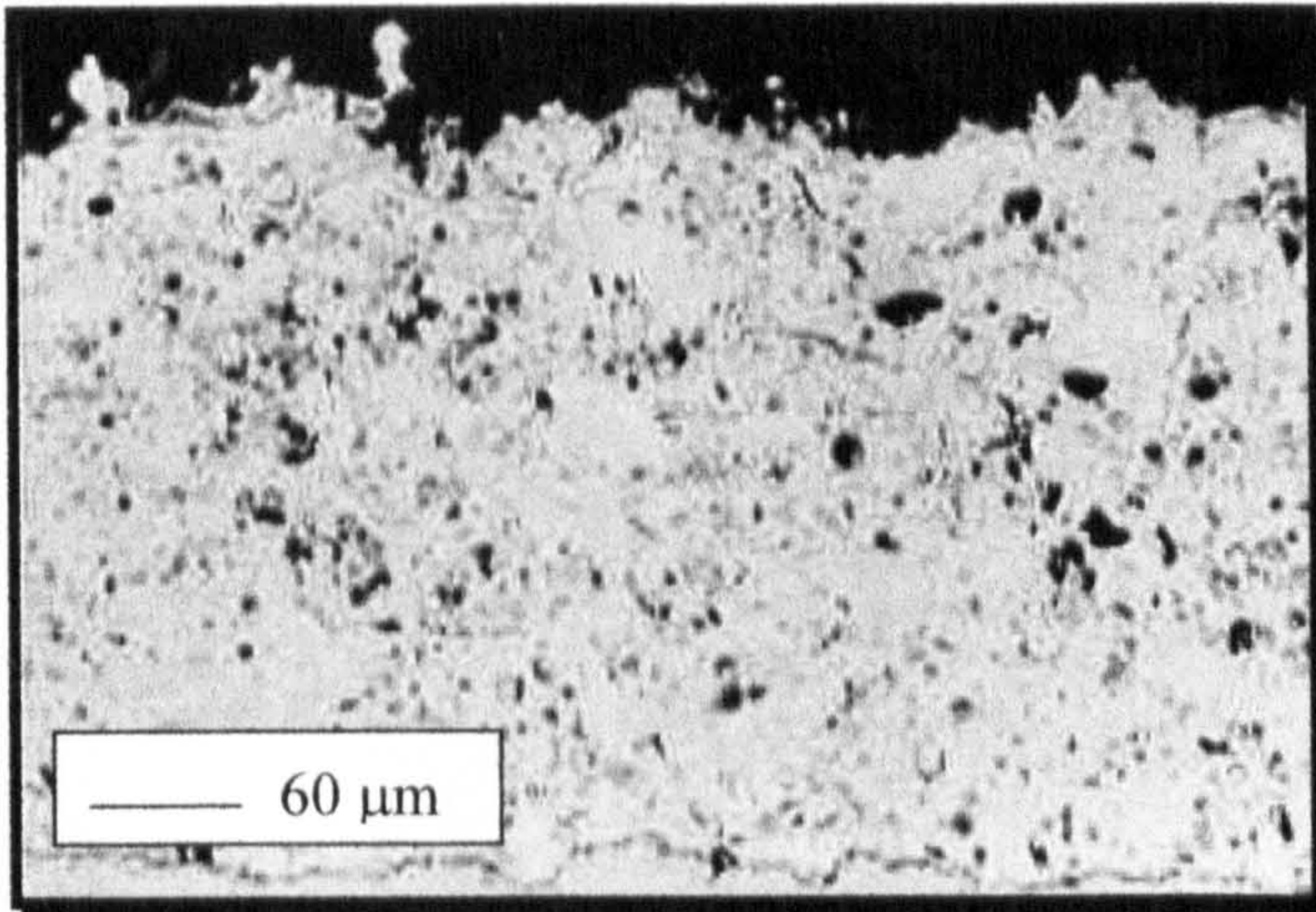
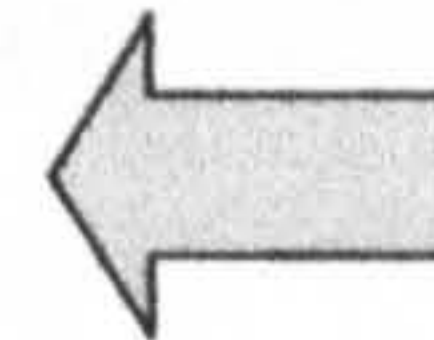


20 cm Reactor

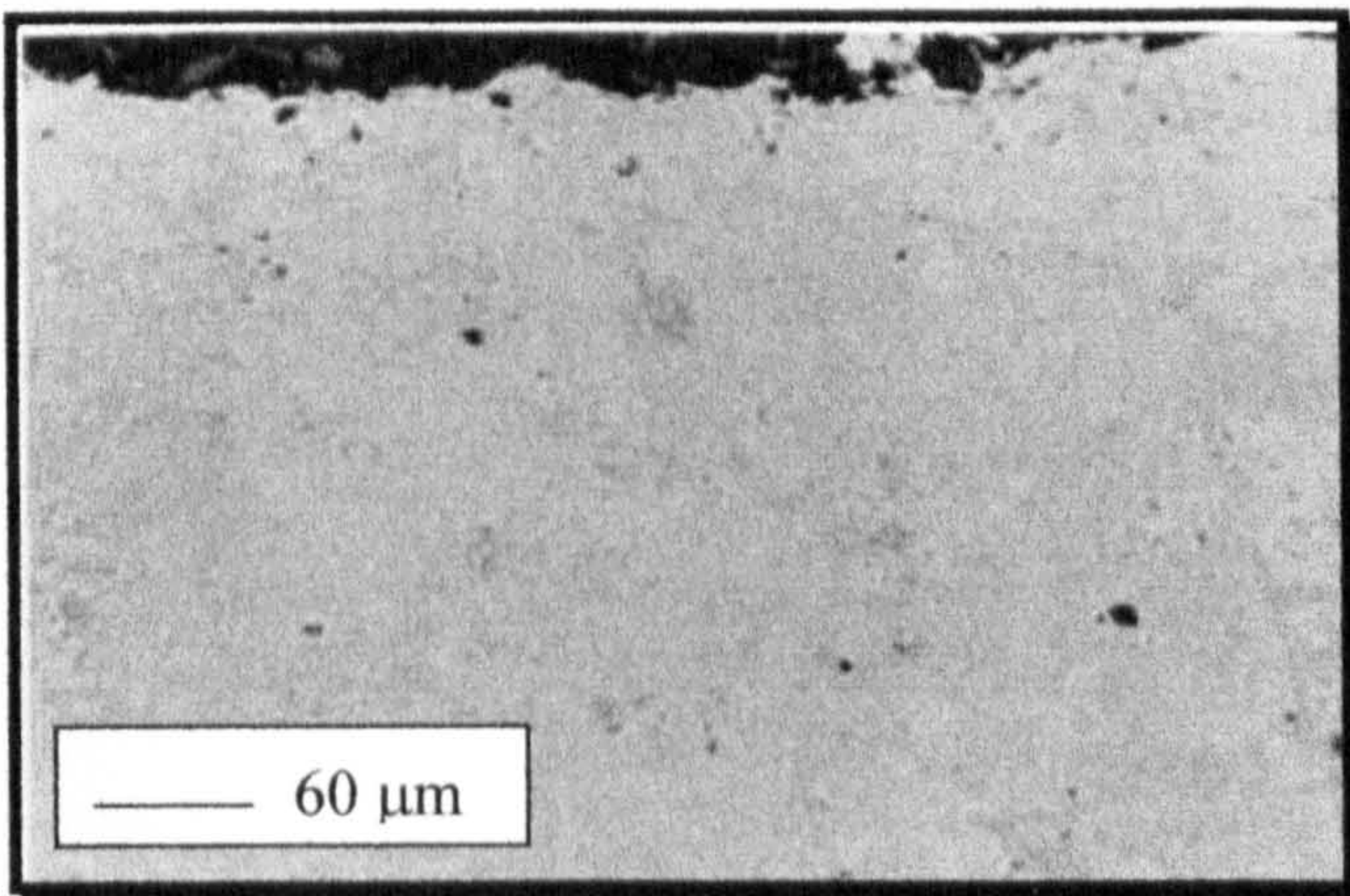
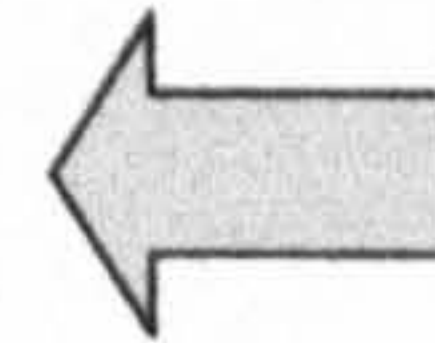
Figure 78 - Effect of reactor length on sprayed coatings



APS



Shrouded Only



RPS

Figure 79 - (a) Conventionally sprayed APS coating; (b) Shrouded only coating; (c) Reactively sprayed coating

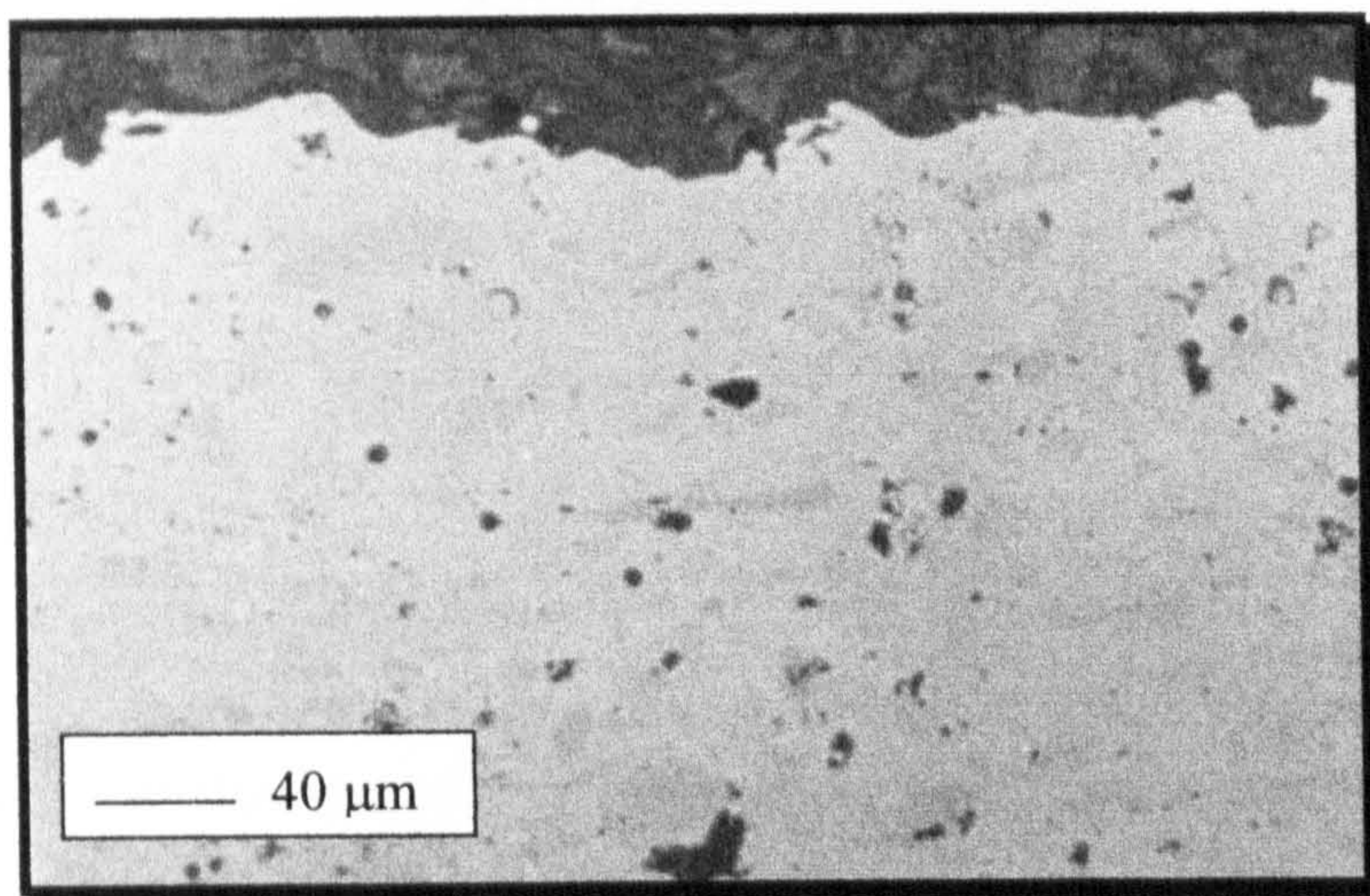


Figure 80 - Coating produced with acetylene, 24 l min^{-1}

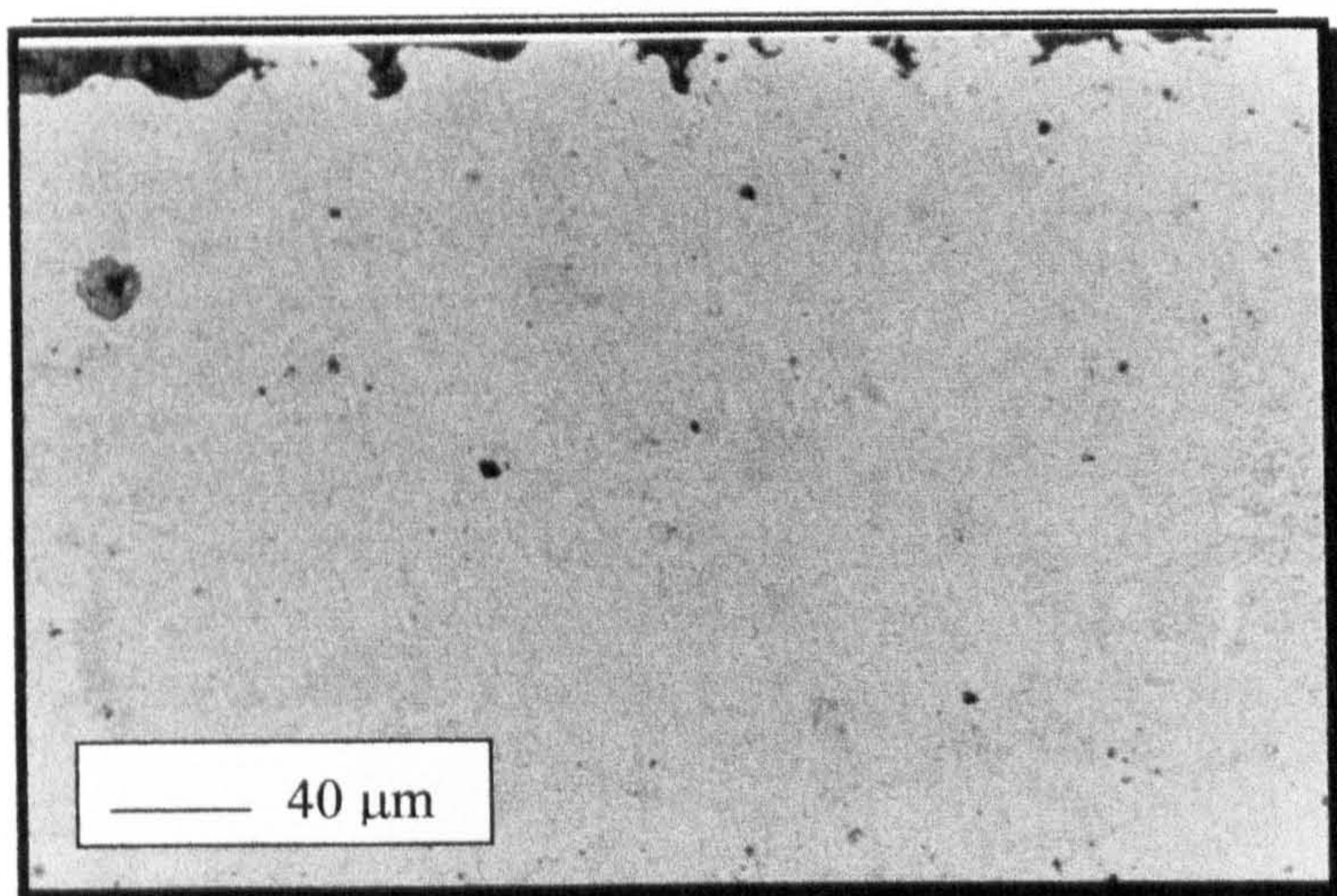


Figure 81 – Coating produced with methane, 24 l min^{-1}

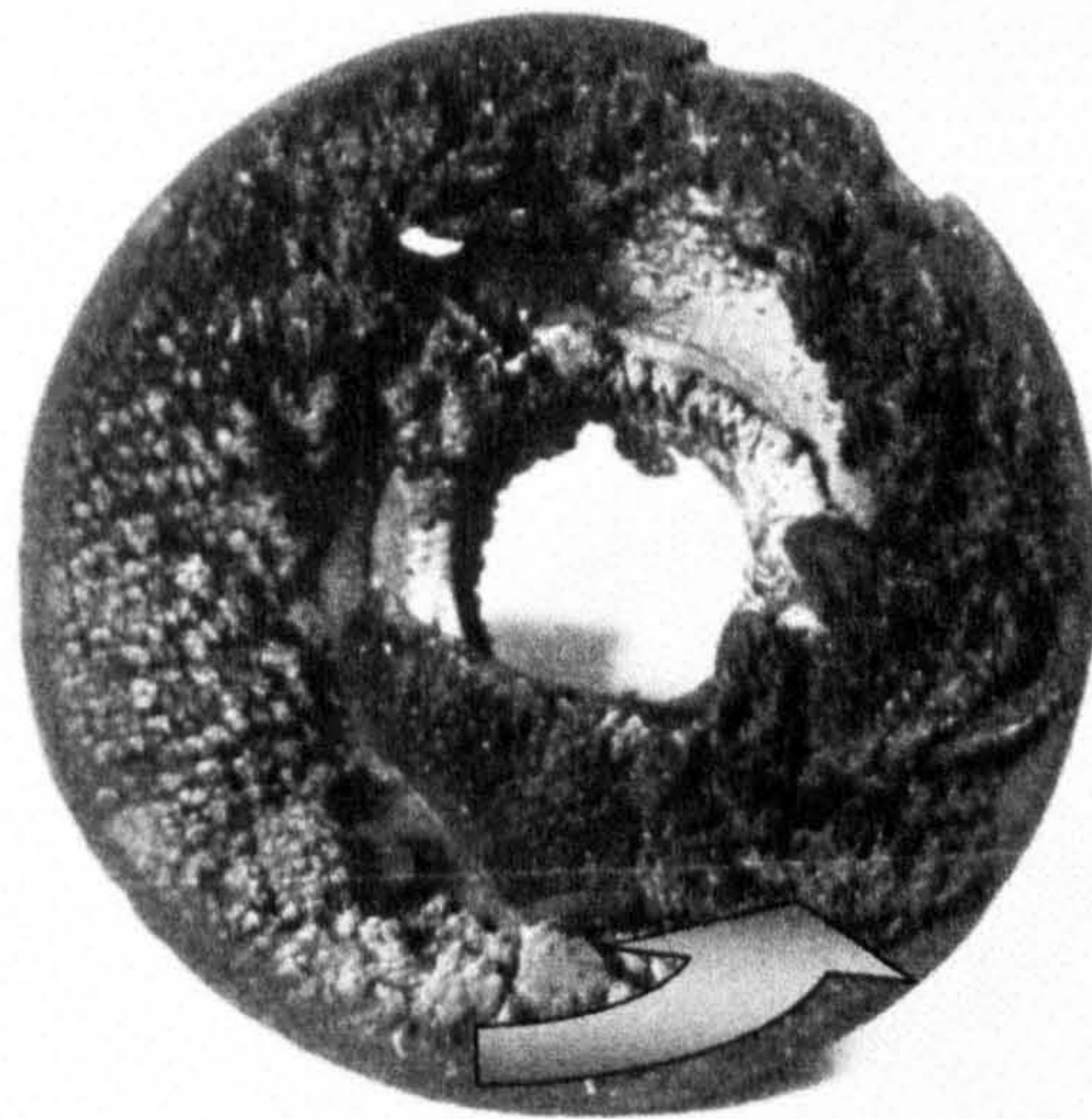


Figure 82 - Carbon deposit build up resulting from high acetylene injection flow rates. Arrow indicates direction of 'swirl'

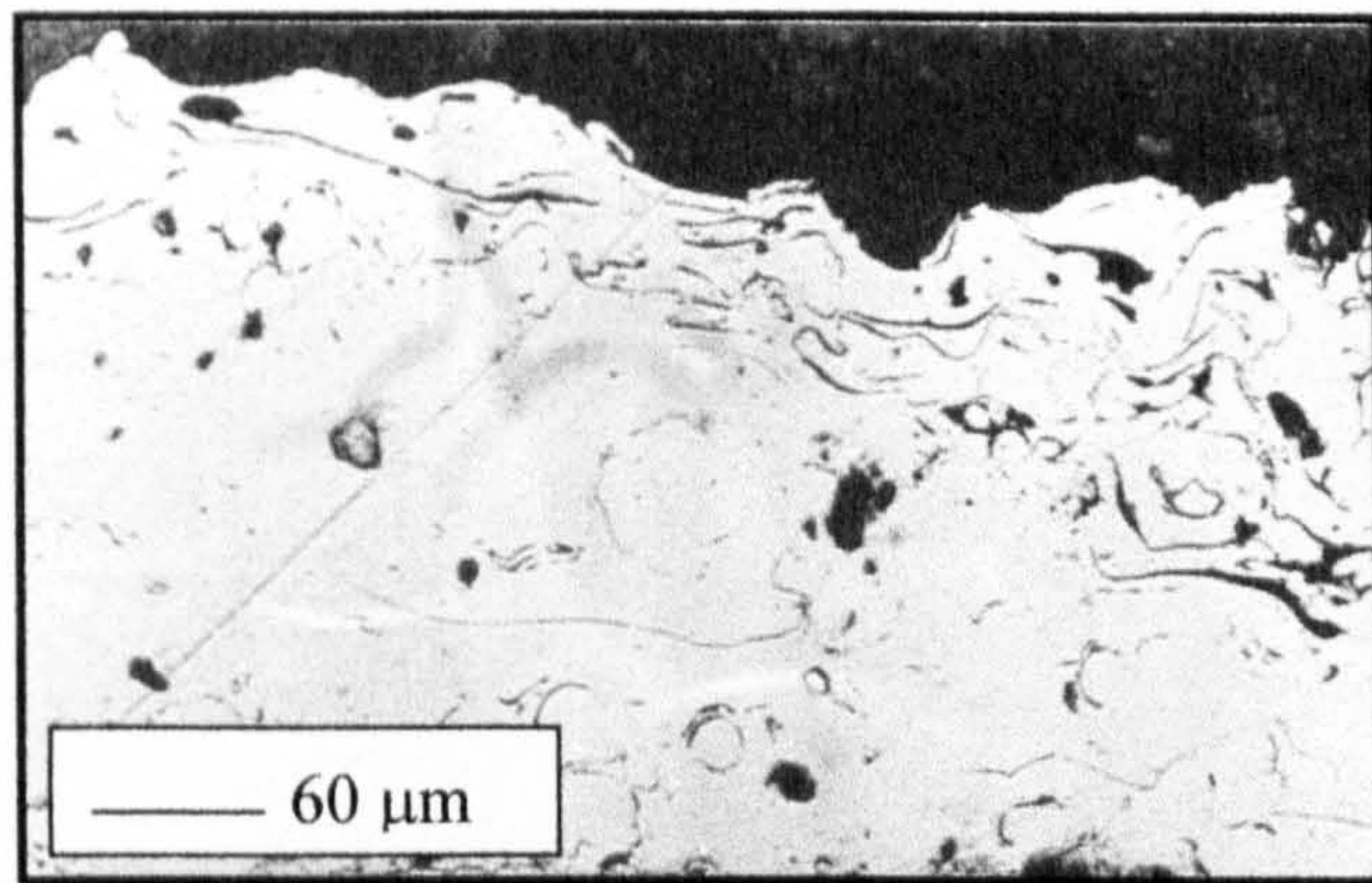


Figure 83 - Optical micrograph of the microstructures produced for a coating deposited with acetylene

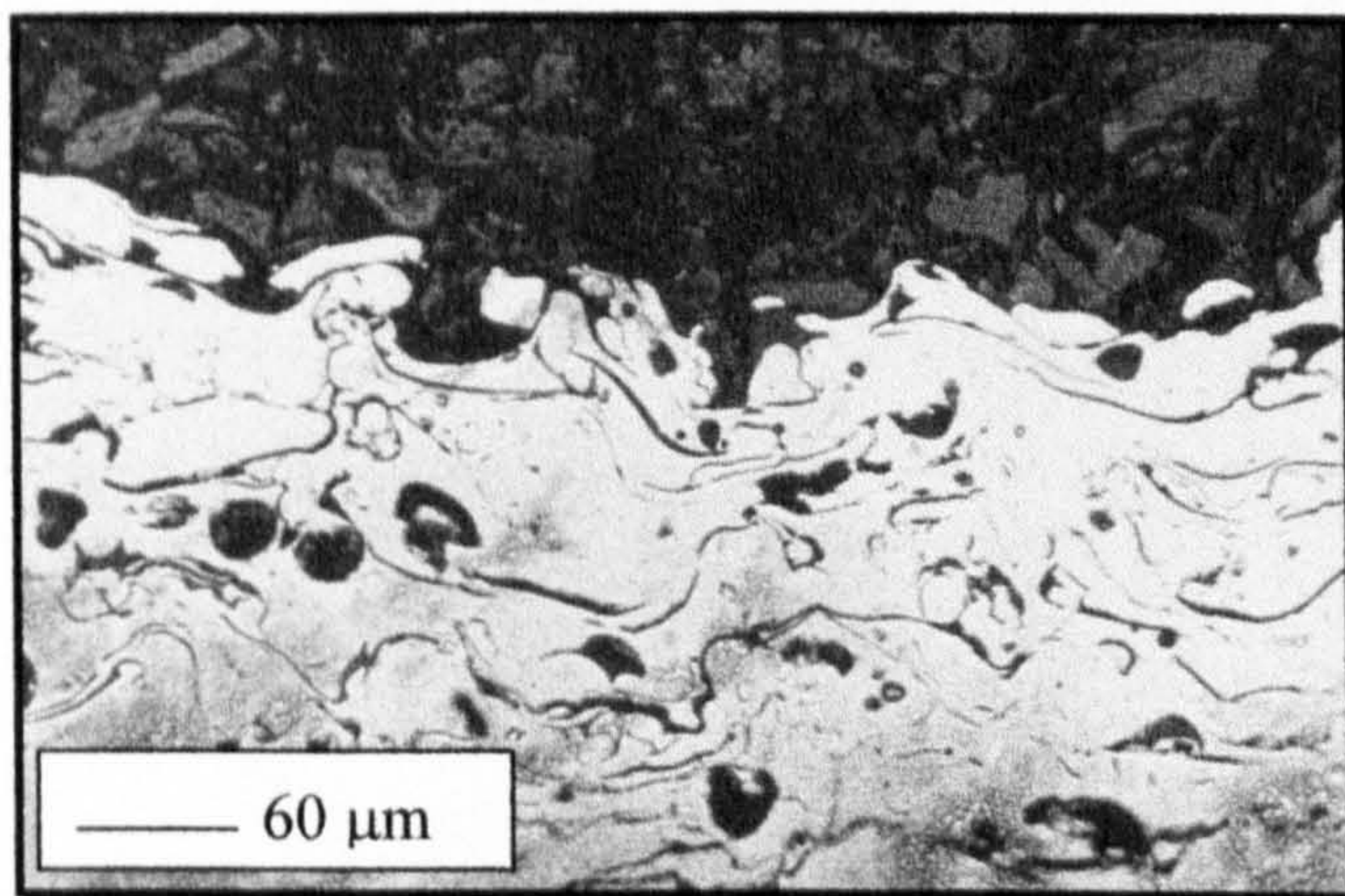


Figure 84 - Optical micrograph of the microstructures produced for a coating deposited with hydrogen

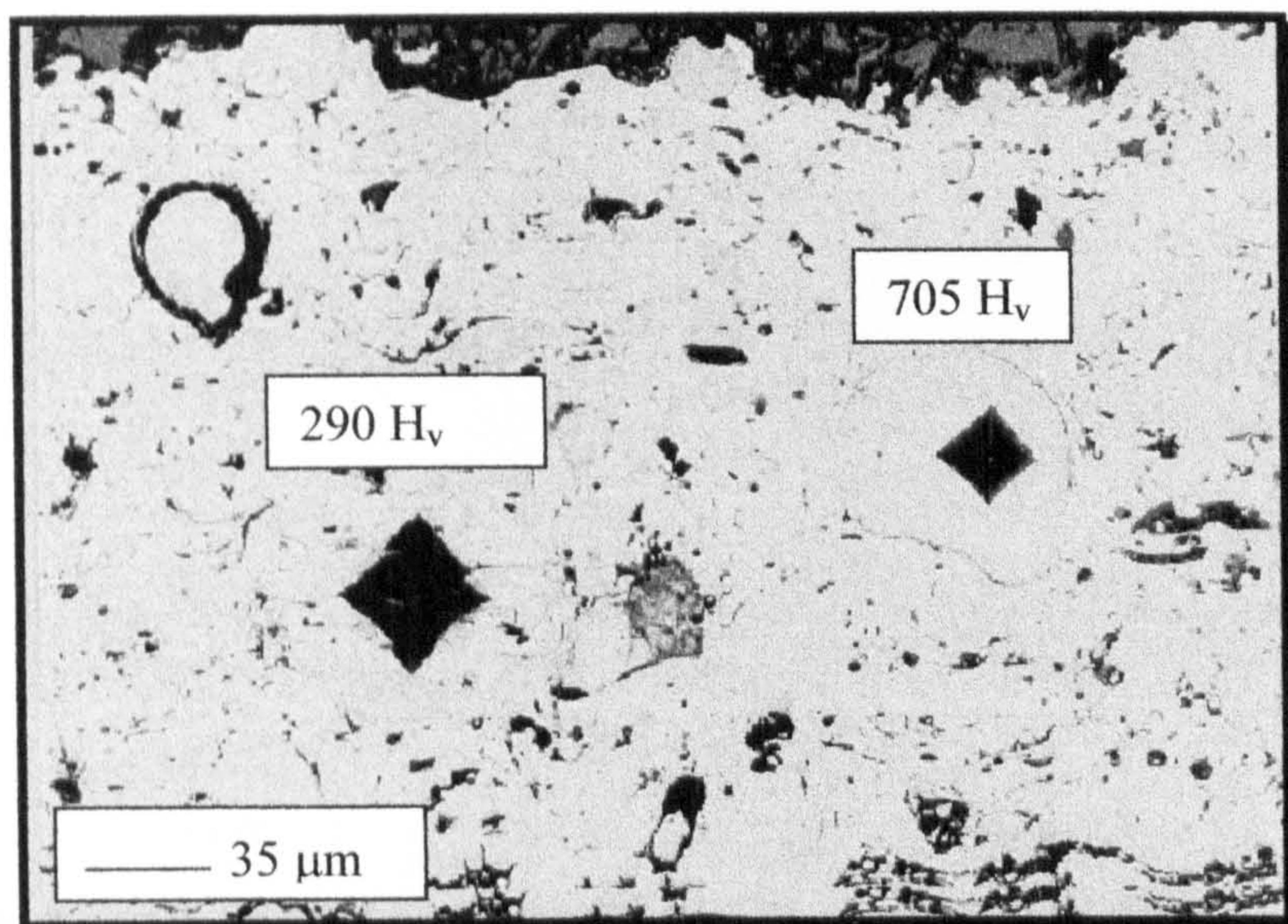


Figure 85 - Coating microstructure and corresponding indents for poorly melted Cr particles

