

Atmospheric Pressure Plasma Etching of Ti-6Al-4V Using SF₆

Author - Alex Bishop ^[1]

Supervisors - Zhaorong Huang^[1], Claudiu Giusca^[1], Tian Long See^[2]

^[1] Surface Engineering and Precision Centre, Cranfield University,

^[2] Manufacturing Technology Centre (MTC)

Submitted on 30th June 2023



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Abstract

Atmospheric pressure plasma (APP) etching using SF_6 has been shown to etch Ti-6Al-4V (Ti64). Operating parameters for input power, SF_6 concentration and standoff distance were determined through previous work as 1.2 kW, 0.8 L min^{-1} and 6mm respectively as the optimum values for etching using the Helios 1200 machine. By using various surface characterisation techniques, information over a broad range of spatial frequencies was obtained. By conducting stationary, dynamic and areal etching, the process has been shown a high degree of precision and material removal rates varying from $0.5 \text{ mm}^3\text{min}^{-1}$ to $2 \text{ mm}^3\text{min}^{-1}$. This process preferentially etches the BCC β phase of Ti64 over the HPC α phase by $\sim 50 \%$. It is proposed that this preferential etching of the β phase is due to both the crystal structure strength being weaker than the α phase and the BCC crystal structure being less dense than HPC, making it easier to remove more volume of material. The etching process is highly temperature dependent and preheating of the samples is required to achieve a clean trench. Significant amounts of redeposition also remain on the surface $< 2 \mu\text{m}$ which comprise of mostly fluorine and oxygen, but this is easily removed. The surface remains optically opaque after etching due to significant roughening of the surface, however negligible contamination remains. The proposed material removal mechanism is through the formation of volatile VF_x and TiF_4 compounds.

Acknowledgments

The author would like to thank:

My supervisors, Dr. Zhaorong Huang and Dr. Claudiu Giusca and the rest of the Ultra Precision research group at Cranfield for their invaluable guidance and support throughout the work. I would also like to say a special thanks to Lydia Frumosu and Sara Hawi. You were always around when I needed to talk through both work and life and you two have made this PhD that much more manageable and enjoyable.

I would also like to thank the MTC and Dr. Tian Long See as well as the EPSRC for funding and making this work possible.

Dr. Adam Bennett and Dr. Marco Castelli for their input throughout the work. I enjoyed our valuable discussions which helped me consider the bigger picture. Also, Prof. John Nicholls for his support at the beginning of this work, helping to direct the scope and the supply of the Factsage software.

Mr. Alan Heaume for his assistance in the laboratories and wishing him a happy retirement.

And finally, Nicole Mattacks for supporting me to complete this PhD, even when I didn't think I could. For always having time to listen to both my complaints and joys and generally putting up with me, I love you.

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Chapter 1

Introduction

This thesis develops an atmospheric pressure plasma (APP) process for the etching of Ti-6Al-4V (Ti64) alloy. Ti64 is the most commonly used alloy of titanium [1]. The applications of Ti64 span multiple industries, such as: aerospace, medicine, and construction. This is due to its high strength, corrosion resistance, and biocompatibility [2]. However, these very properties make it difficult to machine [3]. Ti64 is an $\alpha + \beta$ alloy, meaning it is comprised of a mixture of two crystal structures, Hexagonal close packed (HCP), and body centred cubic (BCC) respectively. Typically, Ti64 is a mixture of 70-95% α and 5-30% β [4].

Contact machining techniques used for finishing Ti64 parts all have drawbacks, such as: high running costs, expensive tool replacements, high tool wear, long processing times or involve the use of harmful chemicals. Abrasive methods for finishing metal surfaces, such as grinding and sand blasting are very common methods to reduce surface roughness, however are unsuitable for removing large amounts of material. Use of lubricant is required when grinding titanium and its alloys to prevent surface burning [5] and grinding of Ti64 can result in μm scale R_a roughness values, but this roughness increases with depth of cut [6]. Comparing the roughness of milled, sand blasted, ground and micro-machined Ti64 surfaces, milling reduces the roughness and improves fatigue life the most, while sandblasting reduces the roughness the least and can introduce significant internal stresses which reduce fatigue life [7]. Achievable roughness values for

common contact machining techniques of Ti64, are shown in Table 1.1. The values in Table 1.1 are shown for LBM (Laser beam melting) Ti64 samples. LBM is a type of 3D printing where a laser is used to selectively melt a powder, into a solid structure with high accuracy.

Table 1.1: Surface roughness measurements for milling, sand blasting, ground and micromachined LBM Ti64 plates. Reprinted from [7] copyright (2017) with permission from Elsevier.

Surface condition	R_a [μm]	R_z [μm]	R_t [μm]
As built	17.9 ± 2.0	121.9 ± 12.6	141.7 ± 11.7
Milled	0.3 ± 0.1	1.9 ± 0.8	2.9 ± 1.5
Blasted	10.1 ± 0.2	73.4 ± 5.7	90.5 ± 6.2
Vibratory ground	0.9 ± 0.7	8.1 ± 5.4	17.4 ± 10.5
Micro machined	0.4 ± 0.3	4.1 ± 3.5	9.5 ± 8.0

Another contact technique for the finishing of Ti64 is MRF (magnetorheological finishing). MRF is a form of polishing which involves the use of magnetorheological fluids (a suspension of micro/nano sized ferromagnetic particles in a fluid such as oil/water) [8,9]. The surface is then polished using this fluid in the presence of a magnetic field, which varies the fluid viscosity. The development of MRF has typically been focused on the finishing of brittle materials such as glass [10,11], silicon and silicon/tungsten carbide [12,13] mostly for optical applications. Work has been carried out to show this process can also be used for aluminium [14], magnetic materials [15] and titanium alloys including Ti64 [16–18]. However this, like grinding, is mainly suitable for reducing roughness and not removing large amounts of material. Turning and milling are the other two main contact machining processes used for finishing of Ti64. Single Point Diamond Turning (SPDT) is mostly used to machine polymers, silicon-based materials and non-ferrous materials. When machining Ti64, numerous problems are encountered including: high tool wear, surface-tool adhesion and subsurface damage/plastic deformation [19,20]. Many of these problems can be traced back to the low thermal conductivity of Ti64. Heat is not readily conducted away from the cutting zone and transferred to the tool [21]. Increase in the tool life (reduction in tool wear) has been achieved by subjecting the Ti64 surface to a magnetic field which reduced vibrations in the workpiece due to eddy

currents [22]. The magnetic field also helps to release the chips (pieces of cut material) and dissipate heat from the cutting zone [23]. Increasing the magnetic field strength can lead to a reduction in surface roughness, however increasing the magnetic field strength too much induces strong vibrations which leads to a rougher surface and increased tool wear [24]. When milling Ti64, use of compressed cold nitrogen gas as a coolant has been shown to improve the tool life by a factor of >2 (the tool lasts more than twice as long) compared to dry machining. Using standard 'flood coolant' is unsuitable for high speed milling of Ti64 [25]. A major problem with all contact machining is the introduction of residual stress and surface/subsurface damages. Electro-chemical polishing (ECP) has also been shown to reduce roughness and improve fatigue life of Ti64 components, although not as much as milling, and material removal rates are low [26,27].

Ion beam figuring (IBF) is a well established technique for nano-scale alterations to a surface. The material removal mechanism of IBF is a non contact process, where a narrow beam of high energy ions is used to bombard a surface and remove material via sputtering [28,29]. The energy from an incident ion is scattered through collisions with surface atoms. If the energy of an atom is above the binding energy, it escapes from the substrate. IBF is carried out under vacuum conditions to prevent the ion beam interacting, and losing energy, with the air. IBF avoids tool wear, since there is no physical tool, but a constant stream of ions. Due to the limited penetration depth of the ions, subsurface damages are also avoided [30]. While material removal is possible for any material, the effectiveness of IBF is sensitive to the substrate properties [31].

However, due to low material removal rates (typically $100\text{'s } \text{\AA}\text{min}^{-1}$) and requiring a vacuum, the process is slow and unsuitable for large samples. IBF is often used in conjunction with some form of patterning where a mask, which is resistant to chemical etching, is removed via sputtering (or another non-chemical process) exposing the material underneath to chemical etching [32].

An alternative technique for removing material is using a plasma jet. Plasma is an ionised gas, where electrons are no longer bound to the nuclei, and is regarded as the 4^{th} state of matter [33]. Plasma is formed by heating a gas above (at least) the first ionisation energy, for most gases this is between 5 - 20 eV ($1 \text{ eV} = 1.6 \times 10^{-19}$

J) [34]. The ions and electrons will recombine over ns scales, so an external energy must be supplied to a plasma to maintain it [34]. Since the ions are positively charged, and the free electrons are negatively charged, and no longer bound to the nucleus, this creates a charge separation. This charge separation has a profound impact on the behaviour of a plasma, compared to a gas, giving rise to some complex phenomena [35]. Plasma can be focused into a jet by ionising a stream of gas and accelerated through an Electromagnetic (EM) field. Depending on the temperature and chemical composition of a plasma jet, it can be used for a variety of applications such as: material removal, material deposition/coating, sterilisation, and changing the surface energy of a substrate. Plasma's can broadly be categorised into either thermal, or non-thermal. In a thermal plasma, the ions/neutral (heavy) particles and free electrons are at the same temperature. Whereas in a non-thermal plasma, the electrons have a much higher temperature than the heavy particles [36]. For sterilisation and cleaning, a non thermal plasma is required to ensure the surface is not damaged. Whereas, thermal plasma is used extensively in higher energy applications, such as: welding, cutting, and material processing industries [37].

Atmospheric pressure plasma (APP) does not require a vacuum chamber which can be slow and expensive [38]. A plasma formed at atmospheric pressure is more thermal than low pressure plasma, due to the increased density, which increases the chance of collisions within the plasma [39]. By carefully choosing which gas (or mixture of gases) to ionise, a chosen surface can be efficiently etched through chemical reactions. APP etching of silicon based materials has been developed successfully in the past and is a key step in the manufacturing of precision optics and transistors [40]. By using fluorine radicals to chemically react with the surface, volatile silicon fluoride products are formed [41]. The volatile products boil away, which is how material is removed. Chemical reactions are the dominant material removal mechanism during APP etching, as opposed to physical (such as sputtering) [42]. Due to this, APP etching does not leave subsurface damages, often created by physical processes.

Work has been carried out in the past at Cranfield University developing APP systems, including the equipment used in this work [41, 43, 44]. Previous work has focused

on silicon based materials for use as optics [41]. In these cases, APP etching has shown competitive advantages over alternative technologies (such as IBF and MRF), resulting in high material removal rates, and high quality surfaces. This thesis builds on previous work which has established optimum operating conditions such as standoff distance (the distance between the torch and the surface to be etched), and input power, as well as characterisation of the plasma torch.

To justify a plasma-based surface finishing method, it must be comparable or superior to currently used methods in terms of quality of surface produced, processing time and impact on the environment. Achievable surface roughness and material removal rate (MRR) for common surface finishing processes are compared in Figure 1.1 for silicon based materials. This shows that Reactive atom plasma (RAP) processing can achieve nm scale roughness while maintaining high MRR compared to IBF and MRF. RAP is a form of APP etching, developed by RAPT Inc (US), where reactive species (such as fluorine compounds) are injected into an argon plasma to etch a surface. It was initially developed for etching of silicon based optical materials [45].

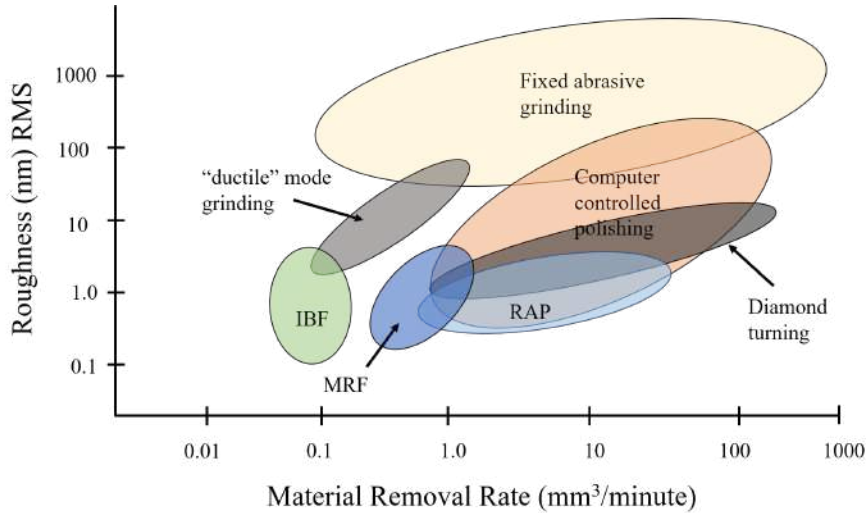


Figure 1.1: Comparison of achievable RMS roughness and material removal rate of RAP against other surface finishing techniques for silicon based materials. Reprinted from [46] copyright (2011) with permission from Elsevier.

Very little work has been carried out in the field of APP etching of metals, with no studies found in literature exploring the etching of Ti64, despite the high demand

for precise finishing of Ti64 surfaces for many applications. Of the work which has been carried out for the plasma etching of metals, most are carried out under vacuum conditions. Under these conditions, chlorine is often used as an etchant for titanium and TiO₂ [47]. However, this could lead to the formation of dangerous bi-products under atmospheric conditions due to chlorine (and especially chlorine radicals) being water soluble [48]. It can be assumed that this is one of the reasons why APP of Ti64 has not been carried out in literature. The significant drawbacks associated with alternative techniques motivated this work, to determine if atmospheric pressure plasma etching of Ti64 using fluorine based chemistry is possible. The aim of this thesis is to extend the APP process for use on metals. More specifically, using fluorine as a reactive species, to develop an APP process which is capable of etching Ti-6Al-4V (Ti64) alloy. To achieve this aim, the following objectives will be fulfilled:

1. To understand the surface chemistry and plasma-surface interactions of a fluorine based etchant with a Ti64 surface. The APP etching process requires volatile products to be formed, in order for material removal to take place.
2. To characterise the etch rate for static, dynamic, and areal etching of Ti64 using a fluorine based etchant. The etch depth, full width at half maximum (FWHM), and the volumetric material removal rate (MRR) will be obtained, and used to compare the APP etching process against other techniques.
3. To characterise the effect of the etching process on the Ti64 microstructure and surface roughness. This will provide a base for assessing the applicability of the developed technology.
4. To propose the material removal mechanism for the etching of Ti64. Understanding the nature of how the APP etching process removes material will help further work to optimise the process.

Chapter Plan

Chapter 1 - Introduction

Introduces the field of plasma etching with reference to relevant previous work and what motivated the work carried out for this thesis. The aim and objectives of the work are also laid out in this section. The introduction discusses alternative techniques for the finishing of Ti64, and outlines the benefits of a possible plasma etching technique. Building on previous work using an APP torch to etch silicon based materials, APP etching of Ti64 using fluorine chemistry is proposed.

Chapter 2 - Literature Review

Explores published literature for plasma etching and the composition of Ti64. This section outlines the basis of plasma physics and plasma etching, APP etching of metals and problems associated with this technique, and introduces Ti64 alloy. Finally, the literature review explores different surface measurement techniques, to provide the reader with enough background knowledge to fully understand the relevance of the presented work.

Chapter 3 - Method

The method and equipment used for: APP etching, surface measurement, chemical and microstructure analysis, and thermodynamic simulations are explained. The design of experiments for static, dynamic and areal etching are shown. Using interferometry, profilometry, and atomic force microscopy (AFM), the surface morphology is characterised, for both low and high spatial frequencies. Scanning electron microscopy and energy dispersive x-ray spectroscopy (SEM/EDS) was used to investigate the chemical composition of the surface, before and after plasma etching. A flow chart, presented in Figure 3.2, outlines the sample preparation method.

Chapter 4 - Results and Discussion

Illustrates the results obtained for stationary dwells, dynamic etching (trenches) and areal etching. The material removed by standard and alternate pass raster patterns, and varying processing speeds for areal etching are compared to a predicted material removal function. The results from SEM/EDS measurements are used to propose a

material removal mechanism.

Chapter 5 - Conclusion

Summary of the thesis, exploring the main results and their significance. This section also addresses all the objectives set in the introduction.

Chapter 6 - Further Work

Description of further work suggested by the author in order to better understand a wider scope of the field.

Chapter 2

Literature Review

The literature review is structured into six sections, covering three main areas. Sections 2.1 - 2.3 cover: what a plasma is, plasma etching in general, and APP etching of metal. This gives the reader an overview of plasma generation and plasma processes. Section 2.4 and 2.5 cover what is Ti64 alloy (it's microstructure and properties), and the problems associated with plasma etching of metal. The final section provides an overview of surface measurement techniques, outlining the benefits and drawbacks of different setups.

2.1 The plasma state

Plasma is an ionised gas, regarded as the 4th state of matter [33]. A plasma is formed by heating a gas until electrons have enough energy to break away from the atoms to which they are bound. Plasma can have up to six different types of particles: free electrons, positively charged ions (an atom which has lost an electron), neutral atoms (in their ground state), excited atoms, negatively charged ions (an atom which has gained an electron), and photons [49]. A charge separation is formed when electrons are removed from atoms, leaving positively charged ions and negatively charged free electrons. These

ions and electrons will typically recombine over ns scales, so an external energy must be supplied to maintain the plasma [34]. The ionised particles create electric fields, and the movement or flow of particles also generates magnetic fields [50]. This leads to plasma exhibiting a collective behaviour, where small perturbations to a plasma at a given point can travel large distances through the Coulomb force [51]. This collective behaviour is analogous to a liquid, as such, plasma is often treated as a fluid in simulations [52]. While treating a plasma as a fluid is an approximation, it greatly simplifies plasma models and equations. By considering a plasma to be fluid, distributions of parameters, such as particle velocity and temperature, can be averaged to produce a quantity used for calculations [50]. Using a distribution function, instead of absolute values for individual particles, introduces the idea of probabilities. The most probable approximation for the distribution, is the Maxwell-Boltzmann (or Maxwellian) distribution function [53]. An example of a Maxwellian distribution of velocity is shown in Figure 2.1, where v_m is the most probable velocity, $\bar{v}$ is the mean average velocity, and v_{rms} is the root mean square average velocity. Equation 2.1, shows the mathematical expression of the Maxwellian distribution function in Figure 2.1.

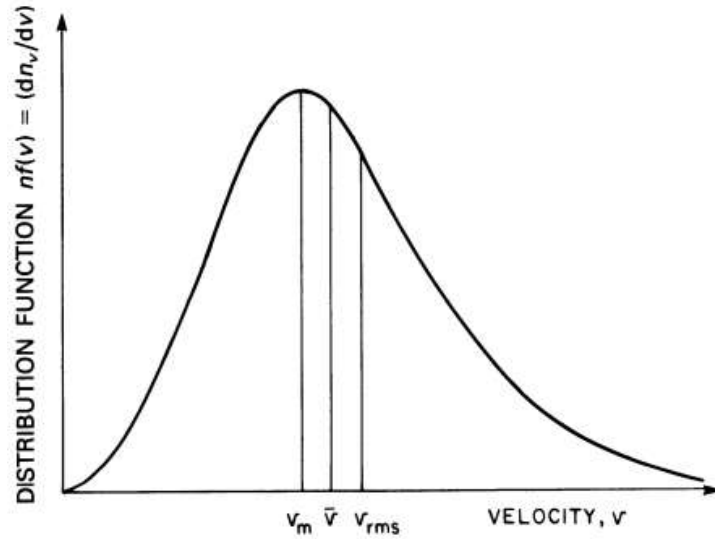


Figure 2.1: Example of a Maxwellian distribution for velocity (v). v_m is the most probable velocity, $\bar{v}$ is the mean average velocity, and v_{rms} is the root mean square average velocity. Reprinted from [49] copyright (1994) with permission from Springer.

$$f(v) = \frac{4}{\sqrt{\pi}} \left(\frac{2k_b \cdot T}{m} \right)^{3/2} \cdot v^2 \exp \left(-\frac{m \cdot v^2}{2k_b \cdot T} \right) \quad (2.1)$$

In Equation 2.1, k_b is the boltmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), T is temperature (in K), m is the particle mass mass (in kg), and v is the particle velocity (in m s^{-1}). Collisions in a plasma are an important factor in plasma physics. When two particles get close to each other, they interact and their properties (such as velocity or temperature) can be transferred. A collision does not mean that the two particles come into physical contact, the particles interact over a larger distance [49]. A collision between two neutral particles of similar mass is illustrated in Figure 2.2. Figure 2.2 shows the particles, m_1 and m_2 , attracting each other before being repelled. Here, the impact parameter is the perpendicular distance between two particles.

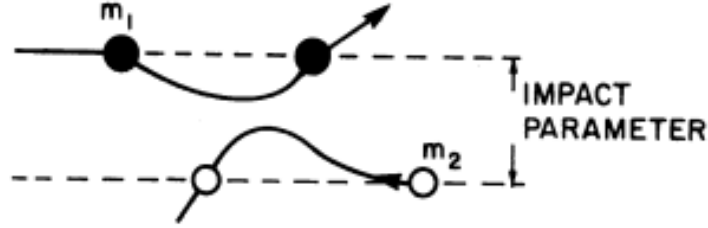


Figure 2.2: Illustration of a collision between two particles. Reprinted from [49] copyright (1994) with permission from Springer.

Since a plasma is comprised of electrons, ions, and neutral particles, there are different types of collisions depending on which particles are interacting. Electron collisions are responsible for most of the transport of energy in a plasma [54], however due to the low mass of electrons, the energy transfer of electron-heavy particle collisions is low [55]. Collisions can be either elastic or inelastic. In elastic collisions, the kinetic energy (or temperature) is conserved. A fraction of the kinetic energy of one particle is transferred to another. This is the case for most collisions of neutral particles at room temperature [49]. One important type of elastic collisions in a plasma are Coulomb collisions [56]. This is due to the Coulomb force, which originates from the charged particles and is proportional to the reciprocal of the distance between them ($\propto 1/r^2$). This covers a much larger distance than the size of the particles [51]. Kinetic energy is not conserved

with inelastic collisions, also called chemical reactions. While the total energy must be conserved, some of the kinetic energy is used to increase the internal energy of a particle. Examples of inelastic collisions include dissociation, ionisation and charge transfer [49]. Collision cross sections are an expression of the probability of a collision. This is a measure of the area of a particle where a collision will take place, and is unique for any pair of particles [57]. The cross section is denoted as σ , and is averaged over all orientations [58].

At equilibrium, a plasma can be considered quasi-neutral (almost neutral). Quasi-neutrality is where positive and negative charges nearly balance in any given volume with sides much larger than the Debye length. The Debye length is the distance a charge particles' EM field influences, and can be calculated as shown in Equation 2.2, where ϵ_0 is the permittivity of free space (8.85×10^{-12}), k_b is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), T_e is the electron temperature (in K), and n_e is the electron number density (m^{-3}).

$$\lambda_D = \sqrt{\frac{\epsilon_0 \cdot k_b \cdot T_e}{n_e^2}} \quad (2.2)$$

Quasi-neutrality can be mathematically shown as $n_e \approx Zn_i$, where Z is the charge number of the ions, and n_i is the number density of ions. A plasma will attempt to reach quasi neutrality if an external influence causes an imbalance of charge. For example, if an object with a positive net charge is placed in a plasma at equilibrium, additional free electrons will be attracted to balance the total charge in the volume [51].

The degree of ionisation of a plasma can be calculated using the Saha equation, shown in Equation 2.3. The Saha equation only applies when the plasma is in thermal equilibrium (i.e. electron and gas temperatures are roughly the same, $T_e \approx T_g$). Plasma equilibrium is explained in Section 2.1.1.

$$\frac{n_i}{n_e} \approx 2.4 \times 10^{21} \frac{T^{1.5}}{n_i} \exp\left(\frac{-U_i}{k_b T}\right) \quad (2.3)$$

Where T is the temperature (in K) and U_i is the ionisation energy (in J). There

is no quantifiable degree of ionisation that constitutes a plasma. There can be some confusion between degree of ionisation of a plasma and how strongly ionised it is. When a plasma is described as a weakly or strongly ionised, this relates to the type of collisions which are dominant. A strongly or fully ionised plasma is described as being dominated by Coulomb collisions, where electron-ion collision frequency (ν_{ei}) $\gg$ electron-neutral collision frequency (ν_{en}). Whereas the degree of ionisation is what fraction of atoms in the plasma are ionised [50].

2.1.1 Plasma equilibrium

While plasma's can broadly be categorised into either thermal or non-thermal, this can be expanded to four states of thermodynamic equilibrium: Thermodynamic equilibrium (TE), local thermodynamic equilibrium (LTE), partial local thermodynamic equilibrium (PLTE), and non equilibrium.

TE exists when the electrons and heavy particles are at the same temperature. In a plasma at TE, elastic collision are responsible for all the energy transport [52]. A plasma is rarely ever considered as in true TE, due to both the mass difference between the electrons and ions/neutrals (heavy particles) and collisions within the plasma. The lighter electrons are far more responsive to excitation or perturbations/instabilities in the plasma. This is why a plasma cannot be considered in true TE if it is confined by a static EM field [59].

LTE or PLTE are often a more accurate description of a real world plasma. LTE is considered close to true TE when considering a small volume. The temperature deviations are very slight and can be considered constant, as in true TE. Fujimoto and McWhirter state the population density of a given quantum level can be described by the Saha-Boltzmann equation [60]. Griem defines LTE as a state where collisional processes dominate over radiative processes [61]. The criterion proposed by Griem for collisional processes to dominate, is shown in Equation 2.4. This gives a minimum electron density for a plasma to be considered in LTE [62]. In Equation 2.4, ΔE is the energy difference between the ground and first ionisation state, E_H is the ionisation potential for a

hydrogen atom ($13.6 \text{ eV} = 2.18 \times 10^{-18} \text{ J}$), and T_e is the electron temperature (in K).

$$n_e \geq 9 \times 10^{11} \left(\frac{\Delta E}{E_H} \right)^3 \sqrt{\frac{T_e}{E_H}} \quad (2.4)$$

Thermal plasma's are often considered close to LTE, where the electrons and heavy particles are at the same temperature [51]. There are three general rules which have to be met for a plasma to be considered thermal: ionisation equilibrium (Saha-Eggert law), dissociation equilibrium (Guldberg-Waage law), and excitation equilibrium (Boltzmann's law). These three laws describe inelastic collisions [55], and state that the reactions: $A \leftrightarrow A^+ + e^-$ (ionisation), $AB \leftrightarrow A + B$ (dissociation), and $A + \Delta E \leftrightarrow A^*$ (excitation) are in equilibrium. Here, A and B are arbitrary atoms, e^- is an electron, ΔE is an amount of energy, and A^* is an excited atom [55]. While thermal plasma is considered in a state of LTE, thermal plasma flows, such as plasma jets, are not necessarily in kinetic equilibrium, especially near an electrode [63]. Thermal plasma's are often used for applications such as: cutting, welding and material processing industries due to their high temperatures (up to 15,000 K), and high energy density (up to 10^8 W m^{-3}) [64].

In PLTE the temperature can no longer be considered constant, the heavy particles are considerable cooler than the electrons. This becomes a more complex situation to model since the density of neutrals and ions can vary locally which can lead to local instabilities or perturbations, introducing non equilibrium effects. Various papers have been published looking at PLTE [60,61,65–68]. However, as Hey notes, that due to the complexities involved, many only consider specific situations [69].

A plasma can also be in a non equilibrium state, sometimes called non thermal plasma. In a non thermal plasma, the electron temperature (kinetic energy) is much higher than the heavy particle temperature, sometimes by two orders of magnitude [55]. A non equilibrium state can be maintained in a plasma, when the energy transfer to the electrons is faster than the energy transfer to heavy particles via collisions [42]. This is the case when an applied EM field has a frequency high enough that the ions cannot respond to it (such as microwave frequency) [70].

2.1.2 Atmospheric and Low Pressure Plasma

The simplest setup for the formation of a plasma involves two electrodes to heat up a gas enough for ionisation to occur. The electrodes create an EM field to transfers energy to the electrons and contain it [35]. A plasma is initially created due to an electron/ionisation avalanche (also called a Townsend breakdown), where an incident electron collides with a neutral atom and releases an electron(s). These free electrons then go on to ionise further atoms [56]. This process is illustrated in Figure 2.3 for a gap with size, d , and an applied electric field with strength E_0 .

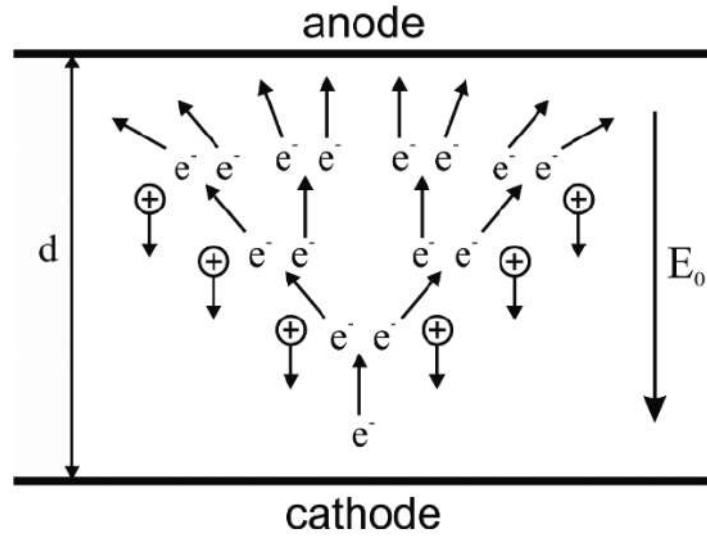


Figure 2.3: Illustration of an electron avalanche [71].

This avalanche occurs when the applied potential difference (voltage) between the anode and cathode, exceeds the Breakdown Voltage (V_b). The breakdown voltage can be found from Paschen's Law, which is shown in Equation 2.5.

$$V_b = \frac{B \cdot p \cdot d}{\ln(A \cdot p \cdot d) - \ln(\ln[1 + 1/\gamma_{sc}])} \quad (2.5)$$

Where: A and B are constants, related to the gas ionisation energy (experimentally found), p is the pressure (in Pa), d is the discharge gap (in m), and γ_{sc} is the secondary electron emission coefficient. The electron avalanche can also be described by the Townsend coefficient, α , which is a measure of the number of free electrons produced

per unit length in an electric field [56]. The Townsend coefficient is related to A and B in Equation 2.5, and can be calculated as shown in Equation 2.6 [56, 72].

$$\alpha = \frac{1}{\mu_e} \cdot \frac{k_i \cdot (E/n_0)}{(E/n_0)} = A \cdot p \cdot \exp\left(-\frac{B \cdot p}{E}\right) \quad (2.6)$$

Where, μ_e is the electron mobility (proportional to $1/p$, with units of $\text{cm}^2 \text{V}^{-1}\text{s}^{-1}$), k_i is the ionisation rate coefficient, and n_0 is the number density of particles in the ground state [56]. There are many ionisation rate coefficients depending on the type of ionisation, and the initial and final ionisation state. An example for the calculation of the ionisation rate coefficient for direct electron impact ionisation (energy transfer from an electron to a neutral atom, exceeding the ionisation potential), is shown in Equation 2.7. This assumes a Maxwellian electron energy distribution for the ionisation of a neutral atom [56].

$$k_i = \sqrt{\frac{8T_e}{\pi \cdot m_e}} \cdot \sigma_0 \cdot \exp\left(-\frac{I}{T_e}\right) \quad (2.7)$$

Where: T_e is the electron temperature (in K), m_e is the electron mass (9.11×10^{-31} kg), I is the ionisation potential of the neutral atom (in J), and σ_0 is the atomic cross section (in m^2) [56]. Paschen's law shows that the breakdown voltage is highly dependent on $p \cdot d$ (pressure-gap length). A Paschen curve shows the relationship between V_b and $p \cdot d$ across all values of $p \cdot d$. Figure 2.4 shows Paschen curves for various commonly used gasses in plasma processing.

The Paschen curves in Figure 2.4, show a minimum value for breakdown voltage, which differs for each gas. A Paschen curve can be split into two sections, a steep decrease in V_b at low $p \cdot d$ values, and a gradual increase in V_b as $p \cdot d$ increases. Different mechanisms are responsible for these two sections. The sharp decrease in V_b at low $p \cdot d$ values is strongly influenced by secondary electron emission of the electrodes, whereas the increase in V_b is dominated by collisions [73]. As the pressure increases, the mean free path, λ_e , of electrons decreases. The mean free path is defined as the distance a particle travels before a collision, meaning at higher pressures, there is less distance between collisions. The mean free path can be calculated with Equation 2.8, as the

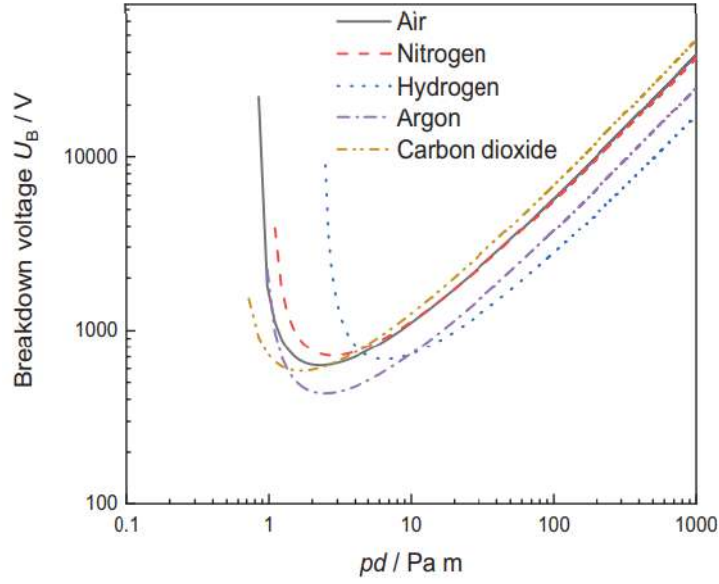


Figure 2.4: Paschen curve for various molecules commonly used in plasma processing [71].

distance particle 'a' travels, before colliding with particle 'b' [49].

$$\lambda_a = \frac{v_a}{v_a - v_b} \cdot \frac{1}{n_b \cdot \sigma} \quad (2.8)$$

Where: v_a and v_b are the average velocity of particles a and b (in m s^{-1}), and σ is the collisional cross section (in m^2). For an electron colliding with a heavy particle, the mean free path can reduce to Equation 2.9, since the velocity of electrons, v_e , is typically much greater than the velocity of heavy particles, so in Equation 2.8, the term $v_a/(v_a - v_b) \approx 1$ [49].

$$\lambda_e \approx \frac{1}{n_n \cdot \sigma} \quad (2.9)$$

Where n_n is the number density of neutral particles (in m^{-3}). There are variations between theoretical and experimental results of Paschen curves. It has been suggested that these variations are due to factors not included in Equation 2.5, such as: electrode configuration, electrode surface features, and charged particle densities [74]. In general, Paschen law shows that for a given discharge gap, a plasma will require a larger breakdown voltage as pressure increase.

Atmospheric pressure plasma (APP) has seen growing interest as a replacement for low pressure plasma systems, since expensive vacuum equipment can be avoided [38]. Increasing the pressure tends to bring a plasma closer to thermal equilibrium, since at higher pressures there is a higher density of particles [39]. Higher densities lead to a decrease in the mean free path and increased chance of elastic collisions. The elastic collision heat the heavy particles, bringing the plasma closer to thermal equilibrium [39]. The excitation frequency and composition of the gas also impact the thermal equilibrium of the plasma [75, 76]. The difference in these two temperatures depends on how the thermal energy is transported through the plasma. The difference between the electron temperature, T_e , and the gas temperature, T_g , in a plasma can be modelled as shown in Equation 2.10, which was derived from energy conservation [75].

$$\frac{T_e - T_g}{T_e} = \frac{\pi m_g (\lambda_e e E)^2}{24 m_e (k_b T_e)^2} \quad (2.10)$$

Where m_e and m_g is the electron and gas (heavy particle) mass respectively (in kg), λ_e is the electron mean free path (in m) and E is the electric field strength (in V m⁻¹) [75]. The term $\lambda_e \cdot e \cdot E$ represents the amount of energy the electrons gain over a distance of one mean free path. Equation 2.10 is an estimate since it does assume only elastic collisions, which is not always the case in a real world application.

Figure 2.5 illustrates how a plasma discharge tends towards thermal equilibrium at higher pressures. Increasing the pressure of the plasma increases the likelihood of a collision of a hot electron with another cooler particle, cooling the electron and heating the heavy particle. As an electron is much lighter than ions/neutrals, it takes many electron-heavy particle collisions to heat the gas temperature, which is why the T_e curve initially decreases with little increase in T_g in Figure 2.5. As the collisions become more and more frequent, the temperatures tend towards an equilibrium, in this case around 10 kPa. Operating at higher pressures also increases the likelihood of local instabilities forming in the plasma [70]. This can also aid in heat transport and increase collisionality, especially notable in very high temperature plasma's, such as fusion plasma [77].

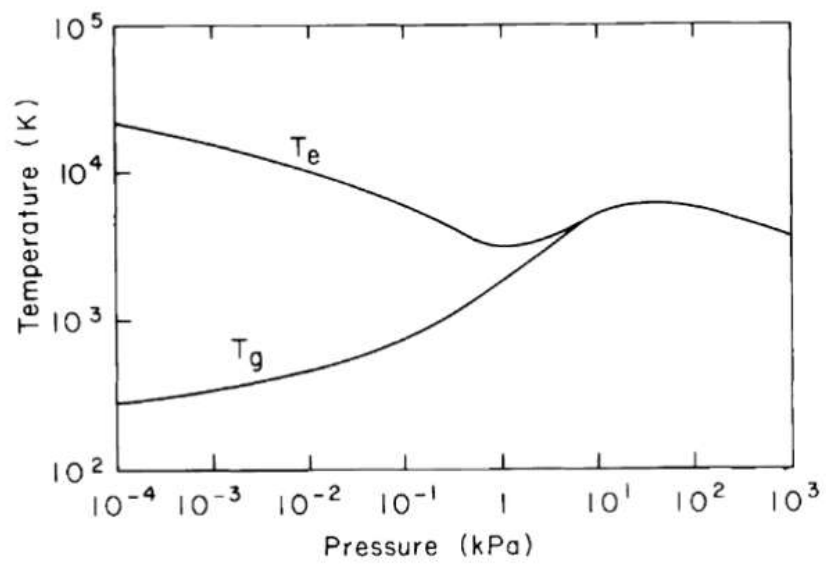


Figure 2.5: Illustration of how electron and gas temperature change as pressure increases. Reprinted from [39] copyright (2006) with permission from Elsevier.

2.1.3 Plasma torches

The characteristics of the plasma generated from a plasma torch is dependent on both the power source, and the design of the torch. The power source frequency impacts the plasma equilibrium (refer to Section 2.1.1). There are many types of plasma discharges, however the most common are: glow discharge, arc discharge, radio frequency (RF), and microwave frequency (MW) [78].

Glow discharges are low power plasmas, typically at low pressure [76]. Glow discharges are often used for spectro-analysis, where a material is inserted into the plasma. Through spectroscopy techniques (such as a mass spectrometer), the materials' composition can be accurately determined [79]. Glow discharges are supplied by both direct current (DC) and alternating current (AC) power sources. A DC power source supplied a continuous current to the electrodes. However, a DC power source poses the problem of arcing between the electrodes at higher powers [42]. With a AC power source, the alternating supplied to the electrodes, means the cathode and anode switch at the input frequency. AC plasma discharges have been shown to have a longer lifetime than DC torches, due to this periodic change in polarisation of the electrodes [80].

An arc discharge is a thermal plasma with a much higher plasma density, and occurs at a higher current than a glow discharge [42]. An electric arc is formed between the electrodes, causing an electron avalanche [81] (refer to Figure 2.3). The most commonly used arc discharge plasmas have a DC power source and operate at higher (atmospheric) pressure [82]. Applications of DC arc discharges include plasma spraying, cutting and welding [63].

An RF plasma discharge has and AC power source (although RF-DC hybrid plasma torches have been developed [83]), operating in the radio frequency band. RF sources operate in the frequency range of between 1 - 100 MHz [84]. RF plasma discharges are thermal, and the energy is primarily coupled into the electrons, then transferred to the heavy particles via collisions. Therefore, RF plasma torches are typically used at high pressures (atmospheric) to increase the collisional coupling of energy to the heavy particles [49]. The energy coupling in an RF plasma discharge can be achieved via

the electric field (capacitive coupling, or E discharge) or the magnetic field (inductive coupling, or H discharge) [84]. Capacitively coupled plasma (CCP), and inductively coupled plasma (ICP) torches are discussed in Sections 2.1.3.1 and 2.1.3.2 respectively. Energy coupling efficiency of an RF discharge is typically 40 - 50% [85]. But the main benefit of a thermal RF discharge is the flexibility of gas chemistry, almost any gas can be used [86].

