

**How the Surface Morphology of Electron Beam Melted Additive
Manufactured Grade 5 Titanium Affects Adhesive Bonding Shear Strength**

by

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ABSTRACT

Electron Beam Melting (EBM) is a powder bed fusion (PBF) additive manufacturing (AM) process, capable of easily manufacturing complex shapes out of strong materials, such as Grade 5 titanium. One way to utilise this process while avoiding its downsides (its high cost and small chamber size – 350mm x 380mm (Ø/H)) is through producing large, stiff and strong structures made of small metal EBM AM nodes adhesively bonded to carbon fibre tubes. These structures offer time and cost savings whilst still being incredibly strong. However, the strength of these structures is only as good as the strength of the adhesive bonds holding it together. Therefore, this thesis aimed to understand the relationship between different as-built surface morphologies producible by EBM AM, and the resulting adhesive bonding shear strength of each surface.

This study tested three EBM as-built surfaces, defined as vertical, horizontal, and trabecular meshed surfaces. These surfaces were shear strength tested using the ASTM D1002 (eccentrically) and D3165 (concentrically) loaded single-lap-joint (SLJ) standards. The samples were macro and micro-roughness tested using a profilometer, with the nano surface roughness features classified and defined by scanning electron microscope. Both a smooth and NaTESI anodised vertical surface were also tested for bonding strength. Finally, a simulation was carried out to analyse the mechanics behind the SLJ failure, showing how the bonding could be improved.

The results showed that the vertical surface had the best micro-roughness and outperformed the epoxy's rated strength by 11.2% (17.9 MPa) in the ASTM D3165 experiments. For the NaTESI anodised vertical samples, no changes occurred to the macro or micro surface roughness, yet the nano surface roughness increased significantly. This resulted in the strongest bond, which was 15% stronger than the epoxy's rated strength, reaching 18.7 MPa. Further, the NaTESI bond failed through 100% cohesion failure of the epoxy adhesive. Therefore, a stronger adhesive would resist even more force. Further, the trabecular meshed surfaces created for this study had a high macro-roughness and porosity, with its struts having a similar micro-roughness to the vertical surfaces. Due to these characteristics, the bond was equivalent to the epoxy's rated strength (15.6 MPa) in the D3165 experiments. The horizontal and smooth surfaces bonded poorly, with the samples reaching only 12.9 MPa and 3 MPa respectively, and both failing through 100% adhesion.

Overall, of the surfaces investigated, the surface with the highest fractal roughness was the most effective for epoxy adhesive bonding. It was proposed that this occurred through increased micro and nano surface roughness impeding the adhesive's deformation motion at the interface. This would then stress relieve the interface, diverting the loading forces into the

bulk of the epoxy adhesive. Additionally, the surface roughness increased the specific adhesion contact area between the epoxy polymer chains and the titanium substrate.

Finally, the simulation found that both the D1002 and D3165 SLJs began failing at the lapping edges due to peeling stresses; the lapping edges were identified as stress concentration points. The D3165 SLJ was exposed to less peeling stresses than the D1002 SLJ due to its loading acting concentrically through the bond line. For both the D1002 and D3165 SLJs, bending moments were present, but increasing the substrate thickness significantly reduced the principal and peeling stresses on the lapping edge, strengthening the joint.

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LIST OF ABBREVIATIONS

AM:	Additive manufacturing
ASTM:	American Society for Testing and Materials
BCC:	Body centered cubic
EDS:	Energy dispersive X-ray spectroscopy
EDTA:	Ethylenediaminetetraacetic acid
FCC:	Face centered cubic
FS:	Flat surface
H₂SO₄:	Sulphuric acid
H₃PO₄:	Phosphoric acid
HBr:	Hydrobromic acid
HCL:	Hydrochloric acid
HCP:	Hexagonally closed packed
HF:	Hydrofluoric acid
HIP:	Hot isostatic pressing
HNO₃:	Nitric acid
LINS:	Laser induced nano structuring
LIPSS:	Laser induced periodic structuring
NaOH:	Sodium hydroxide
NaTESI:	A mixture of sodium hydroxide, sodium-tartrate, sodium silicate, and Ethylenediaminetetraacetic acid dissolved in water
Nd:YVO₄:	Ytterbium-doped fibre
MS:	Meshed structure
PBV:	Parts by volume
PDF:	Powder Bed Fusion
PO₄³⁻:	Phosphate anion
PS:	Powdered surface structure
Ra:	Arithmetic average roughness
SEBM / EMB:	Selective Electron Beam Melting
SEM:	Scanning electron microscope
SLJ:	Single-lap-joint
SO₄²⁻:	Sulphate anion
TPMS:	Triply periodic minimal surface
WS:	Wavy structure
XPS:	X-ray photoelectron spectroscopy

ATTESTATION OF AUTHORSHIP

I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person (except where explicitly defined in the acknowledgements), nor material which to a substantial extent has been submitted for the award of any other degree or diploma of a university or other institution of higher learning.

Kurt Schmidt

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Thank you to my mother-in-law Ruth Cleaver and my brother-in-law Shawn Cleaver for proofreading.

Finally, I would like to thank my partner, Julie Cleaver. I draw inspiration from your hard-work ethic and am always stimulated by our conversations about everything. Nothing beats working with you through the late nights and early mornings. Together, we are greater than the sum of our parts.

Chapter 1: INTRODUCTION

High performance sectors, such as the aerospace, automotive, medical and sporting industries, rely on the use of high-strength, low-density materials. For the sporting industry, an increased power-to-weight ratio can be the difference between a podium finish and last place. And for the aerospace industry, reducing the weight of an aircraft by just one kilogram can save roughly \$1m (£603,000) over a carrier's lifetime (Bowler, 2014).

Grade 5 or Ti-6Al-4V titanium alloy and carbon fibre are both high-strength materials, with an ultimate tensile strength of around 1020 MPa and 1210 MPa respectively (MatWeb, 2018). Unfortunately, these materials are expensive; EBM-manufactured titanium powders average in price at around 200 USD/kg, making heavy components costly (Zenith Tecnica, 2018). For carbon fibre, the cost depends on the complexity of the die and tools required to manufacture a component. However, for both materials, the cost components can be overcome by utilising the advantages of each material. This can be achieved by using AM titanium for small, complex components (such as the joining nodes shown in Figure 1) and carbon fibre tubing for sections of low complexity that require large volumes of material (such as the cross members of the bicycle shown in Figure 2). For products made through these methods, the cost savings and the reduction in manufacturing time makes the use of additive manufactured Ti-6Al-4V titanium alloy nodes bonded to carbon fibre tubes an excellent option.



Figure 1: Left – a light-weight aircraft seat made by joining Ti-6Al-4V titanium alloy nodes to carbon fibre tubes; Right – one of the joining titanium nodes. Both manufactured by Zenith Tecnica



Figure 2: Bastion custom-built bicycle utilising the bonding of additive manufactured Ti-6Al-4V titanium alloy nodes to carbon fibre tubes ("Startup Stars finalist: Bastion Cycles – James Woolcock," 2017)

Adhesive bonding is being recognised as an attractive alternative to conventional mechanical joining methods such as bolting and riveting. This is due to it offering many advantages, such as design flexibility, uniform stress distributions, weight reduction, and a higher joint stiffness (Arenas, Narbon, & Alia, 2010). Therefore, the number of adhesive bonding applications in various industries is growing. For example, the Boeing 787 Dreamliner, shown in Figure 3, was composed of 50% composite materials and 15% titanium, most of which were adhesively bonded together (Hale, 2008).

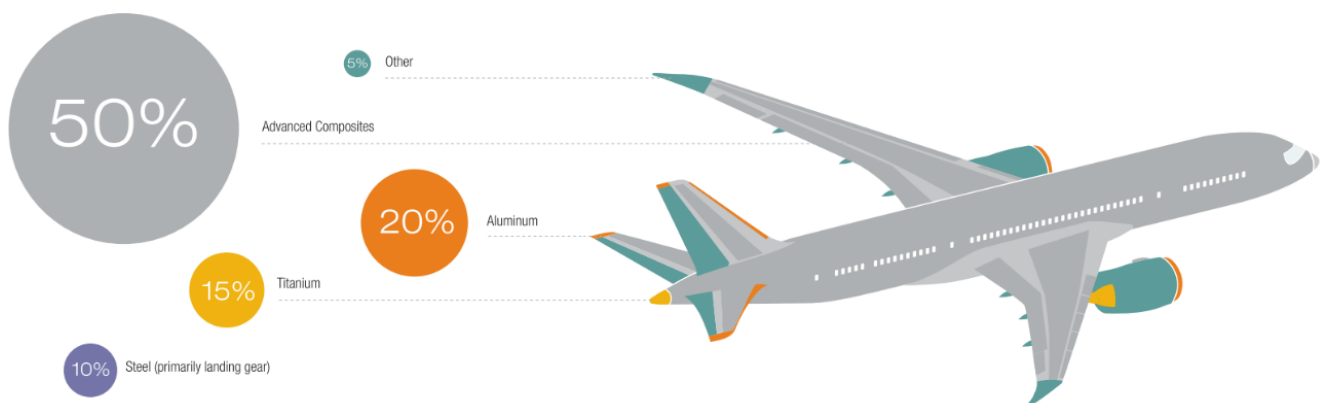


Figure 3: How composite solutions are applied throughout the Boeing 787 (Hale, 2008)

As adhesion is dependent on the chemical interaction of two or three different materials over two interfaces, the bond strength relies on the successful interaction and bonding of these materials. In his review of adhesively-bonded joints, Baldan (2004) states that for a satisfactory joint: first, a surface pre-treatment method should be used which provides a clean surface free

from contaminants; second, that the adhesive should fully wet the solid substrates; and third, that the adhesive joint be designed for shear loading avoiding any transverse peeling loads. Chemical pre-treatments, such as alkaline etching and electro-chemical pre-treatments (like anodising) affect the surface morphology by modifying the naturally occurring oxide layer into a porous nano-structured surface which resembles the look of coral (Kurtovic, Brandl, Mertens, & Maier, 2013) see Figure 4 (a, b, e, f). For the adhesive bonding of titanium and its alloys, surfaces like this, that increase the surface morphologies' nano and micro surface roughness, exhibit greater wetting out of the adhesive, producing higher bonding strengths (Venables, 1984). However, chemical pre-treatments have a downside: they often employ hazardous and non-environmentally friendly chemicals, such as chromic acid. In contrast, there are environmentally friendly methods available, such as the NaTESI, which was proposed by Matz (1988).

A method called laser-induced nano-structuring (LINS) has also shown to improve titanium adhesive bonding. LINS reduced contamination on the surface and increased micro-roughness through the formation of grooves and nano-roughness by the formation of a porous oxide layer (Kurtovic et al., 2013; Rotella, Orazi, Alfano, Candamano, & Gnilitzkyi, 2017) see Figure 4 (c, d). Further, the laser method has the benefit of not requiring toxic chemicals.

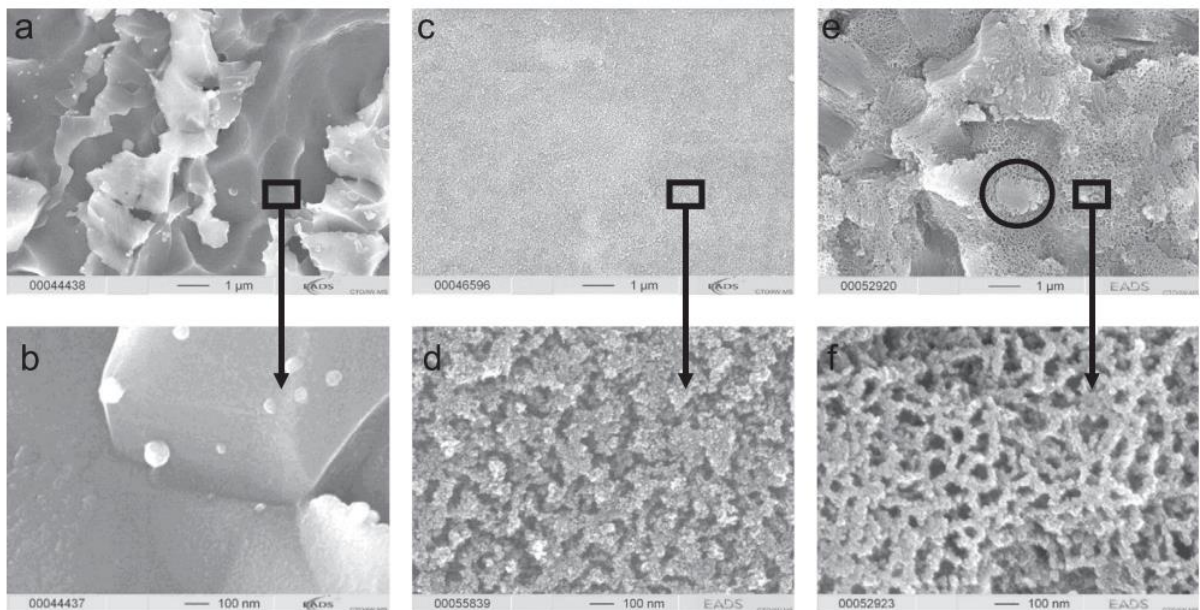


Figure 4: SEM micrographs of Ti-6Al-4V surface: (a), (b) Turco 5578 pre-treatment (c), (d) laser pre-treatment and (e), (f) NaTESi pre-treatment (Kurtovic et al., 2013)

As shown above, micro and nano surface roughness has profound effects on the adhesive bonding strength. For EBM-produced titanium, the surface morphologies/roughness is shown to be dependent on the way the part is orientated with respect to the build direction (Safdar, He,

Wei, Snis, & Chavez De Paz, 2012; Wang, Sin, Nai, & Wei, 2017). Figure 5 visually presents the results of these different build orientations. The surface roughness values are strongly dependent on the processing parameters of the EBM machine, with micro-roughness ranging between Ra 5-40 μm (Wang et al., 2017). The average Ra surface roughness for normal processing parameters is 8-20 μm , with the horizontal build direction producing the smoothest surface, and the vertical direction the roughest. These two surfaces are shown below in Figure 5 along with the other surfaces investigated in this current thesis.

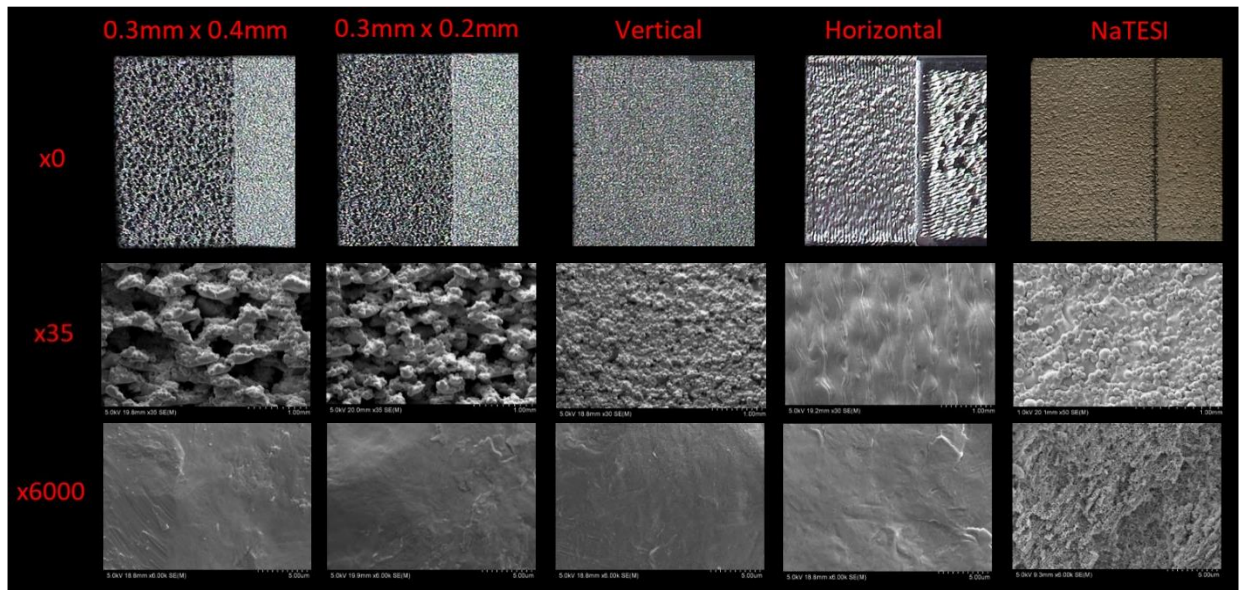


Figure 5: SEM surface images under different magnifications giving the surface morphology of two meshed surfaces, the vertical build surface, the horizontal build surface, and the NaTESI anodised surface (this is experimental data from this thesis)

1.1 The purpose of this research

Although the surface morphology is somewhat understood for EBM materials, it has not been studied in relation to how it affects adhesive bonding, and whether bonds made with the as-built surfaces are strong and reliable. Some companies, specifically Zenith Tecnica (who approached the Auckland University of Technology with this issue) were failing to produce predictable bonds between EBM produced Grade 5 titanium nodes and carbon fibre tubes, specifically on the titanium side, as shown in Figure 6.



Figure 6: Failed adhesion between carbon fibre and EBM additive manufactured Grade 5 titanium, failure through adhesion failure at the titanium interface – obtained from Zenith Tecnica

This thesis set out to solve this problem by investigating the relationship between the surface morphology of EBM produced Grade 5 titanium and the resulting adhesive bonding strength. Further, it aimed to provide Zenith Tecnica with a method for producing predictable structural bonds (10-20MPa in shear) for joints made from these materials. It was successful in this endeavour, defining multiple methods for producing joints with a consistent apparent shear strength of over 15 MPa. Finally, although solving this practical problem was important, the true goal of this thesis was to understand the adhesive bonding phenomenon on a deeper level. Therefore, a possible mechanism of causality is presented for all the results of this thesis.

1.2 Research objectives

The objective of this thesis was to understand the relationship between different as-built surface morphologies producible by EBM additive manufacturing and the resulting adhesive bonding strength for each surface. The three unique as-built surface morphologies investigated in this research were:

- The vertical surface – manufactured with the bonding surface being oriented vertically, and defined by a surface with partially melted powder particles adhered to it;
- The horizontal surface – manufactured with the bonding surface being oriented horizontally, and defined by a surface made up of multiple thin weld-lines;
- The trabecular meshed surface – a 1mm thick surface structure made up of a connected network of many thin 0.3mm struts, with a specifically designed target pore size.

With the adhesive bonding properties defined for the as-built surfaces, the thesis then aimed to see whether the NaTESI pre-treatment method known for improving the adhesive bonding properties of titanium could also improve the bonding of EBM-produced parts. Further, the study investigated smooth titanium surfaces to see how a lack of surface roughness affected the joint's adhesive bonding strength.

1.3 Research structure

Chapter 2 presents the literature review, which covers: two adhesive bonding theories and mechanisms; the importance of removing sources of contamination; the common surface pre-treatment methods for titanium adhesive bonding (looking specifically at laser-induced nano-structuring and anodising); the selective electron beam process and how the process themes can vary the macro and micro-structure; the production of additive manufactured cellular structures; the mechanical, chemical and physical properties of titanium, its alloys and its oxides; the most common adhesive bonding techniques for testing single-lap-joints and the distribution of stress under these load cases; and the objective of the thesis presented as four research questions.

Chapter 3 describes the methods that were used to investigate the four research questions, covering: the materials used in the bonded structures; the preparation method; the testing equipment; the limitations of the two ASTM single-lap-joint shear testing experiments, ASTM D1002 (eccentrically loaded SLJ) and ASTM D3165 (concentrically loaded SLJ); the anodising method; and finally, the results of the preliminary experiment, which investigated the different surface morphologies, is presented and discussed.

Chapter 4 discusses the results of the research, including: an overview of the collected data, including bond strength, surface roughness, maximum force and extension, sample dimensions and characteristics; an in-depth discussion of the force versus extension graphs; an analysis of the results of the simulations used to model the D1002 and D3165 experiments, presenting the failure path and maximum stress locations; and a comparison between the simulation results and experimental findings.

Chapter 5 presents the main conclusions of this thesis and suggestions for future work.

Chapter 2: LITERATURE REVIEW

Adhesive bonding is now an integral part of many industries, finding practical use in many high-performance designs as a way of joining dissimilar materials. With the increased use of EBM AM titanium being involved in these dissimilar joints, it is now paramount to understand the adhesive bonding properties of these uniquely produced parts. This literature review contains the foundation knowledge which was used for investigating the adhesive bonding strength properties of the EBM produced Grade 5 titanium surfaces.

First this literature review will look at what adhesive bonding is, specifically the mechanical interlocking and specific adhesion theories. It will then cover the EBM AM process, looking specifically at Grade 5 titanium, its surface morphology, what microstructure it has, and the resulting mechanical properties. Then common adhesive bonding techniques will be looked at including anodising, and laser surface structuring. EBM cellular structures are then discussed in relation to whether they can create good adhesion surfaces based on their current application towards improving osseointegration of implants. Then the loading and stress distributions of single-lap-joints are discussed. Finally, the objective of the thesis is broken down into four research questions.

2.1 What is adhesive bonding? Theories and mechanisms of adhesion

According to Baldan (2012) no single global theory or model has explained all the phenomena or mechanisms behind adhesive bonding. Pizzi and Mittal (2003) further reinforce this by stating that due to the multiple scientific fields involved in the study of adhesion (including Material Science, Engineering, and Chemistry) the theories, models, or concepts used will vary depending on the researcher's field of expertise. This variety is emphasized by the fact that many models of adhesion have been proposed based on different interpretations of the same phenomenon. Together these theories are both complementary and contradictory. The most common are listed as follows:

1. Mechanical interlocking
2. Electronic theory
3. Theory of boundary layers and interphases
4. Adsorption (thermodynamic) theory
5. Diffusion theory
6. Chemical bonding theory

Although many theories exist, Baldan (2012) states that almost all adhesion research areas aim for the same two basic outcomes. The first aim is to understand and classify the mechanical properties of the adhesive joint, and the second is to allow predictions about the long-term durability of the joint. This is exactly the purpose of this research, which is to classify the mechanical properties of an adhesive joint involving Grade 5 titanium manufactured through electron-beam-melting (EBM) additive manufacturing, and to allow a prediction about its performance. Due to the normal limitation of resources, equipment, and my professional field of study, an emphasis has been put on utilising the theories of mechanical interlocking, thermodynamic theory, and to a lesser extent chemical bonding theory.

2.1.1 The Mechanical Interlocking Theory – how surface morphology affects adhesion

As cited in the book by Pizzi and Mittal (2003), McBain and Hopkins (1924) created the mechanical interlocking model, proposing that the major factor determining adhesive strength was the extent that an adhesive is able to mechanically key or interlock into cavities, pores, and asperities of a solid surface. This phenomenon was named “mechanical adhesion”, an example of this can be seen in Figure 7, which shows the mechanical interlocking observed in the present thesis. McBain and Hopkins (1924) thought of mechanical adhesion as common sense stating, “It is obvious that a good joint must result when a strong continuous film of partially embedded adhesive is formed in situ.” A study done by Borroff and Wake (1949) illustrated the effects that mechanical anchoring had on adhesive bonding strength, showing that the adhesion between rubber and textile fabrics could be improved by increasing the penetration depth of the protruding fibres.

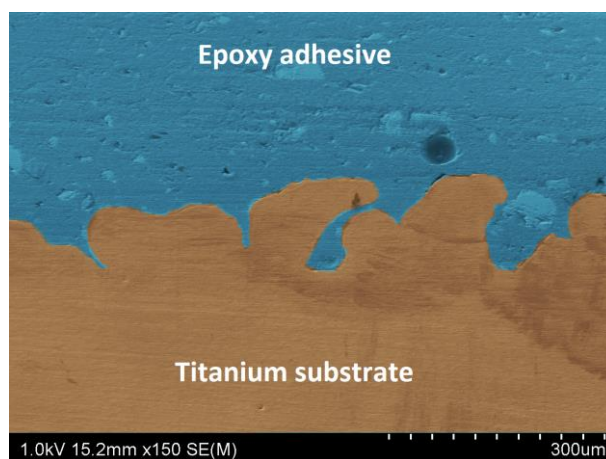


Figure 7: Mechanical interlocking of an epoxy adhesive with a titanium substrate from the present thesis

Unfortunately, the theory of mechanical interlocking was an incomplete picture of the phenomenon of adhesion, as later studies showed that good adhesion could also be achieved between smooth surfaces. It was thought that for the smooth surfaces, another mechanism which was named by McBain and Hopkins (1924) called “specific adhesion” was the cause.

Specific adhesion was thought of as the chemical interaction between the surface of the adhesive and the substrate; and that smoothing chemically charged the surface of metals by removing the natural stable oxide layer. Specific adhesion consequently developed into the model now described in terms of the adsorption or thermodynamic theory. The illustration shown in Figure 8 was produced to visually aid this explanation.

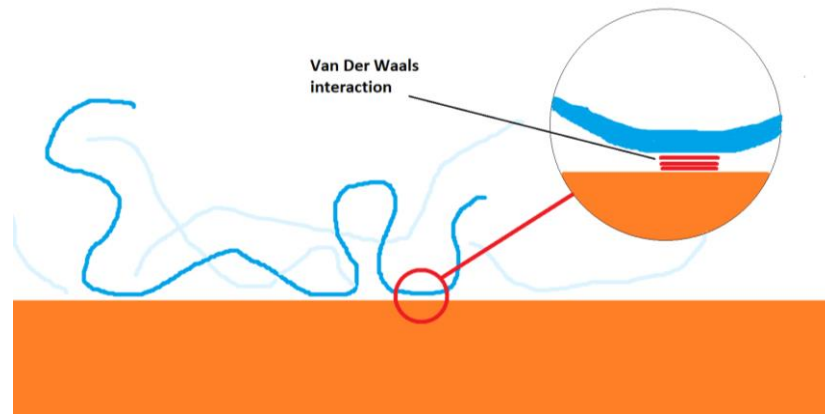


Figure 8: Adsorption mechanism of adhesion between a polymer chain and substrate, using van Der Waals interactions

In his book Wake (1982) proposed that joint strength G could be estimated based on multiplying factors taken from the effect of both thermodynamic interfacial interactions (specific adhesion) and mechanical interlocking interactions (mechanical adhesion), giving a theory that justified that both a smooth and rough surface could improve adhesive bonding. His base relation was given as:

$$G = (\text{constant}) \times (\text{mechanical interlocking}) \times (\text{specific adhesion})$$

This highlighted that a default constant belongs to a substrate and adhesive combination, and that by adjusting both the surface morphology, and the surface properties of the adhesive and substrate, joint strength ' G ' could be improved. However, as stated by Pizzi and Mittal (2003) this was only when the wetting conditions permitted the full wetting out of the adhesive into the substrate. Pizzi and Mittal (2003) add that it is possible that surface roughness and mechanical interlocking, may only improve adhesion strength by increasing the interfacial area available for specific adhesion to take place.

Another criticism highlight by Pizzi and Mittal (2003) towards the mechanical interlocking theory is that improvements to adhesion due to surface roughness do not necessarily result from a mechanical keying mechanism. Instead, they described that surface roughness can increase the energy dissipated viscoelastically or plastically around the crack tip and in the bulk of the material and that this viscoelastic energy loss is often a major component of adhesive strength.

For a long time researchers had difficulty relating surface roughness with adhesive bond strength, because surface roughness was by itself not a very useful physical quantity. For example, it took until the 1970's for the theory of mechanical adhesion to be looked at seriously again, and this was only due to the development of the scanning electron microscope (SEM), which provided a way of viewing surfaces clearly under high magnification. For example, in McBain & Hopkins' day, surface roughness was looked at as a macro quantity being defined in units measuring only to the micron level. However, after the invention of SEM it was proven that surface roughness in some instances extends to the nano realm. Due to some surfaces having surface roughness present at different scales, it became necessary to categorise the surface roughness based on the scale of the frame of view. These categories were first given by Venables (1984) following work carried out on creating porous oxide films in aluminium and titanium. Due to the oxides' porosity and microscopic roughness, adhesives mechanically interlocked well with the surfaces producing much stronger bonds than both smooth and macro-roughened surfaces. The categories Venables (1984) created to define the different surface roughnesses were:

- Group 1: no micro/macro-roughness - smooth
- Group 2: macro-roughness with low or no micro-roughness
- Group 3: micro-roughness

Recently, it was proposed by Mertens et al. (2012) that a fourth group should also be added to the classifications to represent surface pre-treatments which lead to nano-porous structures of dimensions below 100nm.

- Group 4: nano-porous structures smaller than 100nm

In their study of laser etching titanium, Mertens et al. (2012) showed that the laser treatment increased the micro-roughness, nano-roughness and porosity leading to a wedge test crack length of half the length of a sample that was only degreased. For this study the adhesive was able to wet out into surface structures smaller than 100nm.

It is still largely debated how micro and nano surface roughness especially when porous in nature improves adhesive bonding. Explanations of the exact mechanism responsible include: an increased surface area for specific adhesion to act; viscoelastic energy dissipation; entanglement; a mechanical effect of stopping polymer pull-out and forcing scission; and or by a mixture of these effects. However, regardless of the theory used in the explanation, the data from many studies prove that for many material combinations micro and nano surface roughness does improve adhesion strength.

2.1.2 Adsorption (or Thermodynamic) Theory – how surface energies affect adhesion

The adsorption theory was made popular by Sharpe and Schonhorn (1964) who believed that given intimate contact, adhesives adhered to substrates because of interatomic and intermolecular forces established at the interface. The most common interfacial forces being van der Waals and Lewis acid–base interactions, previously shown in Figure 8. The work required to separate these interfacial forces when measured across the entire bonding area was termed the work of adhesion. This study was of interest as the experimental data proved a relationship between the thermodynamic surface free energies of the adhesive and adherent, the work of adhesion, and the bonding strength G . The reversible work of adhesion was measured quantitatively from the surface free energies of the adhesive and adherent, with the surface free energies being measured directly using tests such as a sessile drop test with known values of a liquid's surface tension. Pizzi and Mittal (2003) showed that the adsorption theory can be constructed in three steps of understanding:

1. The surface free energies based on the wetting criterion of the interface
2. Relating the surface free energies to the work of adhesion
3. Relating the work of adhesion to the adhesion strength

Step 1: The surface free energies based on the wetting criterion of the interface

The illustration shown in Figure 9 was produced to visually aid the explanation given by Pizzi and Mittal (2003). They explain that for an idealised perfectly smooth surface, at the surface the molecules differ from the bulk by being drawn closer together due to excess charge. This in turn causes the entropy to drop at the surface as the order of the system increases. This drop in entropy then produces more Gibbs free energy to carry out work, with this energy being present at the surface.

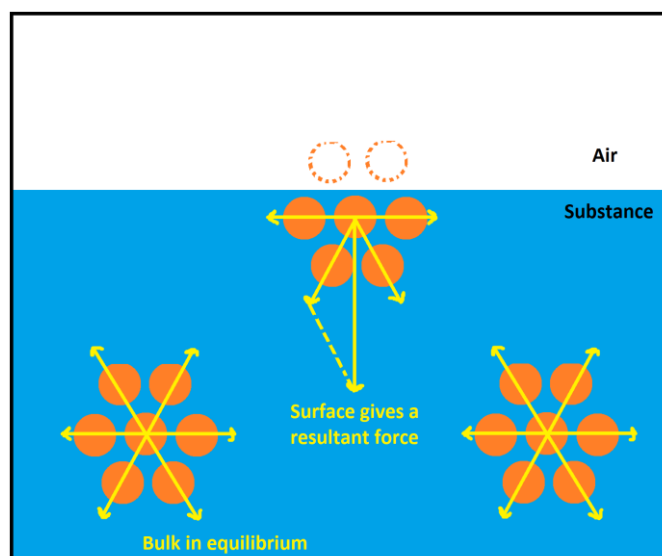


Figure 9: The creation of a surface causing a resultant force that compresses the surface

This can be demonstrated through the following two equations:

$$\Delta G = \Delta H^o - T\Delta S^o$$

Here, G is the Gibbs free energy in the system, H is the enthalpy, T is temperature and S is the entropy. Hence, lowering ΔS increases G. Many believe that by increasing the surface roughness one can decrease the surface entropy by further reducing the number of adjacent bonding sites. For cases where the surface entropy is reduced, the Gibbs free energy (G) in the system is increased, which consequently increases the Gibbs surface free energy (G^s) as shown in the following equation:

$$G^s = \frac{G - G^b}{A}$$

G^s is the Gibbs surface free energy, A is the area of the surface, G is the Gibbs free energy in the system, and G^b is the value the total Gibbs free energy would have if all the constituent particles (atoms, molecules) were in the same state as they are in the bulk of the phase. Hence, if G increases, G^s must also increase.

The formation of adhesive bonds is associated with surface energies, as this quantity determines the extent to which, at equilibrium, a liquid adhesive will meet a solid surface and form a chemical bond. For a solid-liquid system using an ideal surface, wetting equilibrium may be determined from the profile of a sessile drop test. This equilibrium can be shown analytically with Young's equation shown below. The surface tension γ of materials at the three-phase contact point are related using the equilibrium contact angle, Θ , which gives a convenient relation to the surface energies as illustrated in Figure 10.

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos\theta$$

Where

γ_{SV} = Surface free energy at the solid-vapour interface

γ_{SL} = Surface free energy at the solid-liquid interface

γ_{LV} = Surface free energy at the liquid-vapour interface

Θ = the equilibrium contact angle

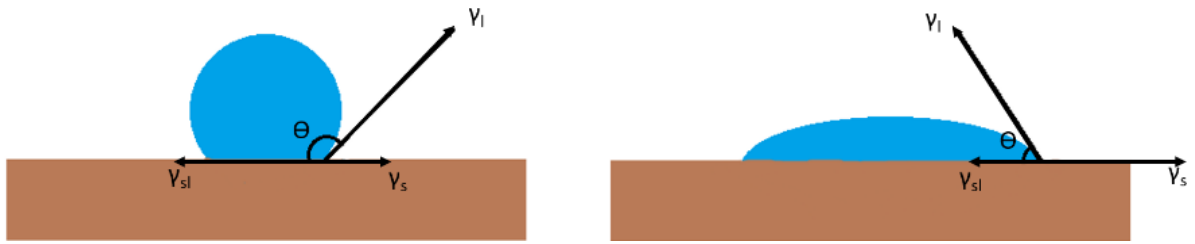


Figure 10: Left – Poor wetting and high contact angle; Right – Good wetting and low contact angle. Assumed vacuum so the vapour subscript v has been omitted

The vapour subscript v represents the surface free energy of the specific item due to the interaction with a vapour phase. This can cause the surface free energy to be lower than the same solid and liquid combination in a vacuum. The decrease is often described as the spreading pressure of the vapour onto the solid surface, given by π , where:

$$\pi = \gamma_s - \gamma_{sv}$$

Another useful measure is the spreading coefficient, S which measures the energy change per unit area when liquids spread over a solid. It is related to the surface tensions by:

$$S = \gamma_{sv} - \gamma_{sl} - \gamma_{lv}$$

These two equations are important as the degree of contact between a liquid adhesive and solid substrate determines the magnitude of the surface energies. The higher the surface energies, the higher the specific adhesion and subsequently the bond strength.

As an adhesive bond requires the forming of new surfaces, the higher the surface energies, the more energy that would be required to break the bond. Table 1 shows the wetting conditions and hence the degree of measuring a successful bond.

Table 1: Contact angle, θ , and spreading coefficient for a liquid on a solid surface showing wetting criterion (Pizzi & Mittal, 2003)

Smooth Surfaces		
" $\theta < 0^{\circ}$ " ^a	Spontaneous spreading	$S > 0$
$90^{\circ} > \theta > 0$	Finite contact angle	$0 > S/\gamma_{LV} > -1$
$180^{\circ} > \theta > 90^{\circ}$	Finite contact angle	$-1 > S/\gamma_{LV} > -2$
" $\theta > 180^{\circ}$ " ^a	Spontaneous dewetting	$S/\gamma_{LV} < -2$

^aThese are in quotation marks because strictly $0^{\circ} < \theta < 180^{\circ}$.

Step 2: Relating the surface free energies to the work of adhesion

The work of adhesion may be either the work of adhesion or the work of cohesion depending on whether the surface separates into two pieces at the adhesive interface, or cohesively in the bulk of one of the materials (see Figure 11 for a visual aid). For a solid-liquid system the adhesion energy W_{SL} under adhesion failure is defined as:

$$W_A = W_{SL} = \gamma_S + \gamma_{LV} - \gamma_{SL}$$

And for cohesion failure, the work of cohesion is defined as:

$$W_C = 2\gamma_S$$

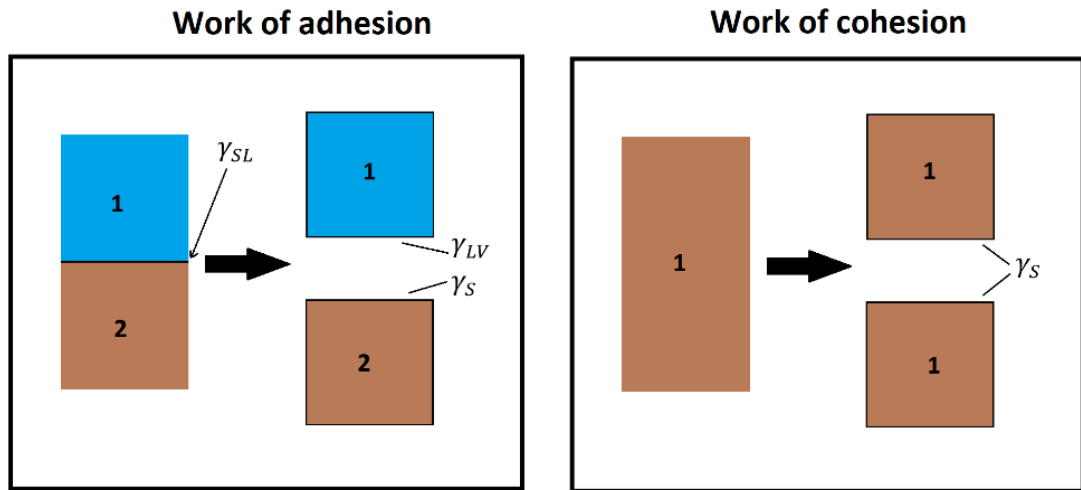


Figure 11: The work of adhesion being related to the surface energies of newly formed surfaces

In over simplified terms, when an object is split in two, the bonds that are broken become the new surfaces. The energy to break these bonds is reflected in the surface energy of the resulting surfaces. Therefore, in the reverse order it follows that the surface energies can be used to predict the work of adhesion or cohesion and subsequently the bonding energies.

Adhesive bonds are just chemical bonds occurring over an interface that formed between a solid surface and a solidifying liquid (the adhesive). For a chemical bond to form the nuclei of one material must come within a certain distance of another materials electron cloud. Therefore, the higher the surface energy of the solid, the closer the liquid adhesive will be drawn towards the solid surface, increasing the probability of the nuclei and electrons of the different materials forming chemical bonds. This is why good wetting in the contact angle test improves the adhesive bonding strength (Baldan, 2012).

Step 3: Relating the adhesion strength to the work of adhesion

Practical adhesion is normally measured using fracture energy G , which comprises of a surface energy term G_o which represents either (W_A or W_C). To this, another term ψ is added to represent the other energy-absorbing processes such as viscoelastic energy dissipation, plastic deformation, and polymer chain entanglement. Here G is given by:

$$G = G_o + \psi$$

Pizzi and Mittal (2003) state based on the work of Andrews and Kinloch (1973a, 1973b) that in most cases ψ is normally magnitudes greater than the work of adhesion or work of cohesion G_o , making the surface energy terms appear pointless for determining the fracture energy. However, Andrews and Kinloch later point out that a small increase in the surface energy G_o may result in large increases in fracture energy G as the energy absorbing term ψ is often coupled by a multiplicative function to G_o . In these cases, they used a mechanically simple system where ψ was mainly associated with viscoelastic losses. For this they found a multiplicative relationship given by:

$$G = G_o(1 + \Phi(c, T)) \approx G_o \Phi(c, T)$$

Here, $\Phi(c, T)$ was a function of temperature and rate-dependent viscoelasticity. From this equation greater magnitudes of surface energy lead to much larger increases in fracture energy because of how it creates a multiplying effect on the bulk energy dissipation processes during fracture.

The Adsorption theory and its use of the contact angle test is a convenient method to quickly determine whether a surface will possess good specific adhesion properties. However, it is limited in practical application to extremely smooth surfaces. This is because when a drop of liquid is placed on a rough and porous surface, air is caught between the surface asperities, restricting the liquid from wetting out. Thus, giving a false hydrophobic measure.

2.1.3 Surface roughness – can it be measured and is it useful?

Surface energy equations are often discussed in terms of energies per area. Normally, when area is imagined, it is imagined as a “perfectly” flat surface. When this is the case, defining interfacial area is simple. However, in reality even the smoothest of surfaces are to a degree rough. Pizzi and Mittal (2003) further comment that many people try to categorize the degree of roughness with geometric factors, others with qualitative values. However, the grading of a surface will change depending on the size of the probe or tile used. Consequently, Pizzi and Mittal (2003) prefer to avoid the use of surface area and instead say “the production of a rough

surface per se increases surface energy, and from this, work of adhesion and fracture energy of the joint". The simple "bond breaking" concept highlights this effect. For a rough surface, more bonds would have to be broken between the molecules of a solid than would need to be broken to produce a smooth surface. Hence, the intrinsic energy of the rough surface is higher.

Further difficulties occur when trying to empirically define a "surface area" as many engineering surfaces are now described as fractal in nature (Pizzi & Mittal, 2003). For fractals, the area depends on the size of the "tile" used to measure it, and the nature of the surface is described by a fractal dimension instead of peak size alone. For fractals, the surface area tends to infinity as the tile size tends to zero. Again, defining the surface area with a fractal dimension is arbitrary as the dimension only represents a unitless measurement of surface complexity. Hence, the fractal dimension is only useful for comparing the complexity of one surface from another, not for defining the actual surface area. For its effect on surface energies it's still best to view surface roughness as increasing the surface energy (per nominal area) but avoiding the desire to quantify accurately the actual change the roughness has on the total surface area.

2.1.4 Summary of the discussed mechanisms for adhesion and their limitations

Although the above theories give a framework with which to view the possible ways the phenomenon of adhesive bonding may work, they are ultimately impractical at giving strength predictions for untested material combinations. For example, the mechanical interlocking theory has experimentally shown that surface roughness and porosity increase mechanical adhesion for specific surface/material combinations. However, no model exists to allow a prediction of bond performance for all surface/material combinations using non-experimental methods.

In the same way, some experiments showed that some smooth surfaces were stronger than their rough equivalent, with the cause linked to greater specific adhesion. Unfortunately, no model exists that, without experimental data, could explicitly present which material combinations would result in this higher specific adhesion.

Finally, even with the thermodynamic theory, although an experimental relationship is found between the surface free energies and the bonding strength, the surface free energy must be measured from a perfectly smooth surface. Also, the surface free energies are still in most cases magnitudes smaller than the final fracture energy. To complicate matters more, this theory describes the surface energy in terms of surface area, which as discussed is entirely dependent on the probe or tile size used to measure it. Changes to the way the surface area is affected by roughness can dramatically change the predicted fracture energy.

The way these theories must be looked at is, instead of being models for allowing the easy design of components; that they are starting points for investigating possible new

material/surface combinations. The theories postulate that certain characteristics should give stronger adhesively bonded joints, but it is still paramount that every joint be tested in its use condition to ensure adequacy.

As stated in the introduction by Baldan (2012) almost all adhesive research areas aim for the same two basic outcomes. The first aim is to understand and classify the mechanical properties of a specific adhesive joint. The second is to allow predictions about the long-term durability of that joint. This thesis sets out to investigate exactly this, namely to classify the mechanical properties of an epoxy adhesive joint made between EBM printed Grade 5 titanium parts, and to use these properties to allow predictions towards future joint performance.

2.2 What is selective electron beam melting SEBM?

Additive manufacturing (AM) is defined as a process of joining materials (with the help of an energy source such as heat, or ultraviolet light) to form a desired object. The formed object is generated via computer instructions rendered from 3D model data. Parts made from additive manufacturing are usually made up layer by layer. It is commonly referred to as 3d printing and Freeform Fabrication (David L. Bourell, Joseph J. Beaman & Ming C. Leu, 2009).

Selective electron beam melting (SEBM or EBM for short) is an additive manufacturing process from the powder bed fusion (PBF) family, which utilises an electron beam as the thermal energy source, see Figure 12.

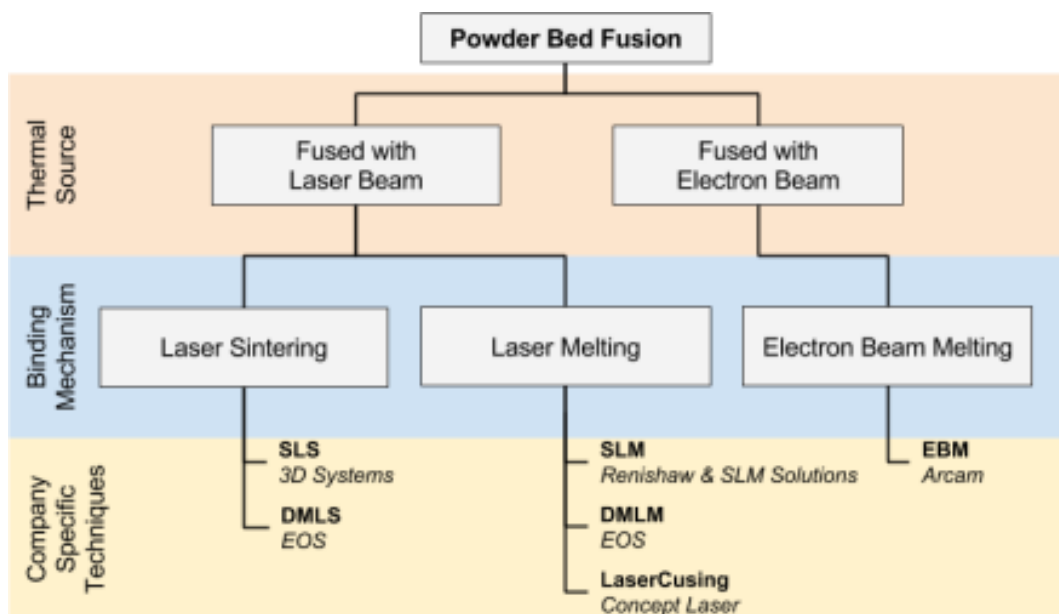


Figure 12: PBF technologies (Wahlström & Gabrielsson, 2017)

The first EBM PBF process was developed at Chalmers University of Technology in Sweden, and commercialized by the Swedish company Arcam AB in 2001 (Wahlström & Gabrielsson, 2017). The machines used for this research were the Arcam Q10 plus and Q20 plus, operated by Zenith Tecnica LTD. The only major difference between these two machines is the chamber size. The schematic of the basic Arcam machine can be seen below in Figure 13.

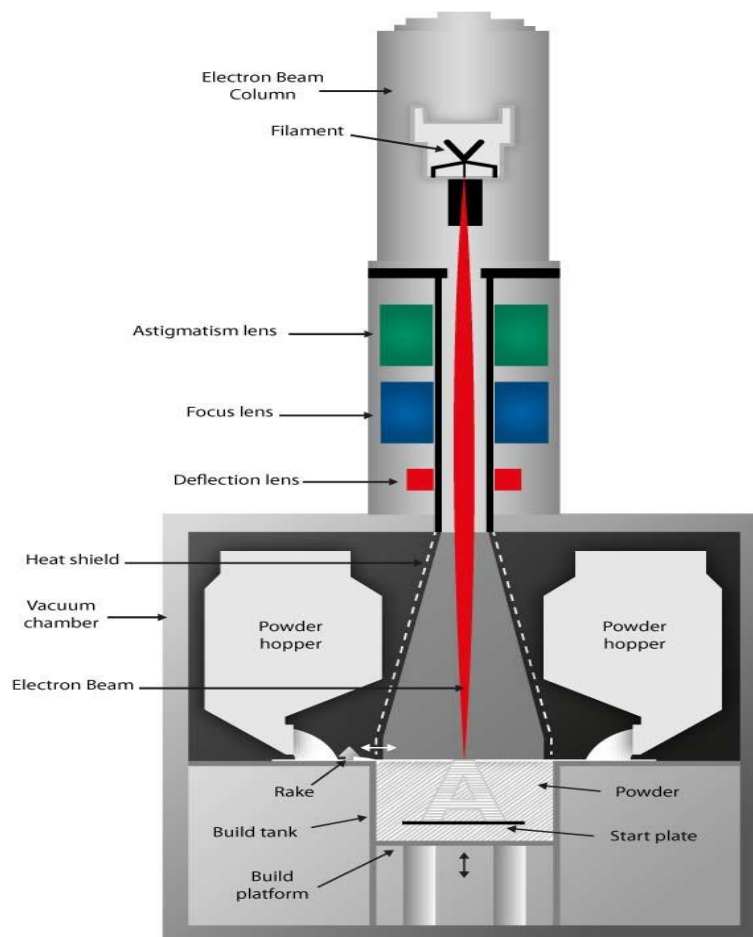


Figure 13: Arcam machine schematic (Arcam AB, 2019b)

Arcam AB (2019b) explain that their PBF process starts by converting a 3D computer model, such as an STL file, into a slice layer file called an abf (Arcam Build File). This is then inserted and read by the machine software. The build then starts by using a *plate heating pre-heat theme* to heat the start-plate. This heating removes any contamination from the start-plate and ensures the first layer of powder and the subsequent part is firmly adhered to the start-plate. Next, fine metal powder (45-100 microns) is gravity-fed from the powder hoppers to the rake arm, which spreads and deposits a thin layer of the metal powder onto the preheated start plate. The thin layer is then selectively melted using an electron beam in specific regions that match the slice file. The beam is controlled by electromagnetic lenses which makes the process accurate and fast.

Three electromagnetic lenses are used in the Arcam machines, see Figure 14. The first being a stigmator to fix the astigmatism (asymmetrical focal point). The second, a focus lens for focusing the beam to a point. And finally, a deflection coil which controls where the beam is directed and how fast it travels (Arcam AB, 2019b).

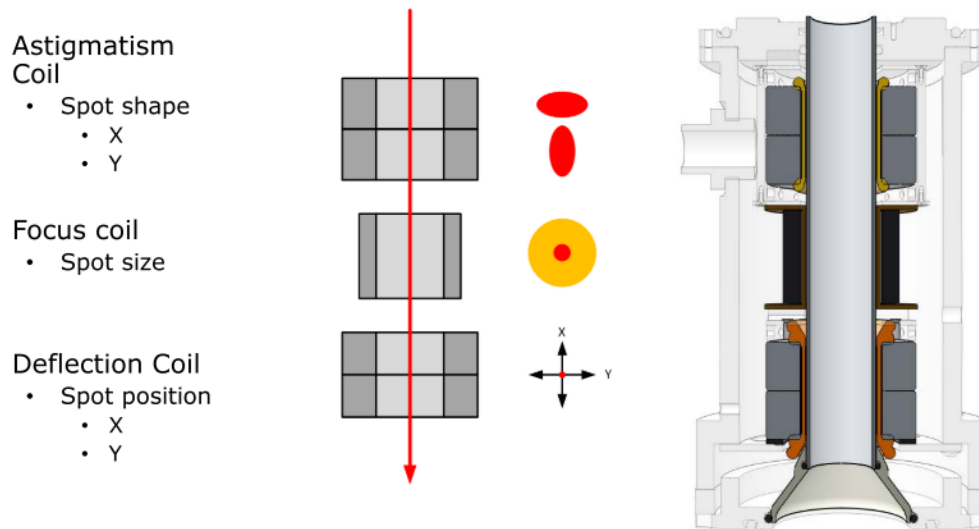


Figure 14: The three electromagnetic lenses of the Arcam machine (Arcam AB, 2019b)

Hernández-Nava (2016) explains that melting in the Arcam system takes place in three steps: *pre-heat*, *contouring*, and *hatching*, as shown in Figure 15. Further, he mentions that the energy input per layer is always kept the same, meaning in build layers with low cross-sectional area, a longer pre-heat is used to ensure the energy input is the same. This is to ensure the thermal distribution is as even as possible.