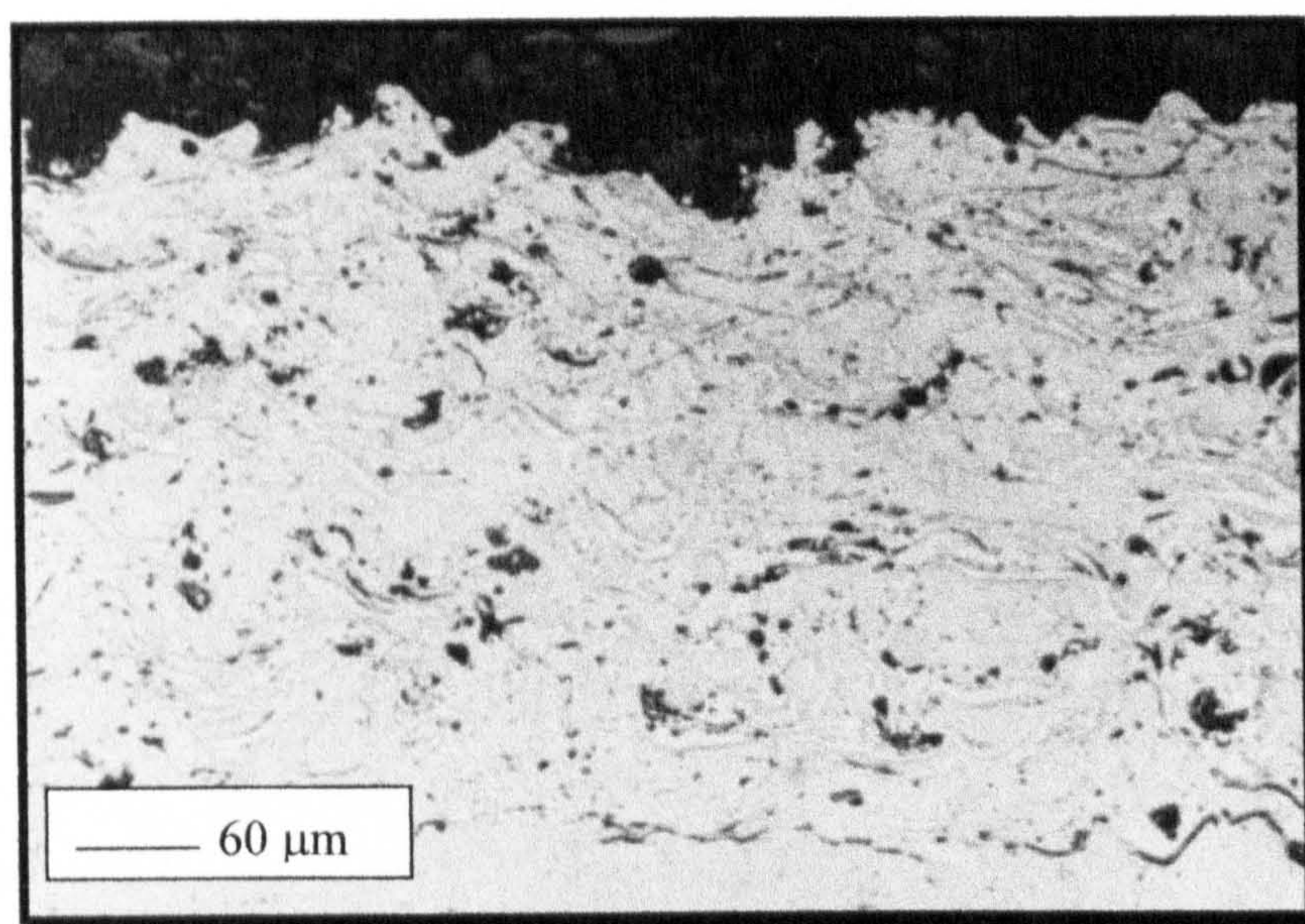


Figure 86 - Optical Micrograph of a reactively sprayed coating, 15 cm graphite reactor, 20 % added Cr

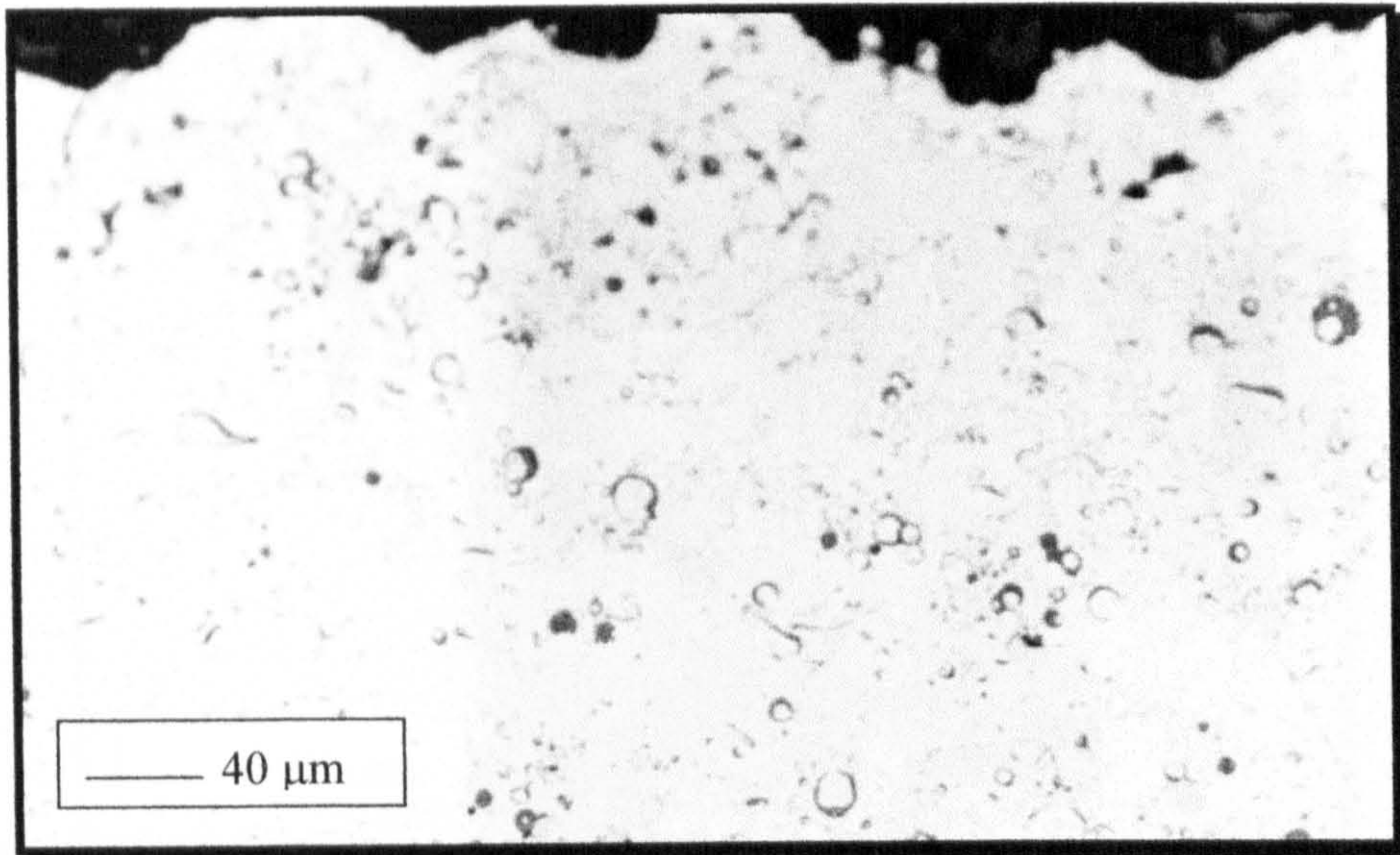


Figure 87 - Optical micrograph of the microstructures for a shrouded only coating deposited with an argon-helium mixture

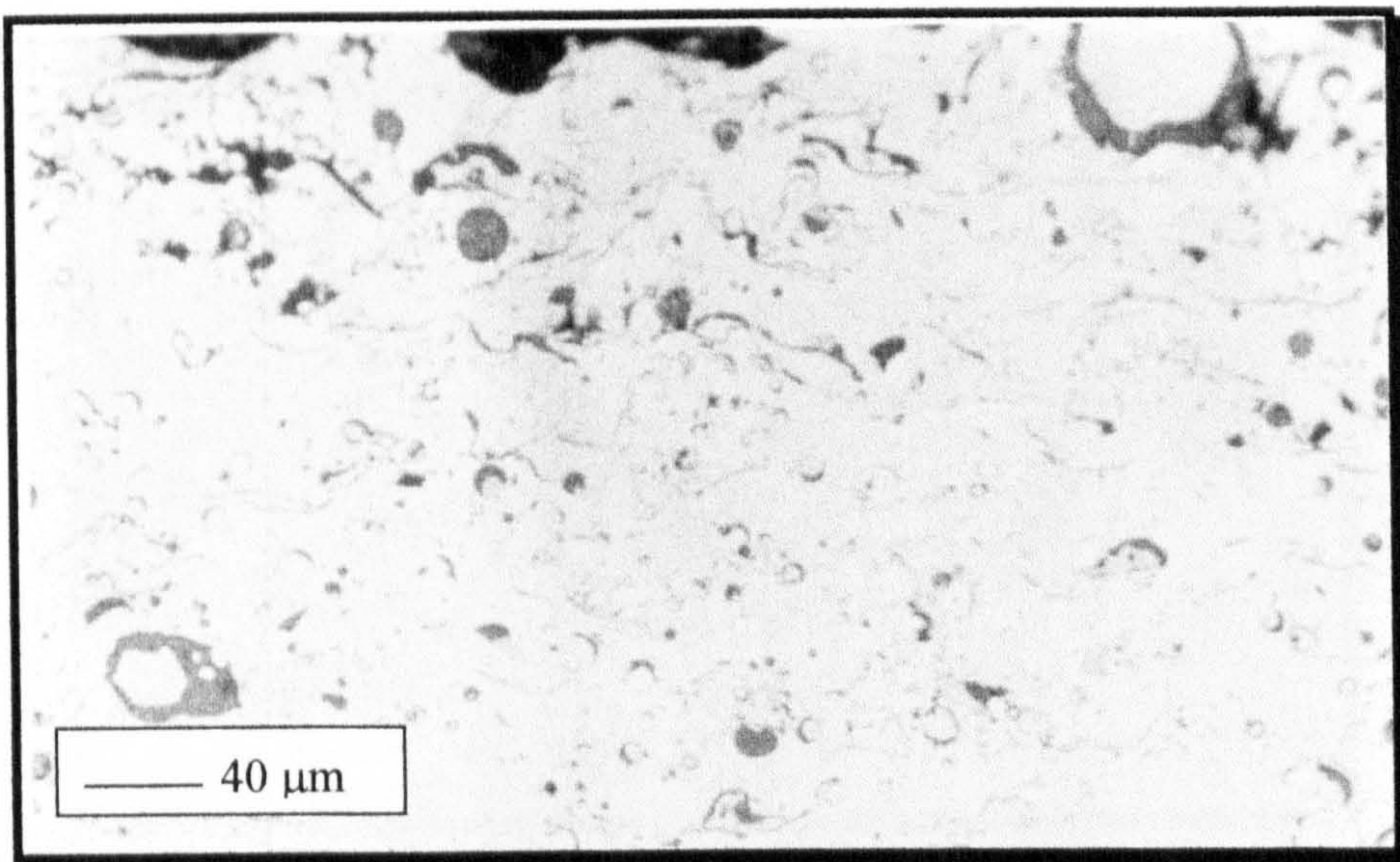


Figure 88 - Optical micrograph of the microstructures for a shrouded only coating deposited with an argon-hydrogen mixture

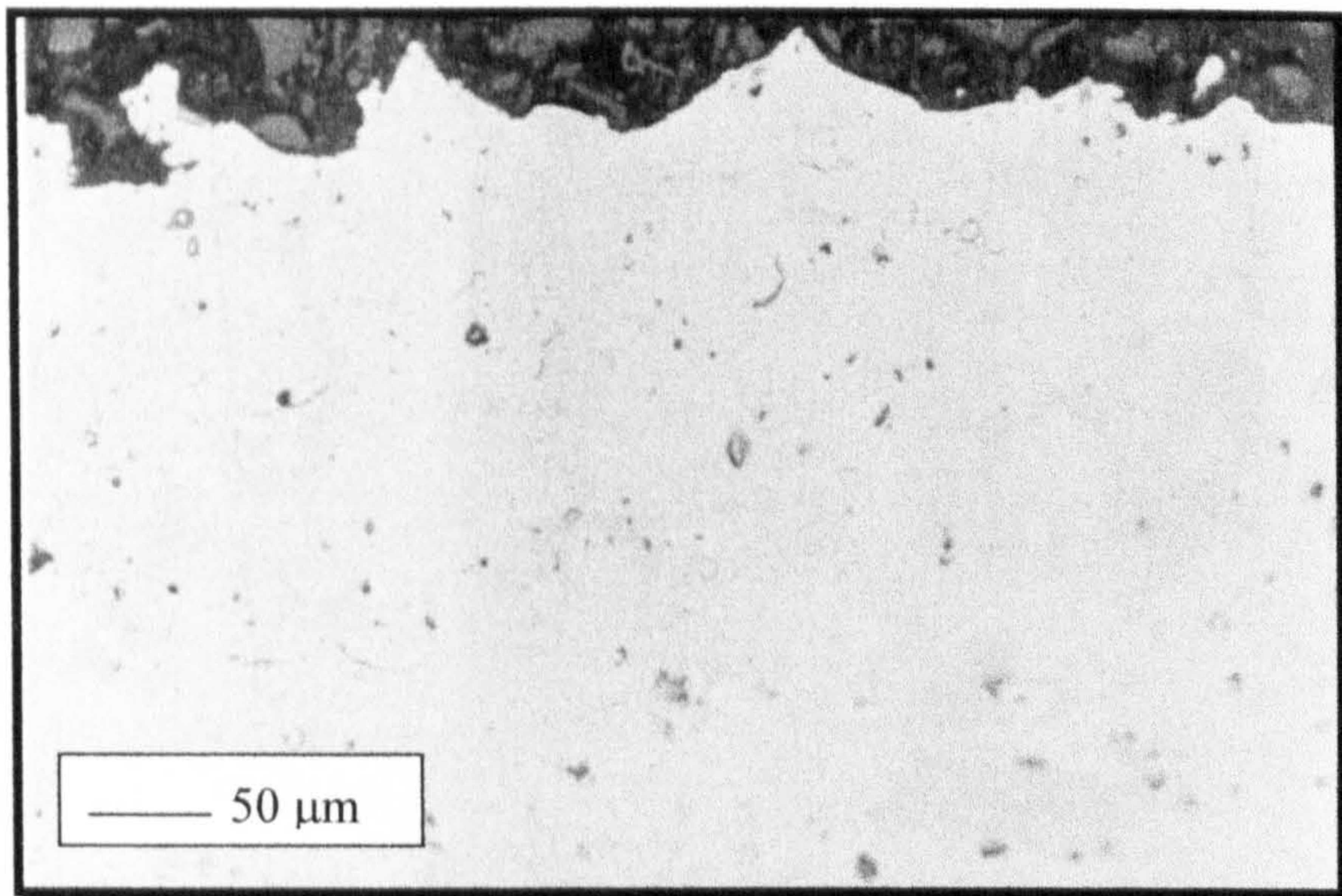


Figure 89 - Optical micrograph of the microstructures for a reactively sprayed coating produced with helium

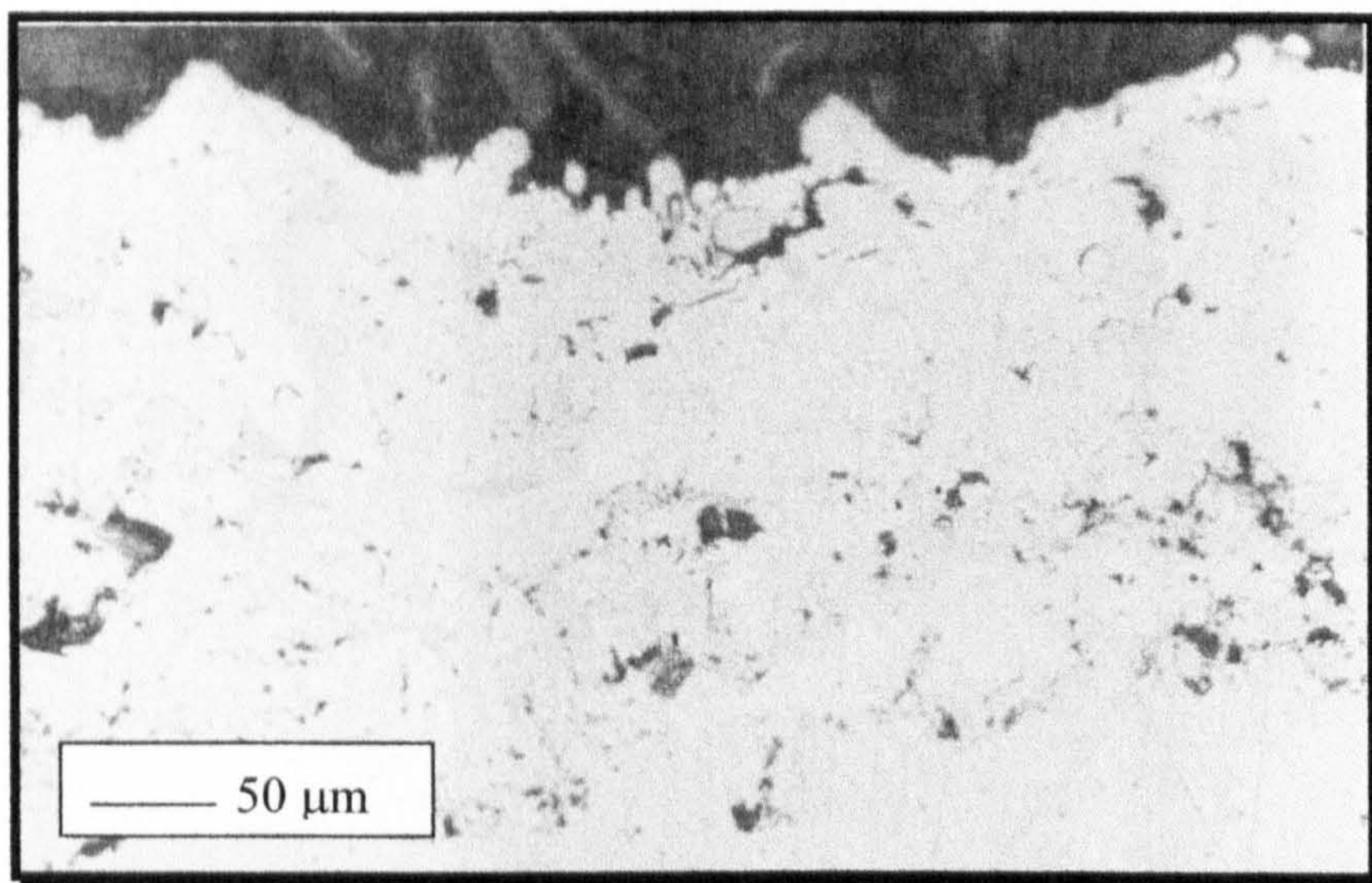


Figure 90 - Optical micrograph of the microstructures for a reactively sprayed coating produced with hydrogen

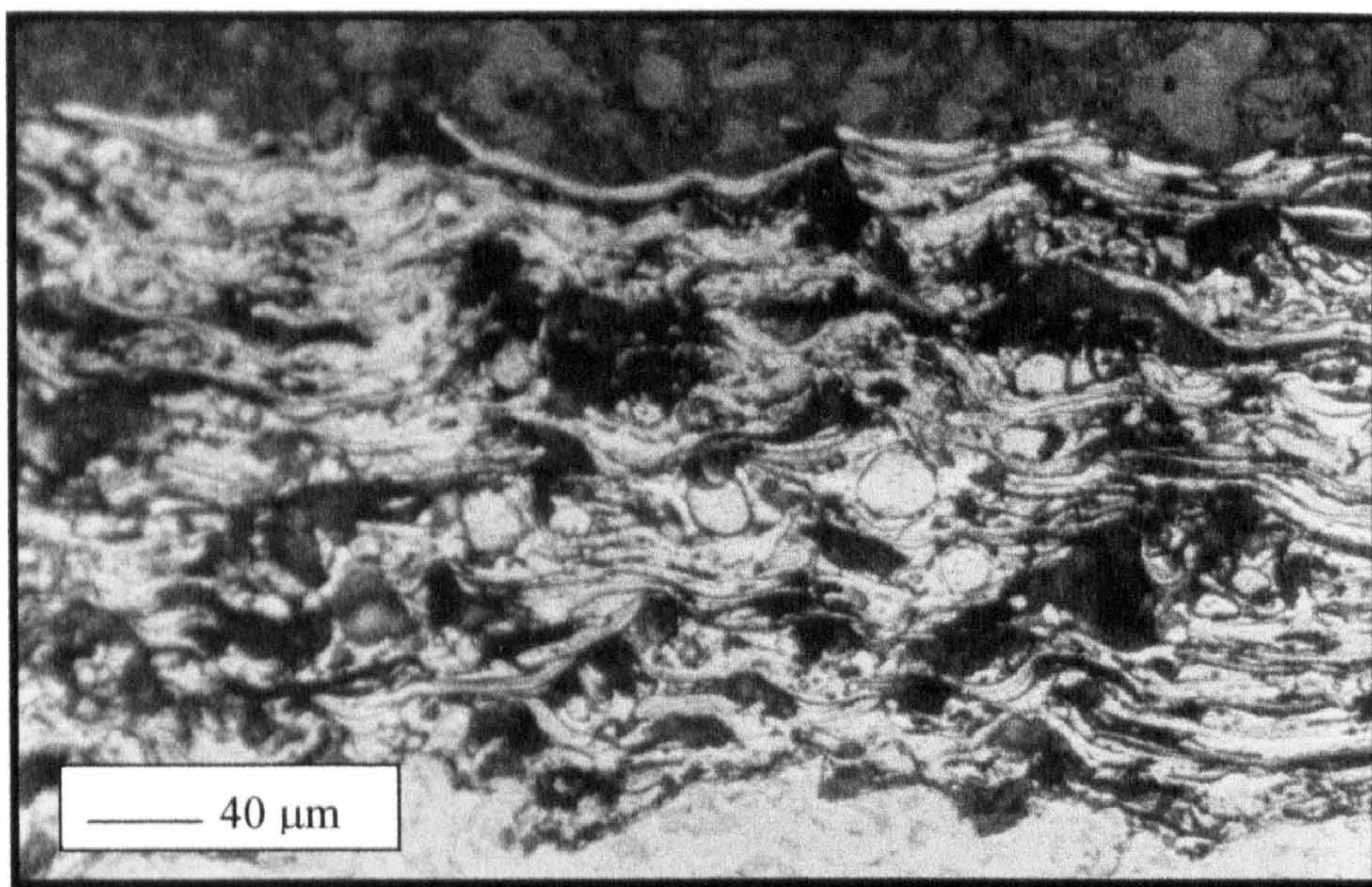


Figure 91 - Optical micrograph of coating post etching

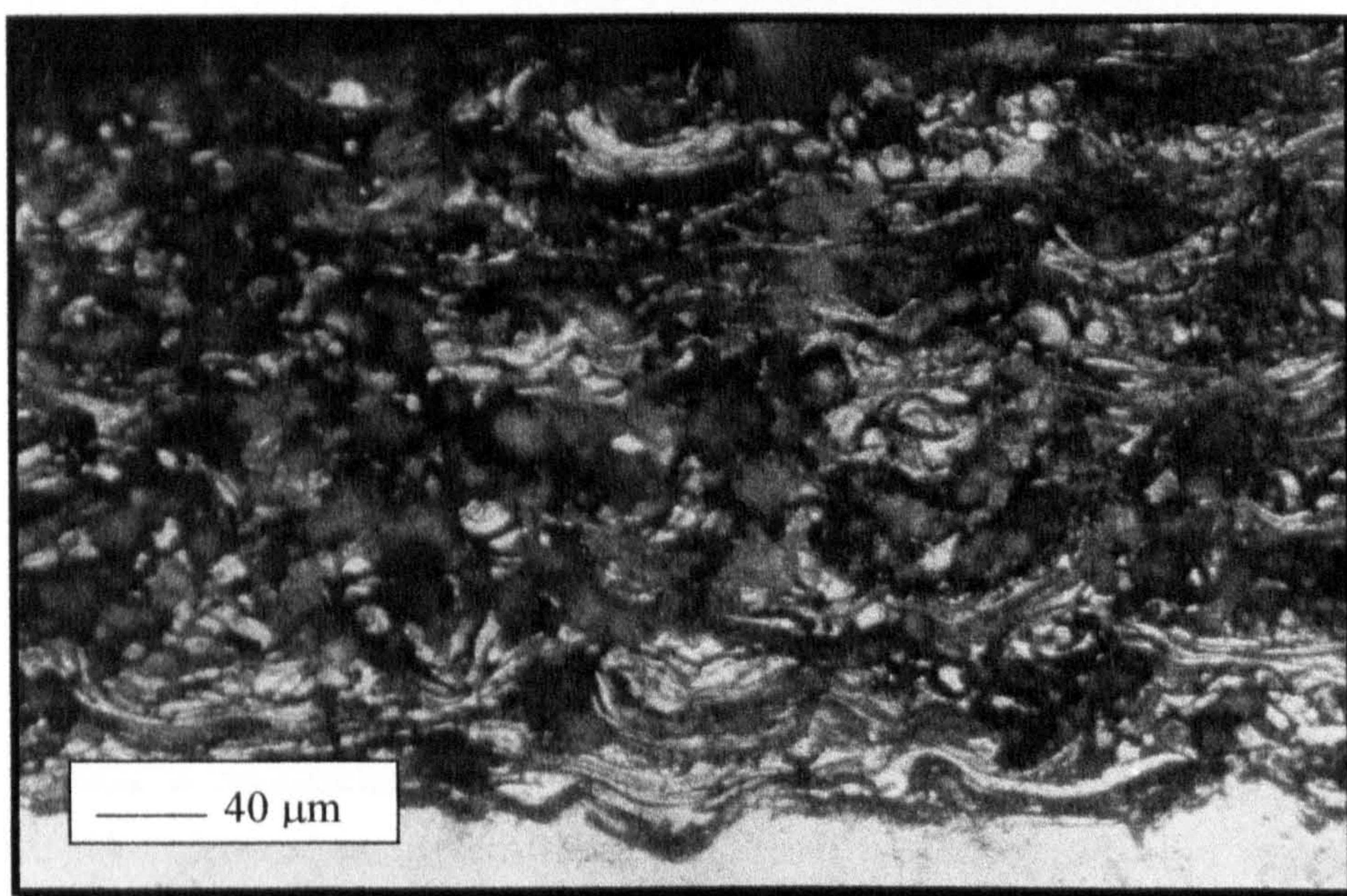


Figure 92 - Optical micrograph showing coating attacked by etching

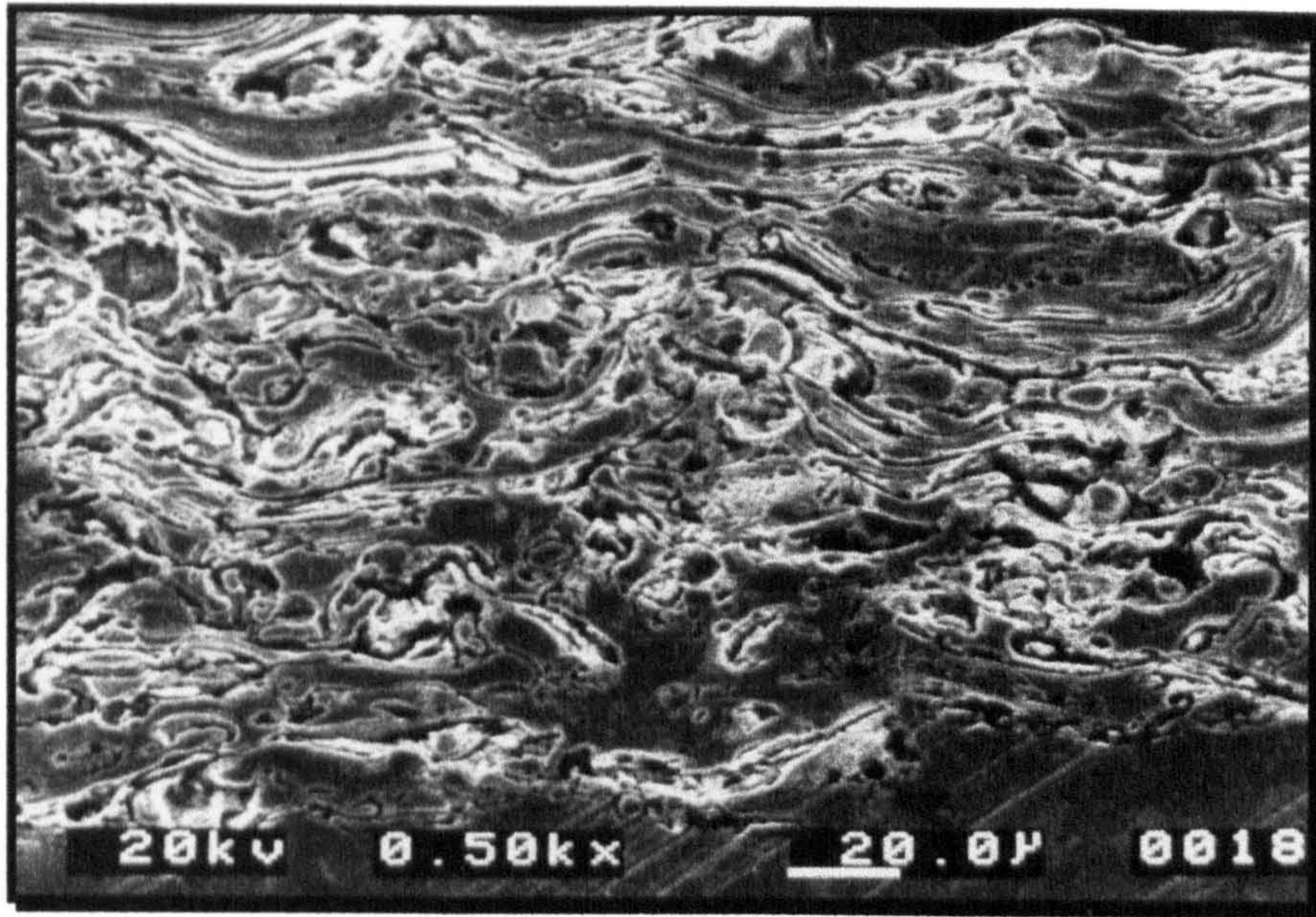


Figure 93 - S.E.M. Micrograph of etched specimen (Carbide phases)