Microwave plasma is typically generated at a frequency of ~ 2.4 GHz [87]. Similarly to RF discharges, the energy in a MW discharge is initially absorbed by the electrons, and transferred to the heavy particles through collisions [49]. While most MW discharges are considered non thermal, MW plasma torches approach a state of LTE at higher powers (kW's) [62]. The energy coupling at MW frequency is typically higher than at RF frequency, with some cases reporting energy coupling efficiency of nearly 100% [85, 88]. MW plasma discharges are used for: spectroanalysis, plasma chemistry, sterilisation, and surface modification [62, 85, 89–91].

Other types of plasma discharges include: surface wave launched [92, 93], dielectric barrier discharge [94, 95], theta pinch [96, 97], laser produced [98, 99] and exploding wires [100]. However, these discharges will not be explored in this work.

Plasma jets are formed where a plasma is accelerated into an energy beam by an EM field. There are many types of plasma torch design, with differing energy coupling mechanisms and plasma density characteristics. For material removal applications, a thermal plasma is preferred due to its energy density [64]. Sections 2.1.3.1 and 2.1.3.2 explore CCP and ICP coupling mechanisms of RF plasma torches.

2.1.3.1 Capacitively coupled plasma

CCP torches couple energy to a plasma through the electric field, between an anode and a cathode, with a potential difference between them. This potential difference ionises an input gas which creates the electron avalanche. An illustration of a CCP plasma torch is shown in Figure 2.6(a).

CCP torches are robust and can operate in a large power regime (10's to 1,000's

of Watts) and frequency regime (10 MHz - 150 MHz) [101]. This kind of setup under atmospheric conditions has four characteristic zones; A 'superficial luminescent' zone close to the tip of the electrode, A 'dark space' around the sharp electrode (possibly caused by electrode ablation or in-homogeneous EM field lines so close to the electrode tip), A hot core and a cooler sheath/coat around the core [102]. A CCP typically has a higher electron temperature compared to an ICP, but a lower electron density [103].

With a CCP torch design as shown in Figure 2.6(a), the cathode must have a sharp tip for efficient plasma coupling, and it will be worn down over time so will need to be replaced regularly. Some designs have removed this sharp tipped electrode and placed an electrode ring outside of the dielectric tube [104]. This torch was specifically designed for nebulisation as well as providing a more stable plasma over time since the electrode was not being worn.

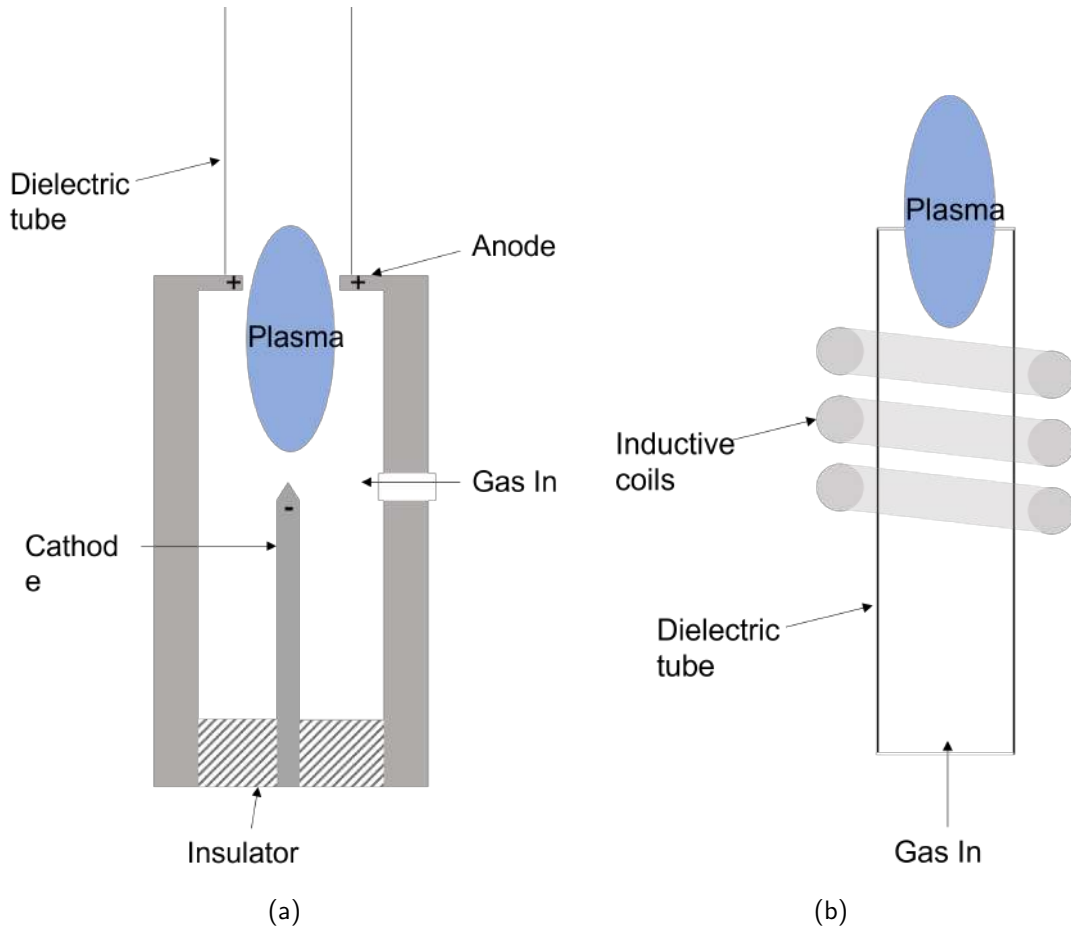


Figure 2.6: Illustration of (a) CCP torch, and (b) ICP torch.

2.1.3.2 Inductively Coupled Plasma

Inductively Coupled Plasma (ICP) torches couple energy to a plasma via a two step process. RF current is supplied to the induction coils, which creates a magnetic field as described in Faraday's Law of induction, the resultant electric and magnetic fields couple energy into the ionised plasma. An illustration of a simple ICP torch design is shown in Figure 2.6(b).

The majority of RF plasma torches are ICP [86]. ICP torches are more common since lower frequencies can produce a thermal plasma, compared to CCP torches. Using the magnetic field to couple energy into the electrons, increases the power dissipation (via collisions) in the plasma [49]. Figure 2.7 shows the power dissipation per unit volume, against the driving frequency for an E discharge (CCP) and an H discharge (ICP). The line between hot and cold is the cutoff for a thermal plasma.

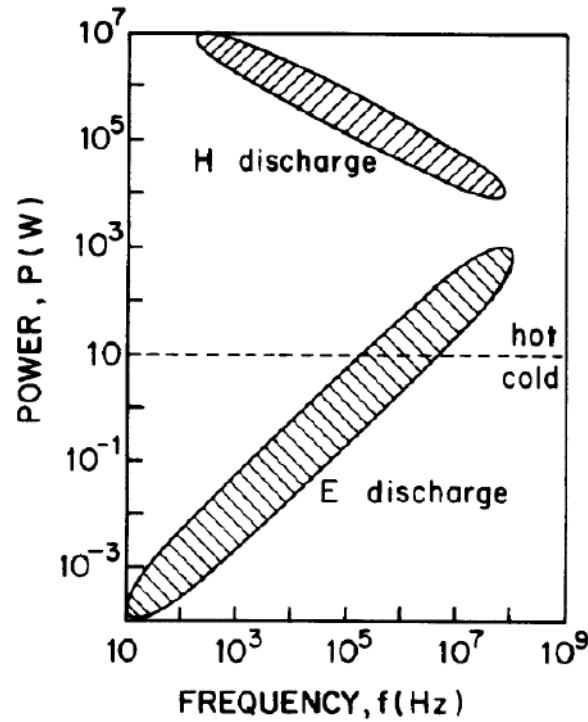


Figure 2.7: Power dissipation per unit volume against input power frequency for E and H discharges. Reprinted from [49] copyright (1994) with permission from Springer.

A problem encountered with ICP torch designs is the large quantities of argon required for cooling and shielding purposes as well as to maintain plasma stability.

Many studies have been published attempting to reduce this via altering the torch geometry [105–107] or using water/air cooling [108–111]. ICP plasma torches can also develop various effects, such as nonlinear plasma polarisation, due to forces from interactions between the plasma and induced EM field such as the Lorentz and ponderomotive forces [112].

2.2 Plasma Etching

Plasma etching was initially developed as a replacement for wet chemical etching [113]. There are 4 main types of plasma etching: Sputtering/Ion bombardment, Chemical, Ion energy driven and Ion enhanced inhibitor etching. These 4 types are illustrated in Figure 2.8. They are all slightly different but are based on the same basic principle:

- An etchant is passed through an EM field strong enough to ionise it, forming a plasma.
- The plasma is then directed at a substrate and the reactive species bombard the surface.
- The ionised particles react with the substrate surface, forming volatile molecules.

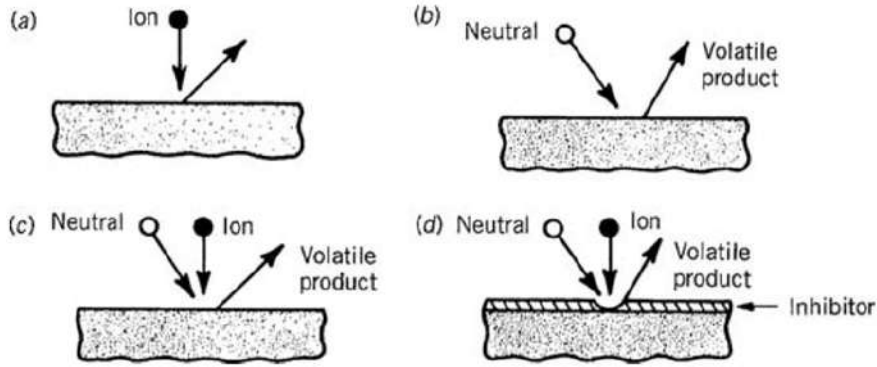


Figure 2.8: Four basic plasma etching processes: (a) sputtering, (b) pure chemical etching, (c) ion energy-driven etching, (d) ion-enhanced inhibitor etching. Reprinted from [42] copyright (2005) with permission from John Wiley and Sons.

The etching rate of a plasma jet is dependent on the chemical reaction rate of the etchant in the plasma and the surface. This follows the Arrhenius equation (Equation 2.11), which shows the chemical reaction rate is dependent on the temperature of the reactants [114]. In Equation 2.11: k is the reaction rate, A is a pre-exponent factor expressing the number of collisions, E_a is the activation energy, R is the universal gas constant and T is the temperature in kelvin.

$$k = A \cdot e^{\frac{-E_a}{R \cdot T}} \quad (2.11)$$

The plasma jet acts as a heat source, heating the substrate as well as providing the species to react with the surface. This leads to the etching process being highly non-linear since the temperature of the surface and reactants are not constant. This non-linearity in etch rate can also be due to variations in the surface of the substrate or instabilities in the plasma jet or environment. Since the plasma etching rate is highly dependent on the plasma temperature, when using a non-thermal plasma a substrate often requires preheating to achieve high etch rates [115].

Sputtering is a well understood process involving an energetic particle, often ions, which are directed at a surface of a material to alter the materials' surface. When talking of sputtering in a material removal process, atoms are ejected from the surface of a substrate due to the physical bombardment of heavy particles [116]. The incident particle collides with the surface which triggers a 'collision avalanche'. Most atoms are trapped within the surface, however some escape. The amount of escaping atoms per incident particle; the sputtering yield ($Y_{sputter}$) and the threshold energy in order for a particle to escape the surface depends mainly on the surface binding energy of the substrate and the mass of the incident particle. Anders [117] proposed a simple equation for calculating sputtering yields, however it is only valid for low ion energy (300eV - 3keV) incident ions, shown in Equation 2.12

$$Y_{sputter} = a \cdot E_i^b \quad (2.12)$$

Here, a and b are fitting parameters dependent on the target material and the mass of the incident particles and E_i is the energy of the incident particle. There have been many papers and reports published listing calculated sputter yields, however Yamamura and Tawara [118] and Ekstein [119, 120] have provided the most thorough accounts, taking into account energy and angular dependencies. During plasma etching, the contribution of sputtering to the overall material removal rate is considered to be negligible.

For chemical, ion-driven and ion enhanced inhibitor etching, a suitable etchant must be used in order to create volatile products with the substrate. Pure chemical etching does not necessarily involve the use of a plasma torch or ionised species. Ion energy-

driven etching does require a plasma, it is a combination of sputtering and chemical etching where an etchant is chosen based on the substrate and injected into a plasma to create energetic ions. This process can produce a much larger etching rate than either sputtering or chemical etching combined, as shown in Figure 2.9, since when the etchant is ionised it is far more reactive. Similar to ion energy driven etching, an ion enhanced inhibitor etching process involves both sputtering and chemical etching, however a mask layer or 'inhibitor' is deposited on the surface which the reactive radicals do not preferentially etch. The material for this mask layer has to be specifically chosen as something that will not create volatile products with the plasma. The mask is often deposited using lithography techniques or by a separate plasma deposition process. A common use for this technique is for the manufacture of transistors. Many published articles investigate this process as it is key for the development of computing power to reduce feature sizes on transistors [40, 121, 122]. Modelling of this process is carried out using Monte Carlo simulations [123]. Table 2.1 shows a comparison of the material removal rate (MRR) of APP etching to alternative techniques.

Table 2.1: Comparison of typical MRR for APP etching and alternative techniques [41].

Technique	Material Removal Rate ($\text{mm}^3 \text{ min}^{-1}$)
APP etching	0.1 - 50
Precision Grinding	2 - 200
Polishing	0.03 - 280
MRF	0.3 - 13
IBF	~ 0.01

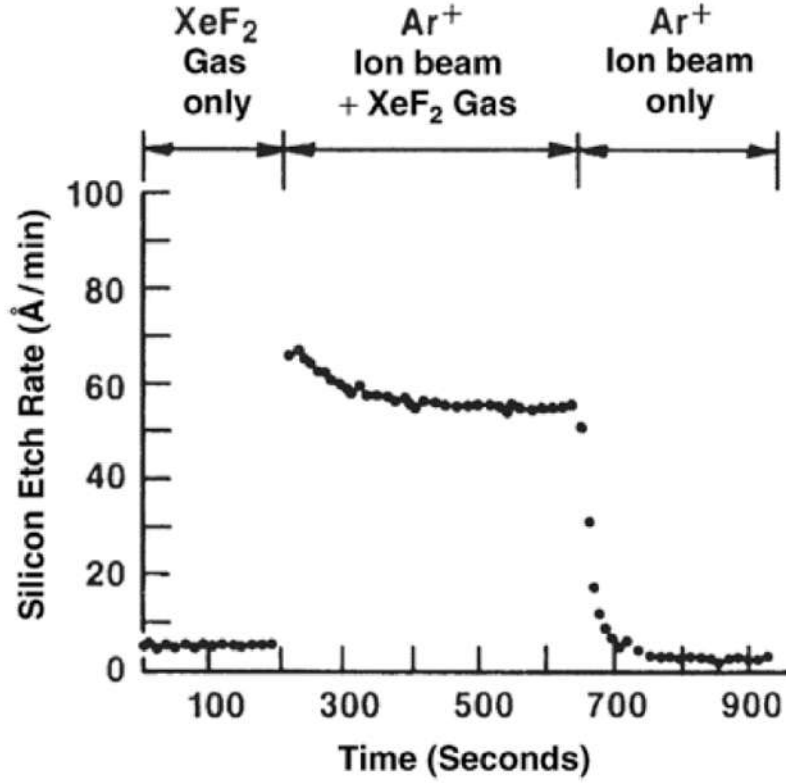


Figure 2.9: Experimental data comparing etch rates of: ion-enhanced plasma etching, pure Ar⁺ sputtering and xenon difluoride chemical etching on silicon. Reprinted from [42] copyright (2005) with permission from John Wiley and Sons.

2.2.1 Plasma Etching of Glass

Plasma etching has been carried out for various silicon-containing materials showing extremely high precision and accuracy [41]. As a non-contact method, plasma etching also leaves negligible surface damages which is imperative for applications such as optics, where nm scale defects can render the optic unusable.

There are many different types of silicon containing materials commonly used for optics, see Table 2.2 for a comparison of their properties. Many studies have been carried out using plasma jets to etch, polish or otherwise alter these silicon based surfaces such as silica [124], SiC [125, 126] and ULE[®] [45].

Fluorine radicals generated from gasses such as SF₆, CF₄ or NF₃ are commonly used for silicon based materials. Plasma etching of silicon based materials has been well established for applications such as manufacture of semiconductors, with a removal

Table 2.2: Properties of commonly used silicon containing materials used for optics applications.

* Variation due to different compositions of Zerodur® and Zerodur® K20.
 ** dependent on method of preparation.

Material	Elemental contents	Thermal Conductivity
Fused Silica	Si-O	1.28 [127]
Crystalline Quartz	Si-O	5-6 [128]
ULE®	Ti-Si-O	1.31 [129]
Zerodur®	Li-Ti-Si-O	1.46-1.63* [130]
Silicon Carbide	Si-C	30-490** [131]
BK7	Si-O-B-Ba-K-Na-As	1.1 [132]

mechanism based on the reaction of fluorine radicals in the plasma and the silicon based substrate to form volatile products. An example for fused silica being $SiO_2 + 4F^\bullet \rightarrow SiF_4 \uparrow + O_2 \uparrow$. Fluorine chemistry is suitable for this due to the high selectivity of fluorine towards silicon and the low thermal conductivity of the samples. This helps 'trap' the thermal energy in the etching zone and prevents unwanted material removal. Oxygen is often added to the plasma jet, as it promotes the dissociation of these gases and removes any sulphur/carbon/nitrogen via oxidation [133], which could otherwise contaminate the surface.

2.2.2 Modelling Plasma Etching

Although the etching rate of a reactive plasma jet is dependent on the chemical reaction rate (which in turn is temperature dependent), the real world etching rate is also dependent on other factors including: substrate surface conditions (e.g. surface roughness), chemical composition and plasma stability. In order to model the plasma etching process and determine the material removal rate these other relevant parameters must be identified.

The material removal rate function of a plasma etching process, $R(x,y)$ can be estimated as the convolution of the beam function, $B(x,y)$ and the dwell time function $\tau(x,y)$ as shown in Equation 2.13. This is based on convolution algorithms used for ion beam figuring, and $*$ signifies the convolution operator [134]. Here, the dwell time function has units of $s\ mm^{-2}$ and describes the amount of time the torch dwells over a given area.

The beam function is taken as the characteristic footprint of a given plasma torch and workpiece, typically a 3D gaussian, and has units of nm s^{-1} . These functions are determined via multiple experiments to achieve a trend of etch depth against time. However, Equation 2.13 requires the assumptions of linear material removal rate and long term spatial and temporal stability. For plasma etching, these assumptions cannot necessarily be made. The plasma torch acts as a heat source which leads to non linearity of the material removal function both spatially and temporally, since the torch itself introduces significant temperature gradients across the substrate during machining [114].

$$R(x, y) = \int_{-x}^x \int_{-x}^x B(x - u, y - v) \cdot \tau(u, v) \cdot du \cdot dv = B(x, y) * \tau(x, y) \quad (2.13)$$

Adaptations of Equation 2.13 have been made to better estimate the material removal function, taking other effects into account. Equation 2.14 includes the dependence of the beam function on the dwell time/velocity function, where the velocity function is proportional to $1/\tau$ [135]. This does however assume that the temperature is only dependent on the dwell time/ processing speed and does not include heat conduction/dissipation effects. Both equations 2.13 and 2.14 also assume that material removal is linearly related to dwell time. This is also not necessarily valid. This assumption would lead to predictions of constant etch depth at a constant processing speed, which is not necessarily true for a real plasma etching process.

$$R(x, y) = \int_{-x}^x \int_{-x}^x B(x - u, y - v, \tau(u, v)) \cdot \tau(u, v) \cdot du \cdot dv \quad (2.14)$$

Due to this, Meister and Arnold proposed a new approach, taking into account both the heat flux from the plasma jet and thermal conduction within the substrate after applying proper boundary conditions, shown in Equation 2.15, where $p_x(t)$ and $p_y(t)$ are the current torch position, $T(x, y, t)$ is the spatially and temporally dependent surface temperature field and $B(x, y, T)$ is the local temperature dependent beam function [114]. Taking all these factors into account obviously makes the determination of the material

removal function far more complex with Meister and Arnold reporting computational times of 16-20 hours, and determination of heat flux from the torch and heat conduction within the workpiece is non trivial.

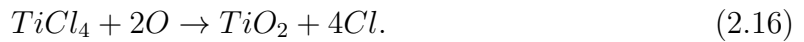
$$R(x, y) = \int_0^{t_{end}} B(x - p_x(t), y - p_x(t), T(x, y, t)).dt \quad (2.15)$$

2.3 Plasma Etching of Metals

There have been many previous studies into the chemical plasma etching of metals. Most have been conducted in a low pressure environment for reasons explained in chapter 2.1.2, with no examples in literature for the plasma etching of Ti-6Al-4V (Ti64). Due to this lack of literature, this section explores the plasma etching of titanium, aluminium and vanadium - the alloying metals in Ti64.

2.3.1 Titanium

Blumenstock & Stephani showed a substantial increase in etch rate of pure Ti when adding fluorine containing compounds to a chlorine based plasma etching process at low pressure [136]. Figure 2.10 shows etch rates for a CCl_4/O_2 plasma and $\text{CCl}_4/\text{CCl}_2\text{F}_2/\text{O}_2$ as a function of pressure. They noted that at higher pressures (above 2.5Pa) a brown layer was forming on the Ti surface which was preventing etching when using a CCl_4/O_2 plasma. They concluded that the addition of fluorine prevented the formation of this brown layer which was determined to be TiO_2 by x-ray photoelectron spectroscopy (XPS) analysis. XPS is a technique used to analyse the surface chemistry and composition, based on the photoelectron effect. By bombarding the surface with x-rays, and measuring the energy of emitted electrons (which relates to the binding energy of an electron in the inner orbital), the substrate composition is determined, since this binding energy is unique for each material [137]. They proposed that the only volatile product being formed was TiCl_4 and that fluorine reduced the reaction rate of TiCl_4 decomposition in the plasma plume. The reaction for the decomposition of TiCl_4 is shown in Equation 2.16.



Fracassi & d'Agostino showed that adding fluorine to a chlorine glow discharge plasma catalyses the etching process of Ti thin films. They suggested that once the oxide layer has been removed through high energy ion bombardment, the TiO_2 layer is replaced by a layer of fluorinated titanium which reacts more readily with chlorine [138].

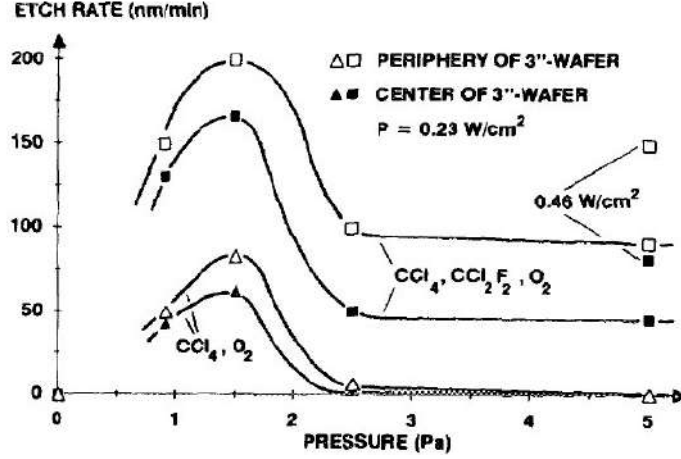


Figure 2.10: Etch rates of titanium in a CCl_4/O_2 , and a $\text{CCl}_4/\text{CCl}_2\text{F}_2/\text{O}_2$ plasma against pressure. . Reprinted from [136] copyright (2011) with permission from American Vacuum Society.

Amirov et al. showed sputtering rate dependencies on the O_2 concentration in an Ar/O_2 plasma at low pressure when etching various metal films. They showed that above about 3.5% O_2 the sputtering rate (V_{sp}) of titanium drops to 0 [139], see Figure 2.11. They explained that this is due to the sputtering yield of TiO_2 being far lower than that of pure Ti. The oxygen in the plasma was causing uncontrollable oxidation on the surface during etching, resulting in an oxide film. They also concluded that the 'memory effect' had an influence, meaning surrounding surfaces and the substrate holder should be pre-treated with pure Ar plasma before each run, removing any residual oxygen impurities.

Parker et al. [47] carried out etching of commercially pure titanium using an ICP system at low pressure (2 Pa). They used a Cl_2/Ar plasma to deep etch Ti and investigated etch rates of the bulk Ti, TiO_2 mask layer and the resultant surface roughness. They concluded that higher ICP power lead to higher etch rates at the cost of an increase in surface roughness, as shown in Figure 2.12. Zhao et. al. showed similar results in terms of Cl_2 flow rate during deep reactive ion etching (DRIE) of bulk Ti in an ICP system, using a negative photoresist instead of a hard TiO_2 mask. They showed the root mean square (RMS) surface roughness increases with Cl_2 flow rate, however increasing the source power, decreased the RMS roughness, although they did not provide

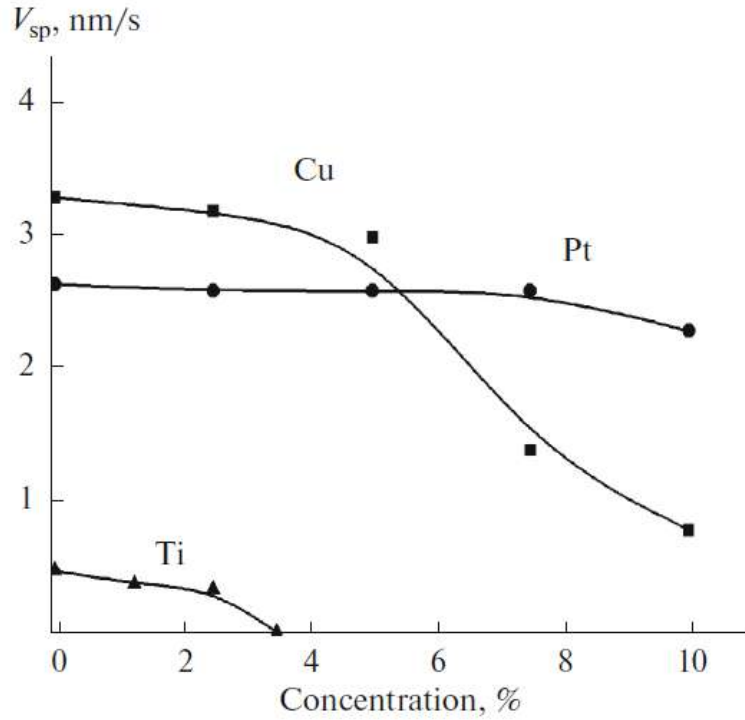


Figure 2.11: Sputtering rate dependency on O_2 concentration for various metal films when exposed to an Ar- O_2 RF-ICP plasma ($p = 0.34$ Pa, $P = 190$ - 250 W) Reprinted from [139] copyright (2011) with permission from Springer Nature.

an explanation as to why [140].

Löffler conducted experiments on the reactive ion etching (RIE) of titanium using an $SF_6/CHF_3/O_2$ mixture. By varying the gas ratios and chamber pressure, they measured the anisotropy of the etch and the etch rate. They showed that by changing these parameters, the etch rate could be increased at the expense of undercutting the mask. They also suggested that a similar process seen with fluorocarbon etching of silicon was occurring with titanium, that CHF_3 was forming a fluorocarbon polymer, protecting the sidewalls of the etch [141].

Li et. al. showed a comparison of fluorine etchants (CF_4 , C_2F_8 and SF_6) during ICP etching of $BaTiO_3$ thin films. Through AFM and XPS analyses, they showed higher etch rates when using SF_6 and less non volatile by-products (e.g. metal oxides/ CF_x compounds) compared with CF_4 and C_2F_8 [142].

Norasetthekul et. al. investigated the dry etch chemistry of TiO_2 films. They found that TiO_2 can be effectively etched using both Ar/ SF_6 and Ar/ Cl_2 discharges, with SF_6

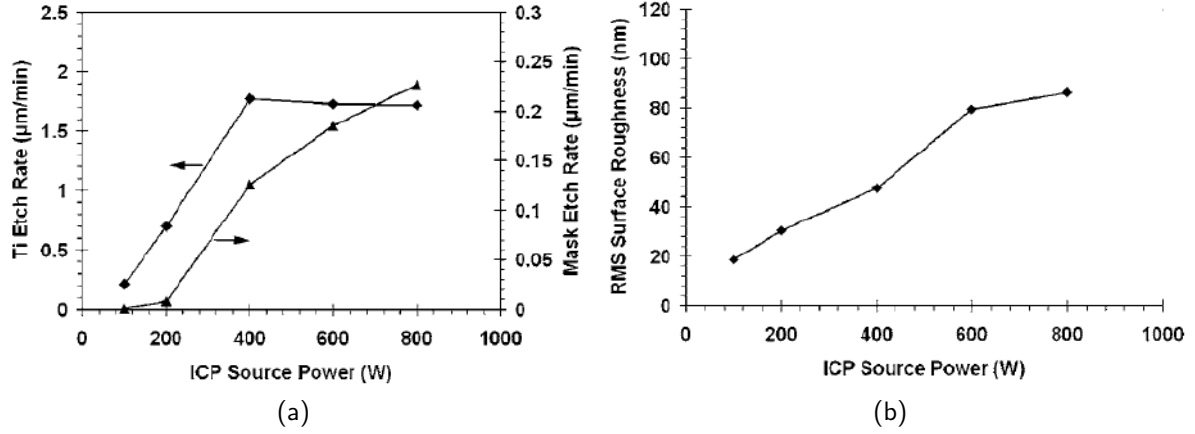


Figure 2.12: (a) Bulk titanium and TiO_2 mask etch rates against ICP power, (b) Resultant rms surface roughness against ICP power after 2 minutes of plasma etching. Reprinted from [47] copyright (2005) with permission from IOP Publishing.

producing the highest etch rate of $\sim 200 \text{ nm min}^{-1}$. They also showed that SF_6 selectively etched Si over TiO_2 and Cl_2 selectively etched TiO_2 over Si. They suggested that SF_6 etches TiO_2 faster (despite being less selective and the products having higher boiling points than Cl_2), because the chlorine is forming more sub-chlorides i.e. TiCl_2 or TiCl_3 , which will not desorb from the surface, as opposed to mostly TiCl_4 [143].

Cheng et. al. conducted ICP-RIE of a perovskite (BaTiO_3) thin films using chlorine (BCl_3/Ar) and fluorine (CF_4/Ar) chemistry. They found higher etch rates and smoother surfaces are produced using BCl_3 than with CF_4 . They also found that when using CF_4 , the etch rate decreased with dwell time, whereas BCl_3 etch rate was constant with time. They suggested this was all due to chlorine creating more volatile Ti compounds than fluorine [144].

These two articles seem contradictory. This discrepancy may be due to the presence of Ba in Cheng's experiment or the microstructure difference between the TiO_2 and BaTiO_3 . Either way, both agree that TiCl_x are more volatile than TiF_x compounds and that both can chemically etch Ti.

2.3.2 Aluminium

Smith showed that under ultrahigh vacuum conditions, chlorine adsorbs onto clean aluminium, then dissociates and chemically reacts. This does not require the chlorine to be ionised [145]. Hess showed that ion bombardment does not promote the etch rate of clean aluminium. This was explained due to the rapid dissociation and chemisorption of chlorine [146]. Hess also stated that hydrogen containing halocarbons used in a plasma lead to polymer coatings on the etch sidewall. This can be beneficial when etching trenches, as it can prevent undercutting. Steinbrüchel conducted experiments using a Kaufmann type ion gun with CCl_4 , CCl_2F_2 and BCl_3 as chlorine sources to etch an Al substrate. Etch yields of > 2 Al atoms per ion were shown when using CCl_4 and ~ 1 for CCl_2F_2 and BCl_3 . Steinbrüchel suggested that this shows the etch mechanisms are a combination of sputtering and RIE, however it was not suggested which was dominant [147]. Bruce and Malafsky demonstrated anisotropic etch profiles of aluminium using a $\text{Cl}_2/\text{CHCl}_3/\text{BCl}_3/\text{He}$ mixture in a parallel plate discharge under vacuum [148]. They suggested the etching was purely chemical. BCl_3 and CHCl_3 were added to remove the oxide layer and to protect the etch sidewalls respectively. They observed no etching with a pure Cl_2 discharge, but an exponential dependence on the initiation of etching against BCl_3 flow rate, shown in Figure 2.13. The authors suggested the presence of BCl_3 was required in the plasma in order to remove the alumina layer due to either sputtering or to prevent re-oxidation of the surface.

Schaible et al. suggested that under vacuum, the RIE of aluminium was limited by the presence of the alumina (Al_2O_3) layer on the surface when using Cl or Br. They found that using an Ar/ CCl_4 plasma was far more efficient at removing material. They concluded this was due to CCl_3^+ being more effective at removing the oxide layer and that the carbon removed residual water vapour present in the vacuum chamber [149]. A year later Schaible and Schwartz showed lateral etching and pitting in the RIE of aluminium alloy (Al/Cu & Al/Cu/Cr) thin films using an Ar/ CCl_4 plasma. They concluded this is due to the grain size of the films [150].

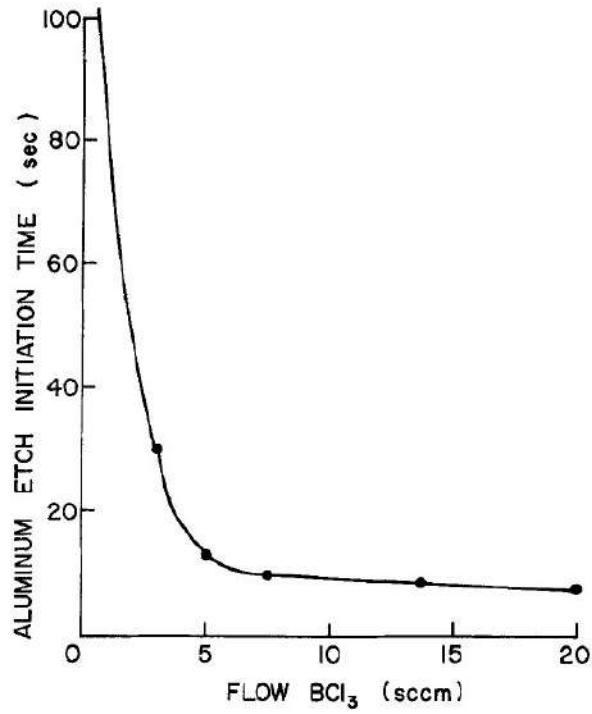


Figure 2.13: Aluminium etch initiation time against BCl₃ flow rate. These results show no etching of the Al surface when only etching with Cl₂. Reprinted from [148] copyright (1983) with permission from IOP Publishing.

2.3.3 Vanadium

Vanadium is most commonly used for alloying, often with steel for manufacture of tools [151]. There are very few studies which have been carried out for the plasma etching of vanadium. Those that have, the etchant concentration has been the main focus having investigated Cl₂ [152] and SF₆ [153] for the plasma etching of VO₂, both of which were carried out at low pressure. No studies have been found investigating APP etching of vanadium.

2.4 Ti-6Al-4V Alloy

Ti-6Al-4V (Ti64), also called titanium grade 5, is a titanium alloy commonly used in industry, specifically the aerospace [154, 155] and medical [156] sectors, due to its high strength, resistance to corrosion, performance at high temperatures and biocompatibility. Ti64 is classified as a 'difficult to machine' material, meaning traditional contact machining can lead to high tool wear and poor surface finish. Ti64 is difficult to machine due to its: hardness, strength and low thermal conductivity, which means heat is not readily dissipated from the cutting zone [157]. There are multiple variations of Ti64 in production, such as Ti-6Al-4V-ELI (Extra Low Interstitial) or titanium grade 23, which contains less oxygen (max 1.3%) giving it a higher fracture toughness. Other small chemical alterations such as; small additions of palladium (0.04-0.08%) *Grade 24*, nickel (0.3-0.8%) and palladium (0.04-0.08%) *Grade 25* and Ti64-ELI with ruthenium (0.08-0.14%) *Grade 29* have also been developed for various benefits such as improved strength or corrosion resistance [158].

2.4.1 Ti64 Microstructure

Ti64 is an $\alpha+\beta$ alloy meaning it is comprised of a mixture of HCP (α) and BCC (β) crystal structures. In general, the HCP phase provides the strength and the BCC phase provides the ductility. For Ti64, aluminium is an α phase stabiliser and vanadium is a β stabiliser. The presence of α stabilisers act to raise the $\alpha - \beta$ transition temperature, whereas β stabilisers lower it. Depending on the quantity of each, the β transition temperature (β transus) can range from $\sim 700^{\circ}\text{C}$ to over 1000°C [2]. While titanium alloys can be classed as α , $\alpha + \beta$ or β , all contain a both α and β phases [159]. $\alpha + \beta$ titanium alloys such as Ti64 contain between 5-30% volume of β phase [4]. Unit cells for HCP and BCC crystal structures are shown in Figure 2.14. The number of atoms in each unit cell is 6 for HCP and 2 for BCC, meaning the HCP structure is more dense than the BCC structure. This is also reflected in the atomic packing factors (amount of space occupied by atoms in a unit cell) for the HCP and BCC structures, given as 0.74 and 0.68 respectively.

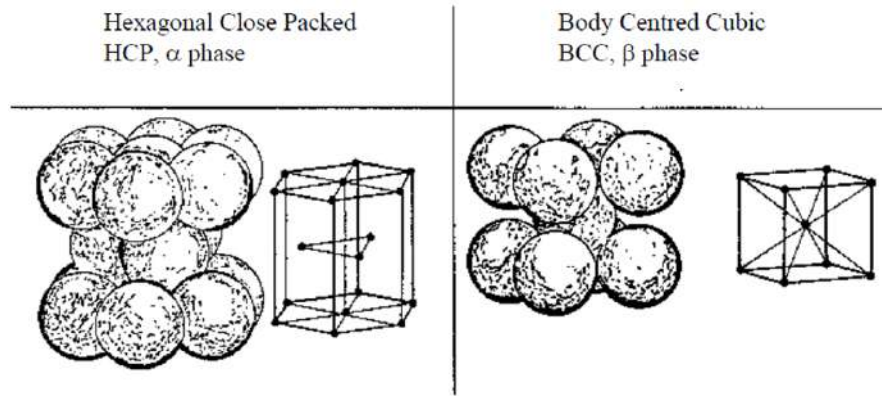


Figure 2.14: Hexagonal Close Packed (HCP) and Body Centred Cubic (BCC) crystal structure unit cells present in Ti64 [160].

The microstructure of Ti64 can be categorised into one of three types: lamellar, equiaxed or bi-modal. Examples of the morphology for these three different microstructures are shown in Figure 2.15 for titanium alloys. The technique for the formation of a desired microstructure requires a multi-step processes of heating and cooling described in detail in chapter 5.1 of Titanium [2]. To summarise, all three microstructures require a four-step process: (1) homogenisation, (2) deformation, (3) re-crystallisation and (4) annealing.

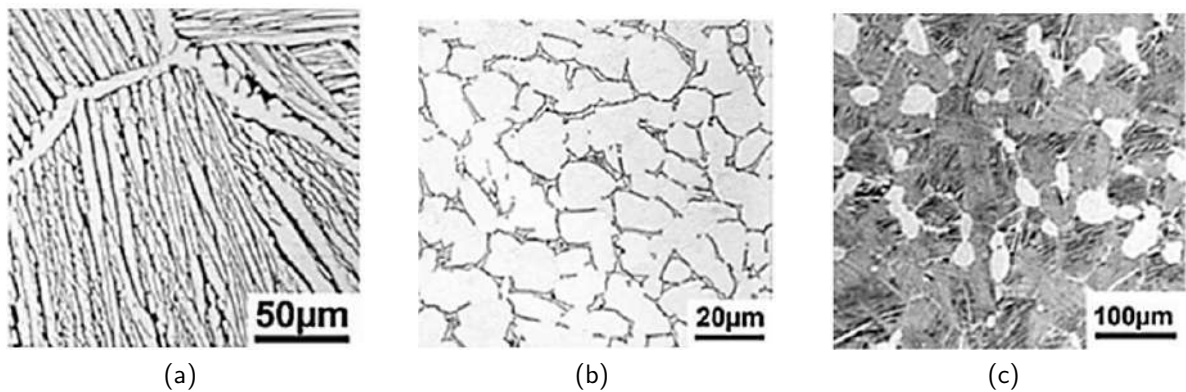


Figure 2.15: Microstructures of a titanium $\alpha + \beta$ alloy (a) lamellar [159], (b) equiaxed [2], and (c) bimodal [159]. Reprinted from [2] copyright (2007) with permission from Springer Nature.