Figure 15: Left to right respectively – Pre-heat, contouring and melting (Hernández-Nava, 2016)

The melting process begins with every layer having two *pre-heat* processes; *pre-heat I* and *pre-heat II*. These processes are used to increase and maintain the chamber temperature, with the pre-heating for titanium reaching around 700°C. This increased temperature reduces both the duration of the melting step and the cooling rate, which then reduces the thermal residual stresses and the formation of non-equilibrium microstructures (such as a martensitic phase). It

also increases the thermal conductivity of the powder, allowing heat to be withdrawn from the part, reducing hot spots which can cause swelling defects. The *pre-heat* also loosely sinters the powder, allowing electrons to flow to ground easier, reducing charge accumulation (Cordero, Meyer, Nandwana, & Dehoff, 2017).

Pre-heat I increases the temperature across all the powder particles using a higher scanning speed with defocused electrons (large focal spot and low beam current). After *pre-heat I*, *pre-heat II* is applied which heats the actual area to become the part at a certain offset of the STL contours. This ensures the part retains the heat and is hotter than the powder surrounding the part. After *pre-heating*, melting of the part layers is then carried out using two melt processes called *contouring* and *hatching*. For *contouring*, only the outer boundary of the part is melted. This is done to accurately constrain the dimensions of a part and to improve the surface roughness. It achieves this by normally setting the beam current lower and melting in *multibeam mode*. In this mode the beam is moving at such high speeds that it can maintain a certain number of spots or molten pools at the same time (refer back to Figure 15b). The final stage *hatching* is, in contrast, carried out using *single beam mode*. *Hatching* melts the powder within the contour using a higher beam current and a hatching pattern with a defined hatch spacing. Once the layer is fully melted, the build table then drops, and another layer of powder is deposited, which is then selectively melted. This process then repeats until the object is fully printed. For both the *pre-heat* and *melt* processes, their parameters can be adjusted by controlling the parent *themes*. Table 2 shows the principal areas for theme development. Adjustable parameters include the beam current, scan speed, and hatch spacing (spacing between beam vectors). More parameters are shown in Table 3, which was given by Hernández-Nava (2016).

For the Arcam Q plus systems, the smallest z-axis increment is currently 50 microns (0.05mm), this being a restriction due to the powder size being used. The powder size has a minimum restriction of 45 microns for two reasons: first, below this size the powder begins to agglomerate, which can impede flow behaviour (Sutton, Kriewall, Leu, & Newkirk, 2016); Secondly, it reduces the electron beam from over-charging the powder, which otherwise would cause material sputtering and arc trips which are commonly named *smokes*. *Smokes* occur because the particles become charged with excess electrons and begin to repel one another. If this charge exceeds the force of gravity then the particles can be driven out of the build envelope. Cordero et al. (2017) demonstrated this by showing that a particle's radius disproportionately increases the gravitational force exerted by the particle, and this occurs at a greater rate than the electrostatic force generated by the beam. Meaning that for larger particles, it requires a disproportionately greater amount of charge per weight to smoke. Hence, larger particles resist smoking more so than smaller particles. Finally, as shown by the MSDS sheet AP&C (2016) smaller particles below 45 microns also become a fire and health hazard.

As stated by Arcam AB (2019a) the electrons in the Arcam Q10 and Q20 are currently generated using a 3000 watt Lanthanum hexaboride crystal, which is used due to the crystal's high electron emissivity. As the system utilises electrons, the process must be carried out at a base vacuum pressure of 5×10^{-5} mbar throughout the build process. This keeps the beam from encountering any interference which would interfere with the build, and reduces the chance of oxidation occurring. During the storage processes a partial pressure of helium is held at 4×10^{-3} mbar, to ensure a clean and controlled build environment, it also ensures the powder does not oxidise or hydrate. Helium is also used during the build to control the build pressure and to reduce powder charging.

The minimum beam diameter is 140 microns (0.14mm) and the minimum beam melt pool size achievable with the Q10 and Q20 plus machines is 300 microns (0.3mm). This is the best resolution achievable for meshes and requires the *point-net theme*. The EBM process results in near-full density parts and is considered a full melting process (Arcam AB, 2019; Sing, An, Yeong, & Wiria, 2016). Once the build is completed the parts or part remain inside a cake of semi-solid sintered powder. A compressed air Powder Recovery System (PRS) is used to remove the parts from the cake by blasting it with titanium powder. All powder is then sieved and recycled.

2.2.1 EBM themes – collection of parameters

As part of the EBM setup, operators can assign *themes* which are a collection of build parameters controlling the machine. *Themes* can be applied individually to different parts of the same build, which allows the easy comparison of the effect build parameters have on a part. The main principal heating areas where themes are applied are shown in Table 2, with the main adjustable parameters being given by Table 3.

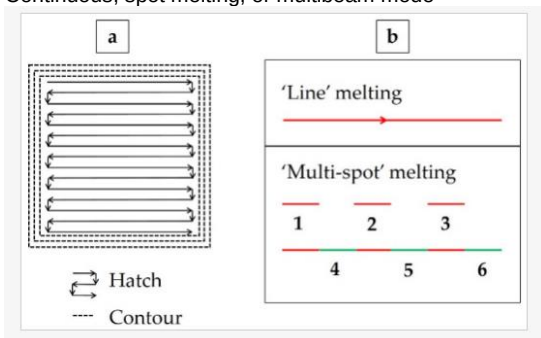
Table 2: Principal areas for theme development (Hernández-Nava, 2016)

Plate heating	Pre-heat	Melting
Constant	Pre-heat I Pre-heat II	Solid – Melt theme Net structures – Net and point-net themes Wafer and support structures – wafer and net themes

Suard (2015) explains that for small sections (less than 1mm diameter struts) the *net theme* is used, which is similar to the standard *melt theme*, consisting of a contouring and hatching sequence. However, the *net theme* has a different contour offset heating area and the beam current and focus are different. For randomly structured meshes such as medical trabecular mesh, the *point-net theme* is used. Here, the 3D model is broken down into a wireframe and everything is interpreted as points. The beam focuses and melts only these generated points, using two settings - spot time and current. This allows for a very small strut size (0.3mm). *Point-net* also reduces the computational memory required for the build. Unfortunately, *point-net*

requires a trade-off between resolution and structural rigidity (Hernández-Nava, 2016). The final theme is the *wafer theme*, which is used to melt supports. This is a partial melt only process, so that supports can be easily removed (Hernández-Nava, 2016).

Table 3: EBM main parameters and definitions (Hernández-Nava, 2016)

Parameters	Description
Scan strategy	Continuous, spot melting, or multibeam mode  Figure 16: melting strategy (Balachandramurthi, Moverare, Mahade, & Pederson, 2018)
Layer thickness	Amount the build tables z-axis drops every layer
Beam current	The beam energy component measured in (mA).
Beam speed	The electron beam speed in mm/sec.
Focus offset	The focal change above or below the intended surface. Can concentrate or diffuse the beam by adjusting the current above or below a baseline current.
Line offset (hatch spacing)	The distance between parallel beam pathways during melting
Line order	The defined order at which the scan lines travel on the melting plane; "1234" indicates an order of 1, "1324" an order of 2, etc.
Offset to contour	Moves the beam to an inside offset of the CAD models contour to account for possible oversized areas. (Normally set close to the weld track width and used in small sections of a part).
Block offset	If applied, prevents sections less than two times the offset to contour from disappearing by driving the beam through the guidance of four spots placed on the starting beam point from the offset to contour.
Contour length	The distance between two points of the four spots formed when block offset is applied.
Contour overlap	The distance the beam is permitted to move times the smallest contour length.
Thickness function	The variation in speed due to changes in angle deposition.
Turning points	The function compensation of beam speed when changes in melting direction take place.

Themes and their respective parameters dictate the final product and can be adjusted to change characteristics such as surface roughness, part tolerance, porosity, defects, swelling, etc. For this thesis, the effect theme parameters have on surface roughness and surface morphology were the main outcomes of interest.

2.2.2 EBM surface roughness

As described by Safdar, He, Wei, Snis, and Chavez De Paz (2012) every EBM sample has visible surface roughness because the process leaves behind a sintered layer of powder on the vertical build direction surfaces, S-II as shown in Figure 17. These types of surfaces are inherent in any additive machine where powder particles overlap with the beam path and the resulting melt pool.

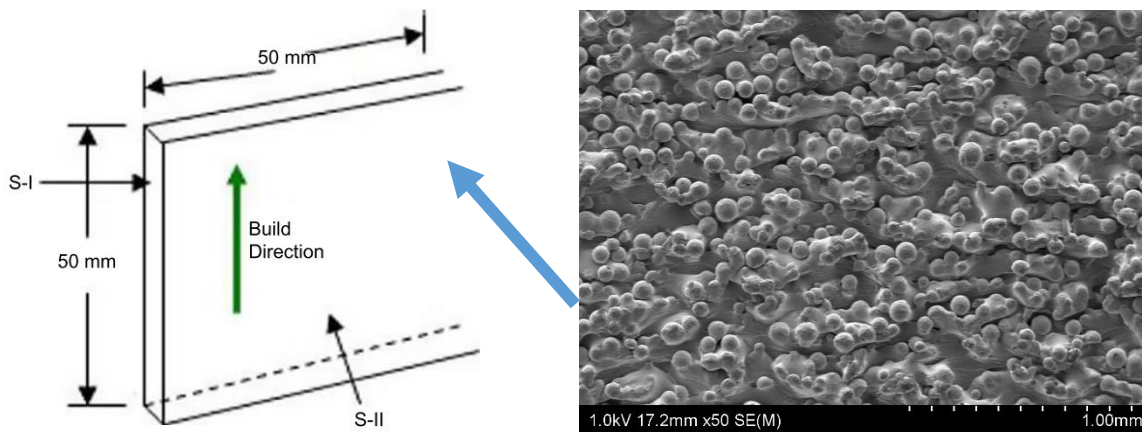


Figure 17: Left – schematic representation of test slab (Safdar et al., 2012); Right – SEM image of S-II surface, which was produced for the present thesis

The surface roughness Ra values for these vertical surfaces can vary from 10-20 μm depending upon the process parameter settings and the thickness of the sample. From the results of Safdar et al. (2012) process parameters which increased the surface roughness included: large powder size, greater build height increments, and higher beam current. Parameters that reduced the surface roughness included: an increased focus offset and scan speed.

The nomenclature given to describe a part's orientation in PBF is dependent on whether the bulk of the material, or feature, is positioned vertically or horizontally (Safdar et al., 2012). The horizontal plane is defined as being perpendicular to gravity, and the vertical plane being parallel to gravity.

2.3 The structure and properties of titanium and its alloys

First discovered in Cornwall, Great Britain by William Gregor in 1791, titanium was named by Martin Heinrich Klaproth after the Titans of Greek mythology. The Titans were hated by their father and exiled into captivity deep within the Earth's crust. So although being the ninth most abundant element, like the Titans, titanium is locked within its earthly mineral forms, requiring large amounts of energy to separate it from its chemical bonds, see embodied energies in Figure 18. The common mineral forms are (TiO₂), ilmenite (FeTiO₃), sphene (CaTiSiO₅) and titanomagnetite (Fe²⁺ (Fe³⁺, Ti)₂O₄ - common to New Zealand) (Leyens & Peters, 2003).

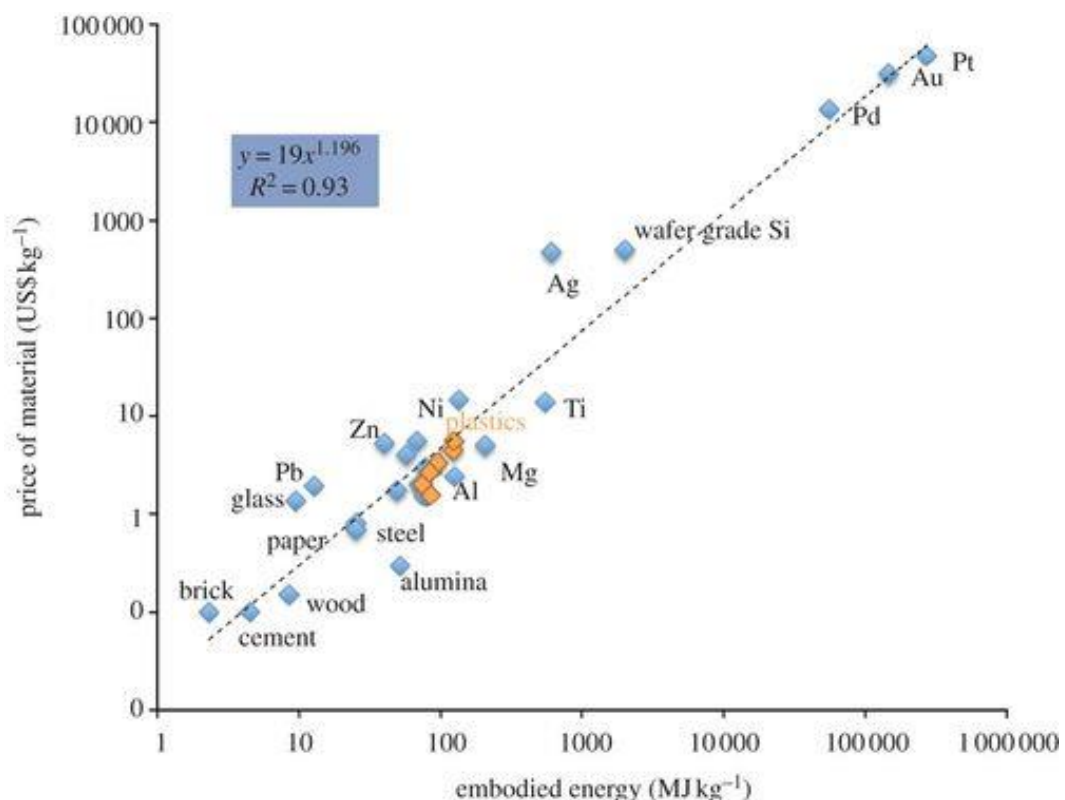


Figure 18: Price of material vs embodied energy of common materials (Gutowski, Sahni, Allwood, Ashby, & Worrell, 2013)

As explained by Leyens and Peters (2003) titanium is a transition metal of symbol Ti and atomic number 22, which is classified as a nonferrous and light metal. It is known for its high strength-to-weight ratio and resistance to corrosion. The most popular of the titanium alloys is Grade 5 titanium (Ti-6Al-4V), which stands out due to its high specific strength (see Figure 19) and excellent corrosion resistance. This is the core reason titanium is used in the medical and aerospace industries and why it continues to expand its use into other markets such as architecture, chemical processing, power generation, marine and offshore, sports and leisure, and transportation (Leyens & Peters, 2003).

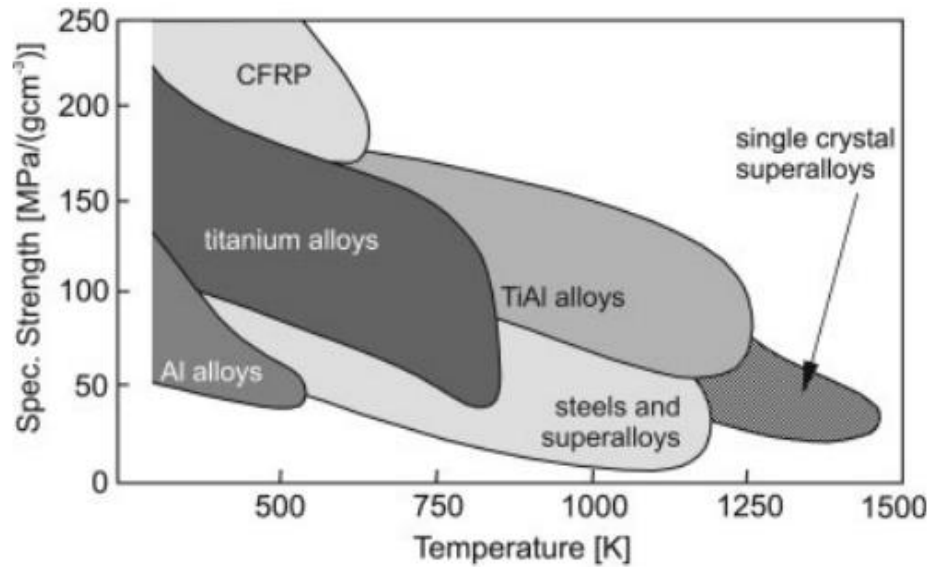


Figure 19: Specific strength versus use temperature for specific materials (Leyens & Peters, 2003)

2.3.1 The crystal structure of titanium

Leyens and Peters (2003) state that depending on the temperature, pure titanium exists in one of two crystal configurations: hexagonal close packed (HCP) which is denoted as an α -phase; and body centred cubic (BCC) which is referred to as a β -phase, see Figure 20.

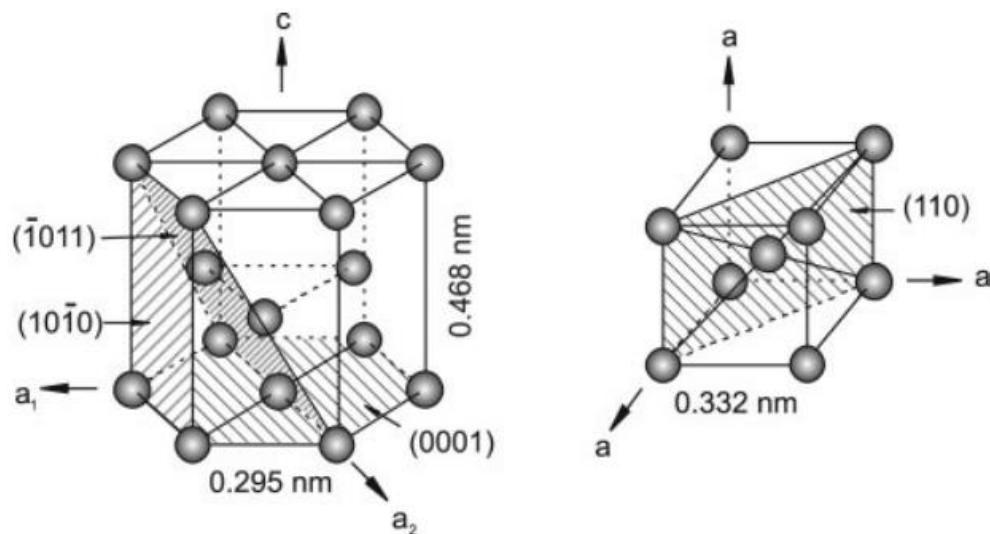


Figure 20: Crystal structure of HCP α and BCC β (Leyens & Peters, 2003)

The allotropic transformation from α to β occurs at $\sim 882^\circ\text{C}$ for pure titanium. The large variety of properties exhibited by titanium is largely due to the existence of these two different crystal structures and this allotropic transition temperature. For example, the resistance to plastic deformation for metals, normally increases from face-centered cubic (FCC), to body-centered cubic (BCC), to hexagonal close-packed (HCP), especially in the presence of impurities (Leyens

& Peters, 2003). Hence, this explains why HCP α titanium when exposed to high impurities has a limited plastic deformability when compared to BCC β titanium.

Generally, the number of slip systems (or dislocation opportunities) in the crystal lattice, dictates the plastic deformation. The number of slip systems can be found by multiplying the number of slip planes by the number of slip directions. For titanium there are 3 slip systems for the HCP lattice, while there are 12 for the BCC lattice. Slips occur on close-packed planes (planes where there are the greatest number of atoms per area) and in closed-packed directions (most atoms per length or most interplanar spacing). Hence, dislocations glide easier on densely packed slip planes (Leyens & Peters, 2003).

The packing density for HCP is greater than BCC being 74% compared to 68% making it appear that deformation would be easier. However, the energy needed for plastic deformation is also a product of the minimal slip path length. For BCC the minimum slip path length is $b_{min} = 0.87 \cdot a$ (0.289), while for HCP the $b_{min} = 1 \cdot a$ (0.295). Here a denotes the lattice parameter of the respective unit cell length. For HCP $a = 0.295$ nm and $c = 0.468$ nm and for BCC β titanium at 900°C $a = 0.332$ nm, see Figure 20 and Table 4. Due to this, plastic deformation is favoured in the minimal slip path length of BCC. However, as discussed by Leyens & Peters (2003) impurities such as oxygen or nitrogen can, due to the limited slip planes in HCP, shift the dislocation movement from the easy basal plane to the difficult prism or pyramidal planes, increasing resistance to plastic deformation and reducing mechanical properties such as ductility. This can be seen with high purity titanium (99.98%) having an elongation of 50%, with the elongation reducing to 20% for Grade 1 (0.18% O) and 15% for Grade 4 (0.4% O). BCC structures are more resistant to impurities as they have six slip planes (Leyens & Peters, 2003).

Table 4: Characteristic parameters of metallic structure types (Leyens & Peters, 2003)

Structure type	N	CN	P	Slip planes Slip directions		Slip system per unit cell	Atom den- sity of slip plane	b_{min}/a
				indices	numbers			
hcp ($c/a=1.633$)	6	12	74%	{0001} <1120>	1 3	$1 \times 3 = 3$	$\approx 91\%$	1
bcc	2	8	68%	{110} <111>	6 2	$6 \times 2 = 12$	$\approx 83\%$	$1/2 \sqrt{3}$ ≈ 0.87
fcc	4	12	74%	{111} <110>	4 3	$4 \times 3 = 12$	$\approx 91\%$	$1/2 \sqrt{2}$ ≈ 0.71

N	Number of atoms per unit cell
CN	Coordination number
P	Packing density
b_{min}/a	Minimal slip component

2.3.2 Alloys of titanium

When alloying elements are dissolved in titanium they act on the phases in four specific ways, which are illustrated in the phase diagrams shown in Figure 21.

1. Are neutral on the α - β transition temperature
2. Stabilize the α -phase by raising the α - β transition temperature
3. Stabilize the β -phase by lowering the α - β transition temperature
4. Act only as solid solution strengtheners without affecting the transition temperature

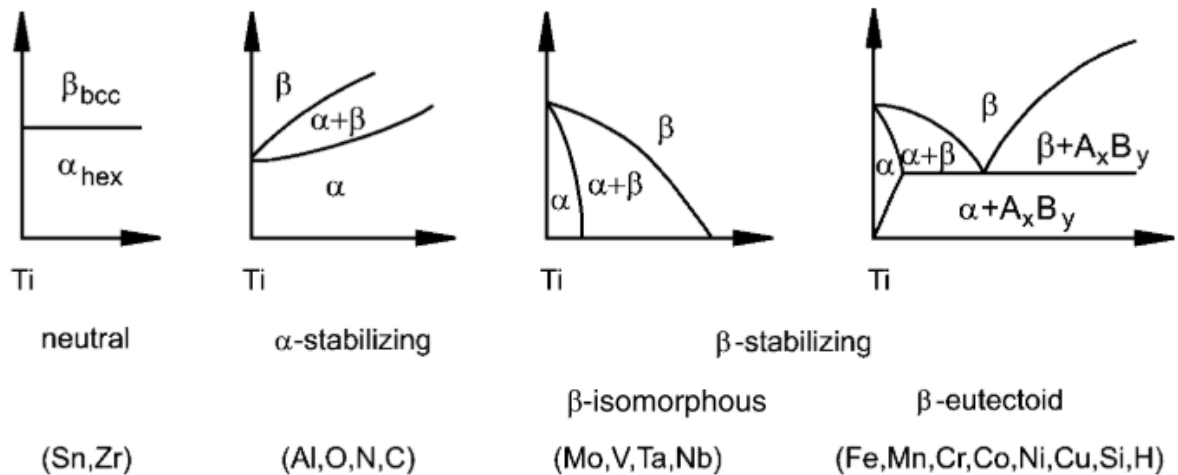


Figure 21: Generalised temperature vs composition phase diagrams showing the effect of alloying elements in titanium (Leyens & Peters, 2003)

Titanium materials are divided into three major groups, which are named after the dominant phase which exists at ambient temperature: these being α alloys, $\alpha+\beta$ alloys and β alloys. As shown in Figure 22, these phases are dependent on the type and number of alloying elements and their effect on the β -transus temperature. β -stabilizing elements are subdivided into two categories. β -isomorphous elements which have a higher solubility in titanium, which act to lower the β -transus temperature, and β -eutectoid elements, which even at very low fractions can lead to the formation of intermetallic compounds. An example of this is in the presence of iron, the formation of the intermetallic compound Fe_2Ti . Figure 22 shows how β -stabilizing alloys are further subdivided into near- α and metastable- β alloys depending on the alloying concentrations.

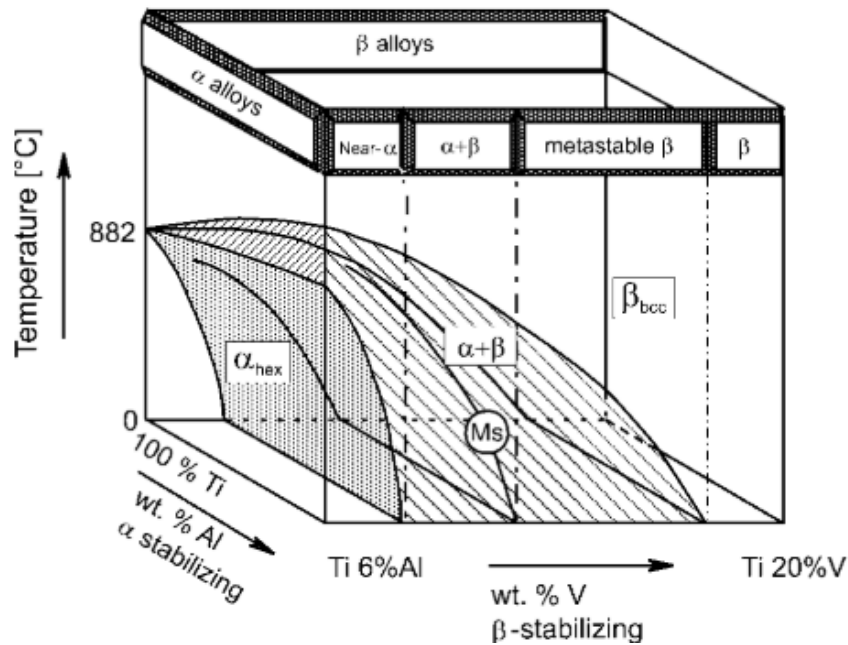


Figure 22: Generalised three-dimensional phase diagram to classify Ti alloys (Leyens & Peters, 2003)

2.3.3 The microstructure of Grade 5 Ti-6Al-4V titanium alloys

As stated by Leyens and Peters (2003) the microstructure dictates many of the properties of a titanium alloy. The primary characteristics describing the microstructure of the α - β alloy Ti-6Al-4V is the size, arrangement, and volume composition of the two α and β phases at the design temperature. For Ti-6Al-4V two qualitative microstructures are present. These are the lamellar microstructure, which forms upon slow cooling from above the β -transus temperature, or the equiaxed microstructure, which results due to either a cold-working and recrystallization process or very fast cooling with specific impurities to drive multiple nucleation points. Both lamellar and equiaxed microstructures can be present as fine or coarse grains - fine from fast cooling and coarse from slow cooling. Table 5 gives some general relationships between the qualitative size and arrangements of grains and the resulting effect on some important mechanical properties.

Table 5: Influence of microstructure on selected mechanical properties of titanium (Leyens & Peters, 2003)

<i>fine</i>	<i>coarse</i>	<i>Property</i>	<i>lamellar</i>	<i>equiaxed</i>
○	○	Elastic modulus	○	+/- (texture)
+	-	Strength	-	+
+	-	Ductility	-	+
-	+	Fracture toughness	+	-
+	-	Fatigue crack initiation	-	+
-	+	Fatigue crack propagation	+	-
-	+	Creep strength	+	-
+	-	Superplasticity	-	+
+	-	Oxidation behavior	+	-

The different microstructures possible can be formed through a variety of thermomechanical treatments as shown in Figure 23. For some applications a variety of these are carried out, which could include several of the following:

- A sequence of heat treatments
- The use of mechanical deforming techniques
- Aging with the correct impurities
- Annealing which removes the internal strains by recrystallizing the grains

These treatments each affect the microstructure and mechanical properties in specific ways, increasing the range of applications of the alloy.

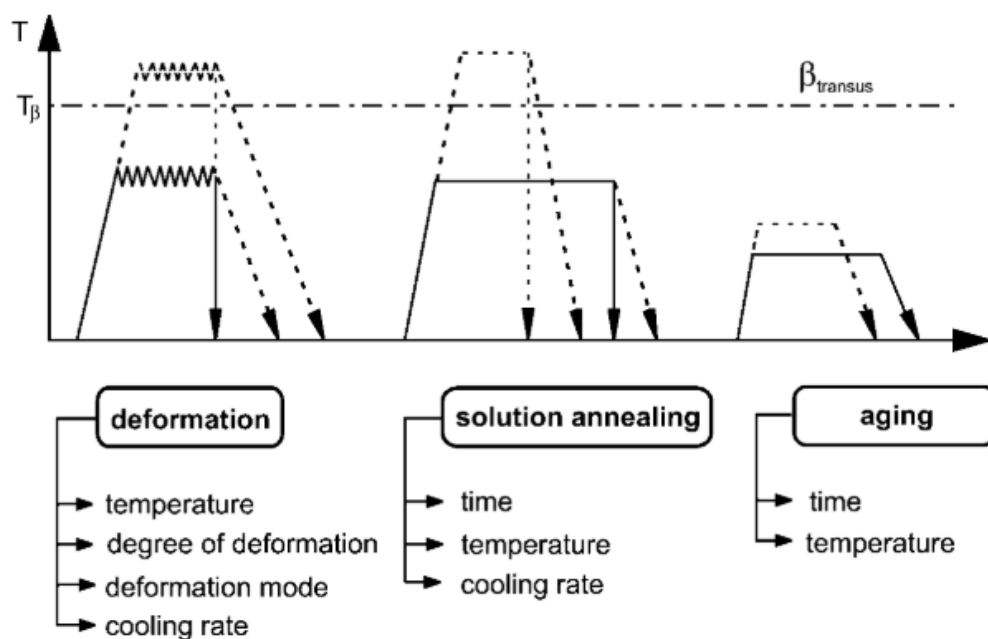


Figure 23: Thermomechanical treatment of titanium alloys (Leyens & Peters, 2003)

As shown in Figure 24, the formation of the lamellae structure begins as the temperature falls below the β -transus temperature. At this temperature traces of α -phase grains begin to nucleate at the grain boundaries of the β grains. As the temperature drops these nucleated grains then grow as lamellae into the prior β grain. Depending on the cooling rate, the lamellae are either fine (fast cooling: cooling rate > 100 °C/min) or coarse (slow cooling: cooling rate < 100 °C/min). An example of a well distributed lamellae structure is shown in Figure 24. Here, the β phase is very sparse and exists at the grain boundary of the coarse α -lamellae.

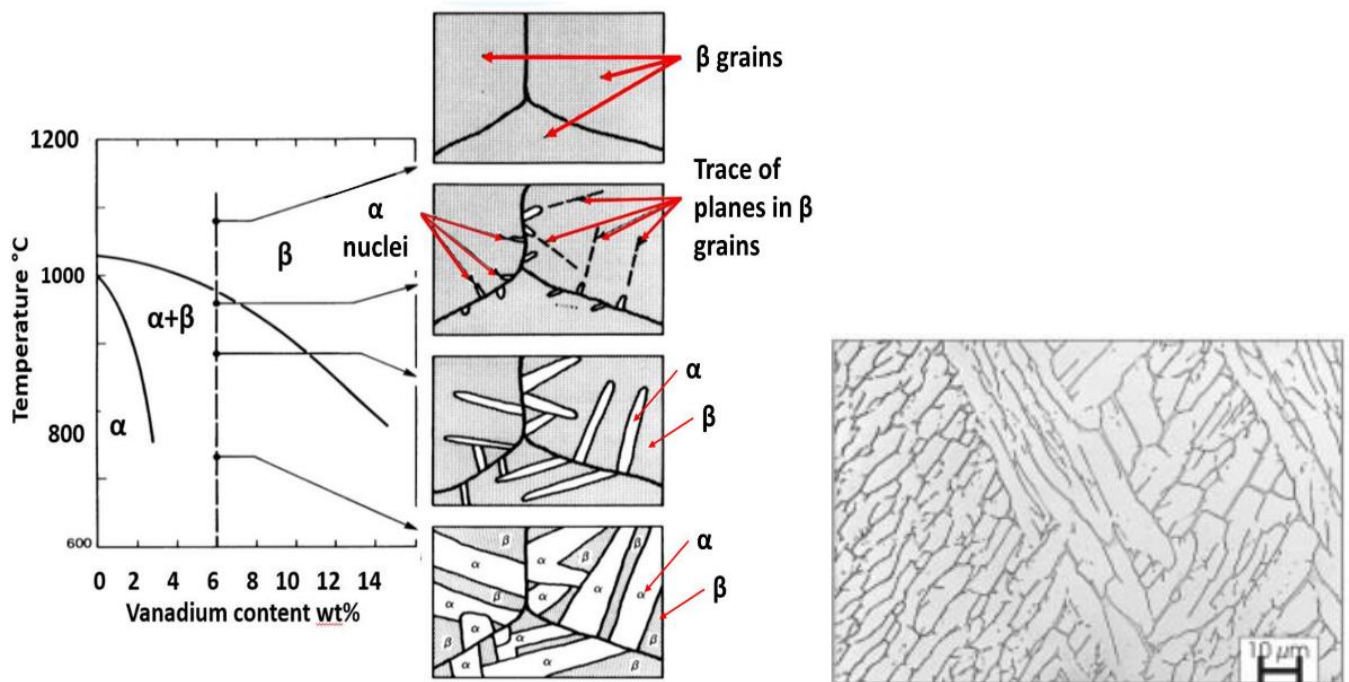


Figure 24: Left – Illustration of the transformation process from β phase to α - β phase for a Ti-6Al-4V alloy (Donachie, 2000); Right – Pure lamellar microstructure of Ti-6Al-4V caused by furnace cooling from 1050°C (Leyens & Peters, 2003)

At extremely slow cooling rates of less than 1 °C/s (60 °C/min) the crystal structure has time to diffuse atoms into configurations that minimise the total elastic strain. For this formation, some of the new α colonies, create further α nucleation points which grow almost perpendicularly from the existing α lamellae. The resulting structure is called the Widmanstatten structure or basket weave. This structure is the type that forms during EBM manufacturing and will be presented later in this thesis.

A non-equilibrium martensitic transformation of the β -phase into a martensitic α is also possible with rapid quenching (diffusion-less cooling: cooling rate > 1000 °C/min). This occurs because as the cooling rate increases, the α lamellae become thinner and thinner until a limit is reached. Here, the cooling BCC β phase can no longer diffuse atoms fast enough to form an HCP α phase, instead a martensitic α' results. This is a very fine needle-like microstructure, see Figure 25. Here, unlike with steel, the martensitic phase of titanium does not induce a large distortion of the crystal lattice and hence the hardening and strength increase is only moderate.

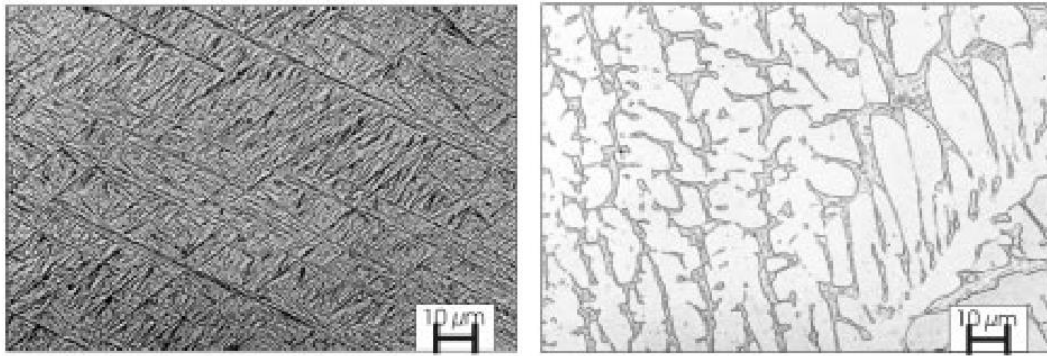


Figure 25: Different martensite microstructures of Ti-6Al-4V. Left: A martensite microstructure, formed from water quenching from 1050°C; Right: A martensite microstructure along the grain boundary (formed from the remaining β), formed from water quenching from 800°C (Leyens & Peters, 2003)

The martensitic structure can exist in two different forms, α' having a hexagonal structure and α'' having an orthorhombic structure (Liu, 2015). The type and amount formed are dependent on the chemical composition of the β -phase and temperature prior to quenching.

As stated previously, unlike the lamellar microstructures, equiaxed microstructures are the result of a recrystallization process. Therefore, the alloy must be cold-worked enough to highly strain the $\alpha+\beta$ grains, thus when the recrystallization temperature is reached these strains can induce the nucleation of new grains at the grain boundaries. This grain rearrangement occurs as the crystal rearranges its atoms to reduce its total elastic strain. Two examples of equiaxed structures are shown in Figure 26.

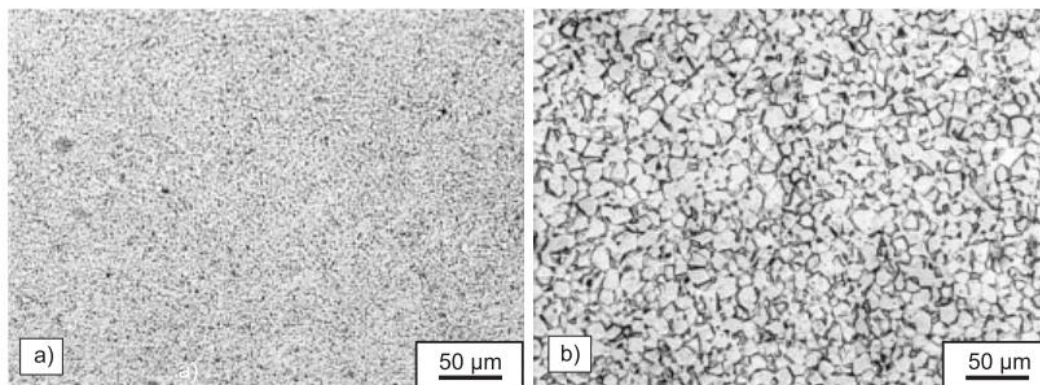


Figure 26: Equiaxed microstructures of Ti-6Al-4V via recrystallization: a) fine grains; b) coarse grains (Leyens & Peters, 2003)

Another microstructure which is achievable for titanium is the bimodal microstructure which can be considered a combination of both lamellar and equiaxed microstructures. The formation of a bimodal structure is the result of a careful cold-working and heat treatment procedure. An example of the bimodal microstructure is shown in Figure 27.

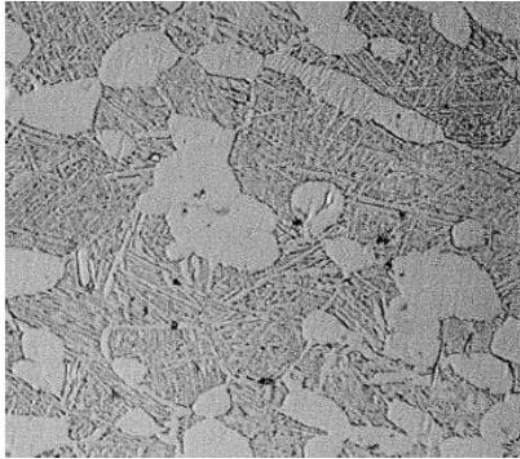


Figure 27: Bi-modal microstructure of Ti-6Al-4V consisting of α surrounded by transformed β (Liu, 2015)

The arrangement, volume fraction, and individual properties of the two phases α and β at design temperature determine the properties of the titanium alloy. This is primarily due to the crystal structure being HCP for α and BCC for β . Table 6 gives some general relationships between the phases and some select mechanical properties.

Table 6: Properties of α , $\alpha+\beta$, and β Ti alloys (Leyens & Peters, 2003)

	α	$\alpha+\beta$	β
Density	+	+	–
Strength	–	+	++
Ductility	–/+	+	+/-
Fracture toughness	+	–/+	+/-
Creep strength	+	+/-	–
Corrosion behavior	++	+	+/-
Oxidation behavior	++	+/-	–
Weldability	+	+/-	–
Cold formability	– –	–	–/+

As given by Leyens and Peters (2003) the α -phase is more densely packed when compared to β due to the HCP structure; it also has an anisotropic crystal structure. Compared with β , α is differentiated by the following properties:

- Impurities increase resistance to plastic deformation at a greater rate
- Impurities reduce ductility at a greater rate
- Anisotropic mechanical and physical properties
- A diffusion rate which is at least two orders of magnitude lower
- Higher creep resistance.

Aluminium is the most common α -stabilizing element with half the specific weight of titanium. α -alloys therefore have a lower density than β -alloys, especially seeing as the latter is often alloyed with heavy elements such as Mo or V (Leyens & Peters, 2003).

$\alpha+\beta$ alloys and β alloys exhibit higher strengths compared to single phased α alloys due to the ability to be hardened to very high strength levels. However, a trade-off is that ductility must be compromised, though this can be improved by reducing the grain size. *Leyens and Peters (2003)* further comment that coarse grains and the lamellar microstructures, when arranged in the correct orientation, demonstrate higher toughness values than fine and equiaxed ones. This is due to the ability of these structures to deflect propagating cracks along differently orientated grains. Further, it's stated that α generates a more stable oxide layer than β , due to the HCP lattice reducing the diffusion coefficient by a half of the value for β .

2.3.4 Microstructure and properties of EBM produced Grade 5 titanium alloy parts

As given by Arcam AB (2019c) who provide their Ti-6Al-4V powders through Advanced Powders and Coatings - A GE (General Electric) Additive company. The chemical specification of their Ti-6Al-4V powder is shown below in Figure 28.

	Arcam Ti6Al4V, Typical	Ti6Al4V, Required *	Ti6Al4V, Required **
Aluminium, Al	6%	5,5–6,75%	5,5–6,75%
Vanadium, V	4%	3,5–4,5%	3,5–4,5%
Carbon, C	0,03%	< 0,1%	< 0,08%
Iron, Fe	0,1%	< 0,3%	< 0,3%
Oxygen, O	0,15%	< 0,2%	< 0,2%
Nitrogen, N	0,01%	< 0,05%	< 0,05%
Hydrogen, H	0,003%	< 0,015%	< 0,015%
Titanium, Ti	Balance	Balance	Balance

*ASTM F1108 (cast material) **ASTM F1472 (wrought material)

Figure 28: Chemical specification of AP&C Ti-6Al-4V powders (Arcam AB, 2019c)

The mechanical properties given by Arcam AB (2019c) for their EBM produced samples built from this powder are given below in Figure 29. For the given data the samples were post processed under hot isostatic pressing (HIP), which was carried out at 920°C, under 100 MPa for 120 minutes.

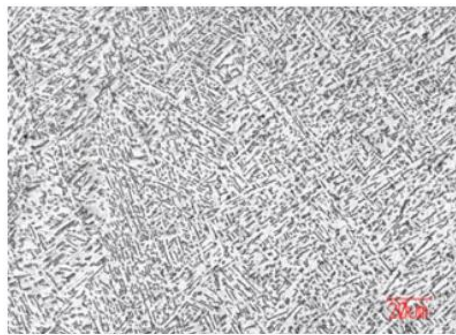
These properties are very favourable for a Ti-6Al-4V part and according to Arcam AB (2019c) are equivalent to wrought annealed parts. The microstructure is given below in Figure 30.

	Arcam Ti6Al4V, Typical	Ti6Al4V, Required**	Ti6Al4V, Required***
Yield Strength (Rp 0,2)	950 MPa	758 MPa	860 MPa
Ultimate Tensile Strength (Rm)	1020 MPa	860 MPa	930 MPa
Elongation	14%	> 8%	>10%
Reduction of Area	40%	>14%	>25%
Fatigue strength* @ 600 MPa	>10,000,000 cycles		
Rockwell Hardness	33 HRC		
Modulus of Elasticity	120 GPa		

*After Hot Isostatic Pressing **ASTM F1108 (cast material) ***ASTM F1472 (wrought material)

The mechanical properties of materials produced in the EBM process are comparable to wrought annealed materials and are better than cast materials.

Figure 29: Mechanical properties (Arcam AB, 2019c)



Micrograph of Arcam Ti6Al4V material, 500x.



Micrograph of Arcam Ti6Al4V material, 1000x.

Figure 30: Microstructure of Arcam Ti-6Al-4V at 500x and 1000x magnifications. Shows a Widmanstatten structure with fine α and β grains (Arcam AB, 2019c)

The microstructure given by Arcam AB (2019c) is a Widmanstatten structure containing lamellar α and β phases. The structure here is slightly different to the Widmanstatten structure produced by EBM that was given by Rafi, Karthik, Gong, Starr, & Stucker (2013) which is shown in Figure 31. Here, the alpha grains are slightly larger and more defined in packets, giving what would be expected of a basket weave structure. The difference in the Arcam AB (2019c) microstructure may be due to the images being taken post HIP, although this was not explicitly mentioned by their catalogue.

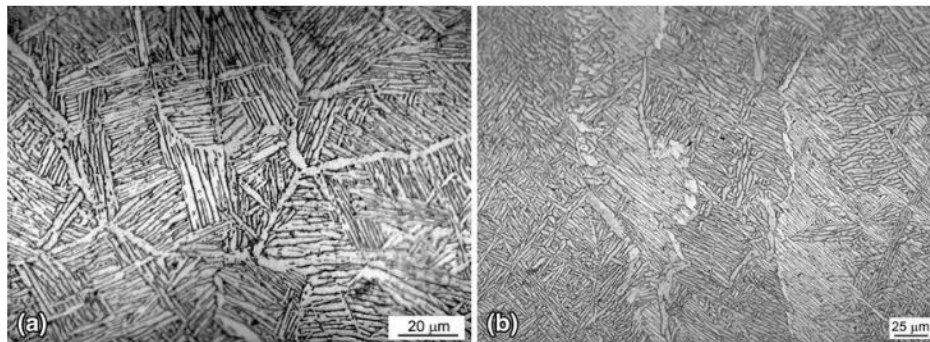


Figure 31: Optical micrograph of EBM produced Ti64 samples. (a) Transverse cross-section; (b) Longitudinal cross-section (Rafi et al., 2013)

For Rafi, et al. (2013) the microstructure is predominantly made up of a α -phase lamellae with the lamella boundary being surrounded by a small amount of β -phase. They stated the Widmanstatten structure was to be expected as the build chamber in their study was maintained at 650-700°C for the entire build and slowly cooled to room temperature at the end of the build. The α -phase lamellae would therefore have had the time to diffuse and form the perpendicular branches of the basket weave structure.

Although the microstructures are similar to the Arcam results, the studies by (Murr et al., 2009; Rafi et al., 2013; Rafi, Karthik, Starr, & Stucker, 2012) show significant differences in the mechanical properties, particularly the fatigue strength. This is most likely because the Arcam samples underwent a HIP treatment and may have been machined and polished, while the other studies were only machined or in an as-built condition. The values from these studies are given in Table 7 below.

Table 7: Mechanical properties of EBM build Grade 5 titanium parts from three different sources

	(Rafi et al., 2013) Vertically built and machined	(Rafi et al., 2013) Horizontally built and machined	(Rafi et al., 2012) As-built vertical	(Rafi et al., 2012) As-built horizontal	(Arcam AB, 2019c) After (HIP) process
Stress at yield (Offset 0.2%), MPa	869 (SD: 7.2)	899 (SD: 4.7)	782 (SD:5.1)	844 (SD:21.6)	950
Ultimate tensile stress, MPa	928 (SD: 9.8)	978 (SD: 3.2)	842 (SD:13.84)	917 (SD:30.53)	1020
Strain at break, %	9.9 (SD: 1.7)	9.5 (SD: 1.2)	9.9 (SD:1.02)	8.8 (SD:1.42)	14
Fatigue > 10⁷ cycles	340 MPa	300 MPa	100 MPa	200 MPa	~640 MPa

Examining the data from Table 7, both machining the surface of the samples, and the HIP process significantly improved fatigue strength. In addition, it appears from the Arcam promotional material that the HIP process improves other tensile properties. It is likely that the HIP process reduced the lack of fusion and void defects, which would act as stress raisers, reducing the ultimate tensile strength. Further, as shown in the data, elongation was improved, which most likely occurred due to the HIP process taking place around the recrystallisation temperature. Therefore, the grains would have become more distributed and homogenous. For the results given by Arcam AB (2019c) only the value of the data was presented, without any mention of the method used. Therefore, it must be treated with caution, with precedence given to the studies which presented their data with experimental evidence. The material properties data from Table 7 was later used for defining the titanium properties in the analytical simulation.

The Arcam fatigue data is given in Figure 32. Again, caution must be taken with this data as no mention was given of the samples' surface roughness or whether the samples were machined, or HIP treated. These two factors would justify the differences seen in Table 7 and why the Arcam fatigue strength values at 10^7 cycles were double the next second best.

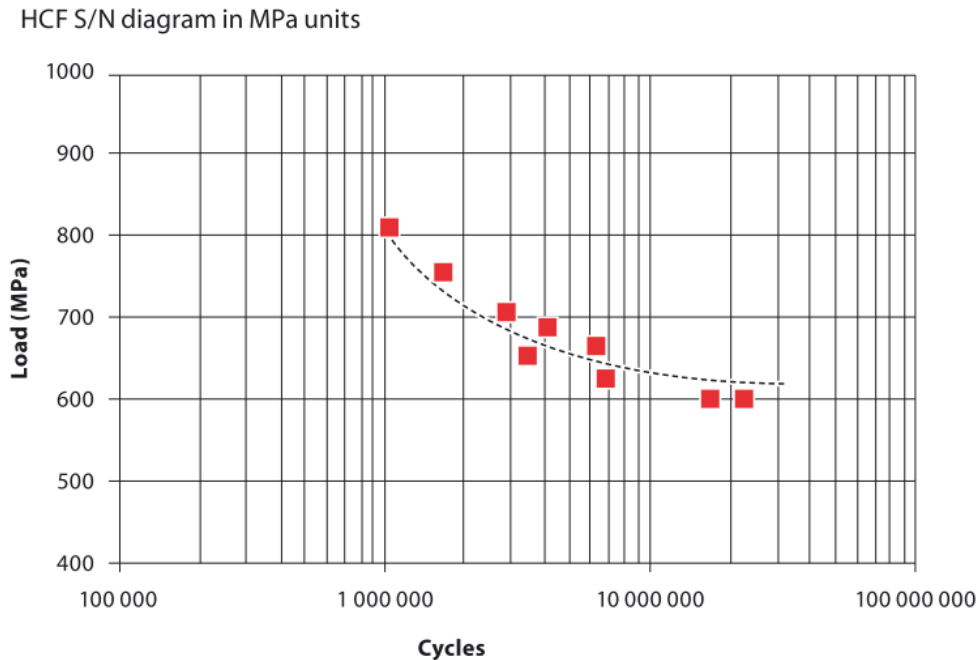


Figure 32: Arcam Ti-6Al-4V high cycle fatigue test

It is important to note that hardness depends on solidification rate, which is affected by part wall thickness or position in relation to the bulk of the material. Martinez et al. (2008) showed a hardness variation from HRC 37 to HRC 42 within a dimensional range of ~4 cm for EBM built samples. Interestingly, Hernández-Nava (2016) discussed that thinner parts should exhibit higher hardness and less elongation due to quick cooling rates. However, his experimental results showed a consistent Vickers micro-hardness of 3.5 GPa regardless of whether the test location was on a thin strut or in the bulk of the material.

2.4 Titanium oxides

As explained by Liu (2015) due to titanium being a transition metal, it can exist in many different oxidation states, and therefore titanium oxide can form in varying stoichiometries. These include: Ti_3O , Ti_2O , Ti_3O_2 , TiO , Ti_2O_3 , Ti_3O_5 and TiO_2 . The most stable is titanium IV dioxide TiO_2 (titania) due to titanium preferring the oxidation state of 4^+ . TiO_2 can exist in three different crystalline states, these being: rutile (tetragonal) which is thermodynamically stable; anatase (tetragonal) which is in a metastable phase; and brookite (orthorhombic) which is also in a metastable phase. The different crystal structures of titanium dioxide are shown in Figure 33.