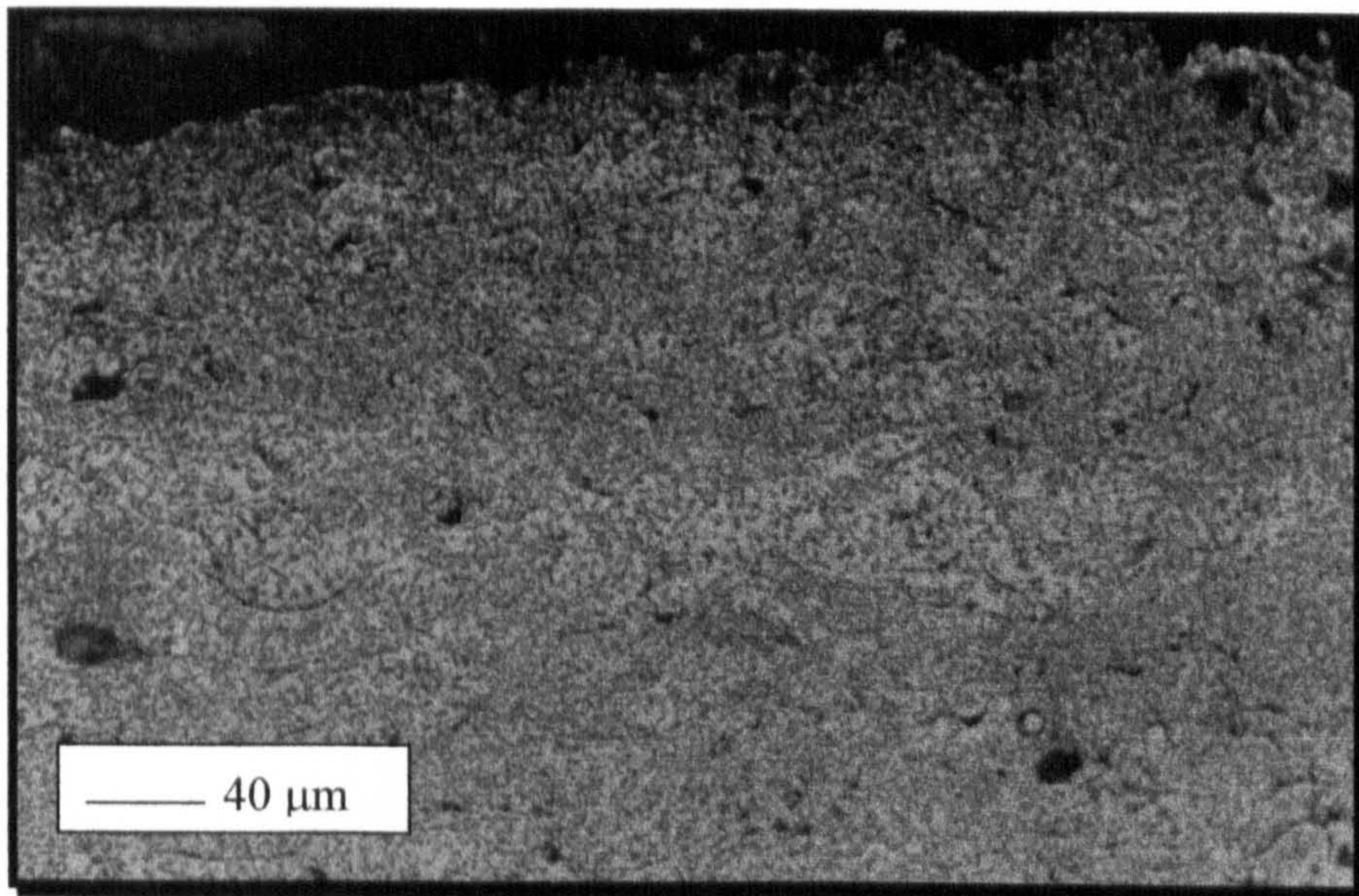


Figure 94 - Optical micrograph of post heat treated reactively sprayed specimen

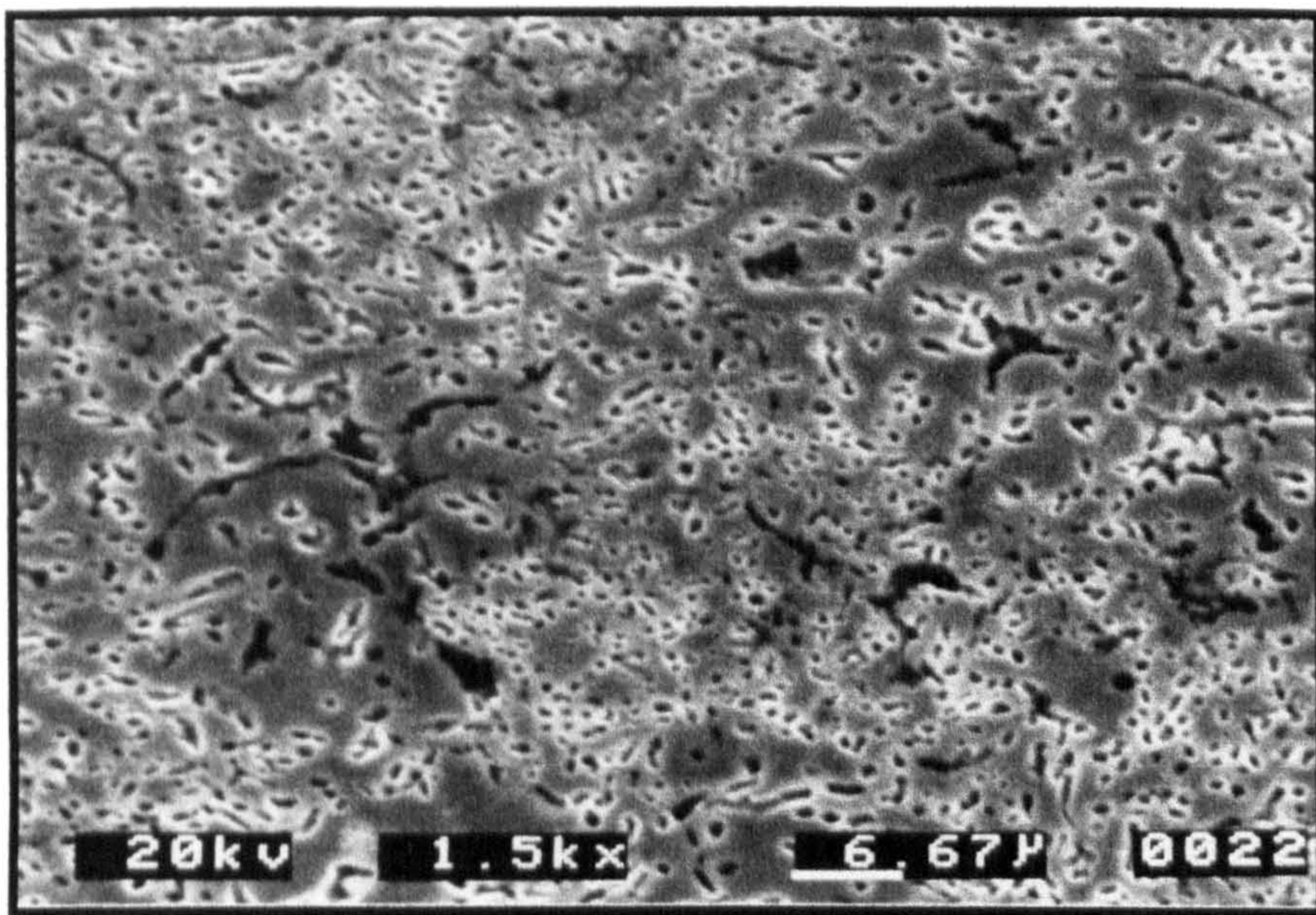


Figure 95 - S.E.M. Micrograph of attacked region

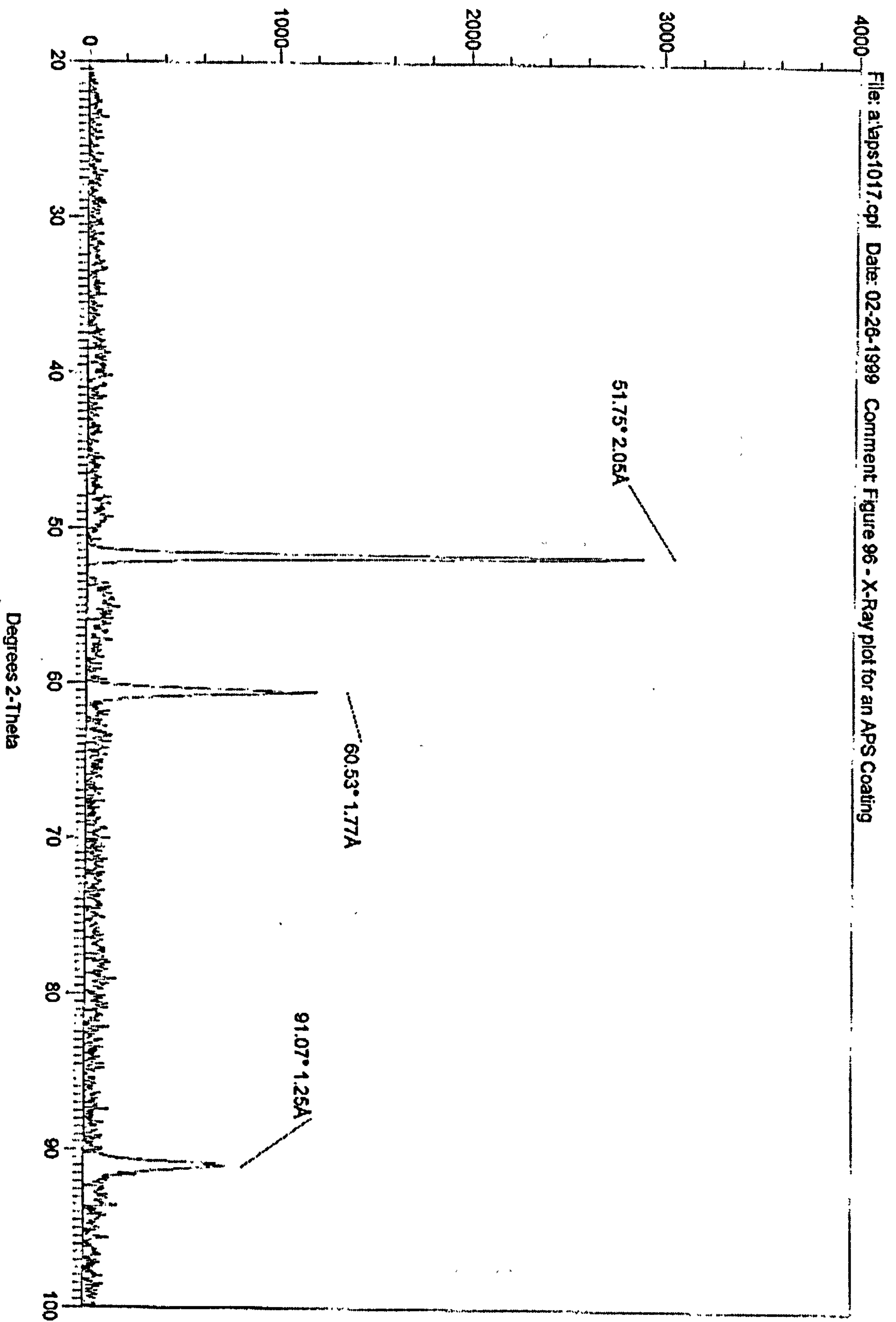


Figure 96 – X-Ray plot for an APS coating

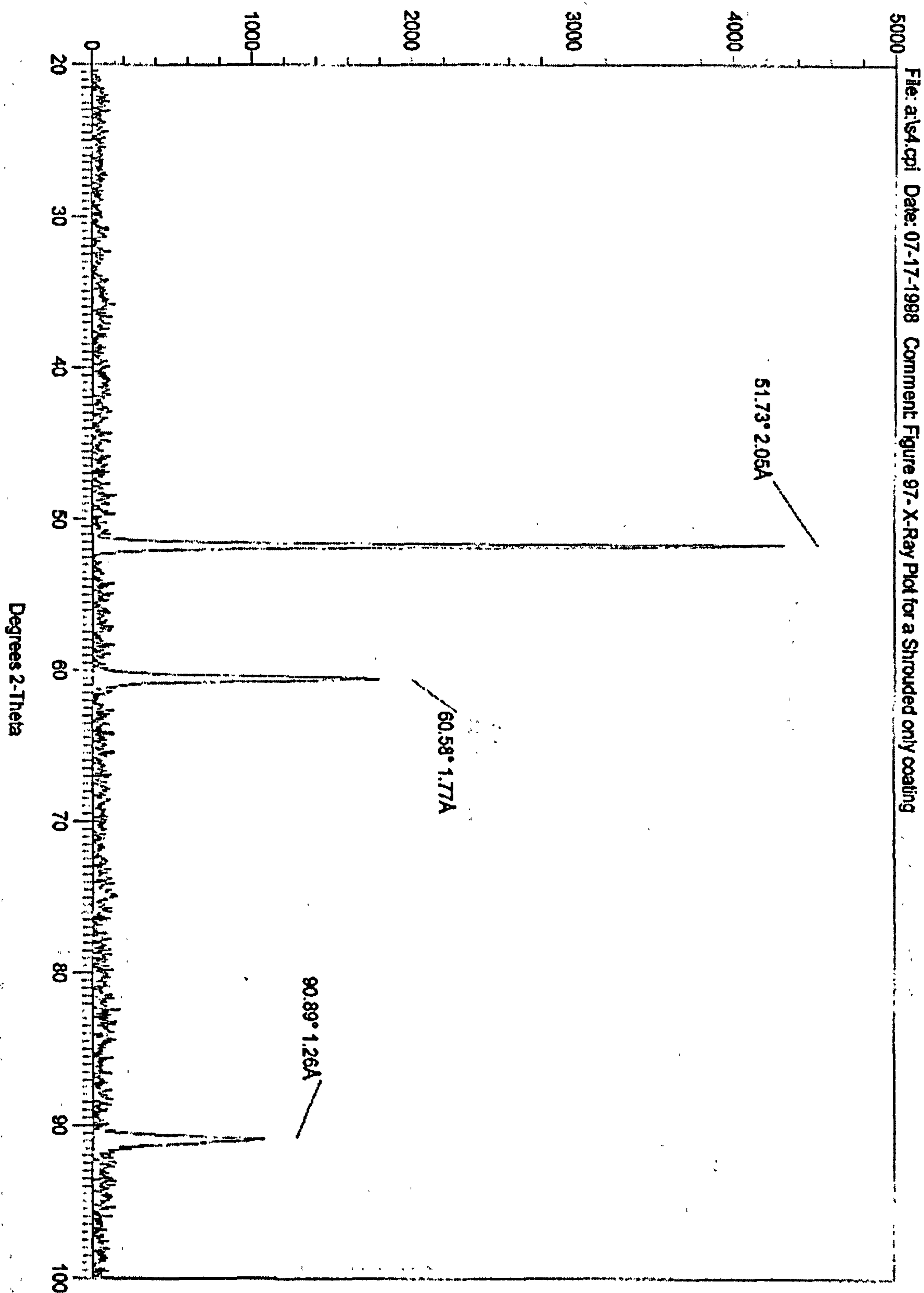


Figure 97 – X-Ray plot for a shrouded only coating

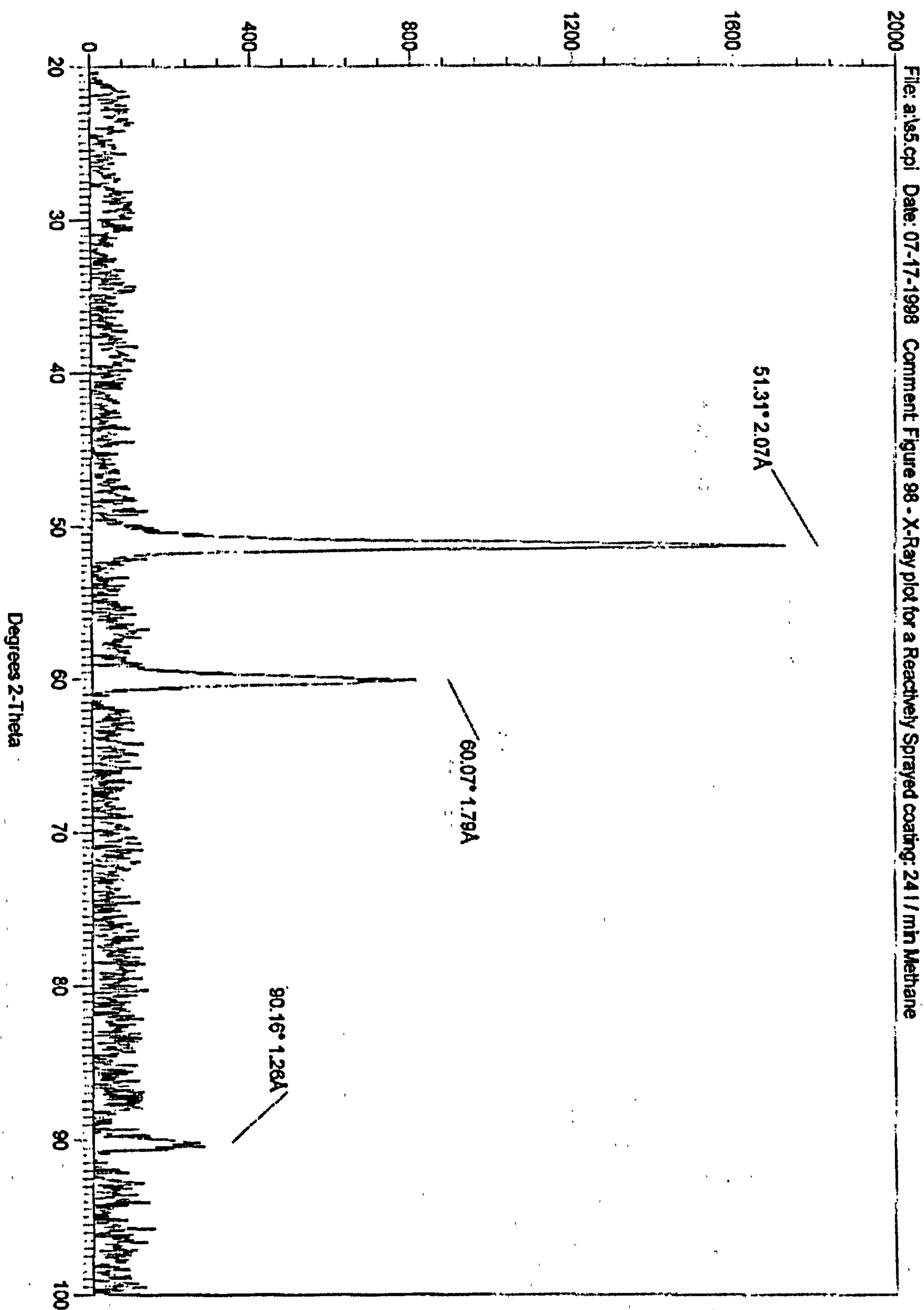


Figure 98 - X-Ray plot for a Reactively Sprayed Coating

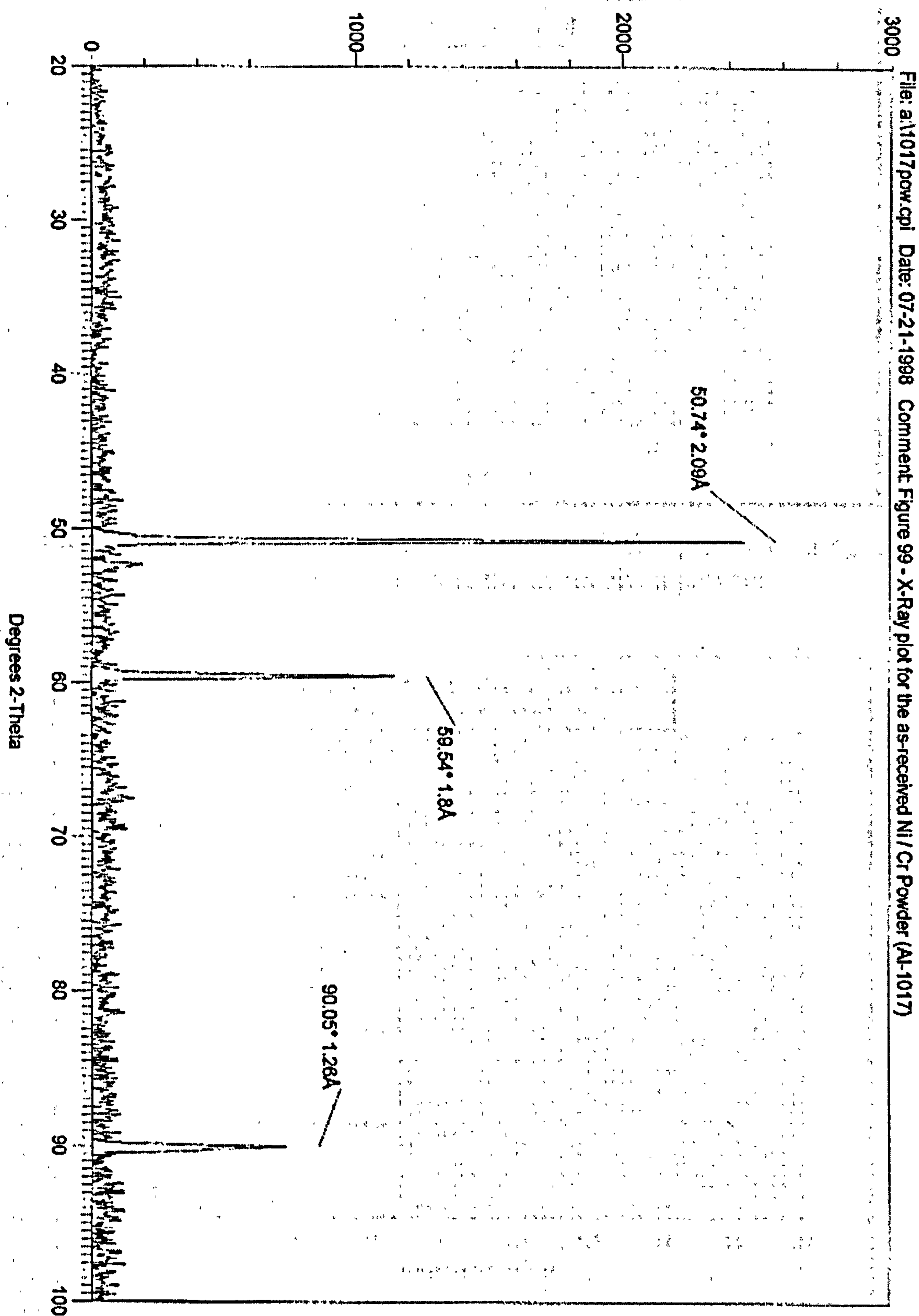


Figure 99 – X-Ray plot for the as-received powder (AI-1017)

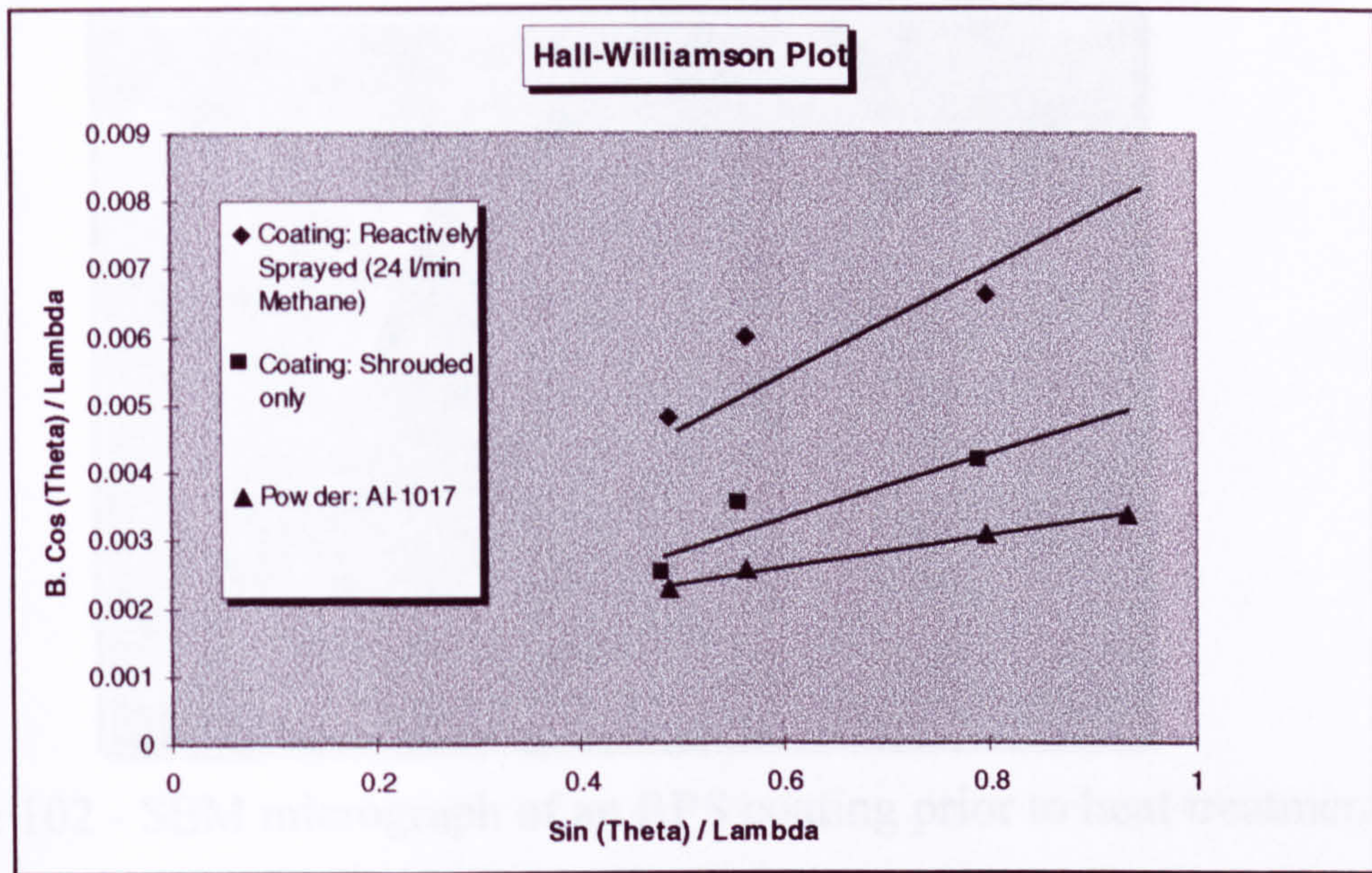


Figure 100 – Hall-Williamson plot for a reactively sprayed coating, a shrouded only coating and the as-received powder.

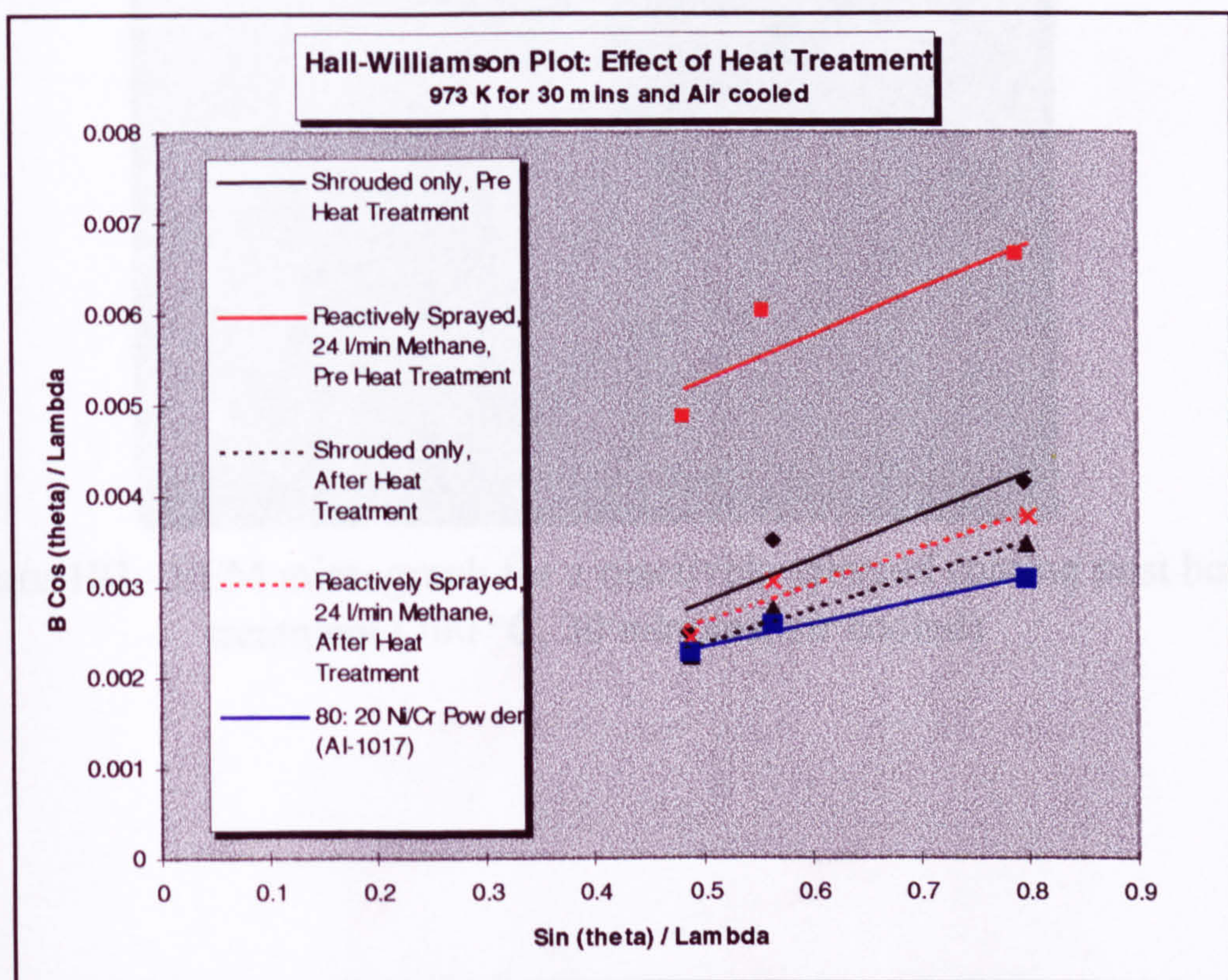


Figure 101- Hall-Williamson plot for a reactively sprayed coating, a shrouded only coating and the as-received powder, before and after heat treatment at 700 °C for 30 mins.

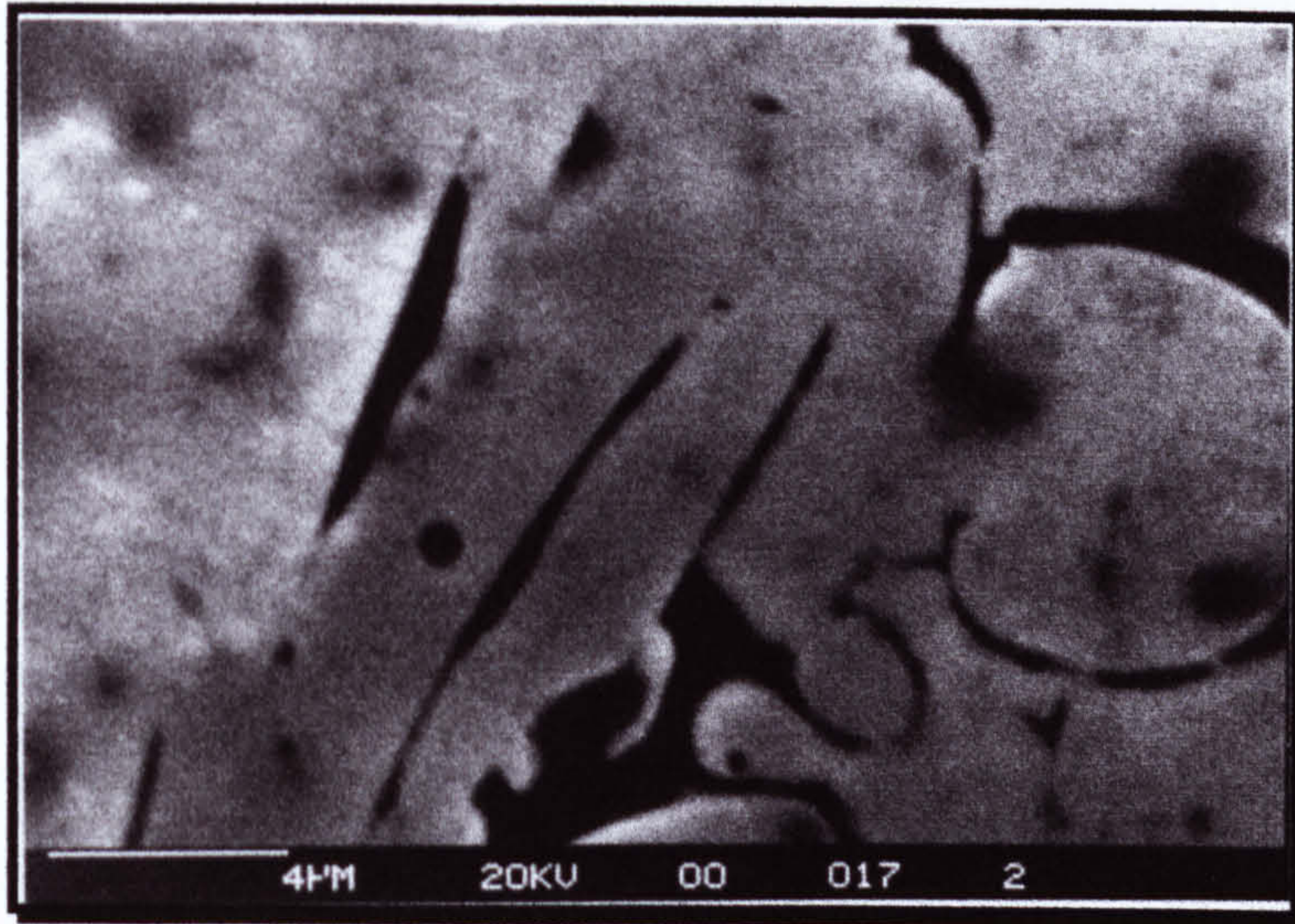


Figure 102 - SEM micrograph of an RPS coating prior to heat treatment

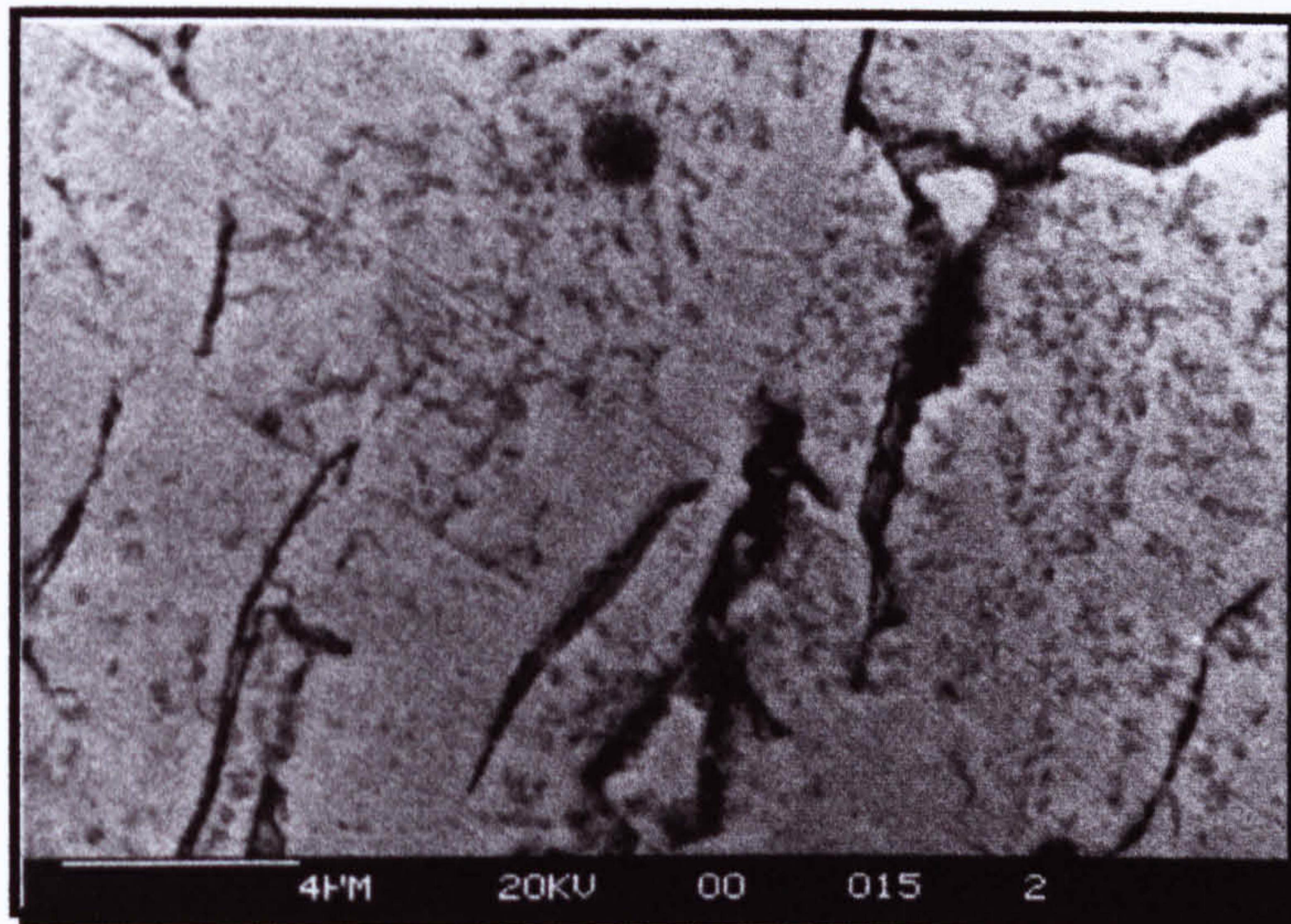


Figure 103 - SEM micrograph for a reactively sprayed coating post heat treatment (700 °C, 30 minutes, air cooled)