With the variation in resultant microstructure being due to how hot the sample is heated and the speed of cooling at each step. The $\alpha:\beta$ ratio and grain size can vary greatly, depending on the manufacturing process and cooling rate [160,161]. Figure 2.16 shows how the cooling rate from various heating temperatures affects the microstructure and grain size for a Ti64 alloy.

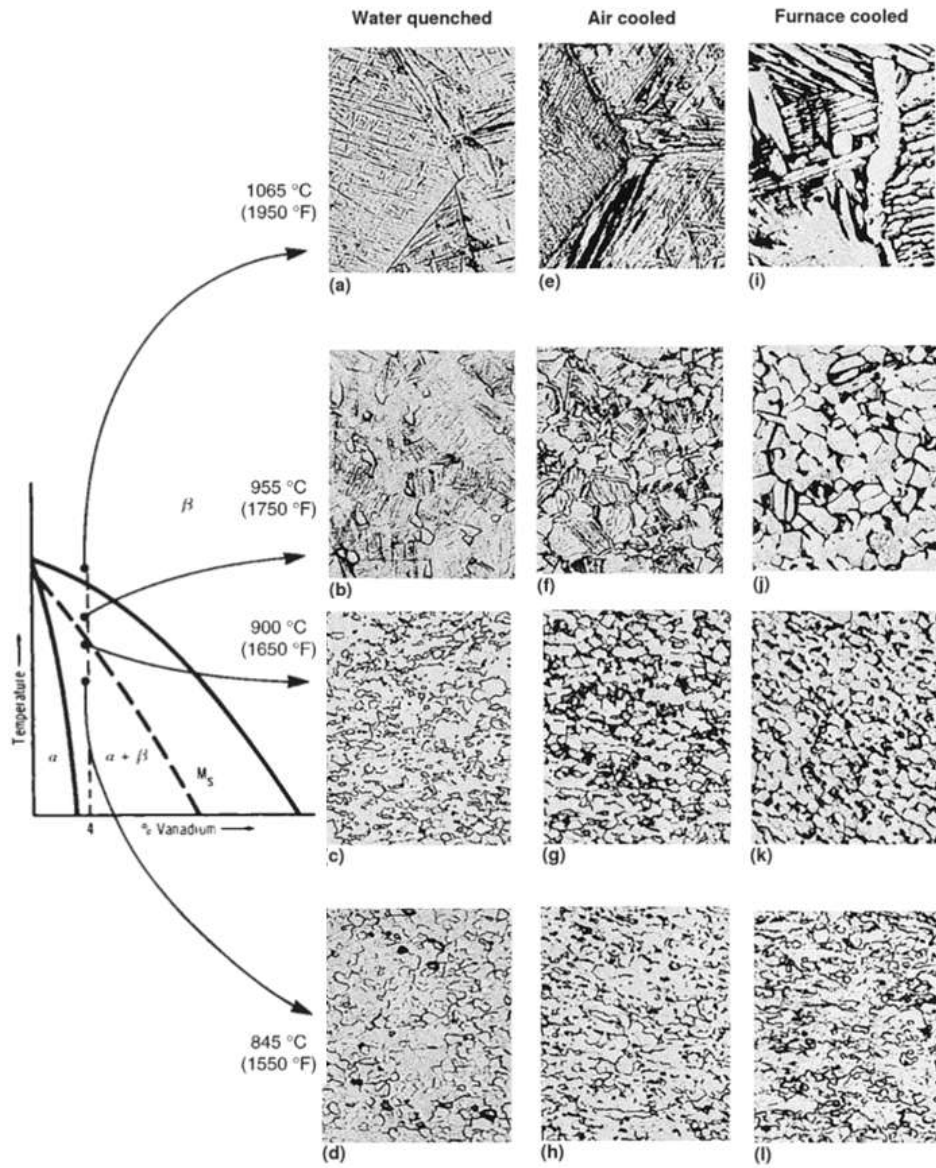


Figure 2.16: Impact of heating temperature and cooling rate on Ti64 microstructure (i.e. 4% V). (a)-(d) show the microstructure when the sample is heated to: (a) 1065°C, (b) 955°C, (c) 900°C and (d) 845°C, then water quenched. Similarly, (e)-(h) show the microstructures when heated, then air cooled and (i)-(l) when the sample is furnace cooled [162].

2.4.1.1 Cooling from beta transition temperature

The $\alpha:\beta$ ratio of Ti64 changes during heating. The α phase gradually transforms to a β phase as the sample temperature increases, until the β transition (transus) temperature (995°C [2]) is reached. At this point the material becomes pure β phase. As the Ti64 is cooled from the β transus temperature, there are three transformations from $\beta \rightarrow \alpha + \beta$ microstructure which have been identified [163]; diffusionless, massive and diffusional. At high cooling rates ($>410\text{ }^{\circ}\text{C s}^{-1}$), fully diffusionless transformation occurs, where hexagonal acicular martensite (α') is formed from the β grain boundaries. Massive transformations ($\beta \rightarrow \alpha_m$) take place at moderate cooling rates (20-410 $^{\circ}\text{C s}^{-1}$) and results in hexagonal α phase but with many dislocations and highly irregular morphology. The fraction of α_m increases with decreasing cooling rates. The massive and martensitic α phases have similar chemical compositions ($\sim 8\text{ \%wt. Al}$ and $\sim 3\text{ \%wt. V}$). Diffusional transformation occurs at low to moderate cooling rates (1.5 $^{\circ}\text{C s}^{-1}$ - 20 $^{\circ}\text{C s}^{-1}$) where heterogeneous nucleation of the α grain begins at the β grain boundary and slowly propagates into the β phase. At these low cooling rates, the $\beta \rightarrow \alpha_m$ transformation is absent. This slow growth of the α phase results in Widmanstätten α colonies with retained β in between. Two types of Widmanstätten structure have been identified (type 1 & type 2). Type 1 occurs at the higher end of this cooling rate range ($\sim 20\text{ }^{\circ}\text{C s}^{-1}$) exhibiting a zig-zag appearance. Type 2 occurs at slower cooling rates, where the Widmanstätten α grows further into the centre of the grains and results in a 'basketweave' morphology. Which α morphology is formed is summarised by Ahmed and Rack in Figure 2.17. The microstructure and morphology of the grains affects the thermo-mechanical properties of the resultant material. As such, heat treatments can be applied to tailor the microstructure to the application [2].

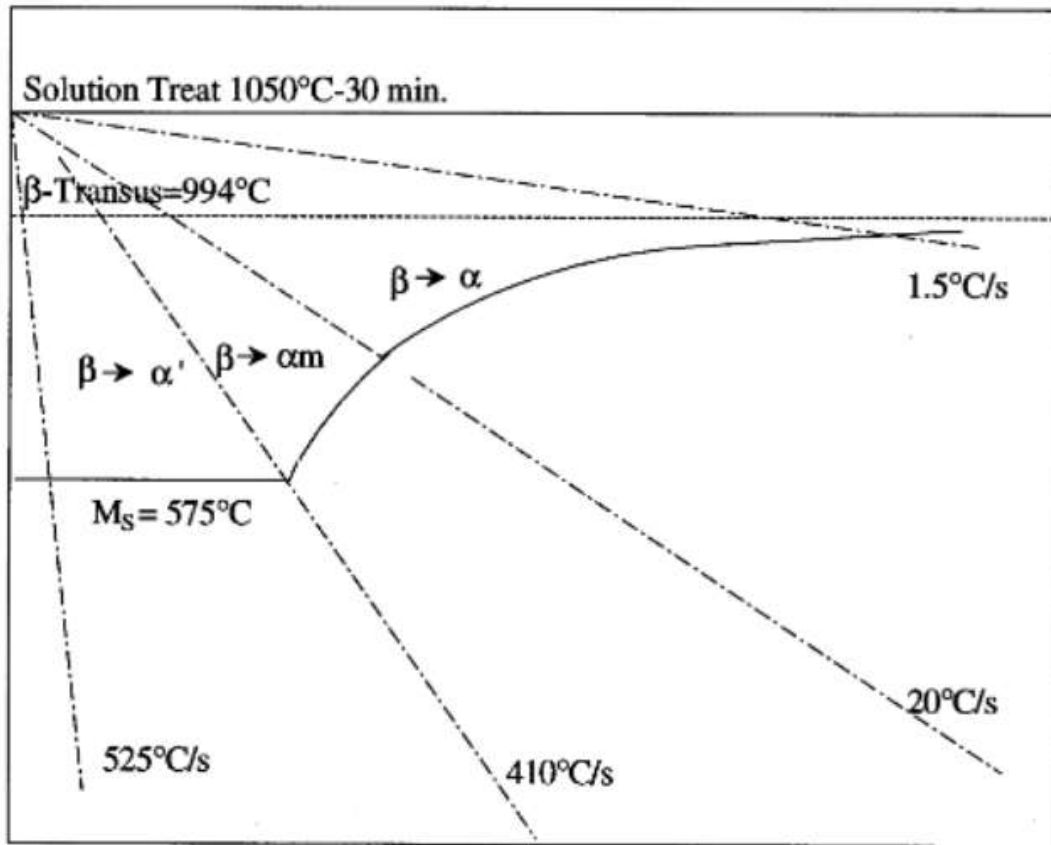


Figure 2.17: Continuous cooling diagram for Ti64 β to α transformation. Reprinted from [163] copyright (1998) with permission from Elsevier.

2.4.1.2 Nucleation and grain growth

Nucleation tends to be heterogeneous and at pre existing nucleation sites, since less undercooling is required compared to homogeneous nucleation [164]. The grains then grow from the interface between the solid nucleation sites and the liquid phase. For a metal, the growth front is continuous and determined by the thermal gradient. The growth of the grains can be: planar, cellular or dendritic [165,166]. Where planar growth is continuous and at a constant velocity, cellular when there exists small instabilities in the growth front and dendritic (or 'tree like') when large instabilities exist in the growth front [167].

2.4.1.3 X-ray Diffraction Spectroscopy of Ti64

X-ray Diffraction Spectroscopy (XRD) is a characterisation technique which involves bombarding the surface of a sample with x-rays. Typically, X-rays are produced by accelerating electrons in an EM field towards a target. X-rays are emitted due to two different mechanisms: Bremsstrahlung radiation, where the incident electrons decelerate and emit the difference in energy as a photon, and from ionising target atoms. When an incident electron collides with an atom in the target, it can eject an electron from the inner shell. An electron from an outer shell then fills the gap, and the difference in electron energy between these two shells is emitted in the form of X-rays [168]. Both these mechanisms emit X-rays over a range of wavelengths. Peaks in intensity (also called the characteristic radiation) exist at certain wavelengths, which is dependent on the target material [168]. These peaks are referred to as $K\alpha$ and $K\beta$ peaks, typically, XRD techniques use the $K\alpha$ peak. An example of a spectrum produced by an X-ray source is shown in Figure 2.18. In this case there are two peaks in the $K\alpha$ peak, labelled as $K\alpha_1$ and $K\alpha_2$.

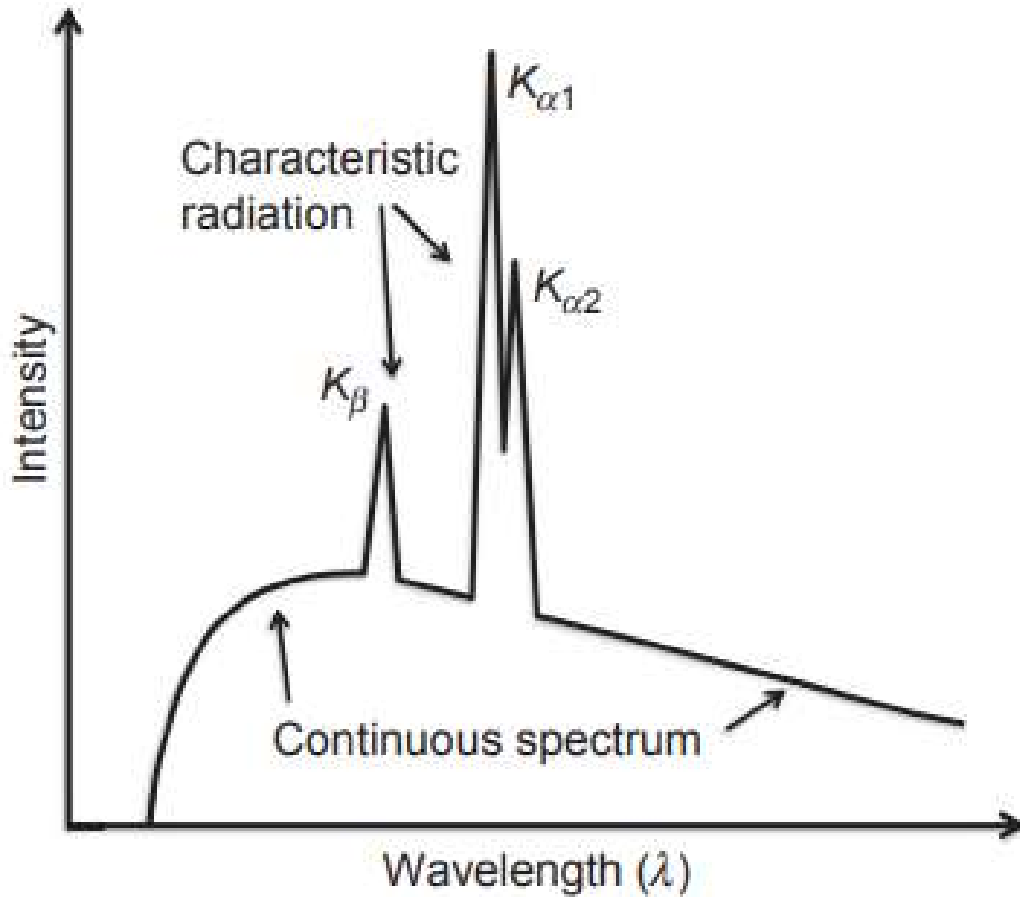


Figure 2.18: Intensity against wavelength for an X-ray source. The characteristic radiation is shown as $K_{\alpha 1}$, $K_{\alpha 2}$ and K_{β} . Reprinted from [168] copyright (2016) with permission from Elsevier

The XRD spectra for Ti64 shows both α and β peaks and their corresponding orientations. Where XRD is commonly used for powder analysis, it also is useful for solid materials although the intensity tends to be reduced. Figure 2.19 shows an XRD spectrum for a Ti64 sample and which crystal structure each peak relates to [169]. The peaks in an XRD spectrum of Ti64 typically relate mostly to the α phase since 70% - 95% of the total volume is α , as mentioned above [169–171].

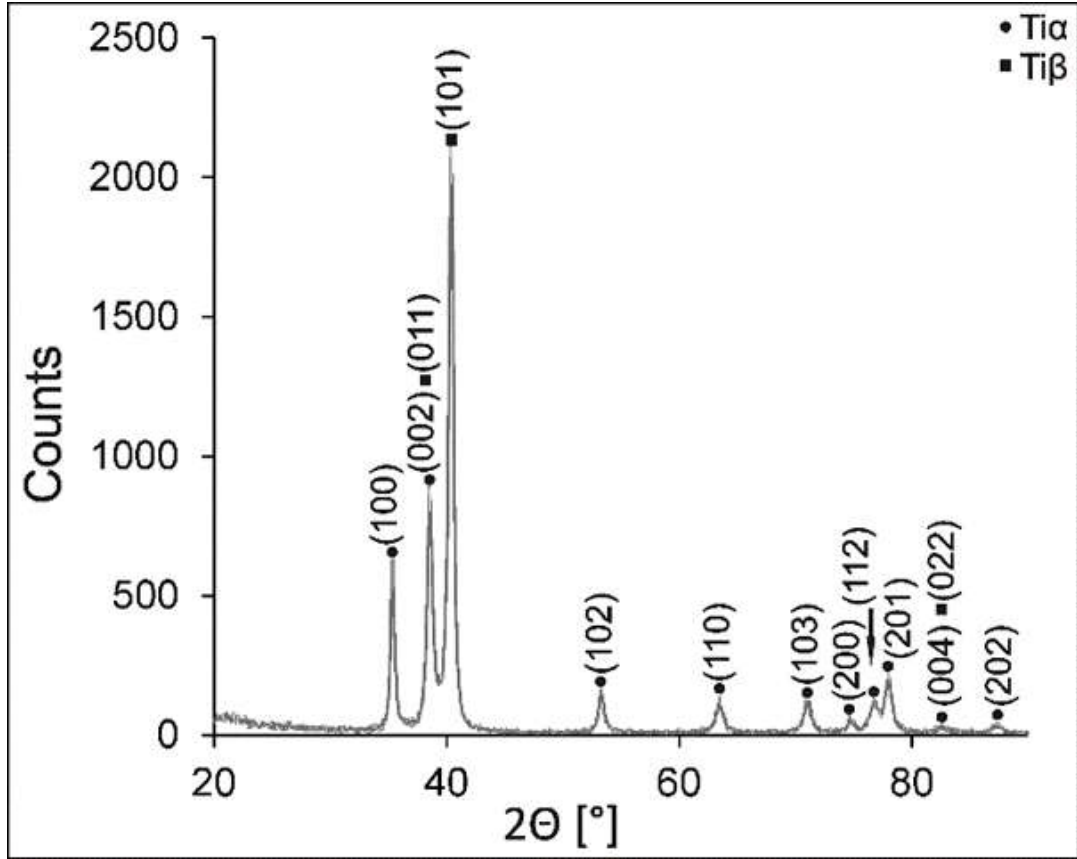


Figure 2.19: XRD spectrum for Ti64 [169].

2.4.2 Thermal Conductivity

A material's thermal conductivity (κ) represents its ability to conduct heat. Heat conduction is a highly complex and difficult field of study where both theoretical and practical measurements are not particularly accurate. For pure metals, the Wiedemann-Franz law, Equation 2.17, simply relates thermal conductivity (κ) and electrical conductivity (σ). Although this is still used to provide estimates of thermal conductivity, this only relates electrical conductivity and electronic thermal conductivity. This equation is only valid for elastic electron scattering which typically occurs at very low or high temperatures [172].

$$\frac{\kappa}{\sigma} = LT \quad (2.17)$$

Heat is mainly transported through metals by two distinct and independent contri-

butions: that of electrons and lattice vibrations (phonons). Other small contributions are often neglected. For pure metals, heat transport is often dominated by electrons whereas in impure metals and alloys the impact of phonons tends to become more significant [173]. For insulators such as glass, only phonons are considered since there are no free electrons to transport the heat. The thermal conductivity of Ti64 is lower than that of its alloying metals as shown in Table 2.3. These values are taken at 20°C i.e. standard room temperature for comparison. This low thermal conductivity in Ti64 is due to electron scattering and dislocations/defects in the lattice structure which can occur during alloying.

Table 2.3: Thermal conductivity of Ti64 in comparison to its component metals at 20°C.

Metal	Thermal conductivity ($\text{W m}^{-1}\text{K}^{-1}$) at 20°C
Ti64	6.6
Ti	15.6
Al	225
V	34.6

The evolution of the thermal conductivity of Ti64 is also important since the plasma etching process in this work will occur at temperatures much greater than room temperature. As the metal is heated up, the thermal conductivity increases. Boivineau et. al. calculated the thermal conductivity of Ti64 from 400-2700K, using the Wiedemann-Franz law, shown in Figure 2.20, from experimental results [174]. This shows a linear increase of thermal conductivity with respect to temperature until the β transus temperature. The peak dsc-signal shown in Figure 2.20, occurs at the β transus temperature. Here, dsc refers to the differential scanning calorimeter used to measure the heat capacity of the Ti64 during the experiments. The temperature range relevant for this work however (up to $\sim 1000\text{K}$) will be below the β transus temperature, where the thermal conductivity range of interest will be between 6.6 and $\sim 13 \text{ W m}^{-1} \text{ K}^{-1}$.

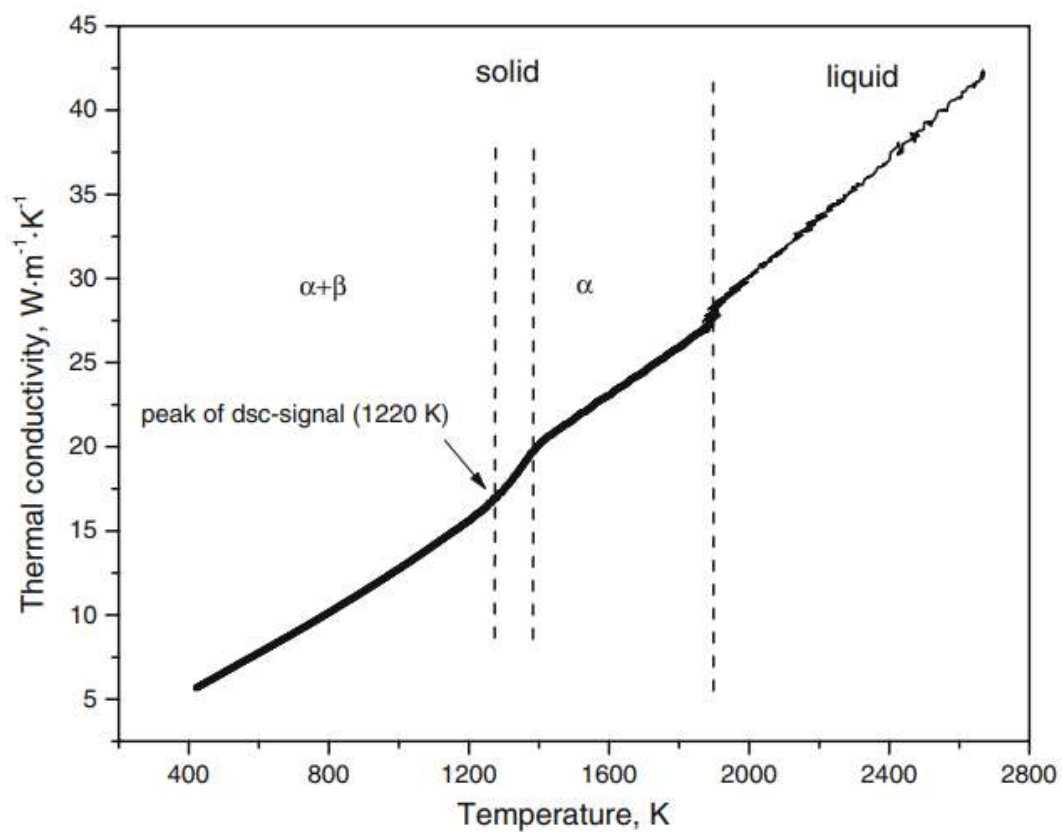


Figure 2.20: Ti64 thermal conductivity against temperature. Reprinted from [174] copyright (2006) with permission from Springer Nature.

2.5 Problems with Plasma Etching Metals

There are numerous examples of plasma etching titanium and aluminium at low pressure (as shown in chapter 2.3), however no modern experiments have been reported to etch Ti64 at atmospheric pressure. While plasma etching of titanium has been shown using fluorine, chlorine and bromine, all three have associated problems. It is important to choose the best reactive species for etching. This is dependent on the chemical composition of the substrate. The most common reactive species for etching metals tend to be F_2 , Cl_2 or Br_2 due to their high reactivity and low ionisation energies. An initial indicator for the selection of an etchant is to assess at the boiling points of the stable products the etchant forms with the substrate [143, 175]. This approach is shown in Table 2.4, where the melting and boiling points of possible titanium, aluminium and vanadium halogenide products are shown. The products which can easily be removed at plasma etching temperatures have been highlighted in red in Table 2.4. This illustrates volatile products will be formed with titanium when using fluorine, chlorine or bromine. Aluminium, however, will not form volatile products with fluorine. Vanadium can be etched with fluorine and chlorine. This is assuming any meta-stable compounds disproportionates before they are removed from the surface of the Ti64 substrate.

A key problem with plasma etching Ti64 is doing it under atmospheric conditions. From previous work it is known that chlorine chemistry is capable of etching titanium under low pressure conditions. For plasma etching at atmospheric pressure no suitable chlorine compound has been identified for use as a reactive species. Also, due to the lack of literature, it is unknown whether other halogen (e.g. fluorine) chemistry will effectively etch Ti64. Under low pressure, chlorine can be ionised at relatively low power. At atmospheric pressure however, the input power required is much higher. This is due to the breakdown voltage increasing with pressure, see Paschen's law in section 2.1.2 (Equation 2.5). Many of the studies mentioned in Section 2.3, were carried out over 20 years ago and used etchants such as CCl_4 or CCl_2F_2 . Due to environmental or health and safety reasons, many previously used compounds have since been either banned or are too dangerous to use. Alternative non-toxic chlorine containing compounds, such as

Table 2.4: Boiling points of titanium and aluminium halogenide compounds [176].
*** VCl_5 Disproportionates into $\text{VCl}_2 + \text{VCl}_4$.**

Etch Product	Melting point ($^{\circ}\text{C}$)	Boiling point ($^{\circ}\text{C}$)
TiF_3	1200	1400
TiF_4	sublimation	284
TiCl_2	1035	1500
TiCl_3	425	960
TiCl_4	-25	136
TiBr_4	39	230
AlF_3	sublimation	1297
AlCl_3	sublimation	178
AlBr_3	98	263
VF_3	sublimation	1395
VF_4	sublimation	325
VF_5	19.5	48.3
VCl_3	300-400	disproportionates*
VCl_4	-24.5	148
VBr_2	827	1227

SiCl_4 or CHCl_3 (Chloroform), are liquid at room temperature. This makes them unsuitable for the available an atmospheric pressure plasma torch. Alternative experiments could involve retrofitting a plasma torch to include a nebuliser to inject liquid particles directly into the plasma jet. However due to time and financial constraints, this will not be investigated in this work. Table 2.5 summarises the problems with using chlorine containing compounds in a plasma jet.

Another problem encountered with using chlorine containing compounds for an atmospheric pressure plasma is the water vapour in the air [48]. Chlorine containing compounds readily hydrolyse to form HCl , which can pose a danger not only to the integrity of the machine but also the operator and other people in the lab. Even if these compounds can be safely removed, metal chlorides can also readily hydrolyse with water vapour in the air forming oxychlorides and hydrated oxides, which stop the etching process [48]. Carbon containing compounds should also be avoided as they can create polymers which coat the etch sidewall.

Bromine containing compounds have also been previously used under vacuum to etch metal. Although many of these compounds are gaseous at room temperature, they are

Table 2.5: Problems with using various Cl containing compounds as a reactive species. Many are either toxic, unstable or banned.

Compound	Problem
C-Cl ₄	Banned
C-Cl ₂ F ₂	Banned
NCl ₃	Highly explosive and unstable
ClF ₃	Highly explosive and toxic
NaOCl	Explosive and unstable
CaOCl	Toxic, Liquid at RTP and corrosive if mixed with acid
PCl ₃	Highly toxic and unstable
ClO ₂	Toxic and explosive at RTP
SCl ₂	Highly corrosive and liquid at RTP
BCl ₃	Highly toxic
SiCl ₄	Irritant and liquid at RTP
CHCl ₃	Liquid at RTP

corrosive. Bromine containing compounds also form a thick metal bromide layer on the substrate in the presence of water. This metal bromide layer also requires chlorine in the plasma to efficiently remove this layer and etch the metal [149]. It was for these reasons fluorine was investigated as an etchant, specifically SF₆. Fluorine based etching is already widely used in industry for precise material removal of silicon based substrates. Since the infrastructure for using fluorine based etchants is already in place with associated risk assessments and setups to deal with fluorinated by-products, the use of a fluorine based etchant is easily adaptable for current industrial setups. Although SF₆ is a potent greenhouse gas, containment procedures in case of a leak would already be in place for industrial applications.

2.6 Surface Measurement

Surface measurement investigates features and dimensions of a sample. Surface features will appear different when observed at macro compared to nano scales. To fully understand the features of a surface (topography), it must be measured over a wide range of spatial frequencies. It is important to clarify what is meant by surface roughness spatial frequency, since the roughness of a surface is often misunderstood. Spatial frequency is the inverse of spatial wavelength i.e. the distance between a repetitive variation in the surface. A measured surface with no cutoffs/filters applied to the measurement is defined as the primary (actual) surface. This measurement (P), includes any affect of form (low spatial frequency) and waviness (mid spatial frequency). By applying filters/cutoffs, these effects can be removed from the measurement to obtain the high spatial frequency roughness (R). Cutoffs apply a filter to only retrieve data between certain wavelengths of surface features. Both a low (λ_s) and high (λ_c) band cutoff are typically applied, between which data will be acquired. The determination of filters/cutoffs is outlined in the national physical laboratory's (NPL) good practice guide no.37 [177].

There are many techniques which have been developed for measuring a surface. They can broadly be categorised into contact and non-contact techniques. Common contact measurement techniques include stylus profilometry, atomic force microscopy - AFM (high spatial frequencies) and Co ordinate measurement machines - CMM (low spatial frequencies). Common non contact measurements techniques include laser scanning, interferometry, and optical microscopy. The technique employed is dependent on the sample surface and the desired information (high or low spatial frequencies). A soft material may require a non contact technique to get an accurate measurement without damaging the surface. Optical measurements may be impossible if the surface is non-reflective. The lateral resolution of an optical measurement is dependent on the pixel size. If a surface feature is smaller than this pixel size, it will be obscured by the surrounding surface and not directly be detected. Figure 2.21 illustrates what spatial frequency domain common measurement techniques are capable of detecting.

The step height of features will also determine which technique can be used. Contact

measurement techniques can be limited by the dimensions of a measurement probe; if a probe cannot fit into a certain feature then the measurement will round the feature. Care must also be taken when choosing the composition of the probe tip. A diamond tipped probe will chemically react with the carbon in ferrous materials, resulting in high tip wear and inaccurate measurements. Optical measurements can also have difficulty detecting steep step heights. These setups rely on light reflecting from a surface back into a detector. If this light is scattered from a sharp step height, it cannot be detected.

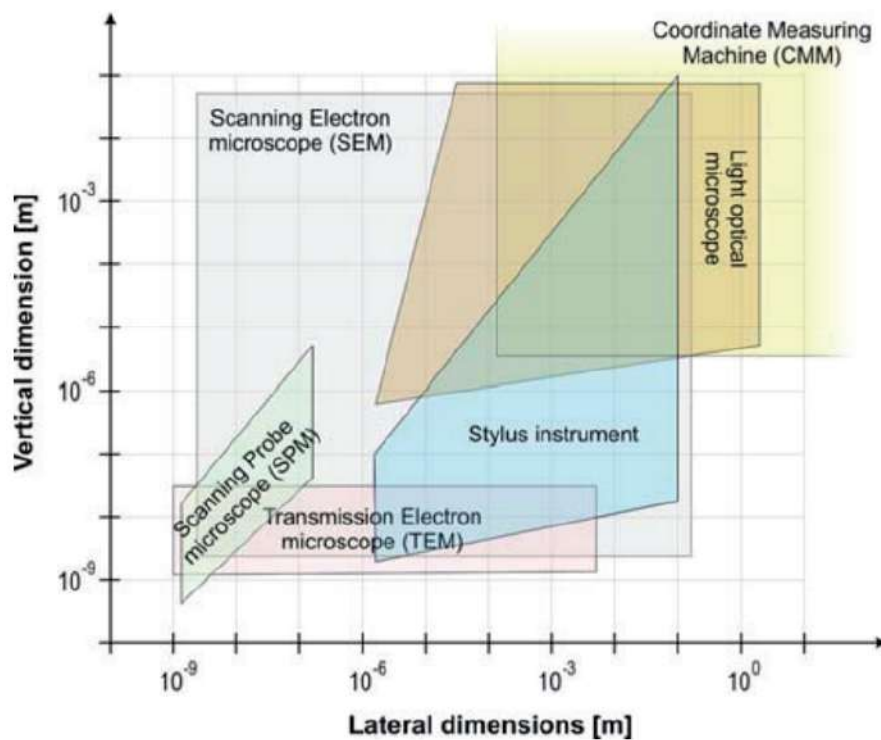


Figure 2.21: Possible feature sizes which can be detected by various measurement techniques. Reprinted from [178] copyright (2006) with permission from Elsevier.

Interferometry is a non-contact, non-destructive technique to measure a surface. Phase shifting interferometry (PSI) is widely used due to its accuracy, large field of view, and fast measurements compared to other surface characterisation techniques [179,180]. PSI setups are extremely sensitive, with picometre (10^{-12} m) level accuracy in some cases [181]. However, due to this sensitivity, noise in dynamic environments can cause errors in measurements [182]. They are also limited by errors in detecting abrupt height discontinuities. PSI works by detecting light reflected from a reference surface, and the surface which is to be measured. Light from the source is passed through a beam splitter, and reflects from both a test surface and a reference optic. Once these two beams are merged together they form an interference pattern (interferogram), based on the surface topography of the test surface. Since the wavelength of the light (often a monochromatic source), and the distance of the reference surface are known, the topography of the test surface can be accurately determined [183].

PSI designs include Michelson, Twyman-green and Fizeau interferometers [179]. A Michelson interferometer uses a movable mirror/reference optic and a stationary test sample. Figure 2.22(a) shows an illustration of a Michelson interferometer, where one mirror would be movable and the other would be the test surface. A Michelson interferometer uses a white light source. A Twyman-green interferometer is a variation of the Michelson interferometer when a monochromatic light source is used (i.e. a single frequency), the setup is the same as shown in Figure 2.22(a). White light has the benefit of a shorter coherence length than a monochromatic source, which makes it easier to determine the position/fringe order. However this higher bandwidth (compared to a low bandwidth source such as a laser) also limits the slope angles which can be detected [184]. A Fizeau interferometer has a different setup, where the reference optic (also called transmission optic) is in the same plane as the test surface, shown in Figure 2.22(b). The monochromatic light source is split, with one beam directed towards the reference optic, and one towards the test surface. This setup is more compact, however the field of view is limited by the size of reference optic, typically 100 - 300 mm diameters [185].

Detailed descriptions of the correct procedure and setup when taking measurements

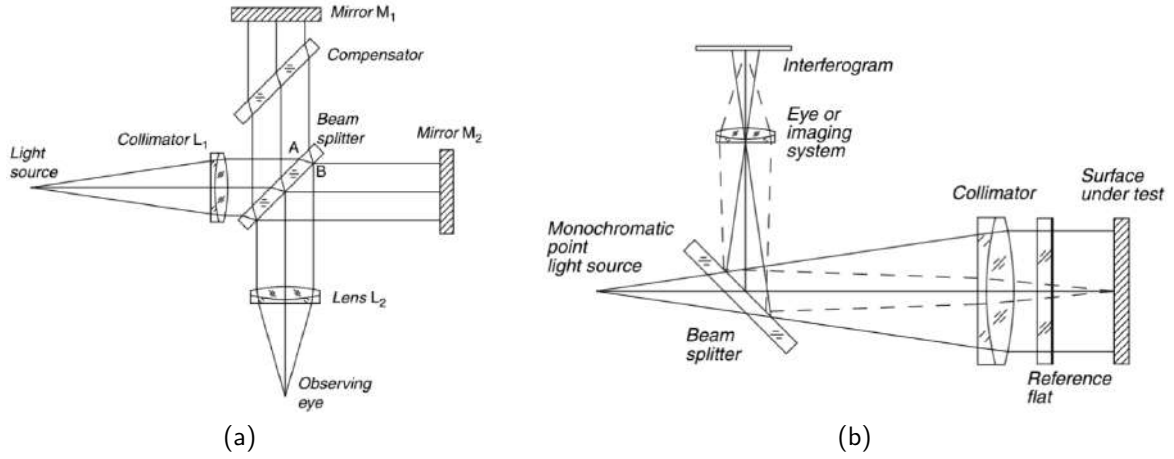


Figure 2.22: Schematics of a typical PSI setups (a) Michelson/Twyman-Green interferometer, and (b) Fizeau interferometer. Reprinted from [183] copyright (2006) with permission from Wiley books

of a surface using interferometry is given in the NPL good practice guides Nos. 108, 116 and 127 [186–188], with good practice guide 80 detailing general metrology good practices [189].

2.7 Summary of literature review

Ti-6Al-4V (Ti64) comprises of a two phase structure HPC (α) and BCC (β) where the majority (70% - 95%) of the total volume is in an HPC structure. Ti64 also has a low thermal conductivity and high strength which make it difficult to machine using conventional methods. Fluorine has been shown to etch titanium at low pressure using plasma. Coupled with the problems of using chlorine containing etchants and the fact that Ti64 is an alloy comprised of 90% titanium, only fluorine has been found as a possibly suitable etchant for the APP etching of Ti64. This also would make the process more applicable to industry, since fluorine compounds are already widely used for silicon based etching and their hazards are manageable with precautions already in place. Also, since literature showed carbon containing compounds could create polymers which coat the etch sidewall and slow down the etching process, SF_6 was chosen as the reactive species over CF_4 , another commonly used fluorine source. The measurement techniques used are designed to detect surface feature spatial frequency over a large bandwidth.

The prediction of the material removal function for plasma etching is highly complex, and many variables must be taken into account. Even when taking into account the thermal, temporal and spatial dependencies of the etch rate, modern plasma etching models cannot accurately predict the material removal.

Chapter 3

Methodology

This section outlines the various methods used in this work. The preparation of the Ti64 samples is explained in Section 3.1, Figure 3.2 (refer to Section 3.1) illustrates the six steps carried out. This flow chart is referred to throughout this thesis to prevent any confusion for the reader. Section 3.2 covers the setup and methodology of the APP etching experiments using the Helios 1200 system. The three sets of experiments are: stationary dwells, trenches, and overlapping trenches (referred to as areal etching). Section 3.3 outlines the surface measurement techniques used. This section is split into two parts based on the spatial frequency of the measurements. Section 3.3.1 covers the phase shifting interferometers (PSI), and coherence correlating interferometer (CCI) used for low spatial frequency measurements. Section 3.3.2 outlines the stylus profilometer and AFM machines used for the high spatial frequency measurements. The final section in the methodology discusses the microstructure and chemical measurement methods. This is split into three sections: FactsageTM simulations, SEM and EDS, and XRD respectively.

3.1 Sample Preparation

Ti64 samples were obtained from Timet (Timet, UK) named TIMETAL[®] 6-4 plates, measuring 50 mm x 50 mm x 16 mm. These samples were annealed at 1300°F (~700°C), then air cooled as stated in the data sheet supplied by Timet. The material composition was given by the supplier in the data sheets as 5.5-6.75%(wt.) aluminium, 3.5-4.5%(wt.) vanadium and up to 1.145%(wt.) other impurities and residual elements, with the remainder titanium 87.605-91%(wt.). The received samples initially had a dull appearance with a rough surface which could not have been measured using optical measurement techniques. However, this would not have provided a sufficiently detailed view of the surface unless many profiles were taken before and after etching and stitched together to create a 3D view of each surface. This process would have been extremely time consuming, therefore, sanding and polishing of the samples was preferable. Despite the time consuming nature of this method, it would enable a more complete view of the process before and after etching. Figure 3.1 shows an example of an (a) as received sample, and (b) a prepared sample after sanding and polishing.



(a)



(b)

Figure 3.1: Ti64 samples from Timet, (a) as received samples with a rough, dull surface and (b) after sanding and polishing.

The sample preparation method used is illustrated in Figure 3.2. The three stages at which measurements were carried out are referred to as: Before plasma etching (Measurement A), Immediately after plasma etching (Measurement B) and After plasma etching & polishing (Measurement C) throughout this thesis so as to avoid any confusion.

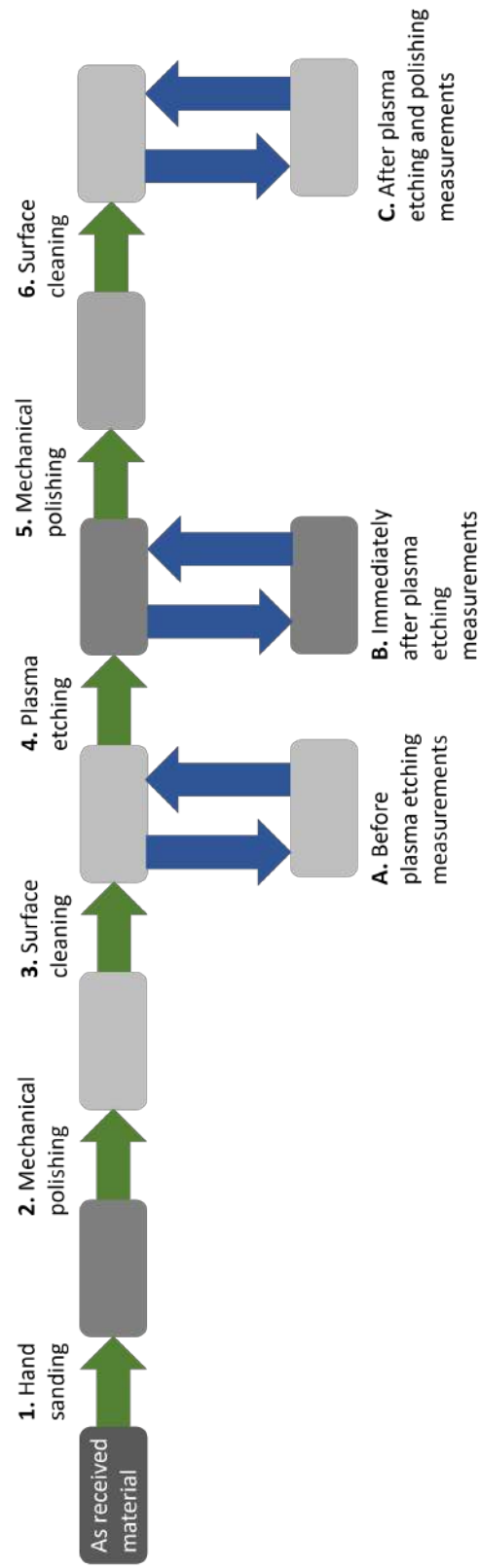


Figure 3.2: Flow diagram of the method and at which stages measurements are carried out.