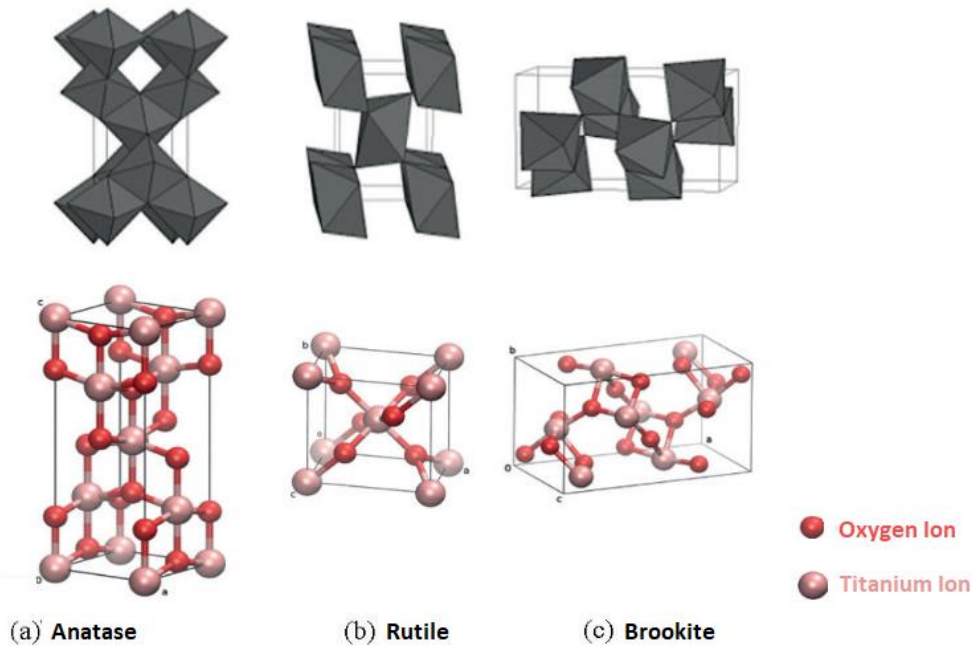


Figure 33: Crystal structure of TiO_2 (Scarpelli, Mastropietro, Poerio, & Godbert, 2018)

Liu (2015) states that the anatase structure can be obtained by anodic oxidation, and the rutile structure can be created by anodic oxidation followed by a thermal treatment. Further, he states that the oxide film is very resistant to breakdown and will only be compromised in highly reducing conditions, for example: strong reducing acids such as HCl, HBr, H_2SO_4 , H_3PO_4 , and in HF solutions at all concentrations (Markle, 2018) and reducing bases like NaOH. In addition, increasing the temperature also increases the reduction rate (Labak, 2010) as does the addition of hydrogen peroxide in some bases and acids (Nazarov, Zemtsova, Valiev, & Smirnov, 2016).

Titanium dioxide is a useful surface for improving adhesive bonding due to its non-continuous morphology of being porous and rough at the nano-scale, as well as being covalently bonded to the titanium substrate (Mertens et al., 2012).

2.5 Anodising of titanium

İzmir and Ercan (2018) and Liu (2015) both describe anodising as an electrolytic passivation process which produces or grows an oxide layer on the surface of a metal part. They explain that anodising is achieved by using a power source and an electrolyte cell to drive a redox reaction. The power source causes electrons to flow from the anode where oxidation takes place to the cathode where reduction takes place. The process is called anodising because the part to be treated forms the anode electrode of the electrolytic cell. This is shown in the illustrated visual aid given in Figure 34.

Anodising requires a fluid containing electrolytes to allow current to flow between the cathode and anode. To assist with oxidation, the electrolytes usually require the solution to contain oxygen-based anions. Common examples are: the hydroxide ion OH^- and oxyanions such as the sulphate ion SO_4^{2-} and the phosphate ion PO_4^{2-} . Deionised water is normally the basis for the electrolyte solution. However, there are exceptions, such as when only 1% water is used with the balance being glycerol (Valota et al., 2009). Strong acids such as HF or HCl, or a strong base like NaOH can also be added. These chemicals are used as etchants to reduce the oxide layer into having a more porous structure. These pores also allow current to continue flowing through the anode, enabling the production of a thicker and more porous oxide layer. Porous titanium oxide nanotubes were achieved in this way by Mahshid, Dolati, Ghahramaninezhad, Goodarzi and Askari (2010) by using a solution with fluorine ions to slowly consume the titanium oxide layer in specific areas.

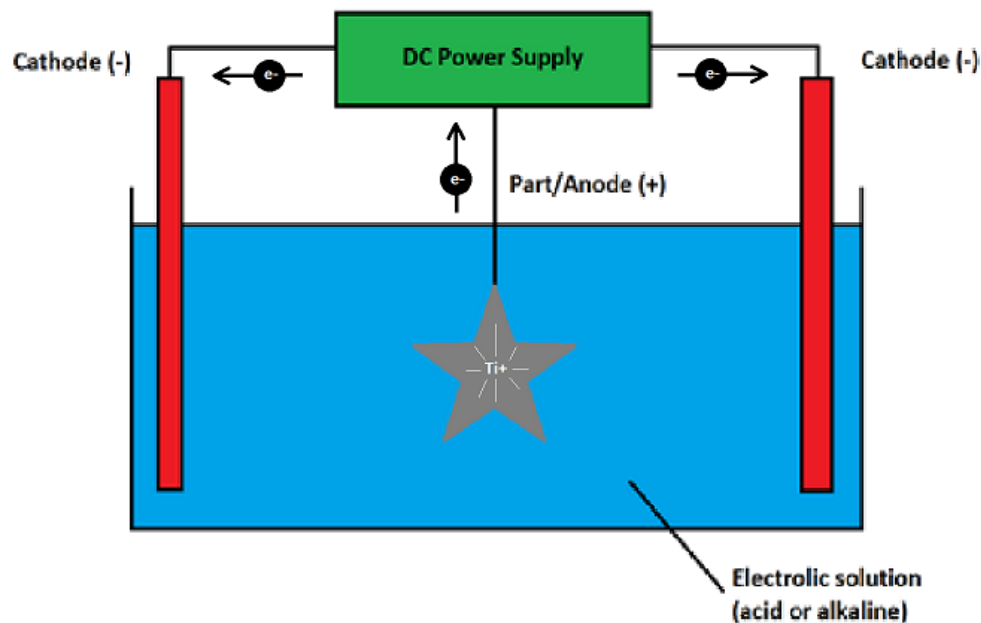
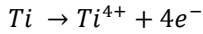
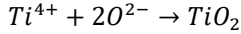
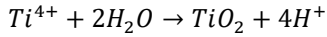


Figure 34: A basic anodising setup

Liu (2015) states that the anodising process starts by supplying power to the closed electrolytic cell circuit. This begins to withdraw electrons from the anode, producing positive titanium ions. These ions then get drawn towards the surface of the part in the direction of the cathode. Negatively charged oxygen anions then move towards the surface of the anode where an oxidation reaction takes place, forming the titanium oxide layer. İzmir and Ercan (2018) add that in some cases the water will split at the metal's surface providing oxygen ions for the oxidation to take place.

The mechanism used to explain the formation of the titanium oxide layer was given by İzmir and Ercan (2018) and Mahshid et al. (2010) and is shown below:

Titanium losing electrons due to the power source and electrolytic cell**Titanium IV reacting with oxygen to form titanium dioxide****Titanium IV reacting with water to form titanium dioxide**

As voltage drives the pull of electrons it also directly relates to the thickness that the anodic layer will grow. This is because the oxide layer acts as an insulator impeding current flow. Hence, a given voltage will result in a given oxide layer thickness (Liu, 2015). However, as stated above, by having reducing agents in the solution, the oxide layer will be etched in specific areas allowing current to continue flowing. A common example of this is NaOH alkaline anodising, which is known for producing thick oxide layers (Mertens et al., 2012).

Some common anodising methods used in adhesive bonding will be discussed in the next sub-chapter, after the importance of removing contamination from the surface is discussed.

2.6 Overview of adhesion techniques**2.6.1 Contaminants and failure types**

Baldan (2012) stated that mechanical and chemical bonding is only effective upon full wetting of the adhesive on the substrate. This is because as per Coulomb's law below, intimate contact (small R) increases the intermolecular forces causing attraction (E).

$$E = \frac{kQ_1Q_2}{R}$$

Therefore, one of the most important steps before any adhesive bonding is carried out is to ensure the substrate has been correctly degreased and had all contaminants removed. Every bonding article reviewed stated this as the essential step in creating a strong bond. Contaminants on the surface lower the surface energy and block any chemical interactions between the adhesive and the substrate, reducing wetting and thus reducing bond strength. The illustration shown in Figure 35 was produced to visually demonstrate how contamination leads to dewetting.

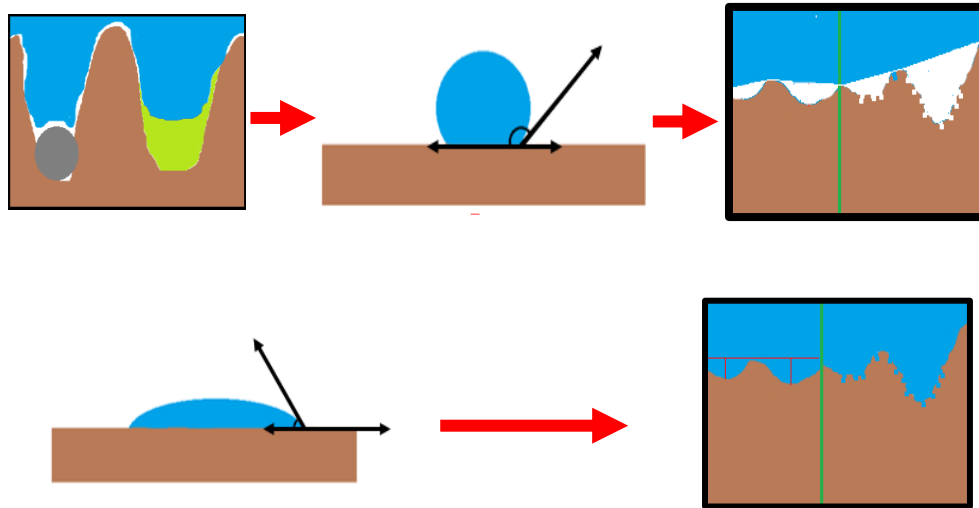


Figure 35: Top image – contaminants, grease and oils reducing the surface energy of a substrate causing incomplete wetting; Bottom image – a clean substrate with high surface energy producing good wetting

As explained by Davis & Bond (1999) the strength of an adhesive bond depends on either the cohesive strength of the adhesive, or the interfacial adhesion strength between the adhesive and the substrate. For a bond to be reliable, failure must occur through cohesive failure of the adhesive, as shown circled in Figure 36. This figure is an illustration that was produced to show the different failure modes visually. Cohesive failure can only be achieved by ensuring the adhesion between the adhesive and the substrate have maximised the properties of mechanical and specific adhesion. Thus, the interface is so strong that failure is forced to occur cohesively within the adhesive. Processing deficiencies are usually characterised by adhesion failures of the bond, in which the adhesive is cleanly removed from one of the substrate surfaces. This is sometimes due to surface contamination but normally due to inadequate surface preparation (Davis & Bond, 1999).

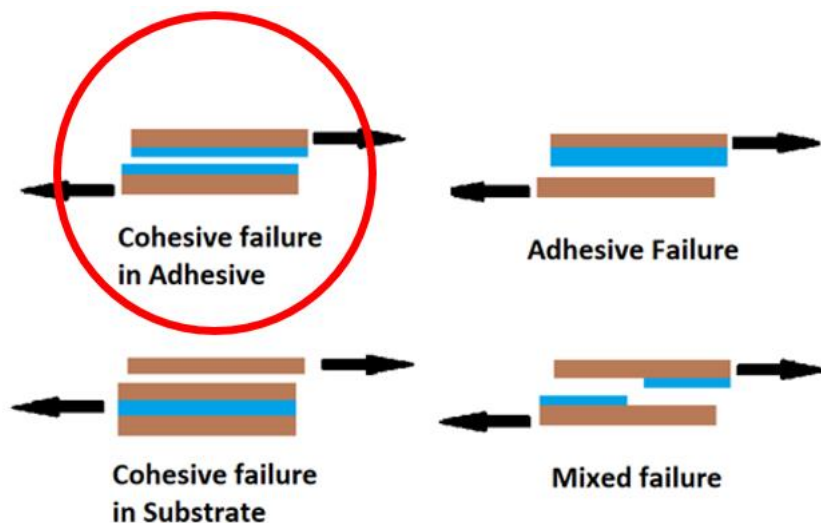


Figure 36: The different failure modes for adhesive bonding. The ideal design criterion is circled

2.6.2 A short history of titanium bonding

According to Wegman and Van Twisk (2012) investigations into optimising the adhesive bonding of titanium, through the modification of its surface morphology, started during the latter part of the 1950s. One of these early treatments was an anodic process, which modified the titanium's surface by adding an oxide layer. These early attempts improved the way adhesives adhered to the surface, as the oxide layer had polar behaviour because of the difference in the electronegativity of the two constituting elements. However, these early anodic joints would fail due to failure of the anodic coating in adhering to the metal surface.

Another early improvement was the introduction of alkaline cleaning techniques. These alkaline cleaned surfaces produced strong initial bonds, but the bonds weakened relatively quickly causing joint failure. It was found that nitric-acid pickling produced similar results to alkaline cleaning. Although these two methods had poor durability, processing time was quick, making them popular during the 60s.

The next discovery was that a phosphate-fluoride conversion coating could be produced on the titanium's surface. This process produced superior wettability and bonding strength, and this was correlated with the presence of titanium dioxide in anatase form. However, the bond life was compromised as the anatase would revert to the more thermodynamically stable rutile, changing the titanium dioxide's volume by 8% and compromising the bond. In 1973, a stabilized phosphate-fluoride process was developed that retarded the conversion of anatase to rutile, improving the bond life. By the 1980s a phosphoric acid anodic process developed by Boeing further improved bonding strength. Other methods such as Turco 5578, Pasa-Jell 107, chromic acid anodising and sol-gel processes were also in regular use. However, due to chromic acid now being known as a carcinogen, it is banned in many countries.

From the 1990's to modern times, due to new environmental and health policies, many of the toxic and hazardous chemicals that were used in some of the above applications were either phased out or have been phased out of use (Marín-Sánchez, Conde, García-Rubio, Lavia, & García, 2016). In response to these new policies, new methods have been created such as laser induced nano-structuring and less toxic anodising methods like NaTESi anodising (Matz, 1988).

The next sub-chapters will cover both laser and anodic treatment methods.

2.6.3 Laser induced nano-structuring

Laser induced nano-structuring (LINS), or laser induced periodic surface structuring (LIPSS), is of particular interest to this research proposal, as it involves restructuring the surface structures through the use of a high-powered energy source.

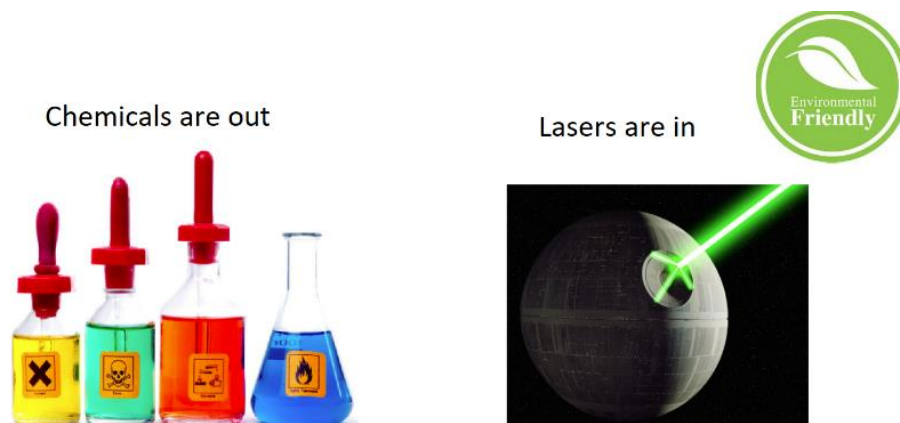


Figure 37: In many countries surface restructuring must use environmentally friendly methods over toxic chemicals.

In an investigation carried out in 2017 by Rotella, Orazi, Alfano, Candamano, & Gnilitzkyi it was shown that through LIPSS, the average failure peel loading could be increased from 15N to 35N, with failure occurring cohesively in the adhesive. Slightly weaker results were found from an acid-base + priming process, showing the LIPSS is an excellent candidate for improving bond strength. It should be noted that in this same study a contact angle test was carried out using ultrapure water, and the LIPSS substrate showed hydrophobic behaviour. However, this was suggested by the author to have been caused by air trapped within the surface asperities and that with pressure being applied to the adhesive joint, the air is displaced allowing the adhesive to wet the surface (Rotella et al., 2017). A visual aid of this phenomenon is given in Figure 38. It was explained by Pizzi & Mittal (2003) that the contact angle test, due to entrapped air on rough surfaces, will give a false reading. Hence, contact angle tests only return useful data about the surface energy on very smooth surfaces.

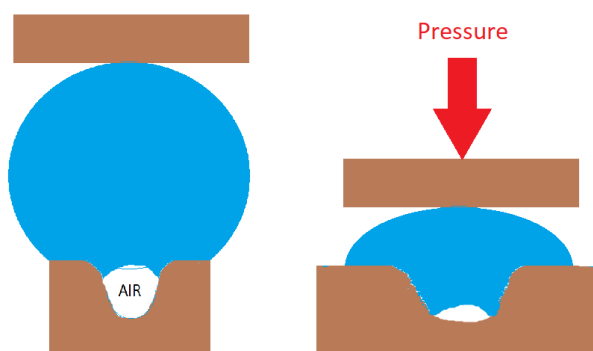


Figure 38: Entrapped air affecting wettability, the first example without pressure the second with pressure

In the 2017 study, a laser with a spot diameter of 6 μm was used which achieved fine porosity control. The results are shown in Figure 39 below.

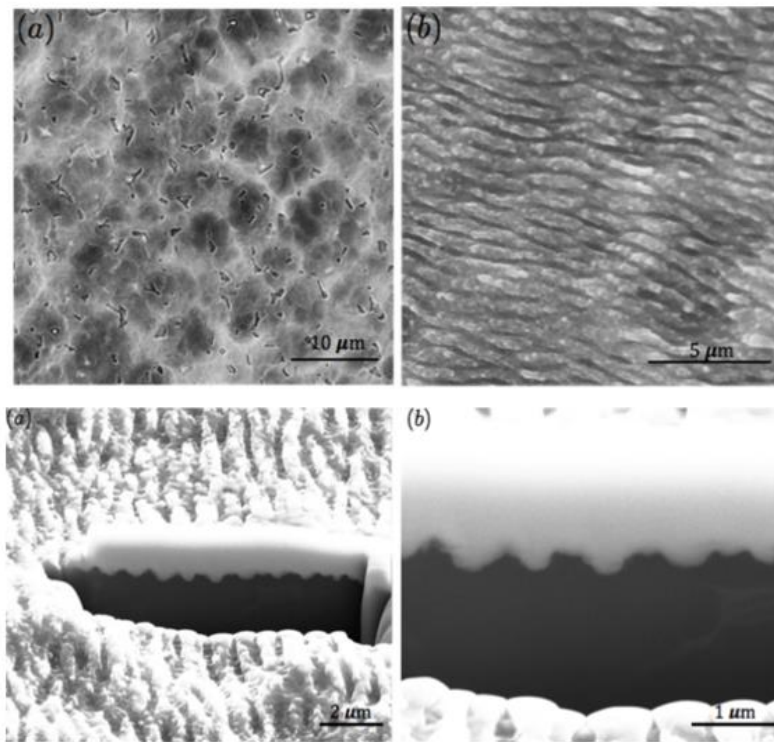


Figure 39: SEM images of substrates. Left – chemically treated through acid-alkaline etch; Right – laser induced nano-structuring (Rotella et al., 2017)

These LIPSS samples displayed consistent fracture surfaces, with failure occurring in the adhesive as illustrated in Figure 40. This was concluded by the author to be due to enhanced mechanical interlocking with the surface asperities caused by LIPSS and not through chemical interactions.

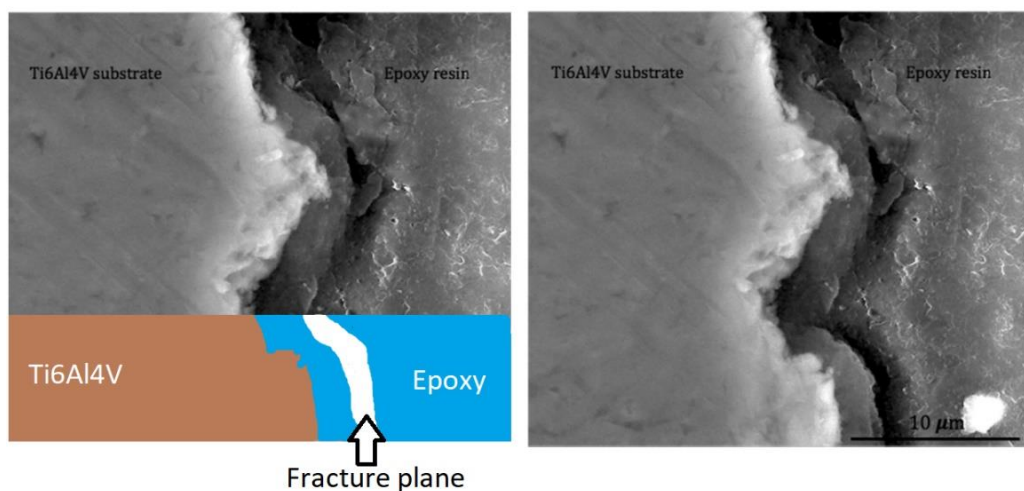


Figure 40: SEM images of a laser treated, bonded cross-section, highlighting the cohesive failure within the adhesive (Rotella et al., 2017)

Another study by Kurtovic, Brandl, Mertens, and Maier (2013) using a different laser showed that when tested using a wedge test, the strength and durability was comparable to NaTESi anodising. In this study the surface structuring was done using pulsed laser irradiation (Nd:YVO₄, 1064 nm). A chemical investigation was also carried out using X-ray photoelectron spectroscopy (XPS) on specimens that had only been cleaned with an isopropanol drenched lint-free cloth. This chemical investigation revealed that when compared to alkaline etching, the laser treated surface had contamination levels that were lower by 10%, and when compared to the untreated samples, the levels halved. For this study the contamination was characterised as the carbon concentration on the surface, and for the laser treatment the levels averaged 19.8 at% (atomic percent).

SEM images were also taken of the surface to further classify the surface morphology. Figure 41(a) shows the macroscopic topography resulting from overlapping laser pulses on the surface. These laser pulses had diameters of about 120 (+/-) 2 μm . Figure 41(b) uses an increased magnification, to view within the borders of one of the laser pulses shown in Figure 41(a). Under this magnification a fine homogenous open porous nanostructure was identified. The side view Figure 41(c) of the surface was obtained by cryo fracture of the surface, where the specimen was broken in two after flash freezing with liquid nitrogen. This side view revealed an oxide layer of about 164 (+/-) 20 nm in thickness that was caused by the laser treatment. Examining closely these oxide layers revealed cavities (pointed out by the white arrow in Figure 41(c)). Evidence was found that the adhesive managed to penetrate these cavities creating both a mechanical and chemical anchor.

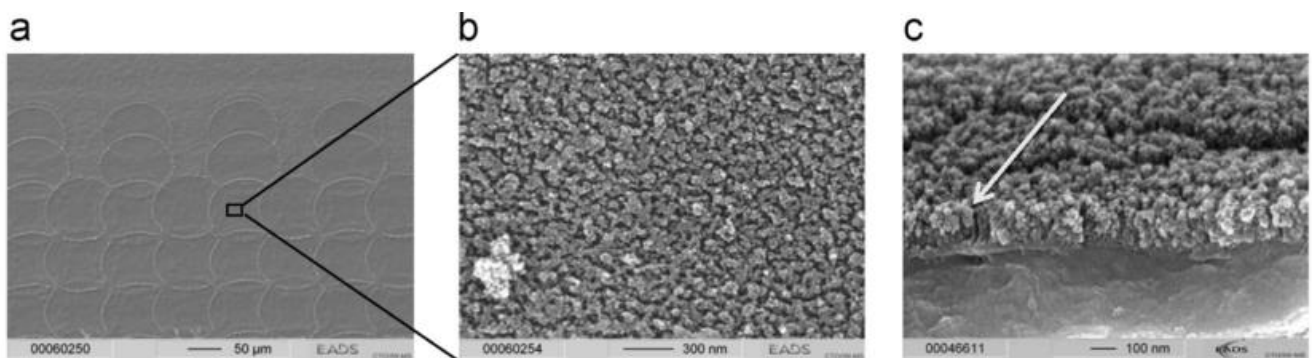


Figure 41: SEM micrographs showing (a) top view of the laser pre-treated Ti-6Al-4V surface; (b) high magnification detail and (c) side view cryo fracture of the nano-structured Ti-6Al-4V surface (Kurtovic et al., 2013)

These results matched earlier efforts carried out a year prior by some of the same researchers. SEM images from Mertens et al. (2012) are shown in Figure 42. These images illustrate the resulting surface morphologies of the Trunco 5578, NaTESi, and the laser pre-treatment methods. Figure 42(a,b) shows the results of the Turnco 5578 pre-treatment method, which

resulted in a morphology with micro-roughness, but no nano-structured surfaces identified. In contrast, the laser pre-treatment method in Figure 42(c,d) resulted in no micro-roughness, but formed an open porous nano-structured surface with the pores having a diameter in the range of 20 to 30 nm. These results were similar to the results from (Kurtovic et al., 2013). Finally, the NaTESi pre-treatment in Figure 42(e,f) produced a micro-roughened surface. Further, it showed a non-homogenous, open porous basket-weave structured surface, that resembled a disordered AM mesh, but at a size below 100nm. Note that the author suggested that the areas of the surface that are dark black are not nano-structured pores but instead dense areas of the substrate.

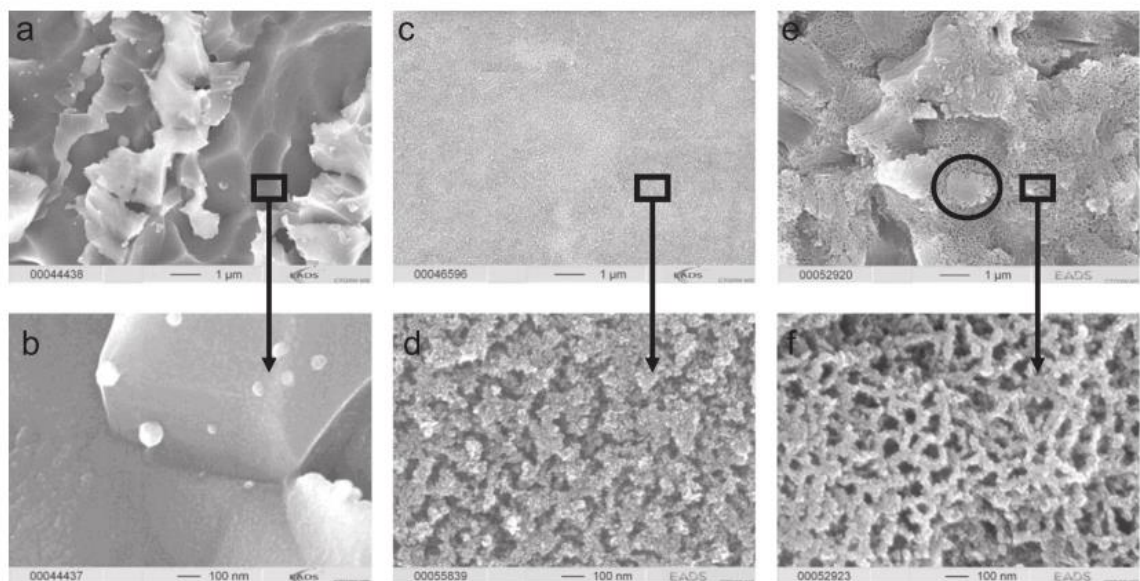


Figure 42: SEM micrographs of Ti-6Al-4V surface: (a,b) Turnco 5578 pre-treatment, (c,d) laser pre-treatment and (e,f) NaTESi pre-treatment (Mertens et al., 2012)

2.6.4 Anodic surface treatments

In an investigation carried out by Marín-Sánchez et al. (2016) It was found that by alkaline anodising Grade 5 titanium in a sodium hydroxide electrolyte mixture, the surface morphology changed through adding a honeycombed porous granular TiO₂ layer, see Figure 43. This method was originally created by Matz (1988) and was called NaTESi anodising. Here, the composition of the electrolyte was mainly made up of sodium hydroxide, which acted as an alkaline etchant and the main donor of oxygen anions (which both etched and encouraged the growth of the oxide layer); sodium-tartrate (an optimiser); EDTA (a chelating agent, to stop debris forming on the surface); and sodium silicate (for evening the etching).

Matz (1988) also showed NaTESi can also be used as an effective etchant, etching at a rate of 10 g m⁻² h⁻¹ at 70 °C and 40 g m⁻² h⁻¹ at 80 °C. It was recommended that a 10-minute soaking

in an acid brightening bath of HNO_3 at 5 mol/L be used to remove any complexing agent residues which are not desorbed by rinsing in water.

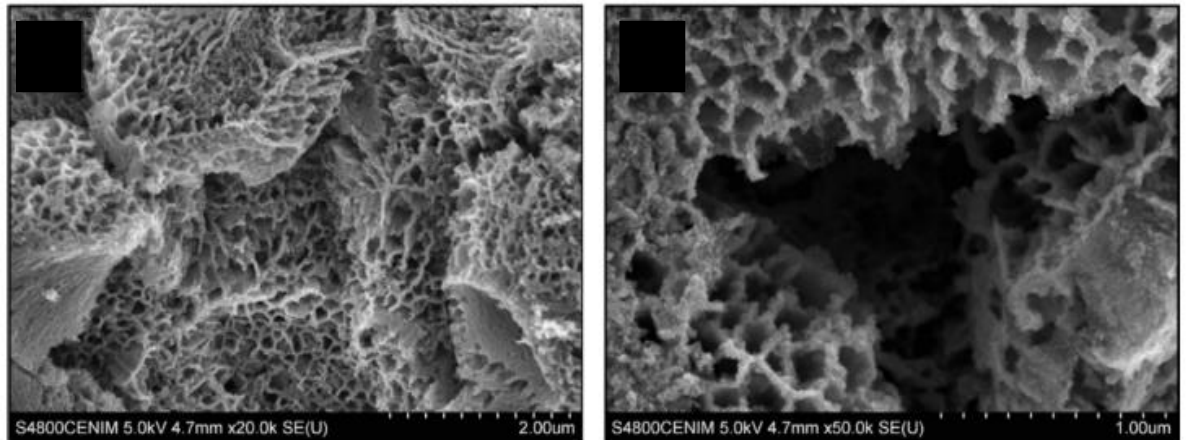


Figure 43: SEM images of Ti-6Al-4V after NaTESi anodisation process (Marín-Sánchez et al., 2016)

From the study by Marín-Sánchez et al. (2016), the forming of the TiO_2 layer from NaTESi anodising doubled the surface energy from 40 to 80 (mN/m). Further, the bonding strength during the wedge crack test also doubled. Anodising in a chromic acid solution was also carried out, and showed almost identical results with the exception that the resulting surface morphology showed a porous/nanotubular TiO_2 layer, as shown in Figure 44.

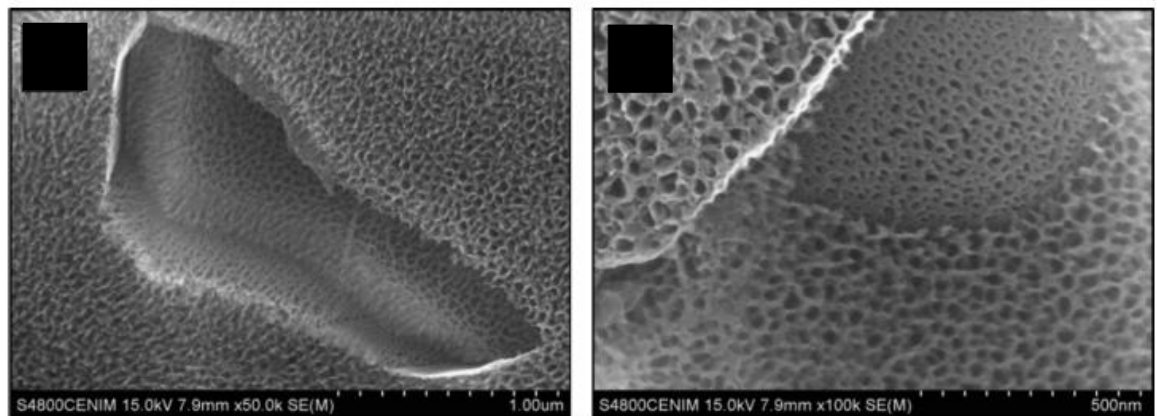


Figure 44: SEM images of Ti-6Al-4V after chromic acid anodisation process (Marín-Sánchez et al., 2016)

In both cases the roughness, especially the nano-roughness of the oxide layers was regarded as the most important design parameters for the adhesive joints, having a big influence on its strength and durability.

The following highlights what was explained above in section 2.6.1, regarding the need to remove contamination, all samples in the experiment by Marín-Sánchez et al. (2016) used the

following decontamination method: samples were degreased with methyl-ethyl-ketone, followed by immersion in a commercial chromate-free alkaline cleaner TURCO4215 NCLTs®, and finally etched with a commercial alkaline product, TURCO 5578®. The samples were then deoxidized in a 7M HNO₃ solution at room temperature, then before the Anodising process was carried out, the natural passive oxide layer was removed by soaking in a solution of 40 %v HNO₃ and 2 %v HF for 45s, at room temperature, with gentle manual shaking. Even after anodising, the samples were rinsed in deionised water for 5 mins and oven dried at 60°C. The surface preparation was finished by applying a chromate-free water-based film primer BR-252 by Cytec and curing for two hours at 60°C. The samples were then bonded using Cytec FM300-2 epoxy adhesive cured in an autoclave for two hours at 180 °C. This method may appear excessive, but it ensures contamination is eliminated, and that the strongest bond possible can be produced.

Initial degreasing and etching surface preparations were common amongst all the literature where bonding strength was successfully increased. Surface treatment methods varied greatly within the literature, and unfortunately many of the most successful surface treatments such as chromic acid anodising involves the use of hazardous materials (Molitor, Barron, & Young, 2001).

For industrial situations, chromic acid anodising was used extensively due to the strength and durability of its titanium adhesive bond. However, due to its toxicity and carcinogenicity, showing that the less harmful NaTESi anodising can produce similar results gives industries a safer alternative. Nevertheless, anodic surface treatment methods still require many controlled parameters for ensuring they produce satisfactory results. This includes extensive surface cleaning and decontamination measures before processing. This explains why laser and plasma treatment methods are attractive, as they can remove contamination and improve adhesive bonding in one go.

From the results of the literature it is clear that removing surface contaminants dramatically improved bonding strength, as did adjusting the surface roughness and porosity through abrasion, grit blasting, acid etching, laser-induced surface nanostructuring, and anodising (Molitor et al., 2001; Pan et al., 2016; Xu et al., 2016). The effects of surface energy and tension of the adhesive and substrate also impacted bond strength. This was shown in the study by Xu et al. (2016) where it was shown that increasing the apparent surface energy by anodising aluminium increased wetting and hence mechanical interlocking. Also, in a study done by Pan et al. (2016) it was found that adjusting surface chemistry through electrografted aryl diazonium salt resulted in an organic primer that covalently attached to the metal's surface. Together, with anodisation, this increased the bond strength to 40 MPa and dramatically increased the adhesive bond's resistance to hot temperatures and humidity.

Numerous studies on cast titanium and other metal alloys have shown that surface roughness, porosity and unique surface morphology, such as the hooks of the oxide layer generated from phosphoric acid anodising of titanium, all dramatically increase bonding strength (Xu et al., 2016). Surface roughness and porosity also contribute to increased diffusion and chemical bonding as the greater roughness increases local surface area. However, as literature is limited on the effects that the unique surface structure of EBM additive manufactured titanium has on bonding strength, this thesis aims to add to it.

2.6.5 Adhesive information

Depending on the loading scenario and the substrate material to be bonded, certain adhesives will be superior to others. Figure 45 shows the different 3M adhesive products and their respective load bearing capacities. The 3M data sheet on their structural adhesives 3M, (2008) also states that as a rule of thumb:

- Epoxy adhesives: Are one and two-part formulations that provide the best chemical resistance and high strength at elevated temperatures.
- Acrylic adhesives: Are still high strength bonding adhesives and do not require the surface preparation needed for epoxies and urethanes; they can be bonded to the widest variety of substrates including hard-to-bond plastics and oily metals.
- Urethane adhesives: Lower in bond strength when compared to epoxy or acrylic adhesives but provide impact resistance and flexibility.

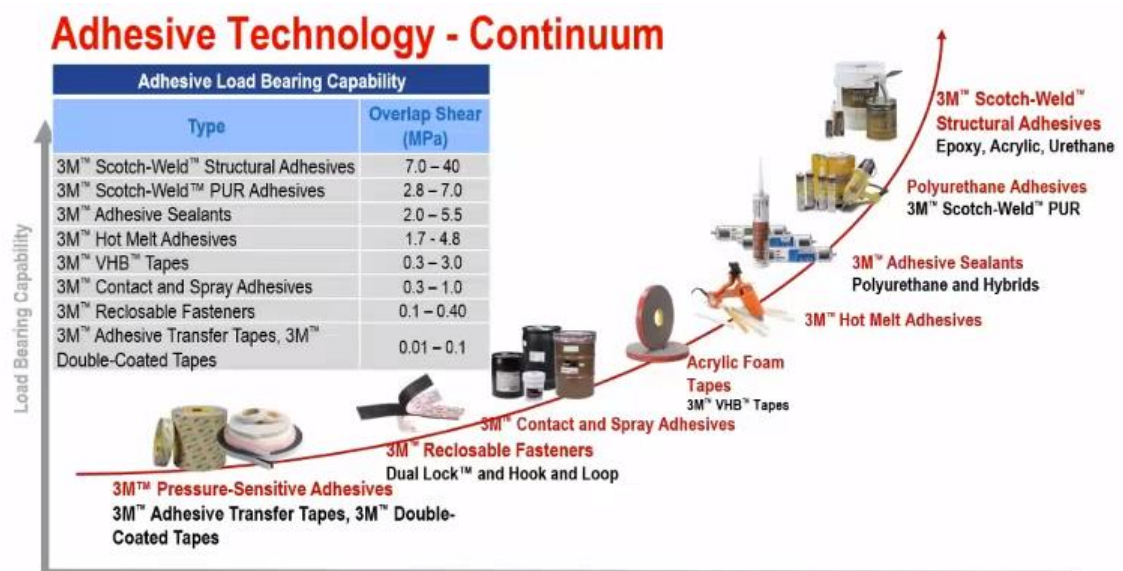


Figure 45: Shows the load bearing capabilities of the different 3M adhesives (3M, 2008)

The differences between the overlap shear strength for epoxy and acrylic adhesives after surface treatments are shown in Figure 46. Here, when the surface is correctly prepared the epoxy adhesives outperform acrylic adhesives. The acrylic adhesives outperform the epoxy adhesives in all other preparation methods shown (3M, n.d.)

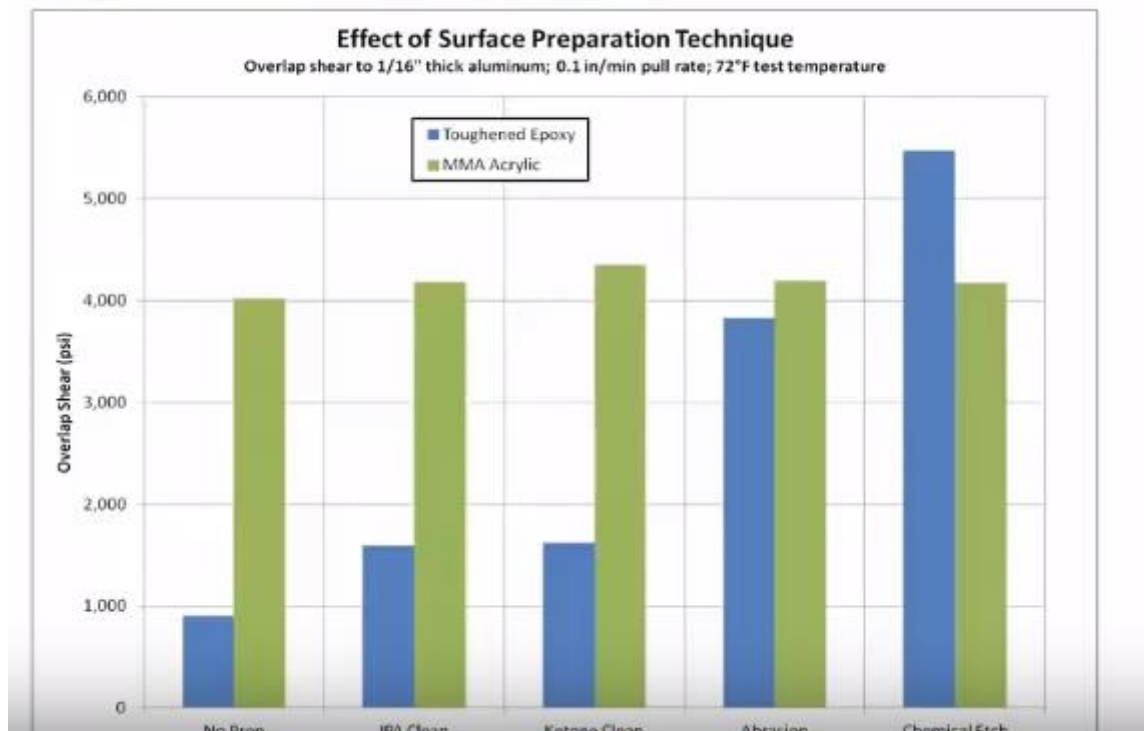


Figure 46: Surface treatments and the resulting overlap shear strength of either epoxy or acrylic adhesives (3M, n.d.)

Adhesive joints can be loaded in many ways with the most common shown in Figure 47. The peel and cleavage loading cases are the most severe conditions as the stress is concentrated into a single line of high stress (Huntsman, 2017). Depending on the loading scenario the adhesive thickness should be varied with at least a 0.0762 mm - 0.127mm gap between the parts for shear loading and a 0.381mm - 0.508mm gap for peel (3M, 2008).

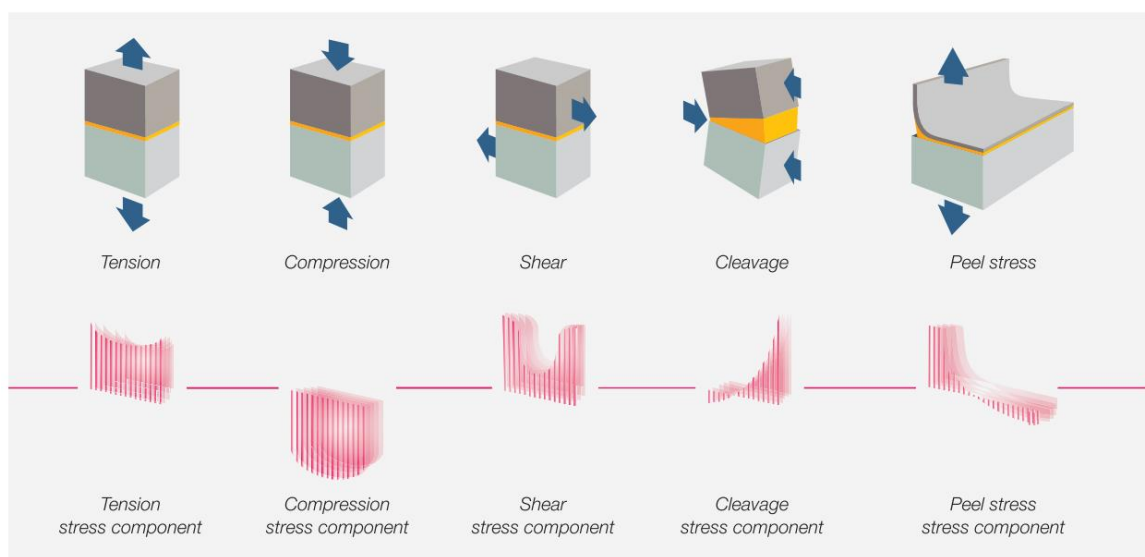


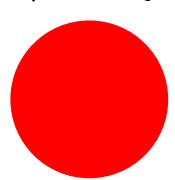
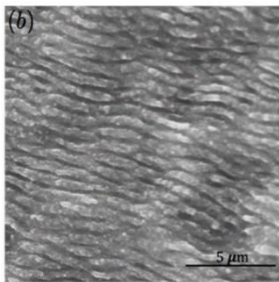
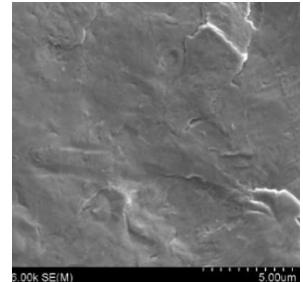
Figure 47: Showing the different adhesive bond loading directions and stress distributions (Huntsman, 2017)

In the study by Arenas, Narbon, and Alia (2010) it was found that an adhesive thickness of 0.1mm produced the highest shear bond strength of 11MPa (which matches the 3M datasheet on recommended adhesive thickness). However, many of the samples were also prone to failing unexpectedly at this gap thickness, with failure occurring through a mixed or adhesion failure path. It was concluded that the optimal thickness for reliability and strength was found to be between 0.4 - 0.5mm for shear loading, which matches more closely the 3M gap thickness recommended for peel loading.

2.7 Cellular structures (Meshes) in additive manufacturing

As stated in section 2.6.3, laser induced nanostructuring is now becoming a modern method for creating surfaces ideal for adhesive bonding. It was speculated in the conception of this project whether a custom theme could be used in EBM to give similar results. However, although these are both high powered devices that use types of radiation as heat sources, EBM currently lacks the focal spot size required to produce results like the femtosecond laser used in LINS. This as well as other differences are listed below in Table 8.

Table 8: Differences between EBM and femtosecond laser

	Femtosecond laser (Rotella et al., 2017)	EBM (Arcam AB, 2019a)
Emitter	Ytterbium-doped fibre (1028nm)	lanthanum hexaboride crystal
Focal spot size (see equivalent sizes)	6 μm 	Min 140 μm Q10/Q20 
Spacing pitch	3 μm	-
Scanning speed	3 m/s	8000 m/s Max
Pulse rate	600 kHz	na
Pulse duration	213 fs	na
Pulse energy/power	0.58nJ	3000 W
Environment	Atmospheric (Oxidizing)	Vacuum (non-oxidizing)
Resulting surface Under x6000 magnification		

As mentioned, the limiting factors are that the processing for EBM takes place under a vacuum meaning the surface is not able to oxidise. Secondly, the focal spot size is too large to create micro or nano patterns. Further, as given by Hypsh and Shannon (2014) femtosecond lasers are known for their ability to carry out cold ablation rather than melt ejection. As a result, it can cut very fine details without damaging surrounding surfaces, as shown in Figure 48.

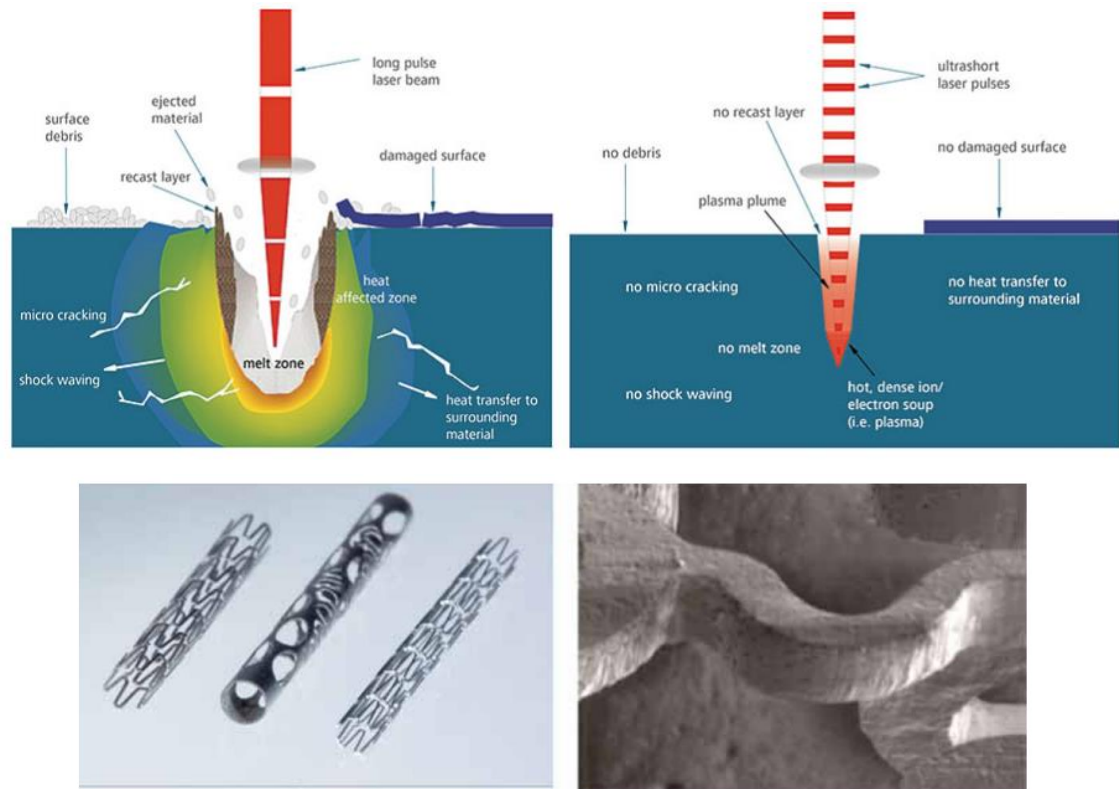


Figure 48: Right - Application with long pulse laser (μs); Left - application with femtosecond laser (fs); Below - cut quality for nitinol stent, with the edge having the same finish as the material surface (Hypsh et al., 2014)

After reviewing the literature, it was concluded that EBM could not produce a nano-structured surface like LINS can. However, this investigation led to another novel idea. Instead of aiming for nanostructures, the EBM machine can manufacture macro and micro-structures in the form of meshes made of struts $\sim 300\text{ }\mu\text{m}$ thick. Therefore, these structures were chosen to be investigated for their influence on improving adhesive bonding strength, see Figure 49 for a schematic of the proposed surface.

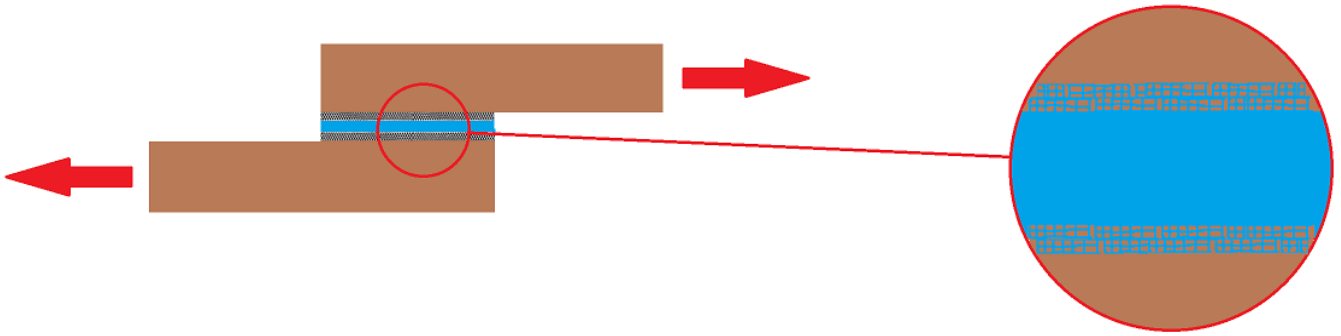


Figure 49: Shear loading of two adhesively bonded substrates, with a close-up showing mechanical bonding which occurs through entanglement with the substrates mesh and surface roughness. Here titanium is shown in brown, and the adhesive in blue

The Arcam EBM machines, specifically the Q10 and 20 plus, are capable of building structures to a minimum resolution of around $\sim 300\ \mu\text{m}$. This means they are very capable of producing cellular structures which are very small in size. Cellular materials are materials in which empty space occupies a significant portion of the volume. They exist in two forms – composed of matter in the faces (closed-cell); composed of matter at the edges (open-cell). Due to the need of removing the sintered powder from within the parts, cellular materials made in EBM are always open-celled.