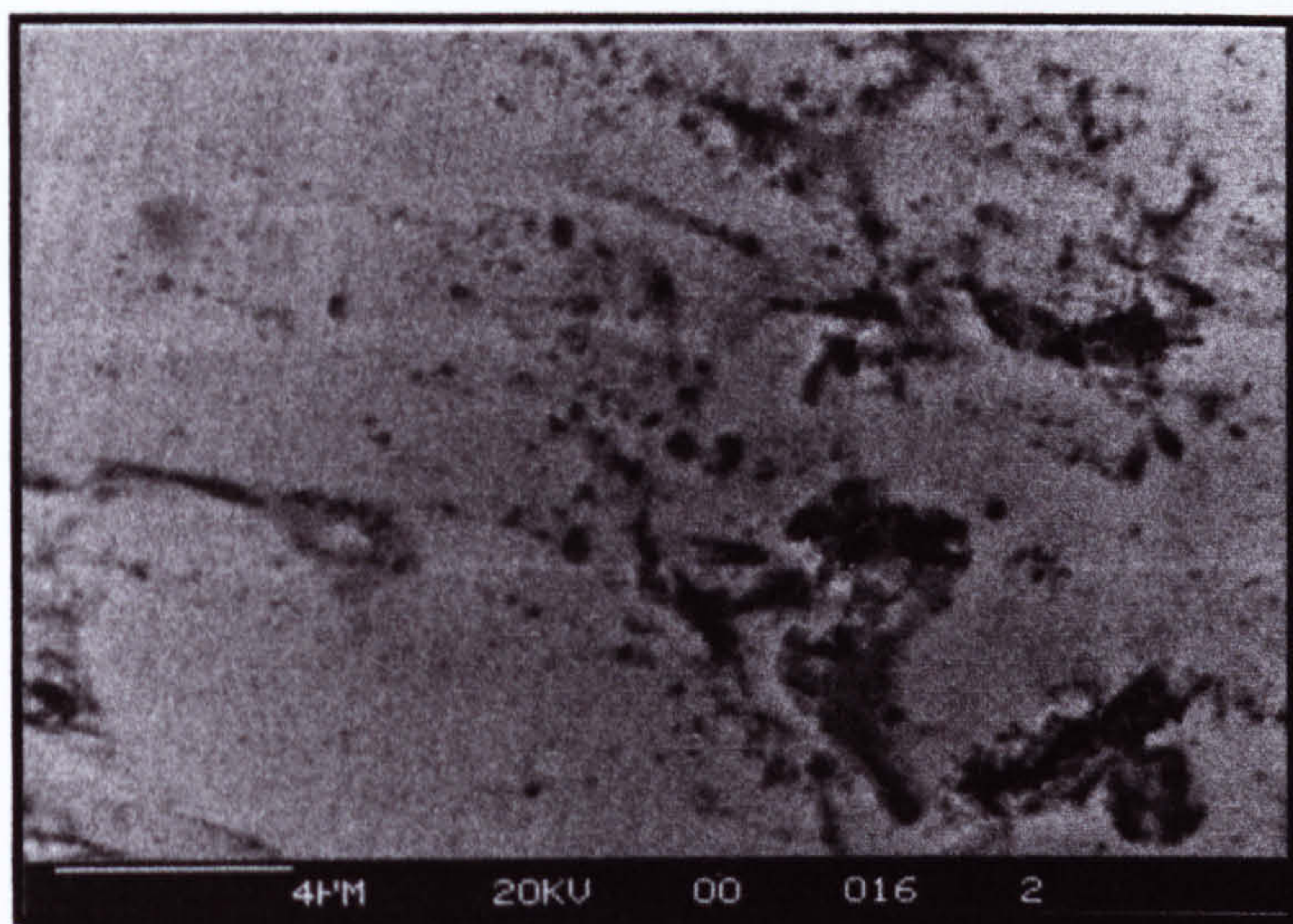


Figure 104 - SEM micrograph of a shrouded only coating post heat treatment (700 °C, 30 minutes, air cooled)

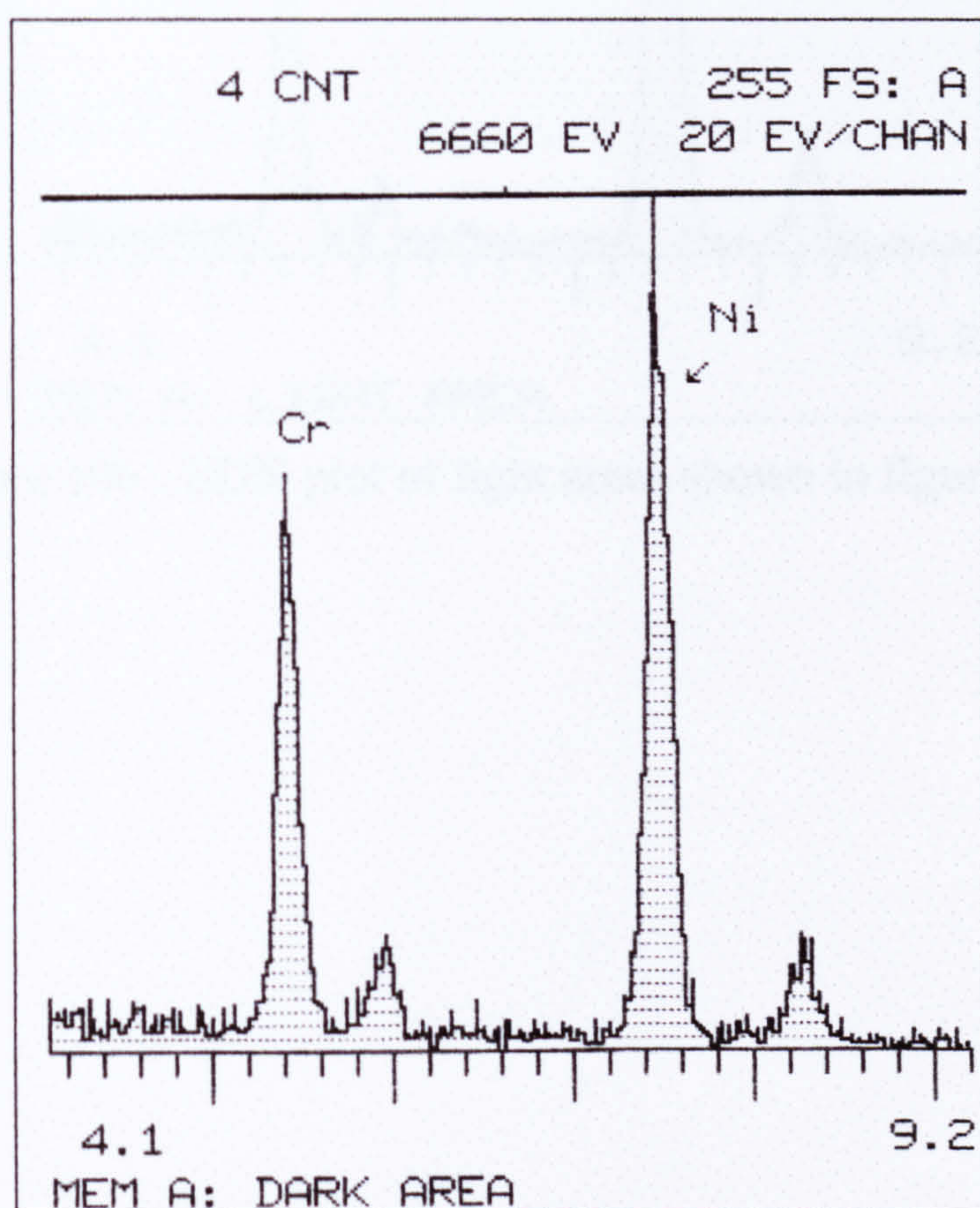


Figure 105 - EDX plot of dark precipitate shown in figure 103

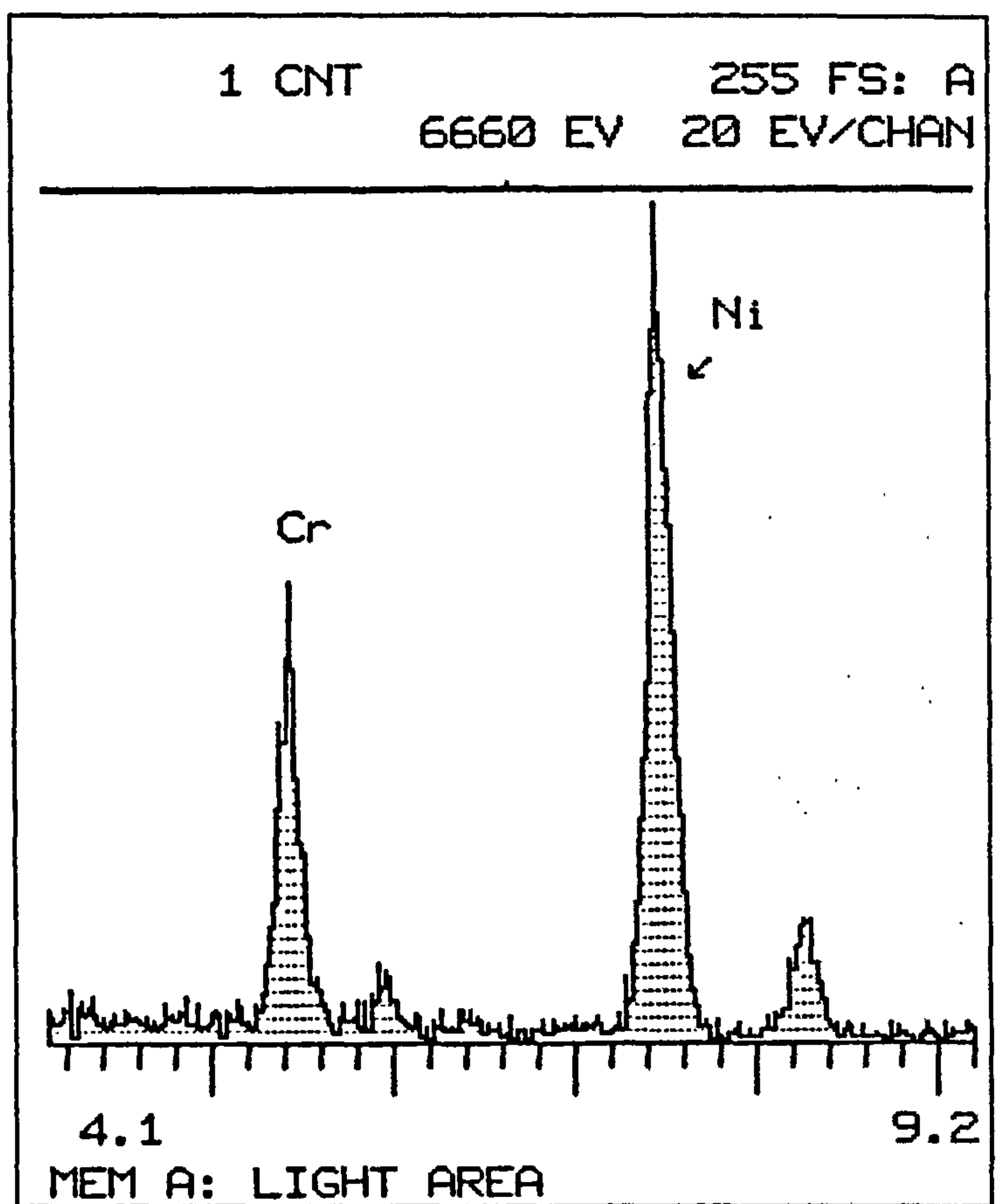


Figure 106 - EDX plot of light areas shown in figure 103

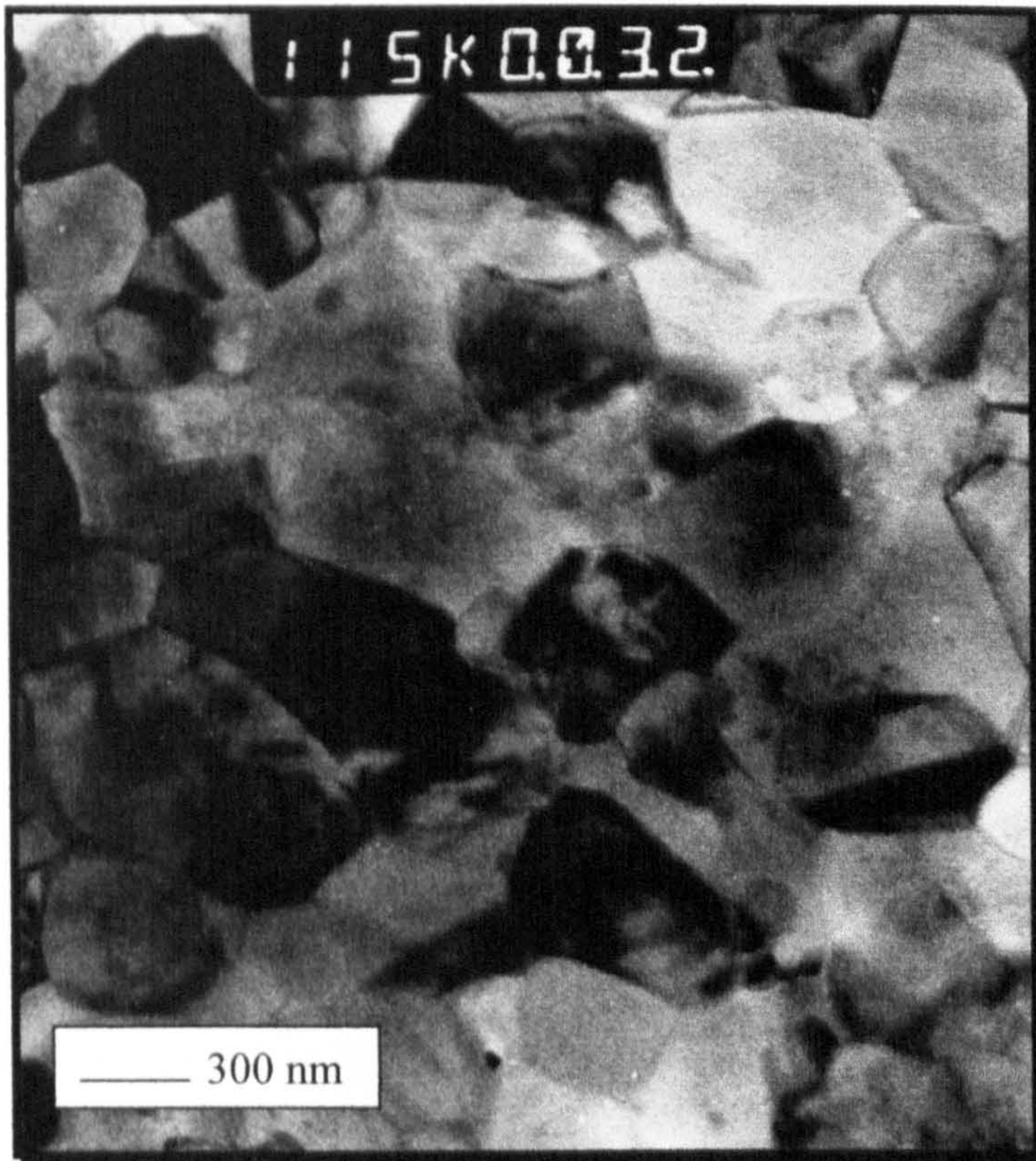


Figure 107 - T.E.M. Micrograph of the fine grain structure of a reactively sprayed sample

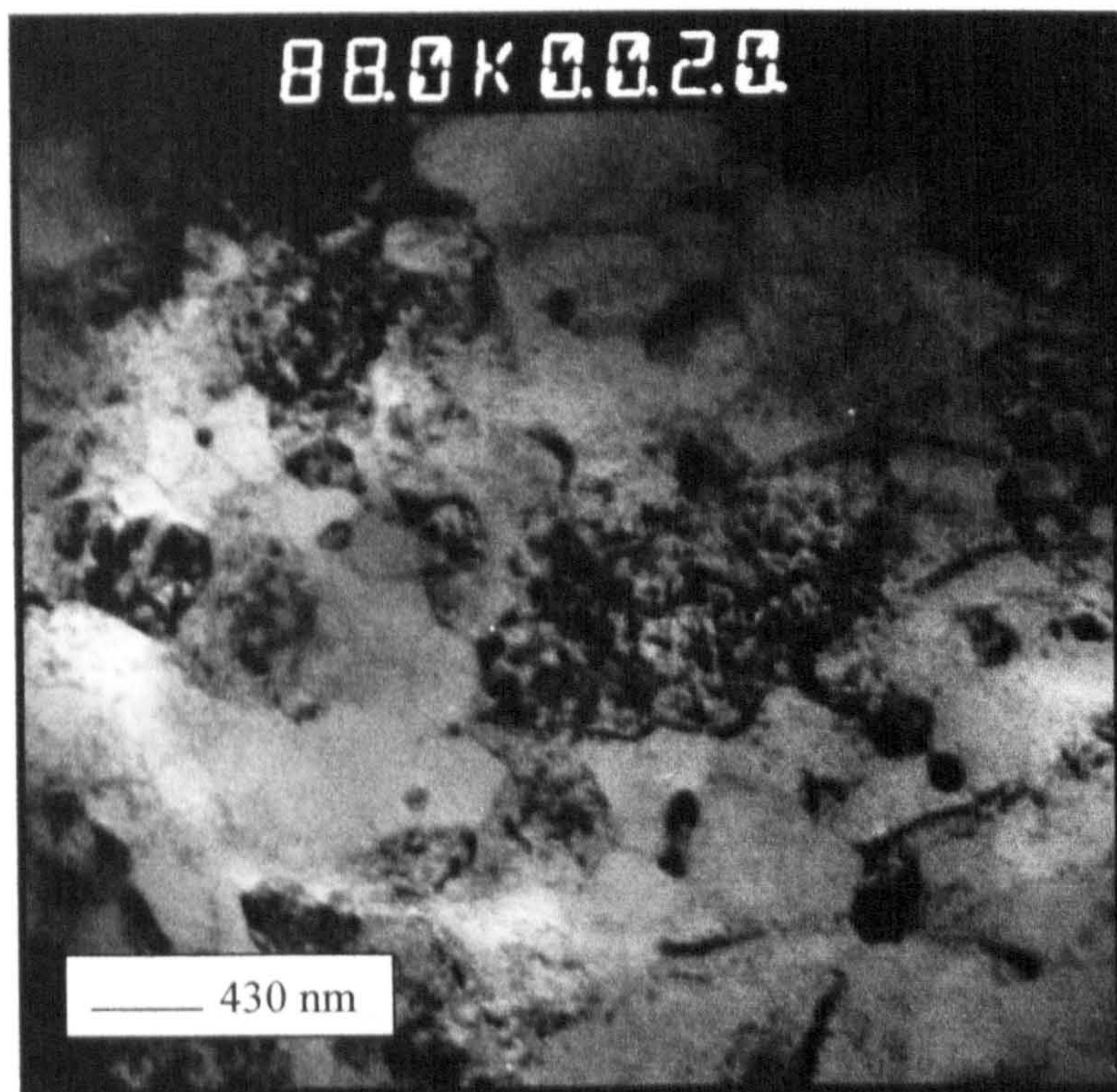


Figure 108 - T.E.M. Micrograph for a shrouded only sample

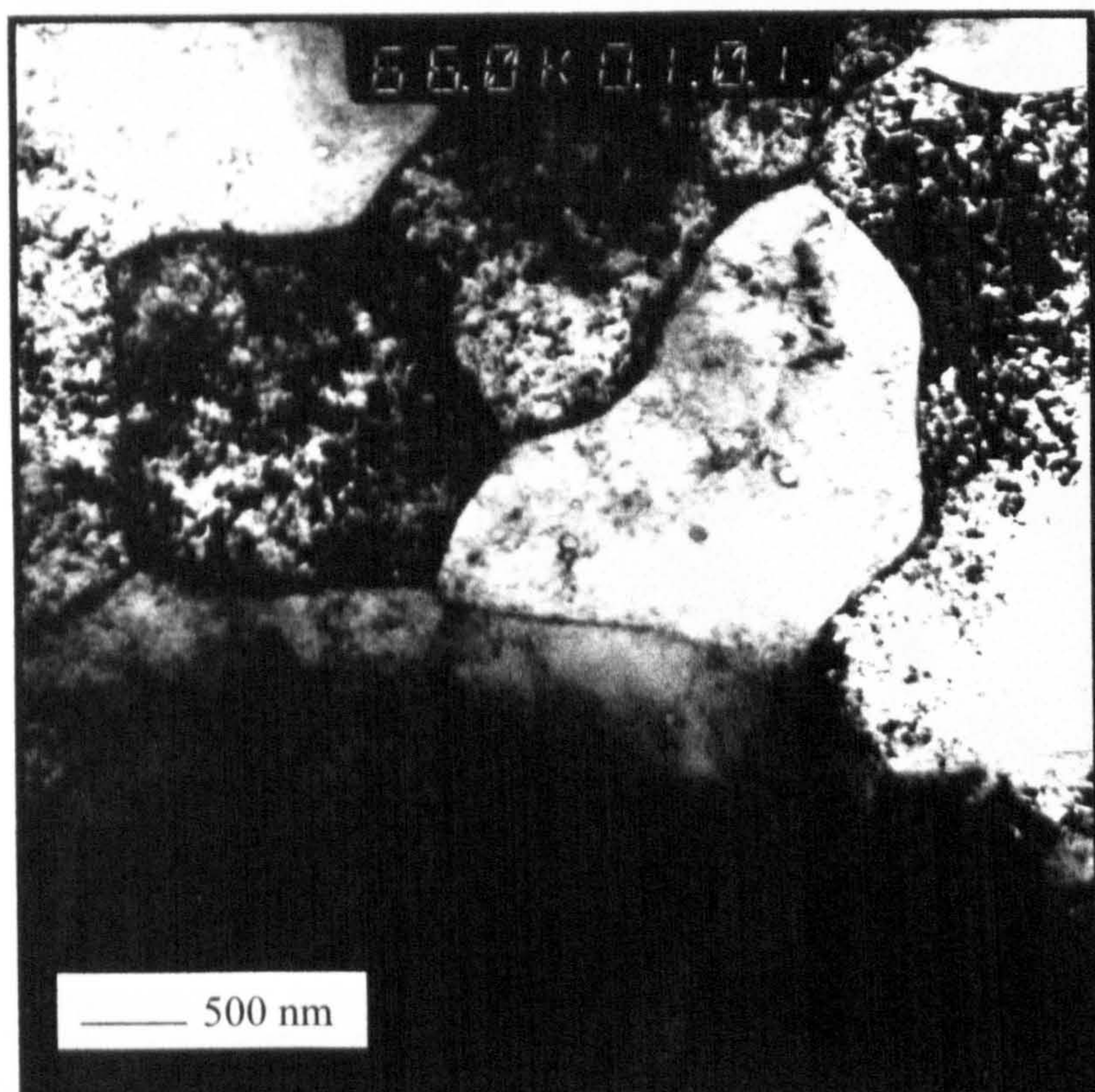


Figure 109 - T.E.M. Micrograph if reactively a sprayed sample

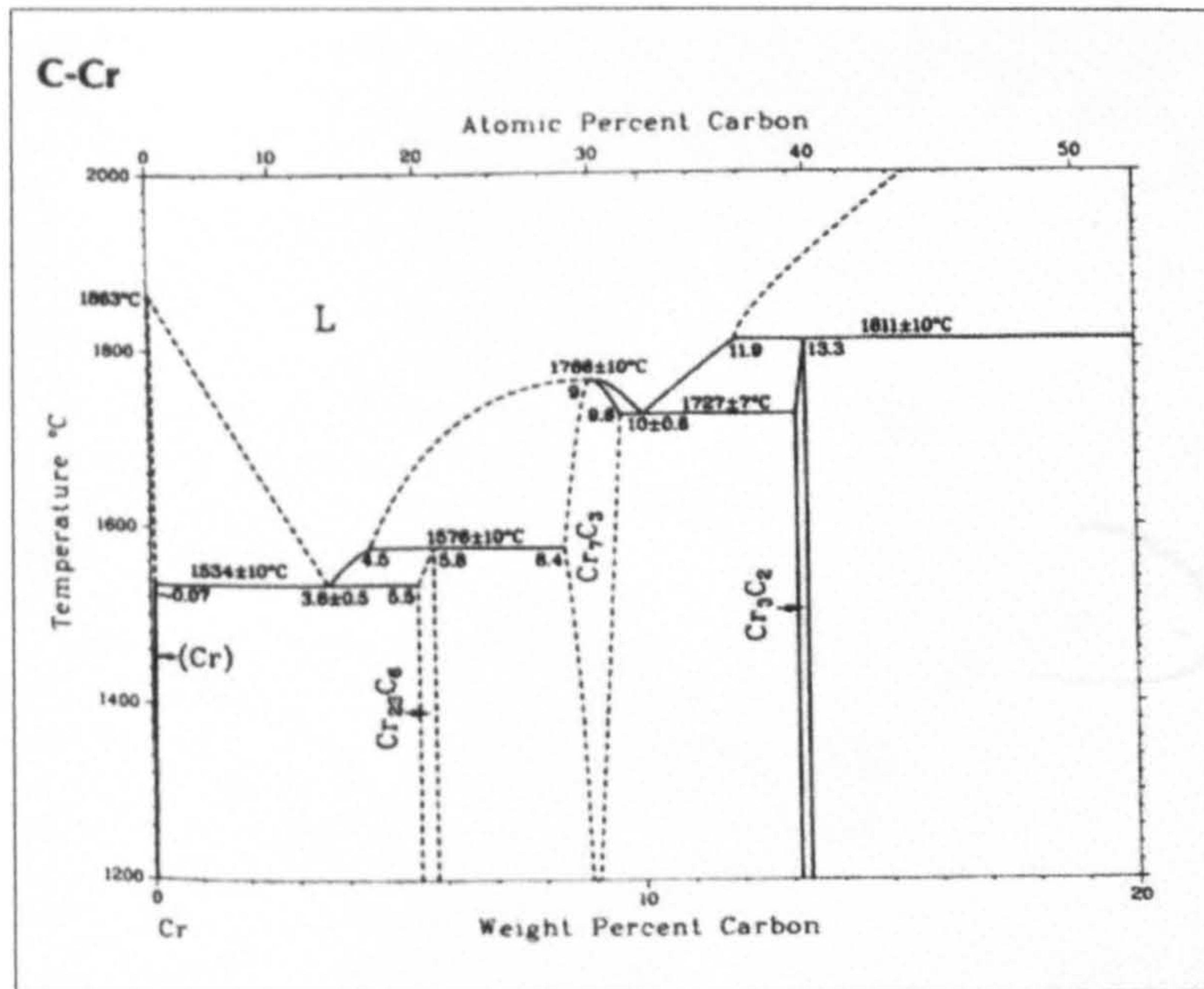


Figure 110 - Cr-C phase diagram

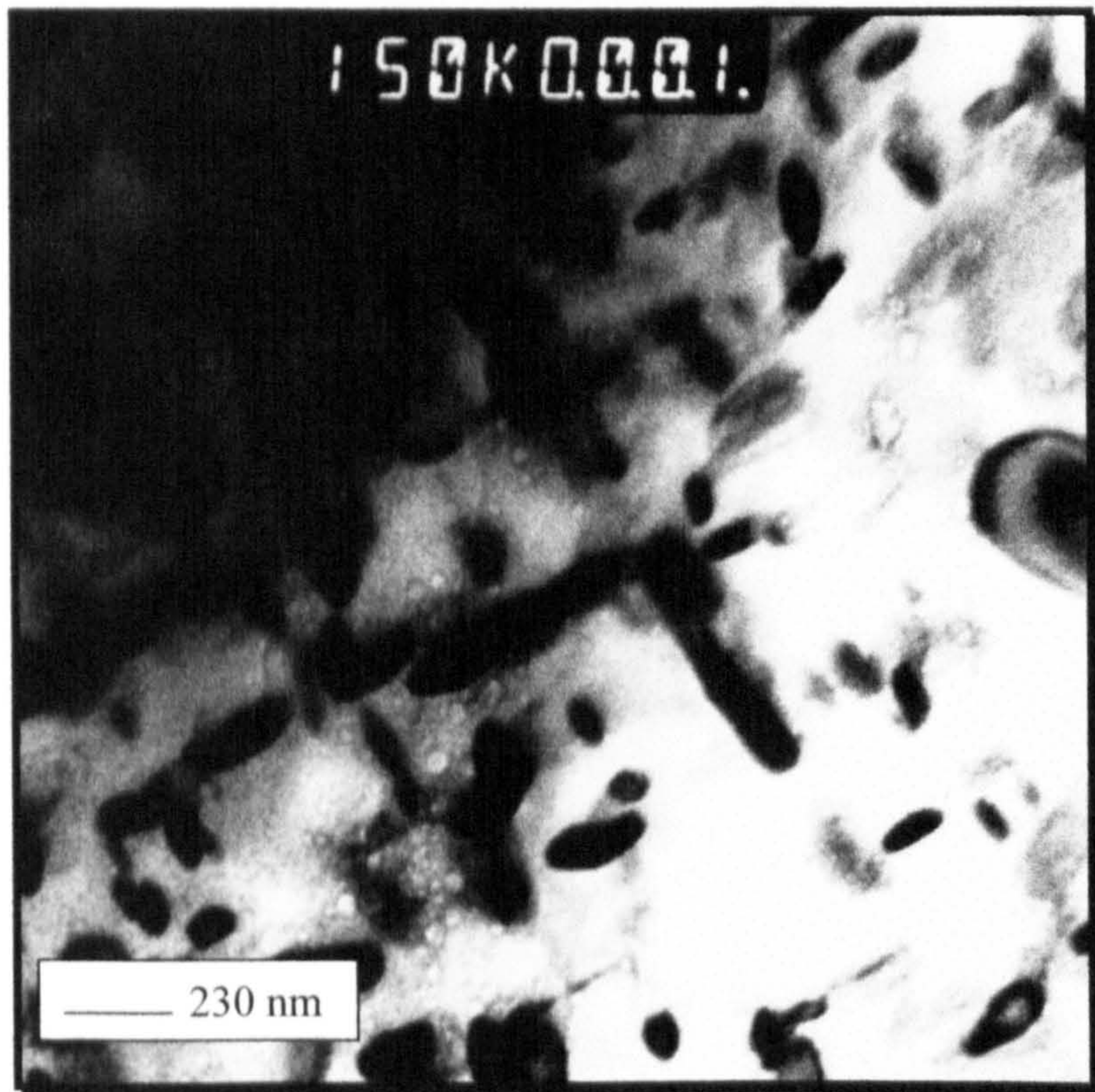


Figure 111 – T.E.M. Micrograph of precipitates showing preferred orientation

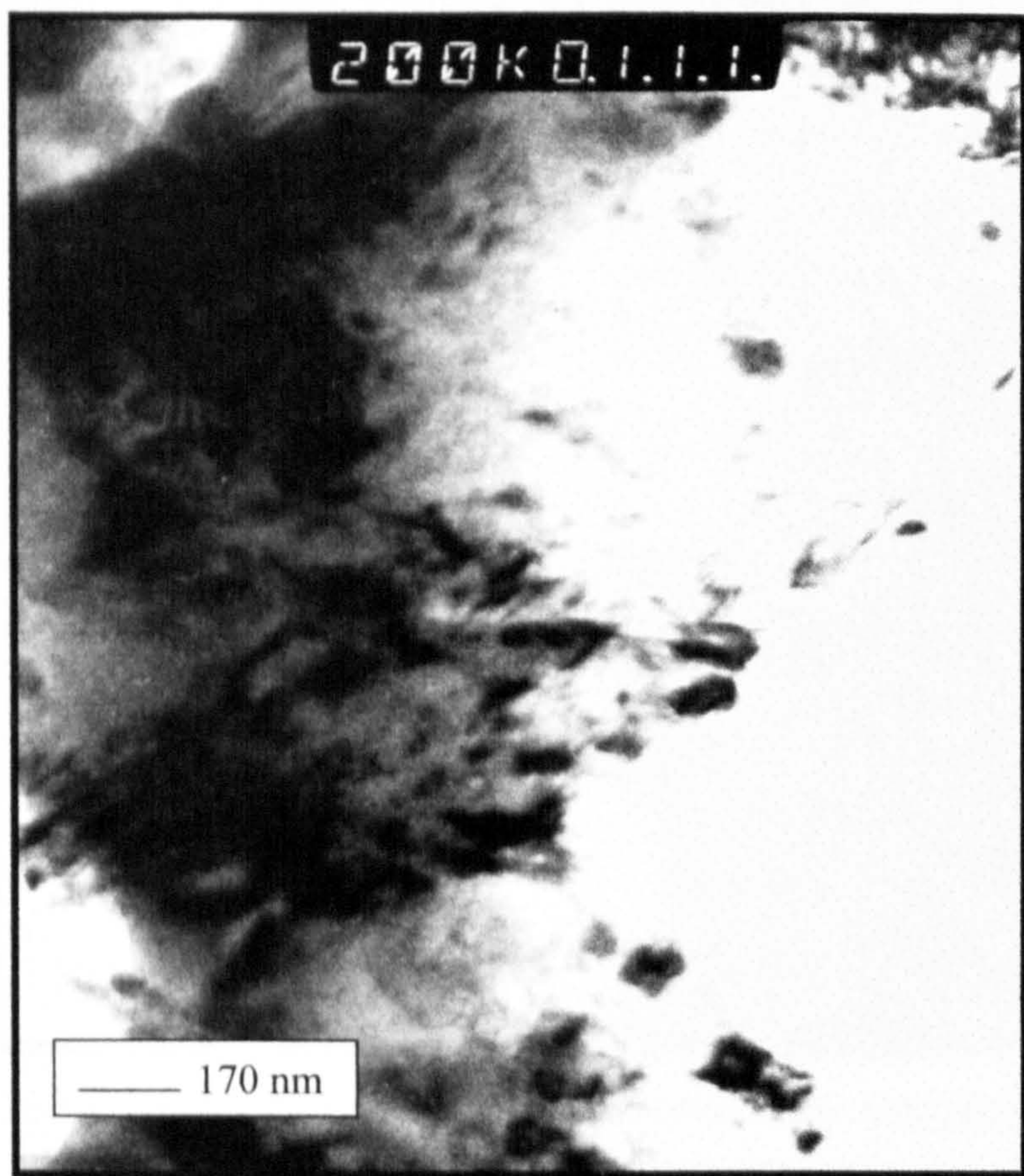


Figure 112 - T.E.M. Micrograph showing precipitates not displaying preferred orientation