The sanding process (step 1 in Figure 3.2) was carried out using various grades of sandpaper from 40 to 2500 grit. The rougher (40-180 grit) used alumina as the abrasive and the finer grades (240-2500 grit) used silicon carbide abrasive. As stated in Section 2.4.1, Ti64 is a mix of α (HCP) and β (BCC) phases. Due to this, the samples were hand sanded, so as not to heat the surface too much. The microstructure of Ti64 will shift to a pure β phase above 995°C (β transus temperature), which may occur in localised areas in conventional grinding. Grinding will also induce thermal damage which can lead to residual stresses of 100's of MPa [190].

The mechanical polishing process (step 2 in Figure 3.2) was then carried out using a "random orbital polisher" from VonHaus (VonHaus, UK) and "superfinish L1 final polishing liquid" from LAM PLAN® (LAM PLAN, France). This compound contains silicon nanoparticles formulated for efficient polishing of titanium and its alloys.

The edge roll off effect is inevitable during sanding, grinding and polishing processes, often observed in the polishing of silicon wafers [191]. This is where more material is removed at the edges of a sample compared to the centre, creating fillets around the edge of a sample. The result of this effect is illustrated in Figure 3.3(a). This effect is caused by non uniformity during the sanding/polishing processes [192]. The edge roll off effect was significant with the Ti64 samples, with mm scale reductions observed at the edges. Due to these observed edge roll off effects, a mask was applied in the PSI measurements to ignore the edges of the samples. This was applied in the interferometer software with a diameter of ϕ 40 mm at the centre of the samples. The measurement area is illustrated in Figure 3.3(b) from a top view.

The surface cleaning (step 3 in Figure 3.2) was carried out using de-ionised water and IPA (Isopropyl alcohol) wash to remove any residue from the polishing process. Subsequently, the cleaned samples were dried using a CDA (clean dry air) jet. This three step process was used to remove chemical contaminants from the surface. This was verified through EDS (Energy dispersive x-ray spectroscopy), discussed in Section 3.4.1.

After the plasma etching (step 4 in Figure 3.2), the mechanical polishing and surface cleaning steps were repeated (steps 5 and 6 in Figure 3.2). This is required since the samples after plasma processing are roughened to such an extent that the surface is optically opaque; i.e. the surface roughness is great enough to scatter light in all directions, such that any optical measurements are impossible. The mechanical polishing at step 5 was very brief (< 30 s), to ensure the surface was not altered more than necessary.

This whole method shown in Figure 3.2 was repeated after plasma etching experiments were completed in order to re-use samples.

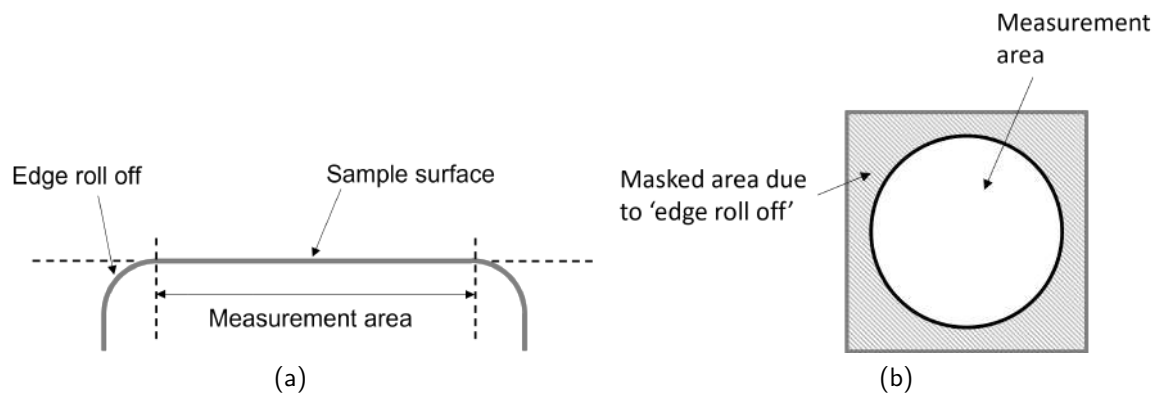


Figure 3.3: (a) Illustration of the edge roll off effect created during sanding and polishing, the edges show a fillet, adapted from [192]. (b) A top view illustrating the location of the measurement mask to ignore edge roll off effects.

3.2 Helios 1200 Setup

Figure 3.4(a) shows the Helios 1200 plasma etching machine. The torch in the Helios 1200 is, as far as literature shows, unique in design. The Helios 1200 can operate in an E dominated mode or H dominated mode, depending on the input power (refer to section 2.1.3). The E dominated mode is characterised by low electron density and a dim plasma plume, compared to a higher electron density when operating in H mode [193]. This is achieved by the design of the coil. Figure 3.4(b) shows a cross section of the plasma torch. The copper coil is made of 5 helical turns; the top 3 turns are hollow with coolant flowing through them, the bottom 2 turns are solid copper. These 2 uncooled 'free turns' have the benefit of making the plasma easier to ignite. The purpose of this design is to allow for plasma ignition in the E dominated mode without the need for an additional ignition device (such as a tesla coil) [194]. The Helios 1200 torch can be split into three distinct regions: a gas supply region below the copper coil, the excitation region around the coil, and the transportation region after the coil. The plasma temperature in the excitation region is $\sim 10,000$ K, and reduces to $\sim 1,000$ K in transportation region [194]. The torch enters an H dominated mode at high powers, occurring ~ 1 kW, and is observed as a sharp increase in brightness and size of the plasma plume. All experiments were carried out in the H dominated mode to provide a higher electron density. When operating at the higher power H dominated mode, the plasma can be considered thermal ($T_e \approx T_g$). The Helios 1200 plasma torch also has a standard De Laval nozzle attached to the end of the torch, shown in Figure 3.4(b). This reduces the full width at half maximum (FWHM) of the jet footprint, and increases the ionisation rate. The FWHM is the width of a Maxwellian distribution at half of the maximum value. The position and dimensions of the coil are the most critical factor influencing the stability and distribution of the plasma jet [194]. The Helios 1200 system uses two COMET CVBA 250AC capacitors to match the impedance of the RF network with the torch, in order to minimise reflected power. Previous work investigated the automation of this tuning network to account for variations in the system impedance [195]. However, for this thesis, the capacitors were adjusted manually since this automated network was not operational.

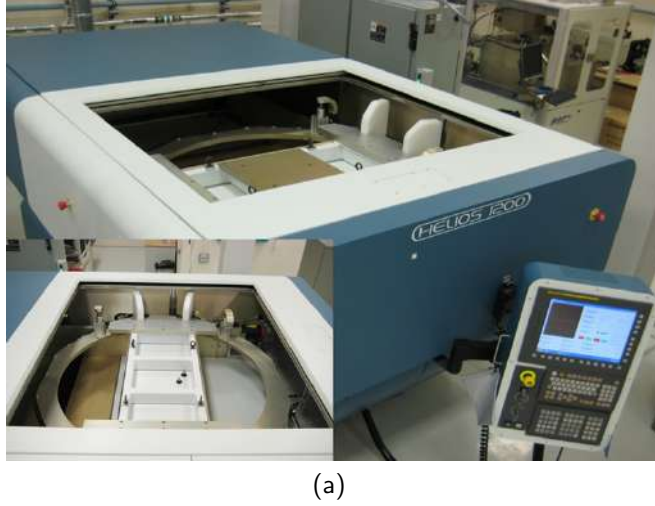
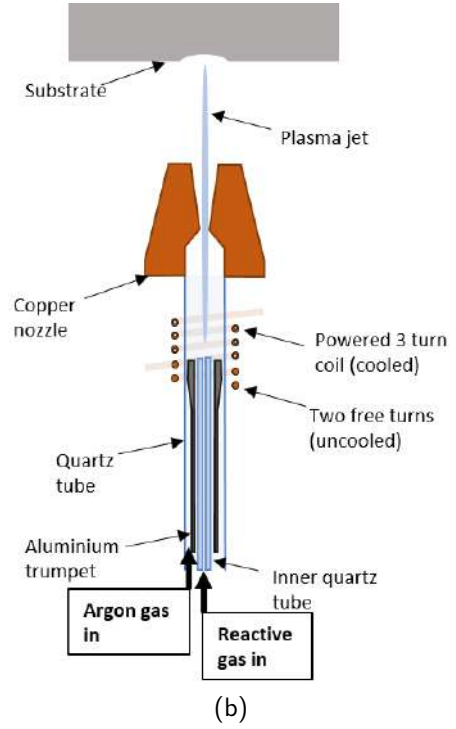


Figure 3.4: (a) Helios 1200 plasma etching machine (b) Illustration of the cross section of Helios 1200 torch design.

The experiments carried out on the Helios 1200 were conducted using an argon/ SF_6 plasma at flow rates of 20 L min^{-1} pure argon and 0.8 L min^{-1} $\text{Ar}(90\%)/\text{SF}_6(10\%)$ mix as the reactive species. The operating power was kept constant at 1.2 kW, at a frequency of $\sim 40.25 \text{ MHz}$ with $\sim 10 \text{ W}$ reflected power. The standoff distance was also kept constant at 6 mm. These have previously been found to be optimum operating parameters from previous work on this machine [41, 44]. The mounting setup in the Helios 1200 comprises of a copper gantry with a $200 \times 200 \text{ mm}^2$ gap hanging below the main 1.2 m mount, shown in Figure 3.5(a). To mount the $50 \times 50 \text{ mm}^2$ samples, a $200 \times 200 \text{ mm}^2$ aluminium plate was milled to hold 4 samples as shown in Figure 3.5(b). The use of aluminium was beneficial due to its resistance to fluorine chemical etching, and its relatively low electrical conductivity. The low electrical conductivity prevents the mounting plate from interfering with the operation of the plasma jet.

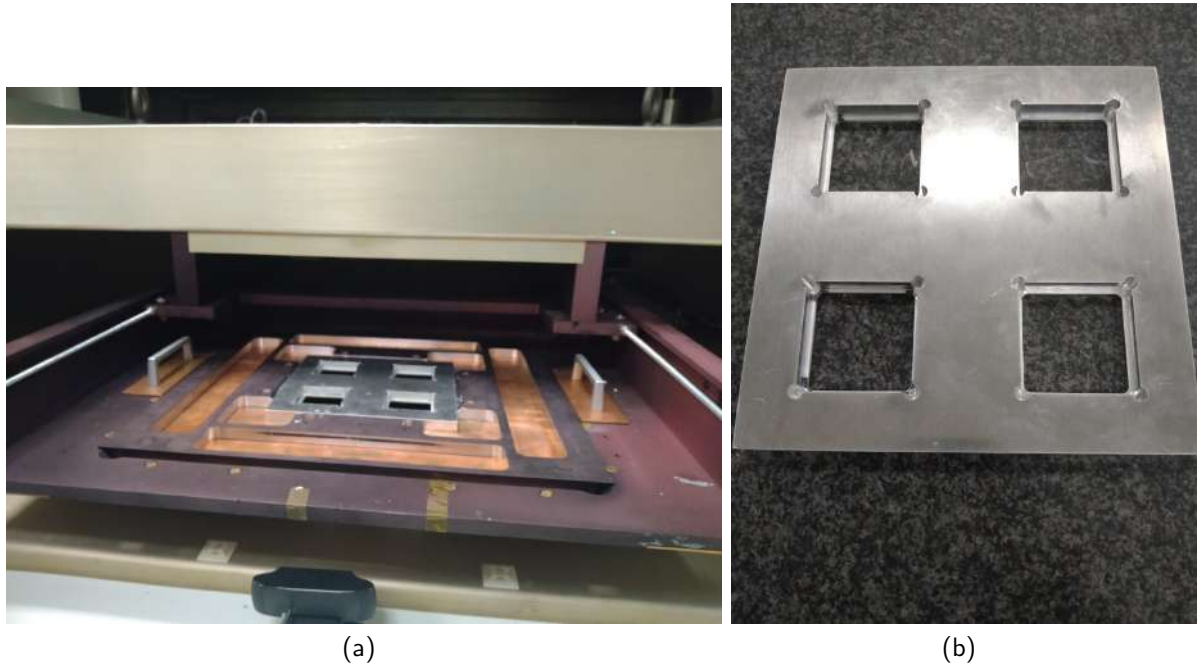


Figure 3.5: (a) Gantry for mounting in the Helios 1200 machine and (b) aluminium mount for 4 50x50 mm² samples.

Initially, stationary dwells were carried out where the torch was turned on and positioned in the centre of a sample. By measuring the material removed at various dwell times, the variation of material removal rate against time was calculated. This will also determine possible processing speeds for etching trenches; showing how long it takes to start the removing material. The operational condition of the Helios 1200 machine was verified by etching a 200 mm x 200 mm block of fused silica. The etch rate of fused silica when using SF₆ etchant is known from previous work on this machine [41]. A 1 s dwell was carried out, the result is shown in Figure 3.6. The maximum etch depth was 182 nm and the FWHM was 11.8 mm and 11.5 mm in x and y respectively. This is comparable to previous work, where the etched footprint was determined to have a FWHM of 10.9 mm $\pm$ 0.4 mm. The result shown in Figure 3.6 was measured using the Zygo PSI, discussed later in Section 3.3.1. Although the dwell was not perfectly gaussian and symmetrical, it was deemed good enough in order to proceed with experiments on Ti64 samples.

The stationary dwells were carried out at dwell times between 1 s - 10 s in 1 s

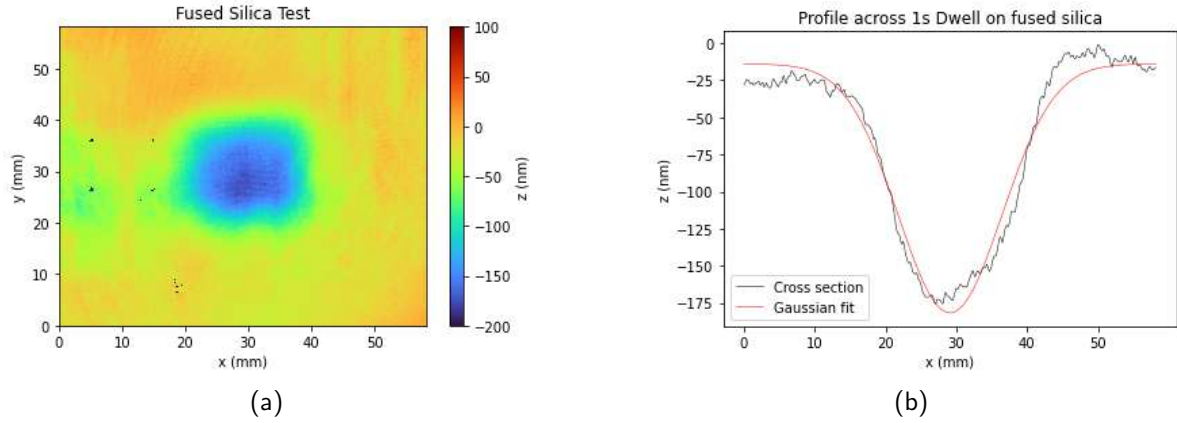


Figure 3.6: (a) 2D Dwell footprint for a 1s stationary dwell on fused silica and (b) cross sectional profile in the x direction with a gaussian fit to show operational condition of the Helios torch.

intervals. Dwell times of 1 s - 4 s showed no material removal. Table 3.1 shows the design of experiments with the measured outputs for three repeats between 5 s - 10 s. Values for maximum etch depth, FWHM in x and y and the MRR were determined.

Table 3.1: Design of experiments for 1 s - 10 s stationary dwells with three repeats at each dwell time.

Dwell time (s)	Maximum etch depth			FWHM _x			FWHM _y			MRR		
	1	2	3	1	2	3	1	2	3	1	2	3
5												
6												
7												
8												
9												
10												

After the stationary dwells, trenches were then carried out at speeds informed from the dwells. The processing speeds for trenches were initially determined based on the measured width of the plasma footprint (the hole etched in the stationary dwells). Equation 3.1 shows the relation between the FWHM and processing speed to ensure the torch spends the corresponding amount of time over a given point.

$$\text{Processing speed} = \text{FWHM} / \text{DwellTime} \quad (3.1)$$

After initial experiments showed a different etch depth to what the stationary dwells suggested, the range of speeds was expanded between 50 mm min⁻¹ to 250 mm min⁻¹ in 50 mm min⁻¹ intervals. These experiments showed the dynamic etching process required preheating to etch a clean trench. The preheating pass used for the trenches was kept consistent throughout the experiments. A pure argon plasma jet at the operating conditions of 1.2 kW and 6 mm standoff was used at 50 mm min⁻¹. This pass was carried out directly before the SF₆ was injected into the plasma stream. Table 3.2 shows the processing speeds and measured outputs for the trench experiments.

Finally, areal etching experiments were carried out to further investigate the etching process. As mentioned in Section 2.2.2, the standard procedure for surface figuring using plasma jets is to perform a deconvolution between the time function and beam function. This is because, as the plasma torch is moved back and forth over a surface, a certain point can be exposed multiple times to the plasma jet. The effect of this overlapping is taken into account by performing a deconvolution. The approach taken by Meister and

Table 3.2: Design of experiments for trench etching with three repeats at each processing speed.

Processing speed (mm min ⁻¹)	Maximum etch depth			FWHM			MRR		
	1	2	3	1	2	3	1	2	3
50									
100									
150									
200									
250									

Arnold [114] has led to the most accurate prediction of the material removal function during plasma etching. However, the amount of investigation required in order to accurately predict the material removal function during plasma etching would be extensive. This would require accurate models of heat conduction within the Ti64 samples and determination of the temporal dependence of the heat flux from the torch. Therefore, it was decided that the development of a full figuring process of Ti64 was unfeasible within the time frame of this PhD. To obtain results for areal etching, simplifications had to be made. These simplifications relate to both the beam function and the time function. The beam function was defined as a symmetrical 3D gaussian, shown in Equation 3.2. In Equation 3.2, B relates to the beam function, A is the pre exponential factor (in this case the etch rate), x and y are the surface position, and σ is the standard deviation of the beam footprint. Here, A is taken as 143 nm s⁻¹, based on the derivative of a linear relationship for etch depth against processing speed and σ was calculated as $FWHM/(2\sqrt{2 \cdot \ln(2)})$.

$$B = A \cdot \exp\left(\frac{x^2 + y^2}{2 \cdot \sigma^2}\right) \quad (3.2)$$

This simplification of the beam function by removing the temperature dependence was required since the thermal dissipation properties of Ti64 during plasma etching had not been defined in literature.

Initial areal plasma etching experiments were carried out by overlapping trenches at a constant speed and pitch, set as 100 mm min⁻¹ and 5 mm respectively. The average FWHM observed during the trench experiments was measured as ~10 mm, leading to the

pitch size of 5 mm (half the FWHM). See Figure 4.9(b) for all FWHM measurements. This back and forth (rastering) at a constant speed is called a neutral removal process which illustrates the thermal build effect on etch depth when overlapping trenches. The neutral removal experiments were initially carried out by overlapping three trenches (to observe if the pitch of 5 mm would result in a smooth removal footprint), then seven to cover the entire measured surface. Both of these experiments were carried out using a standard raster pattern, illustrated in Figure 3.7(a).

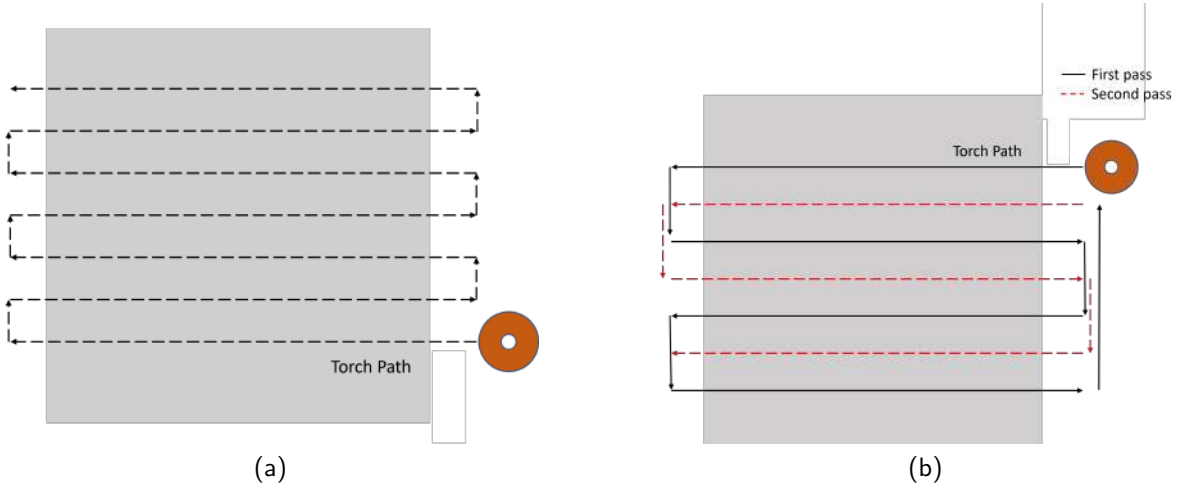


Figure 3.7: (a) Standard and (b) alternate pass raster patterns used for areal etching.

To investigate the non-linearity, the time function had to be greatly simplified. A code was written in python to interpolate the etch depth against processing speed from the trench experiments, see Figure 4.9(a) for these results. The python code is shown in Appendix D. The function fitted was defined as shown in Equation 3.3. This simplified time function was used to investigate the etching process under variable processing speeds.

$$Etch \ depth = 977137 \cdot Speed^{-1.51}. \quad (3.3)$$

Processing speeds were calculated for each pixel in the PSI surface measurement following this relationship, leading to a velocity map. See Section 3.3 for further details about the PSI setup. The processing speeds were set to result in a height of 0 nm for

each pixel i.e. a flat surface. The velocity map was exported as a text file with processing speeds for each x-y coordinate. This velocity map was averaged into areas of 5 mm x 1 mm to input into the Helios 1200 machine, which did not have the capability to change velocity every pixel ($\sim 193,000$ pixels in each measurement area). An illustration of this process is shown in Figure 3.8. The maximum speed was set to 500 mm min⁻¹, this occurred when the height of the pixel was below 0, i.e. no etching was required. This does not include temperature dependence, but also removes the spatial and temporal dependence on the etch rate. This method assumes the etch rate will be the same anywhere on the surface. These simplifications lead to a material removal function as defined in Equation 2.13, shown again in Equation 3.4 for convenience.

$$R(x, y) = \int_{-x}^x \int_{-x}^x B(x - u, y - v) \cdot \tau(u, v) \cdot du \cdot dv = B(x, y) * \tau(x, y) \quad (3.4)$$

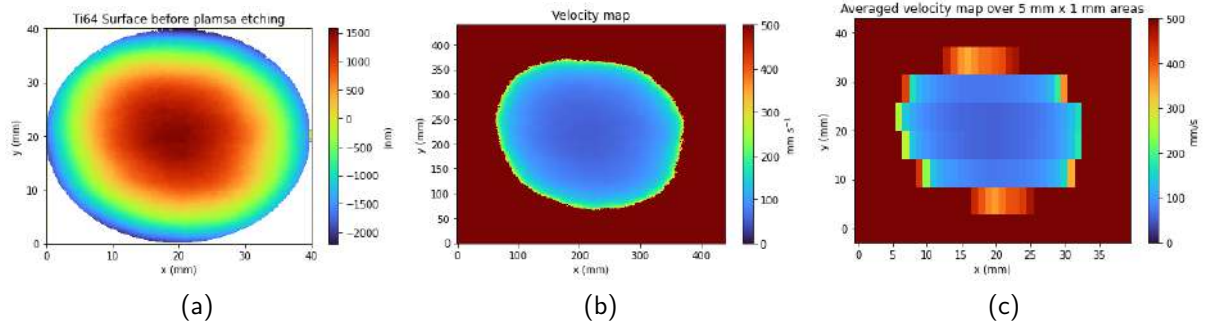


Figure 3.8: Steps taken to build the velocity map used for areal plasma etching: (a) Before plasma etching surface, (b) each pixel assigned a processing speed to reduce the surface height to 0, (c) averaged velocity map for areas of 5 mm x 1 mm.

The assumptions for both the beam and dwell time functions could lead to inaccurate predictions of material removal. However, the validity of these assumptions are tested by comparing the simplified material removal function to the plasma etched surface. Since the simplified dwell time function is used for both the actual plasma etching and the predicted material removal function, the resultant difference is a direct investigation of the simplified beam function. The approach followed for the areal plasma etching is illustrated in Figure 3.9.

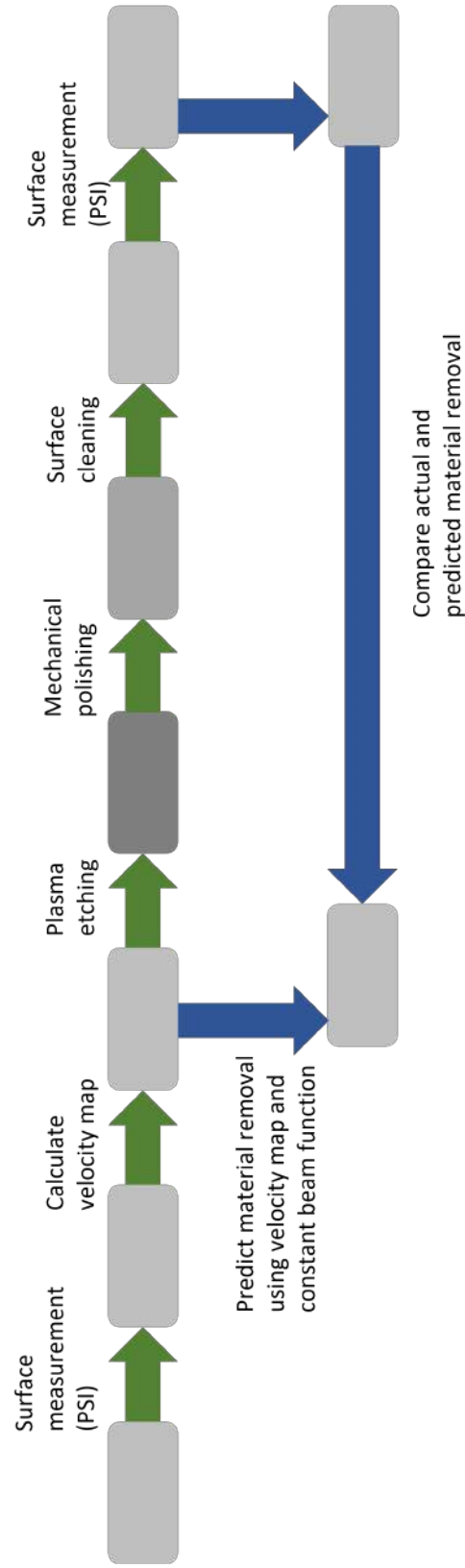


Figure 3.9: Flow diagram of the method taken for areal plasma etching.

The areal plasma etching results when employing a standard raster pattern showed a significant increase in the etch rate towards the centre of the samples. Figure 4.26(b) shows an increased etch depth of >500 nm. In an attempt to reduce this effect, an alternate pass raster pattern was employed, as shown in Figure 3.7(b). Also, by varying the time function between 100%, 125% and 150% of the calculated velocity map, the thermal effects of the plasma etching process could also be investigated. Table 3.3 shows the various parameters used for the time function in the areal plasma etching experiments.

Table 3.3: Processing conditions and speeds for areal plasma etching experiments.

Standard raster experiments	Alternate pass raster experiments
3 pass raster at 100 mm min^{-1}	1 x calculated speed
7 pass raster at 100 mm min^{-1} raster	1.25 x calculated speed
1 x calculated speed	1.5 x calculated speed

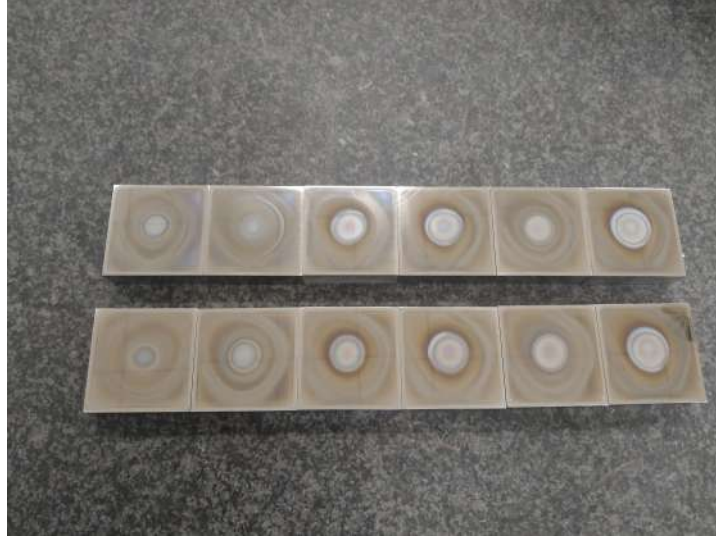
3.3 Methods for Surface Measurement

Throughout this work, various surface measurement techniques are used. To determine material removal, phase shifting interferometry (PSI) is used. For detecting high spatial frequencies, profilometry, coherence correlating interferometry (CCI) and atomic force microscopy (AFM) is used.

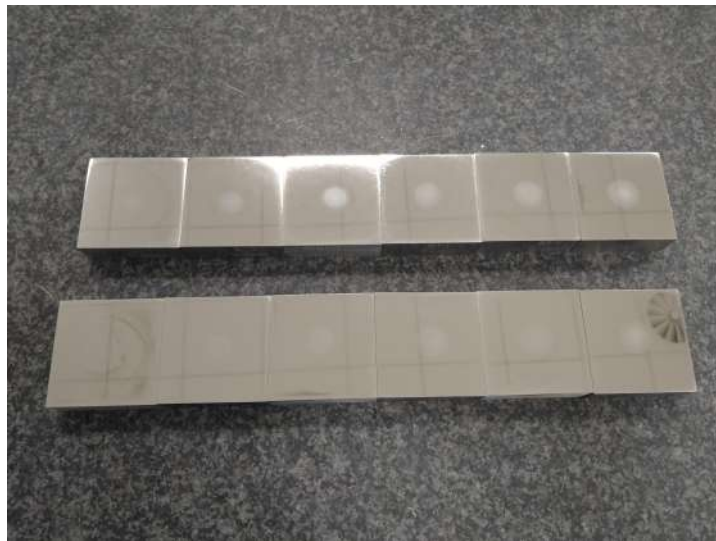
Surface measurements for both form and roughness were taken before and after the plasma etching process in order to determine material removal rates and the plasma torch footprint. To obtain an accurate perception of the surface topography, multiple spatial frequencies must be measured from nano-scale to mm scale. This requires multiple techniques, as mentioned in chapter 2.6. The techniques used throughout this work are: AFM, profilometry and interferometry to understand the surface topography over a wide range of spatial frequencies.

The points in the process at which measurements were carried out is illustrated in Figure 3.2 as: measurements A, B, and C. The measurements are referred to as; before plasma etching, immediately after plasma etching and after plasma etching & polishing.

Optical measurements could not be taken at the "immediately after plasma etching" stage (measurement B). The plasma etched surface was optically opaque and covered in a layer of fine dust. At this stage only SEM images were taken since the dust on the surface made roughness measurements meaningless. Since AFM and stylus profilometry were used for the high spatial frequency roughness measurements, the dust would adhere to the probe tip, leading to inaccurate measurements. Figure 3.10 (a) shows two samples at each dwell time immediately after plasma etching, illustrating the opaque nature of the resultant surface. The samples are arranged from left to right in terms of increasing dwell times. Figure 3.10 (b) shows the same samples after plasma etching and polishing. Although a white spot remains at the centre of the dwell, these samples were reflective enough for PSI measurements.



(a)



(b)

Figure 3.10: Images of the Ti64 samples (a) immediately after plasma etching and (b) Images showing the Ti64 samples immediately after plasma etching and after plasma etching and polishing for dwell times between 5-10s (left to right).

3.3.1 Low-mid spatial frequency measurement methods

Form measurements were taken by two different interferometers: An FST10 from Fisba Optik which is a Twyman-Green interferometer (Fisba Optik, Switzerland), and a Dynafiz[®] from Zygo which is a Fizeau interferometer (Zygo, USA), referred to as the *Fisba* and *Zygo* respectively hereafter. Both pieces of equipment measure low spatial frequencies (form), and were used to characterise the material removal from the plasma etching. Both interferometers were setup in phase shifting mode (PSI). The switch from the Fisba to the Zygo was made because the Zygo was simply faster and easier to take measurements. The Fisba requires re-calibration between every measurement but the Zygo auto-calibrates using a reference optic and a mounted transmission lens. The Fisba and Zygo setups are shown in Figure 3.11(a) and (b) respectively. The measurements using both the Fisba and Zygo were carried out using a $\phi 40$ mm measurement mask, applied in the software (μ Shape Mx[®]). This mask set the interferometers to ignore any pixel outside the selected location. This mask was applied to remove the edge roll off effects present on the sample. The edge roll off effect is described in Section 3.1. No cutoffs were applied to these results since the real amount of material removed was desired. Applying cutoffs to filter out the high spatial frequencies is unnecessary here, since the amplitude of the form is much greater than that of the high spatial frequency roughness.



(a)



(b)

Figure 3.11: (a) Fisba Optik FST10 Twyman-Green Interferometer and (b) Zygo Dynafiz[®] Fizeu Interferometer.

The surface form deviation (also called peak to valley - PV) is the difference between the highest and lowest points on a surface. All the samples had a surface form deviation (PV) of $< 5 \mu\text{m}$ across the measurement area, after the sample preparation process.

The repeatability of the Fisba and Zygo measurements was quantified as PV deviations of $\pm 20 \text{ nm}$ and $\pm 30 \text{ nm}$ respectively, indicating the variation between repeat measurements. These errors can be caused by a number of factors including: the environment (humidity, temperature etc.), local vibrations or inaccuracies in repositioning.

Figure 3.12 shows the difference between two measurements of a Ti64 surface after a sample was measured, removed then remeasured. Figure 3.12 (a) relates to the Fisba and (b) for the Zygo. These repeatability measurements indicate that any surface features below $\sim 20 \text{ nm}$ (Fisba) and $\sim 30 \text{ nm}$ (Zygo) will not be accurately measured. Features below this will be distorted, since repeat measurements can vary by more than the feature size.

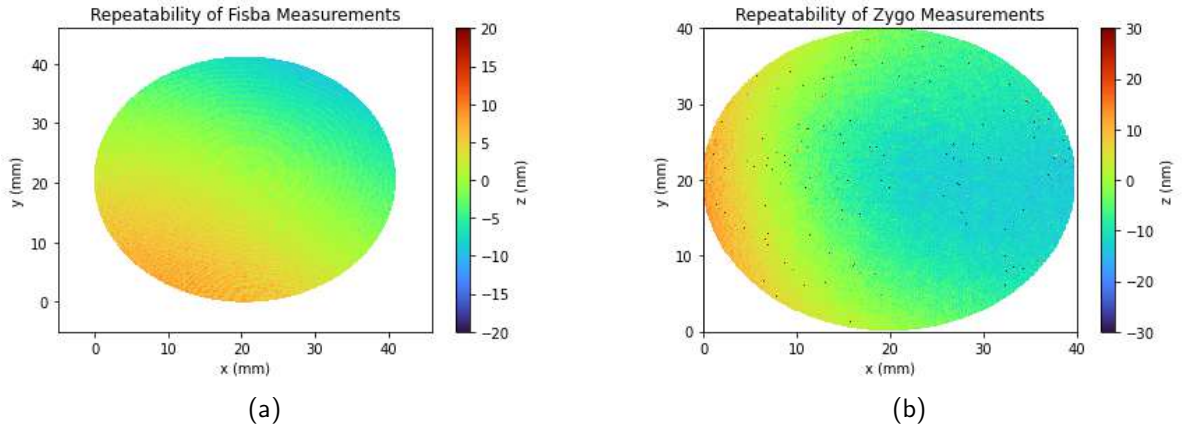


Figure 3.12: Positioning errors for (a) Fisba and (b) Zygo PSI setups.

The setup for the Fisba involved both active and passive damping plates under the interferometer to help reduce noise from vibrations, as seen in Figure 3.11(a). The interferometer used a laser of wavelength 632.8 nm , a precision tilt stage resting on three ball point adjustable screws, and a three point location system to position the sample. This ensures the fringes on the interferogram were as wide as possible. The Fisba measurements resulted in a 820×820 pixel surface, with each pixel measuring $\sim 48 \times 48 \mu\text{m}^2$.

The Zygo setup also used a laser with wavelength of 632.8 nm and a precision tilt stage with 3 point location to ensure repeatable measurements. The Zygo setup is shown in Figure 3.11(b). The highly reflective, polished Ti64 surfaces required a Dynaflect™ transmission flat from Zygo (Zygo, USA) to be included. This was mounted on the interferometer to attenuate the received signal ensuring the interferometer detector is not saturated. Noise was removed from the measurements through the inbuilt "noise tolerant" algorithm in the Mx software used. The measurements using the Zygo resulted in a 440x440 pixel surface, with each pixel measuring 90x90 μm^2 . Thresholding was also applied to the measurements from the Zygo in the Mx software to remove the contribution from any points which did not reflect enough light. In this context, the thresholding value is set at a percentage of the maximum intensity. If a pixel is detected with an intensity below this value, it is removed and filled as a null point. This thresholding was set to the default value of 7%. This is important since points which register as very low intensity will be inaccurate and not a representation of the true surface. Measurements were taken at points A and C (see Figure 3.2), following the good practice guides mentioned in Section 2.6. Each measurement was averaged over 5 repeats to reduce any noise present in the result. By subtracting the surface of measurement A, from the surface of measurement C, material removal rates and the FWHM of the plasma torch footprint were calculated. The values of FWHM were calculated as shown in Equation 3.5 and MRR was calculated using Equation 3.6 for the stationary dwells and Equation 3.7 for the trenches.

$$FWHM = 2 \cdot \sqrt{2 \cdot \ln(2)} \cdot \sigma \quad (3.5)$$

$$MRR_{static} = \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{f(x, y) \cdot dx \cdot dy}{\tau_{dwell}} = \frac{2\pi D_{max} \sigma_x \sigma_y}{\tau_{dwell}} \quad (3.6)$$

$$MRR_{dynamic} = \frac{\int_{-\infty}^{\infty} \frac{f(y) \cdot dy \cdot L}{\tau_{trench}} = \frac{\sqrt{2 \cdot D_{max}} \cdot \sigma_y \sqrt{\pi} \cdot L}{\tau_{trench}} \quad (3.7)$$

A Talysurf 6000 Coherence Correlation Interferometer (CCI), shown in Figure 3.13,

was used to characterise a large area of the surface using a 20x magnification lens with a field of view of $900\text{ }\mu\text{m} \times 900\text{ }\mu\text{m}$. No cutoffs were applied to these results since the real (primary) surface was desired to observe the effect of the plasma etching on all spatial frequencies. A white light source was used since the slope angles present on the Ti64 samples are relatively low so the shorter coherence length was helpful to determine the order of the fringes observed. Samples were positioned on the CCI stage using gauge blocks to ensure they were parallel to the bottom of the stage. The field of view was kept consistent between measurements by using the corner of the sample as a reference. The stage could then be moved a set distance to ensure measurements are being carried out at a known position. The samples were levelled using the inbuilt levelling programme in the mountains software used to plot the results.



Figure 3.13: Talysurf 6000 coherence correlating interferometer (CCI) setup.