Lattice structures are a type of open-cell cellular material which are composed of a connected network of struts. They are classified as either periodic (a repetition of a unit cell or a strut in defined directions), or stochastic/random (an assembly of struts of cells lacking periodicity or symmetry) (Suard, 2015). Additionally, there are also surface based cellular materials such as Triply Periodic Minimal Surfaces (TPMS). The cellular material examples shown in Figure 50 were produced to show the variety achievable with EBM AM.

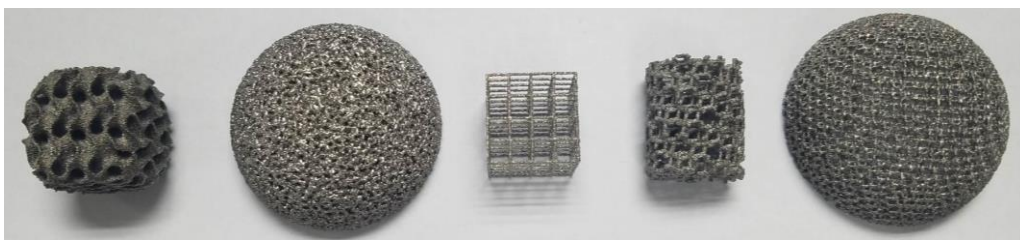


Figure 50: Different cellular materials. 1st, a TPMS cube; 2nd, a stochastic trabecular (strut-based) mesh; 3rd, a periodic (strut-based) lattice; 4th, a periodic (unit cell based) cube; 5th, a periodic (unit cell based) mesh

EBM produced lattice structures were investigated by Hernández-Nava (2016) and it was shown that the mechanical properties of the lattice were heavily influenced by macro defects such as surface roughness, internal pores, and undersized cross-sections. Porosity was shown to increase with reducing strut size, with an even greater increase in porosity when built using the *point-net melt theme*. These defects contrast to the ideal smooth surfaces employed in

calculations such as numerical methods like finite element and can lead to incorrect mathematical predictions of strength. Hernández-Nava (2016) compiled the different compressive strengths of different geometries at varying relative densities showing the varying properties achievable, see Figure 51.

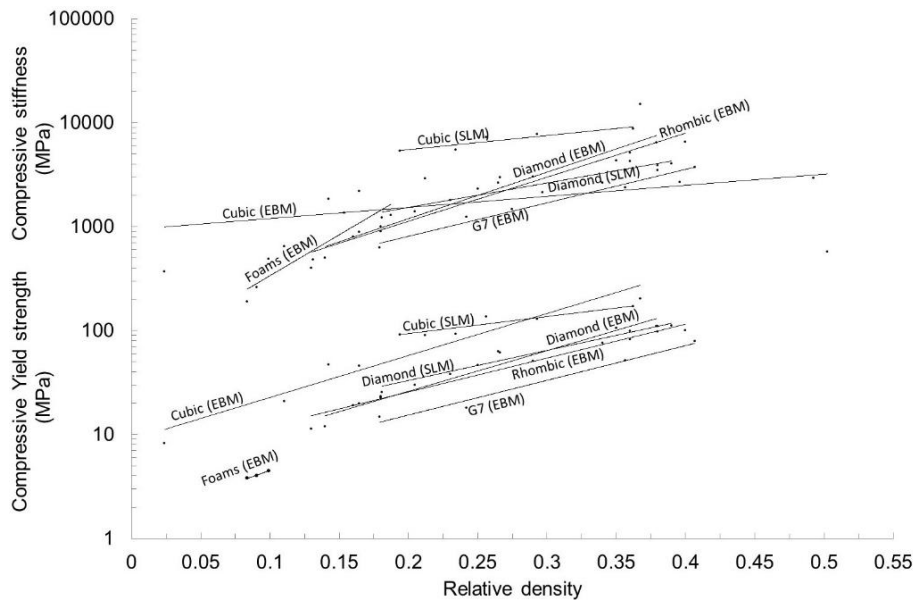


Figure 51: Compressive strength and stiffness of EBM and SLM produced Ti-6Al-4V lattices and foams (Hernández-Nava, 2016)

No literature was found for the adhesive bonding between EBM produced meshed surfaces. However, many articles mentioned the use of trabecular meshed surfaces in promoting osseointegration (bonding between living bone and an implant). This was shown by Browne, Palmquist, Thomsen, Snis, and Emanuelsson (2011) where an EBM manufacture porous cylindrical implant was placed into the femur of a sheep. The successful osseointegration between the bone and implant is shown in Figure 52. It was thought possible that this trabecular meshed surface could also promote improved adhesive bonding between titanium and an epoxy adhesive. Therefore, it was included as a surface to be investigated.

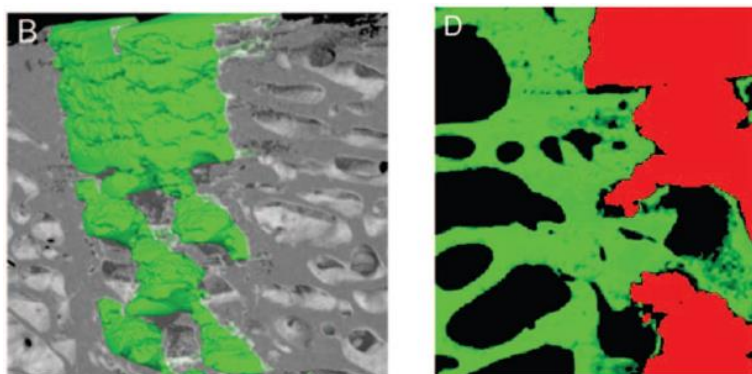


Figure 52: Micro-computed tomographies of the porous implant. Left – implant shown in green; Right – implant is shown in red and bone in green (Browne et al., 2011)

2.8 Loading of adhesive single-lap-joints

2.8.1 Single-lap shear test ASTM D1002 (eccentrically loaded SLJ)

ASTM D1002 is a single lap joint (SLJ) shear strength test which was heavily used in the past due to its simplicity of quickly producing multiple samples from two large bonded sheets. In terms of this thesis, because each part was printed individually no additional ease of joining was gained.

ASTM D1002 is only useful for comparing surfaces and not for defining an adhesive bond's real shear strength. This is because due to the D1002's eccentric loading about its geometry, bending moments develop as the offset forces try to become collinear. The bending of the material then causes the bond line to rotate, placing the bonding interface under perpendicular loading, resulting in peeling and cleavage stresses. Adhesives are weaker under peeling and cleavage stresses, therefore it is important to never design from the strength values obtained from the D1002 tests, as it will give false values of the joint's shear strength. In most cases D1002 is now superseded by D3165 or D5656 (McCann, 2015). The set up for a typical D1002 is shown in Figure 53 (ASTM International, 2010).

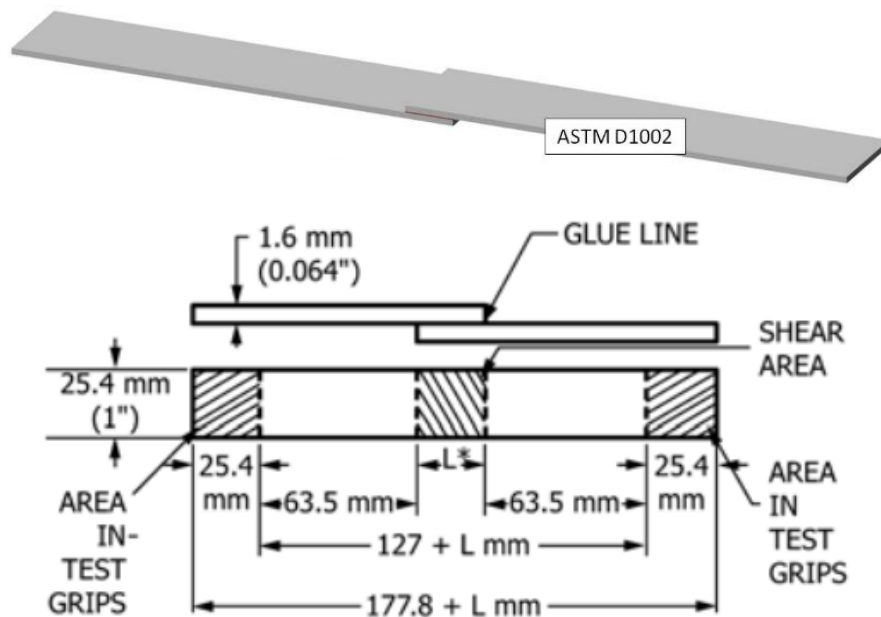


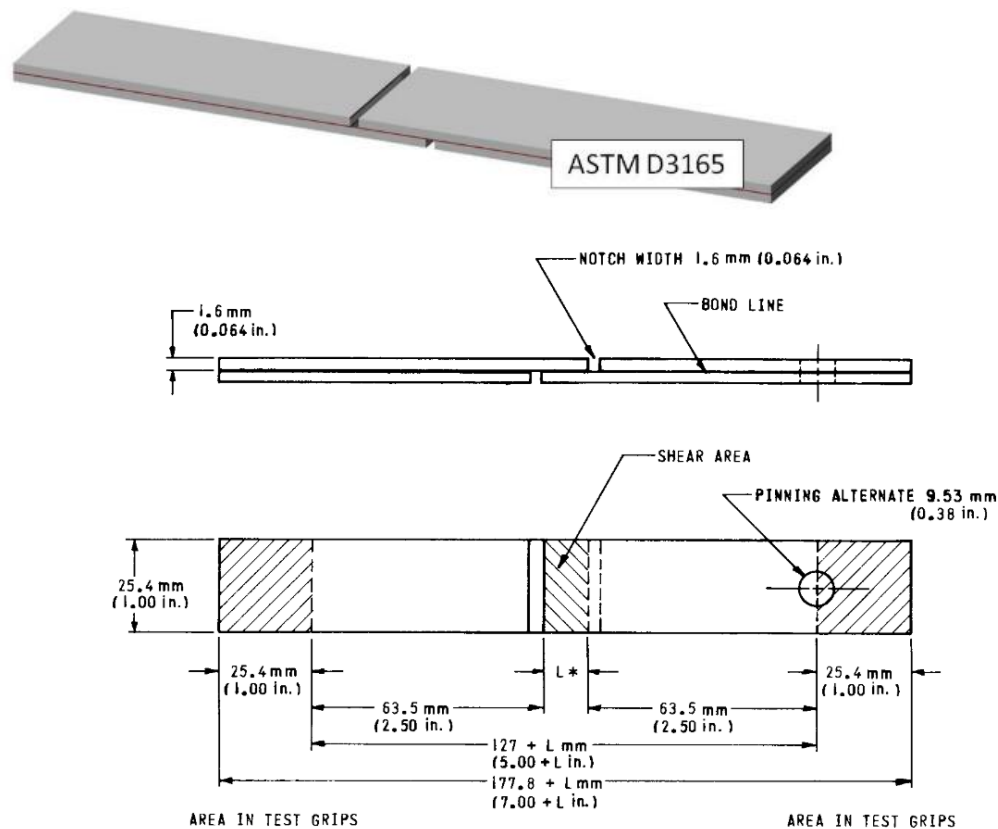
Figure 53: ASTM D1002 coupon setup (ASTM International, 2010)

2.8.2 Single-lap shear test ASTM D3165 (concentrically loaded SLJ)

ASTM D3165 is also a single lap joint (SLJ) shear strength test, except unlike D1002 the substrate is thickened, and a notch is added at half the thickness of the part, see Figure 54. The notch shifts the neutral axes of the forces to act concentrically through the bonding surface. This

in turn reduces the induced bending moments and thus the peeling and cleavage stresses. Hence, D3165 presents a more accurate measure of a bonded joint's shear strength.

In most cases it is still recommended to only use D3165 for comparative apparent shear strength purposes only, especially for materials with a low stiffness modulus. This is because bending moments, and therefore peeling and cleavage stresses, are still present in the overlap region. For experiments that require the measuring of an adhesives in-situ shear stress/strain constitutive data, the ASTM D5656 standard can be used. ASTM D5656 uses the same geometries as D3165, with the thickness of the samples cross section increased until there is enough material and stiffness to resist bending deformation (McCann, 2015). Due to the cost of manufacturing D5656 samples, and that this study only requires a comparison of the different adhesion properties of different surfaces, the D3165 standard was sufficient. The bonding dimensions of a typical D3165 joint is shown in Figure 54 (ASTM International, 2000).



NOTE 1—*L = length of test area. Length of test area can be varied. Recommended length of lap is 0.50 ± 0.01 in. (12.7 ± 0.3 mm).

Figure 54: ASTM D3165 coupon setup (ASTM International, 2000)

2.8.3 Stress distribution in single-lap-joints

As stated by da Silva (2008) for an adhered SLJ, the substrates undergoing loading are often assumed to be effectively rigid, meaning that as the load passes from substrate to substrate a uniform shear stress is generated, as shown in Figure 55.

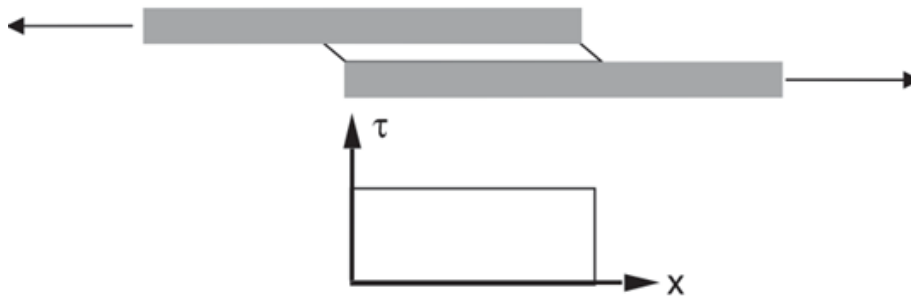


Figure 55: Uniform adhesive shear strength in D1002 SLJ (da Silva, 2008)

However, in reality the substrates don't act perfectly rigid, and stretch more nearer to their loaded ends, then in the centre of bonding, as shown in Figure 56. Therefore, the shear stress is not uniform, instead it is greatest at the overlap ends, and lowest towards the centre.

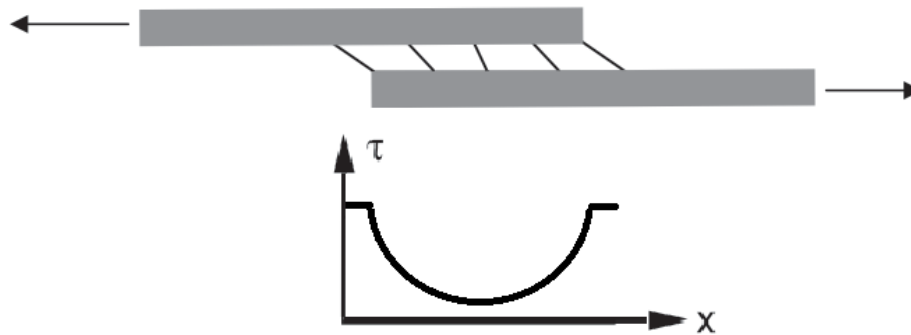


Figure 56: Non-uniform adhesive shearing in D1002 SLJ (da Silva, 2008)

In loading cases like ASTM D1002, in addition to the non-uniform stress distribution, the offset in loading about the neutral axis causes bending in the loaded substrates. This loading induces transverse direct stresses, referred to as peel or cleavage stresses which are maximum at the joints ends, this is shown in Figure 57 (da Silva, 2008).

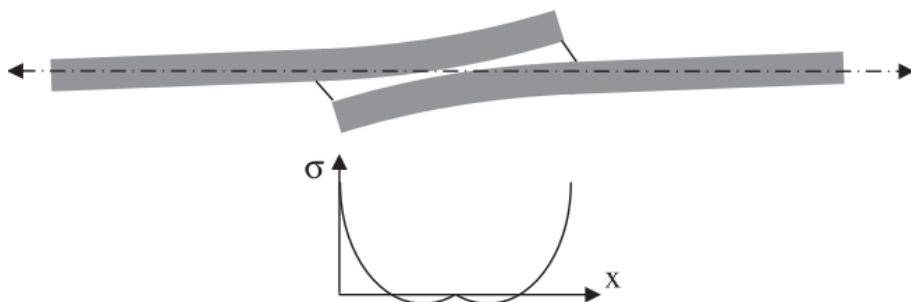


Figure 57: Peel stresses in a D1002 SLJ (da Silva, 2008)

A more detailed explanation of the formation of peeling stresses in eccentrically loaded SLJ's is shown in the illustration by Budynas and Nisbett (2012), see Figure 58. Peeling stresses are stresses that act perpendicular to the bond line as shown in Figure 58c. Adhesives are sensitive

to peel forces as they create a leverage effect that concentrates stress to act in smaller areas of the bond, causing failure at lower force levels than those observed in tension and shear. Materials or geometry changes which increase the force required to cause flexural yielding, reduce the bending deformation, and increase bonding strength, by ensuring the forces act more uniformly over the bond line.

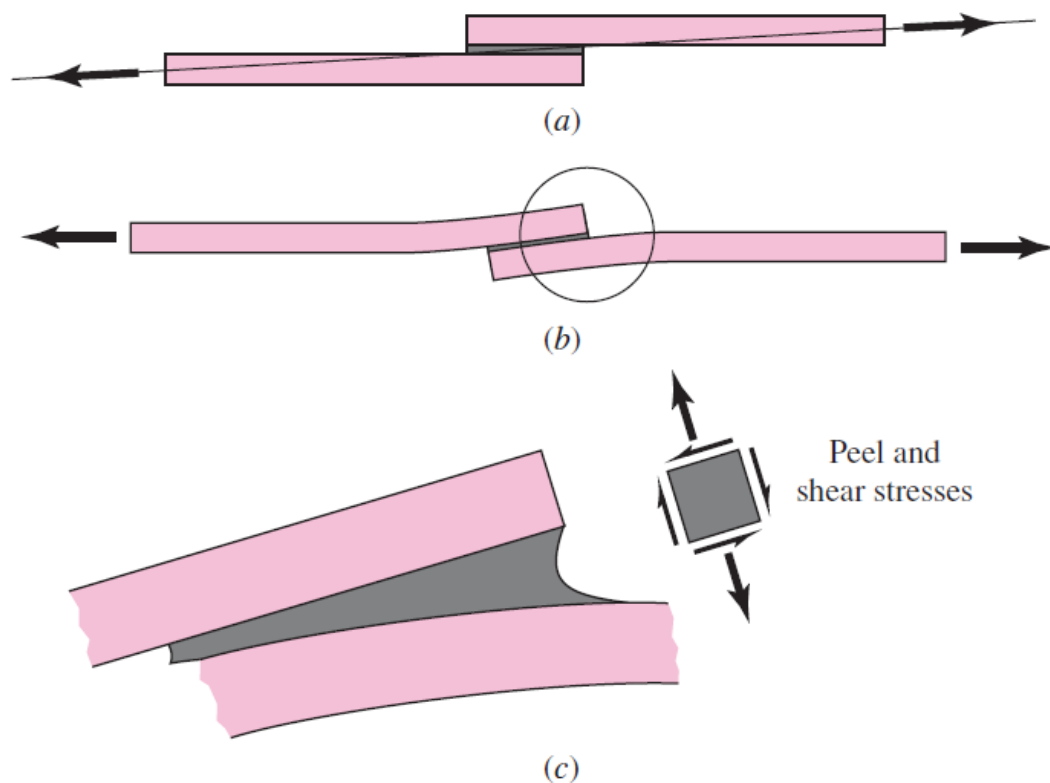


Figure 58: Loading of a D1002 single-lap joint. (a) The geometry of the SLJ causes an offset in the initial loading about the neutral axis; (b) As the load increases the adherents bend as the forces attempt to become collinear; (c) At the end of the bond line, peel and shear stresses appear, these peel stresses often induce joint failure (Budynas & Nisbett, 2012)

The non-uniform stress distributions shown in Figures 55-58 apply to all SLJ's to some degree, more so for thin, flexible, and eccentrically loaded substrates, and less for thick, stiff, and concentrically loaded substrates. However, in most cases this is fine as only an apparent shear strength value is required. This is because most adhesive experiments only aim to compare the performance of different adhesive and surface pre-treatment combinations, and not to define the actual strength of the joint for design purposes.

For the ASTM Dxxxx standards apparent shear strengths are calculated by using the ultimate tensile force and assuming the shear stress to be uniform over the area of bonding. Using apparent shear strength is adequate when it is understood that non-uniform stresses exist, and that the resulting values should only be used for controlled comparative results and not design or prediction purposes (McCann, 2015).

2.9 Thesis objective

From the literature analysed above, the following four unanswered questions were formed.

Answering these questions is the objective of this thesis. These questions are:

1. What are the different surface morphologies achievable through EBM manufacturing?
2. Using the theories of mechanical interlocking and adsorption, how do these different surface morphologies effect adhesive bonding strength?
3. What effect does a trabecular mesh have on the adhesive bonding strength, and is this better than the default EBM surfaces?
4. What effect does NaTESI anodising have on the adhesive bonding strength, and is this better than the default EBM surfaces?

It is apparent that by answering these questions, a better understanding will be gained of the surface morphologies achievable through EBM additive manufacturing, select surface treatments, and the effect these have on shear adhesive bonding strength. It is expected that this information will be practically applicable within the EBM industry.

2.10 Methodology – reasons for the chosen method

The title of this thesis is “How the Surface Morphology of Electron Beam Melted Additive Manufactured Grade 5 Titanium Affects Adhesive Bonding Shear Strength”. The chosen method was selected to provide a controlled experiment to answer both the title question and the four research questions listed above. The bonding shear strength was selected as the outcome or dependant variable, with the surface morphology being selected as the input or independent variable. Controls were used to ensure that only the surface morphology would be influencing the outcome of the bond strength. This gave three elements which had to be defined in order to produce a successful experiment. These three elements are:

- **The independent variable:** the surface morphology of EBM titanium. Questions that will be analysed include: what are the surface morphologies achievable? What are their key characteristics? How are these characteristics best defined and quantitatively measured? How can EBM parameters and themes change the surface morphology?
- **The dependent variable:** adhesive bonding shear strength. This includes analysing: what are an adhesives' key characteristics? How are these best defined and quantitatively measured?
- **Controls:** constraints on the experiment. Factors that will be considered include: how will the adhesive be used? What pre-bonding, degreasing and cleaning method is most effective? What is the best bonding preparation method? What shear testing method or standard is most effective? How will the EBM process be controlled?

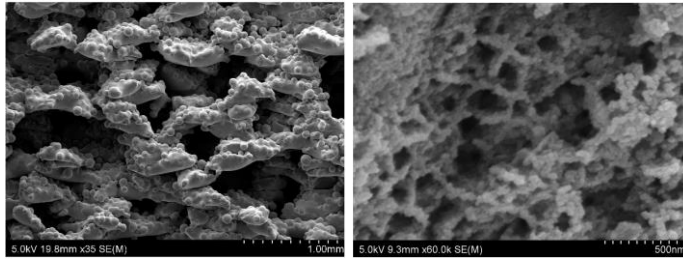
The literature review helped answer the above questions that were posed in regards to the independent variable, dependant variable and controls. The section below shows how these answers were implemented to provide the method of this research.

For the **independent variable** (the surface morphology of EBM titanium) there are two as-built orientation-based surface structures, these being the vertical and horizontal surfaces as discussed in 2.2.2. Further, the EBM process is capable of producing meshed structures as shown in 2.7. Finally, as discussed in 2.6.4, any titanium surface can be anodised to produce a porous nano structured surface. Defining these surface morphologies in terms of surface roughness is difficult, as many of these surfaces exhibit finer and finer detail as the scale of the reference frame reduces. Essentially, the EBM surfaces have a fractal nature, particularly the anodised surfaces, which have nano surface roughness as shown in 2.6.4. This is an issue, as a mechanical probe cannot measure roughness under the micron level. Further, defining the surfaces in pure fractal dimensions is also not practical – at least not for this study – due to limitations in image processing expertise, and time. Therefore, to overcome these limitations and to still provide a useful outcome, a pseudo-fractal surface roughness method was created for this study. In this method a different surface roughness measuring technique was used which depended on the size of the surface structures for a given reference frame. For this thesis the pseudo-fractal surface roughness groups 2, 3 and 4 as defined by Venables (1984) in 2.1.1 were used. These three groups are:

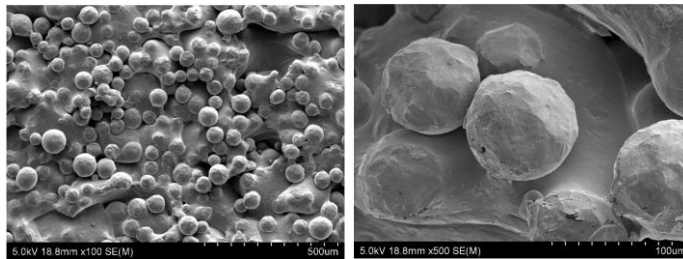
- Group 2: macro-roughness (above 0.5mm sized surface features), which had the roughness measured visually through SEM;
- Group 3: micro-roughness (1 μ m - 500 μ m sized surface features), which had the surface roughness measured using a stylus profilometer;
- Group 4: nano-roughness (below 1 μ m sized surface features), which had the roughness measured visually through SEM imaging.

In addition to Group 2 and 4 being measured visually under SEM, the surfaces were also defined based on the morphology of the structure. The three morphologies used were defined as:

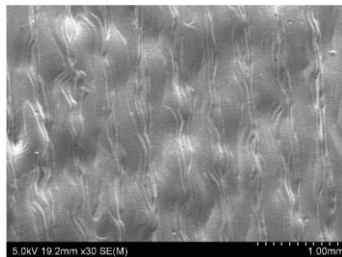
- A meshed structure (MS), categorised by being a cellular structure made of many interconnected struts and defined by the thickness of the struts, the pore size between them, and the thickness of the overall structure;



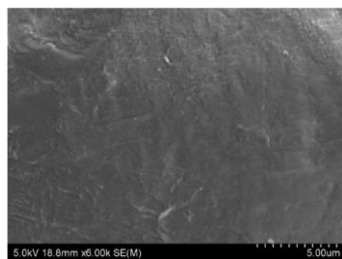
- A powdered structure (PS), categorised by having partially melted powder particles on the surface and defined by the amount and size of the particles, how they have joined to the main body, and the depth of the crevices produced;



- A wavy structure (WS), categorised by having a wavy surface and defined by the spacing and amplitude of the waves;



- Flat structure (FS), categorised by being flat with extremely low roughness values and defined by being a solid and smooth surface.



Due to the pseudo-fractal nature of the EBM surfaces, many of these structures can exist for a single surface.

For the **dependent variable** (adhesive bonding shear strength), the adhesive bonding shear strength was chosen to be measured using the ASTM D1002 (eccentrically loaded SLJ) standard. However, this was changed to ASTM D3165 (centrically loaded SLJ) standard as

this method simplified the bonding process, and reduced the peeling stresses, making the results more consistent as the stress concentrations were reduced.

To **control** the adhesive bonding, only the Adhesive Technologies NZ Ltd's HPR 25 rubber-toughened epoxy adhesive was used. The reason for this selection was that it exceeded the requirements of ASTM D1002 (achieved 15.9MPa), was produced locally, and, due to constraints on funding and resources, the adhesive was provided for free.

The other controls used in the experiment are covered in the Chapter 3, which outlines the method used in greater detail.

2.11 Literature review summary

This literature review outlined the fields of adhesive bonding, EBM additive manufacturing, and several modern titanium pre-bonding surface treatments. It presented evident knowledge gaps in the understanding of the bonding properties of the surfaces of EBM printed Grade 5 titanium, and highlighted a potential novel idea in the creation of a meshed surface for improving adhesive bonding strength. Additionally, it overviewed the methods structure, showing how the basic method was structured to provide a controlled experiment.

The following chapter will cover the materials and preparation procedures used to control the experiment. It will also include all production and testing equipment and how they were used.

Chapter 3: EXPERIMENTAL METHODS AND PROCEDURES

This chapter will look at the preparation of the shear test coupons, how they were bonded, what limitations they possessed, how they were tested, and the special processes used to adjust the surface morphology (specifically the anodising process). Further, what parameters were used for setting up the simulation will also be analysed. Finally, the results of the preliminary surface morphology experiment are then presented, showing the different surface characteristics of the 10 unique surfaces.

3.1 Preparation of the shear test coupons

Titanium shear test coupons were tested for apparent shear strength using the ASTM D1002 (eccentrically loaded SLJ) standard, and later the ASTM D3165 (concentrically loaded SLJ) standard. D3165 replaced D1002 as it was easier to bond, and, due to its forces acting concentrically, peeling stresses were reduced, which made the results more consistent. (The D1002 and D3165 SLJ arrangements are shown in Figures 59 and 60.) Due to the eccentric loading and greater induced bending moments, D1002 was considered a peeling stress dominant loading condition, with D3165 being considered a reduced peeling stress loading condition.

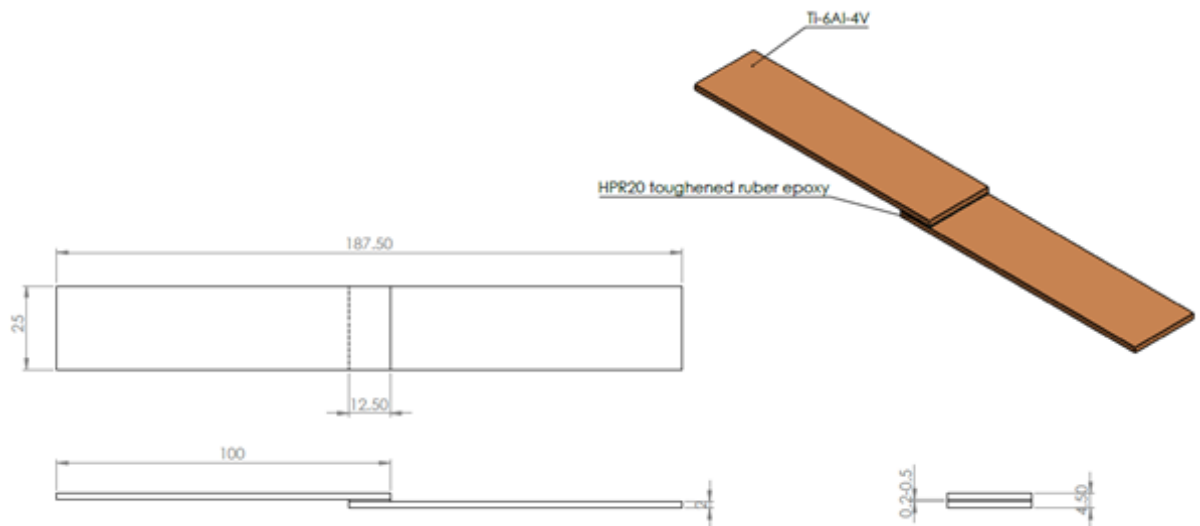


Figure 59 ASTM D1002 single-lap-joint arrangement

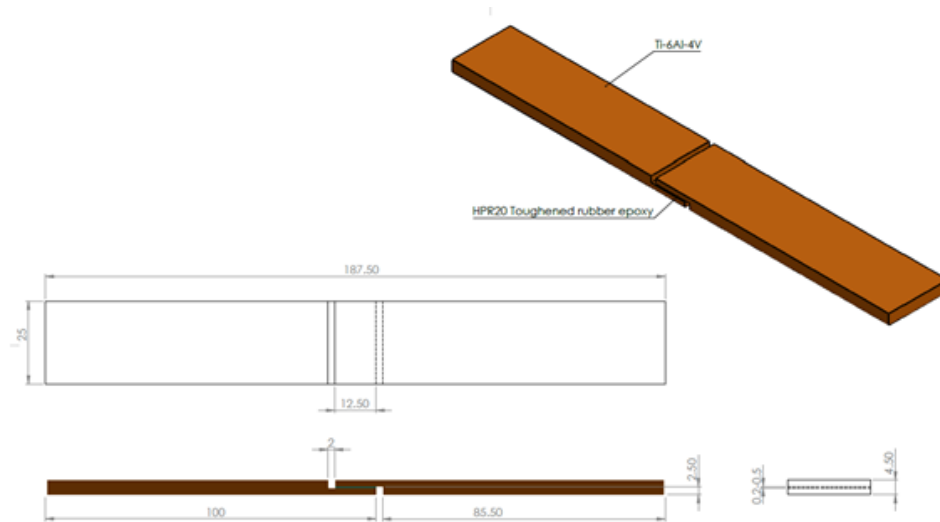


Figure 60: ASTM D3165 single-lap-joint arrangement

The coupons were manufactured from Grade 5 titanium alloy powder provided by AP&C, and were built by Zenith Tecnica Ltd using a standard melt theme on either the Q10 or Q20 plus Arcam machine. The coupons were bonded together with a rubber-toughened epoxy and tested for shear strength using a tensile testing machine.

In total 10 different surface morphologies were tested for their effect on adhesive bonding shear strength. These are shown below in Table 9, along with the number of samples tested for each surface. In total 36 samples were tested.

Table 9: The different surfaces tested for adhesive bonding strength

Name	# of samples
Vertical surface (V)	5x D1002 3x D3165
Horizontal surface (H)	4x D1002 2x D3165
V + rumbling (Va)	1x D1002
H + rumbling (Ha)	1x D1002
V + NaTESI anodised surface (NaTESI)	5x D3165
Smooth surface (S)	5x D3165
Meshed surface (02)	3x D3165
Meshed surface (04)	3x D3165
Stiffened meshed surface (03*)	2x stiffened D3165
Stiffened meshed surface (04*)	2x stiffened D3165

This table displays each surface that was built for this thesis. The eight vertical surfaces listed above were built parallel to gravity, hence its nomenclature of vertical. Further, the six horizontal surfaces were built perpendicular to gravity, hence its nomenclature of horizontal.

For the rumbled surfaces, a rumbling process was used. For this process, a drum is filled with small titanium pieces, plus the coupons to be processed. The drum is then closed and turned at constant rpm for up to an hour. Rumbling reduces the surface roughness by both knocking loose the powder particles which are attached to the surface of the parts, and by compressing the surface of the parts. These samples were abbreviated to *Va* and *Ha*. Rumbling is a common method used by additive manufacturers to reduce the surface roughness of samples.

The smooth surfaces were prepared by taking five horizontal and vertical samples and repurposing them by removing the epoxy from the surface by mechanical abrasion. They were then polished to an *Ra* roughness of around 0.4 microns. These samples were abbreviated to *S* for smooth.

The NaTESI anodised surfaces were prepared by using five vertical build samples and anodising them in a NaTESI solution at 10v for 15 min. This process is described in section 3.3.4. These samples were abbreviated to *A*.

The meshed surfaces were generated using Autodesk's *WITHIN MEDICAL* software. The *Trabecular Topology lattice* was used with thickness set to 0.3mm (beam spot size), and target pore size set to either 0.2mm, 0.3mm or 0.4mm respectively. The mesh was manufactured using an Arcam Q10 plus machine using the point-net melting theme, and a 50-micron layer height (z-direction build increment per layer). Two different D3165 part geometries were used for the meshed surfaces. One had a bonding surface thickness of 1mm thick mesh, and 1mm solid as shown in Figure 61. The second had a bonding surface thickness of 1 mm of mesh, and 2mm of solid melt, as shown in Figure 62. For this revised sample, the extra 2mm of solid melt stiffened the joint reducing the bending moments. The meshed samples were abbreviated to *02*, *04*, *03** and *04**.

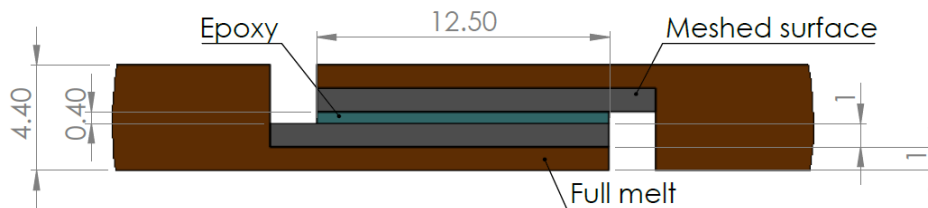


Figure 61: Dimensions of the 02 and 04 meshed samples with a bonding surface thickness of 1mm mesh, 1mm solid

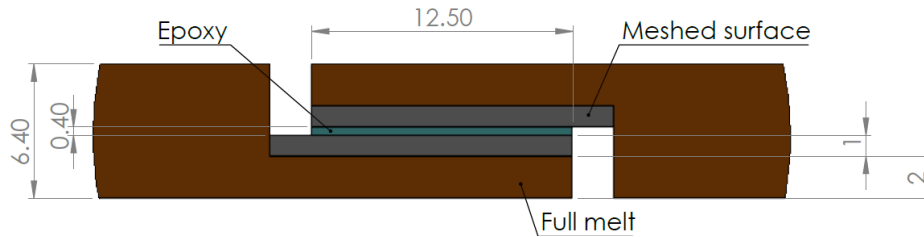


Figure 62: Dimensions of the 03* and 04* stiffened meshed samples with a bonding surface thickness of 1mm mesh, 2mm solid

3.2 The bonding procedure

The coupons were cleaned and degreased by soaking them in acetone for five minutes prior to hot air blow-drying and adhesive bonding. It should be noted that it is industry standard to slightly etch the surface prior to bonding to remove any oxide scale. This is often called pickling or descaling (both are reducing reactions) and for titanium this is normally carried out as per ASTM B600 using a mixture of 30 pbv (70% HNO_3) to 3 pbv (50% HF), where pbv stands for parts by volume.

For 1 litre this would be 300ml (210ml HNO₃ : 90ml H₂O) : 30ml (15ml HF : 15ml H₂O) : 670ml H₂O with the H₂O being deionised water (Bennett, Jay, Figert, John, & NASA, 2007). This results in a 2% HF and 27% nitric acid solution, which although having health and safety risks, is manageable with the correct lab setup. Unfortunately, it was a limitation of this study that the use of HF and nitric acid was prohibited by the university, therefore it is unknown whether the passive oxide layer affected the adhesive bonding strength values obtained.

A custom rig was designed and manufactured to align samples in the correct orientation to one another, and so that the bond line gap could easily be adjusted with shims (see Figure 63). This was built by milling 28x 5.2mm holes into a 12mm thick mild steel plate using a CNC machine. M5x12mm dowel pins were then placed into these holes, and used to constrain the movement of the coupons.

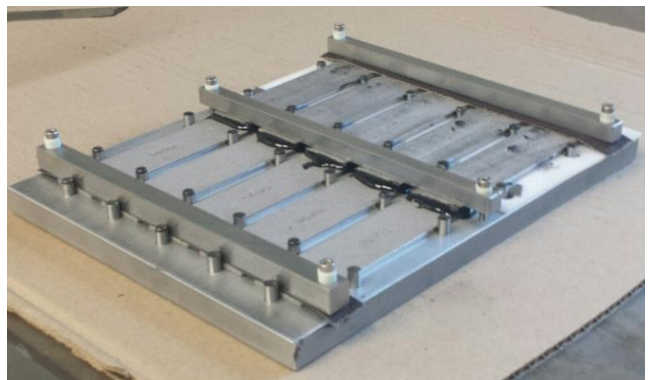


Figure 63: Custom rig for controlling alignment and bonding gap

The HPR 25B adhesive which was used was obtained from “ADHESIVE TECHNOLOGIES NZ LTD.” It required seven days at 20-25°C to reach initial cure, then six hours at 60°C to reach the glass transition temperature which provided full strength (see Figure 64) (ADHESIVE TECHNOLOGIES NZ LTD, 2018). The average failure stress given by the manufacturer for the HPR 25 adhesive was 15.9 MPa.

HPR 25B		ASTM D1002 8 samples 25.0mm wide; overlap 12.2mm
Pot Life 100g @ 20°C	35min	
Thin Film 20°C	3hrs	Failure Stress 15.9MPa ($\sigma = 0.3$) Mode of Failure 80% Adhesion 20% Cohesion ($\sigma = 8.6$)
Typical Cure Cycle	7 days @ 25°C	
Ultimate Performance Cure Cycle	6hr @ 60°C	
Ultimate HDT	75°C	

Figure 64: HPR 25B product specifications (ADHESIVE TECHNOLOGIES NZ LTD, 2018)

15 grams of adhesive was normally prepared from a mix ratio of 1-part hardener to 4-parts resin. This could be considered a small pot size and could be a possible loss of control in the experiment. Further, no autoclave was used, meaning air bubbles were also present in the adhesive (see Figure 65). These bubbles would have acted as stress raisers during loading, reducing the overall performance of the adhesive. However, despite this reduction in overall strength, the comparison between the surfaces should not be affected, as each surface would have been equally impaired by bubbles.

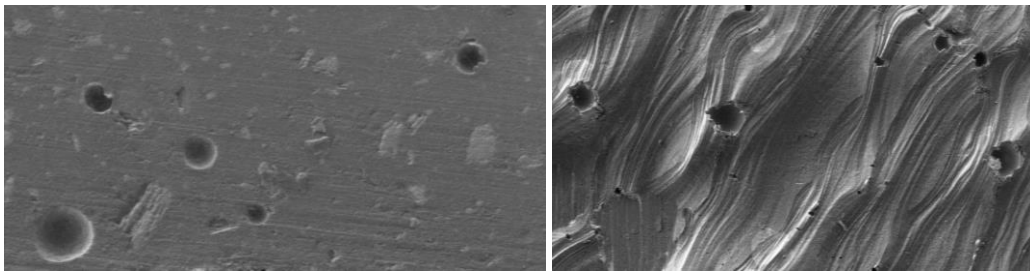


Figure 65: Left – epoxy cross-section of H1 test coupon; Right – epoxy surface of H1 coupon

3.3 Limitations of the experiments

3.3.1 The D1002 (eccentrically loaded SLJ) experiment limitations

- The samples, when bonded, had the adhesive overflow pass the 12.5mm overlap bonding area, increasing the surface area that was resisting the applied force. This error occurred because it is standard practice to bond parts for service with an overflow area. However, for laboratory testing, it is supposed to be excluded. To account for this

error, the real surface area resisting deformation was calculated using the surface area measurement tool in SolidWorks (see the orange areas in Figure 66).

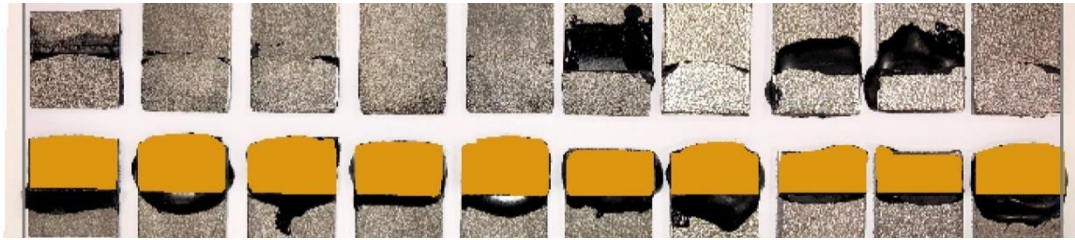


Figure 66: Failed D1002 samples, with the calculated bonding surface area shown in orange

- The adhesive was mixed in a small batch size of 15g. No minimum batch size is specified by the manufacturer, but some adhesives do experience varied properties when mixed in small amounts.
- No autoclave was used. The utmost care was used in mixing the resin with the hardener. However, the adhesive still had air bubbles present.
- The bonding preparation was carried out differently for three samples. These samples had the adhesive applied to both the top and bottom coupons using a push and scrape method. For the other samples, adhesive was only applied to the bottom with the top coupon being placed on top of it. The push and scrape resulted in higher strength values.
- The surfaces were only degreased with acetone and it was not confirmed whether this removed all contaminants from the surface.
- The EBM manufacturing process produced parts with slight deviations from the exact CAD model it was given. Although care was taken to manually grind and sand the parts to dimension, some variations existed between samples. In addition, the surface roughness of the parts deviated within +/- 10% Ra surface roughness when compared to one another. This was an unavoidable manufacturing variance, which reduced consistency between the samples.

3.3.2 The D3165 (eccentrically loaded SLJ) experiment limitations

- The adhesive was mixed in small batch sizes of 15g – 12g white resin to 3g black hardener. No minimum batch size was specified by the manufacturer, but some adhesives do experience varied properties when mixed in small amounts.
- No autoclave was used. The utmost care was used in mixing the resin with the hardener. However, the adhesive still had air bubbles present.
- Surfaces were only degreased with acetone and it was not confirmed whether this removed all contaminants from the surface.
- The EBM manufacturing process produced parts with slight deviations from the exact CAD model it was given. Although care was taken to manually grind and sand the parts

to dimension, some variations existed between samples. In addition, the surface roughness of the parts deviated within +/- 10% Ra surface roughness when compared to one another. This was an unavoidable manufacturing tolerance, which reduced consistency between the samples.

3.4 Testing equipment

Testing was conducted using a Tinius Olsen H50KS tensile testing machine. The data was then exported into an excel file for further analysis. The stress was assumed to act uniformly over the shear area of the coupons, giving an apparent shear stress value calculated from the failure force over the shear area. A tensile jaw speed of 1.3 mm/min was used for every test.

A Hitachi SU-70 Schottky field emission scanning electron microscope (SEM) was used for high magnification surface and cross-sectional imaging of the shear tested coupons, and for characterising the Group 4 surface roughness of the samples. Due to the insulative nature of the epoxy, lower accelerating voltages were used for samples with adhesive remaining on the surface. For the NaTESI samples, due to the insulative nature of titanium dioxide and epoxy, the surface was coated with platinum through physical vapor deposition (magnetron sputtering). This was done to avoid a charging effect, which blurs the image. A low voltage and a very close focal length were also used for high magnification above x6000 times.

A Taylor Hobson Talysurf profilometer was used for measuring the Group 3 surface roughness, ranging from (1µm - 500µm). Three 10mm surface roughness tests were done per sample in two primary directions (along the width and length). The three values taken in each direction were then averaged. The sample average was then taken by combining and averaging these direction-based results. The roughness measurements taken were:

- Arithmetic Average (Ra). This is the average area per unit length that is off the mean centre line, see Figure 67. It can also be calculated by the average height;
- Root means squared (RMS), also known as (Rq). This is the root of the squared sum of heights from the mean line, over the length of sampling;
- Peaks and valleys (Rz). The average value of the absolute values of the five highest heights and deepest depths over the sampling length.

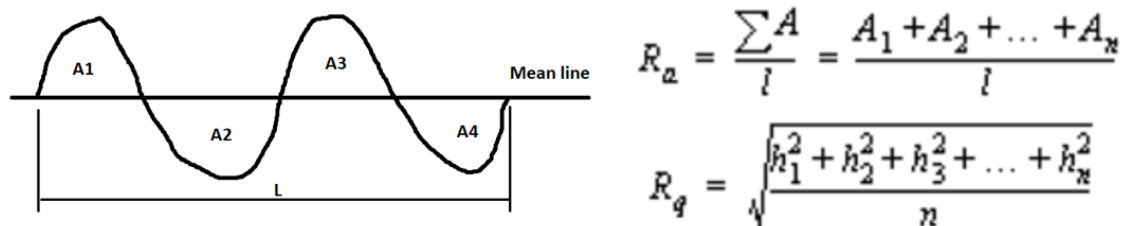


Figure 67: A surface with the mean line and surface areas calculated. The formula for Ra and Rq

3.5 Anodising method

This section describes how the Grade 5 titanium samples were anodised. The objective of this process was to grow a titanium oxide layer in a controlled and repeatable manner to improve the specific and mechanical adhesive bonding properties of the surface. Multiple tests were also conducted to investigate anodic colouring. This was because errors are clearly visible in the coloured samples. Therefore, they were used to understand the anodising process and to develop the correct set-up method and technique. However, data from the colouring experiments are not listed in this thesis due to word limitations.

For improving the adhesive bonding properties, the NaTESI anodic surface treatment was used. During the NaTESI anodising, the samples are actively etched as the anodic layer grows. This allows the current to continue flowing and subsequently a thicker oxide layer to grow. Unfortunately, because the current never dropped in the NaTESI experiments, the current could not be used to confirm that samples are free from contamination. However, the final anodic coatings were uniform in colour and shade, which from the anodic colouring experiments would suggest the surface was free from contaminants.

3.5.1 Safely anodising

Anodising takes place with enough electrical potential to cause an electric shock. The following overviews how electricity interacts with the human body.

“Current” refers to the amount of electricity (electrons or ions) flowing per second. Current is measured in amperes (A) or milliamperes (mA) ($1\text{ mA}=1/1000$ of an ampere). The amount of electric current that flows through the body determines the various effects of an electric shock (Jiang & Brazis, 2018). As listed in Table 10, the magnitude of the current dictates the physiological effect. Most current-related injuries result from the heating of tissues and stimulation of muscles and nerves (Jiang & Brazis, 2018). Stimulation of nerves and muscles can result in cardiac arrest, respiratory problems, or injury from a fall due to recoil from pain. Only small amounts of current are needed to cause physiological effects, as shown in Table 10. It takes a thousand times more current to trip a 20-A circuit breaker than it takes to cause respiratory arrest, hence care must be taken when conducting this experiment.

Table 10: Physiological effect of different shock currents (Jiang & Brazis, 2018)

Current	Required Voltage		Comments	
	1,000 Ω	100,000 Ω		
1 mA	1 volt	100 volts	Threshold of feeling, tingling sensation.	
15 mA	5 volts	500 volts	Maximum current level a human can withstand before sustaining injury.	
15-20 mA	10 volts	1000 volts	Beginning of sustained muscular contraction ("Can't let go" current.)	Extreme Pain
100-300 mA	100 volts	10,000 volts	Ventricular fibrillation, fatal if continued. Respiratory function continues.	
6 A	6000 volts	600,000 volts	Sustained ventricular contraction followed by normal heart rhythm. (defibrillation). Temporary respiratory paralysis and burns.	Burns, Permanent Damage, or Death

8

As a rule of thumb, shock current can be calculated using Ohm's law where:

$$\text{Shock current } I = (\text{Voltage } V) / (\text{Resistance } \Omega)$$

V = volts, A = amps, Ω = Ohms

Below in Figure 68, the human body is shown as a resistor. Shock current can be calculated using Ohm's law. The wetness of the skin dramatically reduces a human's resistance increasing the shock current.

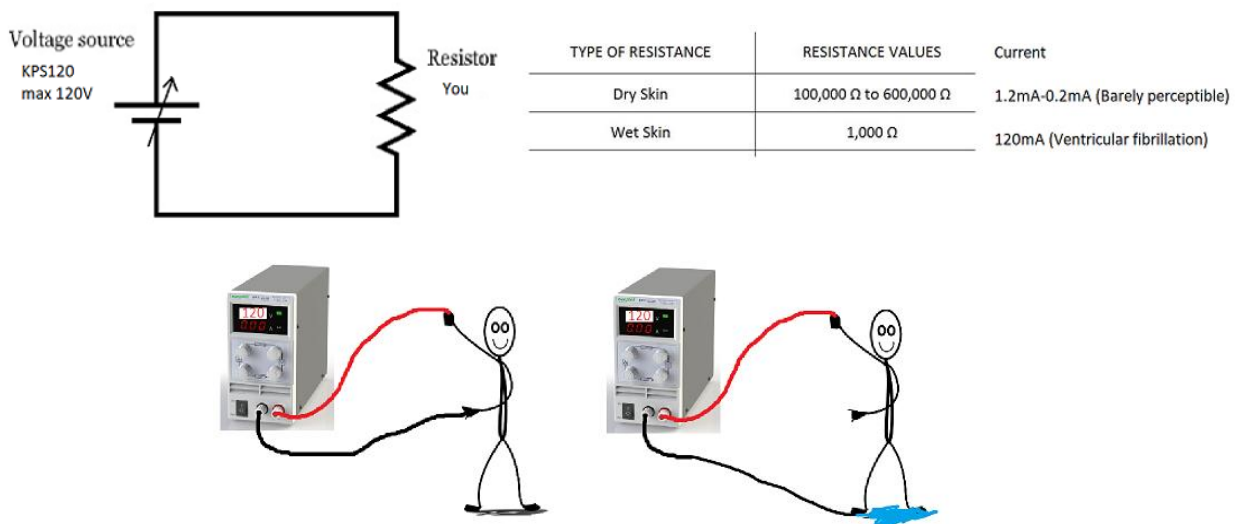


Figure 68: For a voltage supply of 120v, the human body being treated as a resistor and wet skin increasing the shock current

To avoid a shock, avoid touching the positive and negative terminals and ensure the human body is highly resistive and the least favoured path for the electricity to flow. For safety the following points must be adhered:

- Avoid touching either of the terminals (Air and a large gap between you and the terminals has the highest level of resistance)
- Wear gloves
- Be dry
- Wear boots
- Stand on a rubber mat

3.5.2 Anodising equipment

A Wanptek KPS1203D power supply was used for the experiment. This is shown below in Figure 69. This power unit had two methods of providing power, these were:

- C.V (Constant voltage setting) – When illuminated the unit was generating a constant voltage. Current dropped as resistance increased i.e. as the anodic layer grew.
- C.C (Constant current setting) – When illuminated the unit was generating a constant current. The voltage increased or decreased to maintain the selected current i.e. as the anodic layer grew, the voltage would increase to maintain current.