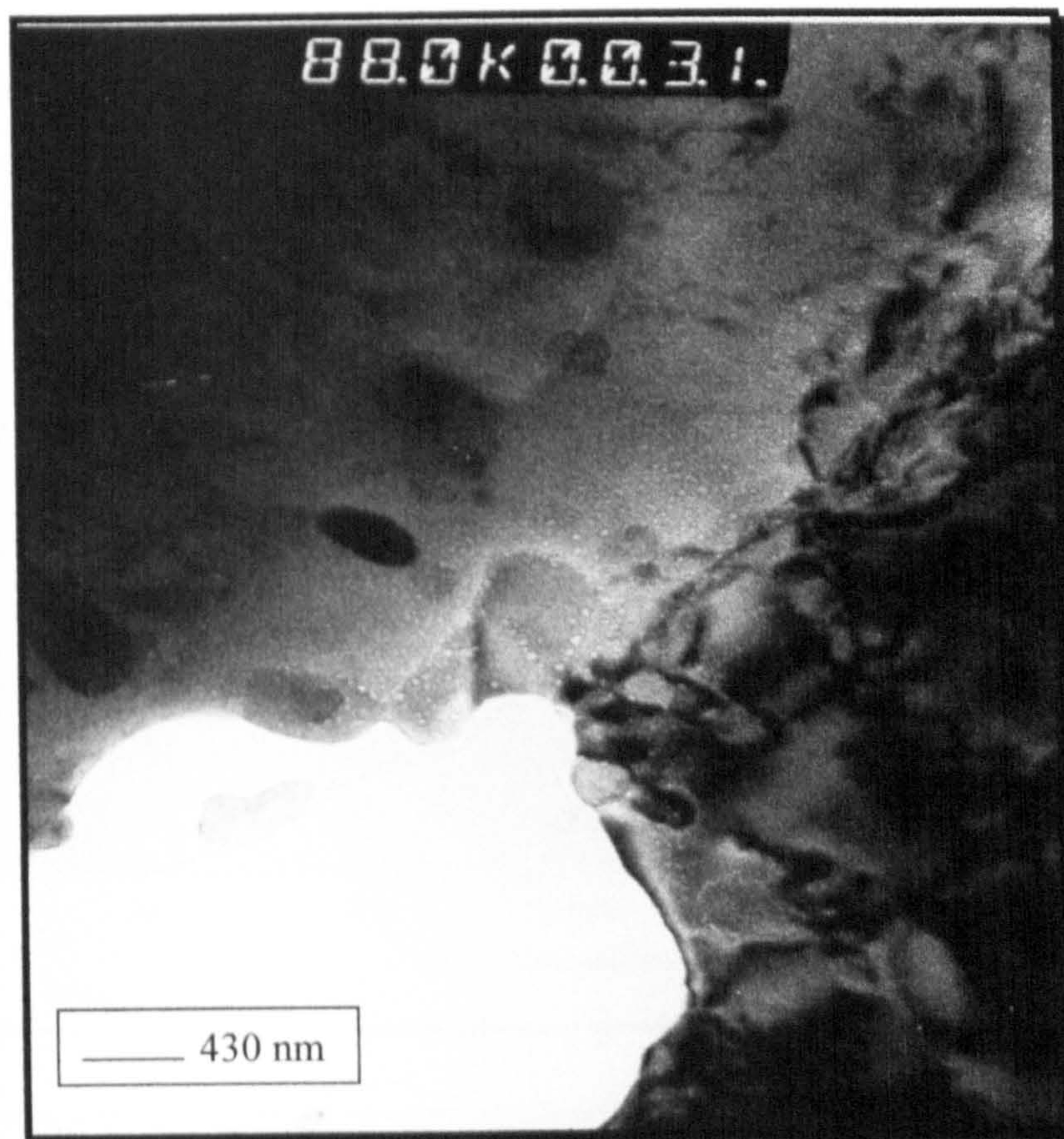
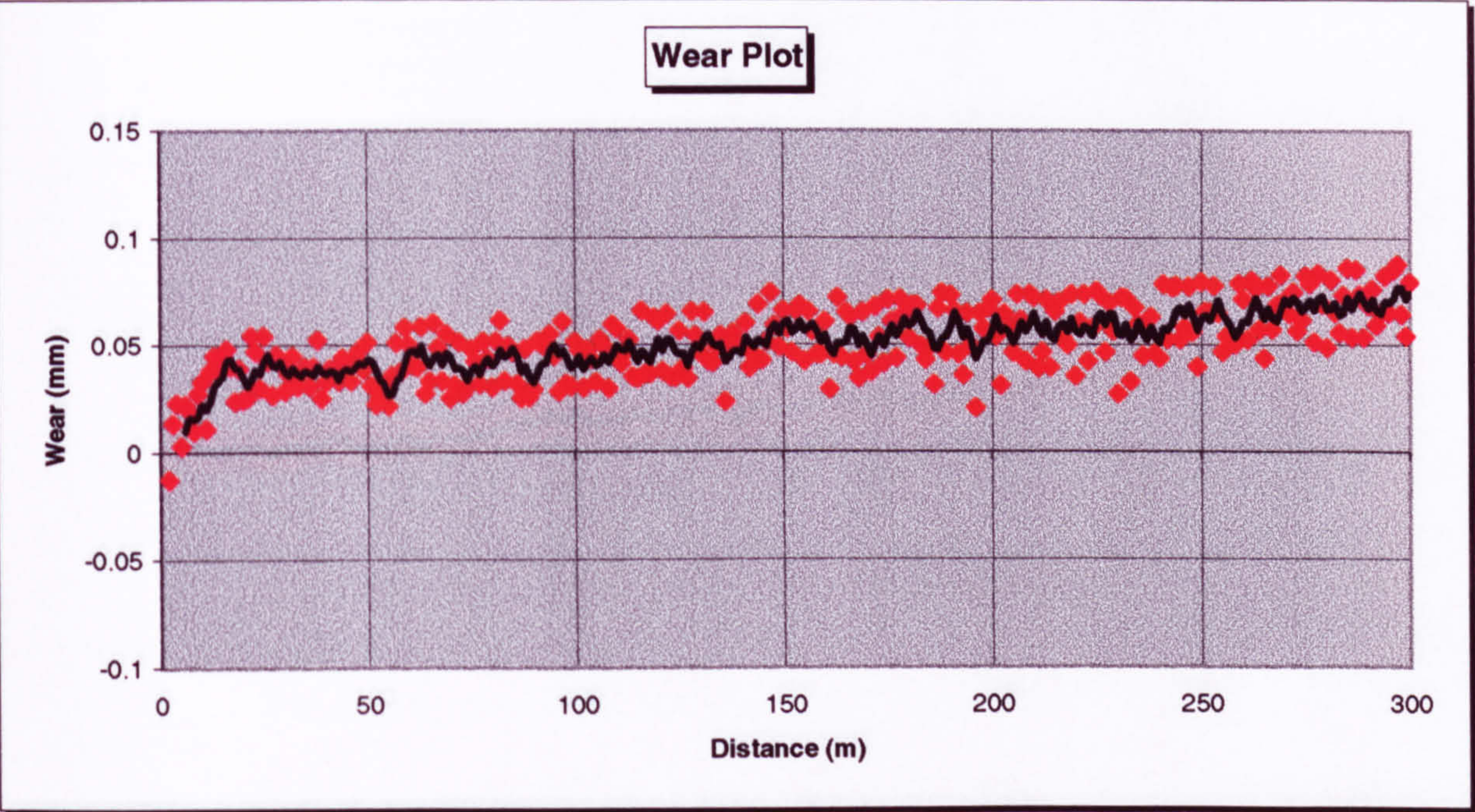
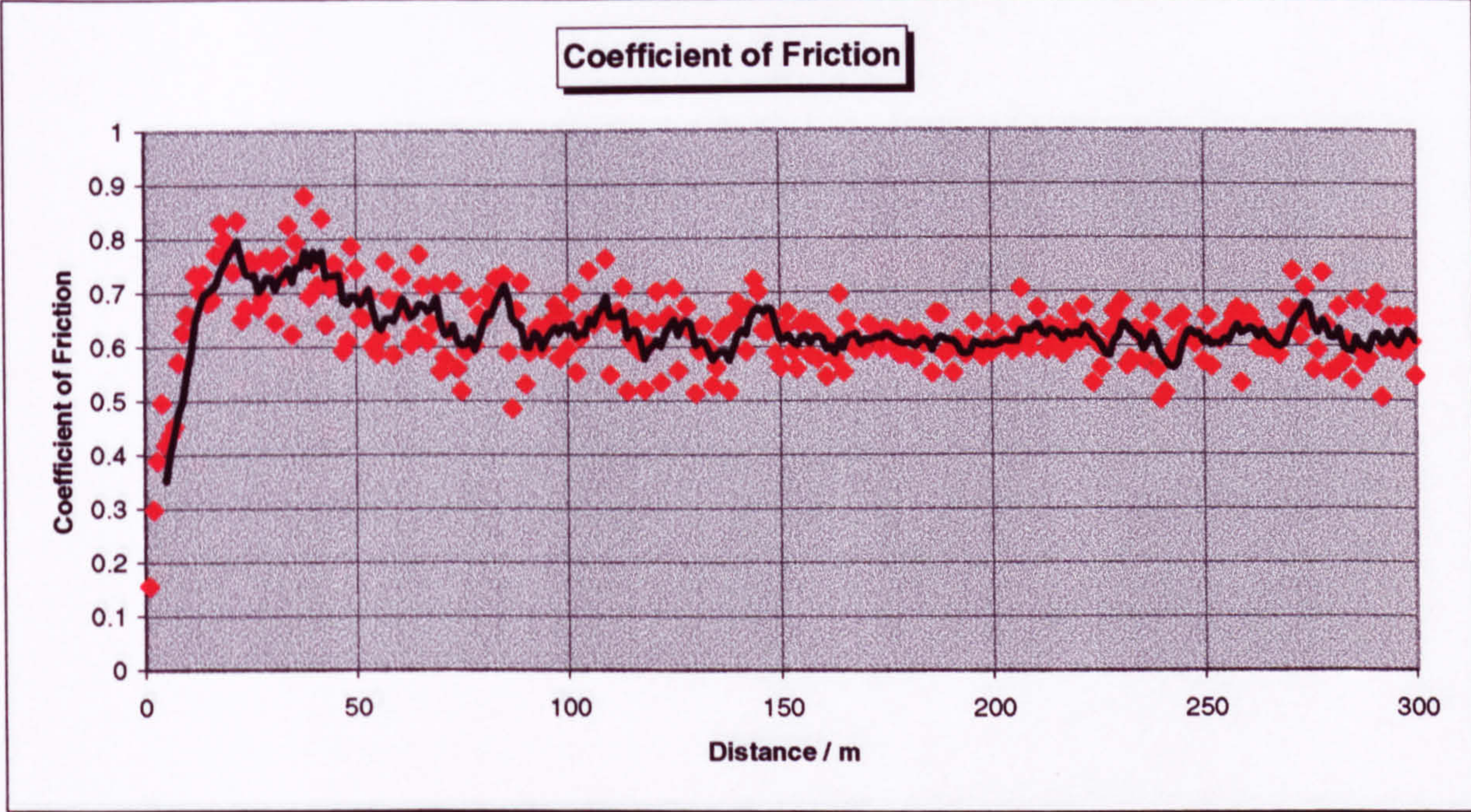


Figure 113 - T.E.M. Micrograph of shrouded only sample post heat treatment

Figure 114

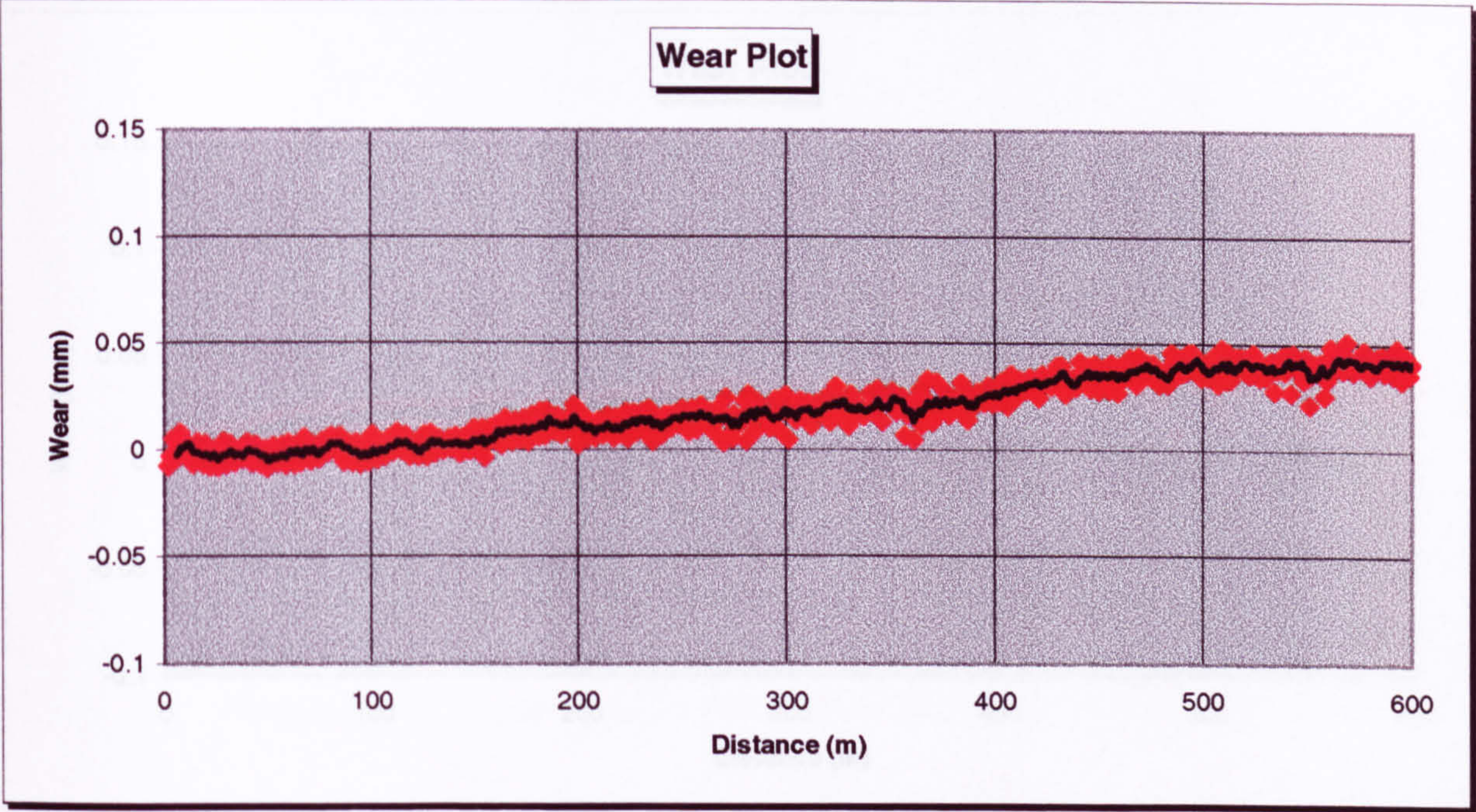
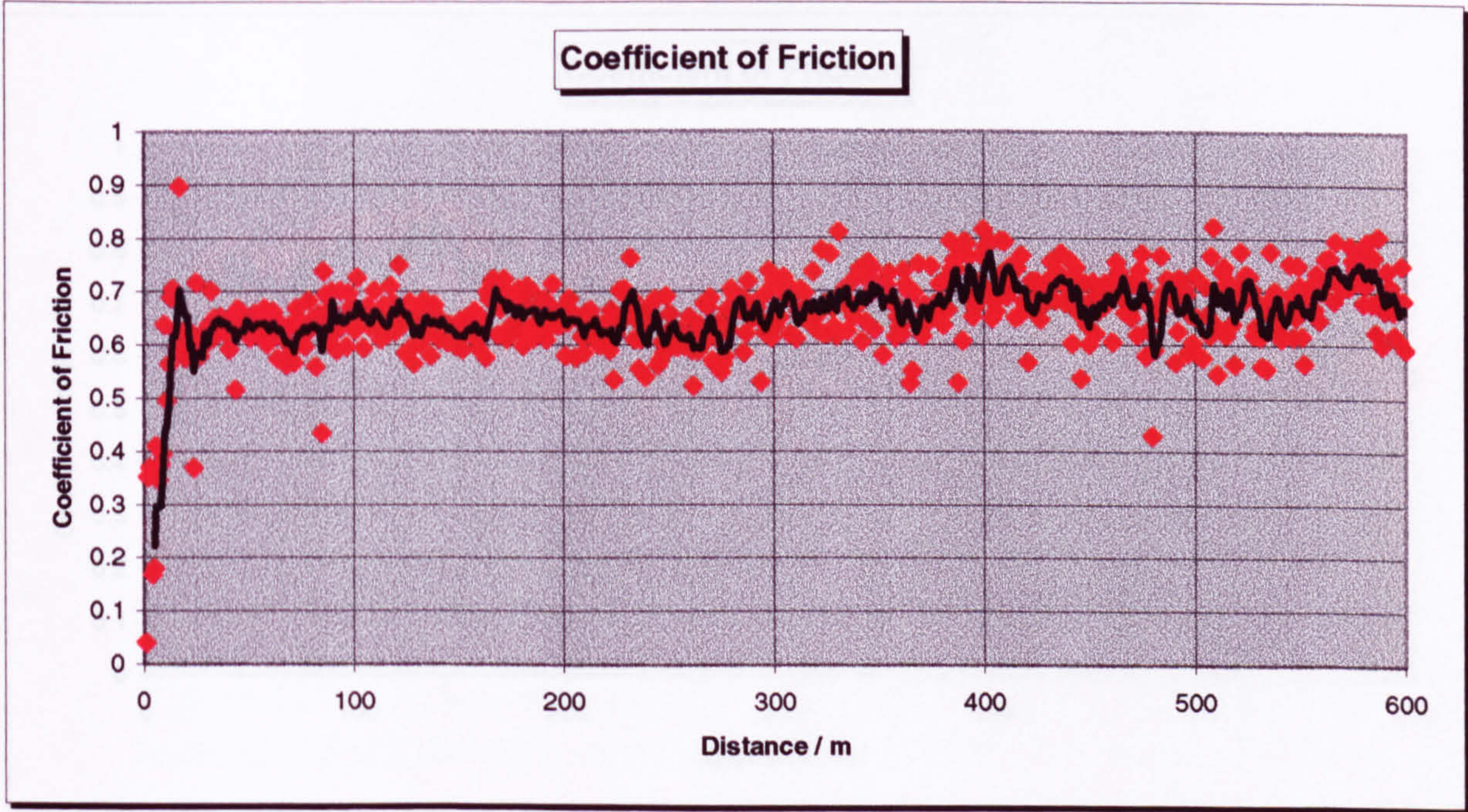
Summary Conventionally Sprayed pin / 20 N Load / 300 m / Counterface: 440C SS / No Lubricant



File	312.dat
Disk cal.	0.154-0.168
I wt. / g	4.84043
E wt. / g	4.8345
Wt loss / g	0.00593

Figure 115

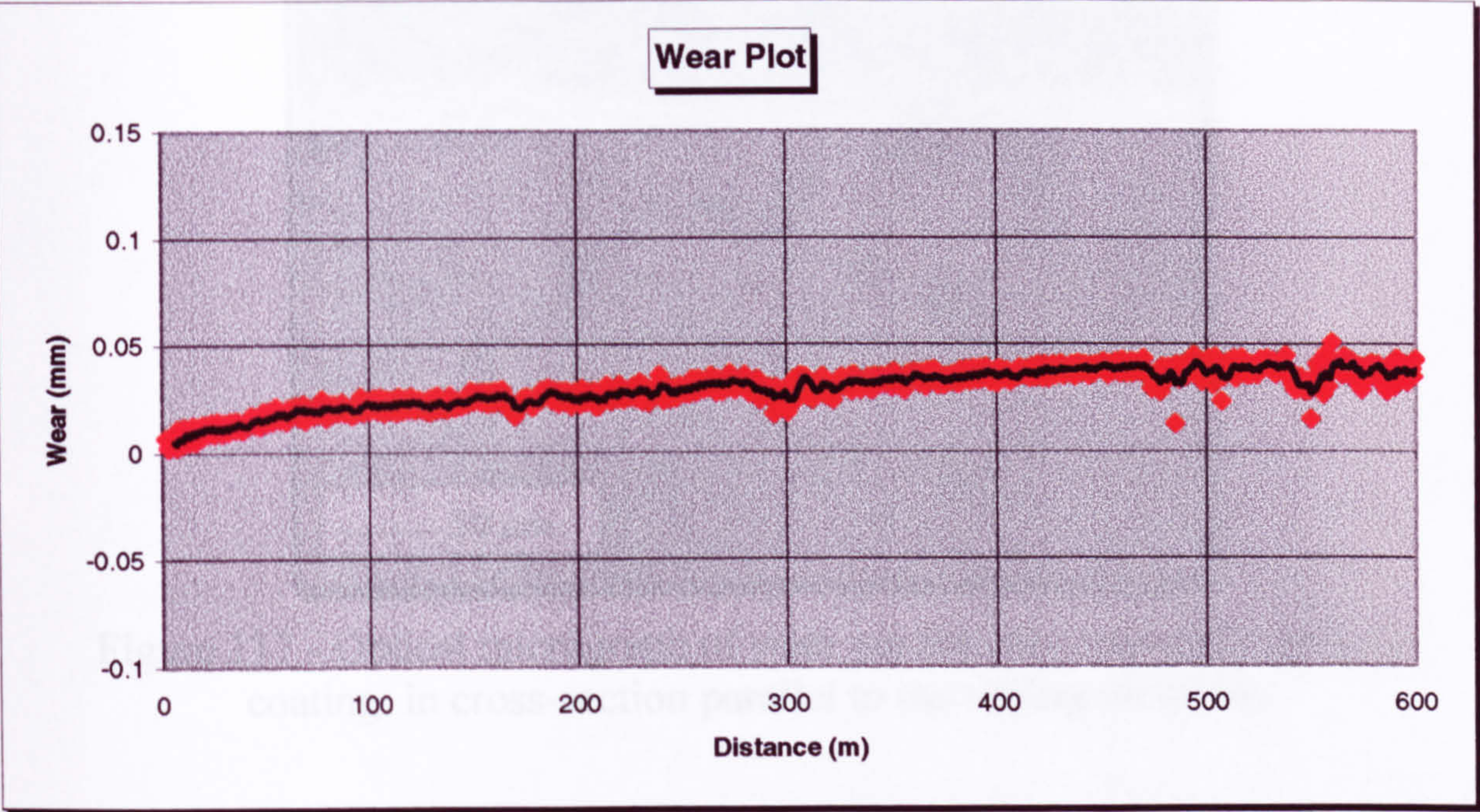
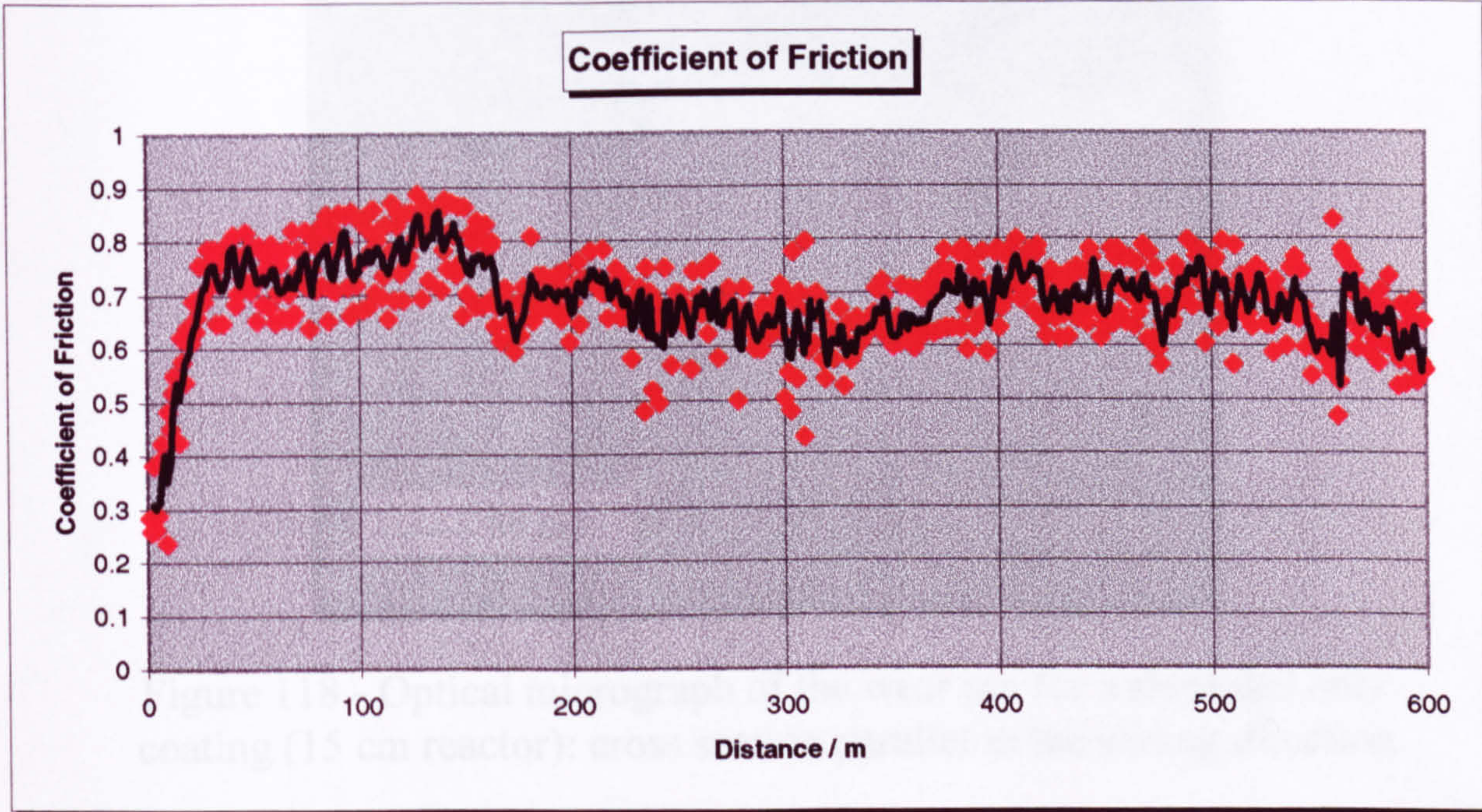
Summary Shrouded only pin / 20 N Load / 600 m / Counterface: 440C SS / No Lubricant



File	308.dat
Disk cal.	0.244-0.258
I wt. / g	4.83883
E wt. / g	4.82607
Wt loss / g	0.01276

Figure 116

Summary Reactively Sprayed pin / 20 N Load / 600 m / Counterface: 440C SS / No Lubricant



File	309.dat
Disk cal.	0.194-0.202
I wt. / g	4.87647
E wt. / g	4.87361
Wt loss / g	0.00286

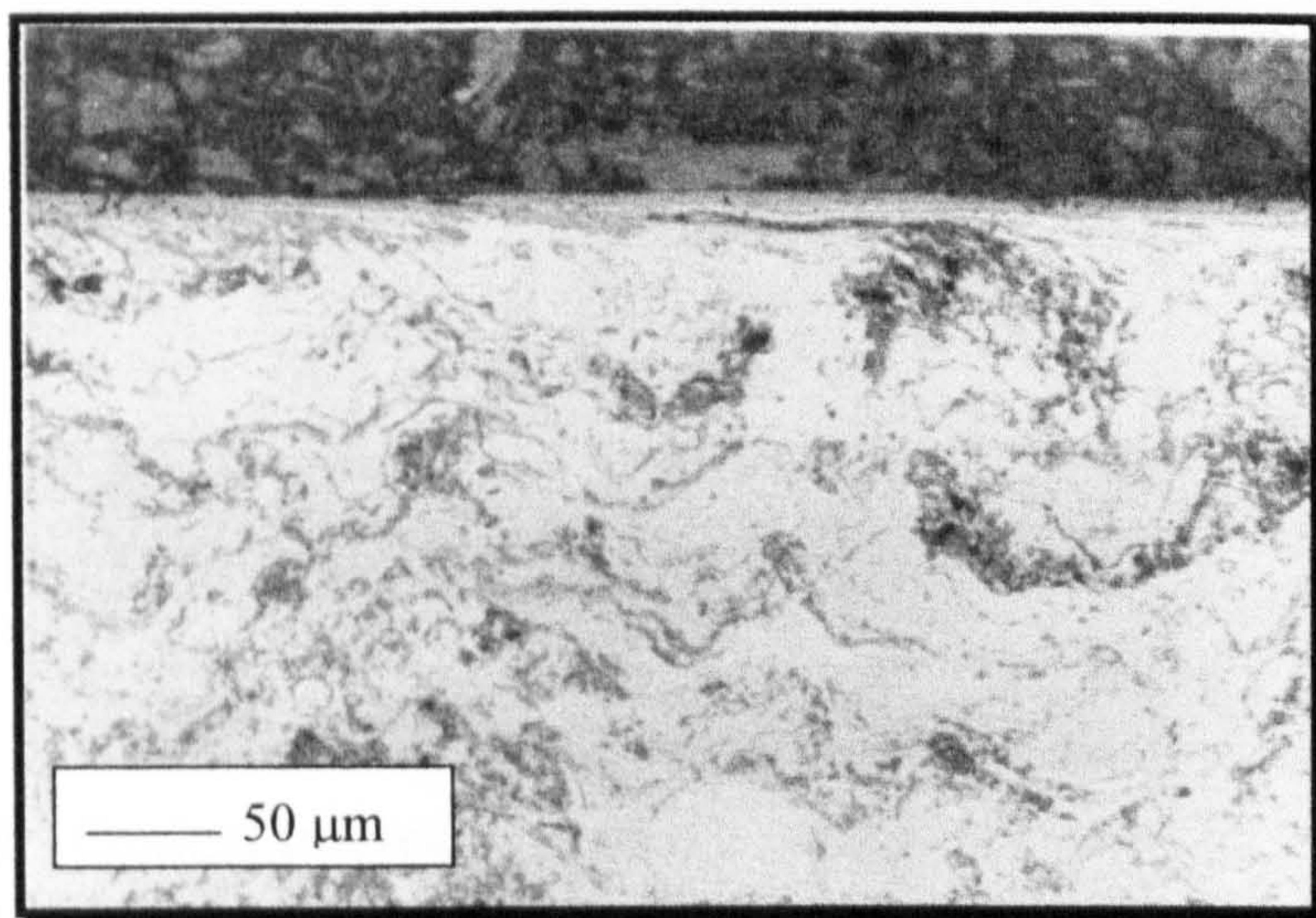


Figure 117 - Optical micrograph of wear pin for conventionally sprayed coating: in cross-section parallel to the sliding direction