3.3.2 High spatial frequency roughness measurement methods

High spatial frequency surface roughness was measured using a Form Talysurf 120L profilometer from Taylor Hobson (Taylor Hobson, UK), shown in Figure 3.14(a). The profilometer was setup with a conispherical diamond tipped stylus, with a tip radius of $2\text{ }\mu\text{m}$ and a measurement speed of 0.5 mm min^{-1} . Samples were positioned on a stage controlled using a micrometer, as seen in Figure 3.14(a). Results were obtained for measurement A and C, shown in Figure 3.2. Five profiles were taken at 5 mm intervals to get a statistically relevant result. These measurements were taken about the centre of each sample as illustrated in Figure 3.14(b). The sample length of each profile was 5 mm. Cutoffs were applied to remove the contribution from low and medium spatial frequencies. The applied cutoffs were $\lambda_s=0.008\text{ mm}$ and $\lambda_c=0.25\text{ mm}$. Cutoffs were explained in Section 2.6. The Ti64 samples were positioned using a 3 point location setup, to ensure precise positioning between measurements A and C. The equipment was levelled by hand for each measurement before applying the above stated cutoffs.

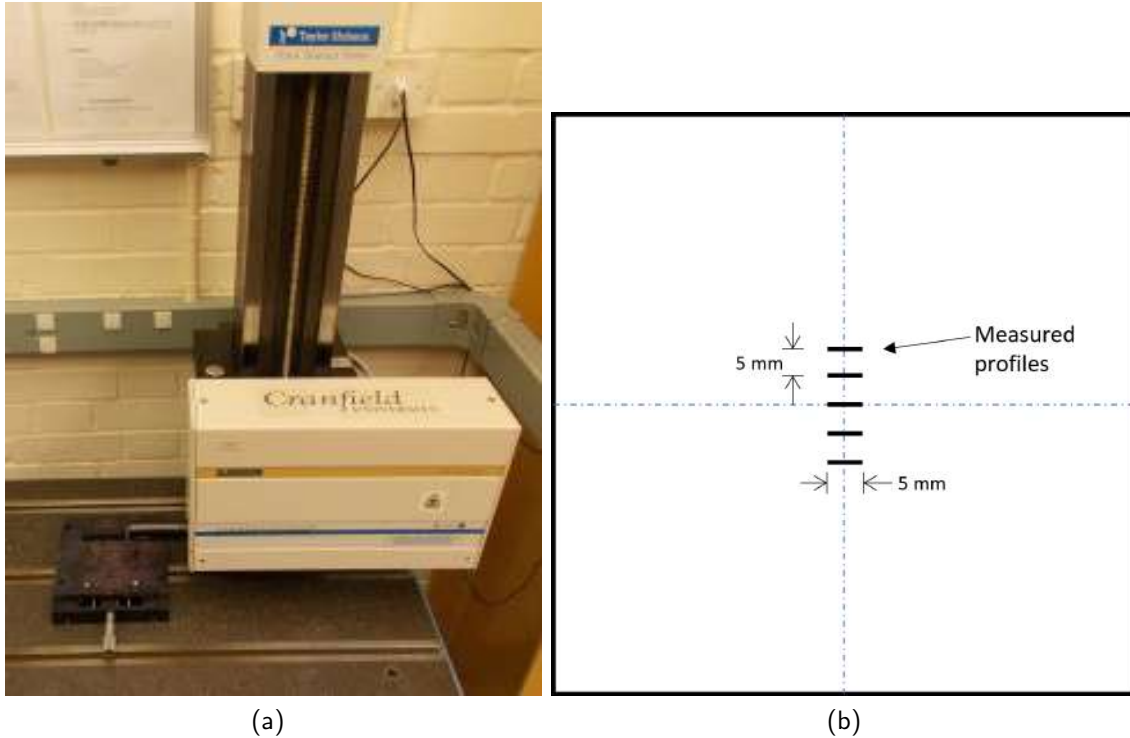


Figure 3.14: (a) Form Talysurf 120L profilometer setup and (b) measurement positions.

Atomic Force Microscopy (AFM) measurements were carried out to closer inspect the grain structure on the etched Ti64 surface. A Bruker Veeco Dimension 3100 system was used (Bruker, USA), shown in Figure 3.15. The measurement area was $25 \times 25 \mu\text{m}^2$, using a nanoSensors AFM Probe PPP-NCHR-10 tip with a nominal radius of $\sim 10 \text{ nm}$ and nominal length of $125 \mu\text{m}$. The scans were carried out in tapping mode. AFM results provide detailed view of the surface microstructure due to the nano-scale tip used.



Figure 3.15: Bruker Veeco Dimension 3100 AFM machine.

3.4 Microstructure and chemical measurement methods

3.4.1 FactsageTM simulations

Thermodynamic simulations at equilibrium were carried out using FactsageTM software, which calculates the products formed under equilibrium conditions given the reactants and their quantities. The calculation of the products is based on the minimisation of Gibbs free energy. Although this software cannot take into account the effects of ionisation, it still provides a useful approximation of the resultant compounds that could be formed. The conditions during the plasma etching process and the quantities of all reactants were input into FactsageTM. The software then outputs a table of all the compounds created. The software does not accept Ti64 alloy as a valid input so Ti, Al and V were input separately in their respective quantities in grams (based on the data sheet provided by the supplier). The amount of SF₆ was determined as the mass per second at the set flow rate, taken as 8.55 mg. These simulations were run at the estimated temperature of the plasma jet at the operating standoff distance (850 K), determined via simulation in previous work on this equipment [44]. Further simulations were then carried out with the same input parameters but varying the temperature from 500 K to 1500 K in 50 K intervals to investigate the evolution of TiF₄ formation.

3.4.2 Scanning Electron Microscopy (SEM) and Energy Dispersive x-ray Spectroscopy (EDS) Methods

SEM images were taken using a Vega 3 from Tescan (Tescan, Czechia), shown in Figure 3.16. These images were taken to observe the effect of the plasma etching process on the grain structure of the Ti64 samples for the samples on which a trench was etched. Although Ti64 has relatively low electrical conductivity, it is still a metal alloy with free electrons, so SEM images can be taken without any impact of charge build up. The Ti64 samples were placed in the SEM and secured to mounting plates via carbon tape.

The SEM operated under low vacuum and beam intensities were varied from 10 kV and 20 kV. By reducing the beam intensity, the SEM images will be more sensitive to the surface. Both secondary electron (SE), and back scattered electron (BSE), imaging was also used. SE images relate to electrons directly from the substrate and provide information about the morphology of the surface. BSE images however relate to electrons from the electron beam which are scattered back to the detector. BSE images provide information from deeper in the sample compared to SE images. SEM images were taken at each measurement step: A, B, and C in Figure 3.2. Wide field SEM images were taken at low magnification (5x and 6x), to view the entire 50 mm x 50 mm sample, then higher magnification images (5000x) were taken at points across the plasma etched trench at 2mm intervals. This shows the variation in the microstructure of Ti64 across the width of the plasma jet.



Figure 3.16: Tescan Vega 3 SEM machine.

Energy dispersive x-ray spectroscopy (EDS) spectra were taken to determine elemental composition. Areal spectra, line scans, and point scans were taken across the plasma etched trenches. This developed an understanding of the chemical impact of

the etching process, and the effect of position relative to the plasma jet. Peaks from the spectra obtained were identified initially using the auto assign feature. Any peaks which the software misidentified, were manually assigned with reference to literature. This manual identification was important since some peaks, such as the titanium $K\beta$ and vanadium $K\alpha$, have very similar energies (4.93 eV and 4.95 eV). The auto assign feature, built into the EDS Aztec software (Oxford instruments, UK), can mis-identify these peaks due to this similarity in energy.

To determine the $\alpha:\beta$ ratio in the SEM images, ImageJ was used. In the unprocessed samples, the α and β phases appeared very similar. Therefore, the boundaries between the phases had to be defined manually. Polygons were drawn around the β phases, then filled with a block colour to provide a contrast from the α phase. The image was then thresholded, based on contrast, to result in a black and white image. The $\alpha:\beta$ ratio was taken as the percentage of the total number of pixels counted in the white and dark areas. Examples of this process are shown in Appendix B. As mentioned in Section 2.4.1, the $\alpha:\beta$ ratio is dependent on the manufacturing process, and has an impact on the properties of the alloy. The implications of this ratio on APP etching are discussed further in Section 4.4.2

3.4.3 X-Ray diffraction (XRD) method

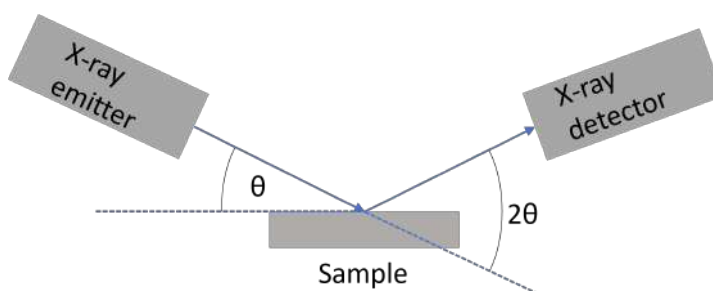
X-Ray Diffraction (XRD) scans were taken using a Siemens D5005 diffractometer (Siemens, Germany), shown in Figure 3.17(a). This machine uses a $\text{CuK}\alpha$ source. This operates by bombarding a copper target with an electron beam, which ejects an electron from an inner orbital, creating a vacancy. X-ray radiation is emitted when an electron transitions to this vacancy from a higher orbital. The XRD machine produces x-rays at 1.6 kW (voltage of 40 kV and current of 40 mA) at a wavelength of $1.5406\text{\AA}$ (0.15406 nm). The peaks produced by the x-ray diffraction pattern are related to specific species, their crystal structure and orientation. Samples were secured on the stage using double sided carbon tape.

Taking the incident angle of the x-rays with the sample as θ , the angle of the detector

with this incident x-ray beam is 2θ . This is the convention used for angles of diffraction in XRD analysis. This is illustrated in Figure 3.17(b). The scans were carried out at 2θ angles between $10-90^\circ$ with a step size of 0.25° . The XRD spectra were taken at each stage; before plasma etching, immediately after plasma etching and after plasma etching and polishing. This was carried out to investigate the affect of the plasma etching process on the crystal structure of the Ti64 samples at a deeper depth than could be observed via SEM, since the x-rays penetrate deeper into the sample than electrons.



(a)



(b)

Figure 3.17: (a) Siemens D5005 XRD machine and (b) illustration of angles used in XRD, where 2θ is twice the angle of incidence.

Chapter 4

Results and Discussions

Here the results are displayed along with relevant discussions about the implications and limitations of the gathered data. The structure of Chapter 4 is set out to provide a logical flow for the reader. Initially the results of the FactsageTM simulations are discussed to show what purely thermodynamic equations suggest would be produced. Sections 4.2 and 4.3 provide the results for the stationary dwells and trenches respectively. Sections 4.3 is split into two parts: material removal, and roughness measurements. The majority of the discussion of the APP etching process is set out in Section 4.4, where the SEM, EDS and AFM analysis is shown. This section provides an explanation of the etching mechanism with AFM results illustrating the preferential etch of the β phase of Ti64. Section 4.5 covers the areal etching, and a comparison of material removal with a predicted material removal function.

4.1 Analysis of the FactsageTM Simulations

The plasma temperature at the operating standoff distance of 6 mm, is assumed to be $\sim 850\text{K}$, as mentioned in Section 3.3.2. Thermodynamic simulations were run in order to obtain an estimate of which products may be formed during the etching process using SF_6 on a Ti64 surface. Table 4.1 shows the top products formed at equilibrium, determined by the FactsageTM software at 850K. VF_x compounds do not feature in this list since the software predicts negligible amounts formed due to the low concentration of vanadium.

Table 4.1: Thermodynamic simulation results at 850K from FactsageTM showing the most formed products from the plasma etching process.

Product	Fraction(%)
TiF_3	80.94
TiF_2	15.16
AlF	3.8×10^{-2}
AlF_3	6.48×10^{-4}
AlF_2	4.19×10^{-4}
TiF	5.60×10^{-7}
TiF_4	4.31×10^{-7}

These thermodynamic simulations were also carried out at temperatures between 500 - 1500K to investigate the formation of TiF_4 . Figure 4.1 shows the calculated fraction (%) of TiF_4 produced follows an exponential trend as temperature increases. This would drop rapidly as the temperature reaches the melting point of Ti64 ($\sim 1600^\circ\text{C}$), but the equipment used here would not approach such high surface temperatures. Working on the assumption that TiF_4 is the only volatile titanium product formed, these simulations suggest that the etch rate is exponentially related to the surface temperature.

As mentioned in section 3.3.2, there are many limitations of this software for a plasma etching application. The software determines the products without taking into account the ionisation of the plasma jet and assumes equilibrium conditions. Both of these assumptions are not valid when considering the Helios 1200 plasma jet. While the calculated quantities cannot be considered accurate, some conclusions can be drawn from these simulations. Without taking into account ionised species, very little of the

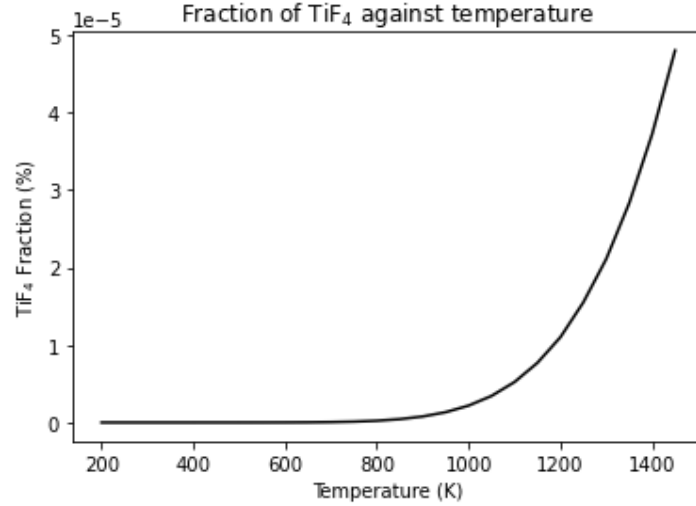


Figure 4.1: Fraction of TiF_4 formed at temperatures between 500-1500K as calculated from FactsageTM.

volatile TiF_4 would be expected. However, large quantities of the non-volatile TiF_3 are predicted.

4.2 Stationary Plasma Dwells on Ti64

Despite the unpromising simulation results, the experimental results proved more encouraging. The stationary dwells were carried out on the Ti64 samples, with dwells times chosen between 1 s - 10 s. The first dwells carried out at 1s showed no etching present, as did the dwells between 2-4s. The machine was checked over to ensure there was no damage, it was in good condition and operating well. Experiments continued and an etch footprint was seen at a 5s dwell time, Figure 4.2 shows the 2D footprint and profiles in x and y with gaussian fits as measured by the Fisba interferometer.

After carrying out three repeats at each dwell time between 5-10s, a plot can be created showing how the FWHM varies against dwell time. This is shown in Figure 4.3. The increase in FWHM, with respect to dwell time, shows the torch footprint is not stable. Eventually this trend would plateau at a set FWHM dependent on the plasma jet. This has been observed with silicon based substrates to be ~ 11 mm after a dwell time of 1 s [41]. However, even after a dwell time of 10s on Ti64, the FWHM has only

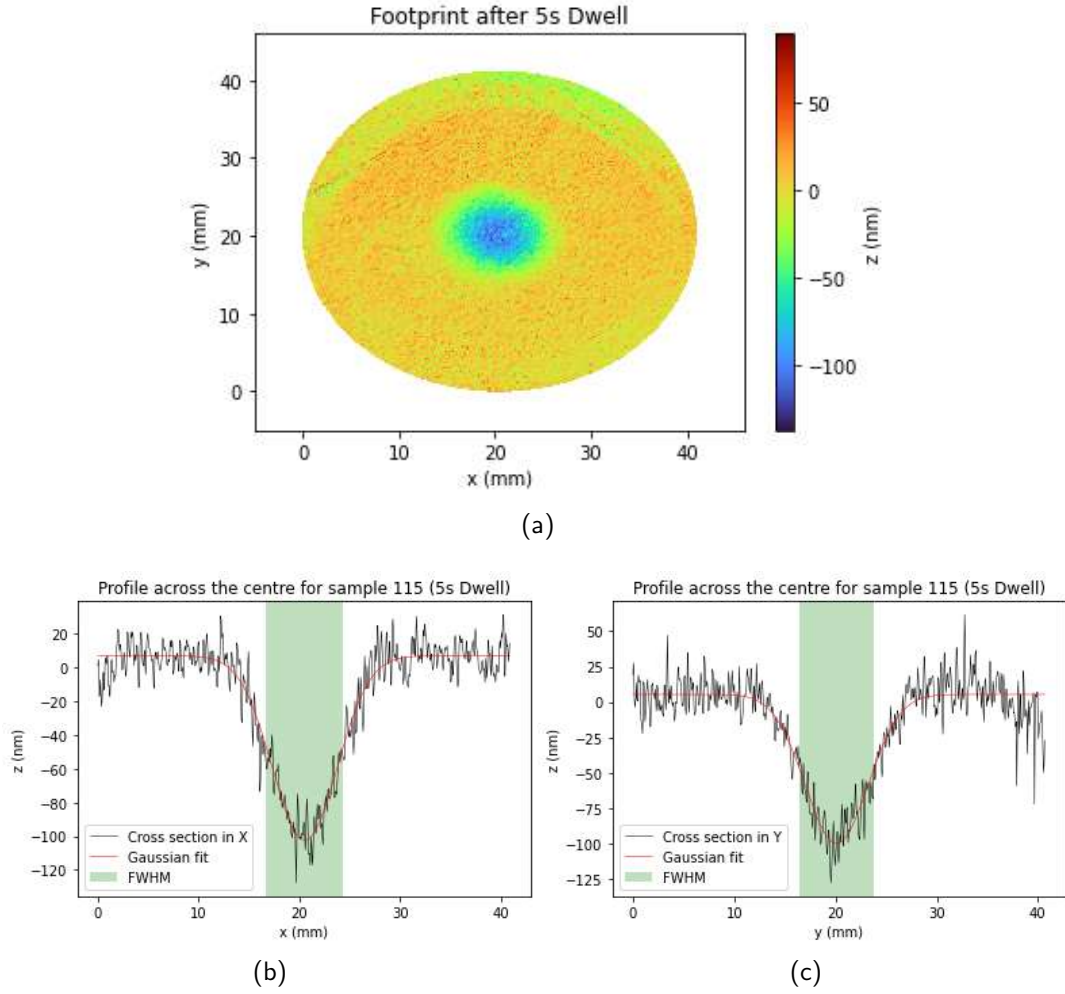


Figure 4.2: (a) 2D Dwell footprint and profiles in (b) x and (c) y directions on a Ti64 sample with gaussian fits after a 5s dwell.

reached ~ 9.5 mm and does not appear to be levelling off. The trend for maximum etch depth against dwell time is shown in Section 4.3 for ease of explanation.

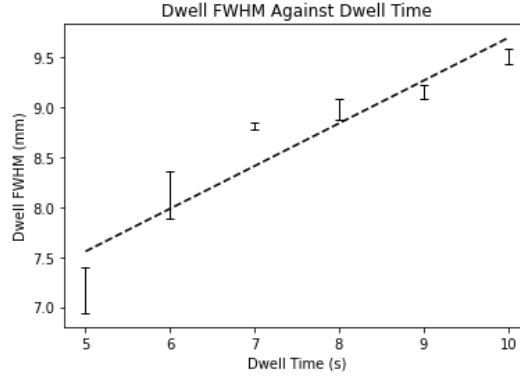


Figure 4.3: FWHM against dwell time for stationary dwells on Ti64 between 5 s to 10 s. The error bars show $\pm$ the standard deviation of the 3 repeats at each speed.

4.3 Trenches

4.3.1 Material Removal

From the dwell depth and FWHM plots, a range of speeds were chosen for experiments to etch trenches (dynamic etching). As mentioned in Section 3.2, the range of processing speeds was initially chosen based on the relationship with the FWHM (Equation 3.1). Table 4.2 shows the processing speeds for the torch to cover one FWHM based on the results in Table 3.1 and Equation 3.1.

Table 4.2: Calculation of processing speeds for trenches.

Dwell time (s)	Average FWHM (mm)	Processing speed (mm min^{-1})
5	7.17	86
6	8.12	81
7	8.81	76
8	8.98	67
9	9.16	61
10	9.51	57

To provide a wider range of speeds, the initial experiments were carried out at 100 mm min^{-1} . Figure 4.4 shows the footprint of a trench at 100 mm min^{-1} , where the torch was moving from right to left. The inconsistency in etch depth on the right of Figure 4.4 indicates that the etching is not initially stable. However, around half way along the trench ($x=20 \text{ mm}$), the etch depth begins to stabilise. Towards the end of the trench ($x=10 \text{ mm}$), a clean trench is observed. The etch depth in Figure 4.4 is far greater than

the dwell experiments would suggest. The FWHM taken at $x=10$ mm, was measured to be 7.8 mm. The equivalent dwell time at 100 mm min^{-1} would be ~ 4.7 s. The results in Table 3.1 would suggest an etch depth of <100 nm for a dwell time of 4.7 s. However, Figure 4.4 shows a maximum etch depth of ~ 500 nm.

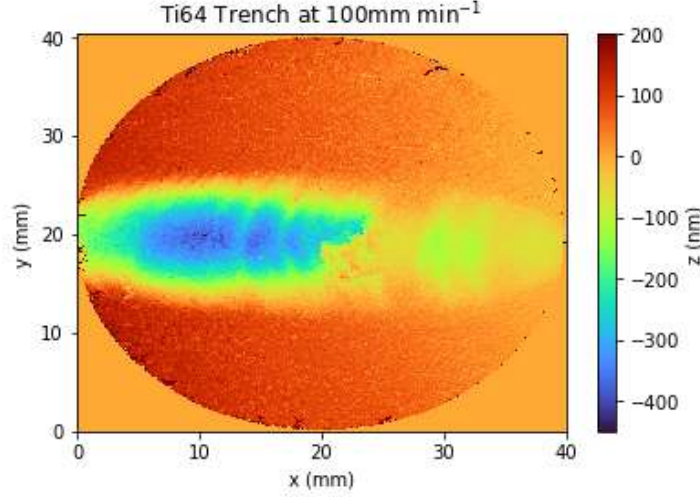


Figure 4.4: Footprint from etching a trench at 100 mm min^{-1} . The torch was moving from right to left.

As stated in Section 2.2, the etching process follows the Arrhenius equation. The chemical reaction rate is dependent on the temperature of the etchant and the surface. The stabilisation of the etch rate around $x=20$ mm in Figure 4.4, shows the time required for the surface to heat up enough for chemical etching to take place. This leads to the conclusion that the dwell times below 5 s are acting purely to heat the sample and emphasises the thermal dependence of the etching process. Here, the results for etch depth against dwell time are presented in Figure 4.5. This shows what initially looks like a linear trend due to: (1) the small range of dwell times explored (5 s - 10 s), and (2) the thermal effects illustrated in Figure 4.4.

A logical next step was seen as preheating the samples before etching, seeing as the etch rate seemed to stabilise as the sample heated up. Figure 4.6 shows the footprint from a single trench at 100 mm min^{-1} after doing a preheating pass using a pure argon plasma jet at 50 mm min^{-1} . This shows a much more stable etch rate with a maximum etch depth of 866 nm and a FWHM of 10.5 mm. 50 mm min^{-1} was chosen to ensure

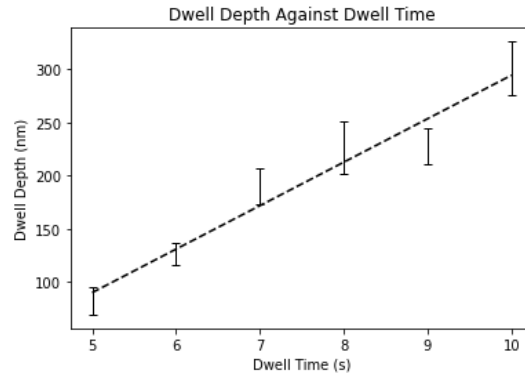


Figure 4.5: Etch depth against dwell time for 5-10s dwells, no etching was observed at dwell times below 5s.

the sample was heated up sufficiently. Figure 4.7 shows that this process did not lead to any significant etching of the surface.

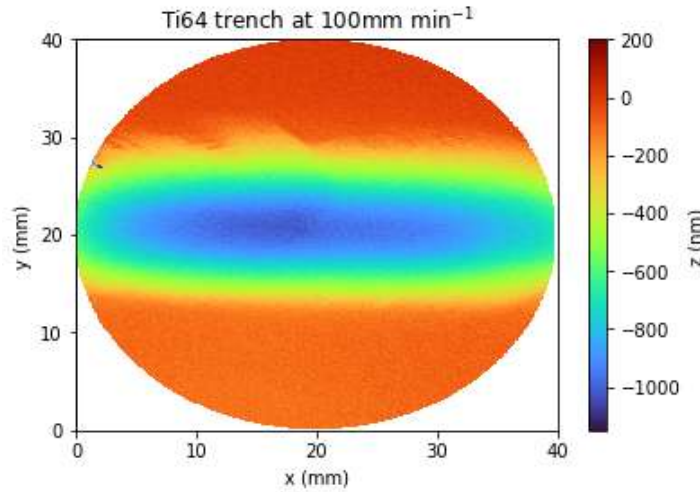


Figure 4.6: Footprint from etching a trench at 100 mm min^{-1} after a single pass using pure argon at 50 mm min^{-1} to preheat the sample. The torch was moving from right to left.

Once etching had been shown to be stable using an initial preheating pass, the time dependence of the etch rate had to be characterised. Figure 4.8 shows the results from each processing speed. The maximum etch depths varied from 2886 nm to 227 nm for processing speeds between $50 - 250 \text{ mm min}^{-1}$. The FWHM varied from 12.5 - 9.6 mm for processing speeds between $50 - 250 \text{ mm min}^{-1}$. While the preheating enabled clean trenches to be etched, Figures 4.6 and 4.8 show there was always an increased etch depth at the centre of the trench. This is due to the low thermal conductivity of the Ti64 and

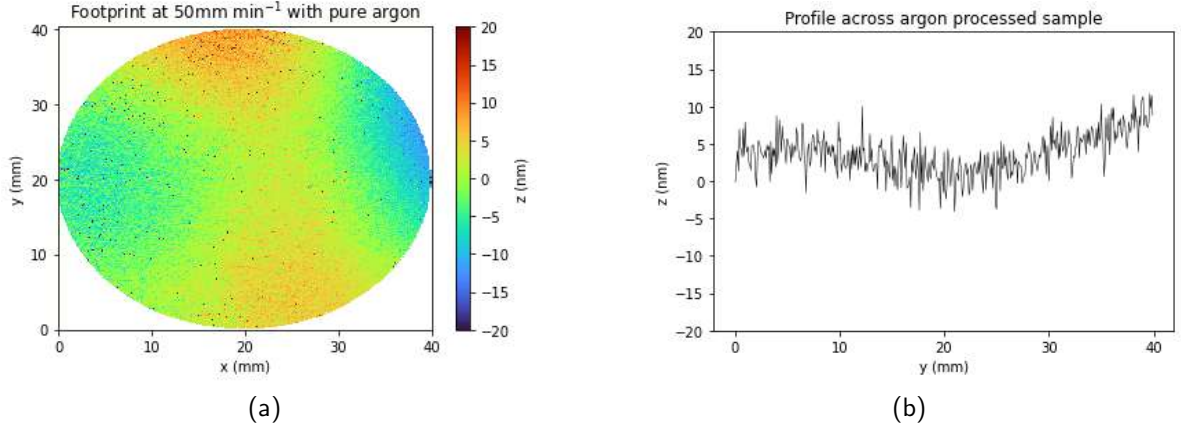


Figure 4.7: (a) Footprint and (b) profile after 50 mm min^{-1} pure argon trench. The torch was moving from right to left at $y=20 \text{ mm}$.

the relatively small size of the samples ($50 \text{ mm} \times 50 \text{ mm}$), in comparison to the size of the plasma jet (area of influence $\sim \phi 20 \text{ mm}$). The heat will not be dissipated as much from the centre of the sample compared to the edges leading to an increased temperature in the centre and thus increased etch rate.

Three repeats were carried out at each processing speed to ensure precise and statistically valid results. Figure 4.9 shows how (a) the maximum etch depth, (b) the FWHM and (c) the MRR varies with processing speed. The error bars show $\pm$ the standard deviation between the three results taken at each speed. In Figure 4.9(a), the trend for the maximum etch depth was calculated as $977137 \cdot x^{-1.51}$, where x is processing speed. The trend line was decided as an inverse power since an exponential trend would not accurately depict the tail of the curve. The etch rate would eventually drop to 0 as the processing speed is increased. This mechanism is more accurately described by an inverse power. The apparent linear trend in etch depth against time observed for the stationary dwells is due to a small sample of dwell times investigated. The etch depth would increase with a similar trend to that observed when etching trenches in Figure 4.9(a) if longer dwell times were carried out. As shown from the plot of FWHM against dwell time, Figure 4.3, the etching takes a considerable amount of time to reach a thermal equilibrium, or at least a partial equilibrium. Since the FWHM of the torch footprint has not reached a plateau after 10 s and the fact that the etching process is

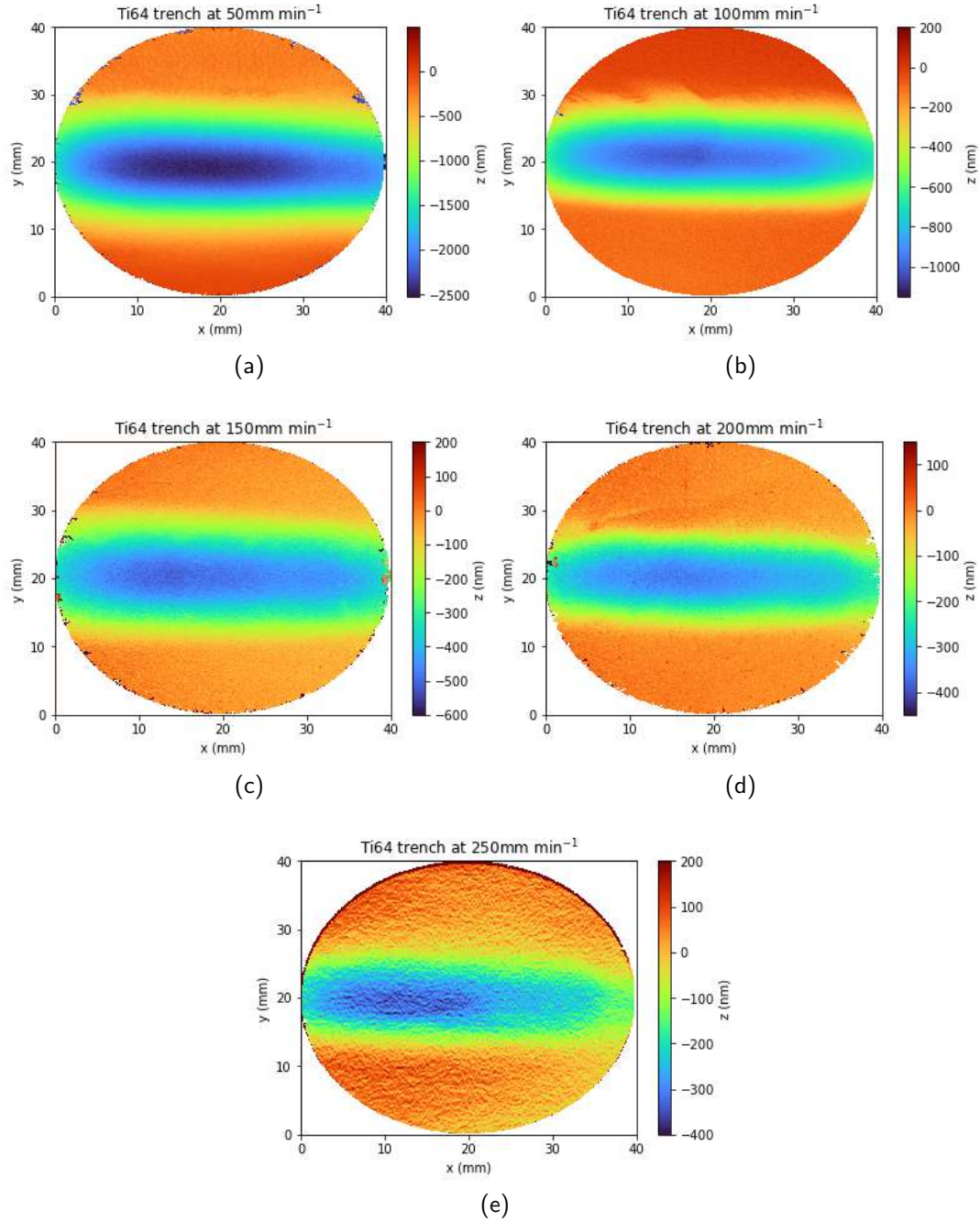


Figure 4.8: Trench footprints for speeds between 50-250 mm min⁻¹ increasing speeds from (a)-(e), after preheating using a pure argon plasma at 50 mm min⁻¹. The plasma torch was moving from right to left in all cases.

thermally dominated, it can be concluded it has not approached any kind of thermal equilibrium in the dwell times investigated.

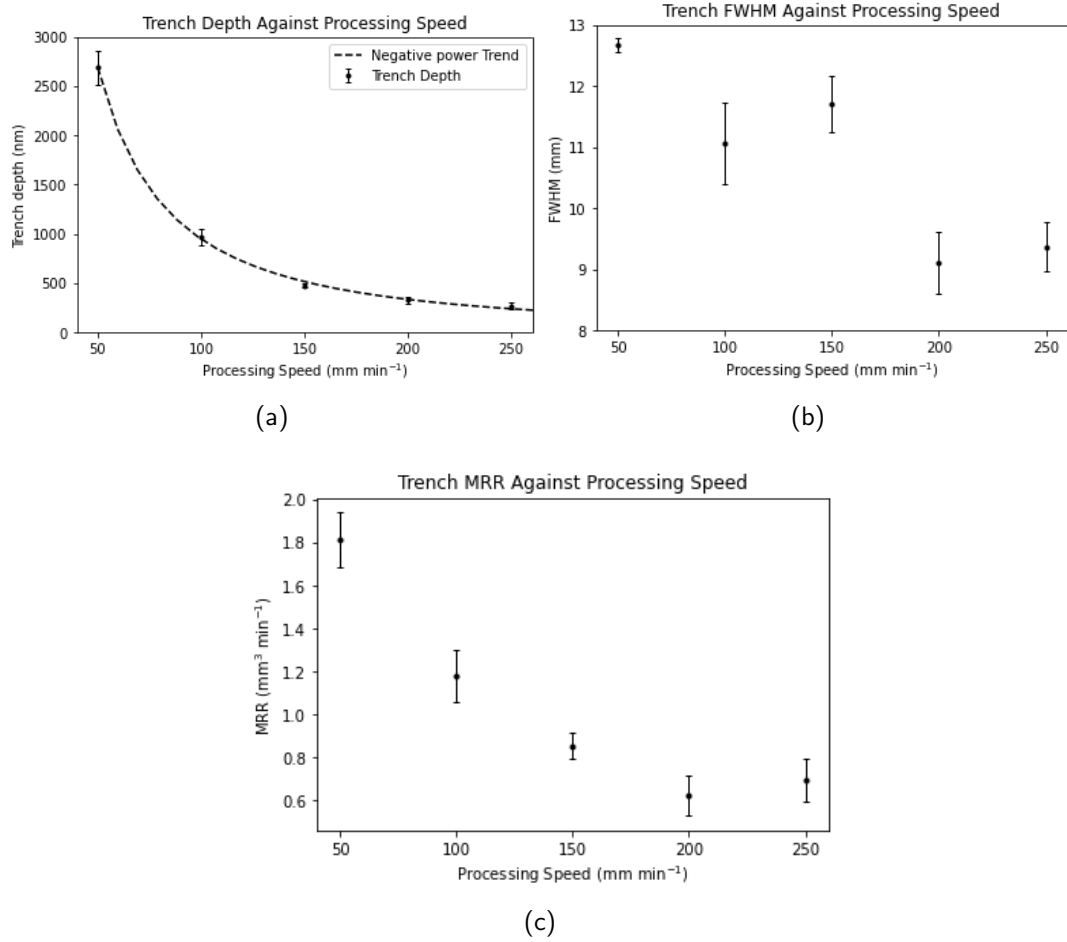


Figure 4.9: Trend of (a) maximum trench depth. The trend shown was calculated as: $977137 \cdot x^{-1.51}$. (b) FWHM against processing speed for trenches between 50-250 mm min⁻¹ and (c) the related MRR after preheating with an argon plasma. The error bars show $\pm$ standard deviation of three separate results at each data point.

A preheating pass was required for clean trenches, shown in Figures 4.4 and 4.6. This is the reason the etch depths seen in the trenches is higher than the results from stationary dwells would suggest. Since the plasma etching process is thermally dominated, the sample must be hot enough for the products to be volatile. As discussed in Section 2.4.2, Ti64 has a low thermal conductivity of $6.6 \text{ W K}^{-1} \text{ m}^{-1}$ at 20° compared to other metals, even compared to that of its constituent metals (refer to Table 2.3). However, compared to fused silica ($1.38 \text{ W K}^{-1} \text{ m}^{-1}$), it has a relatively high thermal conductivity. The etch rate during plasma etching is highly dependent on the surface temperature due to the chemical nature of the etching process. A substrate with a high thermal conductivity reduces the plasma etching rate since heat will be conducted away from the etching zone. Figures 4.3 and 4.9(b) show that the FWHM of the torch footprint is highly variable with respect to exposure time. This shows the surface-torch interface has not reached a thermal equilibrium since the FWHM has not reached a plateau. These results show this increased thermal conductivity is enough to greatly increase the amount of time required for the plasma footprint to stabilise. The results in Section 4.2 show that APP etching of Ti64 is possible, so volatile products must be formed with the SF_6 etchant. However, the composition of the volatile products at unknown at this stage. Figures 4.9 and 4.5 show a repeatable process when etching an individual trench or dwell. The error bars show $< \pm 40 \text{ } \mu\text{m}$ deviation in etch depth for most results (except the trench depth at 50 mm min^{-1}). Figure 4.9(c) shows how the MRR varies with processing speed, with MRR values between $0.5 - 2 \text{ mm}^3 \text{ min}^{-1}$. This is at the lower end of typical APP etching MRR ($0.1 - 50 \text{ mm}^3 \text{ min}^{-1}$, refer to Table 2.1). However, this is still significantly greater than alternative techniques such as IBF ($\sim 0.01 \text{ mm}^3 \text{ min}^{-1}$) and comparable to that of MRF ($0.3 - 13 \text{ mm}^3 \text{ min}^{-1}$).

4.3.2 Roughness Characterisation

The surface roughness of the etched surfaces was characterised using profilometry. As mentioned in Section 3.3.2, the high spatial frequency roughness measurements were carried out after plasma etching and polishing (measurement C in Figure 3.2).

As mentioned in Section 3.1, the polishing process in step 5 was very brief (<30s). This was only employed to remove the opaque layer on the surface. Stylus profilometer measurements were taken across the etched trenches. Figure 4.10 shows the trend of average roughness (R_a), against processing speed. The error bars shown calculated as $\pm$ the standard deviation of the five measurements at each speed. The values of R_a roughness for the samples before plasma processing was measured to be between 6 nm - 12 nm in all cases. Figure 4.10 shows how the plasma etching process significantly roughens the surface. The roughness measurements also show a negative power trend, as seen for the etch depth results, which was calculated as $5841 \cdot x^{-0.85}$, where x is the processing speed.

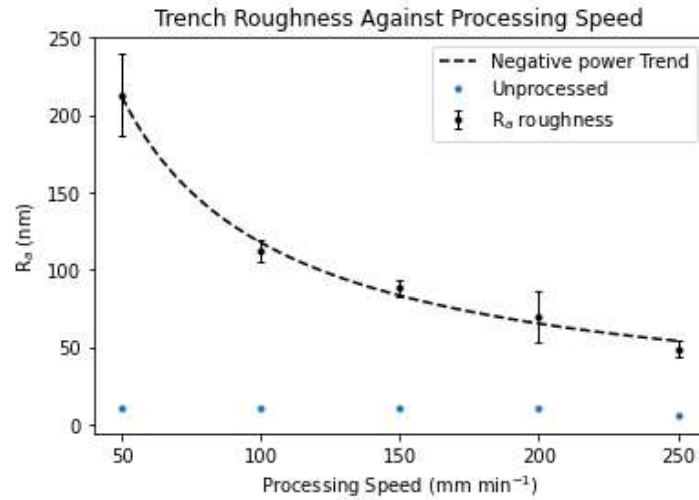
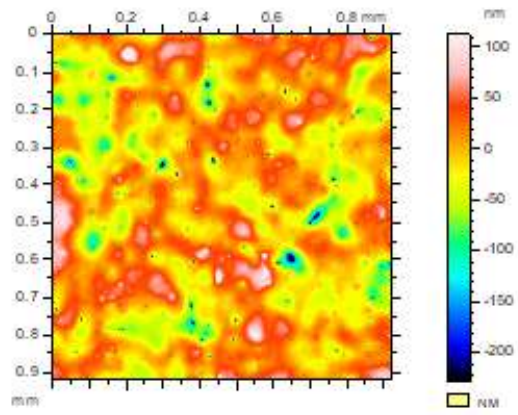


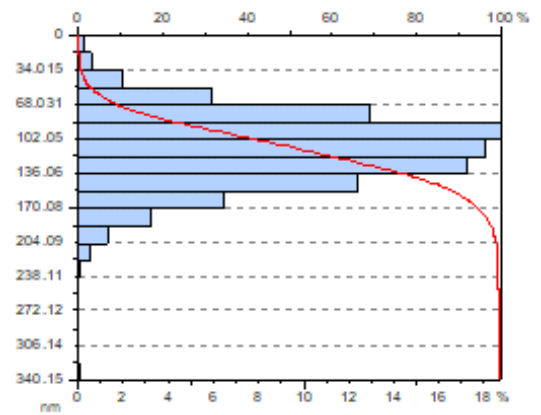
Figure 4.10: R_a roughness against processing speed, error bars are $\pm$ standard deviation for 5 measurements. The trend is calculated as $5841 \cdot x^{-0.85}$.