The NaTESI experiment was conducted using the C.V method.

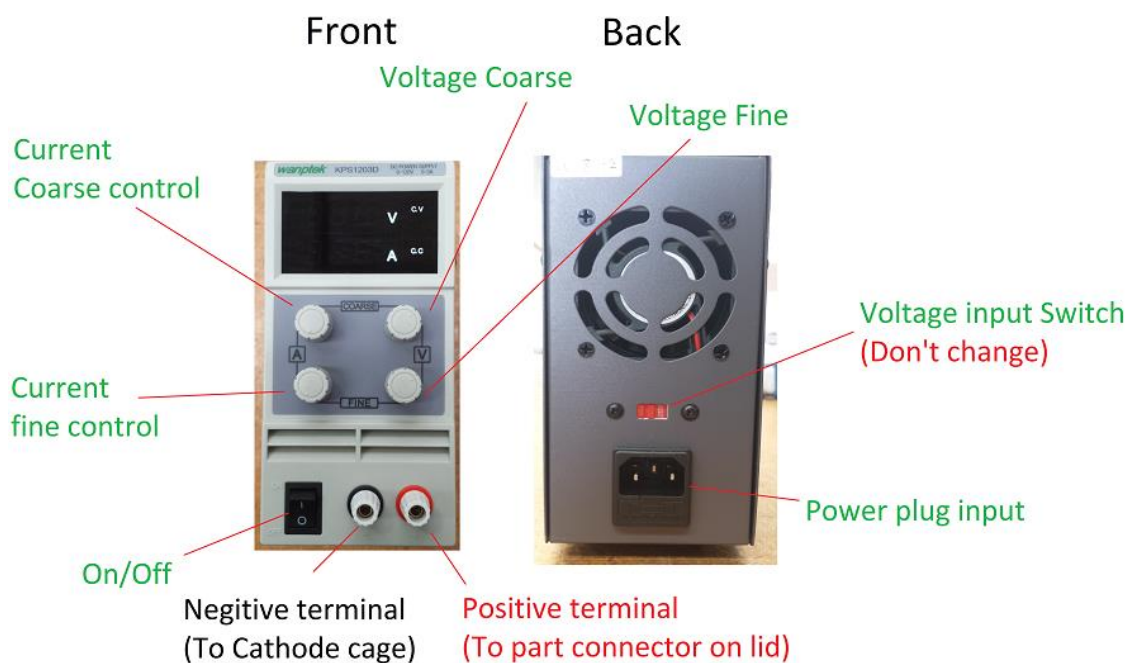


Figure 69: The Wanptek power supply

The voltage input switch at the back of the machine was operated on 230v mode for its supply input.

A custom anodising unit was produced which is shown in Figure 70. This consisted of a HDPE container, with an EBM printed Grade5 titanium cathode cage. Audio banana plugs were used for easy connection and disconnection of the supply from the cell. For operation, the red positive cable (red banana plug) was connected to both the Wanptek unit's red positive terminal and to the red terminal located on the lid of the anodising unit. Then the black or negative cable (black banana plug) was connected from the Wanptek unit to the black terminal located on the side wall of the anodising unit. The complete anodising setup used is shown in Figure 71.



Figure 70: Custom anodising unit



Figure 71: Complete anodising setup

CP titanium TIG wire was used for racking and supporting the parts being anodised. Stainless steel wire could not be used as it leeched current away from stimulating the anodic layer growth, increasing anodising times. The CP Ti wire was reusable, it just required the oxide layer to be removed before use so that it could continue to conduct electricity. This was either mechanically removed or chemically removed by soaking in lye (sodium hydroxide).



Figure 72: CP titanium TIG wire

For anodising to be successful the parts had to be clear of all non-titanium contamination. Therefore, for the NaTESI experiments all parts were anodised directly after the parts were blasted with titanium powder during the powder recovery phase of the EBM manufacturing. This was done instead of the standard process of using hydrofluoric and nitric acid etching, which was not allowed by the university.

It was proven that blasting could remove the coloured anodic surface coating and therefore it was assumed that it would be capable of removing a passive oxide layer or contamination from the surface. Either way contamination would have been very low for a part just leaving the build chamber. Contamination results in shading differences or surface textures to be present on the anodised parts, as the anodic layer cannot grow uniformly. For the NaTESI parts, the shading, colour and surface texture was consistent confirming that the oxide layer was most likely free of contaminants.

All anodising requires an electrolyte to carry the electrical potential and to cause an oxidation reaction at the titanium's surface. The chemicals were mixed in accordance with the AAA rule (Always add acid), which was extended to the bases used as well. This practice of always adding the acid or base to the water and not the other way around was used because when water is added to an acid or base, a concentrated solution is formed, which due to the mixture causing an exothermic reaction, will cause the solution to rapidly boil splashing concentrated acidic material out of the container and possibly onto the person responsible.

Parts were attached to the lid using the CP Ti wire. The wire was always cleared of any surface oxide prior to anodising. This racking method worked well for attaching parts as the wire was springy and therefore secured the parts with its elasticity as shown in Figure 73.



Figure 73: A part being racked on the anodising lid using a piece of CP titanium wire

3.5.3 Anodising errors and tips

When anodising for colouring purposes, a successfully grown anodic layer was confirmed by the current flow reaching zero or close to zero (0.01-0.02A). However, some attempts failed to grow a uniform layer and soot was observed on the tips of these samples. Here, the brown soot material provided a pathway for the current to flow and therefore the current would not drop below 0.2A impeding the growth of the anodic layer. The iron oxide soot can be seen in Figure 74.



Figure 74: Left – sample before anodising; Middle- Wanptek unit showing the current not reducing below 0.2A; Right – The failed anodised part with brown iron oxide soot on the tip

This soot was found to have occurred due to the problem parts being built directly onto the start plate without any form of support structure. Here, diffusion of iron from the start plate into the titanium took place and when anodised this iron would oxidise into iron oxide soot. To fix this, either the first few mm of material that was in contact with the start plate had to be mechanically removed, or at least 20mm of support was needed when printing.

Another issue occurred when anodising at voltages above 55v in some solutions. Here, the electrolyte started to bubble excessively around the anode. This leached current causing the anodic layer to fail growing correctly. This was due to oxygen evolution which was being generated due to the high electrical conductivity of the electrolyte solution. Using distilled water and a lower concentration of electrolyte fixed this issue. For higher voltage ranges it is important to use less electrolytes even though it will consequently increase the anodising time. This was only relevant to the colouring experiments used to design the controls for the NaTESi experiment. The NaTESi anodising took place at a low enough voltage of only 10v therefore this oxygen evolution problem did not occur.

For the NaTESi Anodising, due to the active etching rate, the current never dropped below 0.25A. Therefore, because of this, contamination could not be observed by noting the current. Instead a constant voltage of 10v and a time of 15min was used.

3.5.4 NaTESi anodising

The NaTESi anodising method created by Matz (1988) was used for this experiment. For this the final NaTESi solution had a pH of ~12.3. It was mixed using a 1 litre polypropylene volumetric flask by adding 500ml of deionised water. To this, 300g of NaOH (7.5 M), 65g of Na-tartrate (0.33 M), 30g of ethylene-diamine-tetraacetic acid (EDTA) (0.1 M) and 6g of Na₂SiO₃ (0.05 M) was slowly added, then deionized water was added to make 1 litre.

NaTESi anodising	NaOH (7.5M) 300g	Na-tartrate (0.33M) 65g	EDTA (0.1M) 30g	Na ₂ SiO ₃ (0.05M) 6g	H ₂ O (fill to 1L)
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The mixing of these chemicals was exothermic, so to control the temperature the polypropylene volumetric flask was placed in an ice bath and the temperature maintained at 30°C. The NaTESi anodising was carried out using a constant voltage of 10v for 15 min. After anodising the samples were rinsed in deionised water for 5 mins and oven dried at 60°C. Bonding was then carried out using the same method described for the D3165 samples in chapter 3.2.

3.6 Simulation parameters

The purpose of the simulation was to highlight how the geometry of SLJ joint affects the failure strength of the bond, the stress concentration points, and how these give way to a failure path. The aim was not to simulate the exact material combination and surface morphology response to loading but to demonstrate a simplified model showing how a bond can be improved through geometric changes.

The simulations were carried out using ANSYS Workbench Student 2019 R1 v19.3, using the Static Structural Analysis System. The main limitation of the simulation used was that Ansys

student is restricted to only 32,000 elements. Therefore, the stress distribution of the adhesive was limited to just the outer contact points, giving little detail of the stress distribution within the bulk of the adhesive. However, as the intent was to simulate how the geometry of the joint interacts with loading, specifically due to the eccentric loading, more elements were not required.

The mechanical properties used for both simulations are shown in Table 11. For the adhesive this was a Young's modulus (E) of 52 MPa, Poisson's ratio (ν) of 0.3, Shear modulus (G) of 20 MPa, and a Yield stress of 14 MPa. A Bilinear Isotropic hardening effect was also added to simulate a nonlinear plastic range, here the tangent modulus (E_t) was set to 0.024 GPa. The value for the Young's modulus (E) was very low at only 0.052 GPa, placing the adhesive in the material category of rubber, instead of the normal epoxy category of being a stiff polymer with a Young's modulus of 3 GPa. This low modulus was selected as the HPR25 adhesive used in the experiments was a rubber-toughened liquid epoxy (ADHESIVE TECHNOLOGIES NZ LTD, 2018). Figure 75 visually explains this by showing the failure surface with the micro rubber particles coloured in red. These particles are about 30-60 microns in width and are present uniformly throughout the adhesive.

Table 11: Mechanical properties used in the simulation

Material	Rubber toughened HPR 25 epoxy	EBM Ti-6Al-4V
Young's modulus (E)	52 MPa	120 GPa
Poisson's ratio (ν)	0.3	0.36
Shear modulus (G)	20 MPa	44 GPa
Yield stress	14 MPa	840 MPa
Tangent modulus (E_t)	24 MPa	none

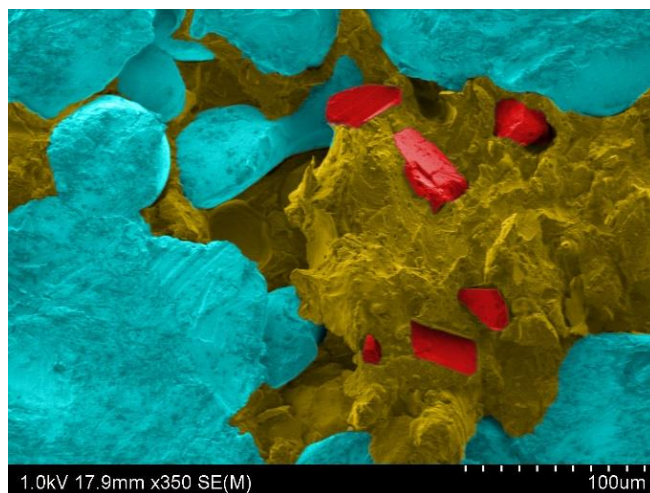


Figure 75: SEM failure surface showing HPR25 epoxy with titanium in blue, epoxy in yellow and rubber particles coloured red.

A bonded contact was used between the two titanium substrate bodies and the adhesive body. For a more realistic simulation Cohesive Zone Modelling (CZM) could have been used instead. However, CZM requires test data about the adhesive for defining the material properties, and this data was not available. Additionally, as the purpose of the simulation was to simply show how the geometry affected the stress distribution, the bonded contact was enough.

A body sized mesh of 0.5mm was applied to the adhesive region, and a body sized mesh of 2.5mm was applied to the titanium bodies, as shown in Figure 76. This was done to provide higher resolution of the stress in the adhesive, where the most deformation was taking place. Smaller elements would have been used were the number of elements available in the Ansys student version greater.

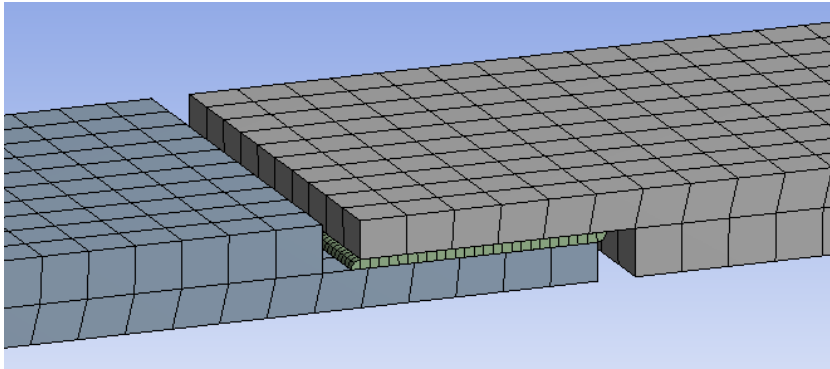


Figure 76: Mesh sizing for simulation

A fixed support was applied to the end of one titanium substrate. Frictionless supports were added to the top and bottom surfaces 25mm from the ends. These supports and the force which was applied to the opposite end are shown in Figure 77.

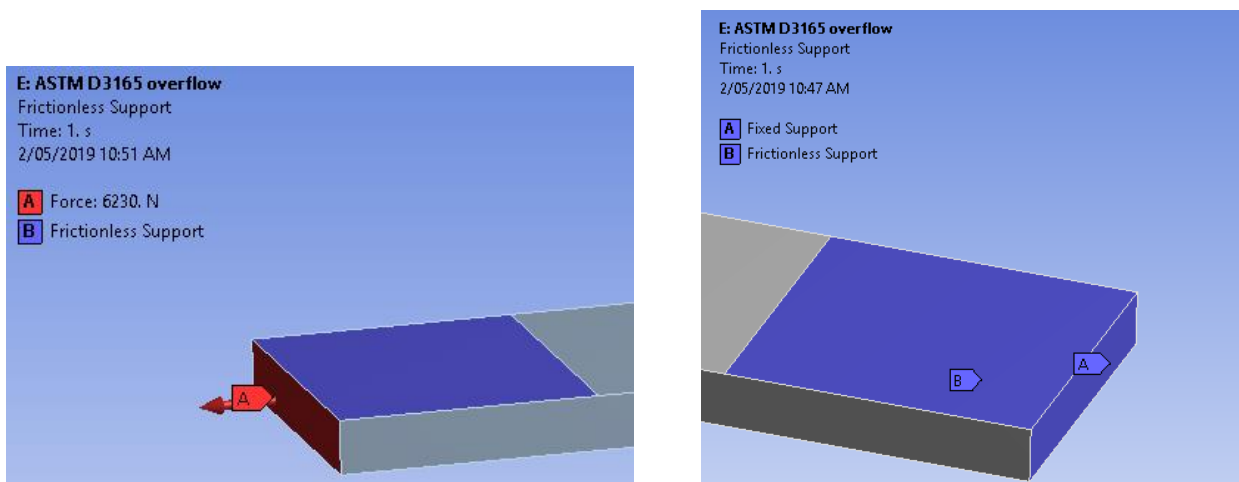


Figure 77: Left - Force applied to SLJ. Right - Supports used for SLJ.

A mesh sensitivity study was not run as the number of elements in the simple configuration already neared the maximum element limit.

The following section will cover the preliminary experiment carried out to investigate the different surface morphologies in this study.

3.7 Preliminary experiment – surface morphology of samples

This section will present the results of the preliminary experiment, which was carried out to define the surface morphologies of the 10 different surfaces studied. The results of this experiment are then analysed in Chapter 4 – along with the shear strength results – to explain how the different surface morphologies affected the bonding strength of the two SLJs.

The shape and build orientation of the ASTM D1002 and D3165 samples were printed, as shown below in Figure 78. The bonding surfaces were named the “vertical” and “horizontal” surfaces, due to the respective surfaces being orientated parallel to either the vertical or horizontal planes, as described in section 2.2.2. The different surface morphologies were defined by taking SEM images of each sample type under different magnification ranges. For each magnification range, the overall qualitative nature of the surface was characterised, as defined in section 2.10.

Figure 78 shows the vertical build had the highest micro surface roughness, due to the outer contour melt pool overlapping with powder particles. The horizontal build had the lowest micro surface roughness, having no beam overlap. Instead, the horizontal surface is formed of multiple thin weld-lines in the hatching pattern of the final layers beam path.

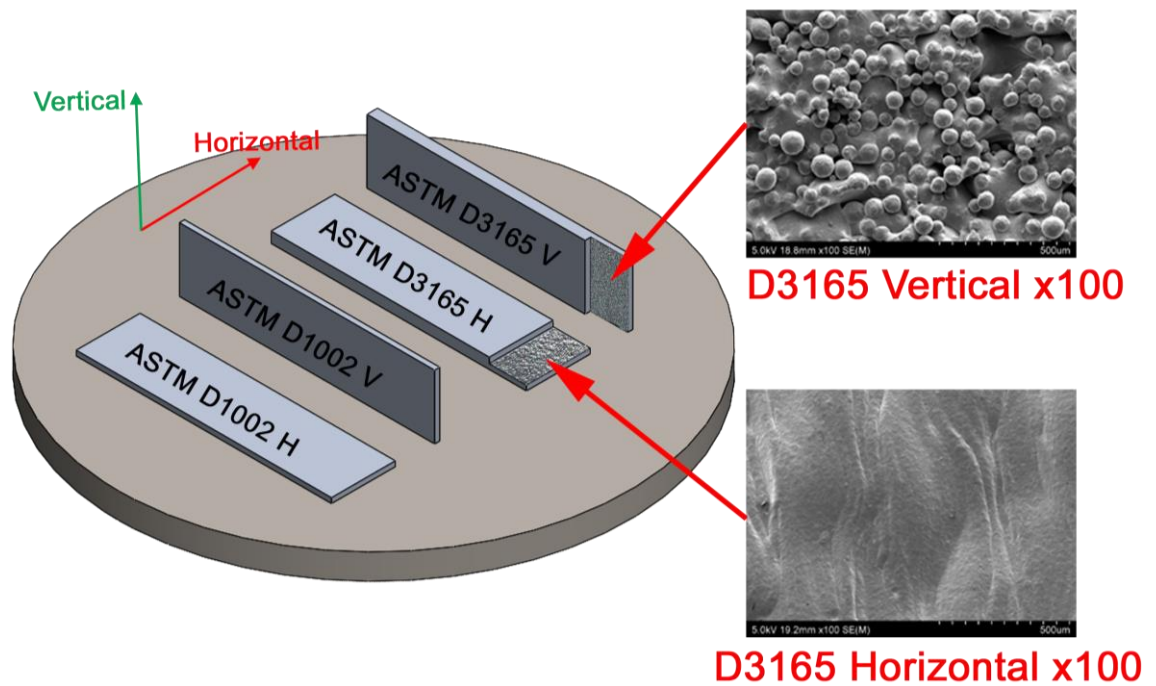


Figure 78: Test coupon build directions, with resulting vertical and horizontal surface morphologies

Figure 79 overviews the meshed and NaTESI modified surfaces. For the meshed surface, as expected, it had a porous and rough macro surface roughness. For the NaTESI modified surface, being derived from vertical samples, the macro and micro surface roughness was unchanged. However, at the nano scale, the surface became very porous and rough.

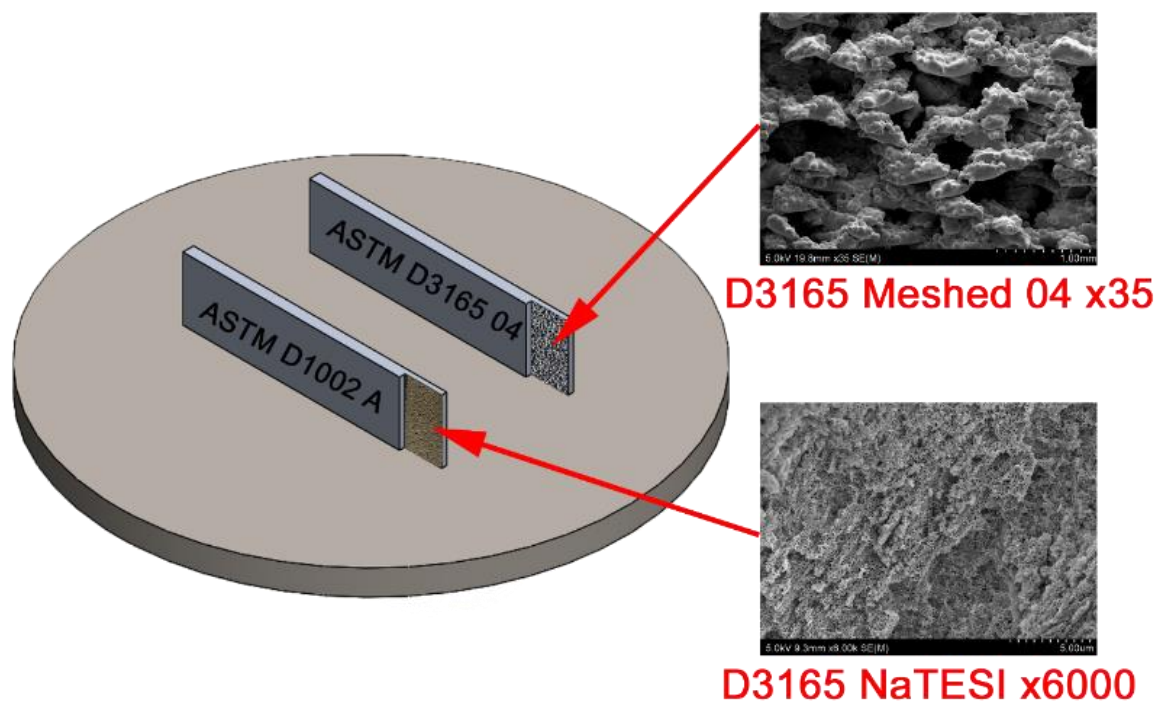


Figure 79: The surface morphology of the meshed and NaTESI modified vertical build samples

Figures 80-83 (below) visually present the surface roughness of the different sample types at different magnification levels, with tables 12-14 describing the surfaces. (Refer to section 2.10 for an explanation of the MS, PS, WS and FS surface structures.)

Figure 80 shows the macro-qualities of the surfaces under x0-x100 magnification, with Table 12 defining the qualities of the different surface types.

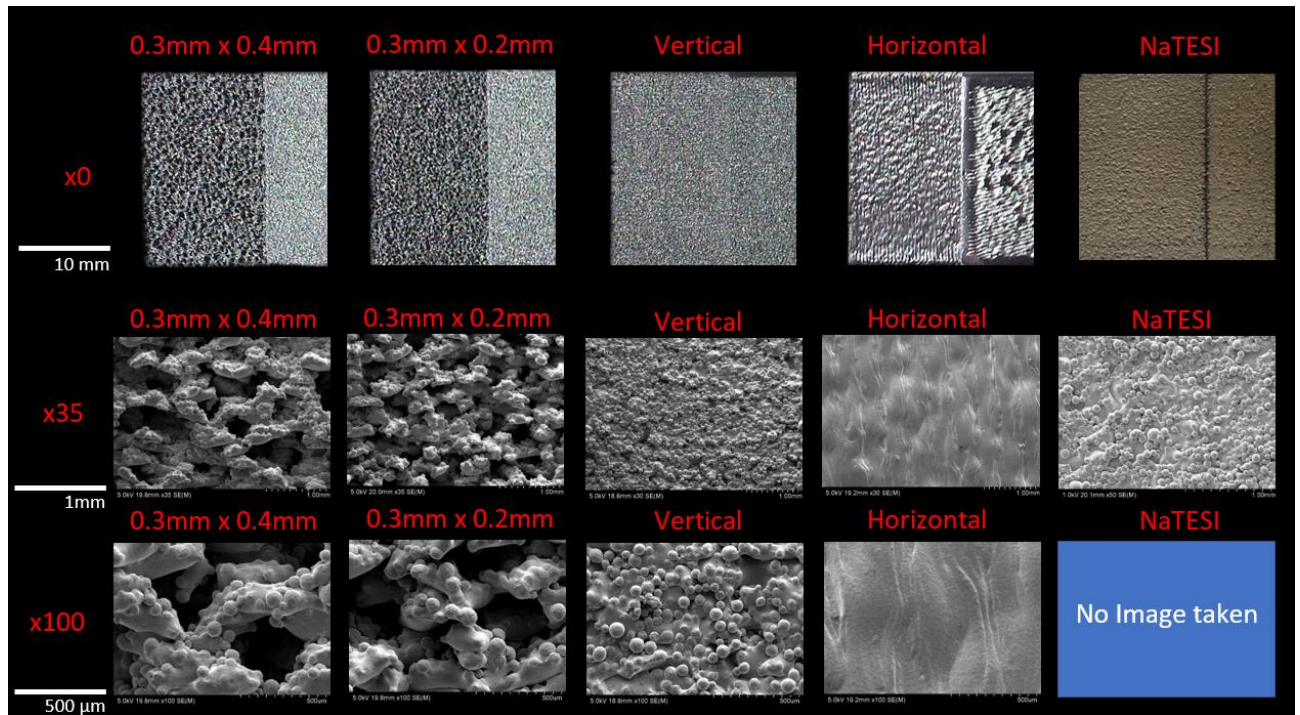


Figure 80: SEM surface images under x0-x100 magnification giving the macro/micro surface morphology

Table 12: The surface structure of the samples from 0x-100x magnification

	04	02	Vertical	Horizontal	NaTESI
Macro-roughness morphology (x0-x100 magnification)	MS surface with 0.3mm struts and 0.4mm pores.	MS surface with 0.3mm struts and 0.2mm pores.	PS surface, ~325 particles/mm ² , average particle diameter of 70μm, joint mid-way through particle. ~Ra of 15 μm	WS surface, ~300μm spacing, with an 8μm amplitude. ~Ra of 5 μm	PS surface, ~200 particles/mm ² , average particle diameter of 70μm, joint mid-way through particle. ~Ra of 12 μm

Figure 81 shows the micro-qualities of the surfaces under x500 magnification, with Table 13 defining the qualities of the different surface types.

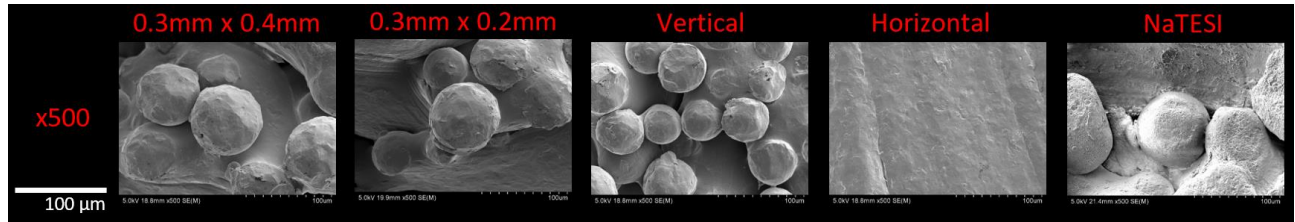


Figure 81: SEM surface images under x500 magnification giving the micro surface morphology

Table 13: The surface structure of the samples at x500 magnification

	04	02	Vertical	Horizontal	NaTESI
Micro-roughness morphology (x500 magnification)	PS surface on struts, ~100 particles/mm ² , average particle diameter of 70μm, joint mid-way through particle.	Like 04.	PS surface, ~325 particles/mm ² , average particle diameter of 70μm, joint mid-way through particle.	FS surface, no protruding structures.	PS/MS surface, ~200 particles/mm ² , average particle diameter of 70μm, joint mid-way through particle. Visible Nano surface consisting of a very fine porous surface roughness.

Figure 82 shows the micro/nano-qualities of the surfaces under x6000 magnification, with Table 14 qualitatively defining these surface qualities. At this magnification level, the meshed, vertical and horizontal surface morphologies became identical, being flat surface structures. However, the NaTESI surface just begins to show its nano-structured surface roughness.

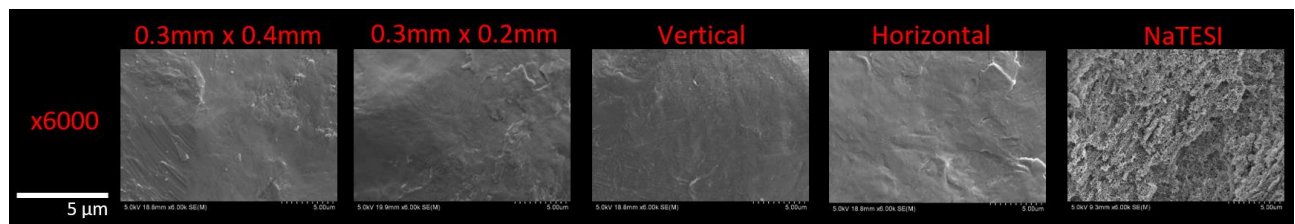


Figure 82: SEM surface images under x6000 magnification giving the micro/nano surface morphology

Table 14: The surface structure of the samples from x6000 magnification

	04	02	Vertical	Horizontal	NaTESI
Nano/micro-roughness morphology (x6000 magnification)	FS surface, no protruding structures.	FS surface, no protruding structures.	FS surface, no protruding structures.	FS surface, no protruding structures.	MS surface consisting of a very fine porous surface roughness with ~50nm struts and ~100nm pores.

At these different magnification ranges, the adhesive interacts with the surface differently, affecting whether the bond is mechanically-interlocking-dominant or specific-adhesion-

dominant. Figure 83 compares the surface of the standard vertical sample to the NaTESI sample, which was derived from the same standard vertical sample. In this figure, it is clearly shown that NaTESi anodising, although having a minimal effect on the macro and micro morphology, significantly affected the nano morphology by forming a porous, titanium-oxide meshed structure.

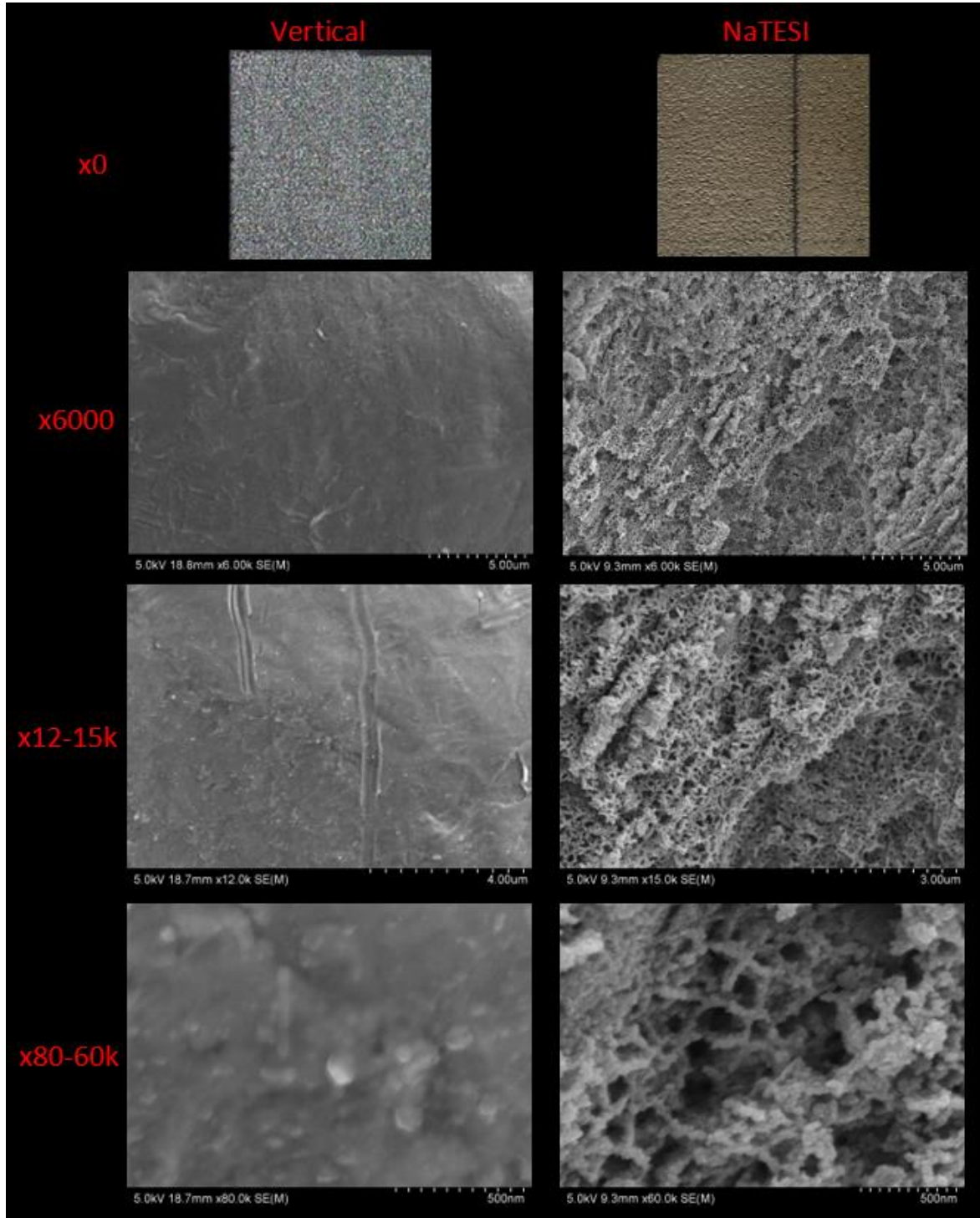


Figure 83: SEM images comparing the standard vertical surface to the NaTESI surface at different magnification levels

3.7.1 Summary of the different surface morphologies

For the as-built, orientation-based surfaces (vertical and horizontal) shown below in Figure 84 (left), the surfaces had distinct differences in surface roughness over the macro and micro range, but an identical surface at the nano range. The vertical build had the highest surface roughness of the two, averaging $R_a \sim 15.5 \mu\text{m}$, due to overlapping powder particles partially melting into the outer melt contour of the part. The horizontal build had the lowest surface roughness, averaging $R_a \sim 6.85 \mu\text{m}$, due to the powder completely melting into multiple thin weld-lines. Although the macro and micro surface roughnesses were different, the nano-roughness of the surfaces was almost identical, as seen in Figure 85, at x6000 magnification.

For the trabecular-meshed surfaces, the macro structure possessed a pore and strut meshed surface lattice, as seen in Figure 84 (right). Additionally, due to the beam profile overlapping with powder particles outside of its outer contour, the struts had a similar micro-roughness to the vertical build surfaces (see x500 magnification in Figure 85). Finally, at x6000 magnification, the nano-roughness was almost identical to the vertical and horizontal surfaces.

For the NaTESI modified vertical surface, the macro and micro surface roughness was unchanged from the vertical build surface which it was derived from, as seen in the x35 and x500 magnifications in Figure 85. However, unlike the three other surfaces, the nano surface roughness changed significantly due to the anodising treatment, with the surface becoming very porous and rough, resembling coral. Here the resulting meshed oxide layer had $\sim 50\text{nm}$ struts and $\sim 100\text{nm}$ pores (see Figure 84). Figure 85 presents an overview of each surface side-by-side at different magnification levels.

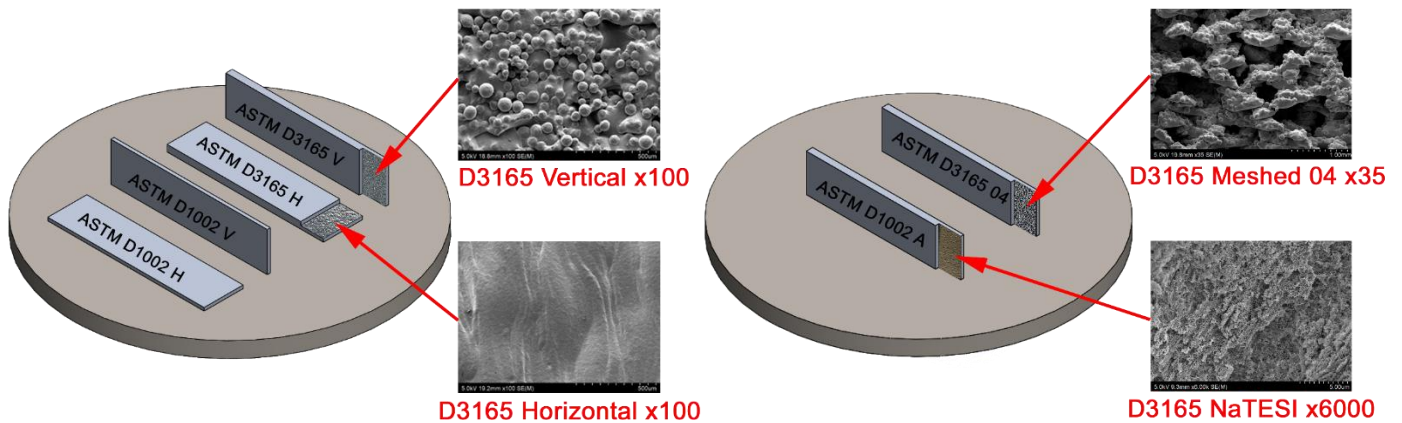


Figure 84: The surface morphology of the vertical, horizontal, meshed, and NaTESI modified vertical build samples

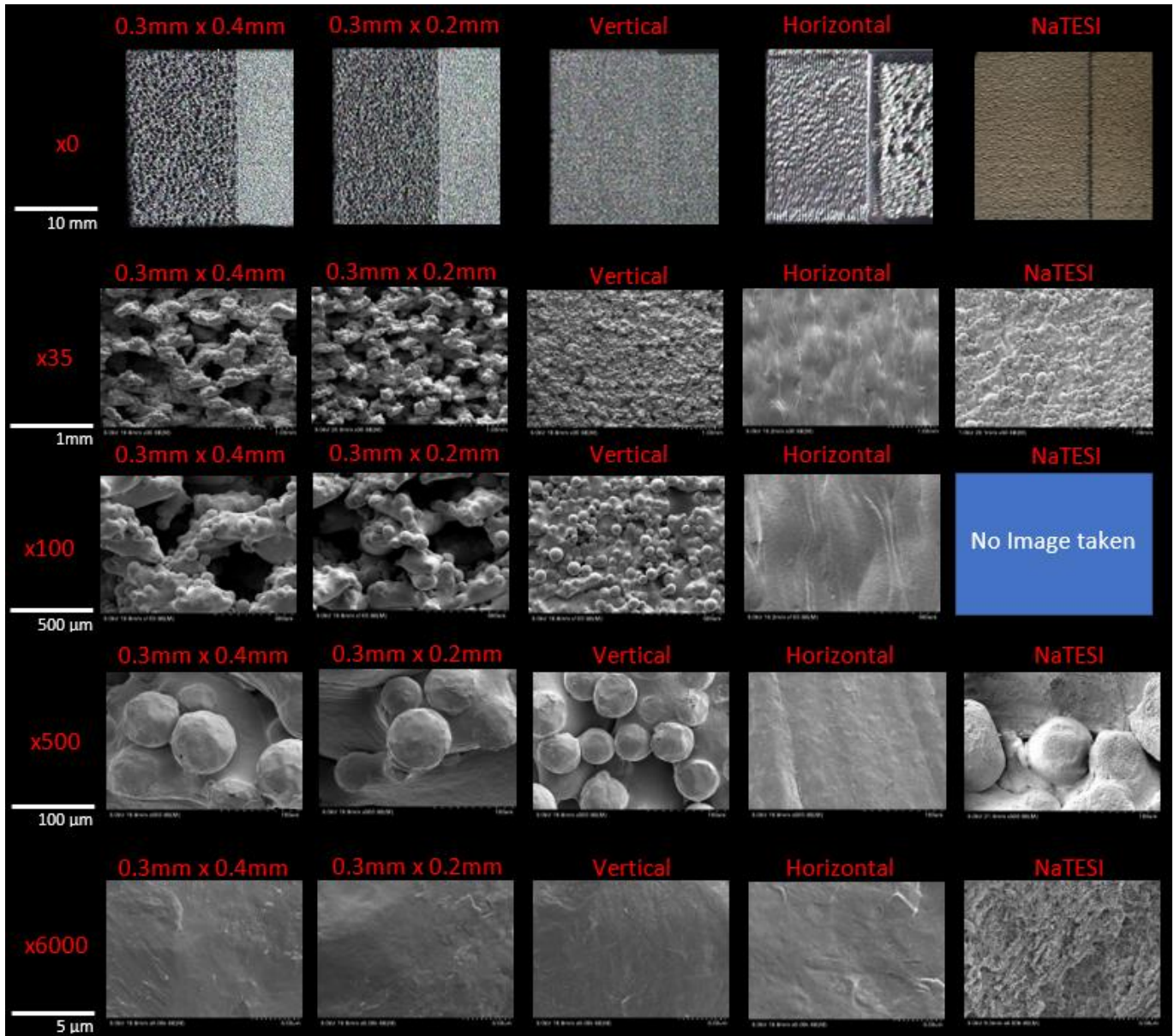


Figure 85: SEM surface images of the four surfaces under x0-x600 magnification showing the macro, micro and nano surface morphology and roughness

To conclude, Table 15 presents the ranking of the four unique surfaces, based on the degree of macro, micro, or nano surface roughness.

Table 15: Ranking of the qualitative surface roughness at macro, micro and nano scales

Surface roughness rank	Meshed	Vertical	Horizontal	NaTESI anodised
Macro	1 st	2 nd	3 rd	2 nd
Micro	1 st	1 st	2 nd	1 st
Nano	2 nd	2 nd	2 nd	1 st

Chapter 4: RESULTS AND DISCUSSION

This chapter presents the shear strength results of the two single-lap-joint adhesive bonding shear strength tests. It relates the characteristics of the surface morphology to the adhesive bonding strength, demonstrating why a particular surface produces a certain result. In addition, it looks at the reproducibility of the strength data, demonstrating how reliable certain surfaces are, and why some surfaces may produce a wide variety of results. Finally, it covers the simulation results highlighting the stress concentration points and failure paths, providing a deeper understanding of how the geometry of the joint affects the failure strength of the bond.

4.1 The effect surface morphology has on the adhesive bonding shear strength of the eccentrically loaded D1002 SLJ samples

Samples were tested for apparent shear strength using an ASTM D1002 eccentrically loaded SLJ shear strength test. Two different strength values were calculated: First, a generic strength value based on the area that the coupons overlapped. Second, a revised shear strength value which used SolidWorks to calculate a more accurate surface area that included the adhesive overflow. This overflow would have aided in resisting the shear forces and therefore needed to be included. This second shear strength value was assumed to be more accurate as it considered the actual material which resisted movement. Revising the strength only affected the V4 sample, all other samples were adjusted by the same ratio.

Before moving onto the results it is important to state that a major processing error occurred in the adhesive joining of the D1002 samples. This error occurred for three of the samples (V4, H2, V5). This error involved the adhesive being applied to both the top and bottom coupons using a push and scrape method. This method would have forced the adhesive into the substrate and may have displaced more air bubbles than the standard method. The standard method involved just placing the adhesive on one of the surfaces and squeezing the samples together. These three samples also showed far higher strength values than the rest of the samples. For the D3165 experiments, the push and scrape method was applied to all samples, and this was believed to improve the experiments reproducibility.

4.1.1 Overview of D1002 (eccentrically loaded SLJ) shear strength and roughness data

As shown in Figure 86, the average Ra surface roughness was higher for all vertical surfaces. Which as explained in section 2.2.2 is the result the process leaving behind a sintered layer of powder on the vertical build direction surfaces due to powder particles overlapping with the beam path and the resulting melt pool. In addition, except for the H2 sample, all vertical surfaces resisted greater stresses than the horizontal surfaces.

surface roughness possessed the best adhesion strength. For Table 17 below, the side with epoxy remaining on it is denoted E and the side with no epoxy remaining is denoted NE.

Table 17: Table of surface roughness results

	Ha E	Ha NE	H1 E	H1 NE	H2 E	H2 NE	H3 E	H3 NE	Va E	Va NE	V1 E	V1 NE	V2 E	V2 NE	V3 E	V3 NE	V4 E	V4 NE	V5 E	V5 NE
Length 1 Ra	7	6	9	8	7	7	12	10	22	10	15	12	17	14	21	15	17	17	16	14
Length 2 Ra	8	6	10	5	8	6	9	11	19	11	15	16	18	15	17	15	18	13	16	16
Length 3 Ra					7		12	10	15	8	14	15	21	16			17	15		
Length ave	7	6	10	7	7	6	11	10	18	10	15	14	19	15	19	15	17	15	16	15
Sample length ave	7		8		7		11		14		14		17		17		16		15	
Width 1 Ra	10	8	6	8	11	8	8	8	17	12	16	12	21	15	18	17	19	18	16	15
Width 2 Ra	11	8	7	9	10	9	8	7	17	11	15	16	14	17	19	13	19	16	18	15
Width 3 Ra					10		7	7	20	10	17	17	19	17			17	19		
Width Ave	10	8	6	8	10	9	8	7	18	11	16	15	18	16	18	15	18	18	17	15
Sample width ave	9		7		9		7		14		15		17		16		18		16	
	Ha		H1		H2		H3		Va		V1		V2		V3		V4		V5	
Ra ave	7.91		7.65		8.15		9.05		14.30		14.90		16.99		16.73		17.00		15.70	

As shown in Figure 87, except for the H2 outlier, there appears to be a correlation between the surface roughness and shearing strength. However, there are too few data points to give absolute causality.

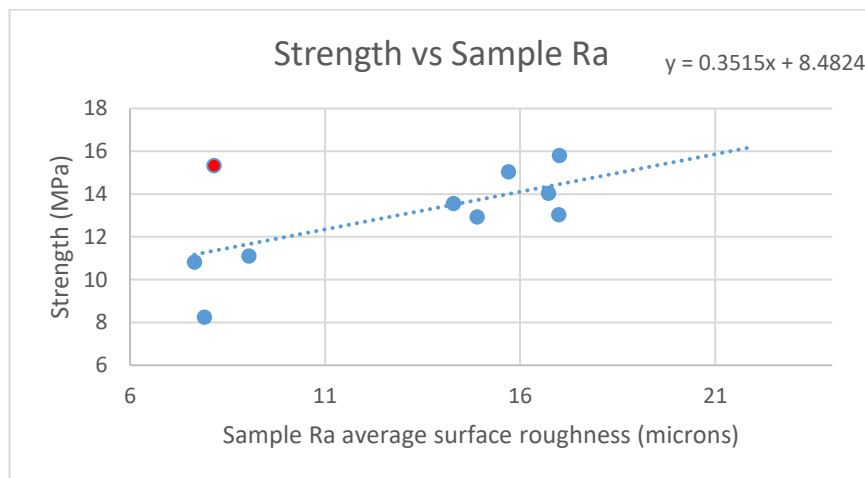


Figure 87: The D1002 samples strength and average surface roughness data curve fitted with a linear line, the red dot shows the horizontal sample outlier

In Figure 88, the graph is plotted with the revised stress. This shows that although there is still a relationship between surface roughness and strength, the slope of the line shows surface roughness has less of an influence on the shear strength than for the unrevised shear strength.

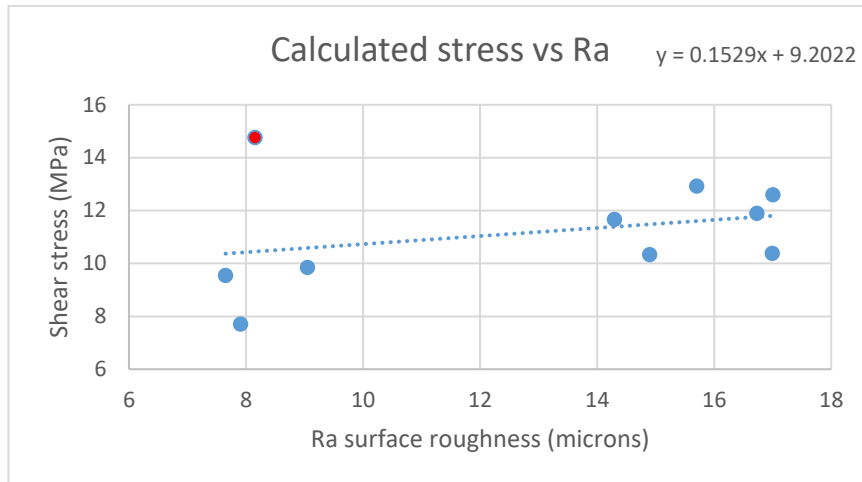


Figure 88: The D1002 samples revised strength and average surface roughness data curve fitted with a linear line, the red dot shows the horizontal sample outlier

In Figure 89, the directionally based surface roughnesses are plotted against the failure strength values. Due to the formula of the fitted linear lines being similar between the two graphs, it appears directionality of the surface roughness has little to no effect on the strength values.

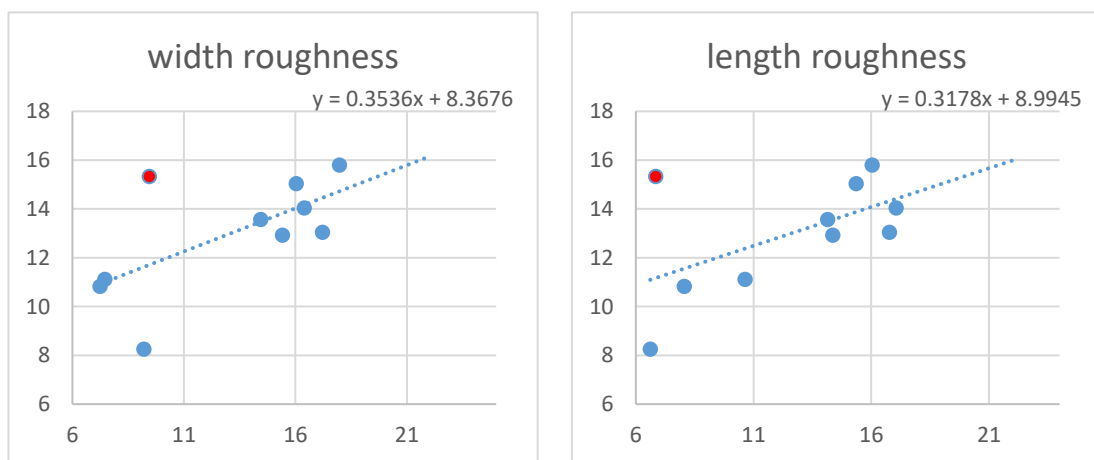


Figure 89: The D1002 samples strength and directional surface roughness data curve fitted with a linear line

Figure 90 presents a box and whisker graph illustrating the range of surface roughnesses for the two primary build directions. The vertical build Ra surface roughness ranged between 14-17 μm with an average of 15.9 μm . The horizontal build surface roughness ranged from between 7-9 μm with an average of 8.2 μm . The horizontal surface had a tighter distribution meaning it was less prone to manufacturing variations.

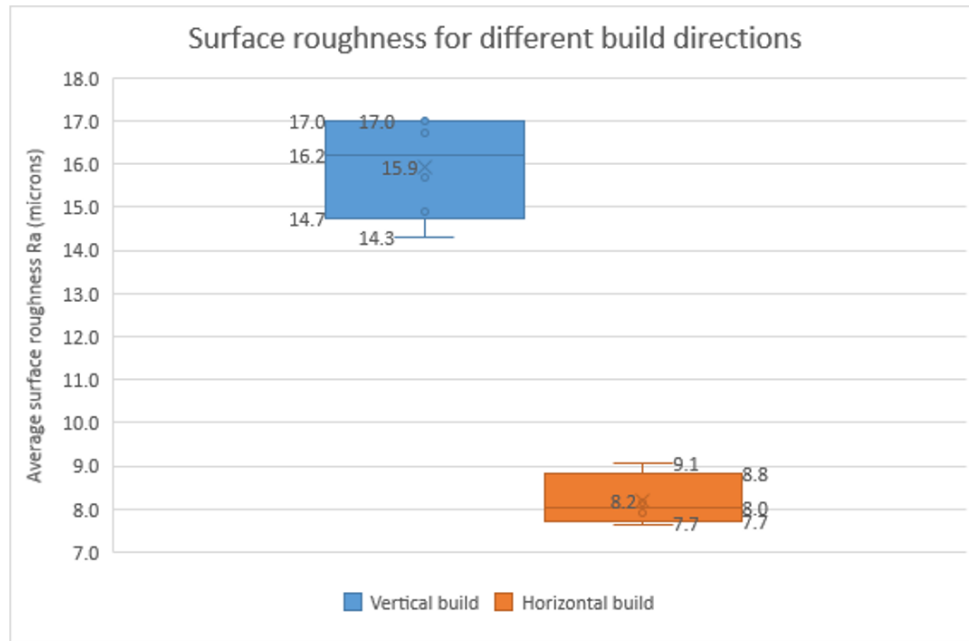


Figure 90: Box and whisker plot of the D1002 Ra average surface roughness

As shown in Figure 91, except for the one outlier on the horizontal surface, the vertical builds outperformed the horizontal builds in terms of apparent shear strength by 19%. This is seen in the mean line of the box and whisker graph being higher for the vertical builds (14.07 MPa) with the horizontal being (11.38 MPa). It also had a tighter distribution, meaning the vertical builds have greater reliability. The adhesive supplier's data sheet gave for eight samples a mean failure stress of 15.9MPa ($\sigma=0.3$) (ADHESIVE TECHNOLOGIES NZ LTD, 2018). Unfortunately, in this experiment most samples failed to reach this mean failure stress. However, the supplier also failed to suggest what substrate material was used and any surface treatments applied.