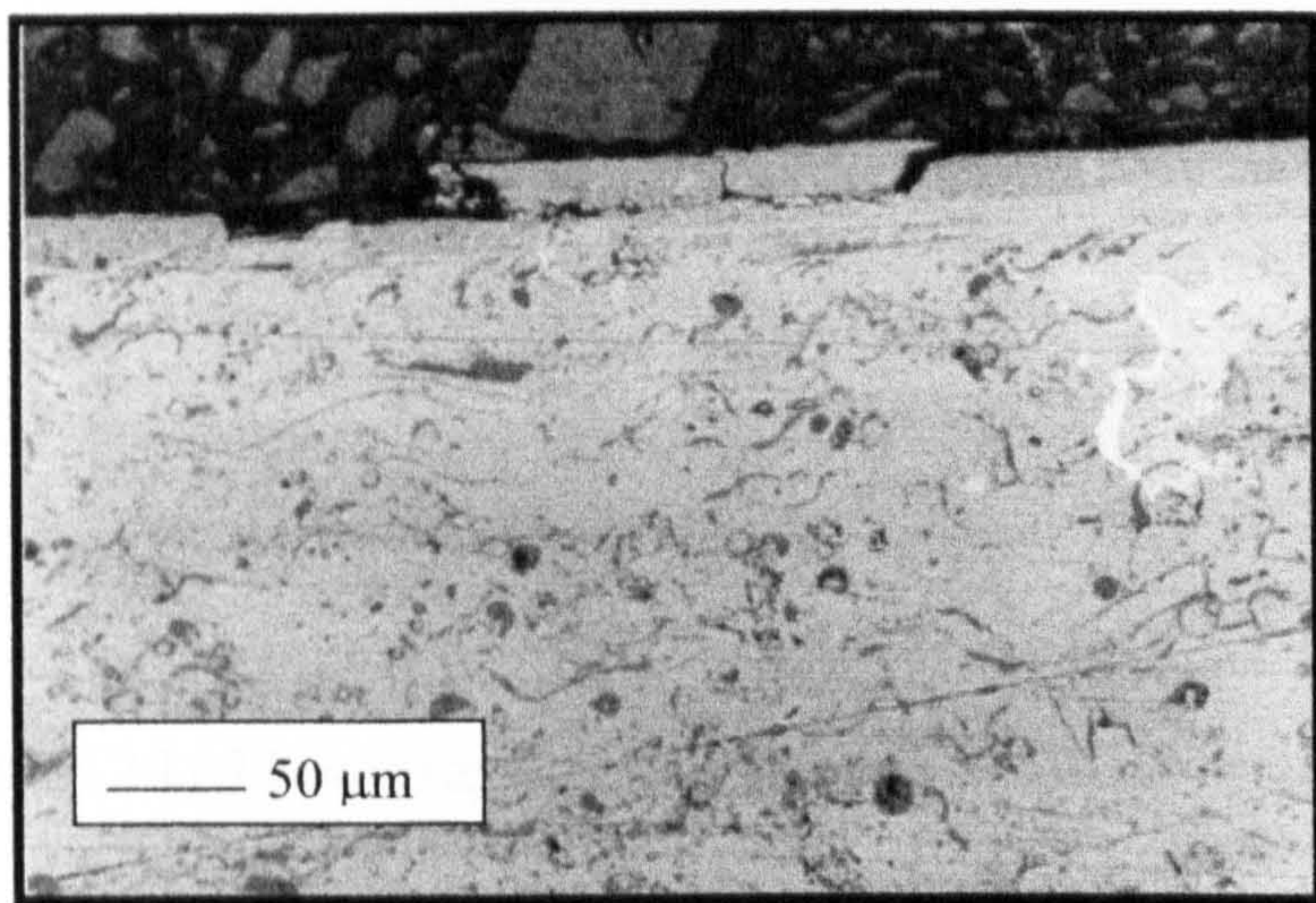


Figure 118 - Optical micrograph of the wear pin for a shrouded only coating (15 cm reactor): cross section parallel to the sliding direction

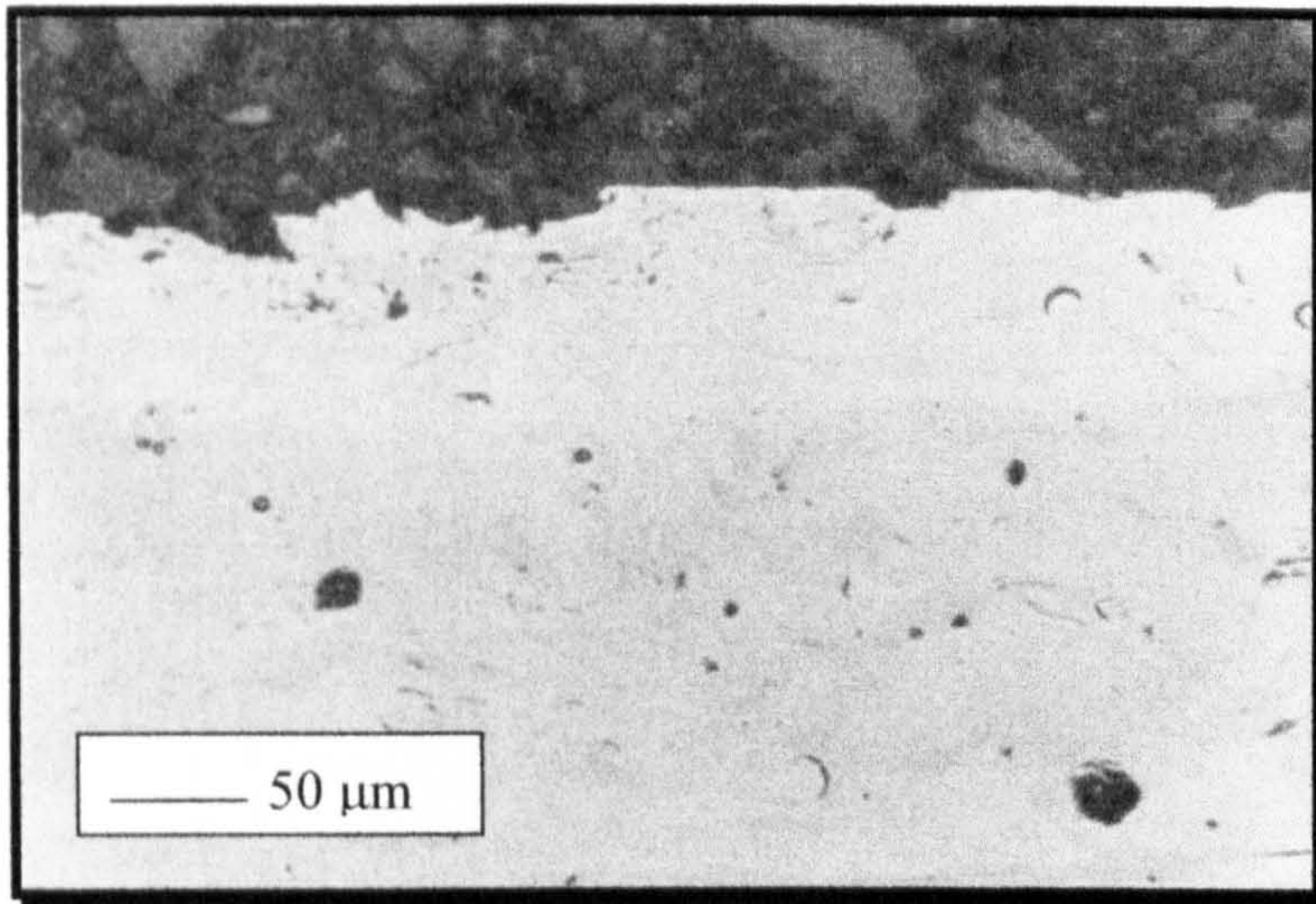


Figure 119 - Optical micrograph of the wear pin for a reactively sprayed coating (15 cm reactor): cross section parallel to the sliding direction

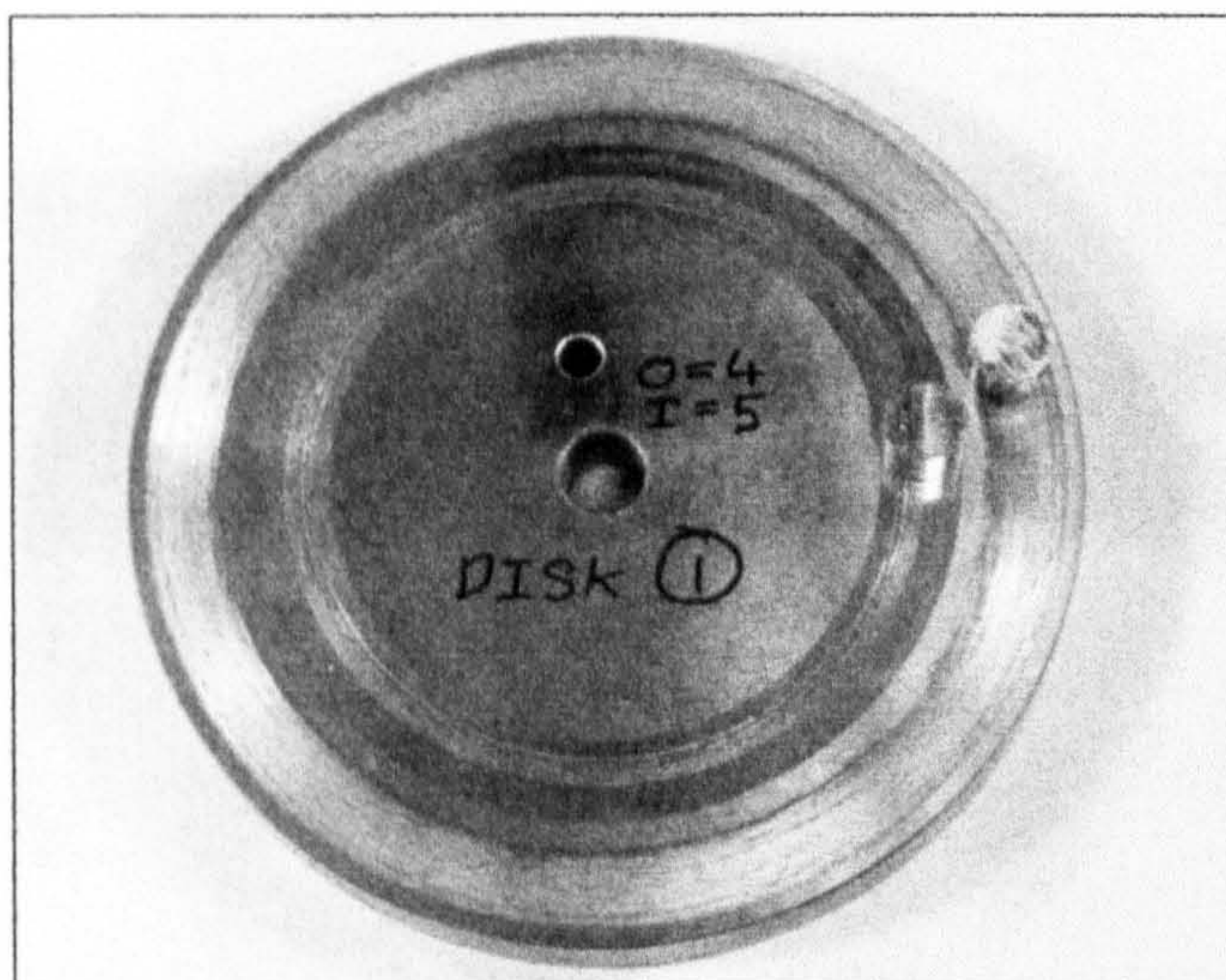


Figure 120 - Photograph of wear disc and pins after testing.

Inner track – Reactively sprayed coating
Outer track – Shrouded only coating

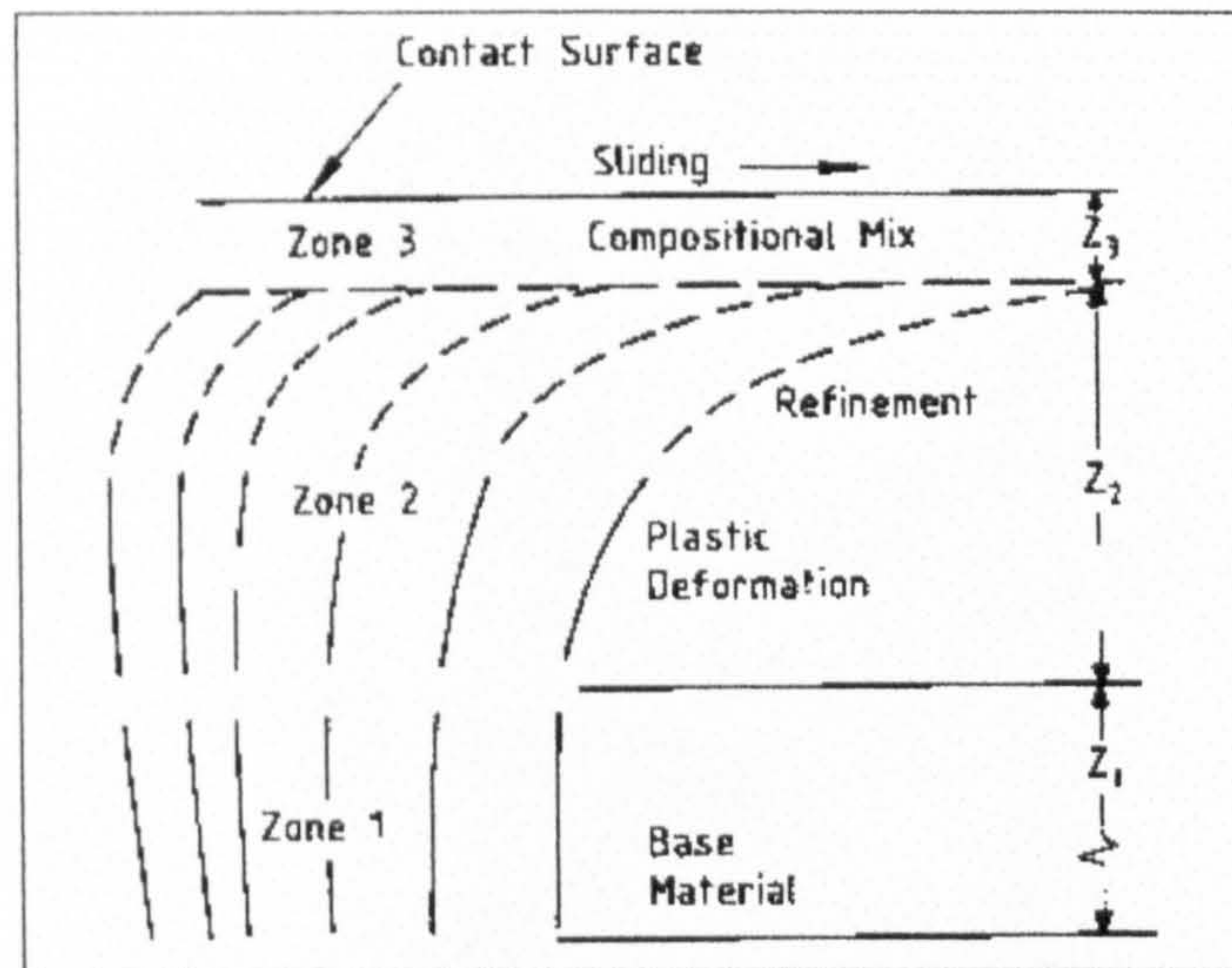


Figure 121 - Schematic diagram of sub-surface zones beneath a worn surface^[64]

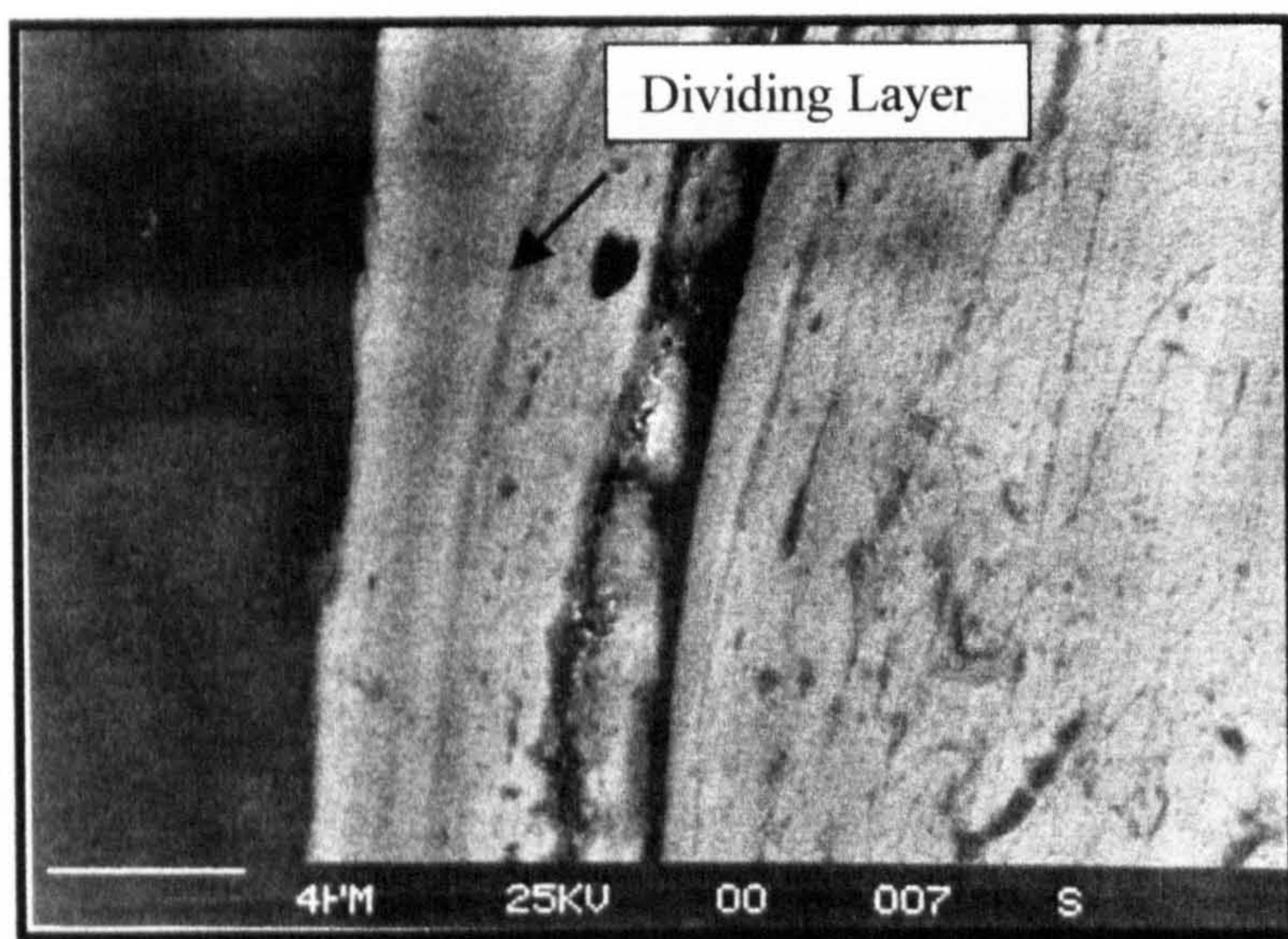


Figure 122 – S.E.M. examination of the conventionally sprayed wear pin in cross section

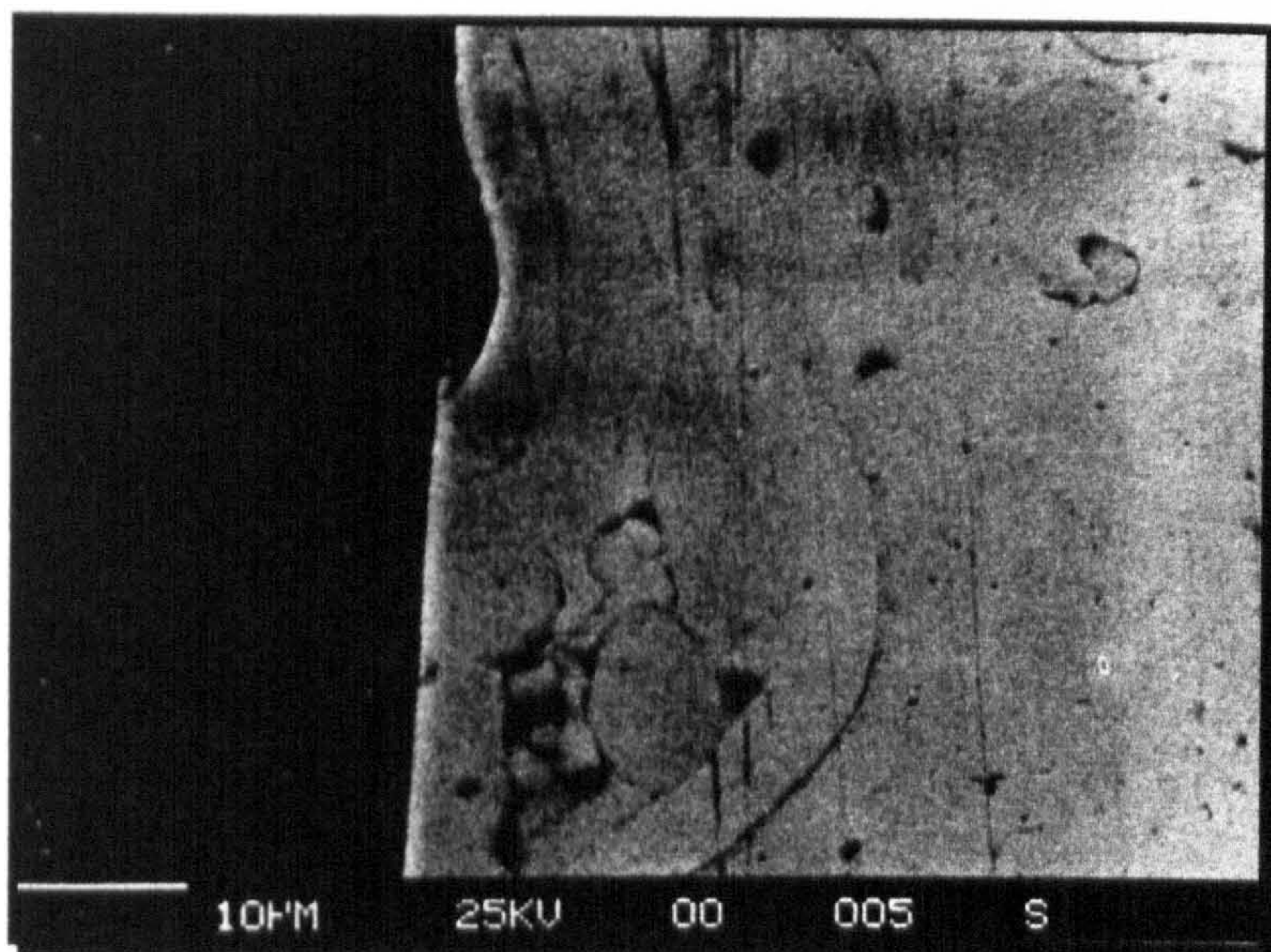


Figure 123 - S.E.M. micrograph shows a section of pulled out coating containing some debris

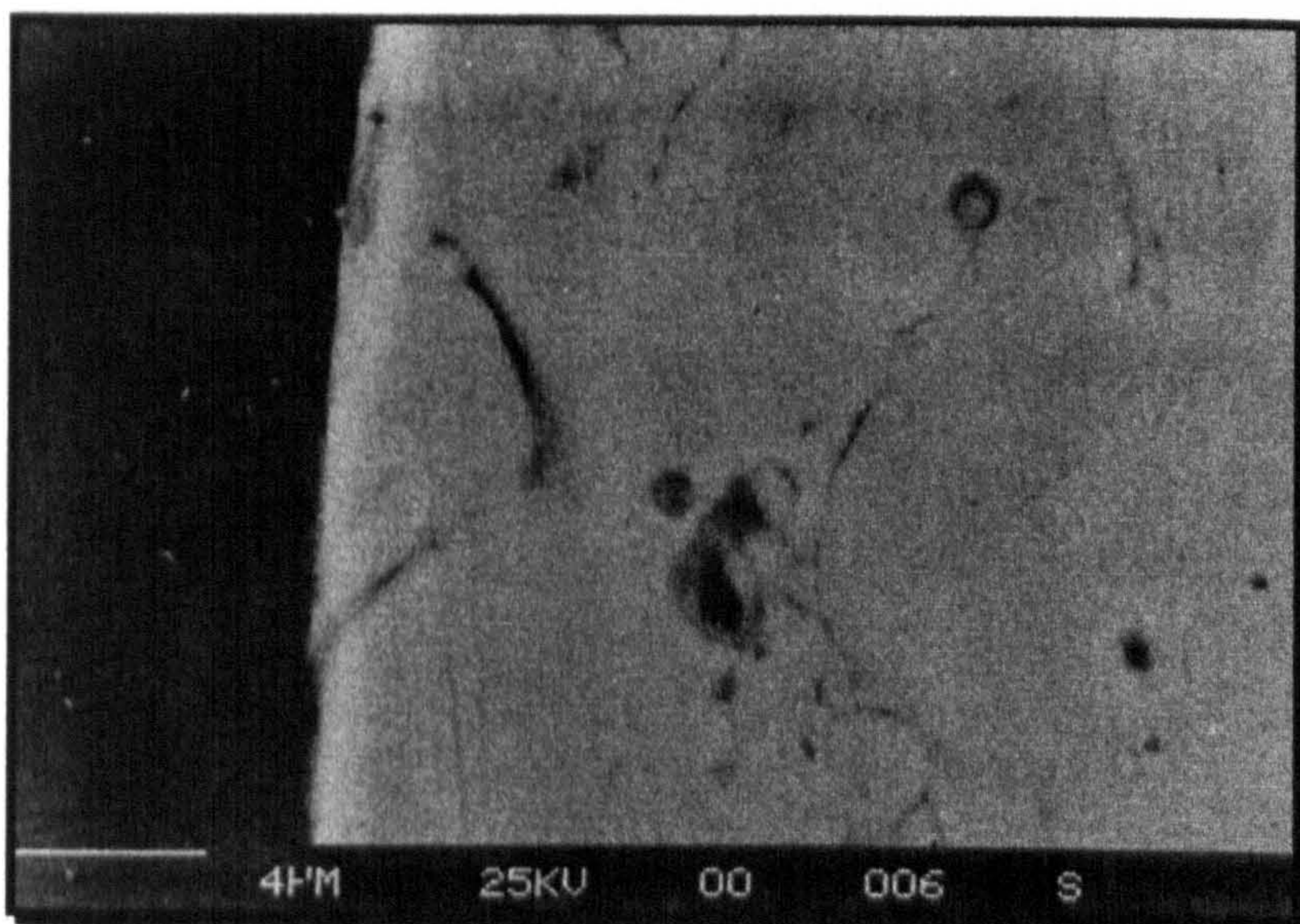


Figure 124 - S.E.M. micrograph showing a splat in the process of delaminating

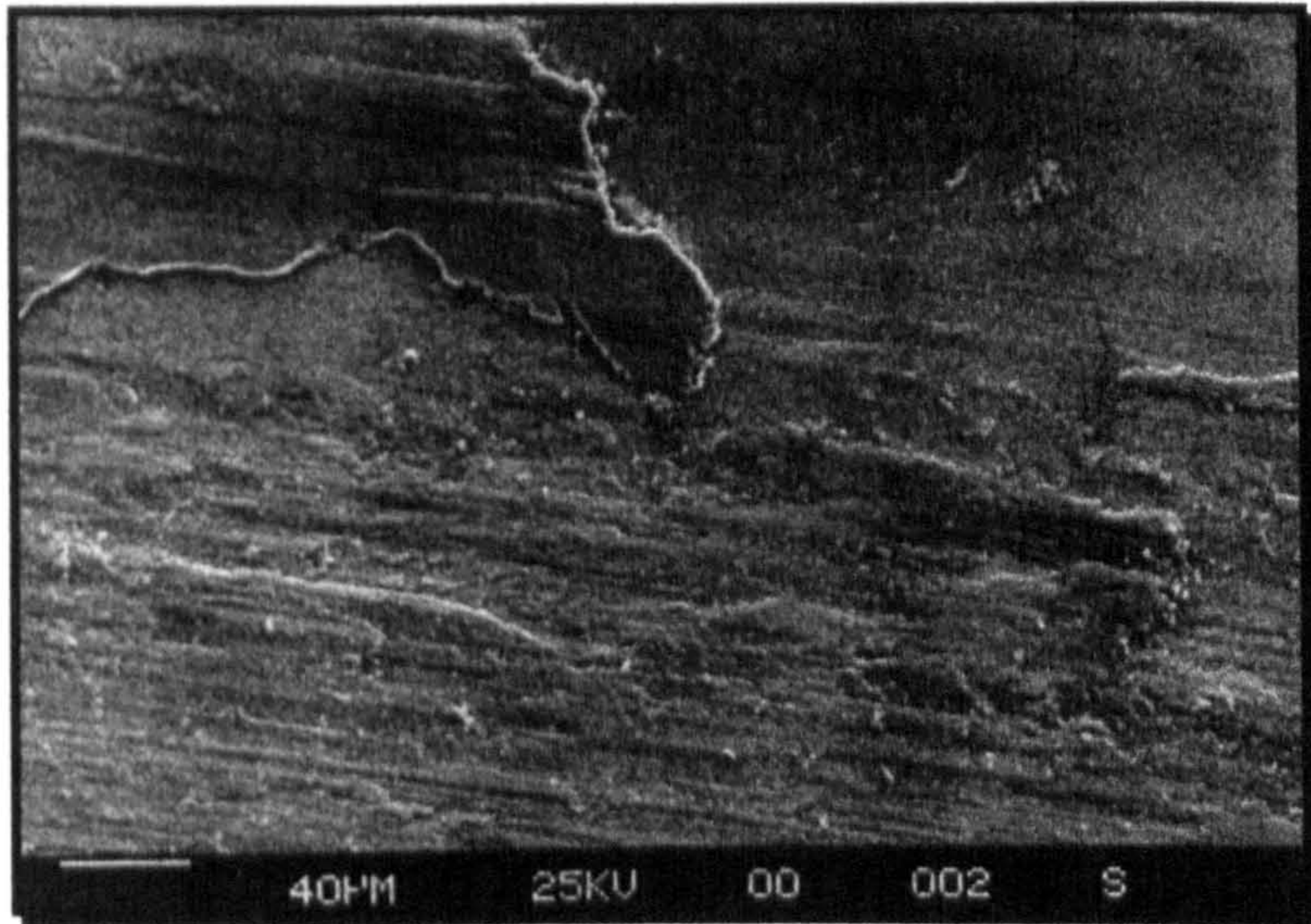


Figure 125 - S.E.M. micrograph of the polished RPS track shown in figure 120

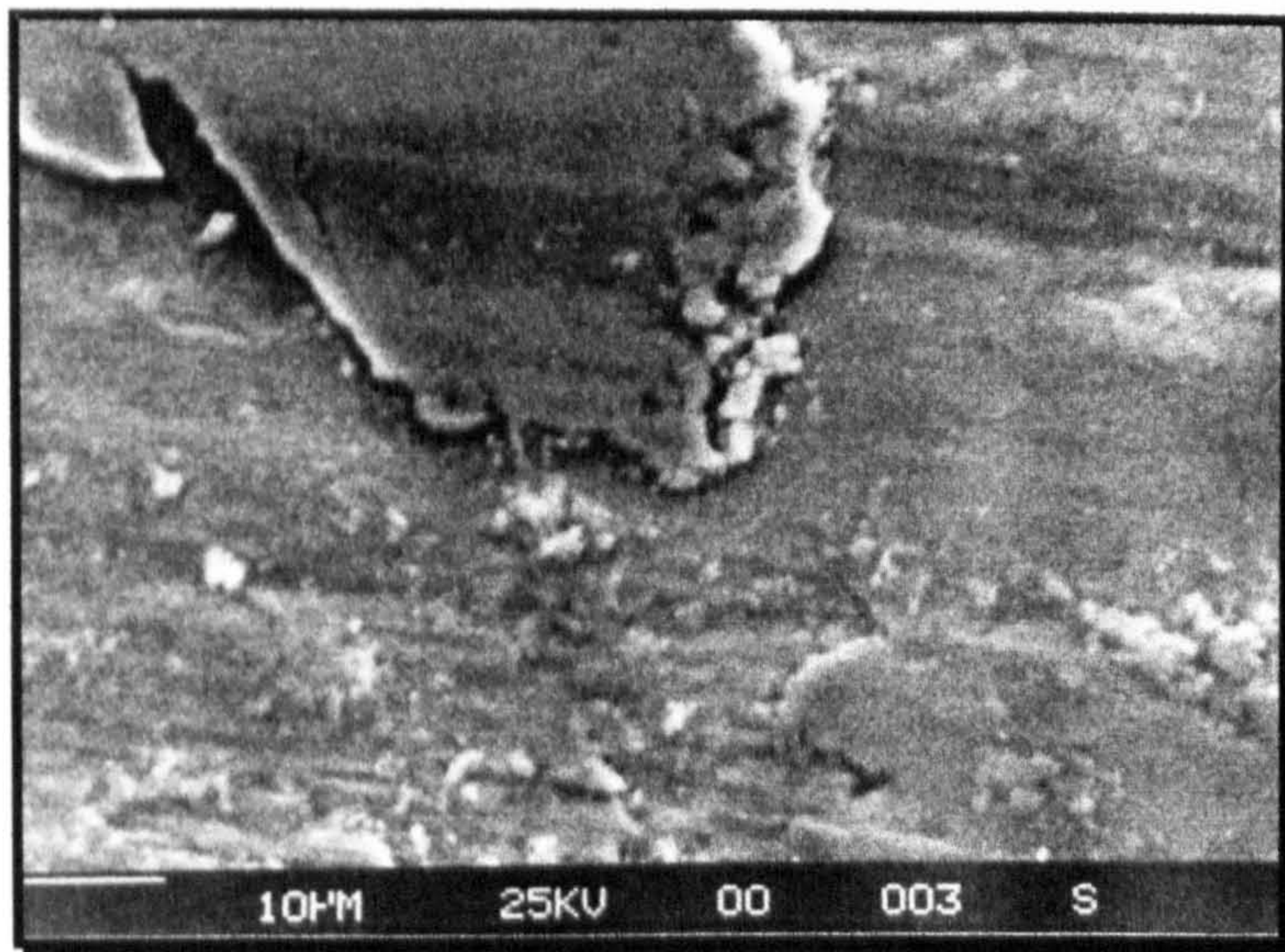


Figure 126 - S.E.M. micrograph of dull areas of RPS track shown in figure 120

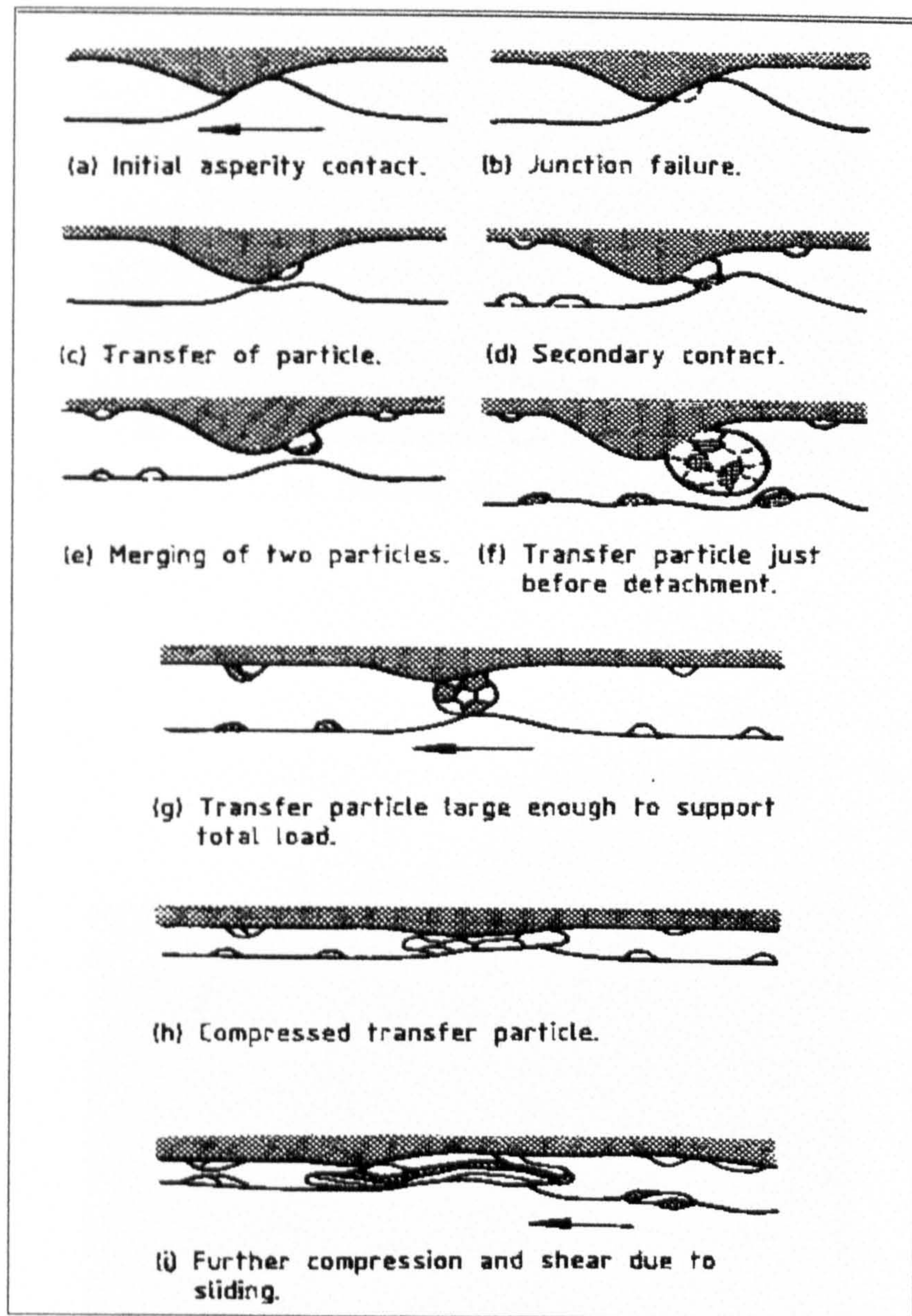


Figure 127 – Mechanism by which composite wear debris may form^[64]