Areal roughness measurements were also carried out using the CCI. However, the samples processed at 50 mm min⁻¹ could not be measured. The surface was too rough for the CCI to accurately measure. CCI measurements were taken at steps A and C in the method flow chart (Figure 3.2). The measured surface and Abbott-Firestone

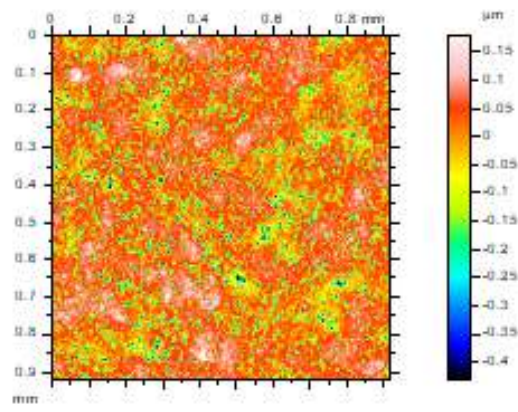
curves with roughness histograms are shown in Figure 4.11(a, b) for step A, and (c, d) relate to step C. Figure 4.11 relates to a trench at a processing speed of 250 mm min⁻¹. Abbott-Firestone curves illustrate the cumulative probability density of the roughness, calculated as the integral of the roughness, i.e. the volume above or below the mean line. The histograms, shown with the Abbott-Firestone curves, shows the amplitude distribution. Figure 4.11(a) and (b) show that the roughness has a normal distribution. This would be expected from a sanding and polishing process, i.e. there is no preferential removal of material leaving a fairly random surface around a mean roughness value. Comparing the Abbott-Firestone curves in Figure 4.11(b) and (d), shows the etching process has introduced a skewness. This skewness is also visible in the histograms, compared to a normal distribution seen before etching. This is repeated in the Abbott-Firestone curves and histograms for the other processing speeds, shown in Appendix C. There is a greater probability density of the surface with low roughness and a small percentage of high roughness. Although the plasma etching process does indeed increase the maximum roughness values in all cases, there is only a small probability of these high roughness areas so the majority of the surface is roughened only slightly. Since this skewness is observed in the Abbott-Firestone curves for all cases explored, this leads to the conclusion that there are certain, small, parts of the Ti64 surface which are more prone to increases in surface roughness and is not due to anomalous surface contamination or plasma jet instabilities. This could refer to multiple possible variations in the Ti64 surface: a particular phase (however, it is impossible to determine if these high roughness areas correspond to either the α or β phases using these results), or elemental composition (possibly the vanadium, since it could be preferentially removed, or the aluminium, since it does not create volatile compounds with the plasma jet, refer to Table 2.4).



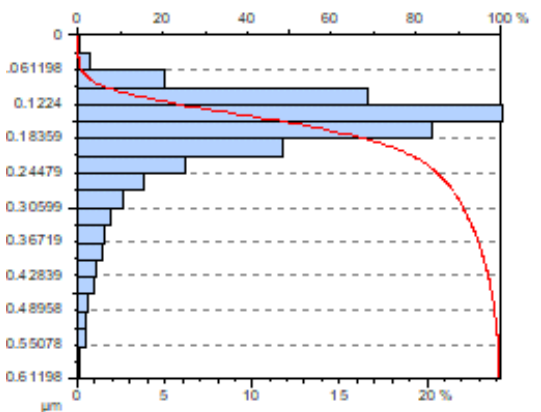
(a)



(b)



(c)



(d)

Figure 4.11: CCI measurements and Abbott-Firestone curves with histograms (a, b) before and (c, d) after etching a trench at 250 mm min^{-1} .

4.4 Surface Microstructure Analysis

4.4.1 Surface Morphology and Chemical Composition

4.4.1.1 Before plasma etching

SEM was used to investigate the surface and grain structure of the Ti64 samples for steps A, B, and C (Figure 3.2). As stated previously, Ti64 contains 2 phases (α and β). These two phases appear very similar in Figure 4.12, which shows a secondary electron (SE) image of the surface of a Ti64 sample before plasma etching (step A). Small surface damages (voids) are apparent in Figure 4.12, visible as pits and scratches. These damages appear darker than the undamaged surface. Surface contaminants appear as bright white points in Figure 4.12. The surface damages and contaminants are due to the sanding and polishing procedure. Figure 4.12 also shows that the Ti64 samples have an equiaxed microstructure (refer to Section 2.4.1). Analysing Figure 4.12(b) using ImageJ, the ratio of the areas of $\alpha:\beta$ was determined to be 82.4:17.6.

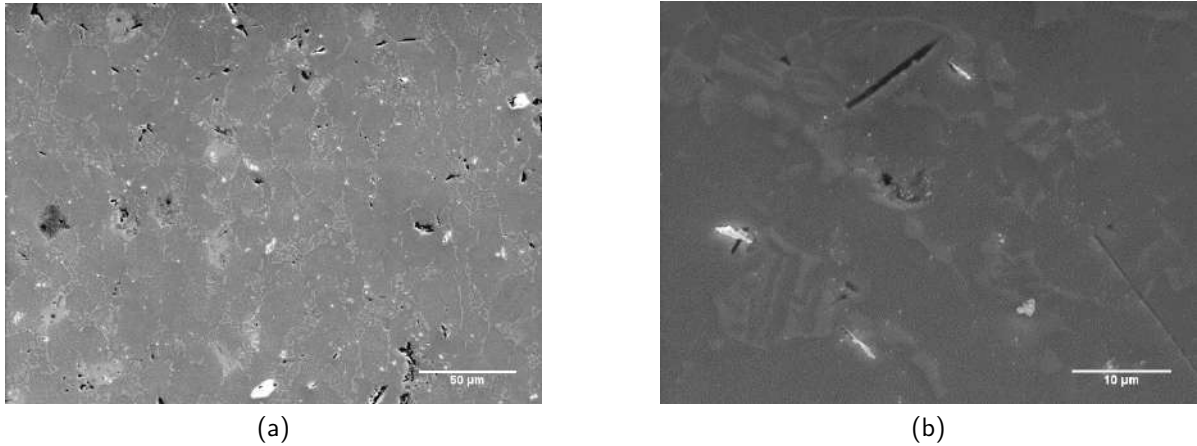


Figure 4.12: SE SEM images at (a) 1000x and (b) 5000x magnification of a clean, polished Ti64 surface before plasma etching, taken at 20kV beam voltage.

Energy Dispersive Spectroscopy (EDS) was carried out on samples to determine the chemical composition at steps: A, B, and C in Figure 3.2. EDS was also used to investigate if the plasma etching process preferentially etched a certain grain type. Before etching, EDS analysis confirmed the composition given by the supplier data sheet as:

6.4%wt aluminium, 3.7%wt vanadium, 0.2%wt iron (impurity from manufacturing) and 0.2%wt silicon with the remainder being titanium. Table 4.3 summarises the chemical composition with reference to quoted values from the supplier. The silicon contaminant is from the polishing compound which, as mentioned in Section 3.1, used silicon nanoparticles as an abrasive.

Table 4.3: EDS measurements showing the chemical composition of the Ti64 samples before plasma etching, compared to the supplier data.

Element	Measured Value	Supplier data	
	% wt.	min %wt.	max % wt.
O	-	-	0.2
Fe	0.2	-	0.4
C	-	-	0.08
Si	0.2	-	-
Al	6.4	5.5	6.75
V	3.7	3.5	4.5
Ti	89.6	87.6	91.0

4.4.1.2 After plasma etching and polishing

Figure 4.13 shows a low magnification (6x), wide field SEM image, of Ti64 surface after plasma etching and polishing. The trench was etched at a processing speed of 100 mm min⁻¹. SEM images were taken at various points across the width of the trench to determine variations in surface morphology and grain structure across the torch area of influence. These points are labelled in Figure 4.13 as A-N. The distance between two adjacent points, such as from A to B, is 2 mm.

The $\alpha:\beta$ area ratio was determined using ImageJ to vary between 8.2-19.5% β for points A-G, with the average ratio being 0.87:0.13. The values of $\alpha:\beta$ ratio for each SEM image is shown in Table 4.4. An example of the thresholded SEM image is shown in Figure 4.14 for point A in Figure 4.13. Figure 4.14(a) shows only the α phase and (b) shows only the β phase. The rest of the thresholded SEM images are shown in Appendix B.

The centre of the trench appears to be between A and B. The etching profile and depth results in Section 4.3, suggested that the etching is symmetric. Similar morphology



Figure 4.13: Wide field SEM image at 6x magnification of Ti64 surface after plasma etching and polishing. The trench is etched at a processing speed of 100 mm min^{-1} .

Table 4.4: alpha:beta ratios before plasma etching and after plasma etching (step B in Figure 3.2), determined through ImageJ.

	Before Plasma Etching	After Plasma Etching						
		A	B	C	D	E	F	G
β %	17.6	13.7	15.5	19.5	13.5	11.2	8.2	9.1

was observed for the pairs of A & B, C & I, D & J, E & K, F & L, G & M, and H & N (where the morphology was very much the same as that for the untreated sample). Figure 4.15 shows the SE SEM images at positions A-G according to Figure 4.13. The images show that the etching is deepest at the centre, and progressively reduces towards the edge of the trench footprint. The SE SEM images also show that the plasma etching process has removed the surface damages seen in Figure 4.12. The microstructure of the Ti64 surface remains equiaxed after etching, meaning that the etching process has not exceeded the β transus temperature of 995°C . This is important since above this temperature, the entire crystal structure will transform to β and the cooling rate from this temperature will greatly affect the type of microstructure and in turn the samples' physical properties.

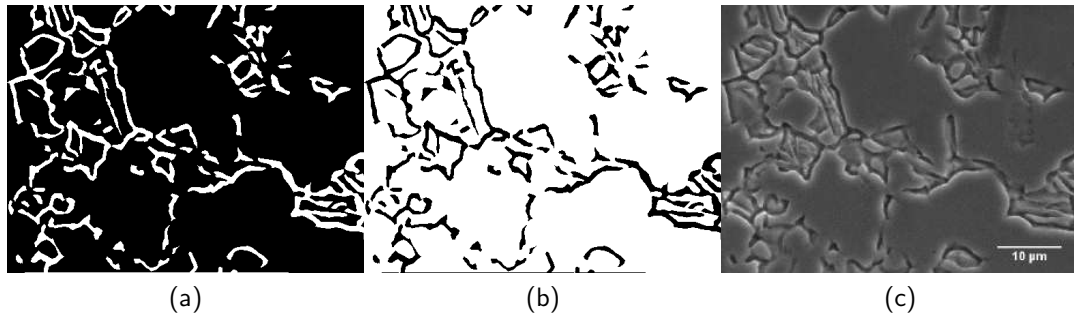


Figure 4.14: SEM images after plasma etching and polishing. The image has been thresholded to show (a) only the α phase in black, (b) only the β phase in black, and (c) original SEM image for position A in Figure 4.13.

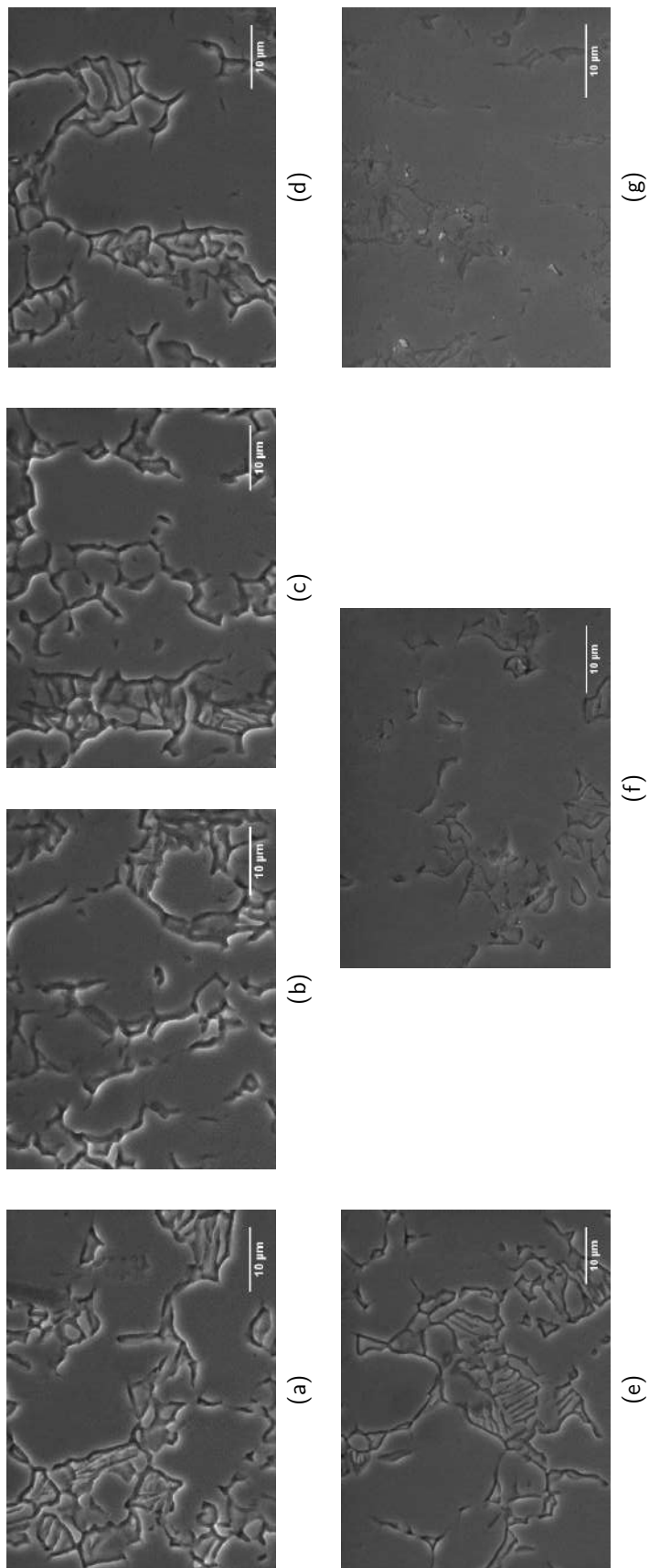


Figure 4.15: SE SEM images of Ti64 surface at 5000x magnification after plasma etching and polishing. (a)-(g) are taken at points A-G shown on Figure 4.13. Each image is taken 2 mm apart using a beam voltage of 20kV.

The SEM images in Figure 4.15, show preferential etching of the Ti64. The etch is deeper at darker places than the brighter places. EDS analysis was employed to determine if there is any chemical composition difference between the dark and bright positions. Figure 4.16 shows the SEM image of the surface where 4 EDS spectra were taken, and Table 4.5 summaries these EDS results. The EDS results must be interpreted carefully, the auto ID peaks option within the Aztec software can lead to incorrect analysis. As mentioned in Section 3.4.1, the energy of the titanium $K\beta$ peak, and the vanadium $K\alpha$ peak, are very similar - 4.93 eV and 4.95 eV respectively. To determine which element a peak seen in this area can be assigned to, the intensity ratio of the peaks for Ti- $K\alpha$:Ti- $K\beta$ can be used, which is 5:1. If this ratio is not met, the peak should be assigned to V- $K\alpha$. The existence of vanadium in the EDS spectra is confirmed using the vanadium $K\beta$ peak at 5.43 eV. If this peak is not detected it is concluded that vanadium is not present in the spectrum.

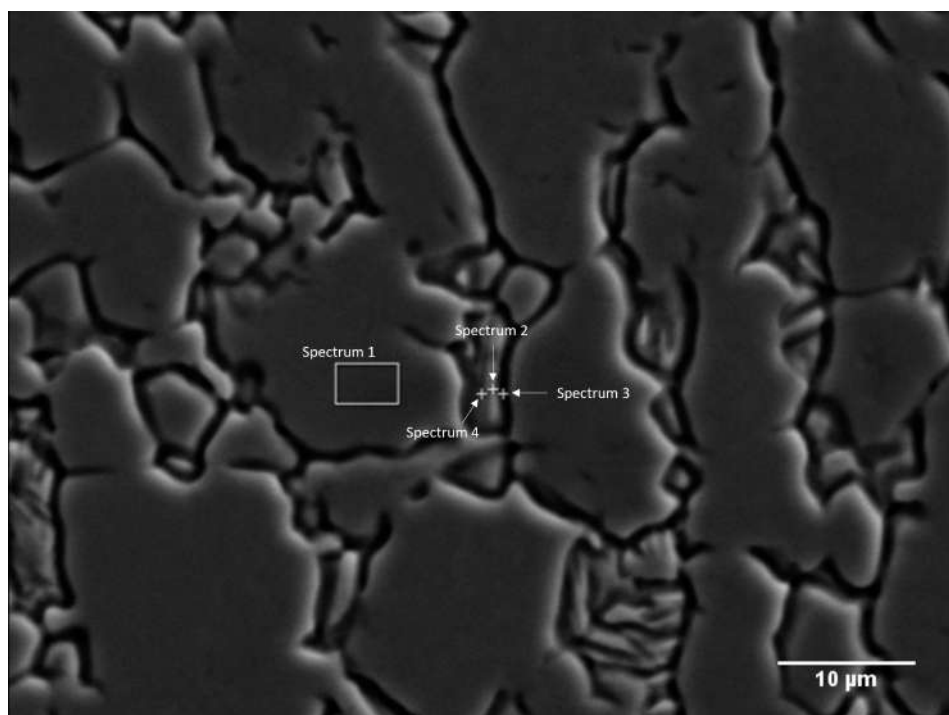


Figure 4.16: SEM image of the area where EDS spectra were obtained from the dark (spectrum 3 & 4) and bright contrasted areas (spectrum 1 & 2) after plasma etching and polishing.

Spectrum 1 is an areal spectrum, taken at large bright area. This result shows that it

Table 4.5: Summary of EDS results for spectrum 1-4 as shown in Figure 4.16 after plasma etching and polishing.

Element	Spectrum Label			
	1 (%wt.)	2 (%wt.)	3 (%wt.)	4 (%wt.)
O	-	-	12.3	-
Fe	-	-	1.0	0.8
Si	-	0.3	0.6	-
Al	6.9	5.7	3.2	5.0
V	2.0	5.8	9.0	8.1
Ti	91.1	88.2	73.9	86.1

contains 91.1 %wt Ti, 6.9 %wt Al, and 2 %wt V, with no other contaminants. Spectrum 2 was a point measurement, taken at the small bright area in between the two dark areas. The EDS results for spectrum 2 shows Ti, Al, V with a small quantity of silicon present (0.3 %wt). As this bright area is very small, $\sim 0.3 \mu\text{m}$ in width, some EDS signals may come from the adjacent dark areas. Spectra 3 and 4 correspond to dark areas. There is oxygen and silicon present in spectrum 3, and a small amount of iron in spectrum 4 (0.8% wt). The silicon is most likely present as a residual of the post etching polishing process. Oxygen is most likely present due to oxidation of the Ti64 surface, either when heated by the plasma jet or general exposure to the air. The other notable point from these results is the much higher vanadium concentration in these two areas. From the literature (refer to Section 2.4) Ti64 contains two phases, α and β , with the α grains often larger in both size and quantity. These results suggest the lighter areas are the α phase, and the darker areas are the β phase.

The PSI measurements carried out in order to obtain material removal rates will only be detecting the surface of the α phase. It is important to note the resolution of the equipment. Since the surface height is averaged over the size of each pixel, features smaller than this pixel size will not be discernible. The Zygo, which was used to measure all the results for trenches and areal etching, has a pixel size of $90 \times 90 \mu\text{m}$. This large pixel size compared to the size of the grains ($>10 \mu\text{m}$ for α and $\sim 2 \mu\text{m} - 5 \mu\text{m}$ for β) means that individual grains cannot be made out.

Further EDS analysis was carried out to confirm the preferential etching of the β phase by investigating the variation in chemical composition between the two phases.

Figure 4.17 shows a BSE SEM image and EDS line-scan results across α and β grain boundaries. The spectra for V, Al and Ti are also shown along this line scan. The spectra in Figure 4.17 show that the dark region (β phase) is vanadium rich and the light region (α phase) is aluminium rich. The y axis shows counts in arbitrary units.

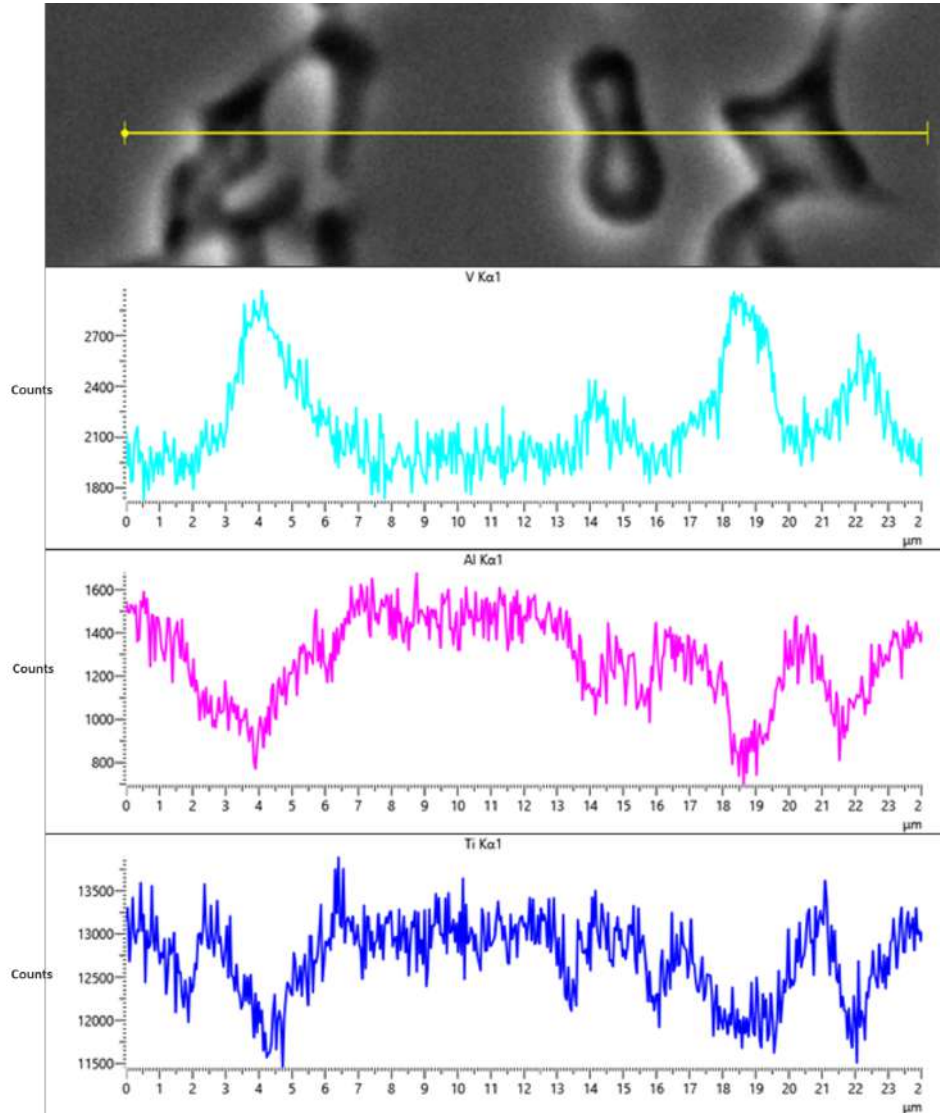


Figure 4.17: EDS line scans showing chemical composition of vanadium, aluminium, titanium (from top to bottom respectively) across the α and β grain boundary.

Combining these SEM and EDS results with the Factsage simulations, the plasma etching mechanism can be proposed. Firstly, it will require time to heat the sample surface to the plasma temperature, which is $\sim 850\text{K}$. At this temperature, some metal fluoride compounds, such as TiF_4 (557K), VF_5 (598K), and VF_4 (321K), are volatile.

Also, as shown in the Factsage simulations in Figure 4.1, the formation of TiF_4 will increase exponentially with regard to processing temperature. Ti64 is comprised primarily of titanium (~90%). Therefore, the main process of material removal is focused on the formation of TiF_4 . Compared to other metal halide products which may be formed via interactions with the plasma, TiF_4 has a low boiling point. Based on this, it can be assumed that the lack of etching seen in dwell times below 5s and in the trench without preheating, is due to the time required to heat the sample to sufficient temperature for significant quantities of TiF_4 to be formed.

It is also assumed that no chemical etching of the aluminium constituent of Ti64 takes place, due to the lack of volatile aluminium fluoride products. However, due to the crystal structures of Ti64, and the position of aluminium within it, it can be assumed that the aluminium is removed by the chemical etching of the titanium and vanadium around it. The vanadium will also be chemically etched and removed in the form of VF_4 and VF_5 , both of which are volatile at the operating temperatures. Vanadium is the easiest to be etched and removed, followed by titanium. However, most likely the removal of titanium required the transformation of TiF_3 into TiF_4 through interaction with fluorine radicals in the plasma jet. After plasma etching and polishing, the average ratio taken over all the SEM images was determined to be 13% compared to 17.6% before any plasma exposure. As stated in literature the α phase grows from the β grain boundaries and into the β grains when cooling from the β transus temperature and the β phase typically makes up 5-30% of the surface area. The $\alpha:\beta$ ratio for the samples etched here lies in the middle of this range. The SEM images cover only a small area of each sample (100's μm^2), so the average $\alpha:\beta$ ratio for the whole surface may vary from the results presented. The conclusion from this is that etching rate and morphology of the resultant surface will vary greatly depending on where in this range the $\alpha:\beta$ ratio lies. The reason for this preferential etch could be due to a number of contributing factors. The composition of the β phase is vanadium rich, compared to the aluminium rich α phase, illustrated in the line scan in Figure 4.17. Vanadium readily forms volatile products with the fluorine radicals in the plasma jet (VF_4 and VF_5). This will make it easier to remove compared to the aluminium and titanium components. The density of

the α and β crystal structures may also play a role in the etch rates. The HCP structure of the α phase is more dense than the BCC structure of the β phase. The increased density means more atoms will be present per unit volume in the α phase. Since the removal mechanism of the plasma etching process is chemical, this increased amount of atoms means more reactions will have to take place to remove the same volume of material in the α phase compared to the β phase. The grain boundaries are where the plasma etching process will initiate. Therefore, the grain size may also have an impact on the etch rate. When a grain is smaller, it will take less time for the surface of an entire grain to react with the etchant, meaning layers of material can be removed faster. Further analysis of the grain size is discussed in Section 4.4.2.

4.4.1.3 Immediately after plasma etching

Immediately after the plasma etching process, the Ti64 surface was optically opaque. The SEM and EDS analysis in this section investigates the composition and microstructure of the etched Ti64 surface at measurement step B (before steps 5 and 6 in the method flow chart, Figure 3.2).

Figure 4.18 shows a wide field SE image Ti64 surface immediately after the plasma etching procedure at low magnification (5x). The trench etched can clearly be seen in the centre of the image which was carried out at a processing speed of 50 mm min^{-1} . SEM images were taken at various points across the width of the trench to determine variations in surface morphology and grain structure across the torch area of influence. These points are labelled in Figure 4.18 as A-G and span a distance of 12 mm, with each area investigated being 2 mm apart.

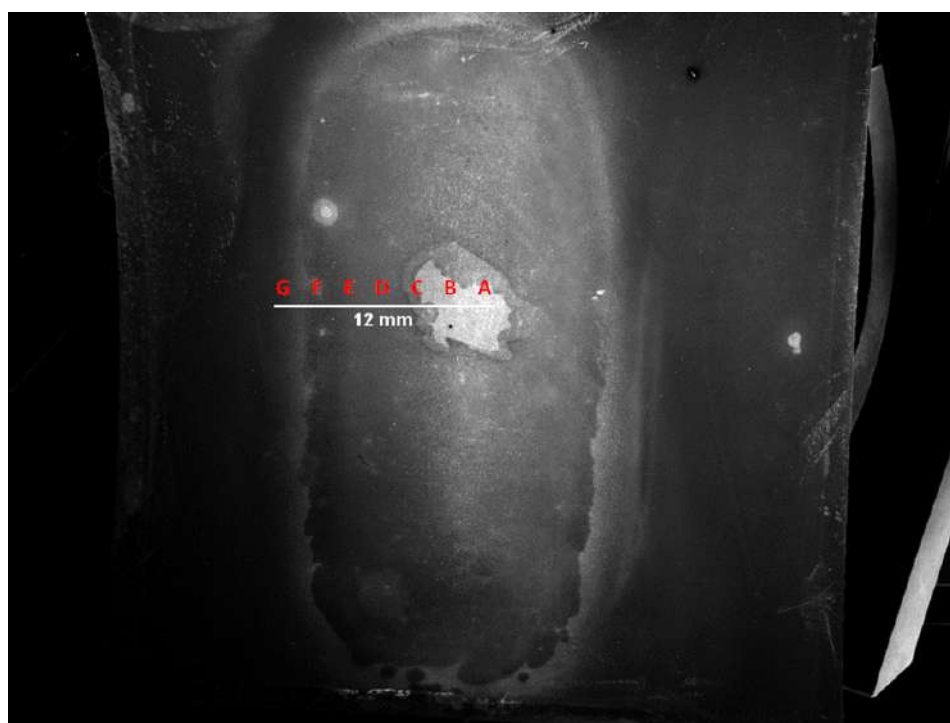


Figure 4.18: SEM image at 5x magnification of Ti64 surface immediately after plasma etching a trench at 50 mm min^{-1} .

The SEM images shown in Figure 4.20 are SE images, taken at a beam voltage of 20kV and a magnification of 5000x. The images are taken at reference points shown in

Figure 4.18 A-G. This shows how across the width of the plasma jet, the morphology of the Ti64 surface appears to change. At first glance, the surface appears cracked towards the centre of the trench, refer to Figure 4.20(a). However, upon further investigation and comparing the morphology to the other SEM images, it can be deduced that this is the redeposition from the plasma etching process. Figure 4.19 shows three SEM images at the centre of an etched trench. Figure 4.19(a) shows an SE image at 20kV beam voltage, (b) shows the same image at 10kV and (c) shows a back scattered image at 10kV. Comparing Figure 4.19 (a) and (b) shows how at the lower beam voltage (and hence more sensitive to surface materials), the structure of the redeposition can be more clearly identified since there is little interference from the Ti64 beneath. This redeposition is thick enough to cover the surface at the centre of the trench such as the electron beam cannot penetrate to the 'clean' etched surface. However, further away from the centre of the etched trench, such as in Figure 4.20 (d-e), the etched surface can be seen beneath the redeposited material. Outside of the trench footprint, Figure 4.20 (g), the morphology resembles that of the clean, un-etched surface. The presence of the redeposition obscured the surface which made $\alpha:\beta$ ratio impossible to determine for this step.

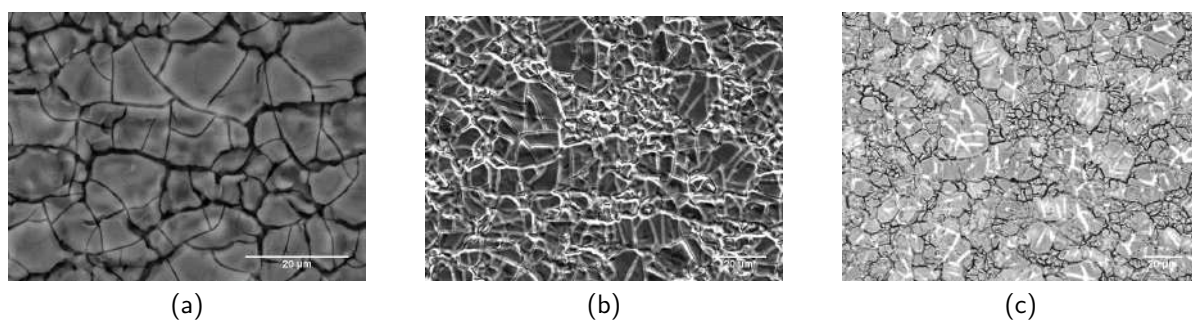


Figure 4.19: SEM images showing the redeposited material taken immediately after plasma etching. (a) SE image at 20kV beam voltage, (b) SE image at 10kV beam voltage, and (c) BSE image at 10kV. These images show how varying the beam voltage and detection mode alters how the surface appears.

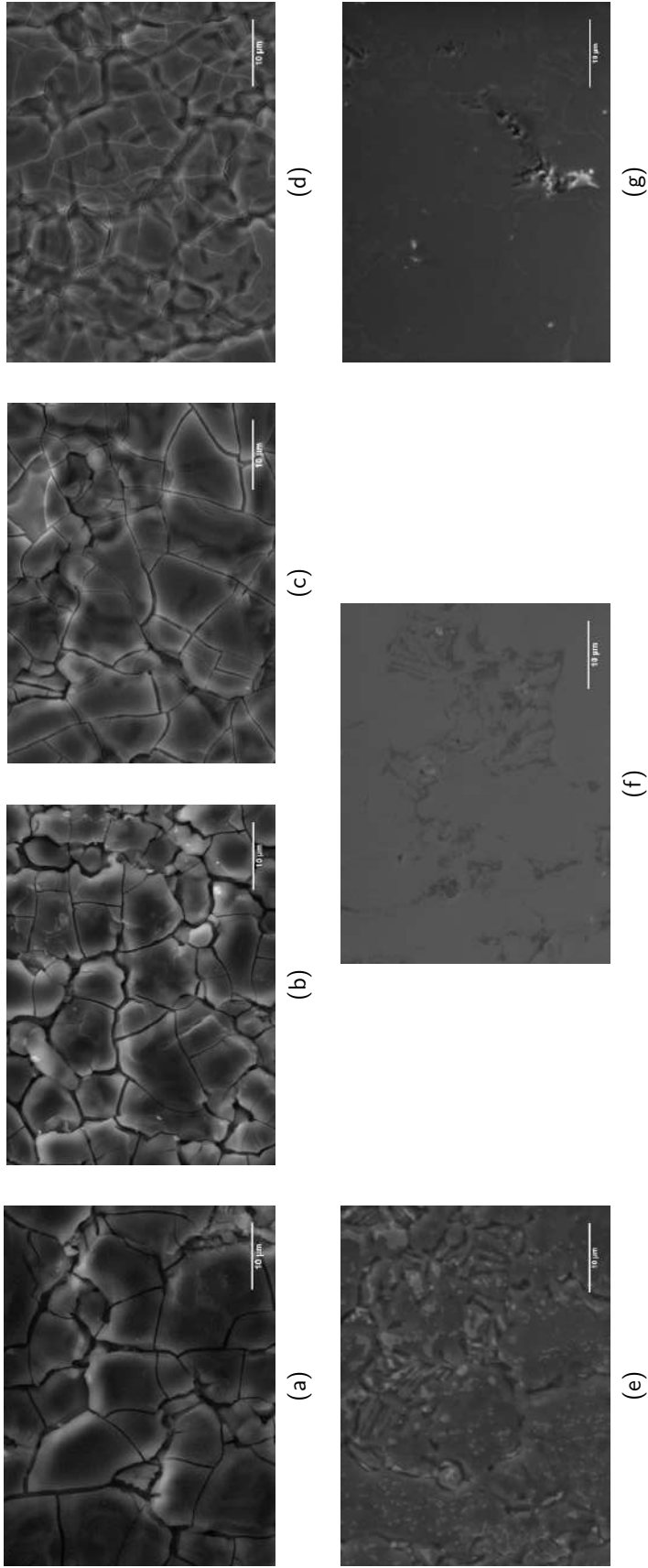


Figure 4.20: SE SEM images of Ti64 surface at 5000x magnification immediately after plasma etching. (a)-(g) are taken at points A-G shown on Figure 4.18. Each image is taken 2 mm apart using a beam voltage of 20kV.

By lowering the beam voltage from 20kV, the penetration depth of the electron beam decreases. There have been multiple ways of determining electron penetration depth in SEM [196]. A common method for estimating the penetration depth of electrons for SEM/EDS is the Kanaya–Okayama model, shown below in Equation 4.1, where R is the penetration depth in nm, ρ , A , and Z are the target material’s density, atomic weight and atomic number respectively and E_0 is the electron beam energy [197].

$$R = \frac{27.6 \cdot A}{\rho \cdot Z^{0.89}} \cdot E_0^{1.67} \quad (4.1)$$

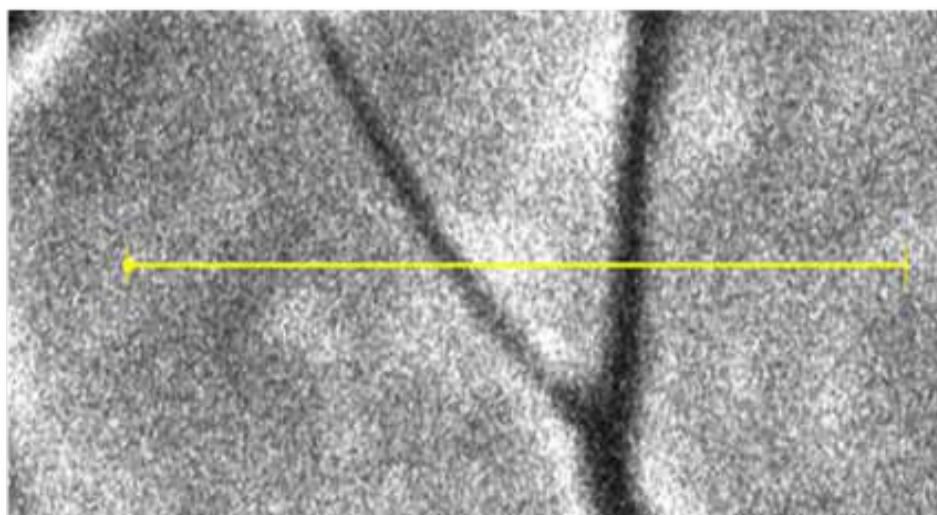
By comparing EDS results when varying the beam voltage, the compositional variation as a function of penetration depth can be investigated. Table 4.6 shows how the chemical composition changes with the beam voltage. These values were taken at the centre of a trench etched at 50 mm min^{-1} and averaged over 3 separate measurements at each beam voltage. The vanadium and iron signals are detected from the etched material beneath the redeposition, since they are only detected at the higher beam voltage. Table 4.6 also shows there is no vanadium and little titanium (4.3%) in the redeposited material, indicating they were evaporated during the etching process. The aluminium concentration is high in this redeposited material, validating the assumption that aluminium fluoride compounds are not volatile at operating conditions. These results also show very high concentrations of fluorine and oxygen in the redeposition. By taking the average atomic weight and number using the atomic percentages shown in Table 4.6 and a density of Ti64 (4420 kg m^{-3}), estimates of the electron beam penetration depth can be made using the Kanaya-Okayama model shown in Equation 4.1 above. These values are also shown in Table 4.6, varying between $0.77 - 2.46 \text{ }\mu\text{m}$. The results in Table 4.6 imply that at the centre of the etched trenches the redeposition is largest and has a thickness of $<2 \text{ }\mu\text{m}$ since at 20kV, vanadium can be detected. The values for penetration depth in Table 4.6 are only estimates, since the absolute density of the interaction volume with the electron beam cannot be determined, so the density of Ti64 was taken for these estimates. Also, there are problems associated with the Kanaya-Okayama model shown in Equation 4.1; this only calculates a first order approximation

of the actual electron scattering which is not applicable at high electron beam energies, it is based on the diffusion model of electron scattering - assuming electrons propagate through the material in the direction of the initial electron beam. This is not necessarily true as analysed by Lukiyanov et. al. [196], who highlighted the inaccuracies of this model at low electron beam energies and low atomic numbers. Inaccuracies will also be introduced by having to assume a constant density across the entire measured area, which will inevitably vary due to the presence of redeposited material.