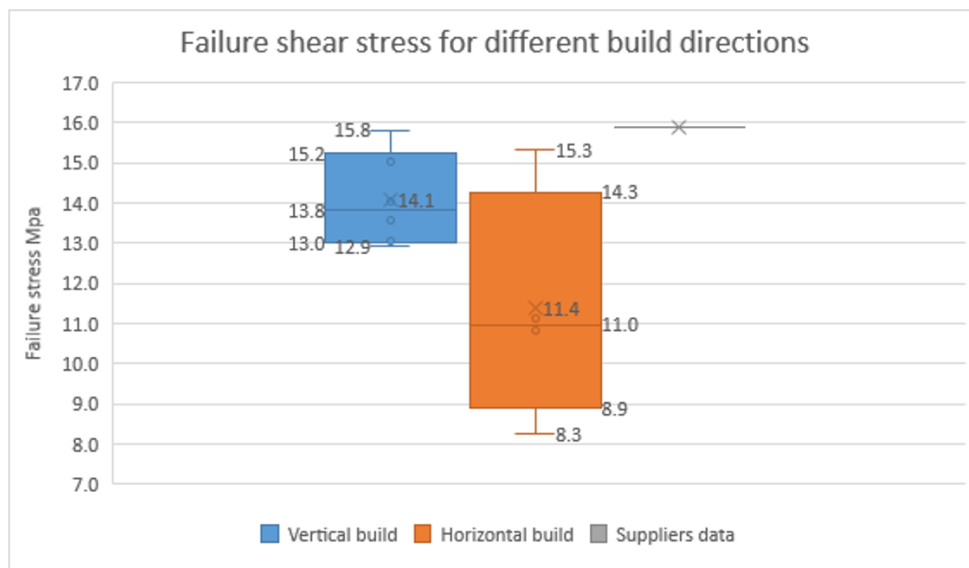


Figure 91: Box and whisker graph of failure shear strength for the D1002 samples

It is clear from the above results that when orientating a part to be built with EBM, less variance, and higher apparent shear bonding strength values are achieved with vertical build surfaces. The following sections 4.1.2 - 4.1.5 will now cover how the materials of the D1002 samples responded to loading, examining specifically at the force vs extension trajectories.

4.1.2 Vertical D1002 (eccentrically loaded SLJ) samples force versus extension data

The graph of the vertical build samples force vs extension graph shown in Figure 92, shows that most of the graphs have similar trajectories, especially over the first 0.2 mm. This suggested that similar mechanical properties existed between all vertical build samples. Therefore, failure was dependent on the number of defects at the adhesive/substrate interface.

Interestingly, samples V4 and V5 followed the same trajectory as the other samples but extended significantly further failing at higher stress values. Upon reflection of the process used for the adhesive bonding of these substrates, an error was found that could have contributed to this discrepancy. This error was that for the samples V4 and V5 as seen below in Figure 92, the adhesive was applied to both the top and bottom coupons using a push and scrape method. For the other samples, adhesive was only applied to the bottom and the top coupon was placed on top of it. Hence, the adhesive would have penetrated deeper into the last two coupons with the potential of displacing more air. Therefore, perhaps the interface defect responsible for premature failure is air, or a lack of penetration of the adhesive into the substrate.

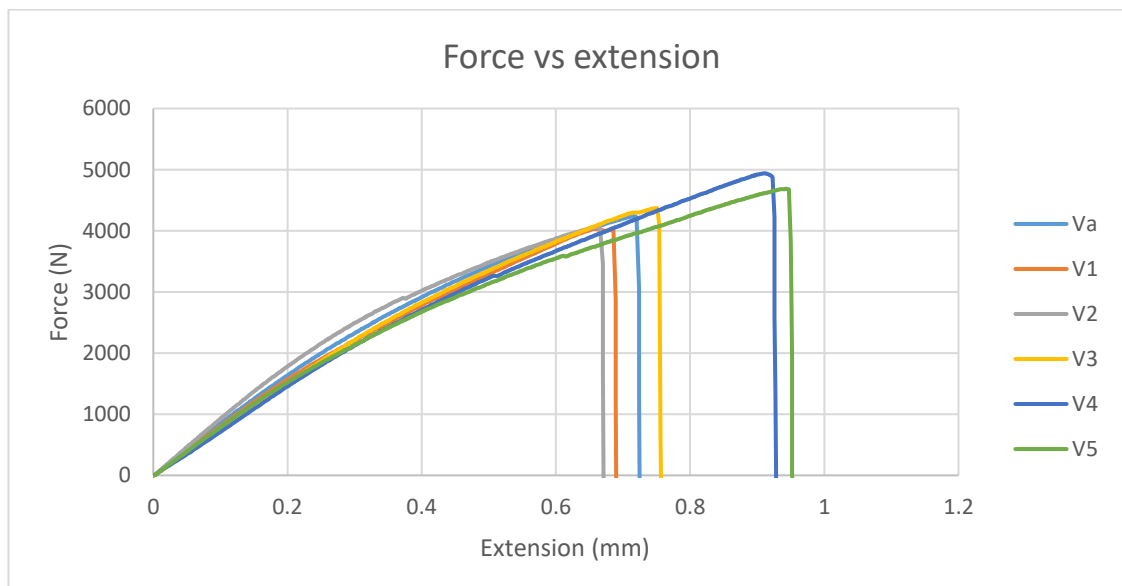


Figure 92: D1002 force vs extension graph for vertical build samples

Below in Figure 93, the rig used for preparing the vertical samples is shown along with a photo of the failed surfaces.

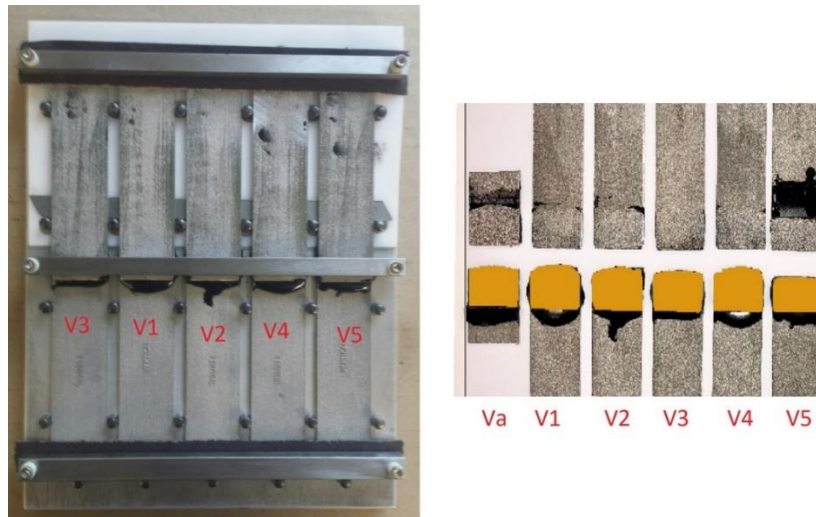


Figure 93: The bonding rig used for the vertical samples and the projected area calculated in solid works

4.1.3 Horizontal D1002 (eccentrically loaded SLJ) samples force vs extension data

The same processing issue occurred with one of the horizontal samples that occurred for two of the vertical samples. The last sample H2 had adhesive applied to both sides using a push and scrape method. This would have again caused the adhesive to penetrate deeper into the substrate, potentially displacing air from the surface. The difference in this case was quite significant and if repeatable, could demonstrate that the horizontal surface is equivalent to the vertical surfaces in terms of bonding strength. Figure 94 highlights the values and how H2 was significantly stronger. Interestingly, just as shown by the vertical build samples, the horizontal plots had similar trajectories to one another. This suggests that all samples exhibit similar mechanical properties with some of the samples failing earlier most likely due to defects along the adhesive/substrate interface.

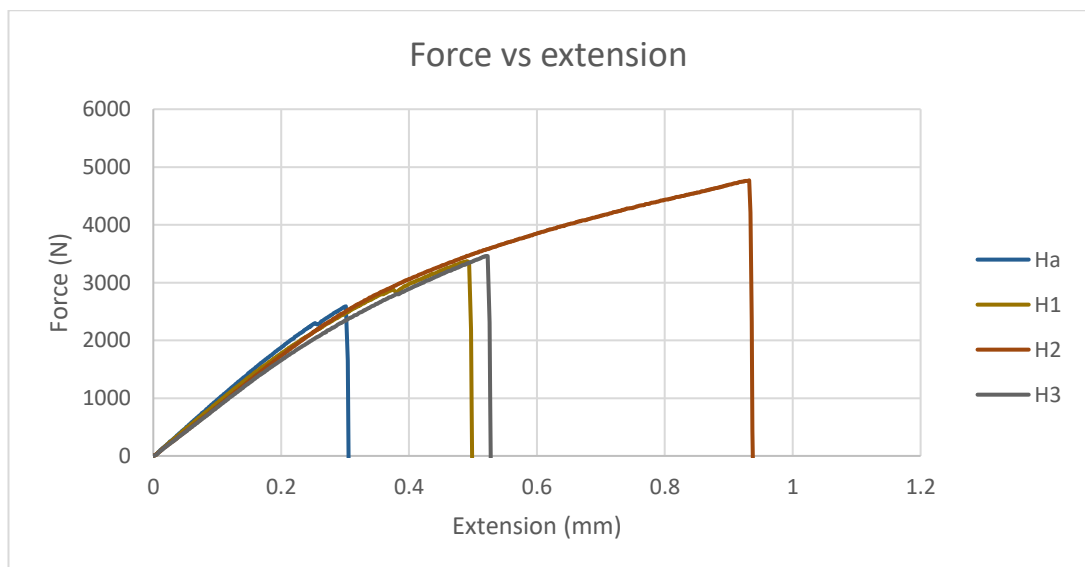


Figure 94: D1002 force vs extension graph for the horizontal build samples

Below in Figure 95, the rig used for preparing the horizontal samples is shown along with a photo of the failed surfaces. Here, the Popsicle sticks acted as the perfect spaces to give a 0.5mm bond-line gap.

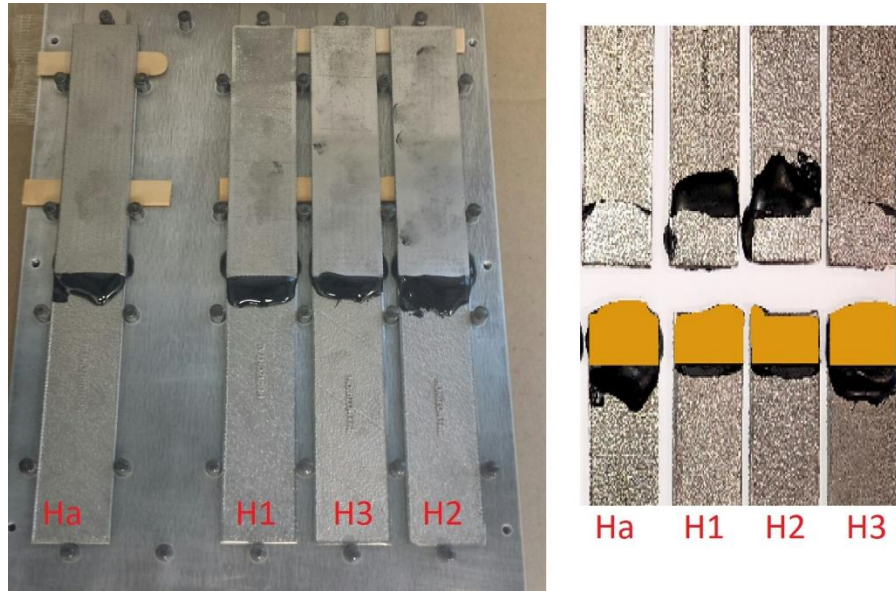


Figure 95: The bonding rig used for the horizontal samples plus their projected area calculated in SolidWorks

4.1.4 All D1002 (eccentrically loaded SLJ) samples force vs extension data

Figure 96 presents the graph of all D1002 samples force vs extension plots. Both the vertical and horizontal samples followed similar trajectories and slopes to one another, showing that for all the samples the bulk mechanical properties of the epoxy/titanium system were the same. Failure therefore occurred due to adhesion failure at one of the adhesive/substrate interfaces, with this failure occurring due to sensitivity to adhesion defects at the interface. Therefore, as shown in Figure 96, certain surface finishes, such as the horizontal build surface were more prone to adhesive/substrate interface defects. The groups shown below highlight this sensitivity to adhesion defects at the interface.

- Group 1 (V4, H2, V5): Possible increased strength due to displacing air from the surface
- Group 2 (V1, V2, Va, V3): This is the vertical range
- Group 3 (H1, H3): This is the horizontal range
- Group 4 (Ha): This was a rumpled horizontal sample that had the lowest surface roughness due to being printed using the 50-micron setting instead of the 90-micron setting.

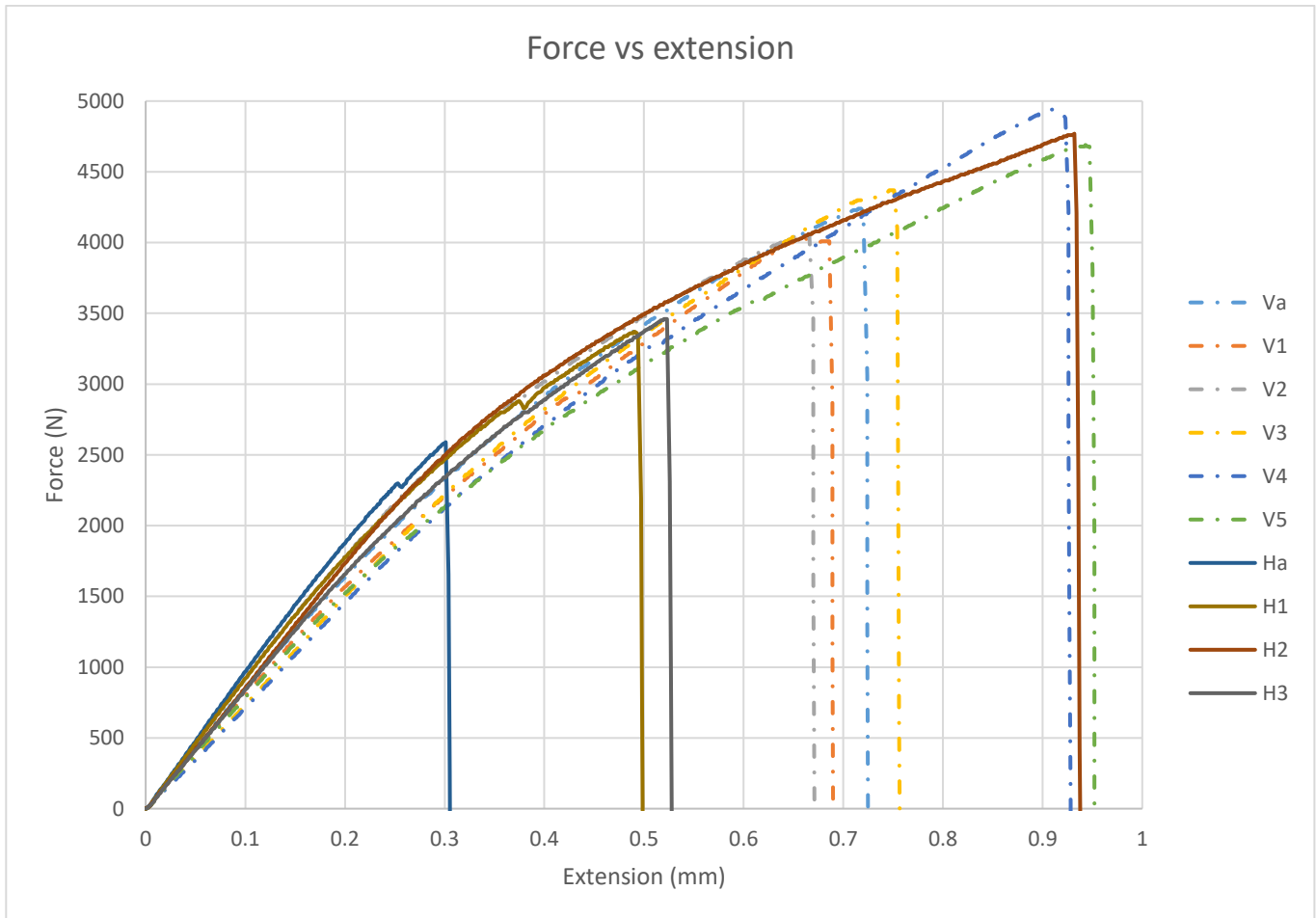


Figure 96: All D1002 force versus extension graphs

The following section 4.1.5 looks specifically at the Va rumbled surfaces and the effect this process has on the surface morphology and the resulting adhesion strength.

4.1.5 The effect rumbling has on the morphology and apparent shear strength of the eccentrically loaded ASTM D1002 samples

The purpose of testing the rumbled surfaces was to see the effect that this common surface roughness reducing method has on the adhesive bonding strength. The rumbling process is described in section 3.1.

The sample Va was prepared using one rumbled surface and one non-rumpled surface as shown below in Figure 97. This was to test which surface would have the most epoxy remaining after failure, hence confirming which surface was the better adhesion surface. For the Va sample, the max load was 4240 N, resulting in an ultimate shear strength of 13.6MPa, when considering the overlap area of 25mm x12.5mm (312.5mm²). However, the actual area that resisted the shear forces was calculated using SolidWorks as 363mm², as shown in Figure 98, giving an actual shear strength of 11.7 MPa.

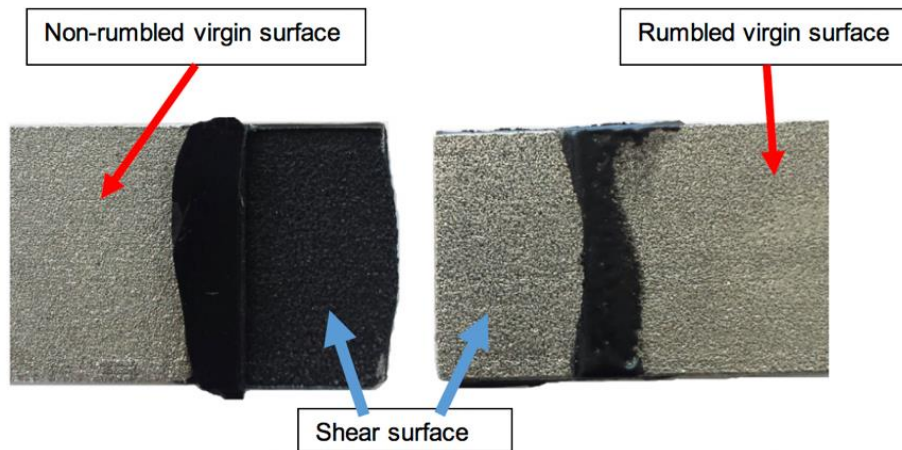


Figure 97: Image of the two parts of the D1002 shear test sample Va



Figure 98: SolidWorks calculated area

Figure 99 presents an Energy Dispersion X-ray Spectroscopy (EDS) analysis used to differentiate the titanium from the epoxy. Due to the high voltage of 15kV and the insulating nature of the epoxy, the surface became charged giving it a bright shiny hue and a lack of focus. Points 1 and 3 showed mainly titanium and aluminium counts as expected, and point 2 had a count consisting mainly of carbon and oxygen as would be expected of an epoxy adhesive. With the parts identified, the shear surface therefore failed through a mixed mode of adhesion failure at the epoxy/titanium interface and cohesive failure of the epoxy. This failure took place on the rumbled side, showing that rumbling reduces the adhesive bonding properties.

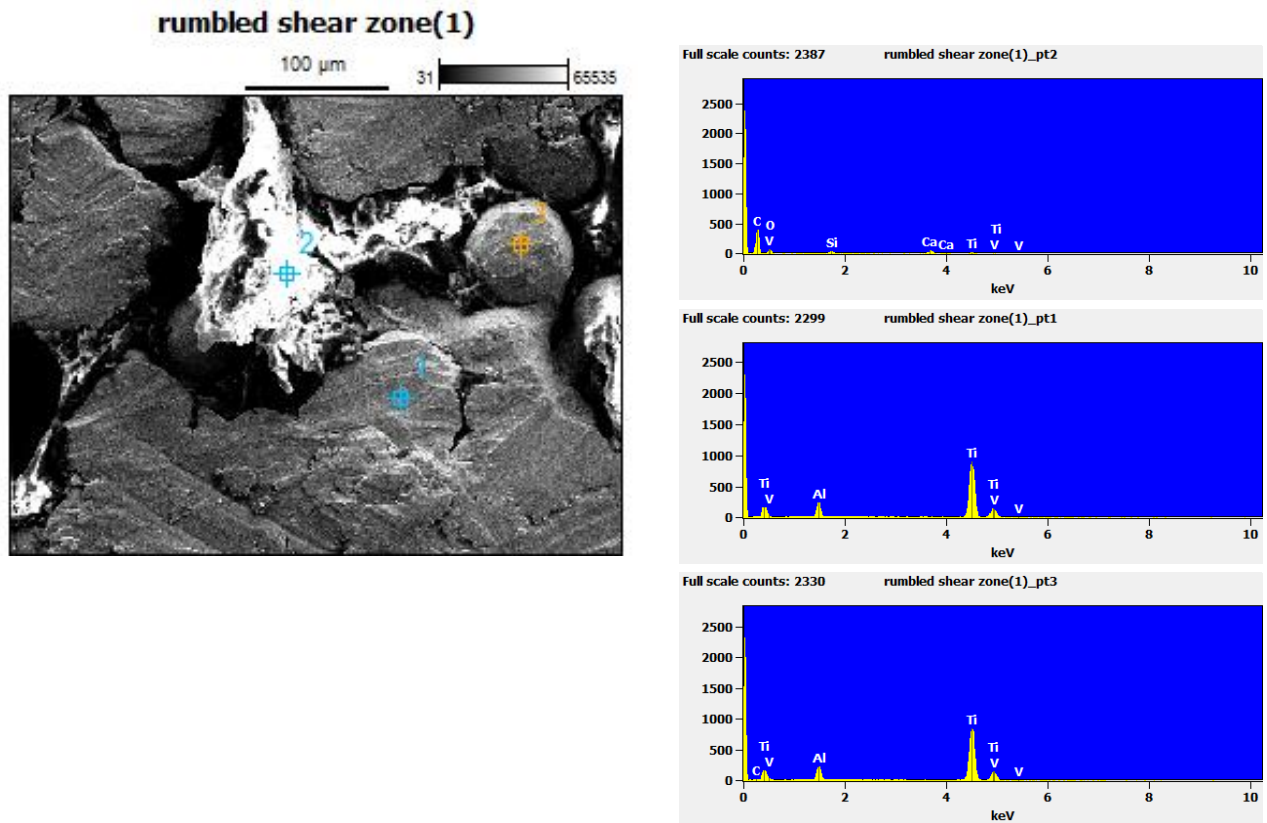


Figure 99: EDS analysis of rumbled shear zone differentiating the titanium from the epoxy

Figure 100 shows the virgin surfaces of the rumbled and non-rumbled surfaces at different magnifications. It is very clear from the images that rumbling reduces the surface roughness by shearing off powder particles and by compressing the surface. This reduction in the surface roughness and overhangs, resulted in less mechanical interlocking between the adhesive and titanium substrate. Hence, the weakest interface of the Va sample was the rumbled side with the strongest being the titanium interface in the as printed condition. This is proven in Figure 101 with the amount of epoxy remaining on the two respective surfaces.

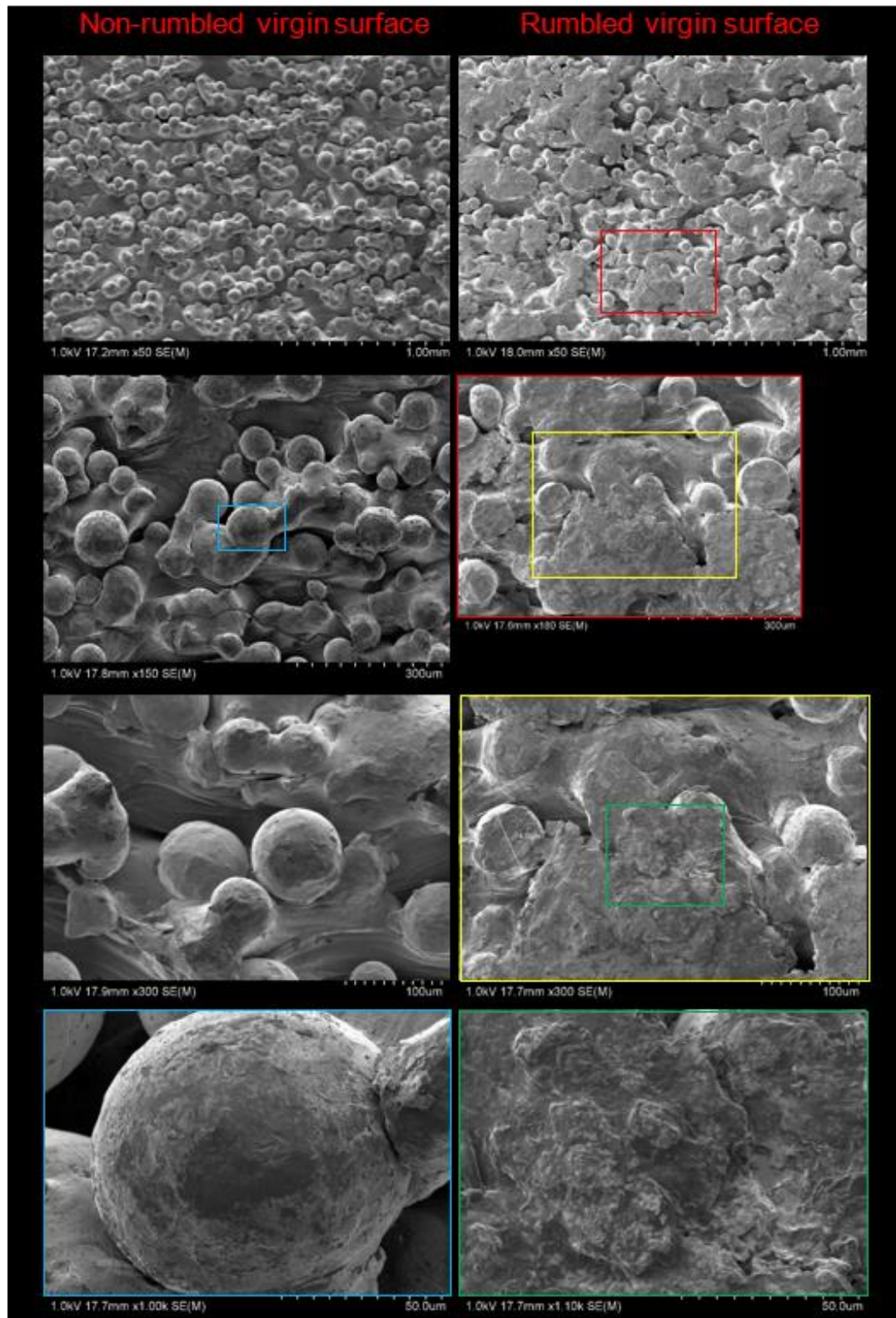


Figure 100: Comparison of the virgin surfaces of the rumbled and non-rumbled surfaces at different magnifications

Figure 101 gives a comparison of the shear surfaces. As expected from a rubber-based epoxy adhesive, no cupping or conning was present. Instead the surface was jagged, and it appears

that failure was mainly induced through a peeling force, as the adhesion failure surface does not show signs of shearing. The failure also occurred on the rumbled side and failure was mostly due to adhesion failure at the epoxy/titanium interface, with a small amount of cohesive failure where the epoxy was caught in small mechanical pockets of the titanium substrate.

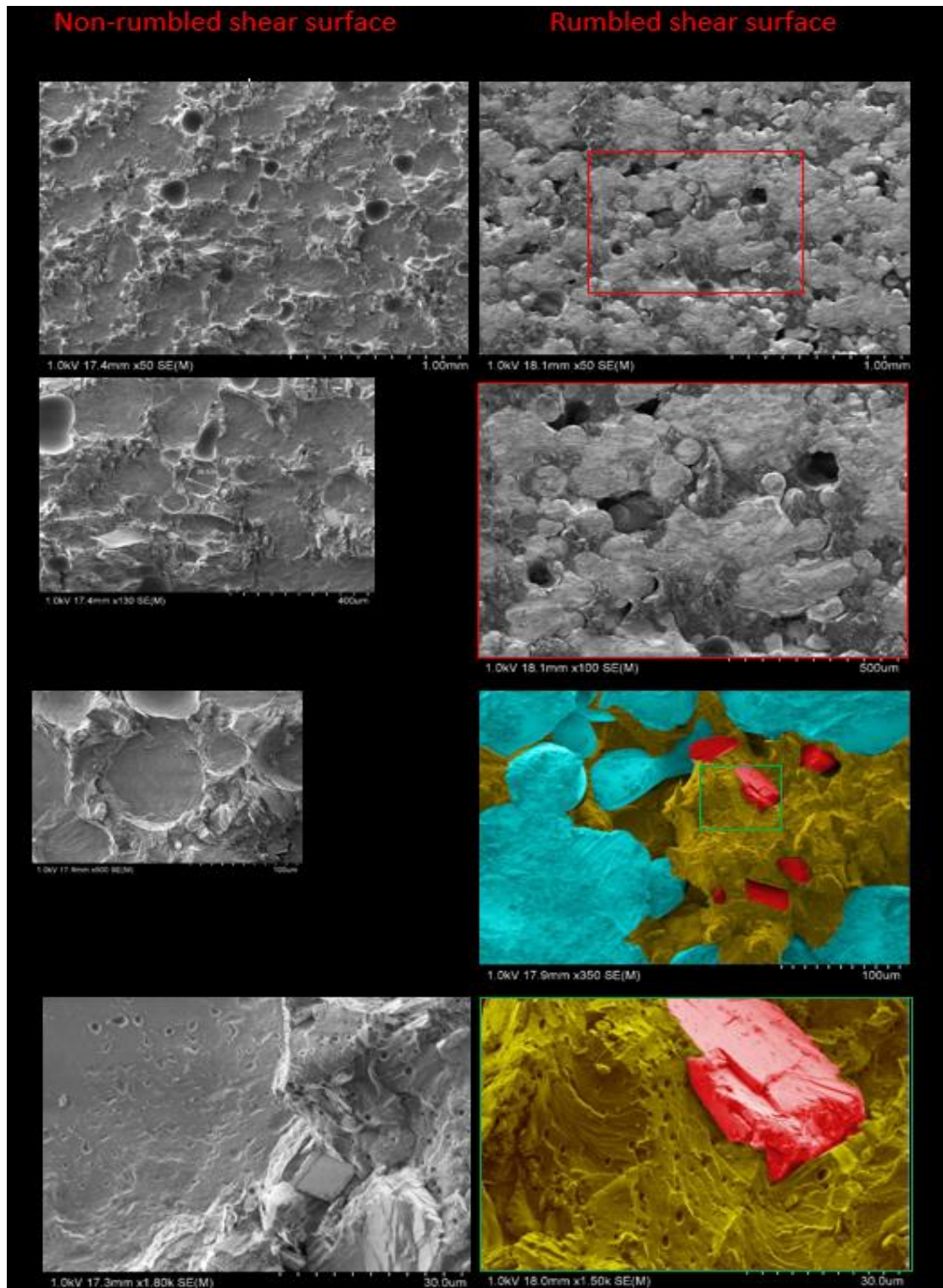


Figure 101: SEM images of the shear surfaces of the rumbled and non-rumbled coupons

As shown in Figure 102, mechanical interlocking was clearly taking place on the non-rumbled cross-sections, with full wetting of the adhesive. Rumbling would have reduced this, as rumbling removes the peaks from the substrate. Therefore, one mechanism by which rumbling may reduce adhesive bonding could be due to the reduction in mechanical interlocking.

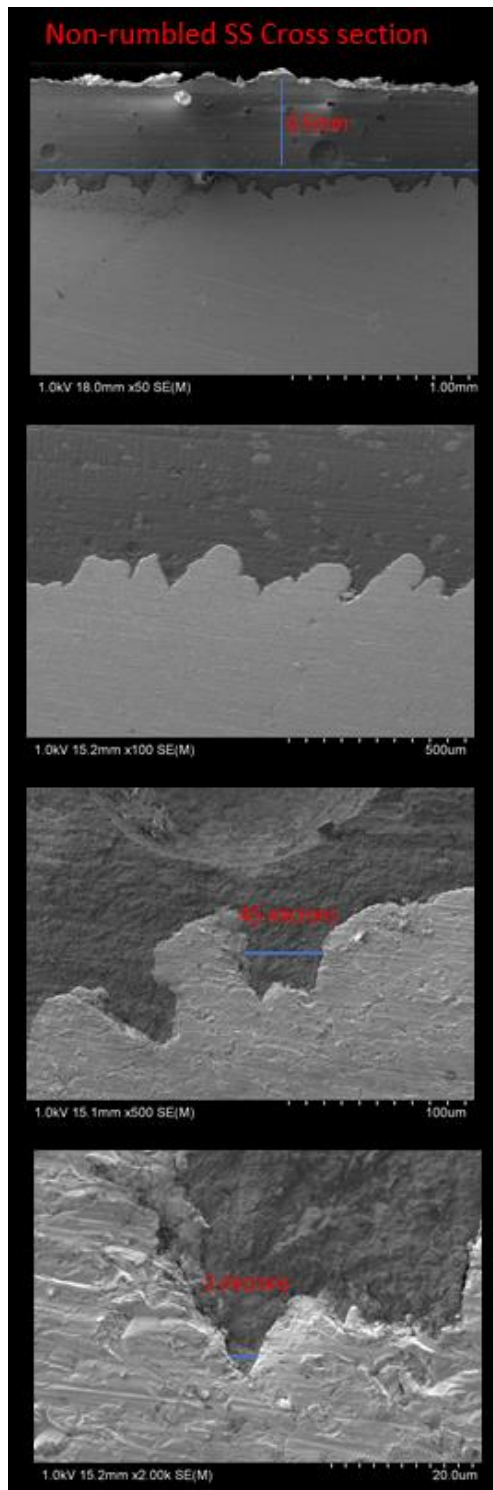


Figure 102: Non-rumbled shear surface cross section, clearly showing mechanical interlocking

4.1.6 Discussion of eccentrically loaded D1002 SLJ experiment

A higher surface roughness correlated to a higher ability to withstand shear stress. This was shown by the roughest non-rumbled and vertical samples withstanding higher loading forces, and by all surfaces performing better than the horizontal builds. Additionally, for all surfaces except one (H1 NE Ra < H1 E Ra) after failure, the roughest surface of the two bonded substrates had the most epoxy remaining. This relationship between roughness and strength was attributed to the surface roughness improving the mechanical interlocking effect of the bond. However, as there were only 10 samples in total with only four being in the horizontal direction, it is not enough to confirm absolute causality. In addition, the lack of control around the bonding procedure for the D1002 experiments could have influenced the data. This was seen in the outlier values of the sample H2. Further, due to the nature of the D1002 being eccentrically loaded, peeling forces were present, introducing unknowns into the data.

The vertical builds outperformed the horizontal builds in terms of apparent shear strength by 19%. This was shown in the mean of the box and whisker graph being higher for the vertical builds (14.07 MPa) than the horizontal (11.38 MPa). It also had a tighter distribution, meaning the vertical builds have greater reliability. Further, all vertical build samples reached over 10 MPa, classifying them as structural bonding surfaces. Only one of the horizontal surfaces reached over 10 MPa and this was an outlier being 30% stronger than the other horizontal samples.

Ra roughness was between 14-17 microns for the vertical samples and between 7-9 microns for the horizontal. Both are considered relatively rough surfaces. The horizontal surface roughness had a tighter distribution meaning it is less prone to manufacturing variations. The direction of the roughness also did not influence the adhesive bonding strength.

In the next sub-chapter, the concentrically loaded D3165 test reduced the peeling stresses giving more accurate apparent shear strength results for the adhesive bond. The adhesive applying method was also consistent for the D3165 test, with adhesive being applied to both sides with the push and scrape method.

4.2 The effect surface morphology has on the adhesive bonding shear strength of the concentrically loaded ASTM D3165 SLJ samples

Samples were tested for apparent shear strength using an ASTM D3165 test. D3165 differed to D1002 by having the bonding surface occur on a step down. This caused the parts to be aligned with the tensile pulling direction reducing most of peeling effects associated with the D1002 tests. In addition, D3165 made assembly easier.

It was found during testing that the first iterations of the D3165 test using the meshed surfaces had excessive peeling forces induced due to the lack of material resisting deformation (this was for samples 02 and 04). The updated design 03* and 04* overcame this issue and thus achieved higher maximum stress values than the 02 and 04 designs.

4.2.1 Overview of the concentrically loaded D3165 samples shear strength data

From the apparent shear strength graph shown in Figure 103, the strongest bonding surface was the NaTESI (A), then the vertical (V), followed by the updated meshed samples (03* and 04*). The 03* & 04* meshed surface had the same thickness of solid titanium in the bonding area as the vertical and horizontal builds. It also had more material across the whole cross section and therefore the highest stiffness out of all the samples. On average the NaTESI, vertical and * meshed surfaces achieved over 15 MPa, which is equivalent to the adhesive manufacturer's best strength values of 15.9 MPa. This suggests that for shear loading at 1.3 mm/min these surfaces perform well. It would be interesting to further investigate the fatigue properties and moisture sensitivity of these bonds. Particularly the NaTESI surface which failed completely due to cohesive failure.

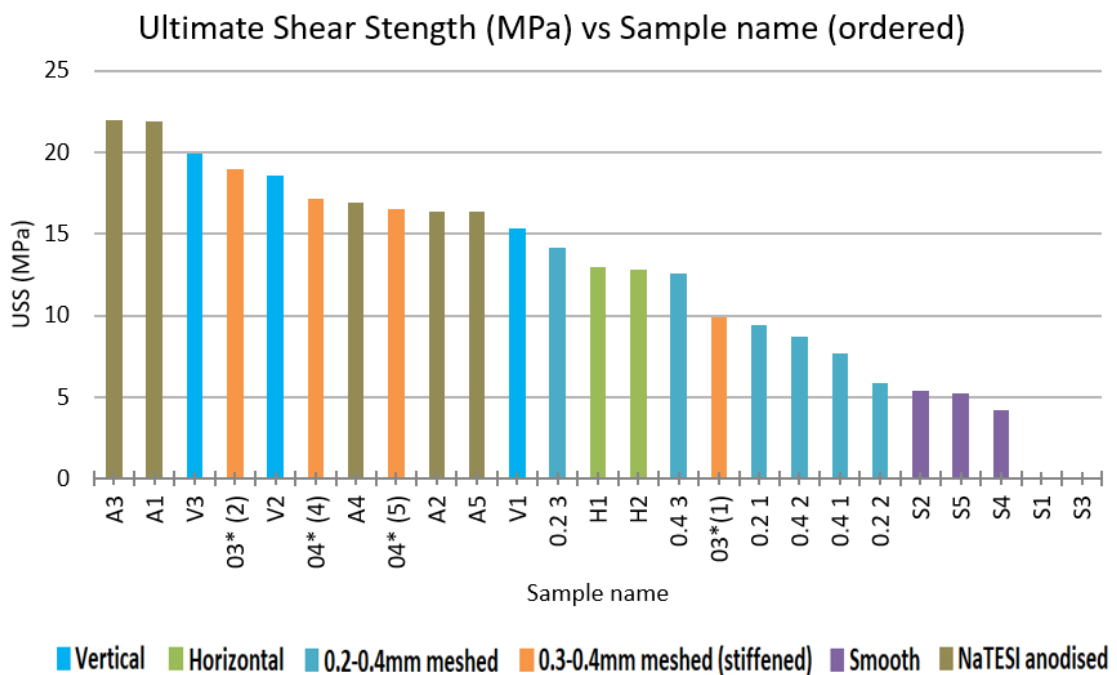


Figure 103: Bar graph of D3165 samples apparent strength ordered from lowest to highest

Figure 104 provides a box and whisker graph of the failure shear stress for the different surfaces. Here, the vertical build surfaces created the most stable strength values with the lowest spread. However, the NaTESI anodised surfaces reached the highest strength values overall. Not enough data points were available for the horizontal surfaces to determine whether the surface produced consistent strength values. The meshed samples all had the least

consistent strength values with the largest spread. The smooth surfaces were the lowest performing surfaces, suggesting that a low surface roughness was not favourable. It was possible with the values of the smooth samples being so low that a processing error occurred reducing the strength of the bond. A possible cause could have been contamination. It was recommended that a future study collects further data with the surface preparation involving an HF and nitric acid etching before bonding to ensure all contamination is removed.

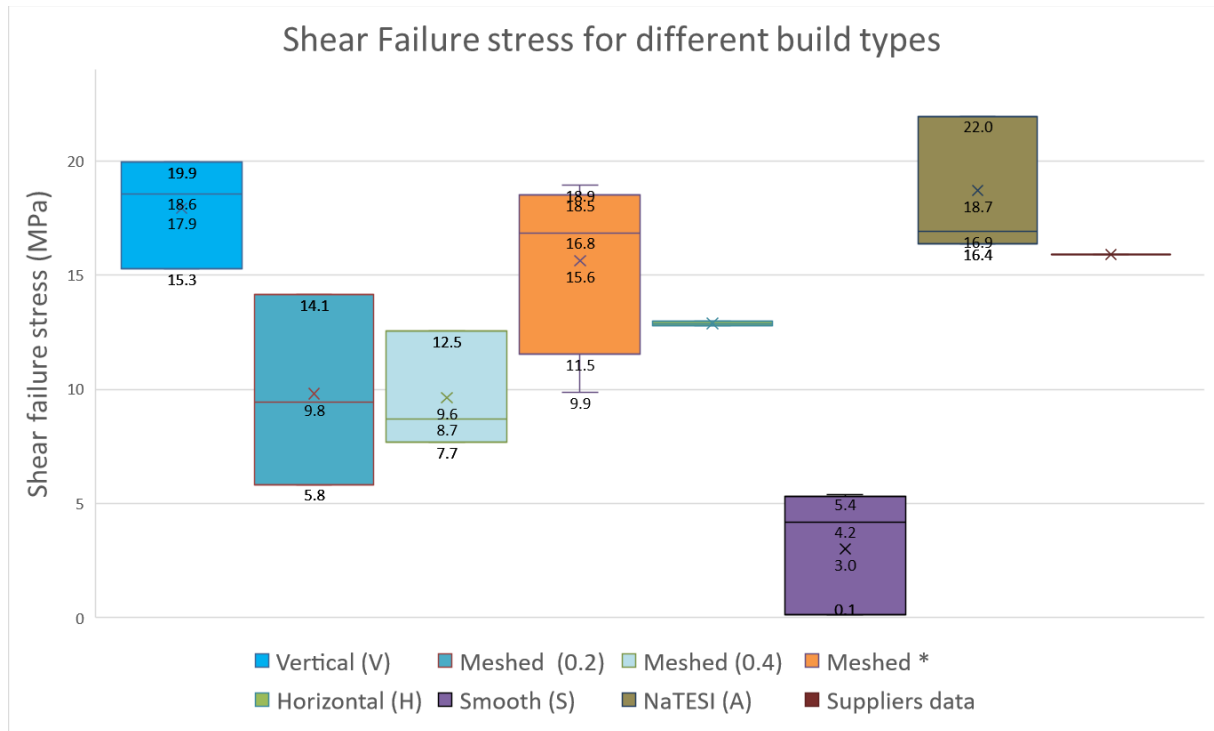
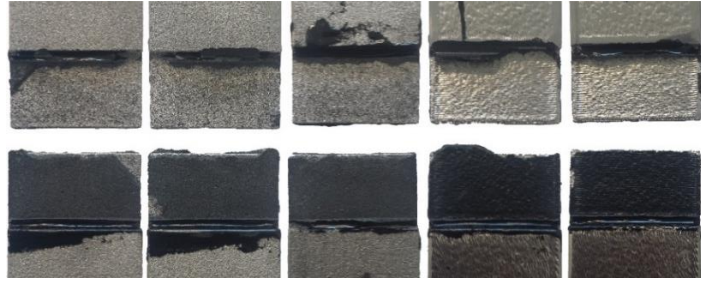


Figure 104: Box and whisker graph of the failure shear stress for all build surface morphologies investigated

The following Tables 18-22 present all the ASTM D3165 data, including a photo of the failed surfaces. The NaTESI anodised surfaces were the only surfaces which failed cohesively in the adhesive. All the other surfaces failed either due to a mixed failure mode or through complete adhesion failure at the interface as seen with the horizontal samples.

For Tables 18, 21, and 22, the surface roughness tests were done as defined in section 3.4. For the vertical build direction, roughness averaged 15 μm , and for the horizontal build direction it averaged 5 μm . These values were consistent with the D1002 tests. Finally, for the smooth surfaces, surface roughness averaged around 0.4 μm . The NaTESI samples had the same average surface roughness as the vertical samples, showing that the NaTESI anodising barely affects the macro or micro surface roughness.

Table 18: Vertical build (V) and horizontal build (H) samples ASTM D3165 data



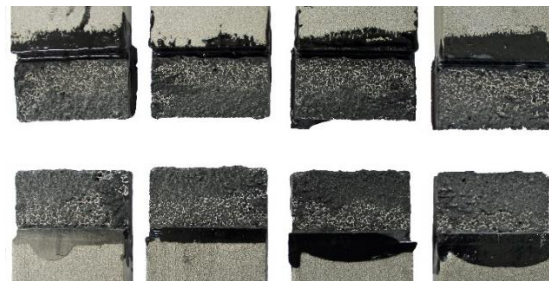
Sample name:	V1	V2	V3	H1	H2
Max load (N)	4780	5800	6230	4060	3990
Ultimate shear strength (MPa):	15.3	18.6	19.9	13	12.8
Strength rank	3	2	1	4	5
Break elongation (mm)	0.8	1.0	1.1	0.7	0.3
Sample average roughness (μm)	15	16	15.1	5.4	5.7

Table 19: 4mm thick meshed samples (02 and 04) ASTM D3165 data



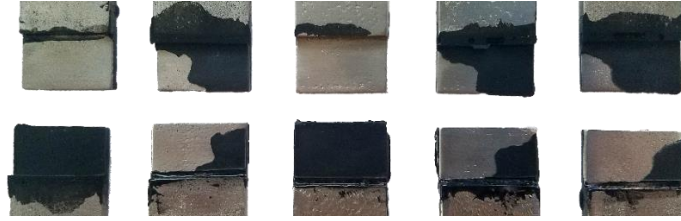
Sample name:	0.2 1	0.2 2	0.2 3	0.4 1	0.4 2	0.4 3
Max load (N)	2950	1823	4420	2400	2720	3920
Ultimate shear strength (MPa):	9.4	5.8	14.1	7.7	8.7	12.5
Strength rank	3	6	1	5	4	2
Break elongation (mm)	1.0	0.7	1.3	1.3	1.3	1.5

Table 20: 6.3mm thick meshed samples (04* and 03*) ASTM D3165 data



Sample name:	04* (4)	04* (5)	03* (1)	03* (2)
Max load (N)	5360	5170	3080	5920
Ultimate shear strength (MPa):	17.2	16.5	9.9	18.9
Strength rank	2	3	4	1
Break elongation (mm)	1.3	0.8	0.5	0.8

Table 21: Smoothed samples (S) ASTM D3165 data



Sample name:	S1	S2	S3	S4	S5
Max load (N)	38	1688	36	1312	1638
Ultimate shear strength (MPa):	0.1	5.4	0.1	4.2	5.2
Strength rank	4	1	5	3	2
Break elongation (mm)	0.0	0.2	0.0	0.2	0.3
Sample average roughness (µm)	0.2	0.4	0.4	0.4	0.4

Table 22: NaTESI anodised samples (A) ASTM D3165 data



Sample name:	A1	A2	A3	A4	A5
Max load (N)	6850	5120	6860	5280	5120
Ultimate shear strength (MPa):	21.9	16.4	22	16.9	16.4
Strength rank	2	4	1	3	4
Break elongation (mm)	1.6	1.3	1.4	1.2	1.2
Sample average roughness (µm)	14	16	15.5	14.5	15

For the apparent shear stress graph shown in Figure 105, the green line represents the highest strength values for the H, 02 and 04 samples. The purple represents the average of the mesh samples excluding the revised mesh * coupons. These two lines demonstrate that the H, 02 and 04 samples are weak in comparison to the A, V and revised * samples.

It is worth being reminded again that the NaTESI anodised samples failed through cohesive failure of the adhesive. This means if tested with a stronger adhesive, the joint would reach higher strength values until the adhesion between the adhesive and the titanium oxide layer failed. This means currently the NaTESI surface is stronger than the *HPR 25* adhesive. This is the perfect failure criterion when designing, as cohesive failures are more predictable than adhesion failures, giving better predictability over the strength of the joint.

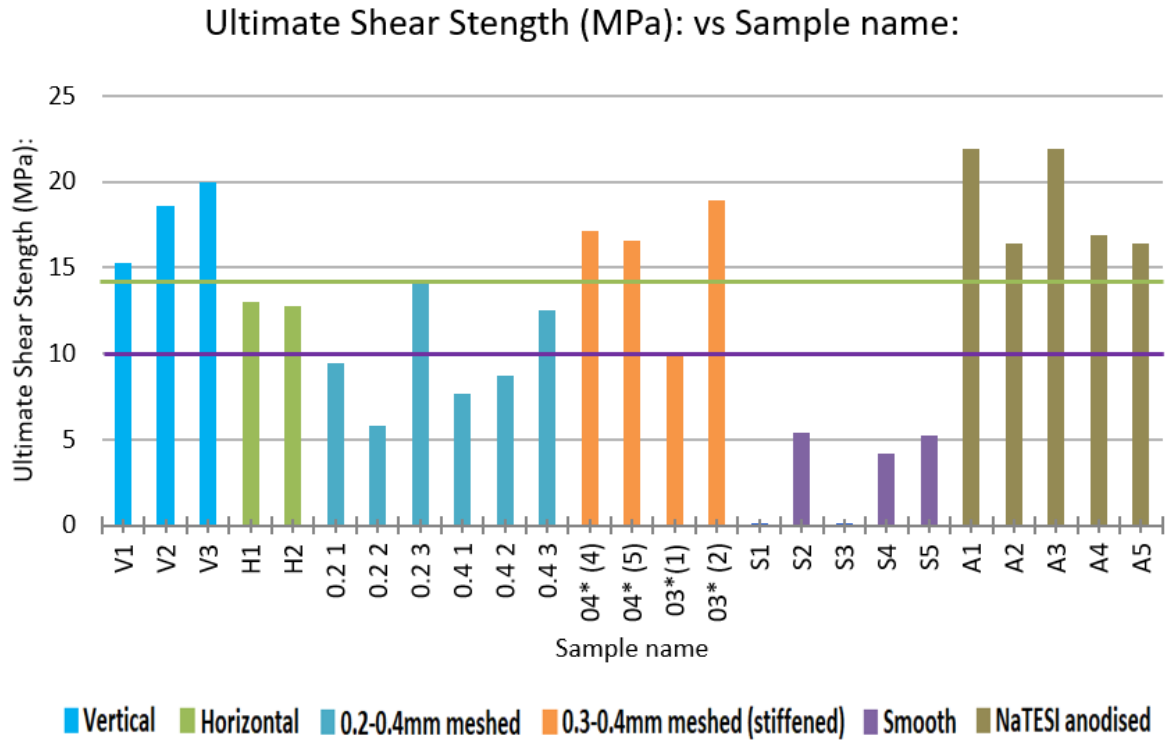


Figure 105: Bar graph of D3165 samples apparent strength

The 02 and 04 meshed coupons failed early due to peeling effects as the titanium was essentially only 1mm thick with a 1mm mesh. Here, the mesh provided less stiffness than the solid titanium. Therefore, the part rotated as it was loaded, causing peeling forces. This can be seen in Figure 106 below.