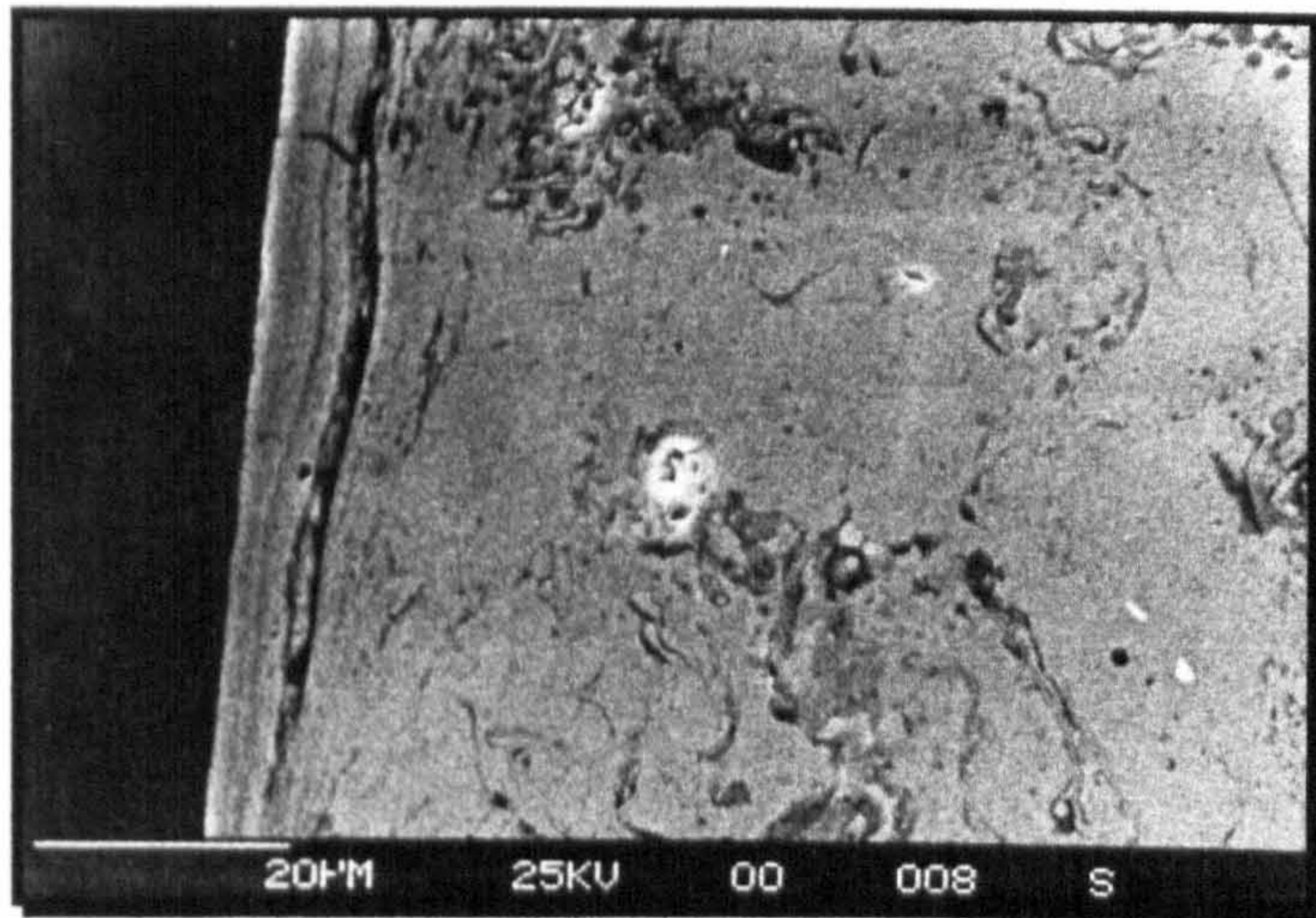


Figure 128 - S.E.M. micrograph of the shrouded only pin

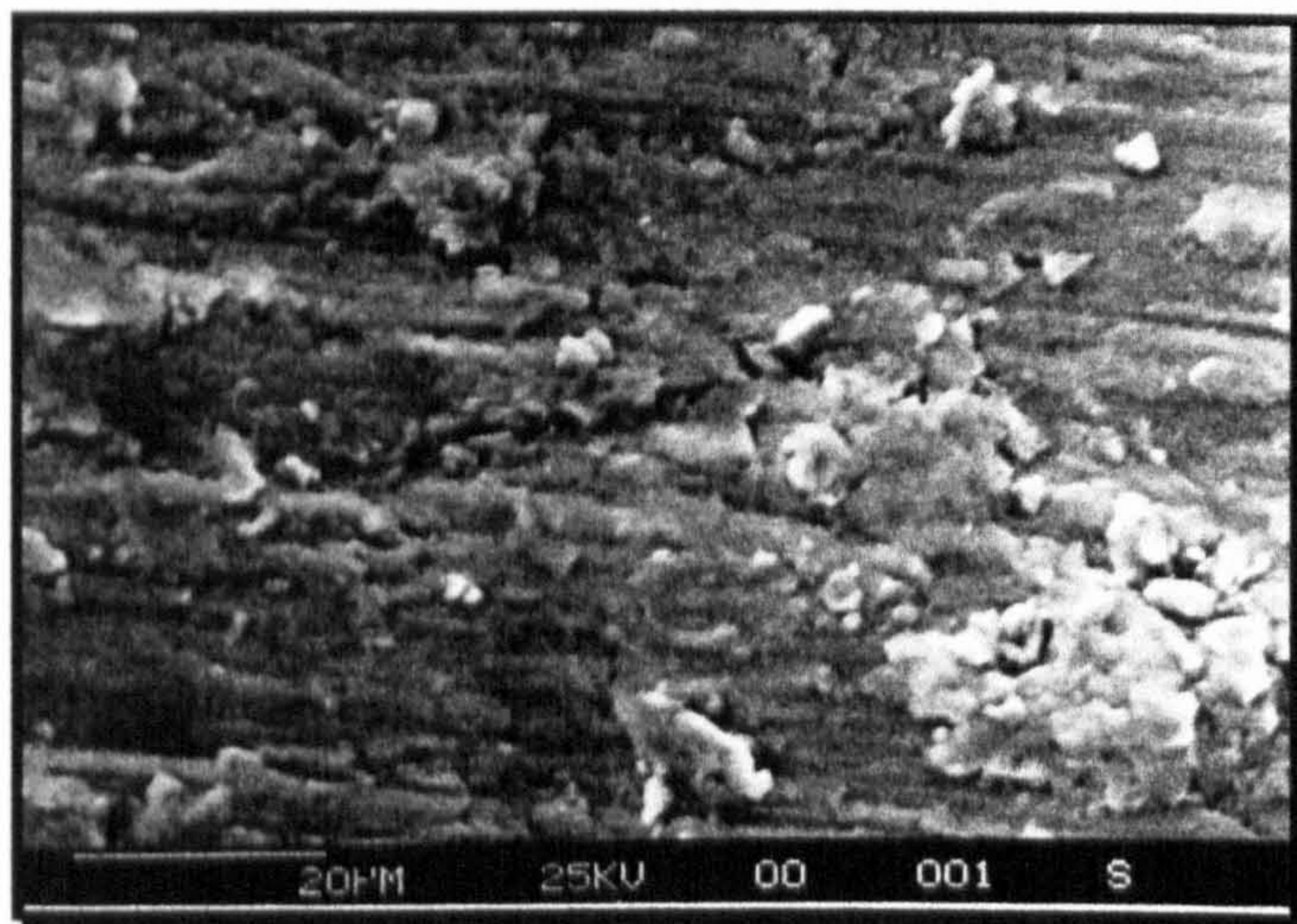
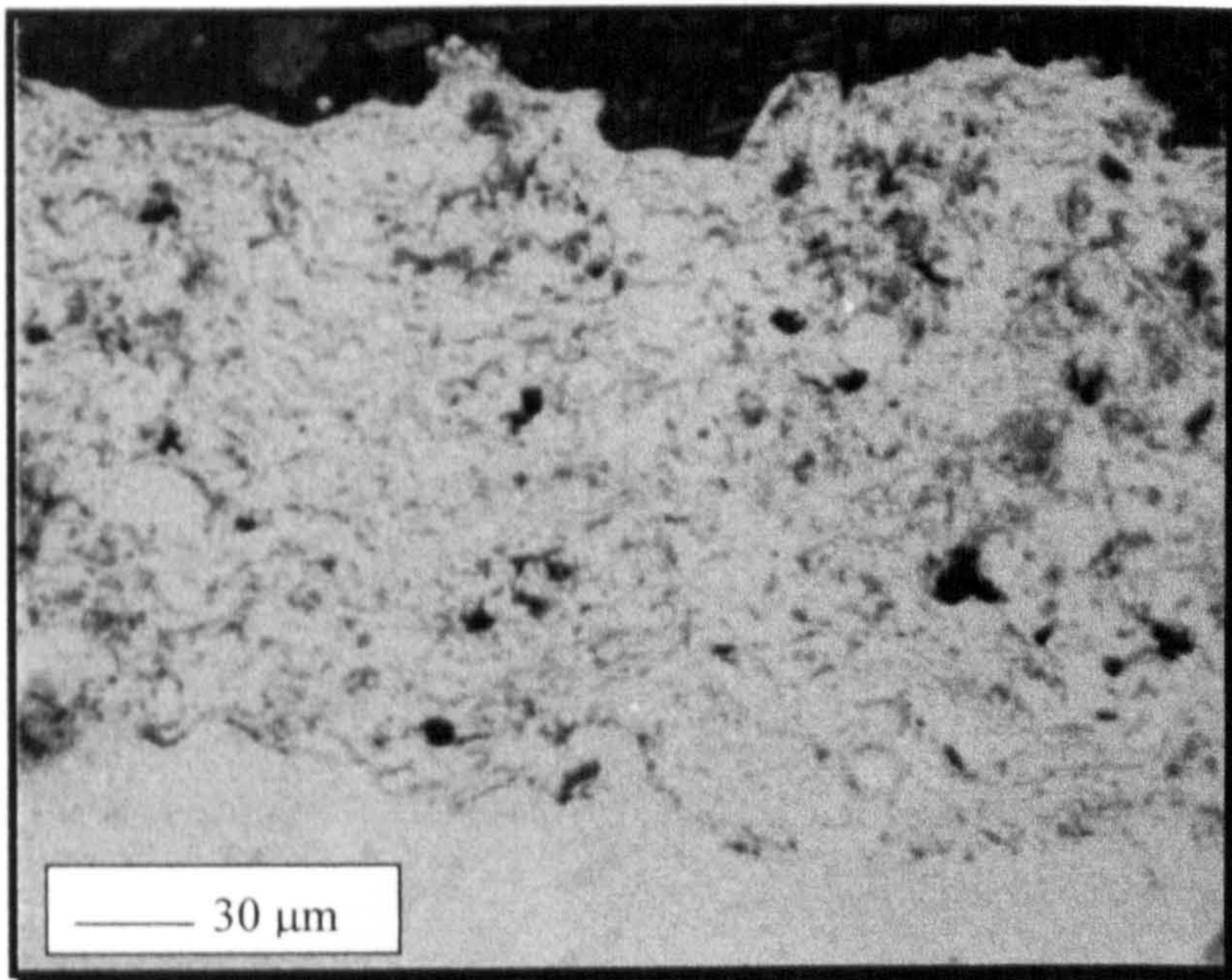
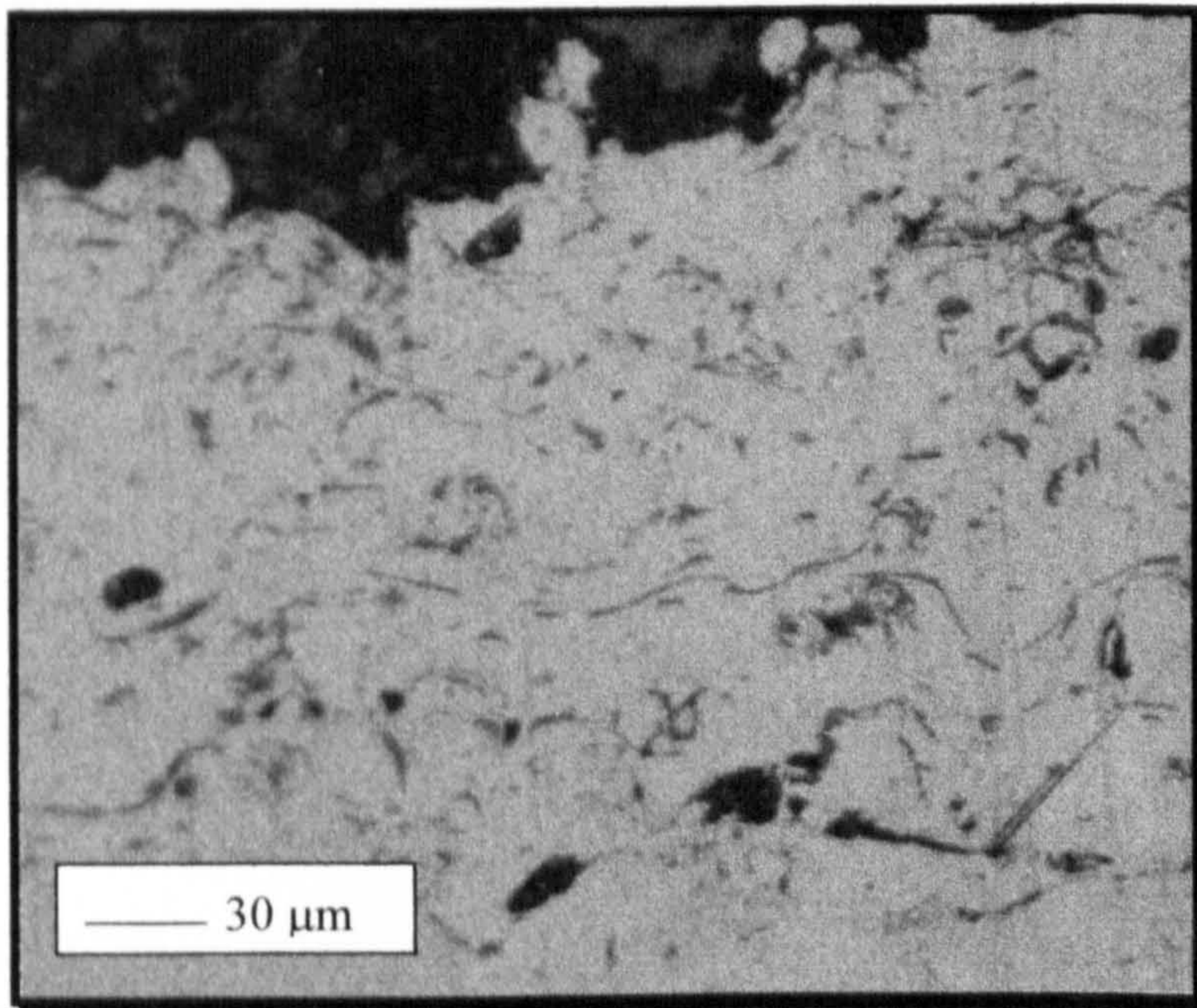


Figure 129 – S.E.M. of the disk surface shown in figure 120 (outer track)

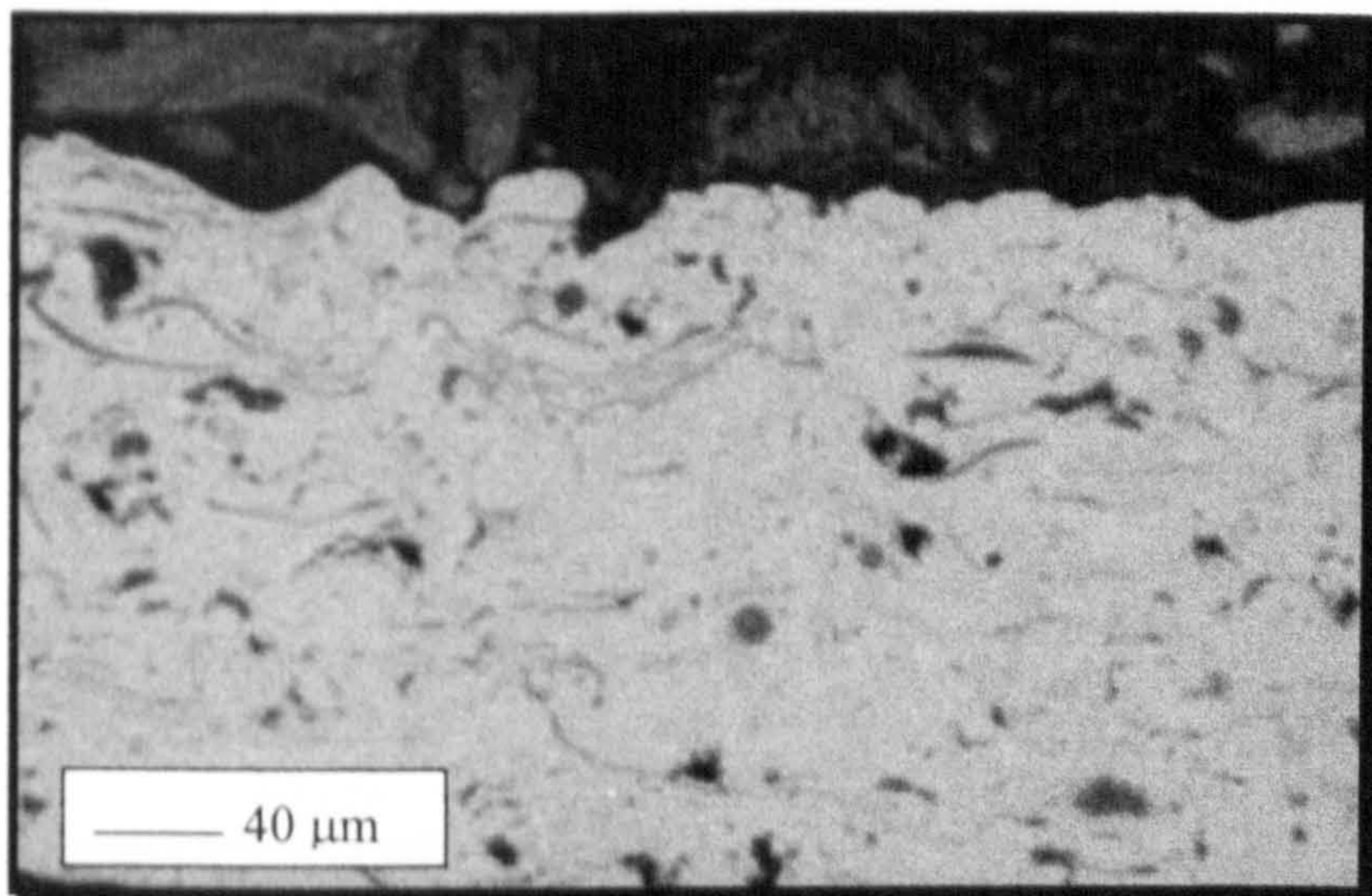


(a)

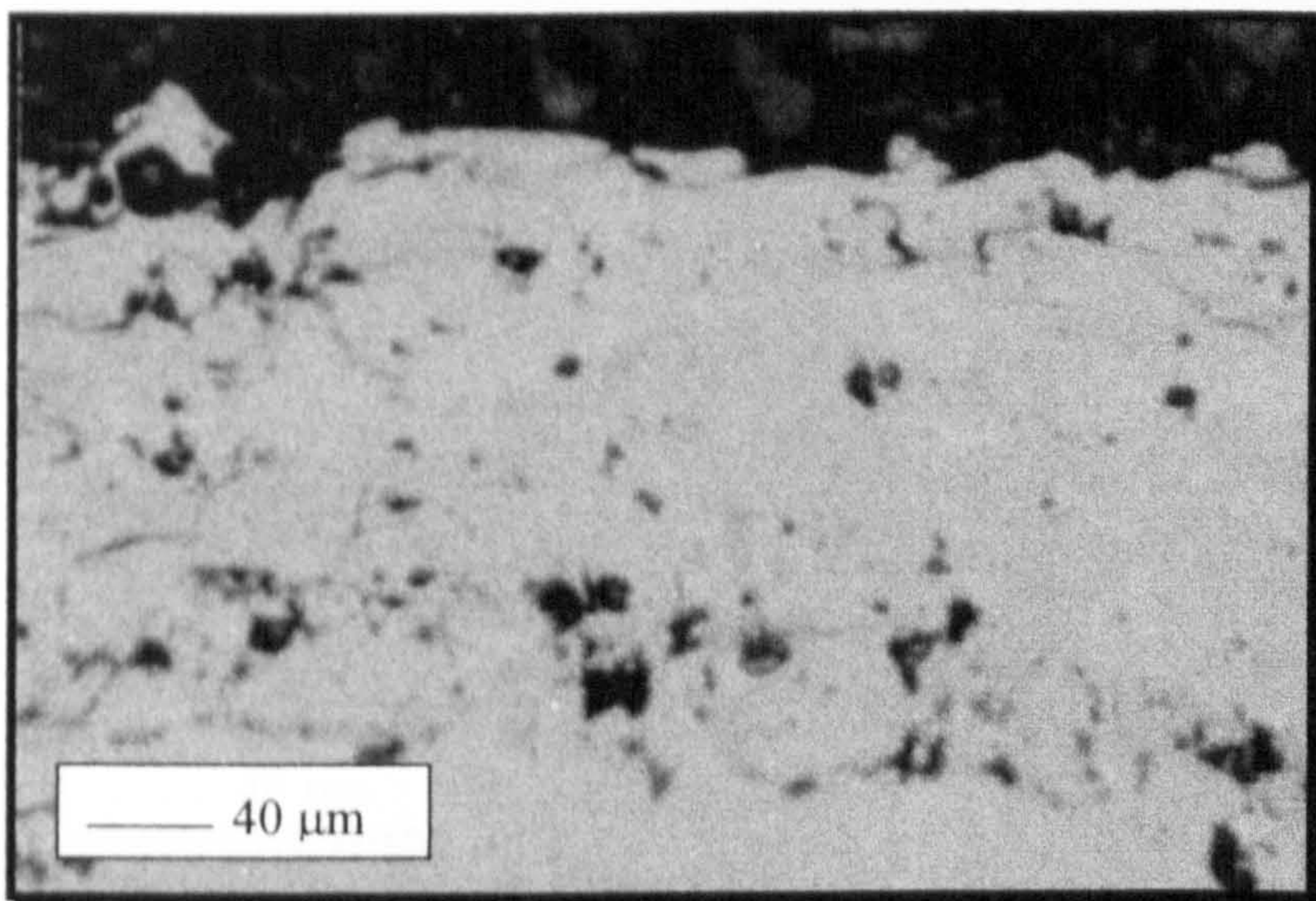


(b)

Figure 130 - MCrAlY, optical micrographs of two conventionally sprayed coatings - Set up 1 Conditions: (a) Amdry 995/1 (b) Amdry 995/47

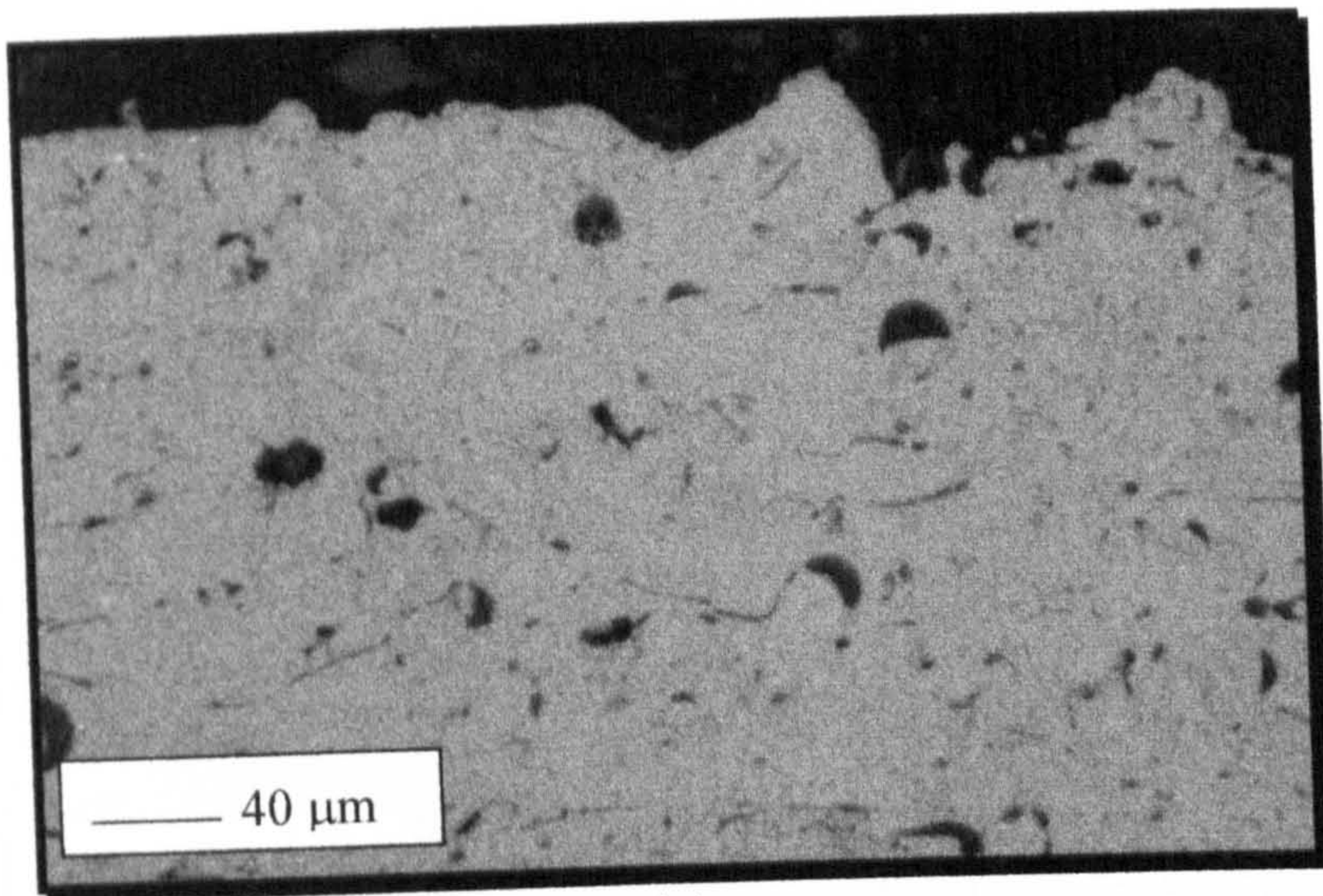


(a)