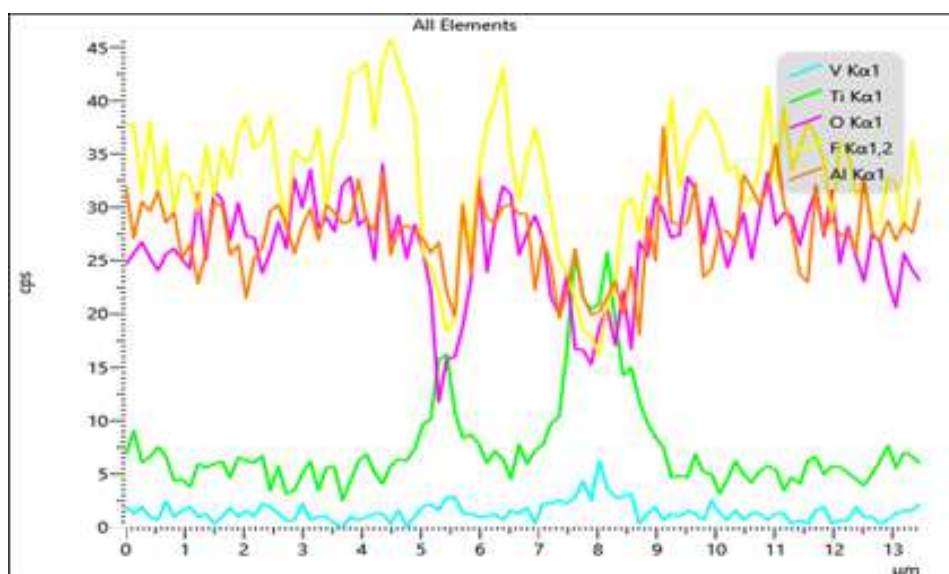
Table 4.6: EDS results at varying beam voltage for a Ti64 sample directly after plasma etching a 50 mm min^{-1} trench. Each value is taken as an average over 3 areal measurements within the same field of view. Values are given here as atomic %. Estimated penetration depths are also shown, calculated using the Kanaya-Okayama model (Equation 4.1), the atomic % was used to determine an average atomic weight and number for the surface.

Element	Atomic %		
	10kV	15kV	20kV
O	28.7	30.6	32.2
F	51.8	49.1	46.5
Al	14.6	13.8	9.9
V	-	-	0.3
Fe	-	-	0.1
C	0.6	0.4	0.3
Ti	4.3	6.1	10.7
Penetration Depth (μm)	0.77	1.52	2.46

Further EDS line scans of the redeposition seen in Figure 4.19 confirm that the dark areas in between what appear to be grains in the redeposition, are in fact gaps. Strong titanium and vanadium signals are detected here along with reductions in oxygen and fluorine, which is concentrated in the 'grains' of the redeposition. The strong Ti and V signals originate from the clean, etched surface beneath the redeposited material, shown in Figure 4.21.



(a)



(b)

Figure 4.21: Line scan of EDS analysis for the redeposited surface, (a) SE SEM image of the surface (b) element distribution profiles along the line in (a).

EDS measurements were taken at each point (A-G), shown in Figure 4.18 for the plasma etched sample, corresponding to 0-12 mm in 2 mm steps. The results given in Table 4.7 show the atomic % of each element present at each location.

Table 4.7: EDS results for the plasma etched sample A-G correspond to areas A-G shown in Figure 4.20. Values are given here as atomic %.

Element	Atomic %						
	A	B	C	D	E	F	G
O	37.9	41.8	41.6	34.6	22.8	5.2	-
F	42.7	35.2	34.0	25.7	21.10	11.9	-
C	-	-	-	-	3.0	1.6	-
Al	7.9	6.4	5.2	5.5	6.2	9.3	11.7
V	0.1	0.2	0.2	0.9	1.3	1.7	2.4
Ti	11.4	16.4	18.7	33.3	45.6	70.3	85.9

To more clearly illustrate how chemical composition varies with respect to the position across the plasma torch pitch, Figure 4.22 was plotted. This illustrates how the amount of fluorine and oxygen correspond to the amount of etching taking place. At position G (outside of the plasma footprint), only titanium, aluminium, and vanadium are present. The composition of any redeposited material may have a significant effect on the chemistry and resultant etch rate. It is important to stress that plasma etching can lead to significant amounts of redeposited material which requires post processing (cleaning/polishing) to remove. The amount of redeposition is dependent on the torch positioning (above or below the workpiece), the plasma flow rate, and the composition of said redeposition. In this specific case, the plasma torch was below the workpiece, pointing up. This positioning would likely have reduced the amount of redeposition on the samples. During the etching process, the redeposition is not completely removed and will remain on the surface until after the etching process is completed. If this redeposited material is not chemically reactive with the reactive species in the plasma jet (such as Al, or AlF_3 in this case), this can lead to reductions in etch rate or even prevent etching all together.

The redeposition after etching by comparing elements present at different beam voltages (refer to Table 4.6), and across the width of the trench (refer to Table 4.7) shows that vanadium and titanium concentrations are low in the redeposited material.

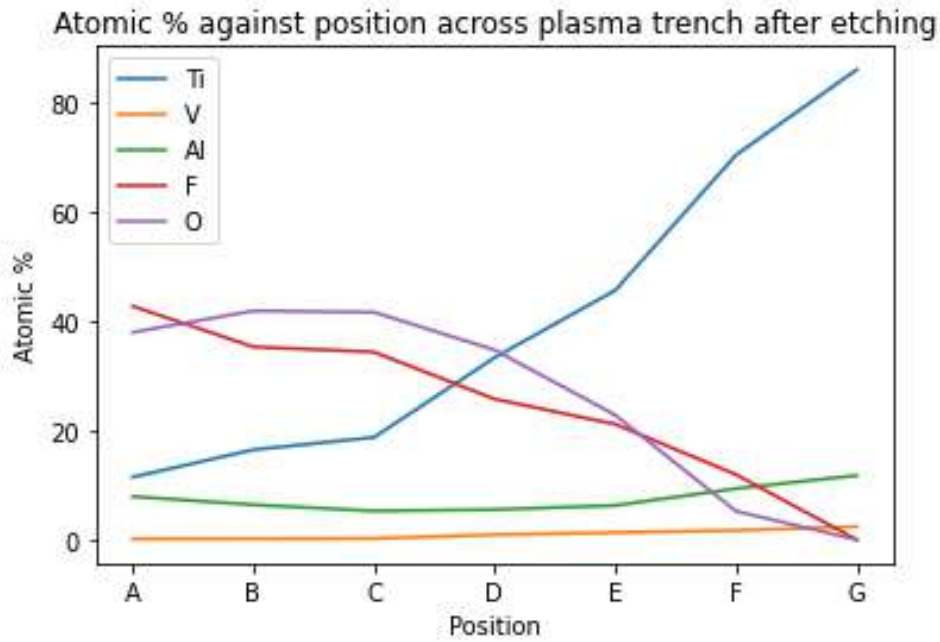


Figure 4.22: Chemical composition across the width of the plasma torch footprint for positions A-G in Figure 4.18 directly after plasma etching. This graph illustrates how the atomic % of fluorine and oxygen decreases away from the centre of the etched trench.

From these EDS results, the etching mechanism can be implied.

The Factsage simulations suggest the majority (~80%) of the products formed will be in the form of TiF_3 (refer to Section 4.1). However, Table 2.4 shows that the only volatile product at the operating temperature of ~850 K, is TiF_4 with a boiling point of 284°C. The formation of volatile products with titanium is vital for material removal, since Ti constitutes ~90% of the alloy. The results from the thermodynamic simulations using Factsage™ suggest that very little TiF_4 would be formed ($\sim 4 \times 10^{-7}\%$) at operating temperatures of ~850K. The proposed mechanism for the formation of greater quantities of TiF_4 is the reaction of fluorine radicals in the plasma jet with the large amounts of TiF_3 formed, as shown in Equation 4.2. Although TiF_3 would remain stable at the operating conditions, it is proposed that it becomes an important step for the formation of greater quantities of TiF_4 .

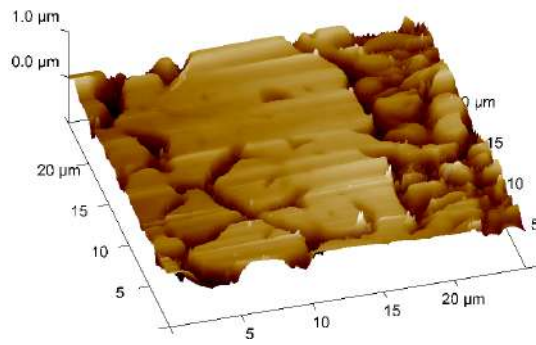


The process of cleaning and polishing after the plasma etching returns the ratio of

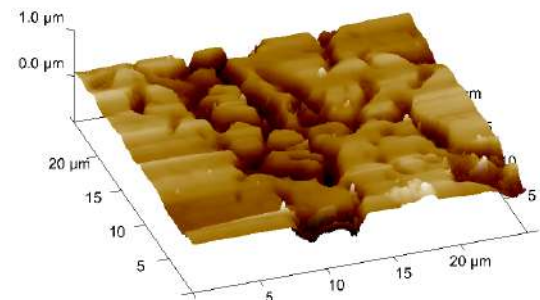
elements to pre-etching composition after the redeposition is removed. This proves that this presence of oxygen and fluorine detected, originates from the redeposited material. This fine powder is easily removed, validating that it is only adsorbed onto the surface and not chemically bound to it.

4.4.2 Atomic Force Microscopy (AFM) Analysis

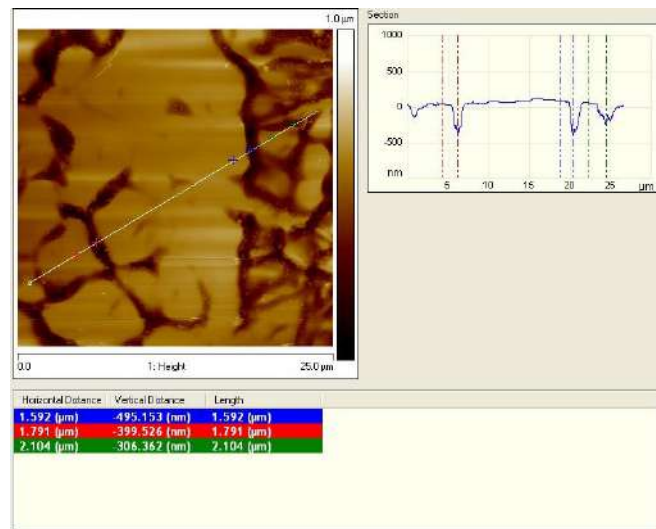
Ti64 is an $\alpha+\beta$ alloy, comprised of a mixture of two different crystal structures. AFM scans were taken to investigate if the plasma etching process preferentially etches one of these phases. The scans shown in Figure 4.23 were carried out at two different areas along the centre of a trench of a sample after plasma etching and polishing. The trench was etched at a processing speed of 100 mm min^{-1} . These scans were taken in the centre of the trench (refer to point A in Figure 4.13). The results in Figures 4.23(a, b) clearly shows the β phase was etched significantly more than the surrounding α phase. Line scans confirm that the β phase has been etched up to $\sim 500\text{nm}$ deeper than the surrounding α phase, as shown in Figures 4.23(c,d), where the blue, red and green points are taken to compare the relative height of the α and β phases. Figure 4.23(c) relates to the 3D image in Figure 4.23(a), and Figure 4.23(d) relates to Figure 4.23(b). The large step height from the $\alpha - \beta$ phase also confirms that PSI measurements will not be able to detect the β phase.



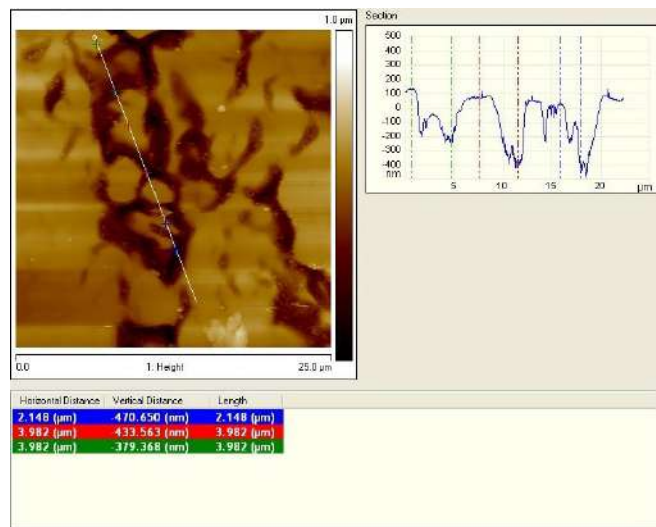
(a)



(b)



(c)



(d)

Figure 4.23: AFM scans in (a,b) 3D and (c,d) 2D taken at the centre of a trench etched at 100 mm min^{-1} . (c) shows the profile across (a) and (d) shows the profile across (b).

The microstructure of the Ti64 samples is an important factor in the etch rate since the results presented in the SEM images (refer to Section 4.4.1), show a preferential etching of the β phase. This is confirmed and quantified by these AFM scans in Figure 4.23, showing the β phase is etched up ~ 500 nm deeper than the surrounding α phase. The trench in Figure 4.23 was etched at a speed of 100 mm min^{-1} which results in a trench depth of $\sim 1 \mu\text{m} \pm 100 \text{ nm}$ as seen in the processing speed against depth trend. This shows that the β phase is etched up to $\sim 50\%$ faster than the α phase. The fact that preferential etching has been observed here leads to the conclusion that the ratio of $\alpha:\beta$ phases and the grain size of each phase for a particular Ti64 sample will affect the etch rate and surface topology. Depending on the cooling rate during any surface treatments, such as annealing, the size and amount of each phase will vary (refer to Section 2.4).

4.4.3 X-Ray Diffraction Analysis

X-ray diffraction (XRD) scans were also taken to investigate the structure of the surface and redeposition. As discussed in Section 2.4, the XRD spectrum for Ti64 is typically comprised mostly of peaks relating to the α phase. This would also be expected here since the β phase comprises of only $\sim 15\%$ of the surface. XRD scans were taken for an as received sample, before and after plasma etching as well as after redeposited material was removed. These scans are shown in Figure 4.24. The spectra show no clear deviation between any step in the plasma etching process, with comparable intensities at each peak. All of the large peaks relate to the α phase. Based on comparison to literature [169–171], the only peaks relating to the β phase are at 2θ angles of $\sim 57^\circ$ and $\sim 71^\circ$, although the peak at 71° is shared with a contribution from the 103 orientation of the α phase.

Although these results show no significant difference at any stage, the EDS results clearly show a deviation in the elemental composition (refer to Section 4.4.1), and AFM scans show a preferential etch of the β phase (refer to Section 4.4.2). The XRD results may show little variation since the penetration depth of X-rays is significantly higher

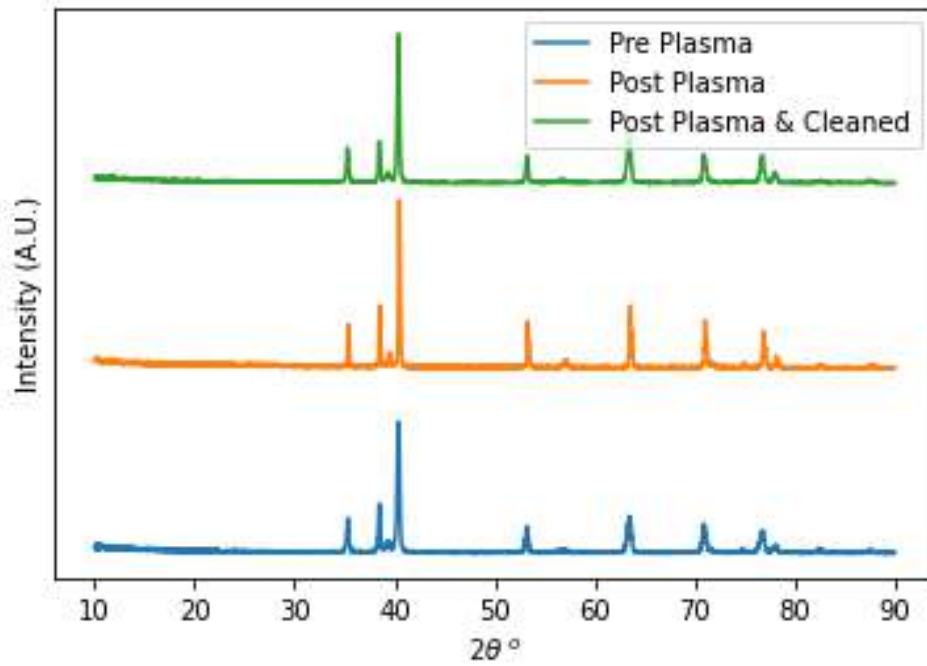


Figure 4.24: Measured XRD spectra of the Ti64 surface before plasma etching, immediately after plasma etching and after plasma etching and polishing.

than that of electrons, meaning a far greater volume is detected. This means that any signal from the surface of each sample is most likely obscured by signals diffracted from the bulk material, which will have far greater intensity.

4.5 Areal plasma etching

The footprint shown in Figure 4.25 shows the material removal after three (a) and seven (c) trenches overlapped at a speed of 100 mm min^{-1} . Figure 4.25(b, d) shows the cross sections of the footprints at $x=20 \text{ mm}$, showing how the etch rate increases with each pass. The trenches started from the bottom right hand side of the sample and progressed to the top left hand side. The final pass for Figure 4.25(c) was carried out at $y=35 \text{ mm}$ which is why the material removal rate decreases towards the top of the image. The sharp increase in surface height represents the edge of the gaussian beam. The three pass neutral removal footprint (refer to Figure 4.25(a)) showed a relatively flat footprint - $\pm 100 \text{ nm}$ deviation in the material removal over the centre $\phi 20 \text{ mm}$ area. This became less consistent after the seven pass raster (refer to Figure 4.25(c)).

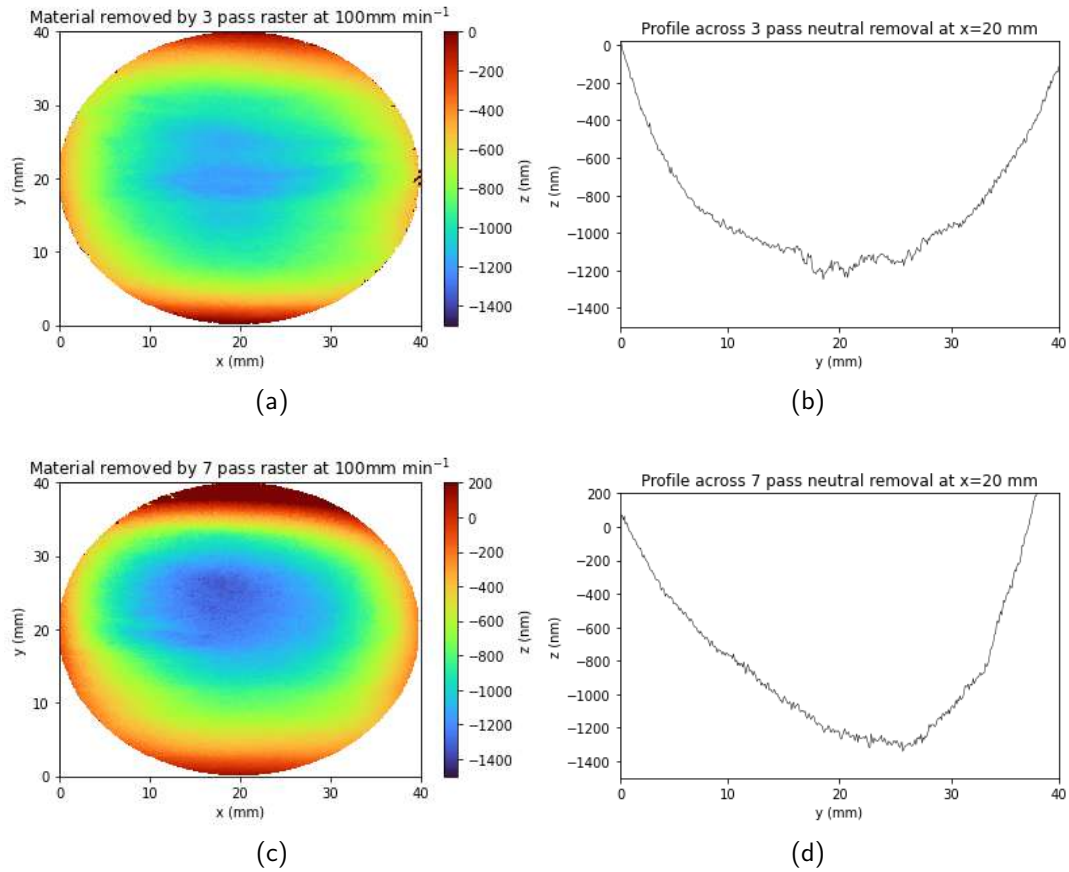


Figure 4.25: (a) Plasma etch footprint after three passes, rastering at constant speed of 100 mm min^{-1} , (b) cross section at $x=20\text{ mm}$ in (a), (c) plasma etch footprint after seven passes, rastering at constant speed of 100 mm min^{-1} and (d) cross section at $x=20\text{ mm}$ in (c).

Figure 4.26 shows PSI measurements (a) before and (b) after plasma etching and polishing when applying variable processing speeds. The method for determining these speeds is described in Section 3.2. The increase in etch depth towards the centre of the sample is most likely due to the build up of thermal energy, increasing the etch rate.

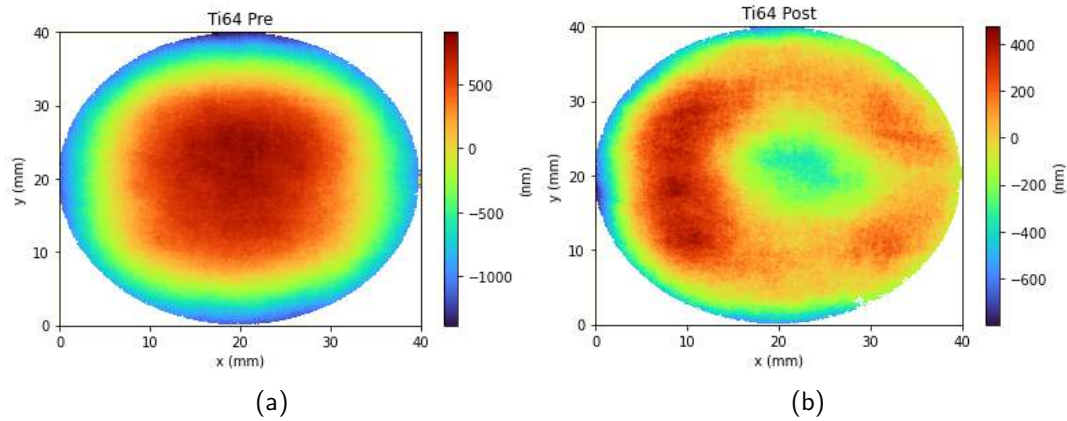


Figure 4.26: Surface measurements of (a) unprocessed sample, (b) sample after standard raster pattern when varying processing speed.

The material removal of the areal plasma etching experiments were compared to a calculated material removal function, using Equation 2.13, (refer to Section 2.2.2). Although, this equation makes assumptions for the temporal stability, spatial stability and linearity of the etch rate with respect to time, it provides a simple estimate which is not computationally intensive to compare actual and predicted material removal. Figure 4.27 shows (a) the material removed in Figure 4.26, and (b) the difference between the actual material removed, and the predicted material removal function (taken as the convolution of the dwell time map and the beam function, Equation 2.13). In Figure 4.27(b), the positive values on the z axis correspond to a greater amount of material removed than predicted and vice versa for the negative values.

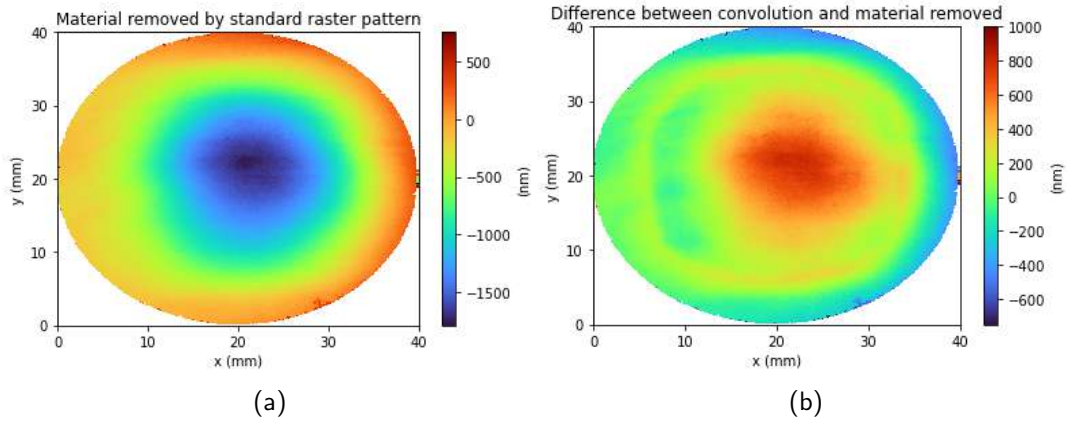


Figure 4.27: (a) Material removed by standard raster pattern (b) difference between the actual material removed and the material removal as defined by Equation 2.13.

Further experiments were carried out in an attempt to reduce the thermal build up effect, by increasing the rastering speed and alternating raster passes. Figure 4.28 shows: (a) the surface before plasma etching and (b) after plasma etching and polishing when applying the alternate pass raster pattern at the calculated velocity map. Figure 4.28(c) shows the material removed by the plasma etching and (d) shows the difference between the predicted and actual material removed using the same process as described previously.

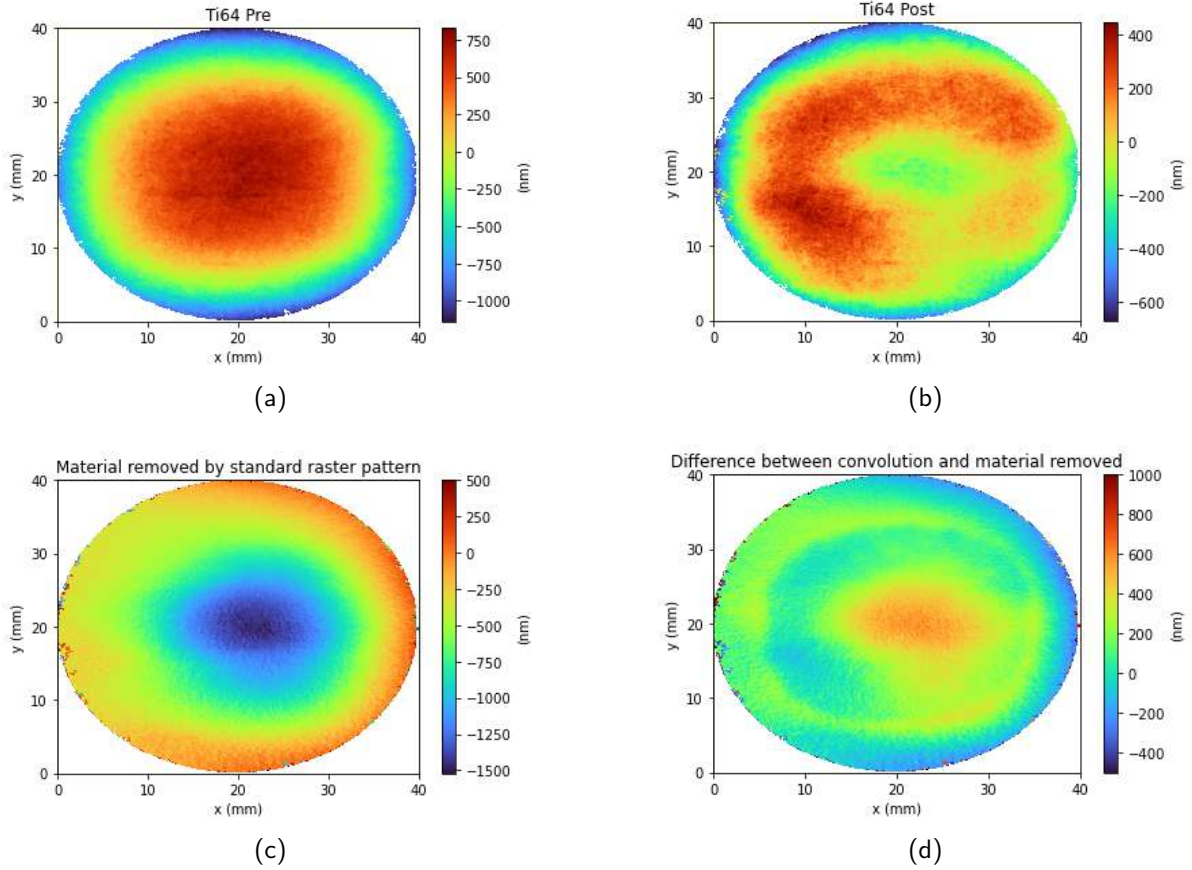


Figure 4.28: Surface measurements (a) before plasma etching, (b) after alternate pass raster plasma etching at the calculated speed, (c) material removed, and (d) difference between the actual material removed and the predicted material removed.

Figures 4.29 and 4.30 (a and b), show the surface measurements before plasma etching and after plasma etching and polishing for the samples which were processed at 125% and 150% of the calculated processing speeds respectively. Figures 4.29 and 4.30 (c and d), show the related material removed and the difference between the actual and predicted material removal for the same samples.

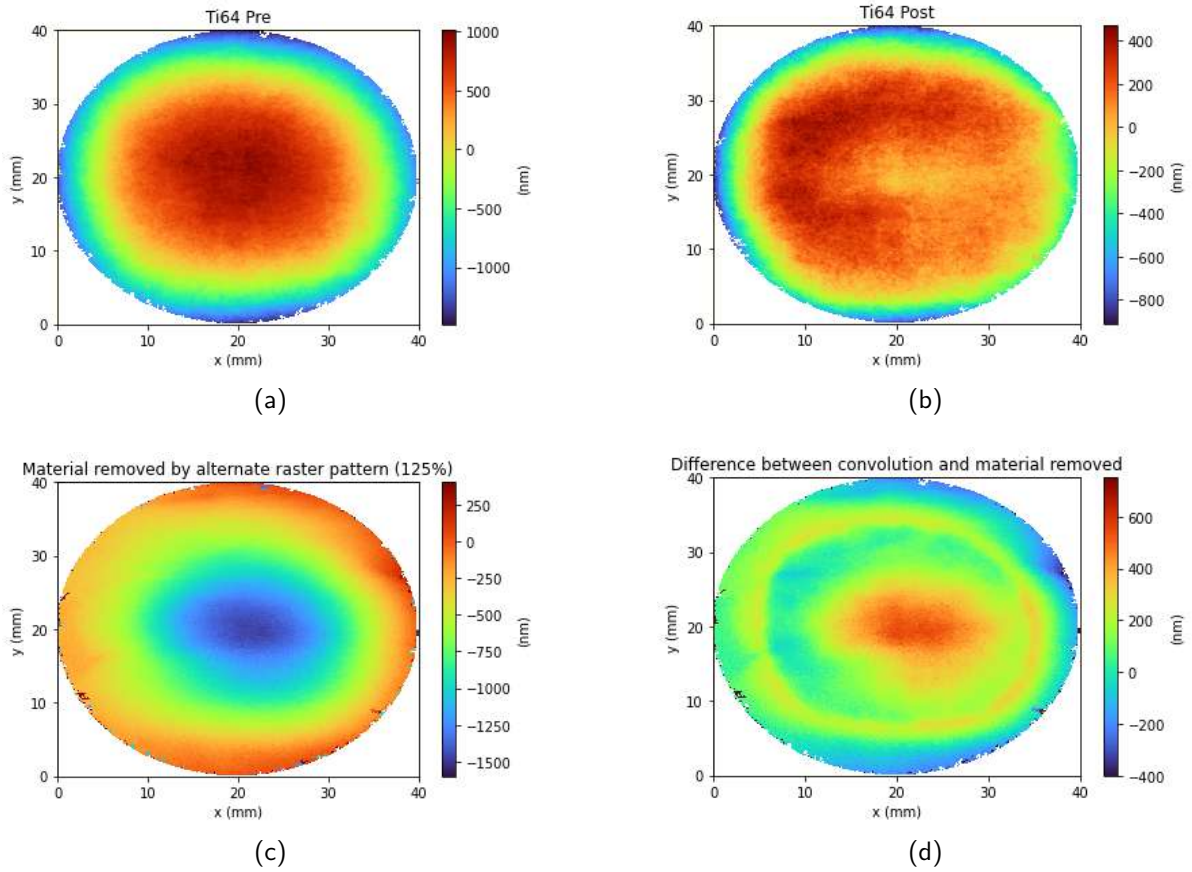


Figure 4.29: Surface measurements (a) before plasma etching, (b) after alternate pass raster plasma etching at 125% of the calculated speed, (c) material removed, and (d) difference between the actual material removed and the predicted material removed.

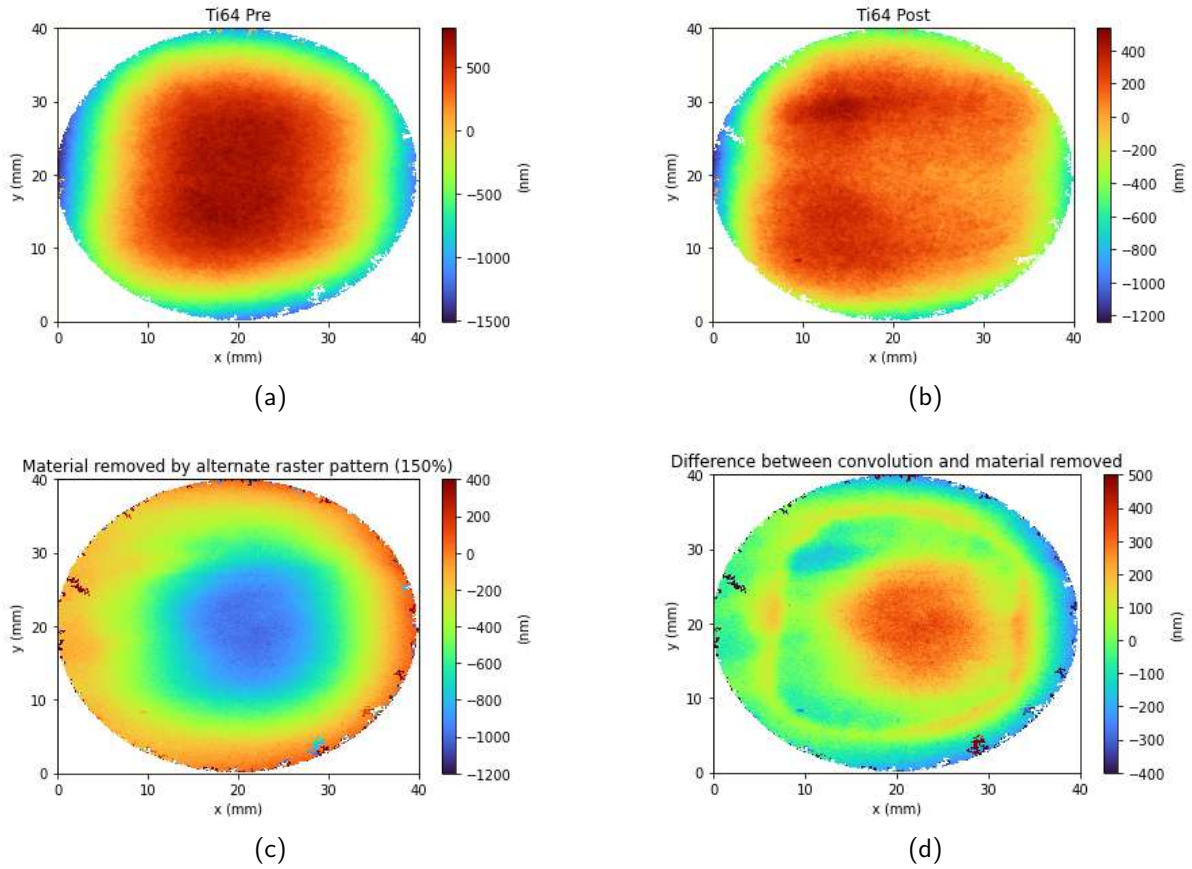


Figure 4.30: Surface measurements (a) before plasma etching, (b) after alternate pass raster plasma etching at 150% of the calculated speed, (c) material removed and (d) difference between the actual material removed and the predicted material removed.

For all experiments carried out (refer to Appendix E for further repeats), there is significant deviation from the predicted material removal function based on Equation 2.13, especially in the centre of the sample, with all the cases presented here showing increased etch depths of >500 nm. Another feature shown in Figures 4.27 - 4.30, is a ring around the centre where material is removed at a higher rate than its surroundings. It can be shown that this ring is due to the method used and limitation of the equipment. The maximum processing speed was set to 500 mm min^{-1} when the measured height of the surface was below 0 nm (refer to Section 3.2). However, this meant the Helios 1200 axis was set to slow down from 500 mm min^{-1} to the processing speed, when the initial measured height dropped to 0 nm or below. This step change was too sudden for the acceleration in the Helios axis. Figure 3.8 (refer to Section 3.2) shows steps of $>300 \text{ mm min}^{-1}$ over a 1 mm distance. This is illustrated in Figure 4.31, where Figure 4.28 is overlaid with points showing where the initial height was measured to be 0 nm.

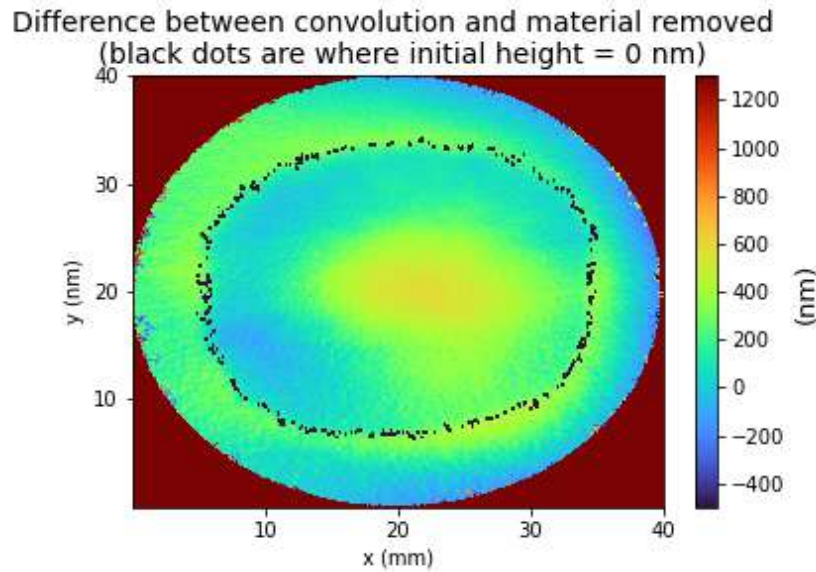


Figure 4.31: Illustration of the origin of the ring effect seen in the areal etching. The points initially measured to be 0 nm are overlaid to Figure 4.28

The increase in processing speed from the calculated speed brought the material removal closer to the calculated removal from the convolution. Figure 4.32 shows cross sections in y (a) and x (b) directions for the difference between predicted and actual material removal rates, shown in Figure 4.28(d), Figure 4.29(d), and Figure 4.30(d).

The cross sections were taken at $x = 20$ mm and $y = 20$ mm for Figure 4.32(a) and (b) respectively. The sudden decreases at ~ 5 mm and ~ 35 mm in Figure 4.32 correspond with the ring shown in Figure 4.31. The results shown in Figure 4.32 show a similar footprint at each speed in both x and y cross sections. However, by increasing the processing speed, the difference is brought closer to 0 (where the actual and predicted material removal rates are the same).

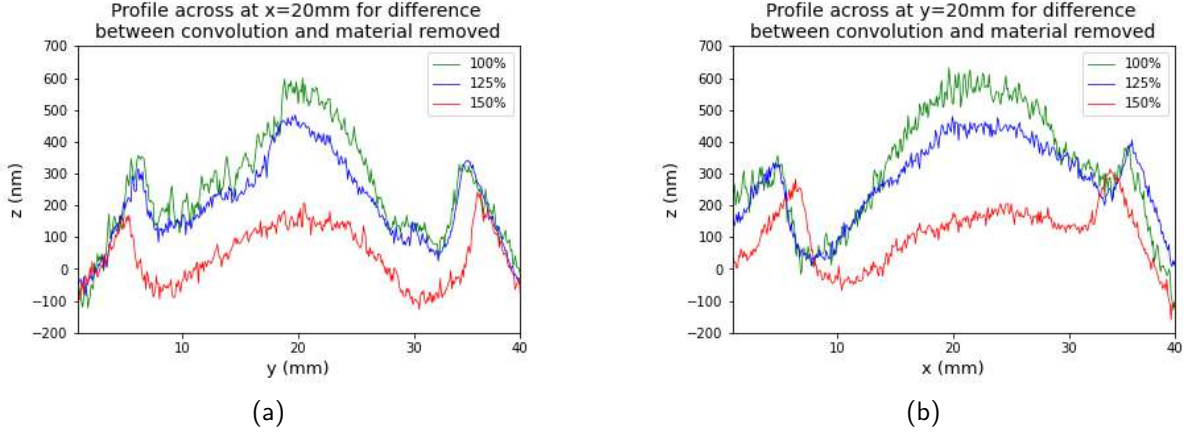


Figure 4.32: Cross sections of the difference between the actual and predicted material removed for 100%, 125% and 150% of calculated speeds in (a) x, and (b) y directions.