Figure 106: Left – solid 2mm thick vertical V2 sample, little to no rotation; Middle – meshed sample with 1mm solid 1mm mesh with bending moments being induced; Right – thickened meshed sample with 2mm thick solid and 1mm thick mesh with little to no rotation

The following sections 4.2.2 - 4.2.11 will now cover how the D3165 concentrically loaded SLJ responded to loading, examining specifically the force vs extension trajectories, and the mechanical properties of the eight different D3165 surfaces investigated.

4.2.2 Vertical D3165 (concentrically loaded SLJ) samples force versus extension data

As seen in Figure 107, all vertical samples followed a very similar trajectory suggesting that the adhesive/surface combination appears to have a predictable stress strain response and base mechanical properties. With all samples following the same general curve, the failure strength appears to depend on the presence of interface defects, which can cause early failure, and the amount of cohesion vs adhesion failure. The box and whisker graph of Figure 108 shows a mean failure stress of 17.9 MPa, with the lowest sample reaching only 15.3 MPa and the highest reaching 19.9 MPa. The adhesive manufacturer rated the adhesive at 15.9 MPa. Therefore, this surface is performing well in exceeding this.

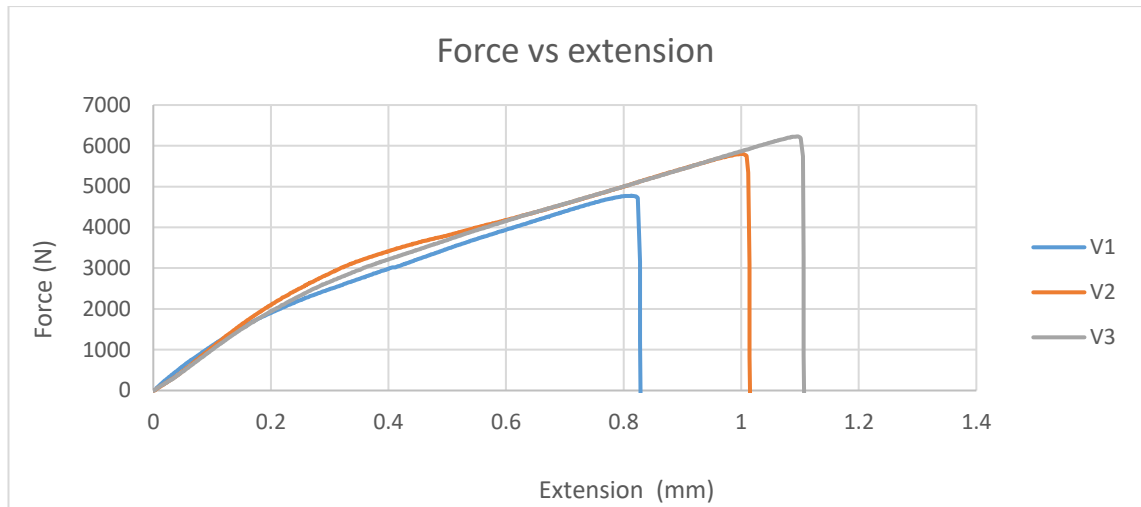


Figure 107: D3165 force vs extension graph for the vertical build samples

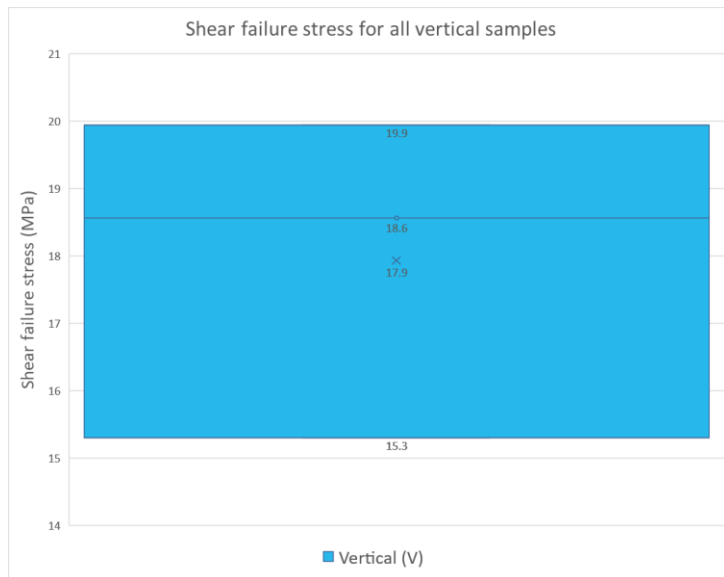


Figure 108: D3165 Shear failure stress box and whisker graph for the vertical build samples

For all three samples as shown in Figure 109, the mode of failure was a mixture of cohesive failure in the epoxy, and adhesion failure at the adhesive/substrate interface. This is clearly

visible in the *No epoxy shear surface* and the *Epoxy shear surface* images of Figure 109. Here, the partially melted powder particles caused high points on the titanium's surface trapping the epoxy adhesive into mechanically interlocked bonds. For the epoxy trapped in the surface asperities, failure was diverted from the interface and into the bulk of the adhesive. For areas of the surface structures where the geometry was unable to mechanically impede the epoxies deformation movement (low gradient), failure occurred at the epoxy/titanium interface.

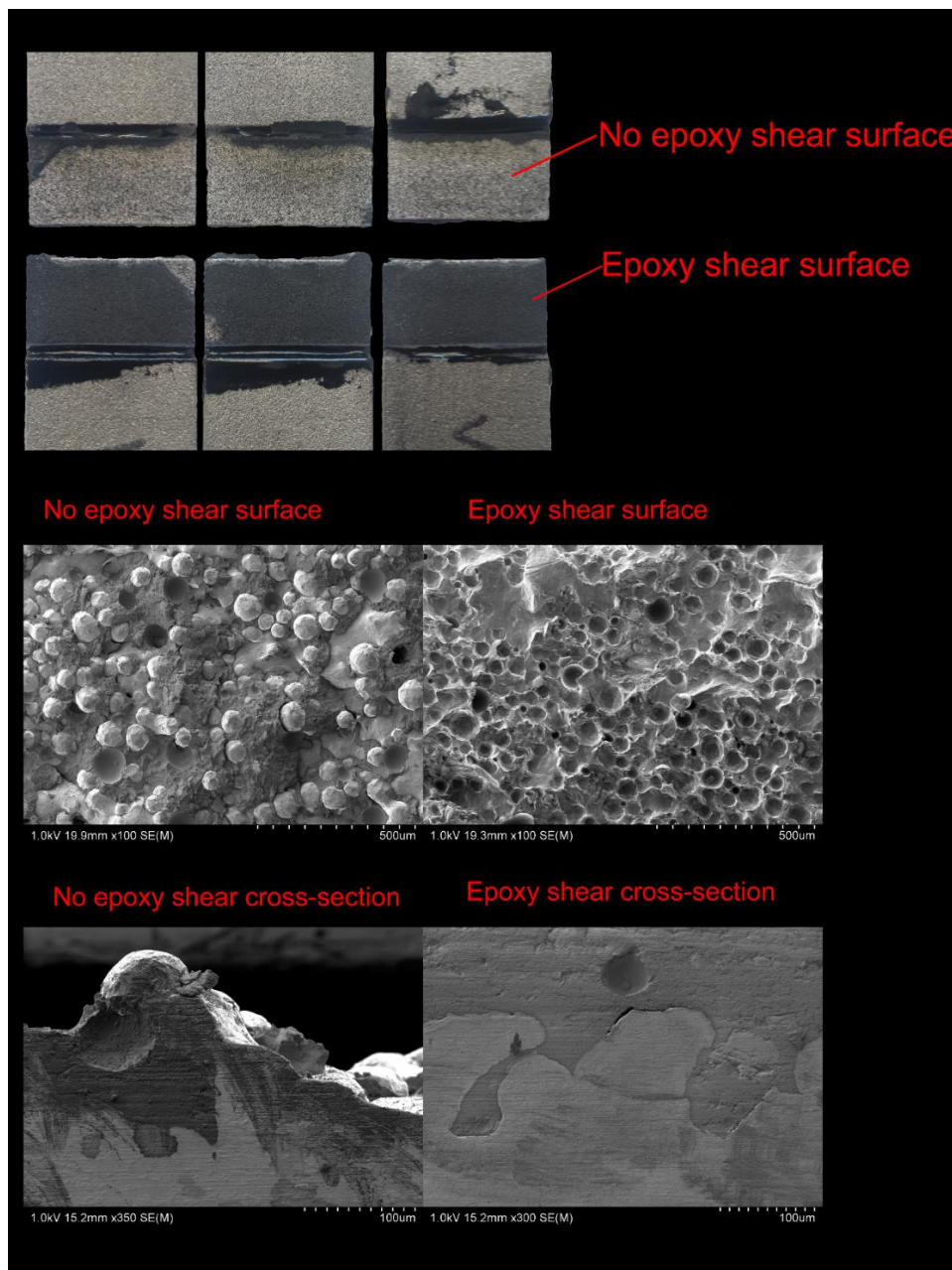


Figure 109: SEM images of a vertical build samples failure surface and cross-section

Figure 110 below is a diagram to help explain why the vertical samples failed through the mixed failure mode. In this diagram there are two different surface roughness shapes shown: (a) a

vertical walled feature, and **(b)** a sloped feature. For most bonded systems the cohesion strength of the adhesive is normally stronger than the specific adhesion between the adhesive and the substrate. Therefore, under shearing forces, failure for a flat or slightly sloped surface should be through specific adhesion failure between the adhesive and the substrate, see Figure 110b. However, when the surface exceeds a certain slope, the specific adhesion is stress relieved, due to the geometry diverting the loading from acting on the interface (weakest area) and into the bulk of the polymer chains (strongest area), see Figure 110a. For the vertical samples the ratio of failure through adhesion versus failure through cohesion, was dependent on the surface's ratio of pockets versus flats. Therefore, improvements to this ratio should improve bonding strength.

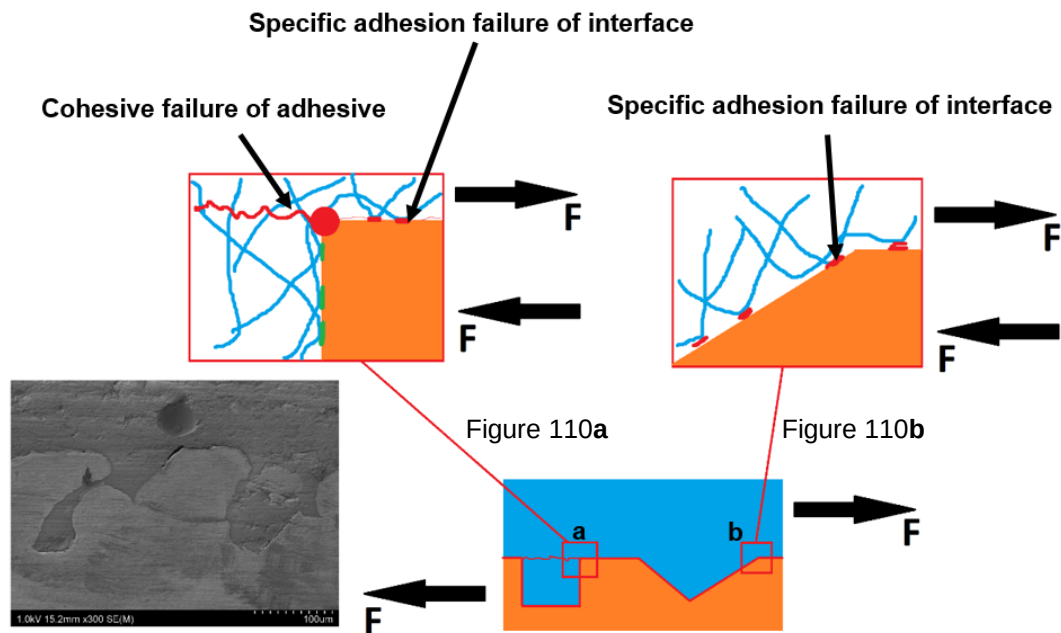


Figure 110: How surface roughness can relieve specific adhesion at the interface forcing failure to occur cohesively in the adhesive

- The vertical surfaces' adhesive shear strength outperformed the horizontal surfaces by 28% with a mean apparent failure shear stress of 17.93 MPa.
- The vertical build surface also had the tightest shear strength distribution making it the most reliable. However, only two horizontal surfaces were tested, therefore absolute confidence in comparison should be avoided.

In the next section, the horizontal samples results are discussed. For these horizontal samples the bonding strength was on average 28% weaker, with failure occurring through complete specific adhesion failure at the interface. This further confirms how surface roughness increases mechanical interlocking, which stress relieves the specific adhesion, increasing the overall apparent shear strength of the bond.

4.2.3 Horizontal D3165 (concentrically loaded SLJ) samples force versus extension data

Figure 111 shows there was a recording issue for the extension between the tensile testing machine and the computer software. Here, the second sample (H2) was offset due to this error. The sample size for this experiment was only $n=2$, so although the horizontal samples adhesive/surface combination appears to have a predictable stress/strain response and base material property, more data is needed to prove this. Additionally, due to the sample size the box and whisker graph in Figure 112 also fails to show useful information about data spread. The mean failure stress was 12.88 MPa, with the lowest sample reaching only 12.77 MPa and the highest reaching 12.99 MPa. This failed to reach the manufactures strength of 15.9 MPa.

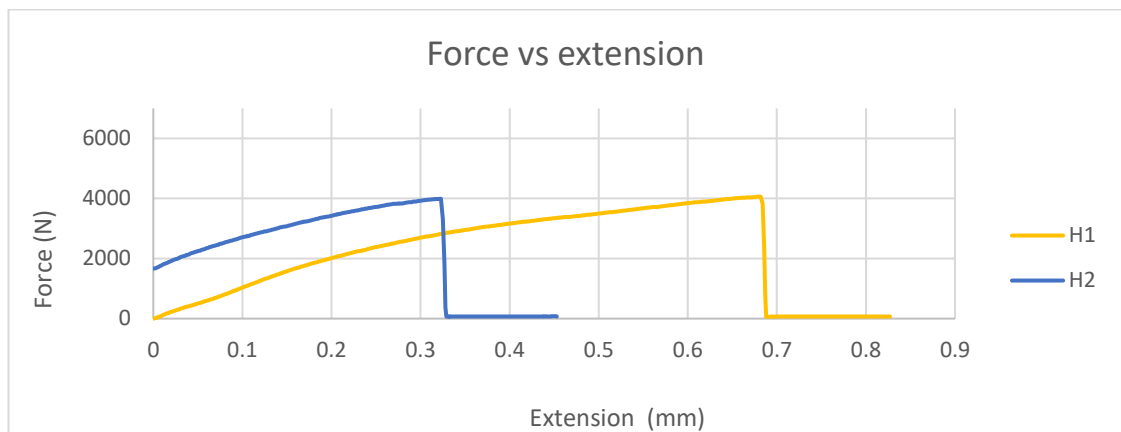


Figure 111: D3165 force vs extension graph for the horizontal build samples

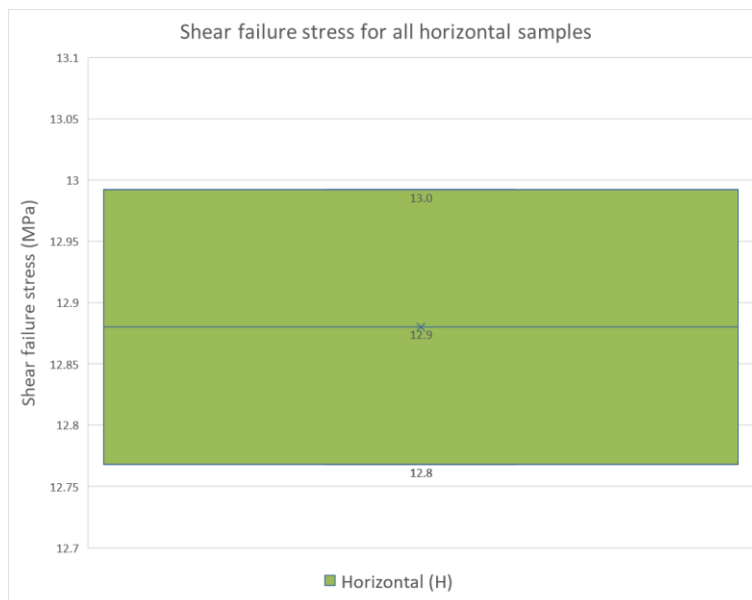


Figure 112: D3165 Shear failure stress box and whisker graph for the horizontal build samples

The surface and cross-section images in Figure 113 show failure occurred entirely through adhesion failure on one of the adhesive/substrate interfaces, with epoxy remaining on only one

surface. Little mechanical interlocking took place which would have caused all loading to be resisted through specific adhesion. This lead the joint to be on average 28% weaker than the vertical samples joint.

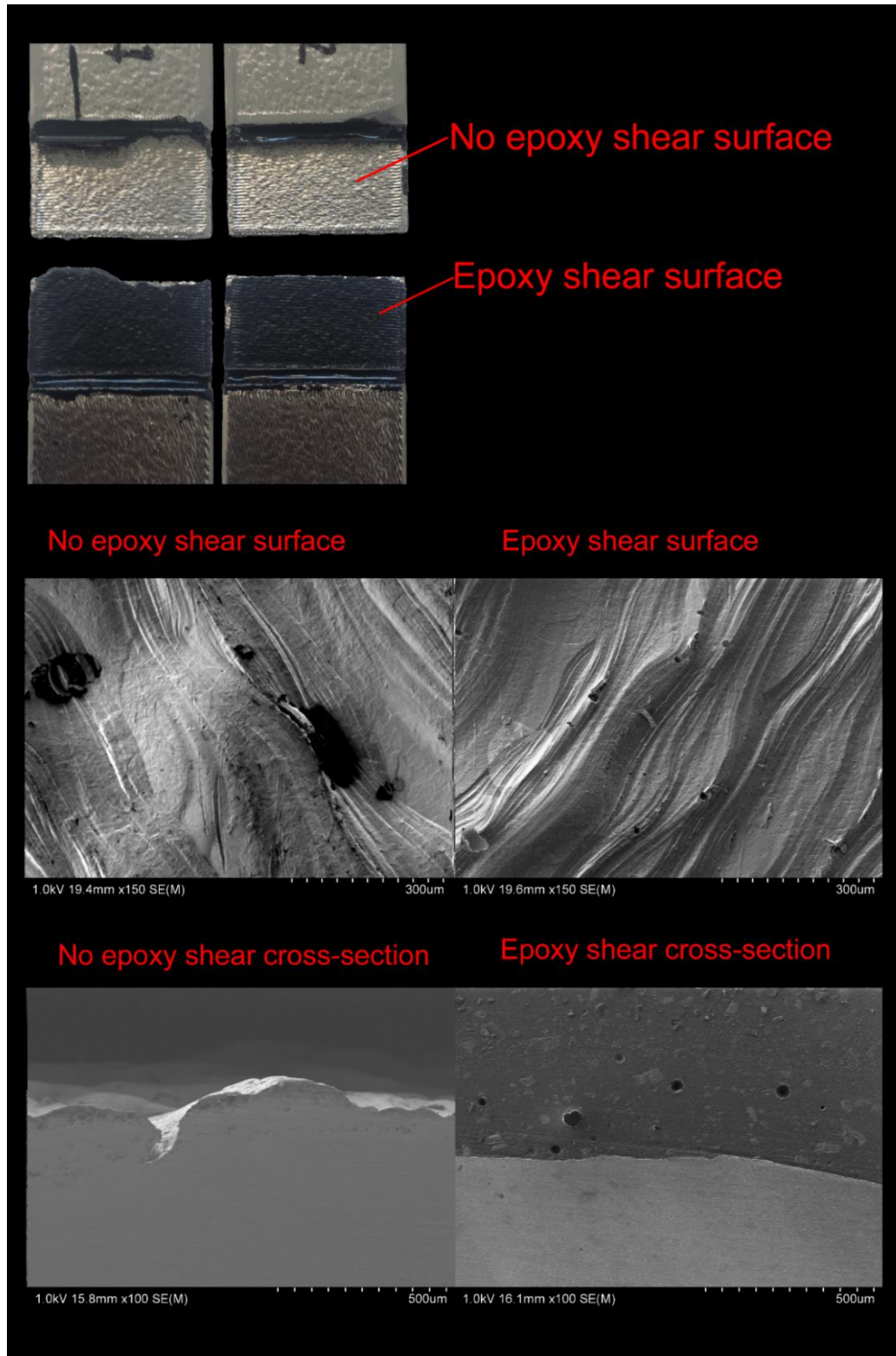


Figure 113: SEM images of a horizontal build samples failure surface and cross-section

Figure 114 below is an illustration showing why the horizontal samples failed through specific adhesion failure at the interface. Due to the low surface roughness of the surface, the polymer chains were unable to mechanically interlock with any surface features. Therefore, all loading was placed on the chemical bonds between the adhesive's polymer chains and the substrate. Figure 113 above clearly shows this with no epoxy adhesive remaining on one of the interfaces of the SLJ.

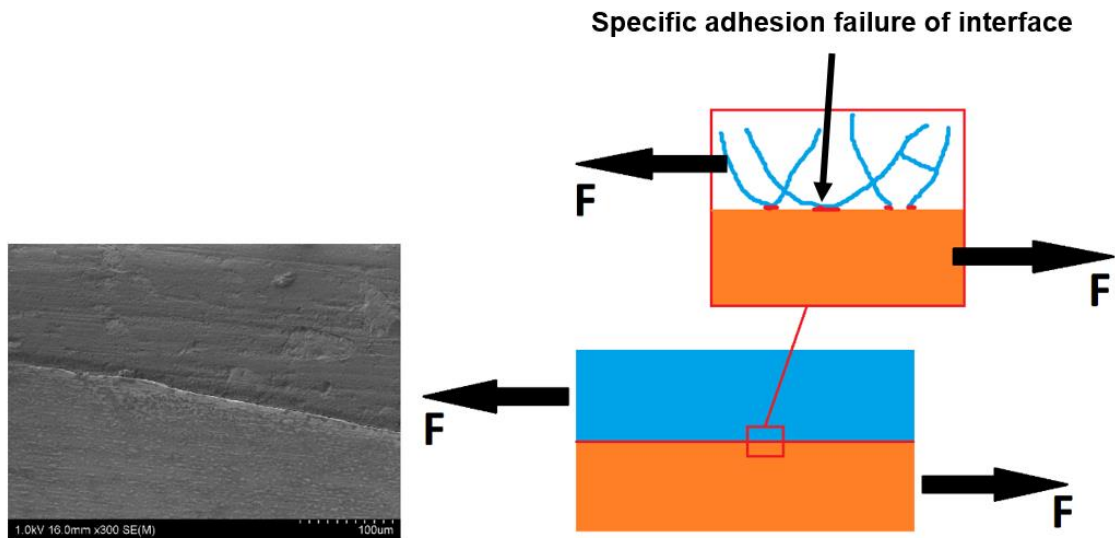


Figure 114: How a lack of surface roughness forces loading to be concentrated on the specific adhesion between the polymer chains and substrate

- The horizontal surfaces performed the worst out of all samples. This was likely due to the low surface roughness of $R_a 5 \mu\text{m}$ causing no mechanical interlocking. Therefore, all loading was placed on the weakest part of the system being the bonds between the epoxy and the titanium surface.
- The horizontal surface having low bonding strength is a good result as it is not practical for most real-world objects. This is because the part must be orientated so that the surface is flat with the electron beam hitting it perpendicularly, which is only possible for flat parts.

In the next sections, the meshed sample results are discussed. For the 02 and 04 samples, due to excessive bending, the samples failed under less loading than the horizontal samples. However, for these samples only 1mm of solid melt was resisting bending versus the 2mm on the horizontal samples. The 03* and 04* revised meshed surfaces which implemented 2mm of solid melt, were the third strongest samples and outperformed the horizontal surfaces by 18% with a mean apparent failure shear stress of 15.62 MPa, which was equivalent to the adhesive manufactures average strength of 15.9 MPa.

4.2.4 02 meshed D3165 (concentrically loaded SLJ) samples force versus extension data (0.2mm pores)

The mean stress for the 02 samples was 9.81 MPa, which was lower than the horizontal surface. Figure 115 showed there was significant variation in the stress values reached and the trajectories of the 02 meshed samples plots. The different trajectories suggest that the mechanical properties of each sample were slightly different. This is possible as the trabecular mesh and epoxy adhesive form a 1mm thick composite material. Therefore, if any processing defects are present, the composites properties could be affected, which appears to be the case.

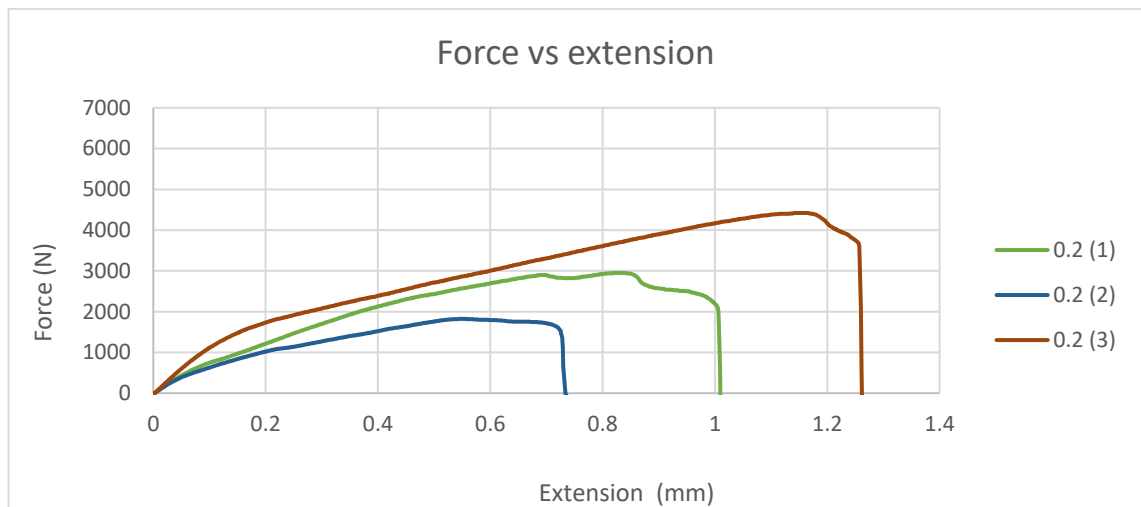


Figure 115: D3165 force vs extension graph for the 02 meshed samples

Figure 116 highlights the variation in results with the spread of data points in the box and whisker graph going from a lowest stress of 5.83 MPa to a highest stress of 14.14 MPa. This was a large distribution and it would be interesting to see a future study with the same test carried out but using an autoclave to reduce the presence of air bubbles in the composite.

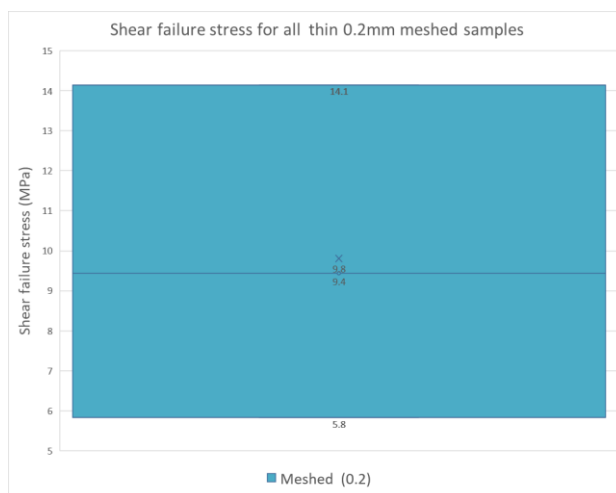


Figure 116: D3165 shear failure stress box and whisker graph for the 02 meshed samples

The failure surfaces shown in Figure 117, displays that failure was a mixture of cohesive failure in the epoxy, and adhesion failure at the interface, with the bulk of material remaining at the tips of the coupons. This material remaining at the tips confirms that large peeling forces were involved.

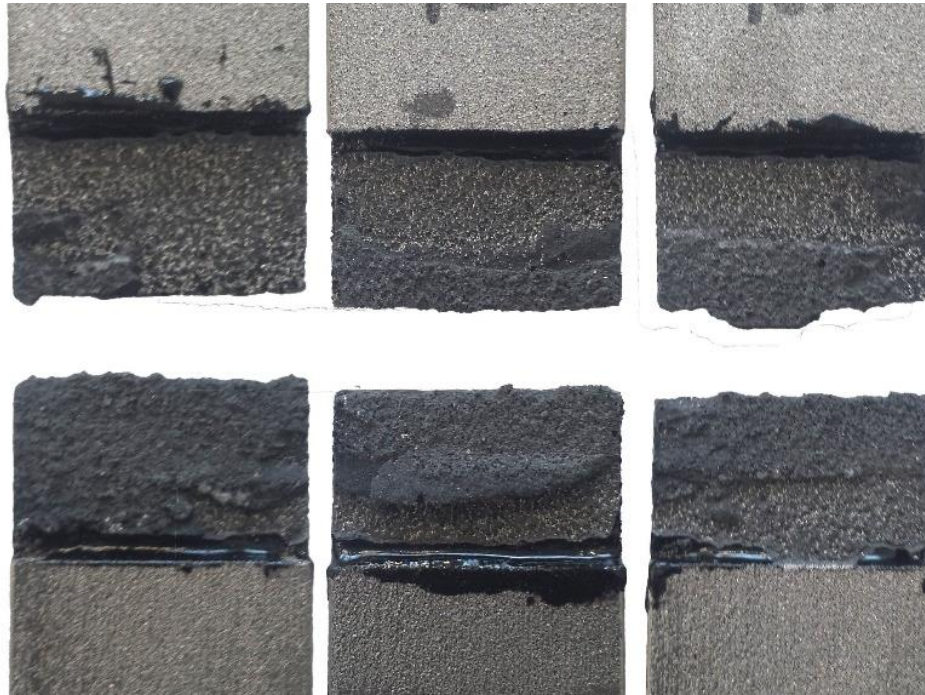


Figure 117: Macro images of the failure surfaces of the 02 meshed samples

Peeling forces arise due to large bending moments. For the 02 meshed samples this occurred because the material resisting the bending moment was only 1mm of solid with 1mm of titanium/epoxy composite. The composite has a very low modulus, so more deflection occurred compared to the vertical and horizontal build samples, which had 2mm of solid material resisting the bending moments. For the redesigned meshed * samples the peeling issues were fixed but some of the samples still varied greatly in their trajectory, therefore there is a degree of randomness with meshed samples which appears to be due to the composite part of the structure.

4.2.5 04 meshed D3165 (concentrically loaded SLJ) samples force versus extension data (0.4mm pores)

04 behaved very similarly to 02 but reached greater extension values, as shown in Figure 118. This was to be expected as 04 had twice the pore size and therefore less material. Hence, for the same bonding force, less titanium was available to resist the stress resulting in more extension.

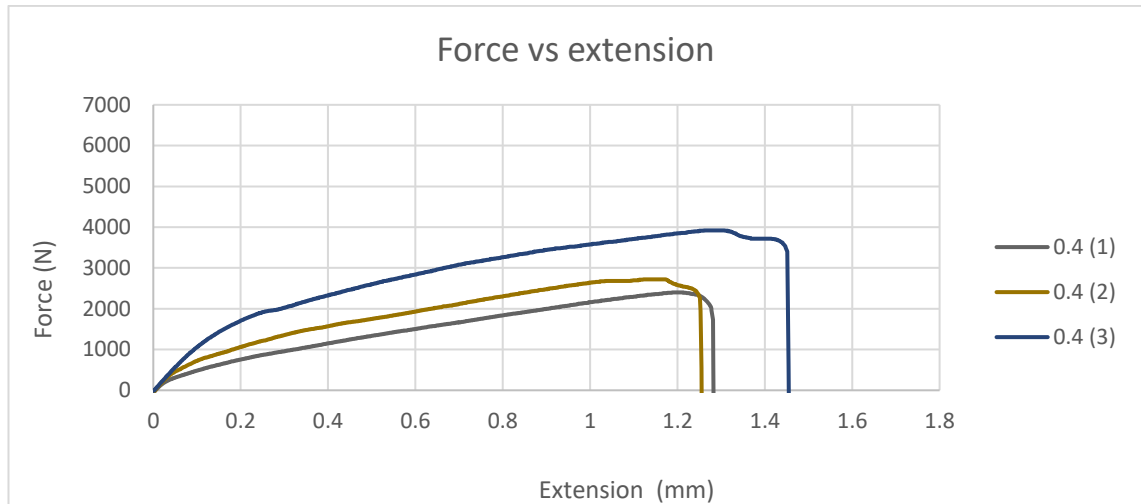


Figure 118: D3165 force vs extension graph for the 04 meshed samples

As shown in Figure 119, the mean failure stress for the 04 samples was 9.64 MPa and like the 02 samples the spread was large ranging from 7.68 - 12.54 MPa. This performance was below the adhesive manufacturers average strength values of 15.9 MPa. Therefore, this surface did not perform adequately.

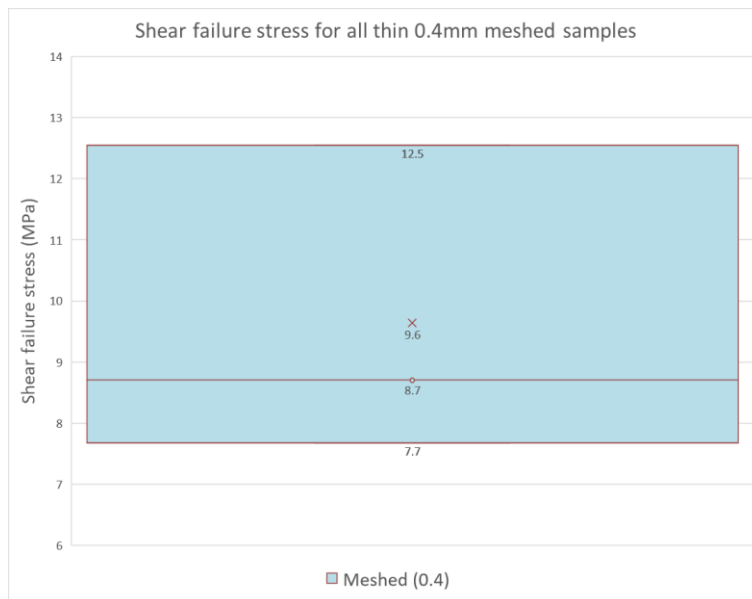


Figure 119: D3165 shear failure stress box and whisker graph for the 04 meshed samples

The 04 meshed samples also failed through a similar mixed failure mode as the 02 meshed samples did, as shown in Figure 120. This failure occurred as a mixture of cohesive failure in the epoxy and adhesion failure at the interface, with the bulk of material remaining at the tips of the coupons.

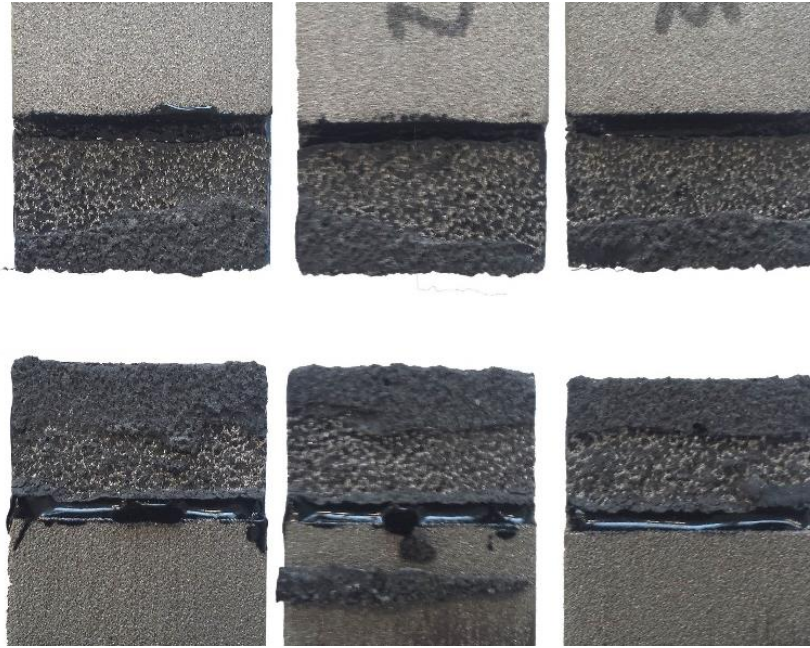


Figure 120: Macro images of the failure surfaces of the 04 meshed samples

4.2.6 04 and 02 meshed D3165 (concentrically loaded SLJ) samples force versus extension data

Figure 121 gives the force versus extension curves for both the 02 and 04 samples. It is clear from these curves that there was a lack of consistency in the meshed samples material response to force. Hence, the adhesive/substrate composite surface seems to be taking on different material values for each sample. Figure 122 shows that this distribution was greatest with the 02 samples.

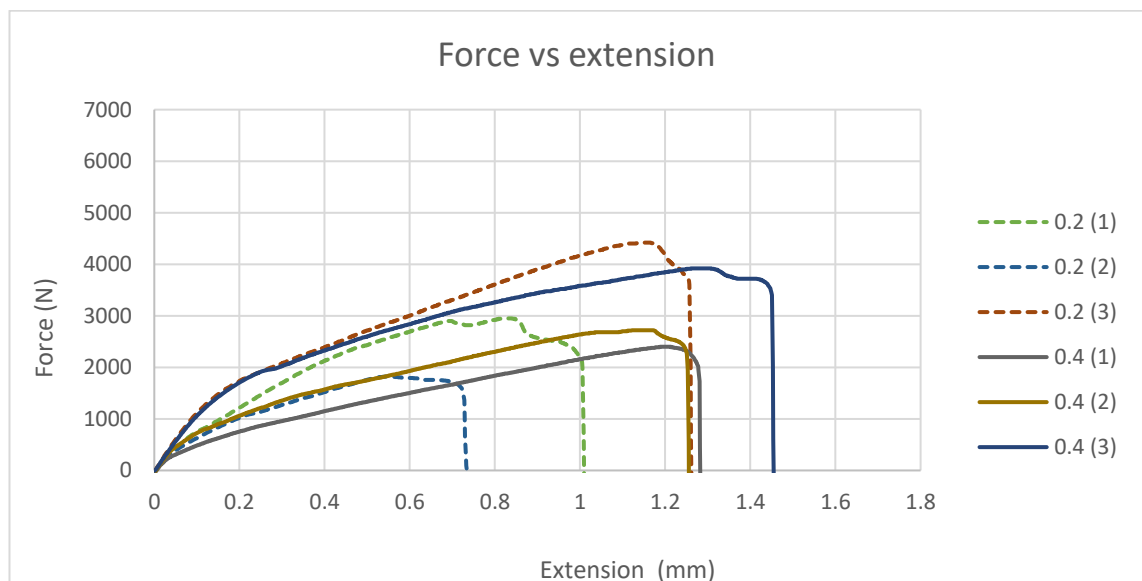


Figure 121: D3165 force vs extension graph for the 02 and 04 meshed samples

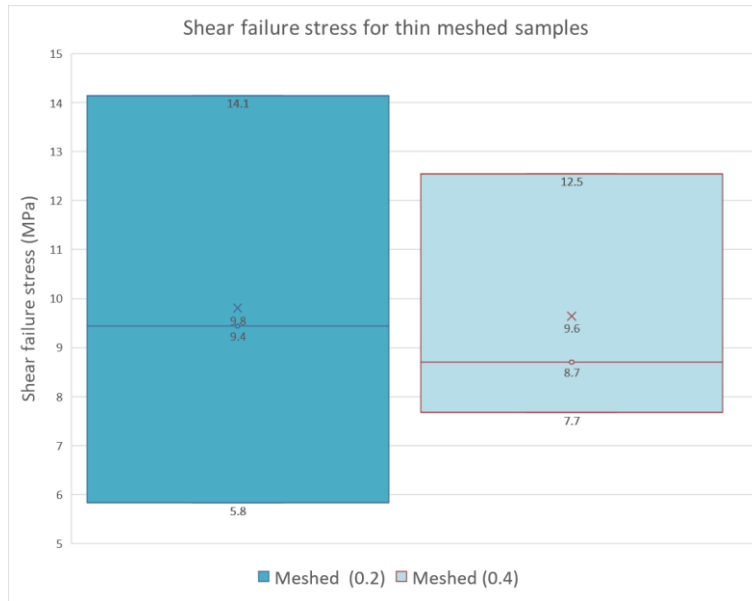


Figure 122: D3165 shear failure stress box and whisker graph for the 02 and 04 meshed samples

4.2.7 03* and 04* meshed D3165 (concentrically loaded SLJ) samples force versus extension data (Stiffened samples)

For the 03* and 04* there was only a small 0.1mm difference in pore size between the two samples, and the machine variation itself further made the difference between the 03* and 04* samples almost indistinguishable. This can further be seen in the fact that the results show no trends within their respective groups (although for both groups $n=2$). Therefore, it was decided to group both samples together into one group.

The revised meshed samples performed well, as shown in Figure 123. However, as observed for both the 02 and 04 meshed samples, the 03* and 04* meshed sample plots all took different trajectories, signifying that each sample had its own inherent mechanical properties.

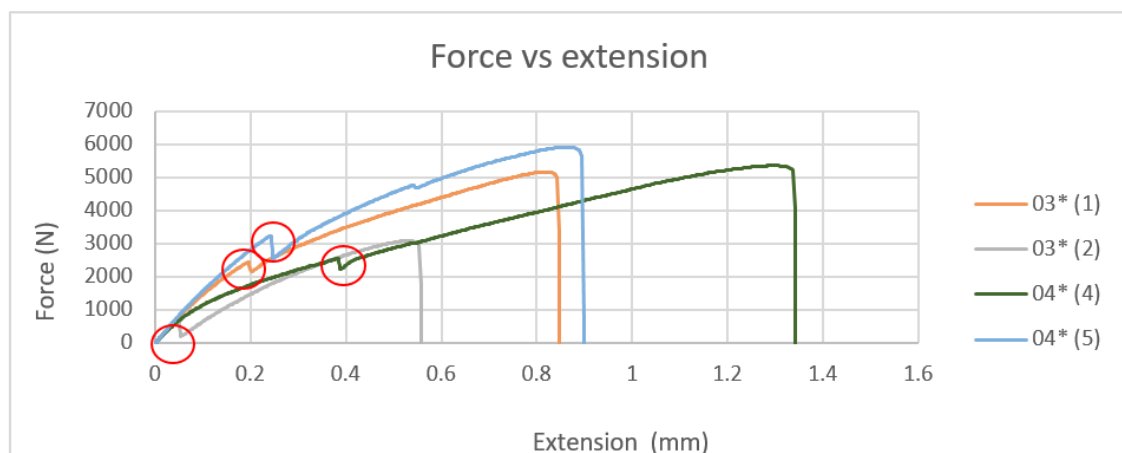


Figure 123: D3165 force vs extension graph for the 03* and 04* meshed samples

The sudden drops in force, circled above in red in Figure 123, were observed to occur due to the adhesive that remained at the bottom of the joint resisting force under tensile loading, as shown in Figure 124. This was confirmed as the drop-in force corresponded to a crack forming at this location during testing.



Figure 124: Adhesive that was remaining at the bottom of the joint acted in tension contributing a small amount of resistance to the forces

As seen in Figure 125 the revised meshed samples had a mean failure stress of 15.62 MPa, with the lowest stress reached being 9.86 MPa, and the highest stress reached being 18.94 MPa. This was the largest distribution of values out of any of the surfaces tested.

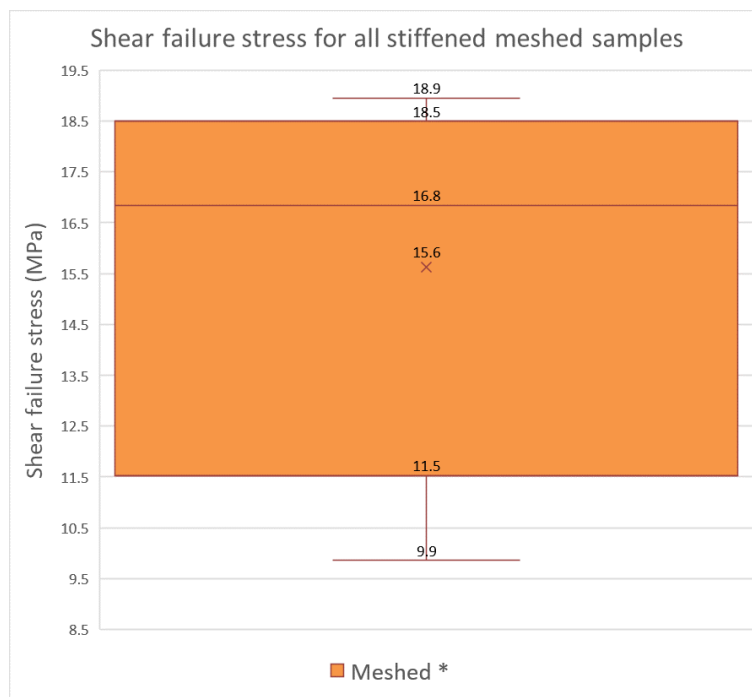


Figure 125: D3165 shear failure stress box and whisker graph for the 03* and 04* meshed samples

As with all the meshed samples, the failure surfaces shown in Figure 126, presents the failure mode as a mixture of cohesive failure in the epoxy and adhesion failure at the interface, with the bulk of material remaining at the tips of the coupons. However, the material remaining at the tips was less pronounced than with the thinner meshed samples 02 and 04. Some of the samples

even showed a zebra-striped pattern suggesting that material shearing was taking place. This pattern happened to occur on the sample that reached the highest stress value (04* (5)) which is the final sample on the right in Figure 126. This further confirms that peeling forces lower the adhesive bonding strength.

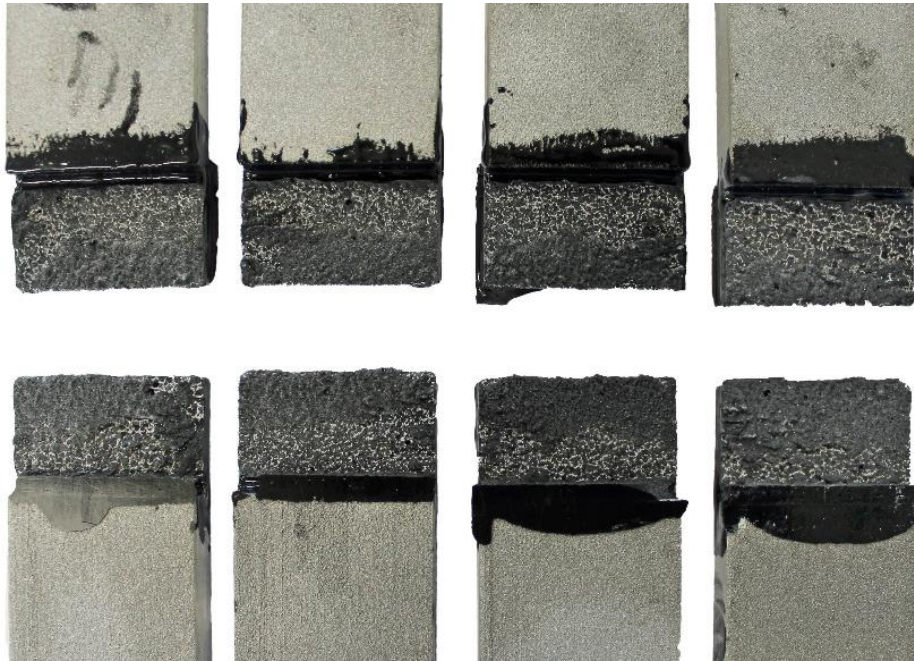


Figure 126: Macro images of the failure surfaces of the 03* and 04* meshed samples

4.2.8 All meshed D3165 (concentrically loaded SLJ) samples force versus extension data

It can be seen in Figure 127 and Figure 128, that the revised 03* and 04* meshed samples dramatically increased the resisted force. This was because the increased cross-sectional area reduced the material bending, which in turn reduced the peeling stresses. Interestingly, a few of the 02 and 04 meshed samples also showed a large amount of extension before failure, which was most likely due to the reduced cross-sectional area of the titanium resisting the force and therefore the greater effect it had on extending the material for a given force. Here, large peeling forces would have been present suggesting the meshed samples are good at resisting peeling forces. A future study of interest could be testing the meshed samples bonding surface under tension and under faster loading conditions.

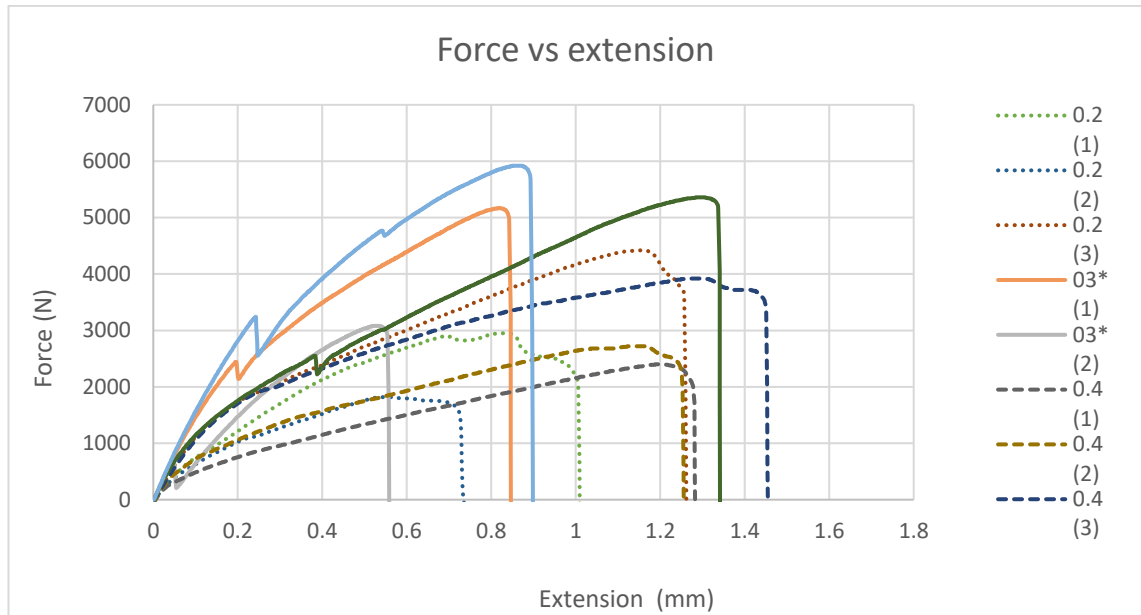


Figure 127: D3165 force vs extension graph for all meshed samples

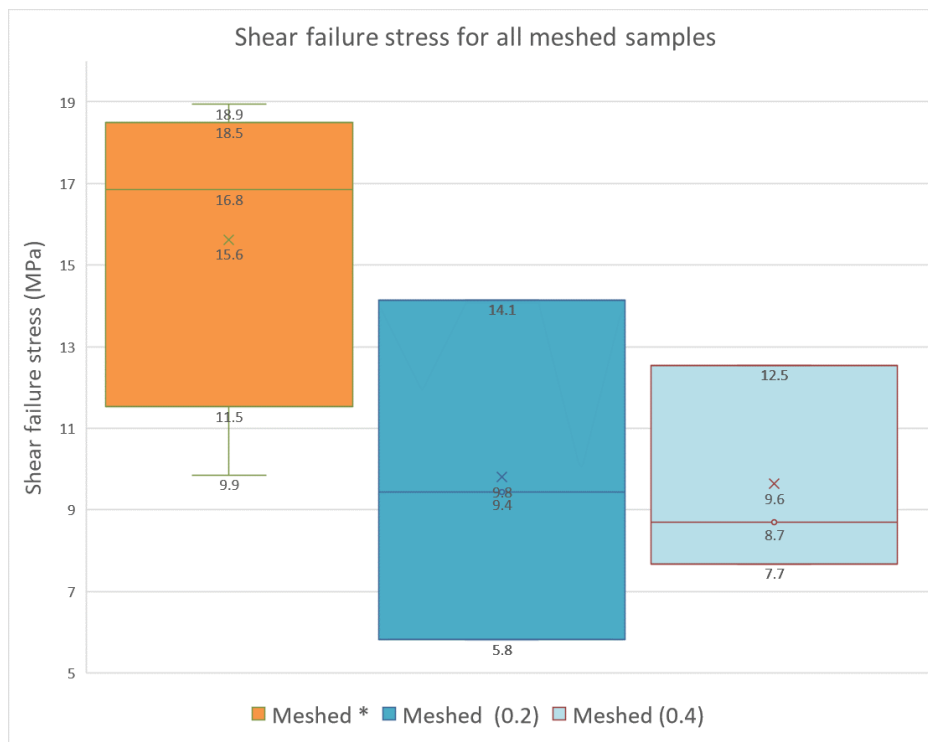


Figure 128: D3165 shear failure stress box and whisker graph for all meshed samples

- The revised 03* and 04* meshed surfaces were the third strongest surfaces outperforming the horizontal surfaces by 18% with a mean apparent failure shear stress of 15.62 MPa
- The 02 and 04 meshed surface did not provide the substrate with as much stiffness as the fully melted titanium. Therefore, these samples were exposed to greater peeling

forces and performed worse than both the vertical and horizontal surfaces, with a mean apparent failure shear stress of only 9.8 MPa

- The meshed surfaces had the largest distribution of strength values, suggesting the surfaces are sensitive to process variations. Perhaps air particles in the composite structure reduce the resisted load by acting as stress raisers.