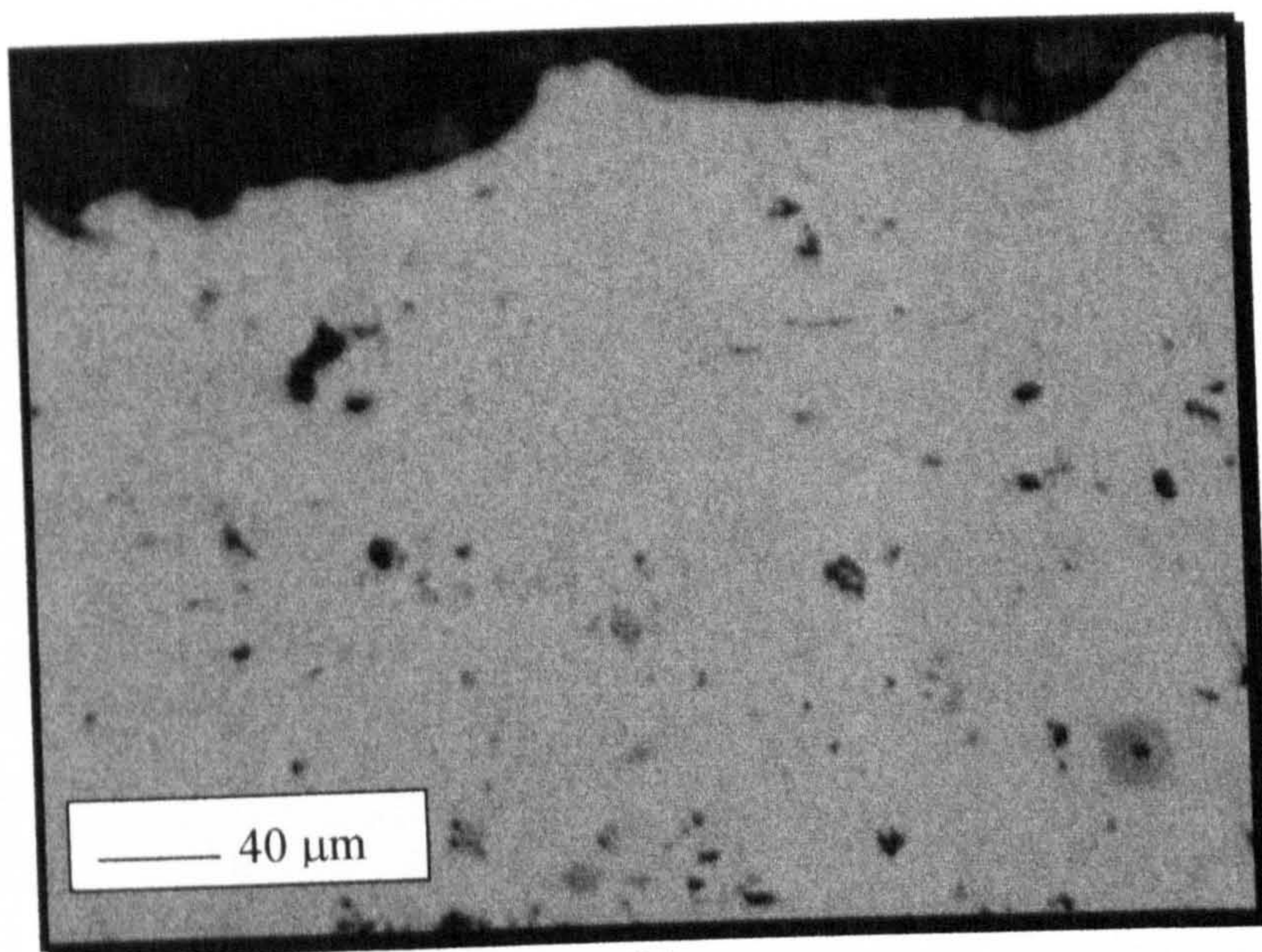


(b)

Figure 131 - Optical micrographs comparing (a) shrouded only and (b) a reactively sprayed coating - Set up 1, (smaller particle range)

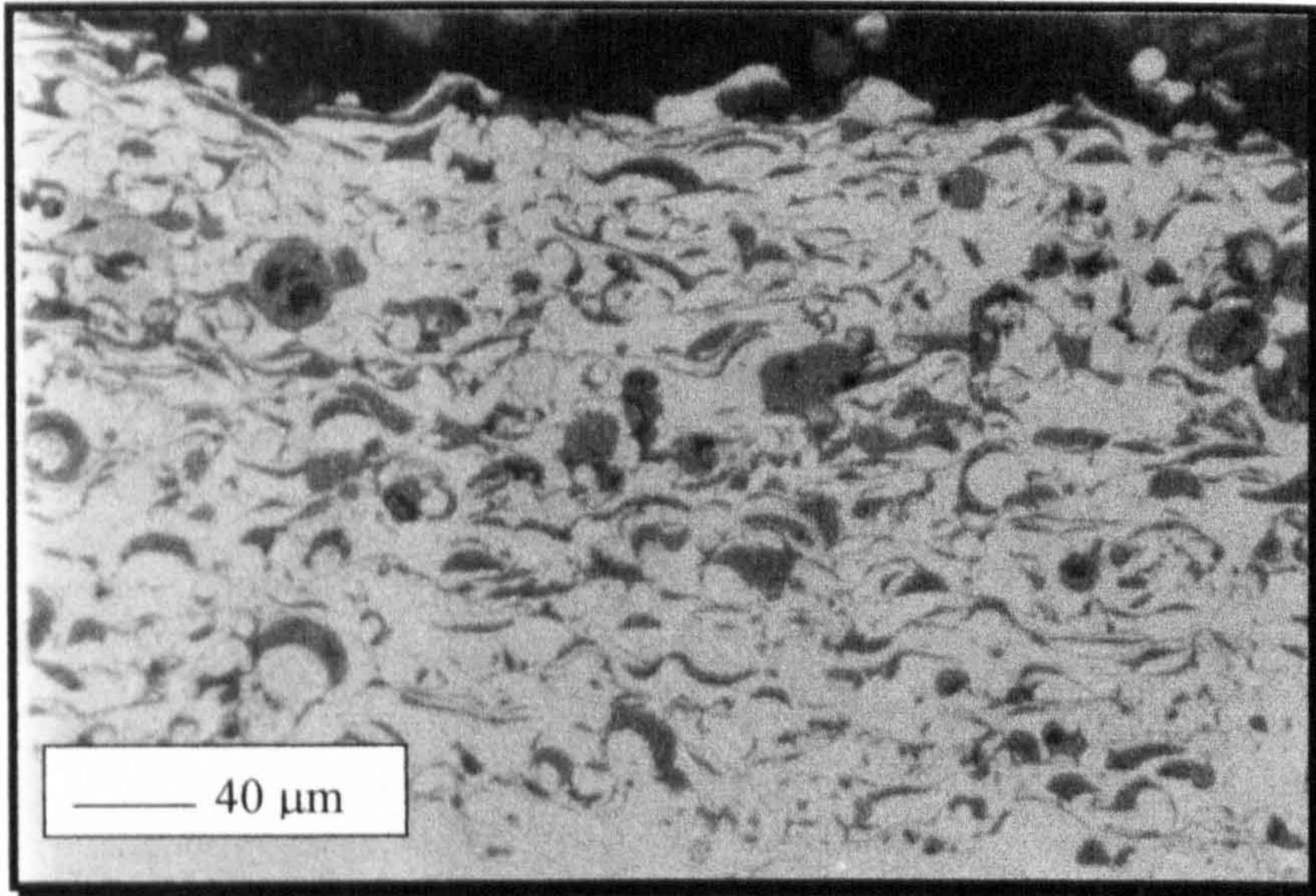


(a)

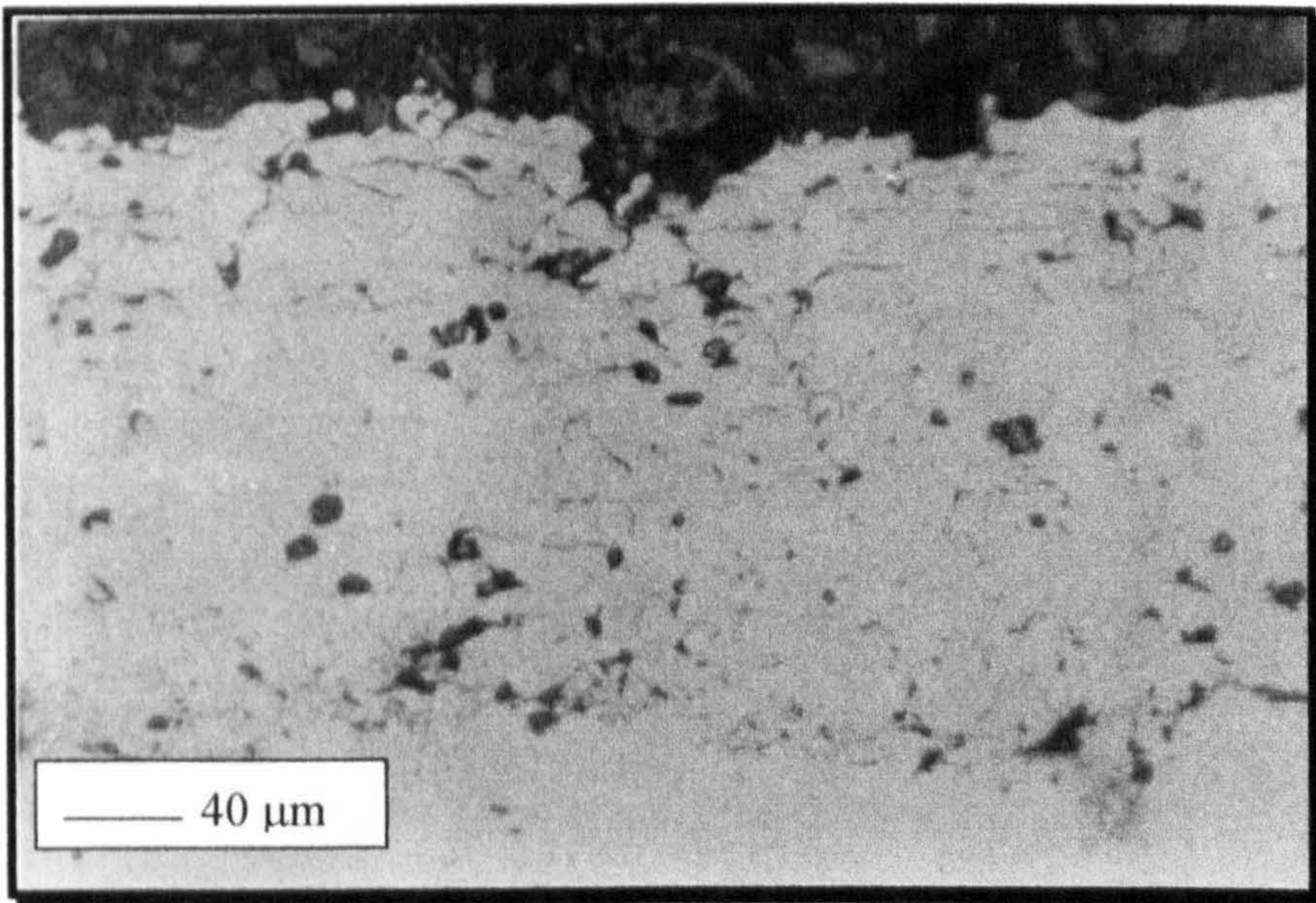


(b)

Figure 132 - Optical micrographs comparing (a) shrouded only and (b) a reactively sprayed coating - Set up 1, (larger particle range)

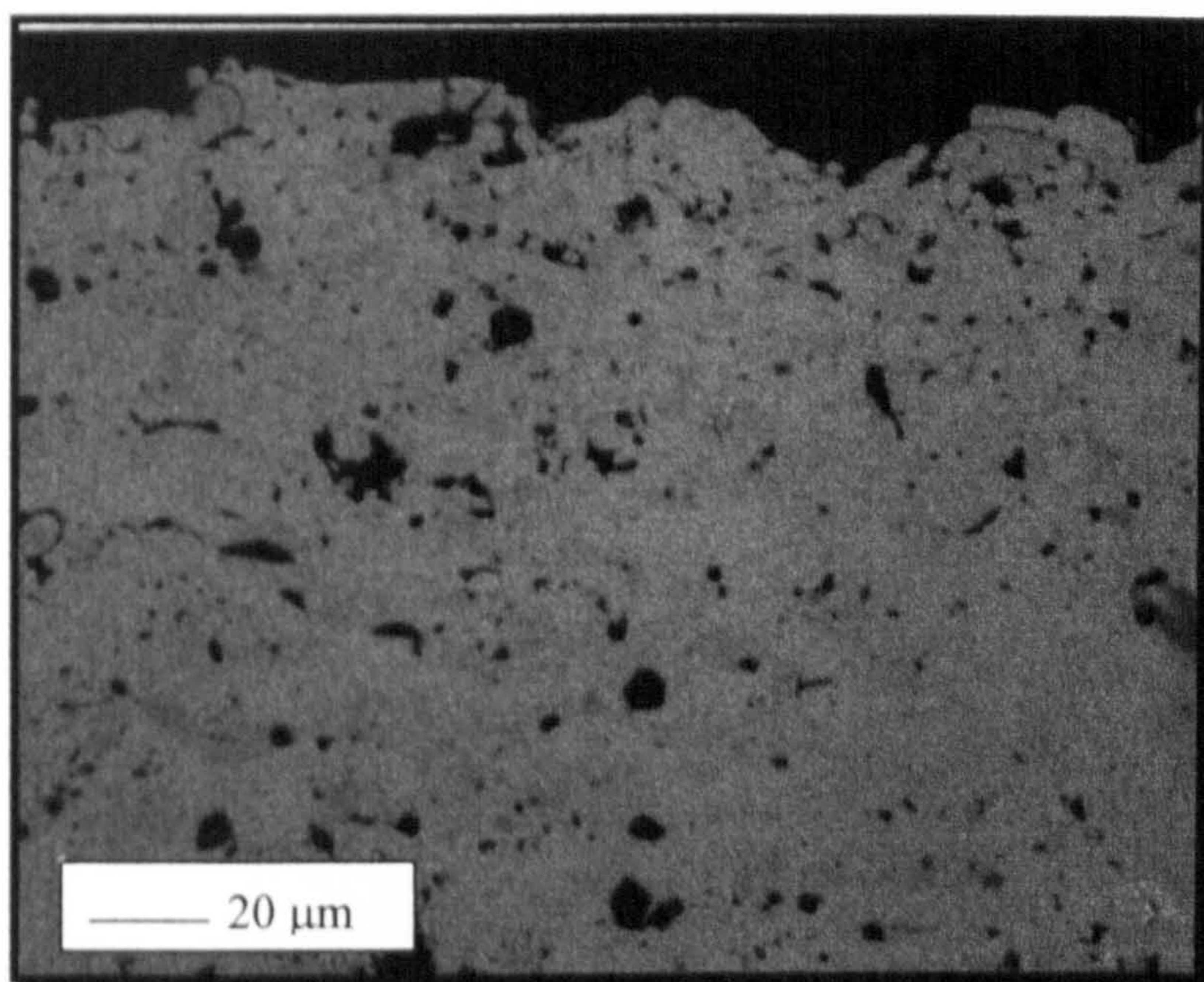


(a)

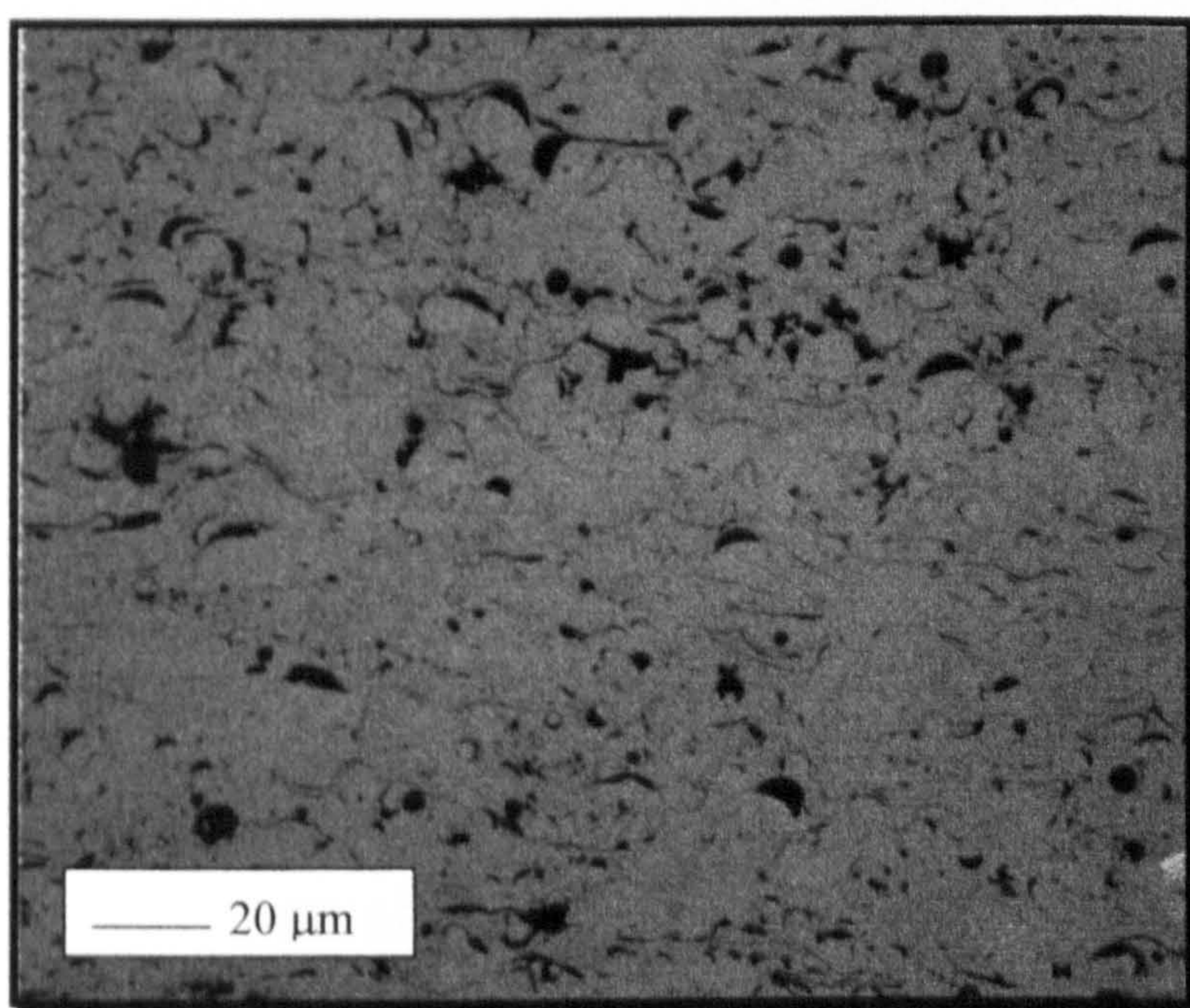


(b)

Figure 133 - Optical micrographs comparing (a) shrouded only and (b) a reactively sprayed coating - Set up 3, (smaller particle range)



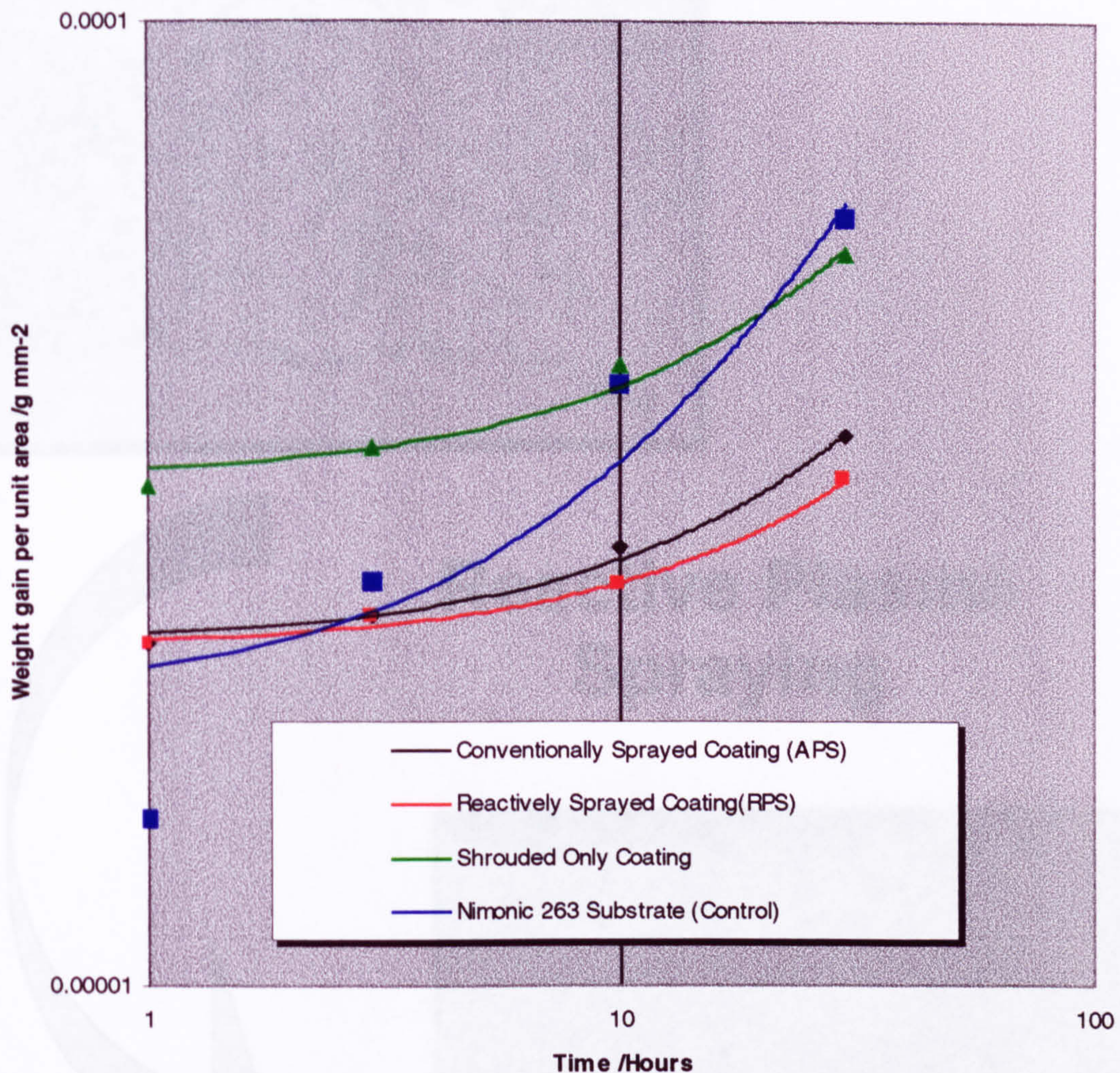
(a)



(b)

Figure 134 - Optical micrographs comparing (a) shrouded only and (b) a reactively sprayed coatings - Set up 3, (larger particle range)

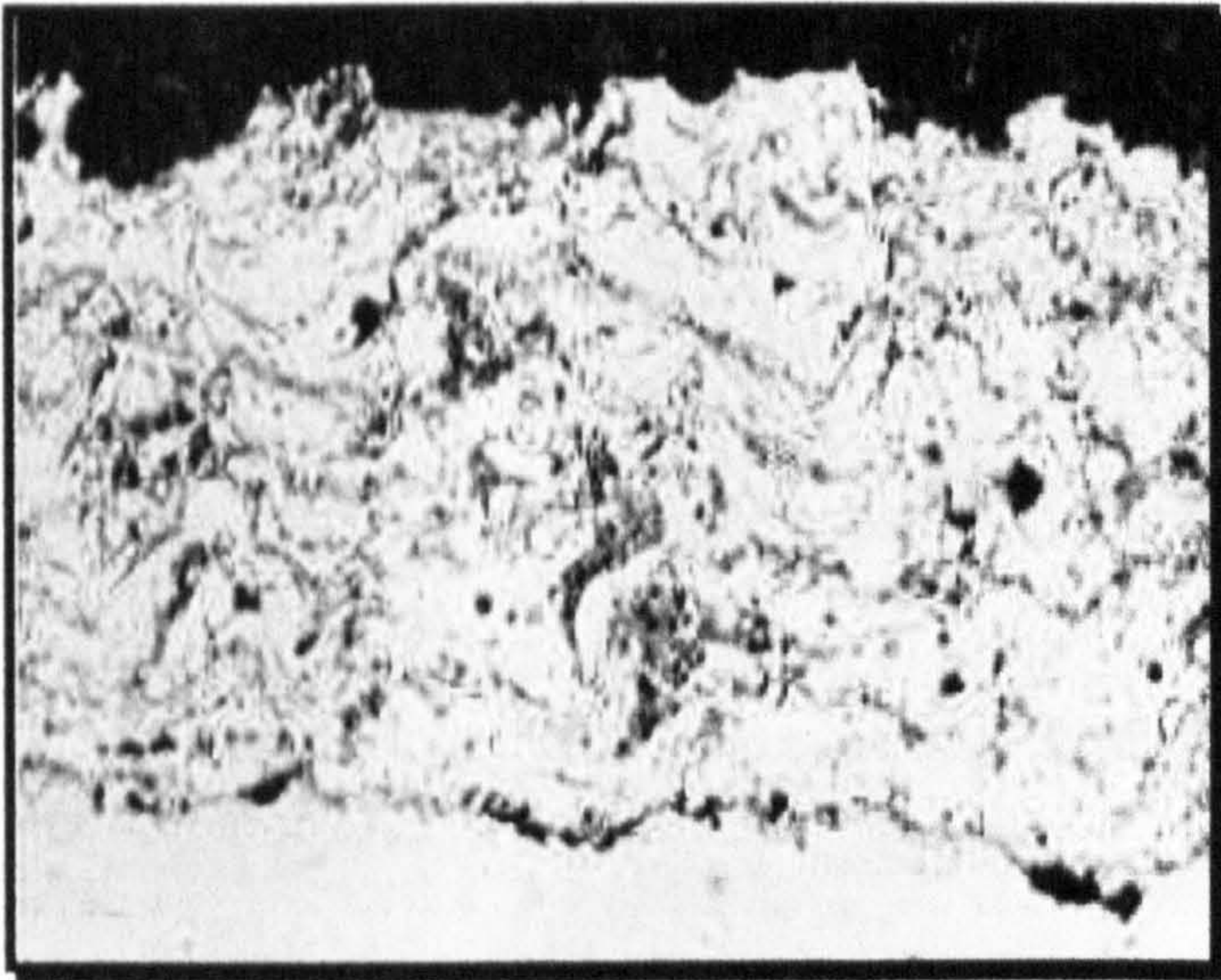
Discontinuous Oxidation Tests Results



Note: The weight changes for the coated samples represent the weight change of the MCrAlY coating and therefore do not include the weight change of the substrate, which has been deducted.

Figure 135 – Discontinuous Oxidation test results: Graph of weight change per unit area plotted against time.

Figure 136 - (a) APS coating spraying parameters (b) reactively sprayed coating spraying parameters



Reactive Plasma Spraying

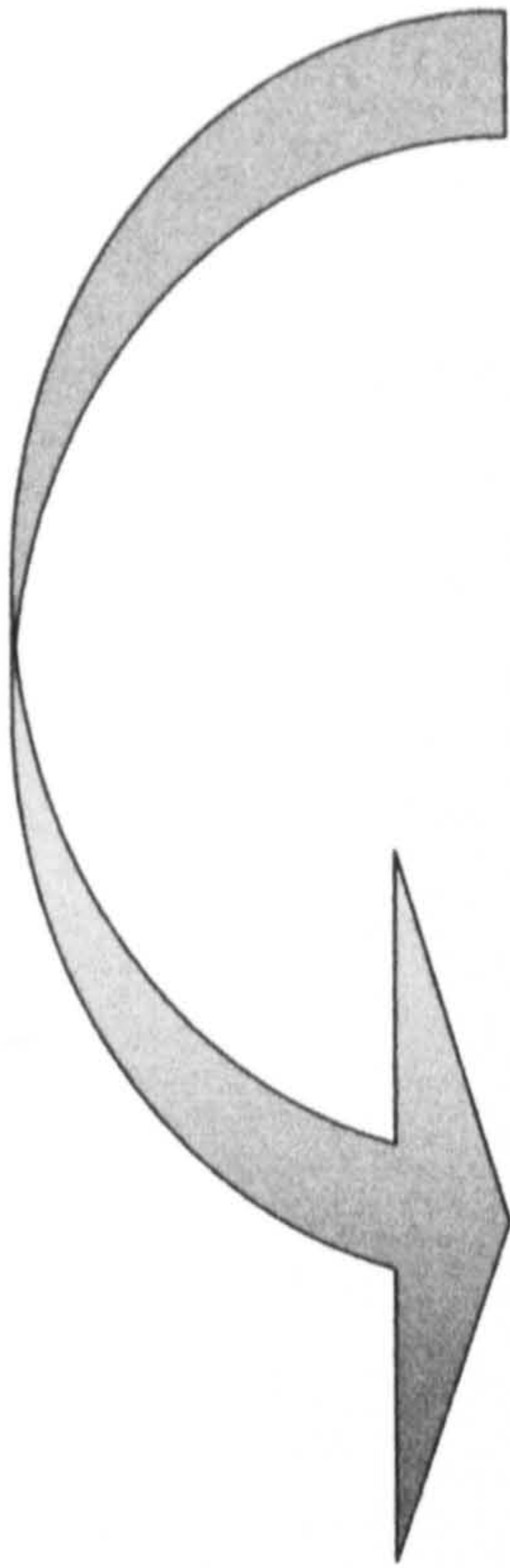
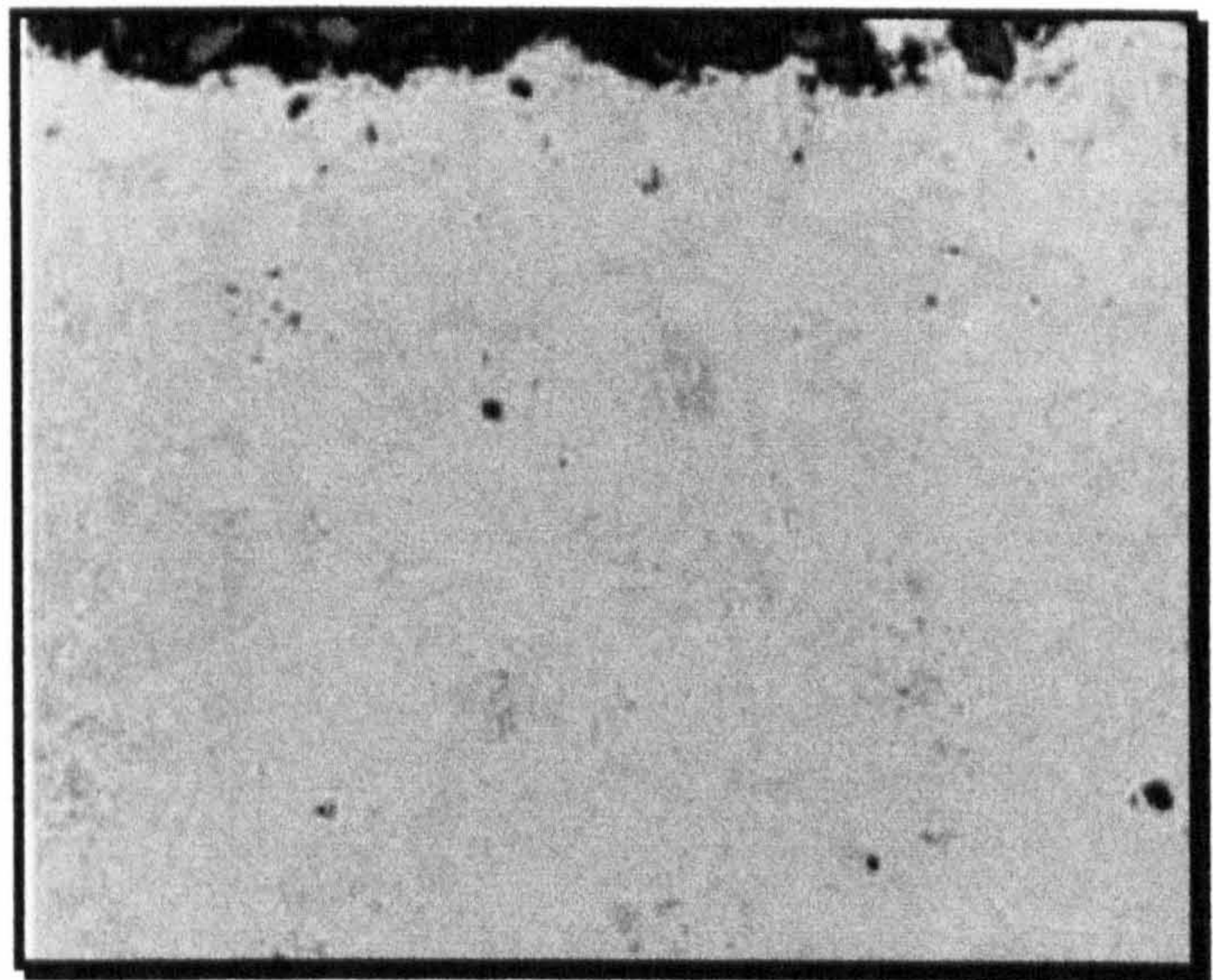


Figure 136 - (a) APS coating sprayed using manufacturers recommended parameters (b) reactively sprayed coating using the most optimised spraying parameters to date

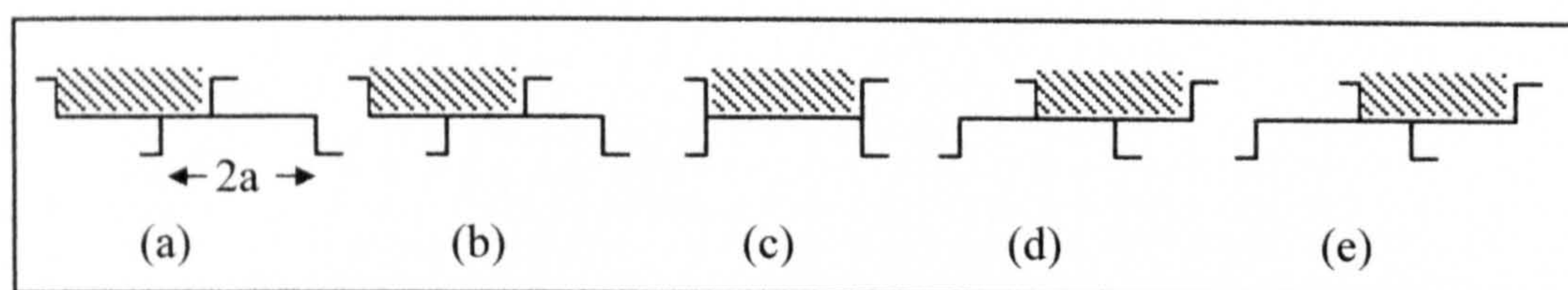


Figure 137 - APPENDIX - Schematic diagram of the evolution of a single contact between two asperites as they pass over each other