Figure 4.32 also shows an increase in material removal towards the centre of the sample. This is due to the thermal flux from the plasma torch. As the sample heats up, the material removal rate increases. The equation used to determine the predicted material removal function, does not take into account the thermal flux from the torch, which accounts for the deviation in the centre of the samples (refer to Section 2.2.2). Equation 2.13, repeated as Equation 4.3 for ease of reference, assumes the beam function and dwell time function are only functions of the torch position (x and y).

$$R(x, y) = \int_{-x}^x \int_{-x}^x B(x - u, y - v) \cdot \tau(u, v) \cdot du \cdot dv = B(x, y) * \tau(x, y) \quad (4.3)$$

To include the heat flux from the torch, the beam function $B(x, y)$ should include a temperature parameter, $B(x, y, T)$ (refer to Equation 2.15). In essence, this includes the effect of the heat from previous trenches on the etch rate. However, the determination of the heat flux from the torch is complex, requiring full characterisation of the heat flux

from the torch during dynamic etching. Due to time constraints, the assumption that each trench was independent of the heat flux from previous trenches was made.

Comparing the difference between the actual and predicted material removal, for the standard and alternate pass rastering shows a slight change. Figure 4.33 shows cross sections for the difference between the predicted and actual material removal in (a) x, and (b) y directions for the standard and alternate pass raster patterns shown in Figure 4.27(b) and Figure 4.28(d) respectively. Figure 4.33 shows that changing from a standard raster pattern, to an alternate pass raster pattern, reduces the increase in etch rate in the centre of the samples by $\sim 25\%$, and $\sim 20\%$ for Figure 4.33(a) and (b) respectively.

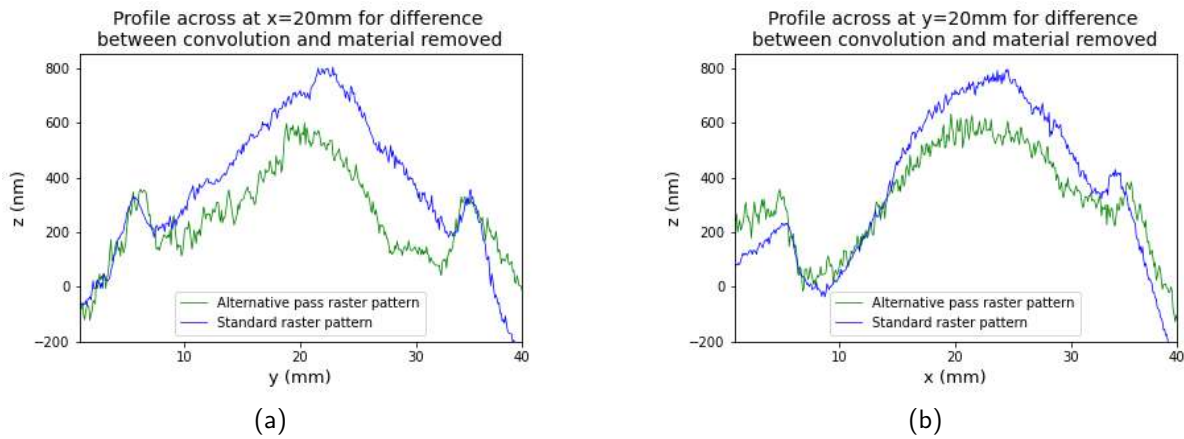


Figure 4.33: Cross sections of the difference between the actual and predicted material removed for standard and alternate pass raster patterns in (a) x, and (b) y directions.

Figure 4.33 shows that the material removal when employing an alternate pass raster pattern, is closer to the predicted material removal. This is because Equation 4.3 assumes that the etch rate for each trench, is independent from the heat flux from previous trenches. By alternating the trenches, the impact of the heat flux from the torch is reduced. However, the heat flux from the torch still heats the sample over time, meaning a surface temperature parameter (as used by Meister and Arnold in Equation 2.15), is still required to accurately predict the material removal. In this way, Equation 4.3 does not account for the path pattern.

Chapter 5

Conclusion

This work has shown the plasma etching Ti64 under atmospheric conditions using a fluorine based etchant (SF_6), for the first time. The results presented show etching for stationary, dynamic and areal etching. The results presented in Section 4.3 show how clean trenches can only be etched if the Ti64 surface is hot. The preheating pass using pure argon heats the surface enough for sufficient quantities of volatile products to be formed. The chemistry involved in the process of etching the Ti64 surface is complex. However, the key results show the etching process preferentially etches the β phase (BCC), which is vanadium rich, compared to the aluminium rich α phase (HPC). This preferential etch is significant, with etch depths of the β phase, shown to be $\sim 50\%$ greater than that of the α phase. The reasons proposed for this preferential etch are due to the difference in chemical composition, density and the grain size of the two phases.

The plasma etching process also leads to a significant amount of redeposition ($< 2\ \mu\text{m}$ thickness) comprising of high amount of oxygen and fluorine in the centre of an etched trench. The concentration of fluorine and oxygen reduces across the width of the plasma affected area with negligible contamination present outside of the etched trench. The EDS analysis shows the vanadium on the Ti64 surface is completely removed by the etching process, along with a majority of titanium. However, the aluminium does not form volatile products with fluorine at the operating temperatures and a large proportion remains on the surface. The mechanism for removal of titanium is proposed to be in the

form of TiF_4 via the interaction of fluorine radicals in the plasma jet and TiF_3 .

The thermodynamics of plasma etching is a highly complex field and the exact temperature dependence on etch rate is highly variable based on the chemistry, dimensions, structural properties, and operating conditions of the plasma jet and the substrate. Most of the operating conditions throughout the results presented were kept constant, with the dwell times/processing speeds being the only variable. Other operating parameters such as: stand-off distance, input power, and reactive gas composition/concentration were not varied, since previous work showed the optimised value for each. The trends of FWHM and etch depths for various processing speeds show the non-linearity of the etching process and comparisons between areal etching and a predicted material removal function require assumptions of a constant beam function and a linear relationship of etch rate and time. When making these assumptions, significant deviations between the actual and predicted material removal are presented. For more accurate predictions of the material removal function, many more parameters must be taken into account, such as the thermal dissipation within the Ti64 substrate, boundary conditions, non-linear etch rates and a variable beam function. The effect of rastering using a standard raster, and alternate pass raster showed a slight impact on the resultant material removal as well.

Chapter 6

Further Work

This thesis showed the APP etching of Ti64 using SF_6 as an etchant. Further work needs to be carried out to fully understand the nature of the etching and to optimise the process. The author recommends the following aspects that further work should focus on:

- Temperature characterisation of the surface during etching. This will enable a better understanding of the thermal dependence of the etching process and enable more accurate estimations of the material removal function. This will be difficult since temperature measurements involving a plasma must involve indirect techniques otherwise the plasma jet will be affected.
- Optimisation of the plasma etching process will involve varying standoff distances, operating power and etchant concentrations. Although these will be limited by the equipment (in this work 0.8 L min^{-1} of 10% SF_6 :Ar mix and 1.2 kW are the maximum safe values), the optimisation will show the dependence of etch rate on each parameter (although these parameters are not independent from temperature)
- Further analysis of the redeposition will give a clearer understanding of the composition. XPS is suggested to identify the valence states and understand the origin of the excess oxygen and fluorine observed.

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Appendices

Appendix A

Stationary dwell footprints

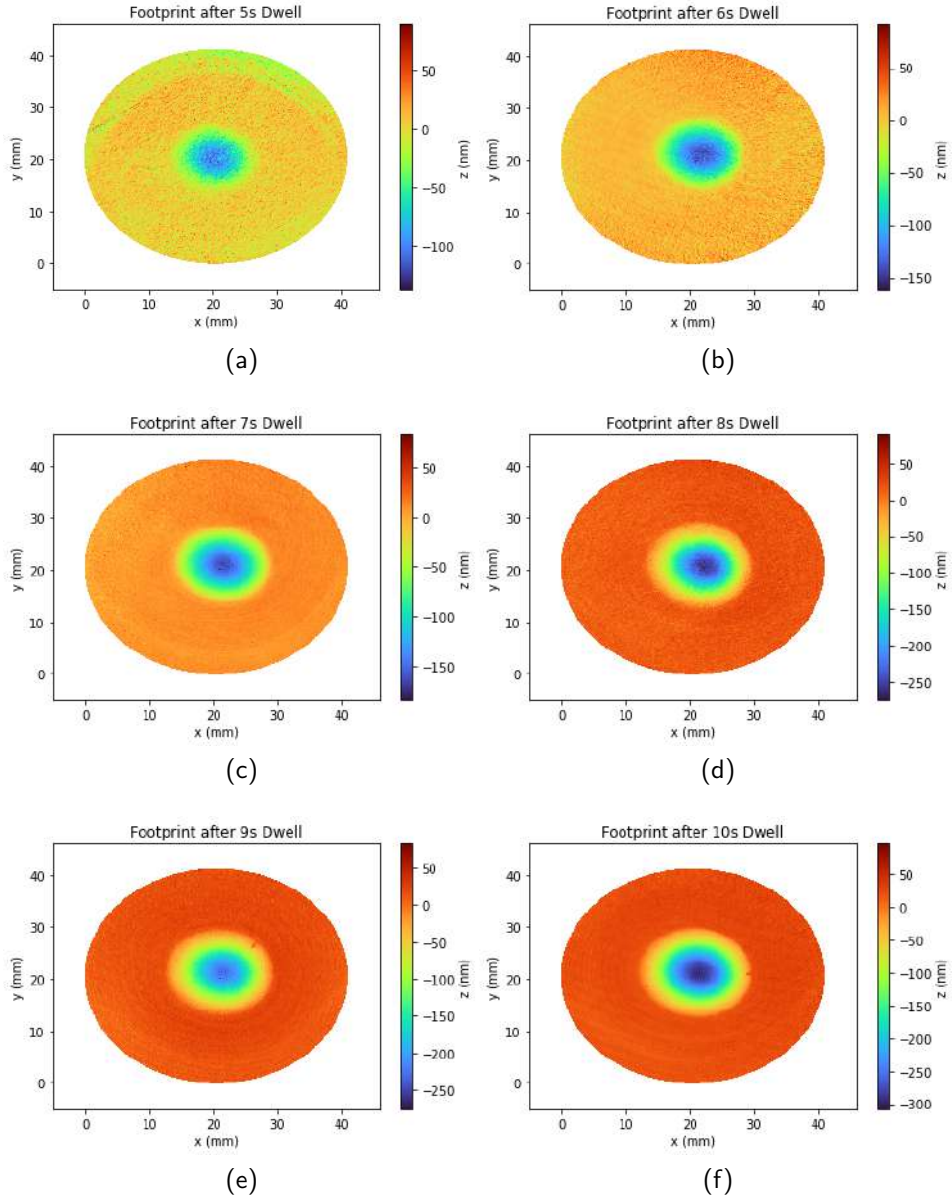


Figure A.1: Footprint from stationary dwells between 5-10s (a)-(f) in 1s intervals.

Appendix B

ImageJ analysis of Alpha:Beta Ratio



Figure B.1: SEM images after plasma etching and thresholded for (a) only the α phase, (b) only the β phase and (c) original SEM image for position A in Figure 4.13

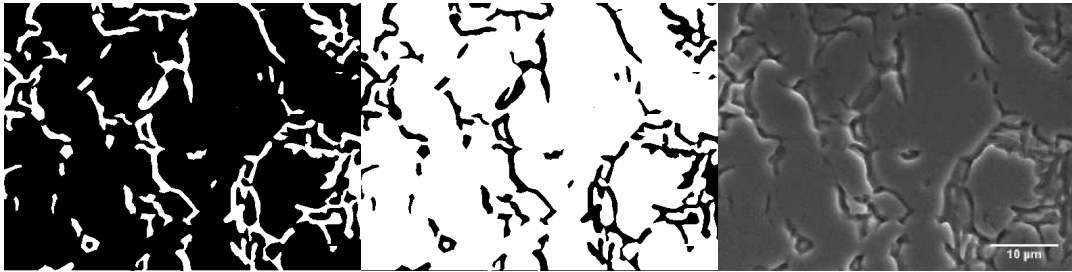


Figure B.2: SEM images after plasma etching and thresholded for (a) only the α phase, (b) only the β phase and (c) original SEM image for position B in Figure 4.13



Figure B.3: SEM images after plasma etching and thresholded for (a) only the α phase, (b) only the β phase and (c) original SEM image for position C in Figure 4.13



Figure B.4: SEM images after plasma etching and thresholded for (a) only the α phase, (b) only the β phase and (c) original SEM image for position D in Figure 4.13



Figure B.5: SEM images after plasma etching and thresholded for (a) only the α phase, (b) only the β phase and (c) original SEM image for position E in Figure 4.13



Figure B.6: SEM images after plasma etching and thresholded for (a) only the α phase, (b) only the β phase and (c) original SEM image for position F in Figure 4.13

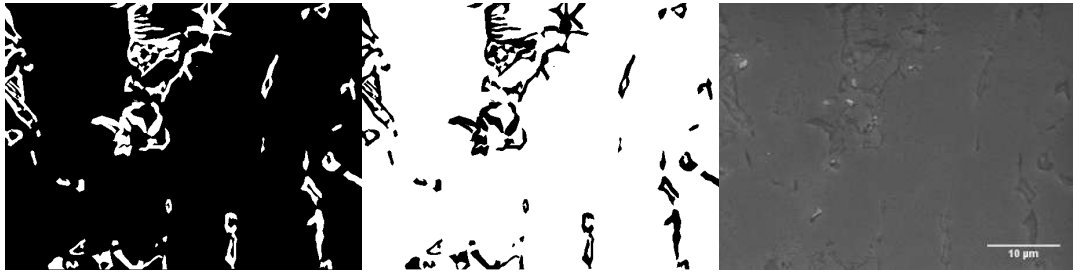


Figure B.7: SEM images after plasma etching and thresholded for (a) only the α phase, (b) only the β phase and (c) original SEM image for position G in Figure 4.13

Appendix C

Abbott Firestone Curves

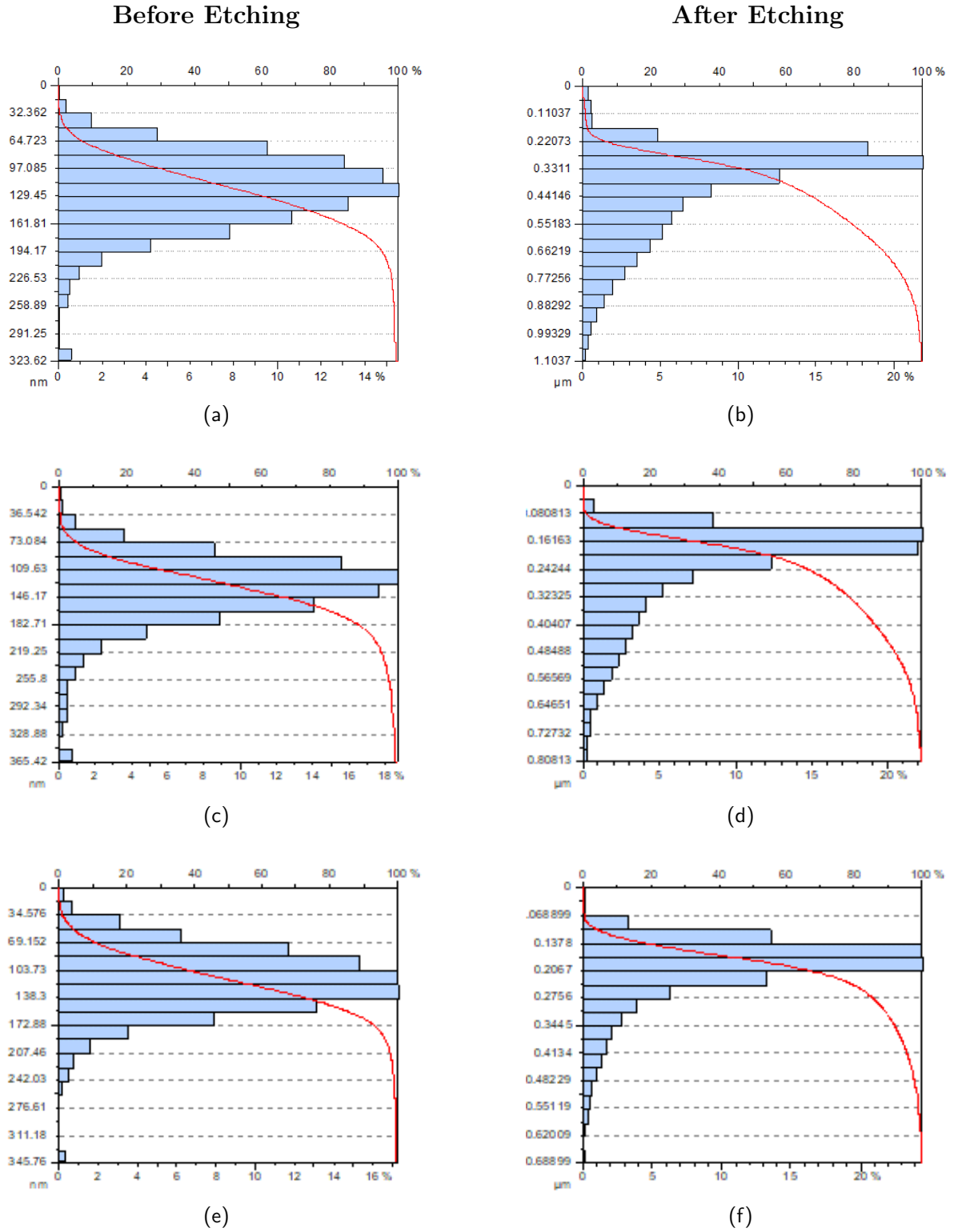


Figure C.1: Abbott-Firestone curves and histograms (a, c, e) before and (b, d, f) after etching trenches at (a, b) 100 mm min^{-1} , (c, d) 150 mm min^{-1} and (e, f) 200 mm min^{-1}

Appendix D

Python Codes

D.1 Defining trends

Below is the python code used to calculate the trends for etch depth, FWHM and MRR during the trench experiments. The same procedue was used for the dwells.

```
# Input the processing speeds and the values for etch depth, FWHM and MRR
Speeds = np.array([50, 100, 150, 200, 250])
Depth_50 = [2469.3, 2703.9, 2885.8]
FWHM_50 = [12.5, 12.8, 12.7]
MRR_50 = [1.64, 1.84, 1.95]
Depth_100 = [866.0, 972.5, 1065.2]
FWHM_100 = [10.5, 10.7, 12]
MRR_100 = [1.08, 1.11, 1.35]
Depth_150 = [495.4, 486.3, 442.9]
FWHM_150 = [11.8, 12.2, 11.1]
MRR_150 = [0.91, 0.88, 0.77]
Depth_200 = [310.9, 295.4, 366.8]
FWHM_200 = [8.6, 8.9, 9.8]
MRR_200 = [0.56, 0.55, 0.75]
Depth_250 = [259.4, 313.8, 226.9]
FWHM_250 = [9.6, 9.7, 8.8]
MRR_250 = [0.68, 0.82, 0.58]
# Group the etch depth, MRR and FWHM into single arrays
Trench_depth = np.array([np.mean(Depth`50), np.mean(Depth`100),
np.mean(Depth`150), np.mean(Depth`200), np.mean(Depth`250)])
Trench_MRR = np.array([np.mean(MRR`50), np.mean(MRR`100), np.mean(MRR`150),
np.mean(MRR`200), np.mean(MRR`250)])
Trench_FWHM = np.array([np.mean(FWHM`50), np.mean(FWHM`100),
np.mean(FWHM`150), np.mean(FWHM`200), np.mean(FWHM`250)])
# Calculate the standard deviation for each speed and group into single arrays
Trench_std = np.array([np.std(Depth`50), np.std(Depth`100), np.std(Depth`150),
```

```

np.std(Depth`200), np.std(Depth`250)])
Trench_MRR_std = np.array([np.std(MRR`50), np.std(MRR`100), np.std(MRR`150),
np.std(MRR`200), np.std(MRR`250)])
# Define inverse power equation
def inv(x, a, b):
return a * x**(-b)
# Set initial guesses for variables a and b
b = np.log((Trench`depth[0]-c)/(Trench`depth[1]-c))/(Speeds[-1]-Speeds[0])
a = (Trench`depth[0]-c)/np.exp(-b*Speeds[0])
# Set range of speeds to plot
speeds = np.linspace(50, 1000, 100)
# Obtain optimised values for a and b (popt) as well as the covariance (pcov)
popt, pcov = curve_fit(inv, Speeds, Trench`depth, p0=[a, b])
# Create the best fit using the optimised parameters for a and b (popt)
fit = inv(speeds, *popt)

```

D.2 Calculating predicted material removal

The python code below was used to calculate the predicted material removal function, based on Equation 2.13, and plot the figures in Section 4.5.

```

# Import the phase data using pandas for before etching
df = pd.read_csv("File location - before etching")
# Remove header
df = df[2:(len(df))]
# Reshape to a 444x400 matrix
z = np.ravel(np.array(df), order='c')
z = np.ndarray.reshape(z, (444, 440), order='f')
# Convert to an array
z = np.array(list(z[:]), dtype=np.float)
# Convert phase data to nm
z = z*632.8/(18202.4)
# Crop to 440x440 array
z = z[0:440, 0:440]
# Import the phase data using pandas for after etching
df = pd.read_csv("File location - after etching")
# Remove header
df = df[2:(len(df))]
# Reshape to a 444x400 matrix
z1 = np.ravel(np.array(df), order='c')
z1 = np.ndarray.reshape(z1, (444, 440), order='f')
# Convert to an array
z1 = np.array(list(z1[:]), dtype=np.float)
# Convert phase data to nm

```

```

z1 = z1*632.8/(18202.4)
#Crop to 440x440 array
z1 = z1[0:440, 0:440]
#Subtract post-pre
res = z1-z
#Set x and y axis
x = [i for i in range(0, 440)]
y = [i for i in range(0, 440)]
#Set colour map
cmap = plt.cm.get_cmap('turbo')
#Before etching 2D plot
v`min, v`max = np.nanmin(z), np.nanmax(z)
fig = plt.figure()
ax = plt.axes()
CS = ax.pcolormesh(x, y, z, vmin=v`min, vmax=v`max, cmap=cmap, shading='auto')
ax.set_title('Ti64 Pre')
ax.set_xlabel('x (mm)')
ax.set_ylabel('y (mm)')
ax.set_xticks([0, 110, 220, 330, 440])
ax.set_xticklabels(['0', '10', '20', '30', '40'])
ax.set_yticks([0, 110, 220, 330, 440])
ax.set_yticklabels(['0', '10', '20', '30', '40'])
cbar = fig.colorbar(CS)
cbar.ax.set_ylabel('(nm)')
plt.show()
#After etching 2D plot
v`min, v`max = np.nanmin(z1), np.nanmax(z1)
fig = plt.figure()
ax = plt.axes()
CS = ax.pcolormesh(x, y, z1, vmin=v`min, vmax=v`max, cmap=cmap, shading='auto')
ax.set_title('Ti64 Post')
ax.set_xlabel('x (mm)')
ax.set_ylabel('y (mm)')
ax.set_xticks([0, 110, 220, 330, 440])
ax.set_xticklabels(['0', '10', '20', '30', '40'])
ax.set_yticks([0, 110, 220, 330, 440])
ax.set_yticklabels(['0', '10', '20', '30', '40'])
cbar = fig.colorbar(CS)
cbar.ax.set_ylabel('(nm)')
plt.show()
#Define the beam function (B) as a 3D gaussian with a constant etch rate
x, y = np.array(x), np.array(y)
sigma = 10/(2*np.sqrt(2*np.log(2)))
X, Y = np.meshgrid((x-220), (y-220))

```

```

R = np.sqrt(X**2+Y**2)
B = 143*np.exp(-(R**2)/(2*sigma**2))
#Define the convolution function
def convolve(star, psf):
star_fft = fftpack.fftshift(fftpack.fftn(star))
psf_fft = fftpack.fftshift(fftpack.fftn(psf))
return fftpack.fftshift(fftpack.ifftn(fftpack.ifftshift(star_fft*psf_fft)))
#Create the velocity map based on the interpolation of Figure 4.9(a)
a = 977137
b = 1.51
proc_speed = (z/a)**b
#Remove nan's and infinities
proc_speed = np.where(proc_speed==np.inf, 1000, proc_speed)
proc_speed = np.nan_to_num(proc_speed)
proc_speed = np.where(proc_speed==0.0, 1000, proc_speed)
#Convert velocity map to pixels per second (from mm per minute)
proc_speed_conv = (1/((proc_speed/60)*(440/40)))
#Perform convolution of velocity map and beam function
proc_speed_conv = -np.real(convolve(proc_speed_conv, np.array(B)))
#Actual material removed plot
fig = plt.figure()
ax = plt.axes()
CS = ax.pcolormesh(x, y, res, vmax=600, vmin=-1500, cmap=cmap, shading='auto')
ax.set_title('Material removed after alternate raster pattern')
ax.set_xlabel('x (mm)')
ax.set_ylabel('y (mm)')
ax.set_xticks([0, 110, 220, 330, 440])
ax.set_xticklabels(['0', '10', '20', '30', '40'])
ax.set_yticks([0, 110, 220, 330, 440])
ax.set_yticklabels(['0', '10', '20', '30', '40'])
cbar = fig.colorbar(CS)
cbar.ax.set_ylabel('(nm)')
plt.show()
#Difference between actual and predicted material removed plot
diff = proc_speed_conv-res
fig = plt.figure()
ax = plt.axes()
CS = ax.pcolormesh(x, y, diff, vmin=-500, vmax=1300, cmap=cmap, shading='auto')
ax.set_title('Difference between convolution and material removed')
ax.set_xlabel('x (mm)')
ax.set_ylabel('y (mm)')
ax.set_xticks([0, 110, 220, 330, 440])
ax.set_xticklabels(['0', '10', '20', '30', '40'])
ax.set_yticks([0, 110, 220, 330, 440])

```

```
ax.set_yticklabels(['0','10','20','30','40'])  
cbar = fig.colorbar(CS)  
cbar.ax.set_ylabel('(nm)')  
plt.show()
```

Appendix E

Areal Plasma Etching Repeats

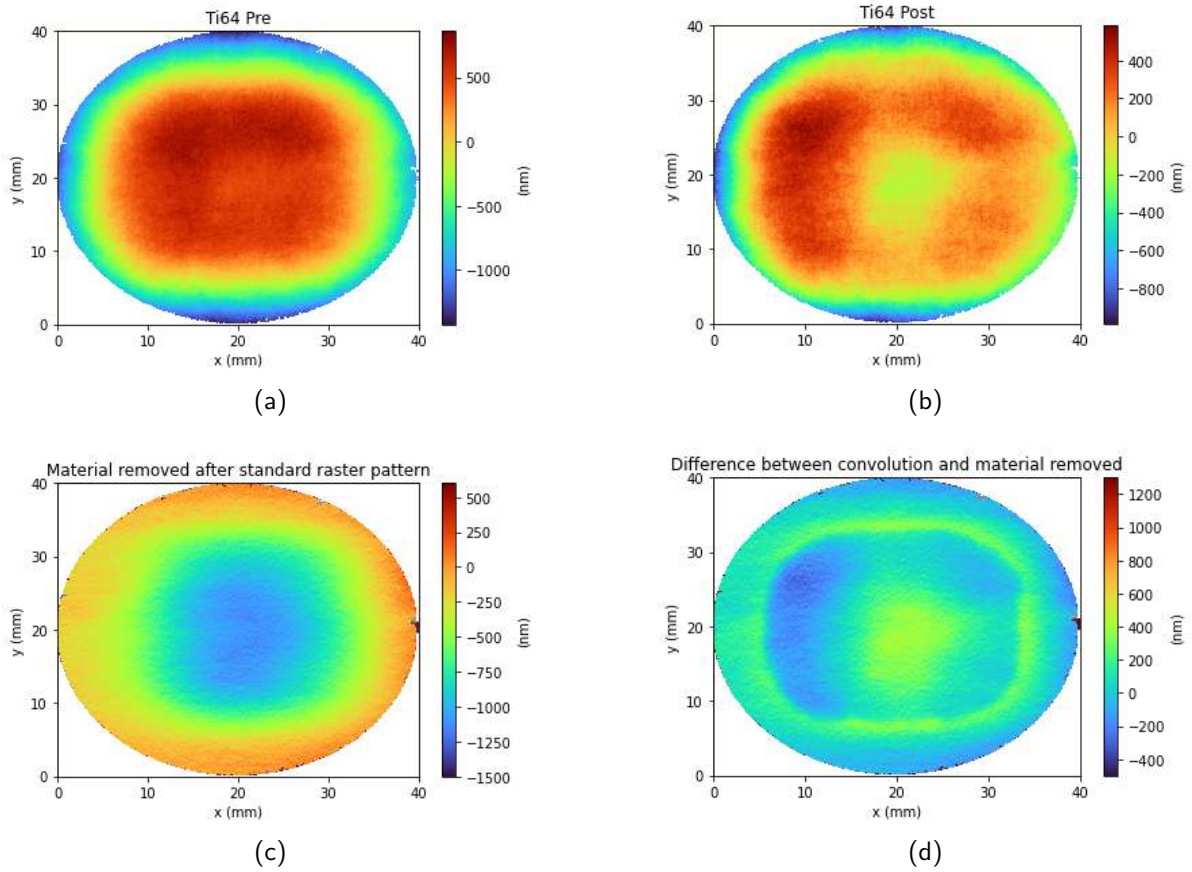


Figure E.1: Repeat surface measurements (a) before plasma etching, (b) after standard pass raster plasma etching at 100% of the calculated speed. (c) Material removed and (d) difference between the predicted and actual material removed

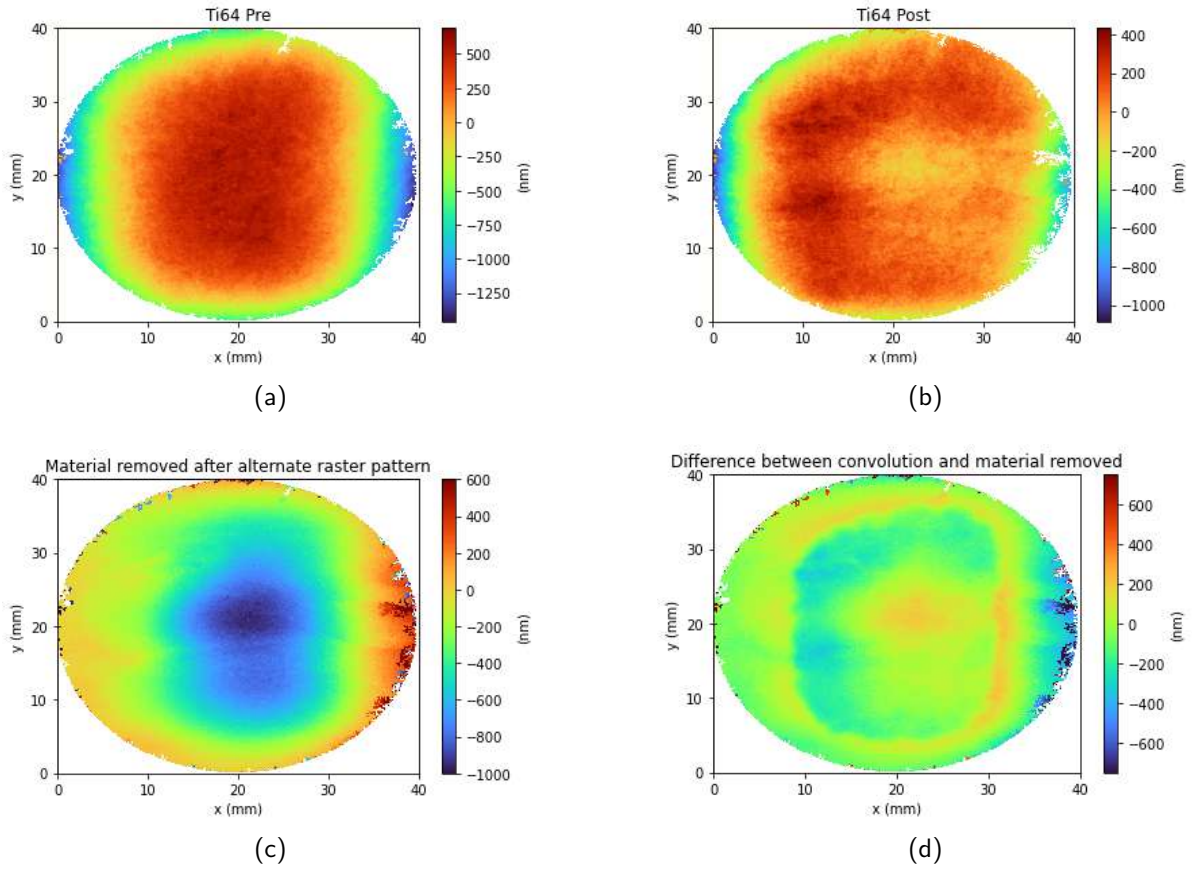


Figure E.2: Repeat surface measurements (a) before plasma etching, (b) after alternate pass raster plasma etching at 100% of the calculated speed. (c) Material removed and (d) difference between the predicted and actual material removed

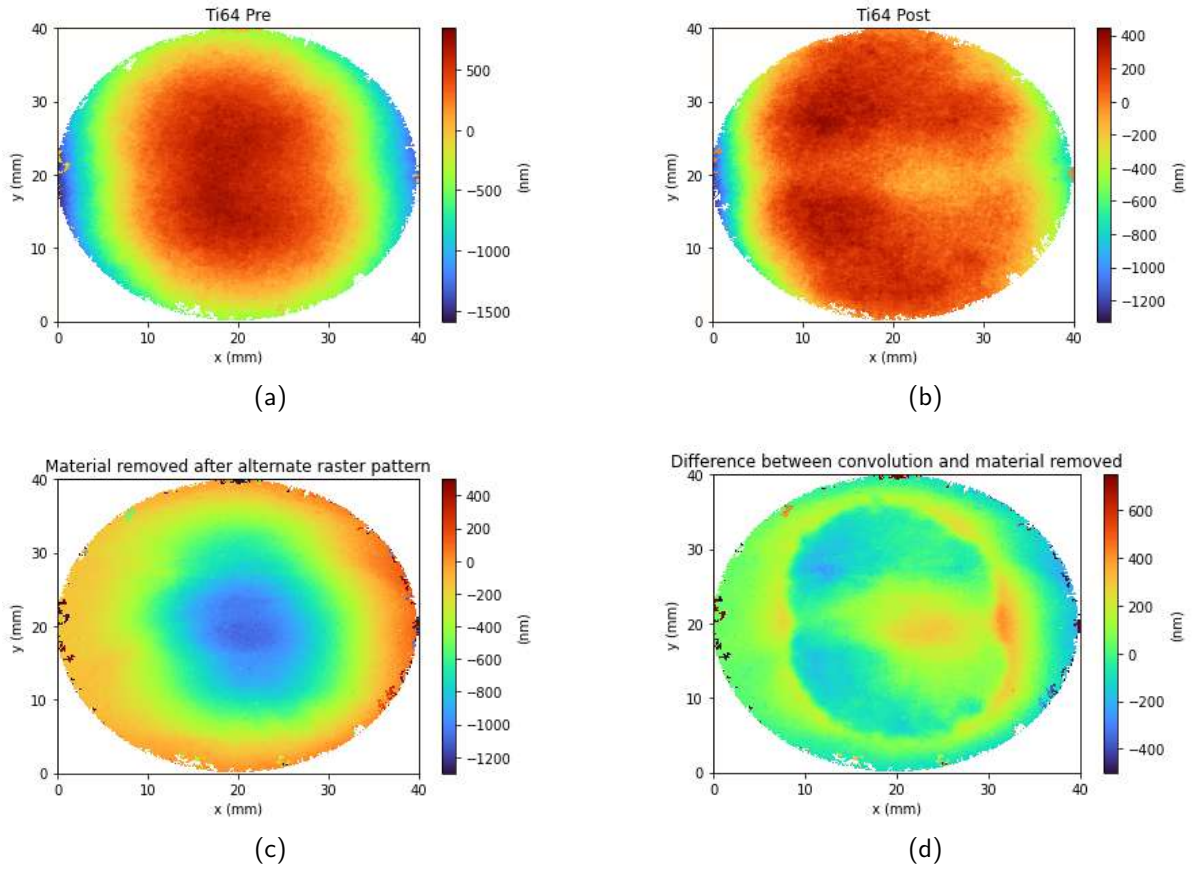


Figure E.3: Repeat surface measurements (a) before plasma etching, (b) After alternate pass raster plasma etching at 125% of the calculated speed. (c) Material removed and (d) difference between the predicted and actual material removed

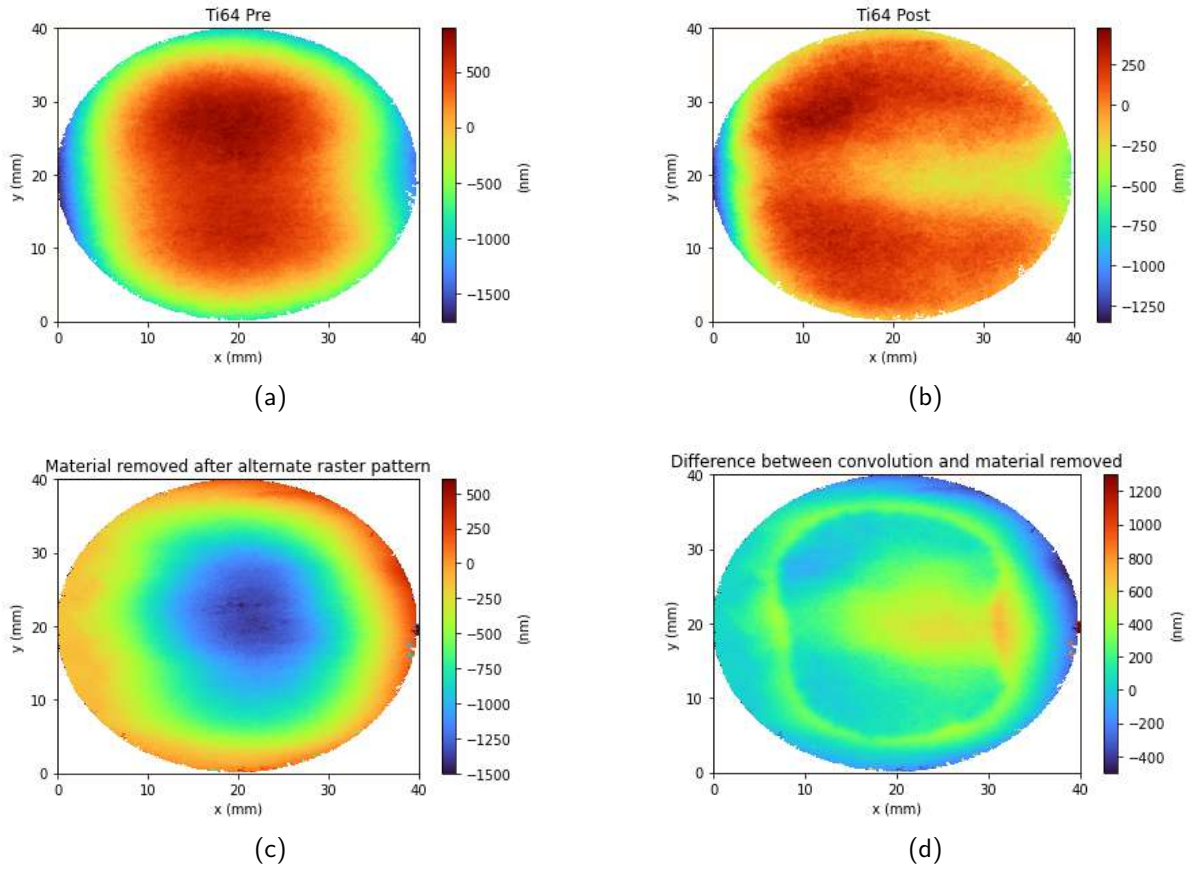


Figure E.4: Repeat surface measurements (a) before plasma etching, (b) after alternate pass raster plasma etching at 150% of the calculated speed. (c) Material removed and (d) difference between the predicted and actual material removed