4.2.9 Smooth D3165 (concentrically loaded SLJ) samples force versus extension data

As shown in Figure 129 and Figure 130, the smooth D3165 samples were the lowest performing surfaces, with two of the samples failing almost immediately. The mean failure stress reached was 3.02 MPa with the highest stress reached being 5.40 MPa. It is possible with the values of the smooth samples being so low that a processing error occurred reducing the strength of the bond. A possible cause could be contamination. Further, two different curve trajectories are present suggesting that the bond is acting with two different mechanical properties. This again suggests that there could be a material processing error occurring. It could be possible that the mechanical abrasion method used left residue on the surface that the acetone could not remove.

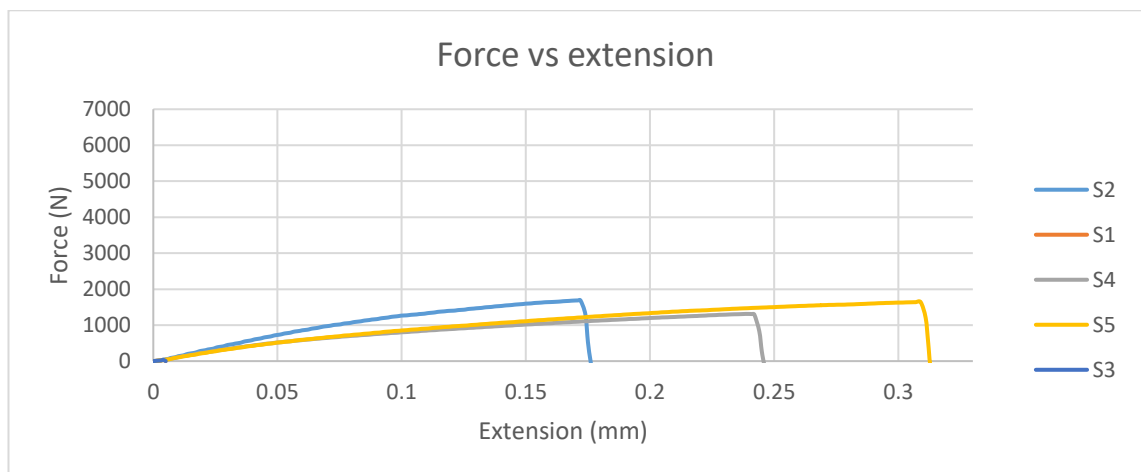


Figure 129: D3165 force vs extension graph for smooth samples

In Figure 131, the mode of failure for the samples that resisted force (S2, S4, S5), showed complete adhesion failure at the adhesive/substrate interface on both samples with a fracture path moving through the bulk of the material. This seems to suggest that certain areas of the bonding surface had higher specific adhesion, suggesting a possible contamination problem. Further, the samples that didn't resist any force, failed completely due to adhesion failure on one of the adhesive/substrate interfaces.



Figure 130: D3165 shear failure stress box and whisker graph for the smooth samples

It is recommended that a future study collects further data with the surface preparation involving an HF and nitric acid etching before bonding to ensure all contamination is removed. This will either confirm the results found; that smooth surfaces are poor bonding surfaces; or confirm that the samples were contaminated.

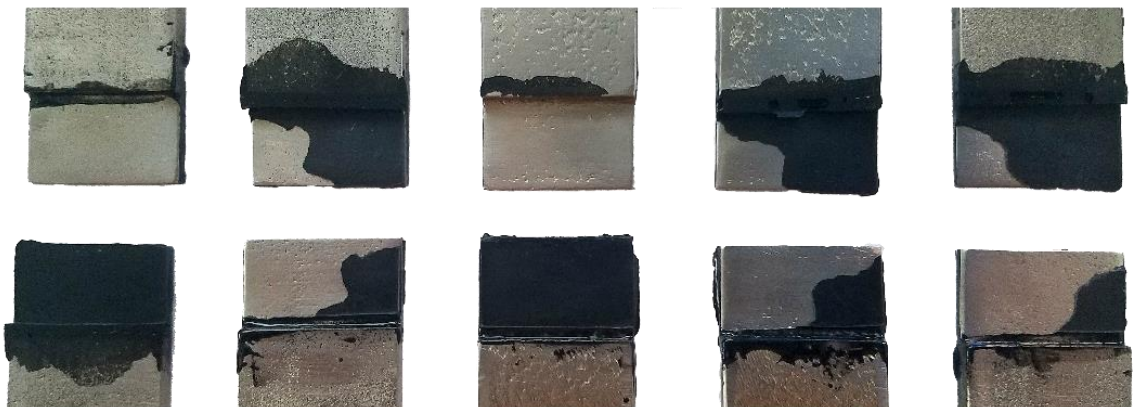


Figure 131: Macro images of the failure surfaces of the smooth samples. Left to right S1-S5

- The smooth surfaces performed very poorly with two samples breaking before testing. It was believed that the surfaces were potentially contaminated, and it is suggested that future work be carried out where before bonding the surface is confirmed to be free of contamination. This way it can be confirmed that contamination caused the low performance, or that in fact the surface is just a low performing surface.

4.2.10 NaTESI D3165 (concentrically loaded SLJ) samples force versus extension

As seen in Figure 132, all NaTESI anodised samples followed a similar trajectory, suggesting consistent mechanical properties amongst them. The distribution was not as tight as the vertical build surfaces ranging from a failure stress of 16.38 MPa at the lowest and 21.95 MPa at the highest, see Figure 133. The distribution is close enough to say that the adhesive/surface combination appears to have a somewhat predictable stress strain response and base mechanical properties. However, unlike the vertical surfaces that showed a mixed failure system, the NaTESI adhesive bonds failed through full cohesive failure of the adhesive as seen in Figure 134. This means the component that resulted in failure was the adhesive. Therefore, the slight changes in the material response trajectories shown in Figure 132 are all due to the mechanical properties of the adhesive slightly differing.

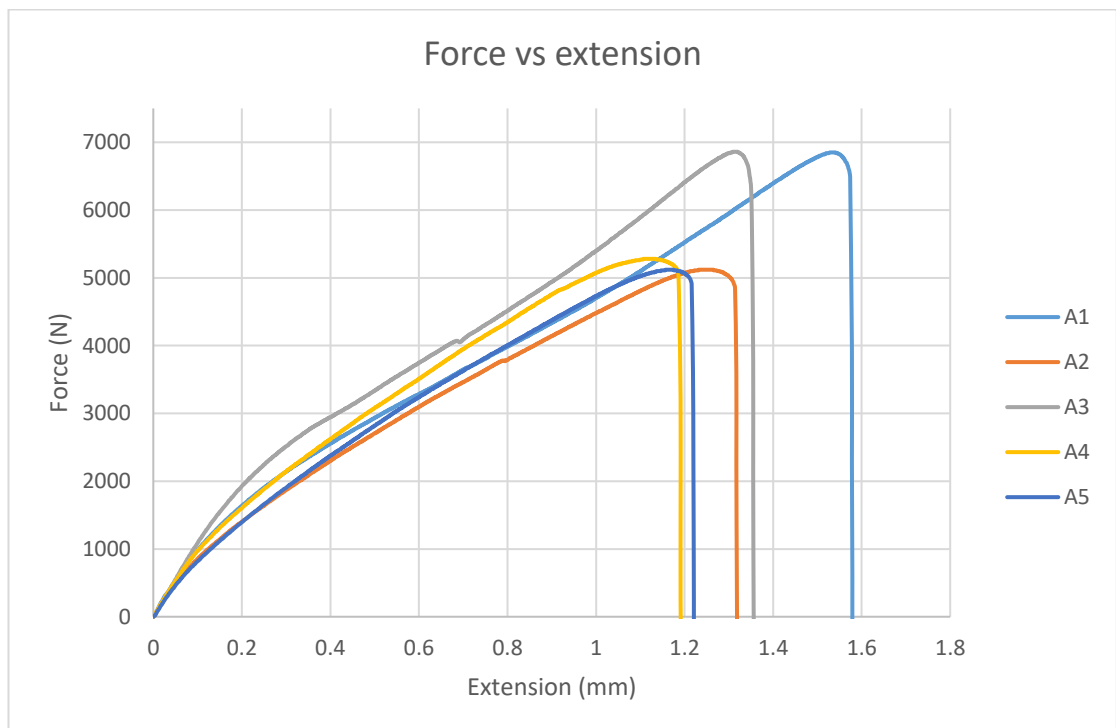


Figure 132: D3165 force vs extension graph for the NaTESI samples

Through achieving complete cohesive failure of the adhesive, the anodised surfaces achieved strength values greater than the vertical surfaces, making them the strongest surfaces investigated. This is further demonstrated by the box and whisker graph shown in Figure 133. Here, a mean failure stress of 18.71 MPa is shown (4.3% stronger than the vertical surface), with the lowest sample reaching only 16.38 MPa and the highest reaching 21.92 MPa (9.2% greater than the best vertical surface). However, unlike the vertical surfaces where failure was a mixed mode, the mode of failure was entirely cohesive failure in the epoxy, as shown in Figure 134. This means given a stronger adhesive, the NaTESI surface would further outperform the vertical surface, at least until failure becomes a mixed mode or an interface failure.

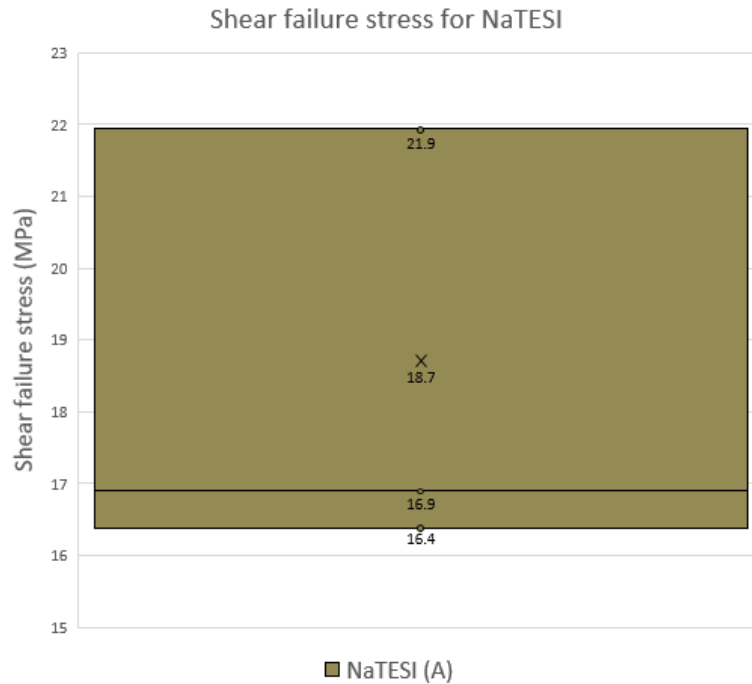


Figure 133: D3165 shear failure stress box and whisker graph for the NaTESI samples

From the cross-section images in Figure 134, mechanical interlocking is clearly occurring with the adhesive becoming entrapped in both the micro and nano pores and crevices of the coral-like NaTESI surface structure. This was visually found to occur up to a magnification of 15000x at which point the conductive nature of the epoxy (even when coated with platinum) prevented the clear image capturing at a higher magnification. This wetting out of the adhesive may have continued to occur even further. From these images it is confirmed that the epoxy used can easily wet the surface of the NaTESI anodised surface.

The epoxy shear surfaces shown in Figure 134 show a clear distribution of air bubbles across the surface. Using an autoclave would reduce these bubbles, increasing the strength of the joint even further. Looking carefully at the 0x magnification, a slight zebra-striped pattern can be seen on the samples. This suggests that a significant part of the loading was shear loading. However, a greater amount of material was still present on the tips of the samples, suggesting that peeling stresses were still involved in the failure as well.

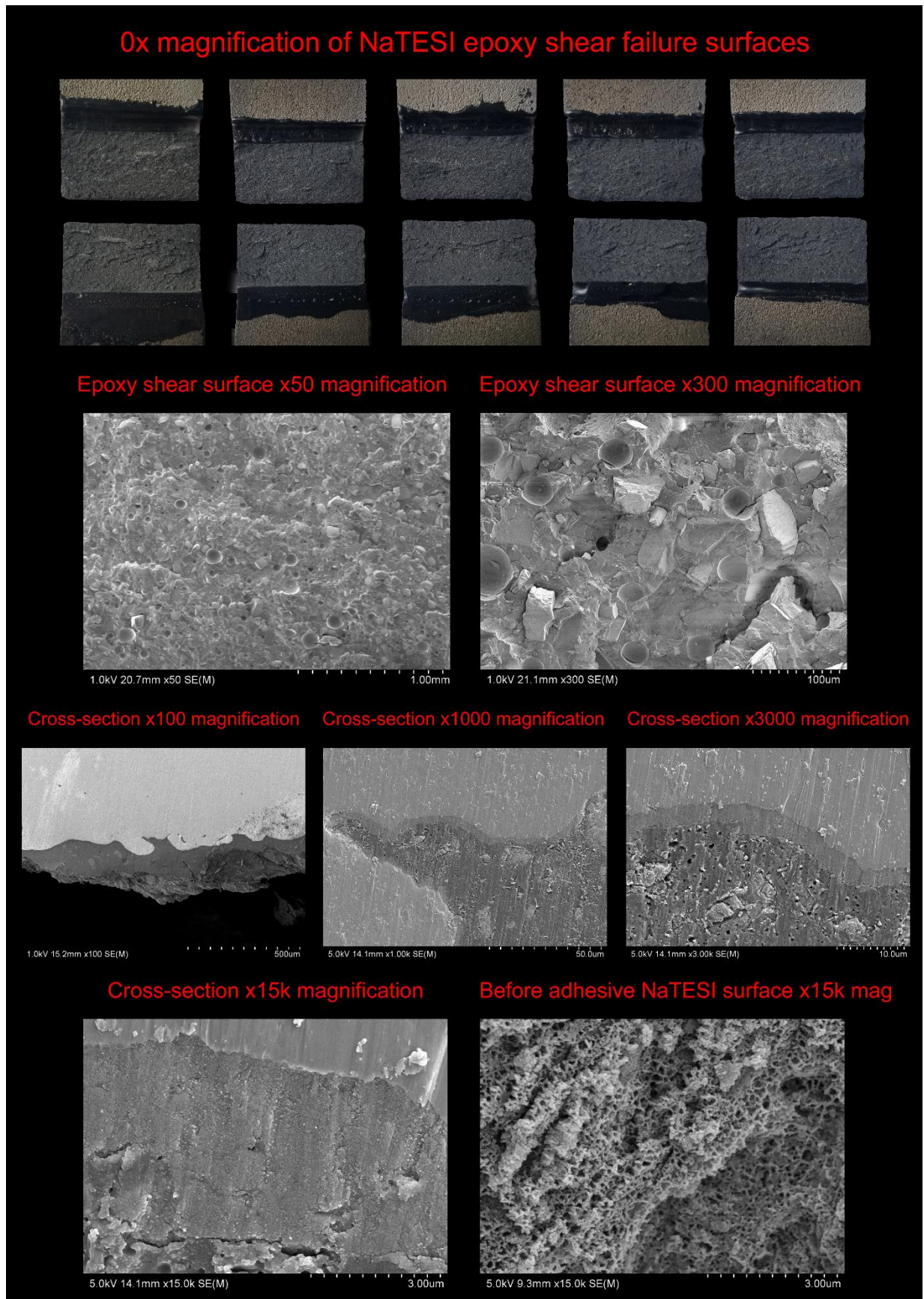


Figure 134: SEM images of a vertical build samples failure surface and cross-section

The illustration in Figure 135 shows how the micro and nano-roughness of the NaTESI surface can mechanically interlock with the epoxy adhesive, forming an interlocked composite. This composite then possesses mechanical properties that are superior to those possessed by the bulk of the adhesive. Hence, failure is diverted from the interface into the bulk of the adhesive where the strength of the system is the weakest.

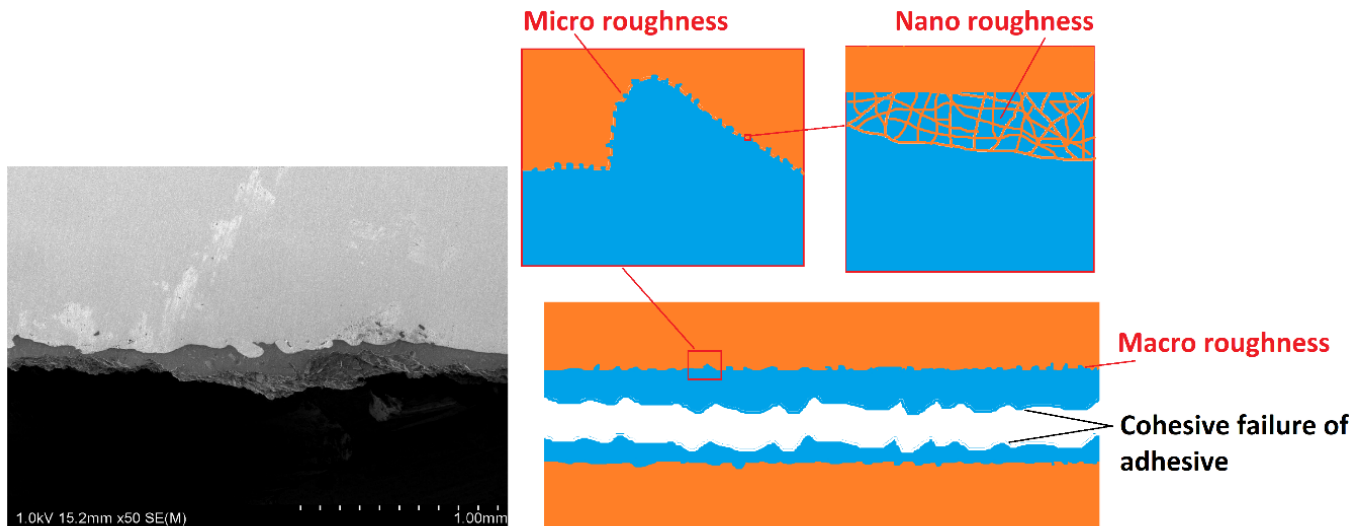


Figure 135: Fractal surface roughness in NaTESI samples relieving the specific adhesion at the interface to such a degree failure is forced to occur cohesively in the adhesive

- The NaTESI anodised surface was the strongest performing surface with a mean apparent failure shear stress of 18.71 MPa (4.2% stronger than the vertical surface mean) and a maximum apparent failure shear stress of 21.95 MPa (9.15 % stronger than the strongest vertical surface sample). Further, the joint failed entirely cohesively, meaning the key component that resulted in failure was the adhesive. Hence, with a stronger adhesive the NaTESI anodised surfaces should reach even higher strength values.
- The NaTESI anodised surface reached the maximum strength of the adhesive.

4.2.11 All D3165 (concentrically loaded SLJ) samples force versus extension data

Figure 136 demonstrates that for the same materials, macro geometry, adhesive thickness, and bond overlap area, the surface morphology of the substrate has a profound effect on the strength of the adhesive bond. This can vary the failure force from 36N to 6860N (0.12 MPa to 21.95 MPa) and the max extension from 0.004mm to 1.58mm.

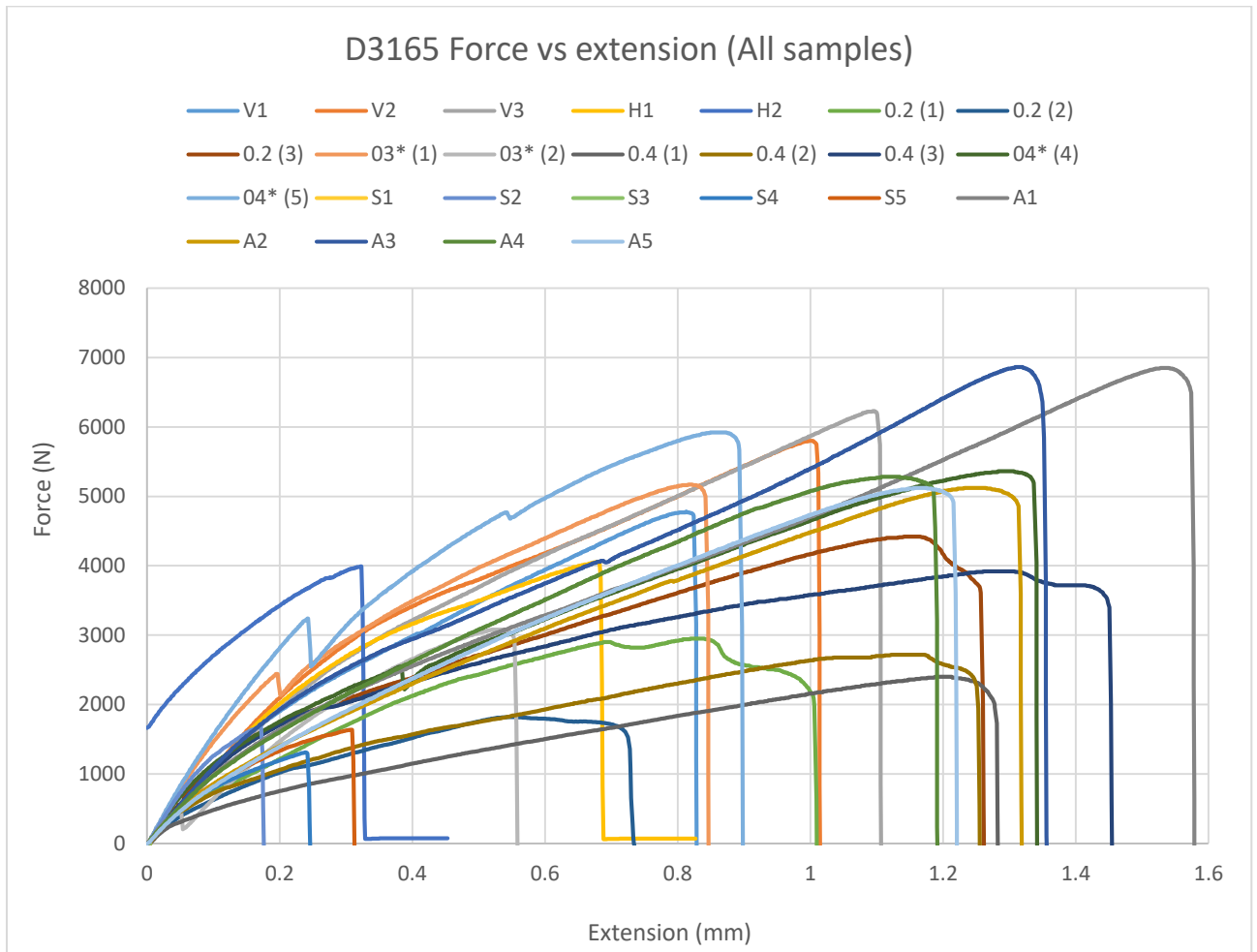


Figure 136: D3165 force vs extension graph for all samples

Figure 137 reduces the scope to include only the strongest D3165 samples from the different surface types. It appears that the vertical, NaTESI, 02 and horizontal build surfaces share similar mechanical properties over an elastic range of 0.2mm. Beyond this the force and extension responses begin to diverge from one another.

The meshed samples had the highest divergence in their trajectories when compared to the other samples because the surfaces were composite surfaces. Even amongst their own samples the differences between the trajectories of the meshed samples were large. This was

possibly due to sensitivity to processing defects such as air bubbles in the adhesive, or even processing defects from printing. The smooth surface also follows a different trajectory to the other samples. It was expected that it would follow a similar path to the horizontal and vertical build surfaces, but that it would fail earlier or unexpectedly at the interface. As suggested before, the smooth samples require further testing with greater contamination control, to either confirm or disprove the poor performance. This is because unlike the other samples that were bonded after removal from the printer, the smooth samples were old samples that were mechanically abraded smooth, and therefore have a higher chance of being contaminated.

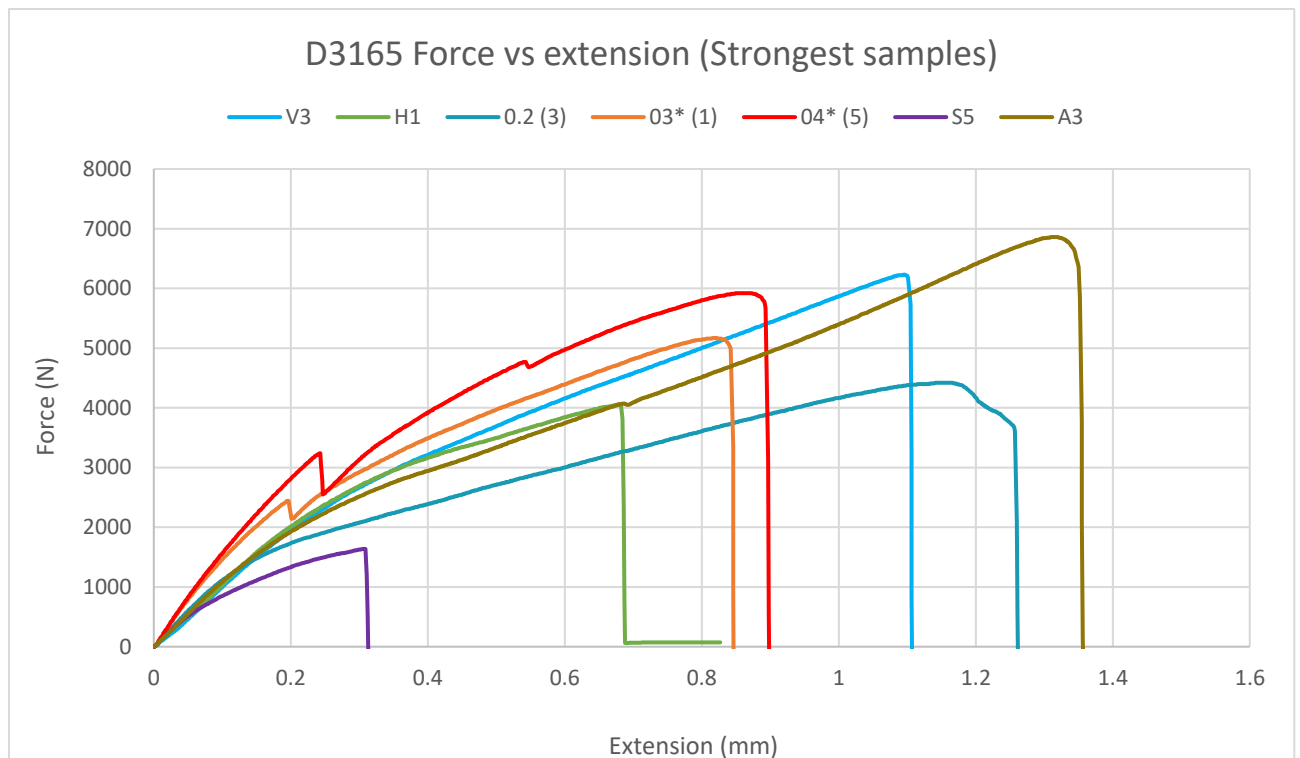


Figure 137: D3165 force vs extension graph for the strongest sample from each surface type

Figure 138 restricts the domain of the graph to 0.2mm to view whether these elastic relationships exist for other surface types. Here, it is even clearer the relationship between the vertical, NaTESI, 02 and horizontal surfaces. The 03* (1) and 04* (5) samples also seem to share a similar force and extension response but only up to an extension of around 0.02mm at which point they begin to diverge.

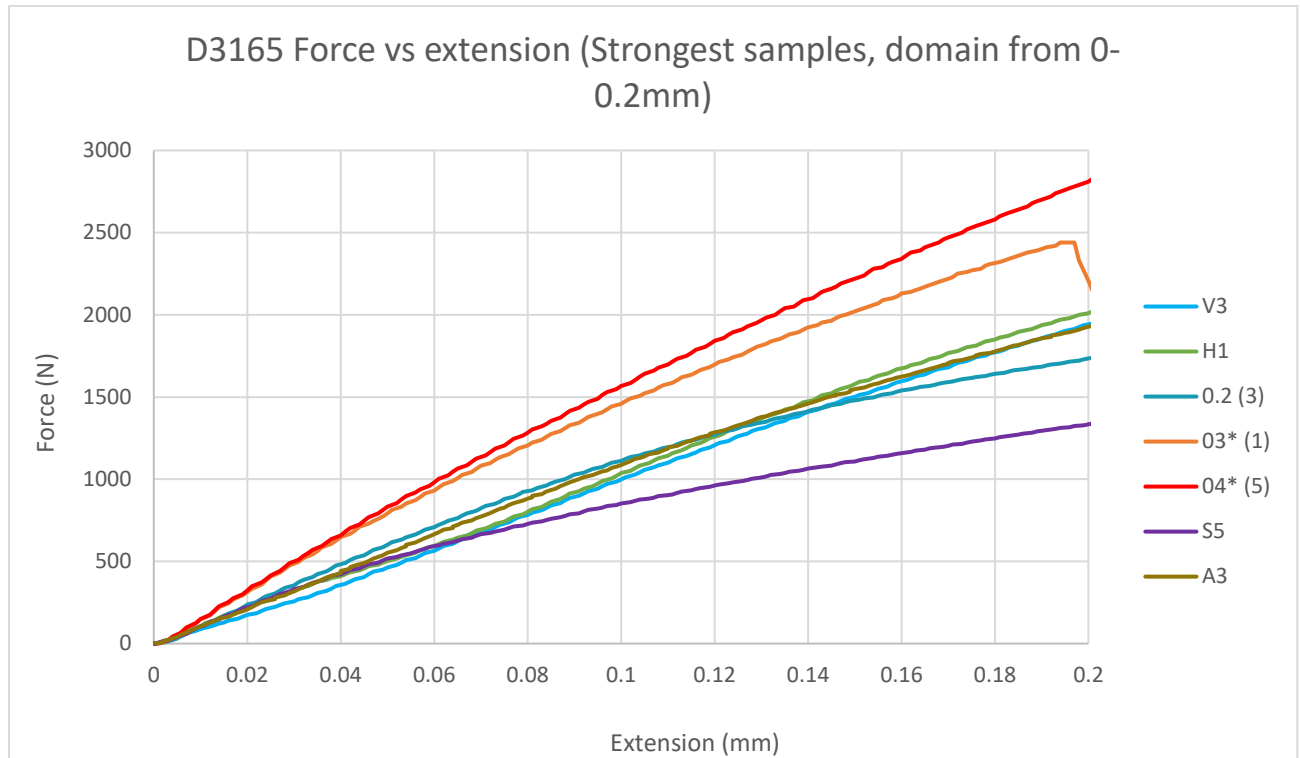


Figure 138: D3165 force vs extension graph for the strongest sample from each surface type. Showing force by extension over the first 0.2mm

The following section will now discuss and summarise the results of the D3165 (concentrically loaded SLJ) experiments.

4.2.12 Discussion of D3165 (concentrically loaded SLJ) experiment

The NaTESI anodised and vertical surfaces performed the best, followed by the meshed surfaces, with their best respective apparent shear strength values being 21.95, 19.96, and 18.9 MPa. The vertical and NaTESI surfaces were the roughest when measured for micro-roughness using a surface profilometer, being (Ra 15.4 μm and Ra 15 μm) respectively. Further, the NaTESI surface was the only sample to possess nano-roughness when visually measured with the SEM under high magnification.

For the vertical samples, the mode of failure was a mixture of cohesive failure in the epoxy adhesive, and adhesion failure at the adhesive/substrate interface. The surface of the vertical samples was very rough at the micro level due to the partially melted powder particles. It was this micro-roughness which caused the mixed failure mode as the gaps between the powder particles were able to trap the epoxy into mechanically interlocked bonds. This allowed the specific adhesion between the polymer chains and the titanium substrate to be stress relieved, shifting failure into the bulk of the adhesive. It is also possible the mechanical interlocking provided more contact area between the epoxy polymer chains and the titanium substrate for specific adhesion to act.

The NaTESI surfaces had the same micro-roughness as the vertical build samples that they were derived from. However, for the NaTESI surfaces, the mode of failure was full cohesive failure of the adhesive. This means the interface and bonding strength between the epoxy and titanium was even stronger for the NaTESI samples than for the vertical samples. It is possible that similar to the interaction between the micro-roughness and the adhesive, for the nano-roughness, the epoxy is able to wet out and mechanically interlock with the nano-structures. Thus, the roughness of the interface is able to impede the deformation movement of the polymer chains. This causes the adhesion between the polymer chains and the titanium to be so stress relieved that failure occurs cohesively through the bulk of the adhesive. Additionally, because this failure occurs due to the adhesive's cohesion strength, a stronger adhesive would see even greater values of resisted force for the NaTESI surface.

The horizontal surface performed the second worst with an average shear strength of only 12.77 MPa. This is most likely due to its low surface roughness (R_a 5.5 μm) causing no mechanical interlocking. This was a good result as the horizontal surface is also not a practical surface for real-world objects, as a part would need to be orientated so that the surface is flat with the electron beam hitting it perpendicularly. Hence, only flat surfaces can be produced.

The meshed surfaces in some cases performed well with high levels of strength reached, such as 18.9 MPa for the 03* (2) sample. However, the meshed samples varied in both resisted force and the material force and extension response. This makes the use of the meshed surfaces in design have less predictability when compared to the other surfaces which had a tighter distribution.

The smooth surfaces performed the worst with only 5.4 MPa in apparent shear strength. These surfaces failed through full adhesion failure, which most likely occurred because there was little to no mechanical interlocking present. This suggests that the specific adhesion between the epoxy and the Grade 5 titanium is not a very strong bonding force. Therefore, to improve bonding strength the specific adhesion needs to have more bonding locations (increased surface area) or to have the loading on it stress relieved by impeding the deformation movement of the epoxy. Both of these mechanisms are provided by rougher surfaces, explaining why surface roughness was shown to improve the bonding strength.

It is still recommended that all experiments be carried out in the future with the use of an autoclave and with the surfaces being acid etched before bonding. The thought is that this may tighten the distribution of the weak and varied samples such as the meshed and smooth surfaces, by eliminating possible contamination and/or air bubble defects.

4.3 Simulation

This chapter will cover the simulations which were used to deduce both the mechanical properties of the adhesive, the maximum stress locations, and types of stresses causing failure. It was found that the adhesive had a very low modulus and would materially be categorised as a rubber. Further, the failure locations matched the experimental results showing that failure was occurring due to predominantly peeling forces. Therefore, geometry changes that reduce peeling stress will increase the force resisted. Peeling stresses are tension stresses which act on the lapping edges towards the y-axis direction. Refer to section 2.8.3 for an explanation of peeling stresses. For the following simulations the normal stress in the y-axis will be used to represent the peeling stresses.

4.3.1 Simulation results

The graph shown in Figure 139, shows the force vs extension results of the strongest samples from both the D1002 and D3165 experiments and the simulation results using the D1002 and D3165 geometries. The simulations produced results consistent with the experimental results, confirming that the mechanical properties selected in section 3.6 are consistent with the real properties of HPR 25. This was unexpected as many simplifications were made in the model.

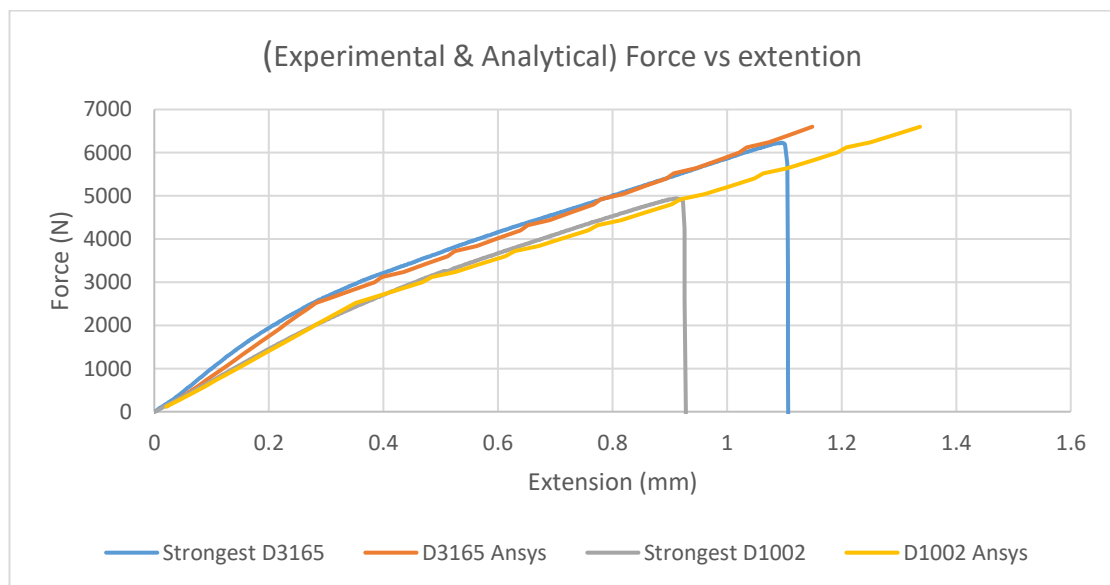


Figure 139: Experimental and analytical force versus extension graph

In both the experiment and the simulation, the D1002 samples reached greater extensions than the D3165 samples for an equivalent force, see Figure 140. This was because the cross-sectional area of titanium was greater for D3165 (105 mm²) versus D1002 (50 mm²) and therefore the geometry strained less for the given load. This can be seen from the basic Young's modulus relationship below:

$$E = \frac{\sigma}{\varepsilon} \quad \& \quad \varepsilon = \frac{\sigma}{E} = \frac{F}{EA}$$

The strain (ε) is equal to the force over the product of the Young's modulus (E) and cross-sectional area (A). Therefore, for a given load if cross sectional area (A) increases, strain (ε) decreases. This is clearly shown in Figure 140, with the D1002 sample extending an extra (0.18mm) along the x-axis.

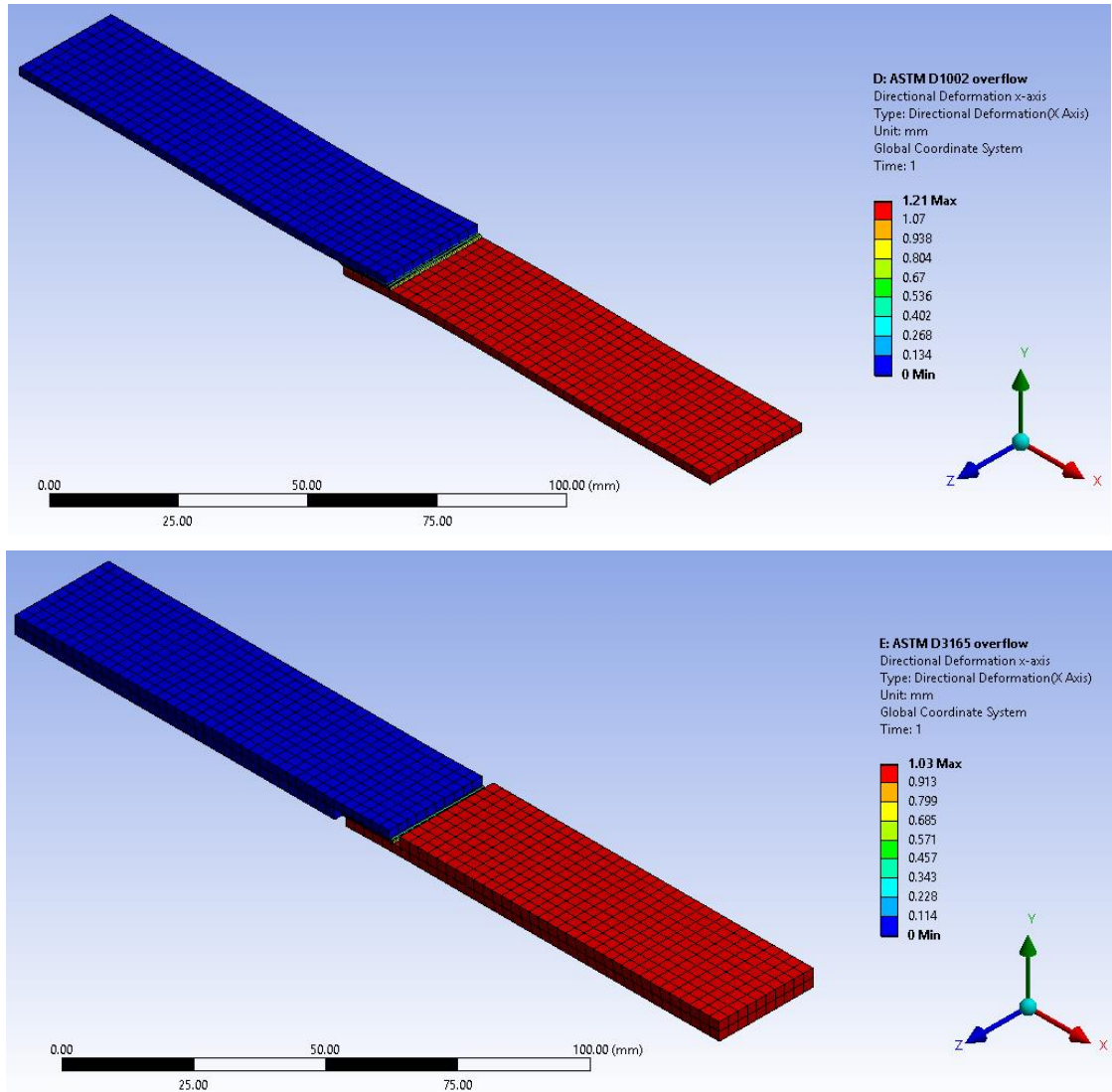


Figure 140: Analytical results for extension along x-axis

As shown in Figure 141 below, D1002 was exposed to an extra 0.74 MPa peeling stress (normal stress in the y-axis). Adhesives are most prone to failure from peeling stresses, so this would be a major contributor in the earlier failure of D1002 when compared to D3165. The peeling stress was calculated in the simulation using a path coinciding with the top adhesive/substrate interface.

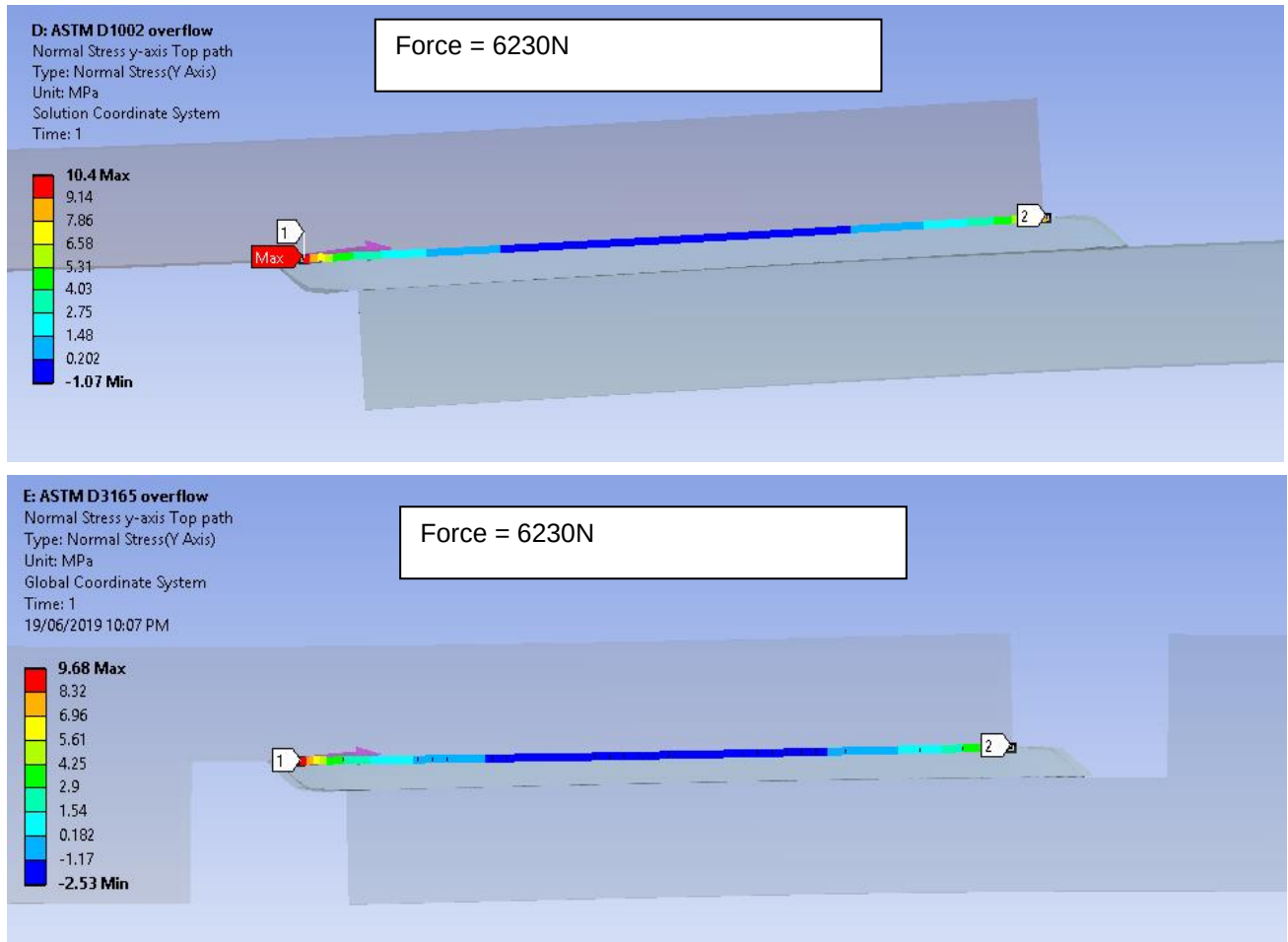


Figure 141: Analytical results for normal stresses along y-axis (peeling stresses) for D1002 and D3165

When both models were loaded with the maximum force obtained from the D3165 experiment (6230 N), the D3165 model was exposed to fewer peeling forces, as seen in Figure 142.

Further, Figure 143 gives a bar graph of the maximum peeling stress for the greatest D1002 and D3165 loading forces. For the same forces D3165 had fewer peeling forces than D1002, which proves that the concentric loading of the D3165 joint does indeed reduce the bending moments and subsequently the peeling stresses experienced.

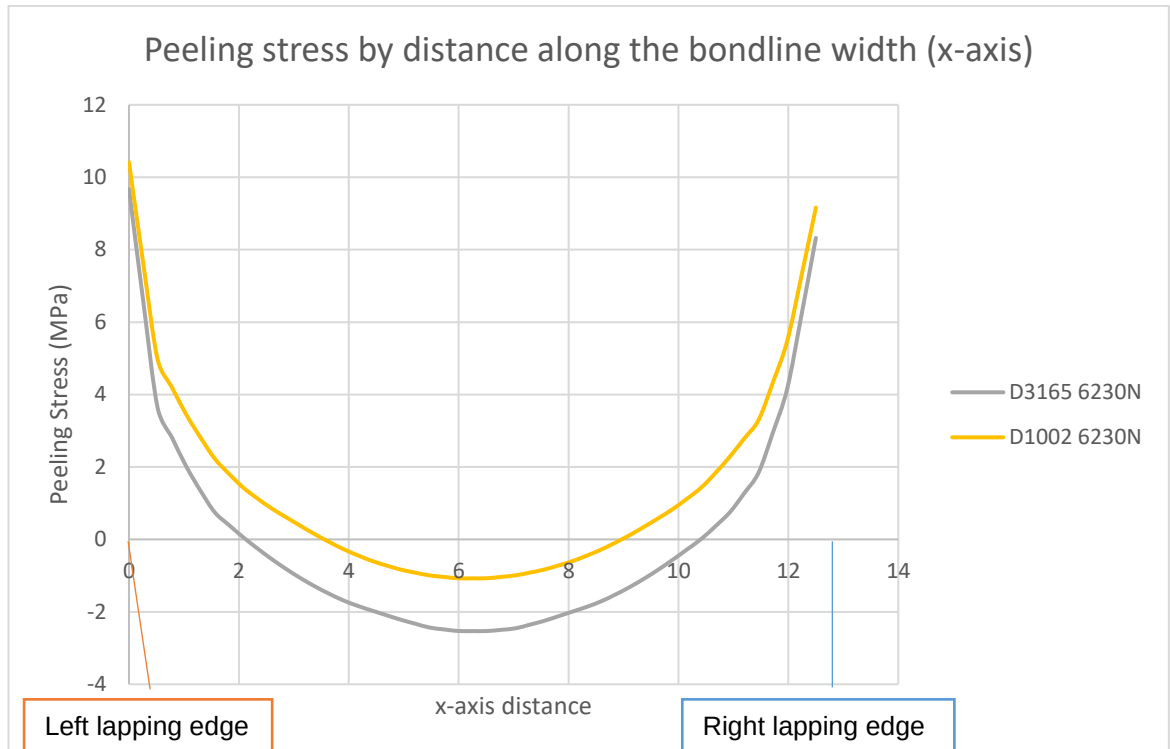


Figure 142: Peeling stresses versus x-axis distance along bonding surface

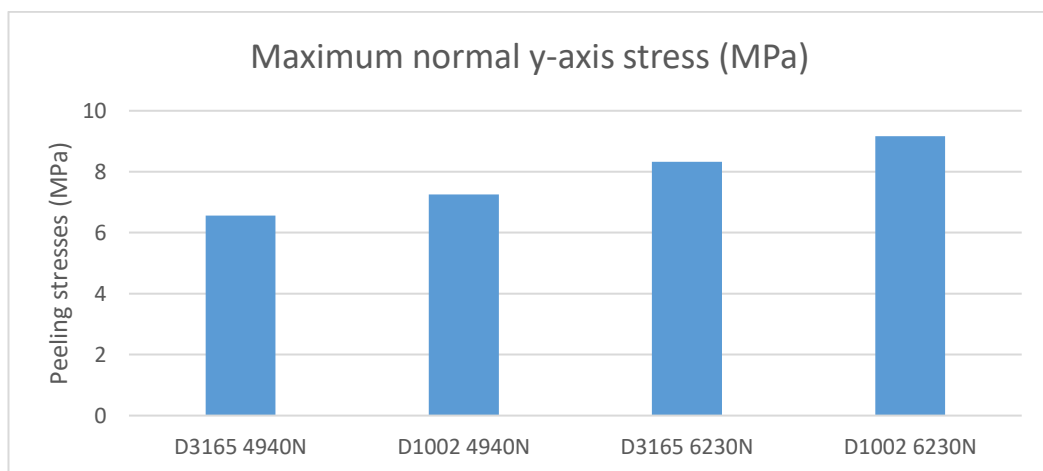


Figure 143: Bar graph of the analytical maximum peeling stress for the greatest D1002 and D3165 loading forces

These peeling stresses are a consequence of the bending moments which are induced due to the placement of material away from the neutral axis of the applied load. These bending moments cause deformation to occur along the y-axis, inducing peeling stresses. Below Figure 144 demonstrates that this deformation is greater at the bond line for D1002 (~0.35 mm) than for D3165 (~0.12 mm).

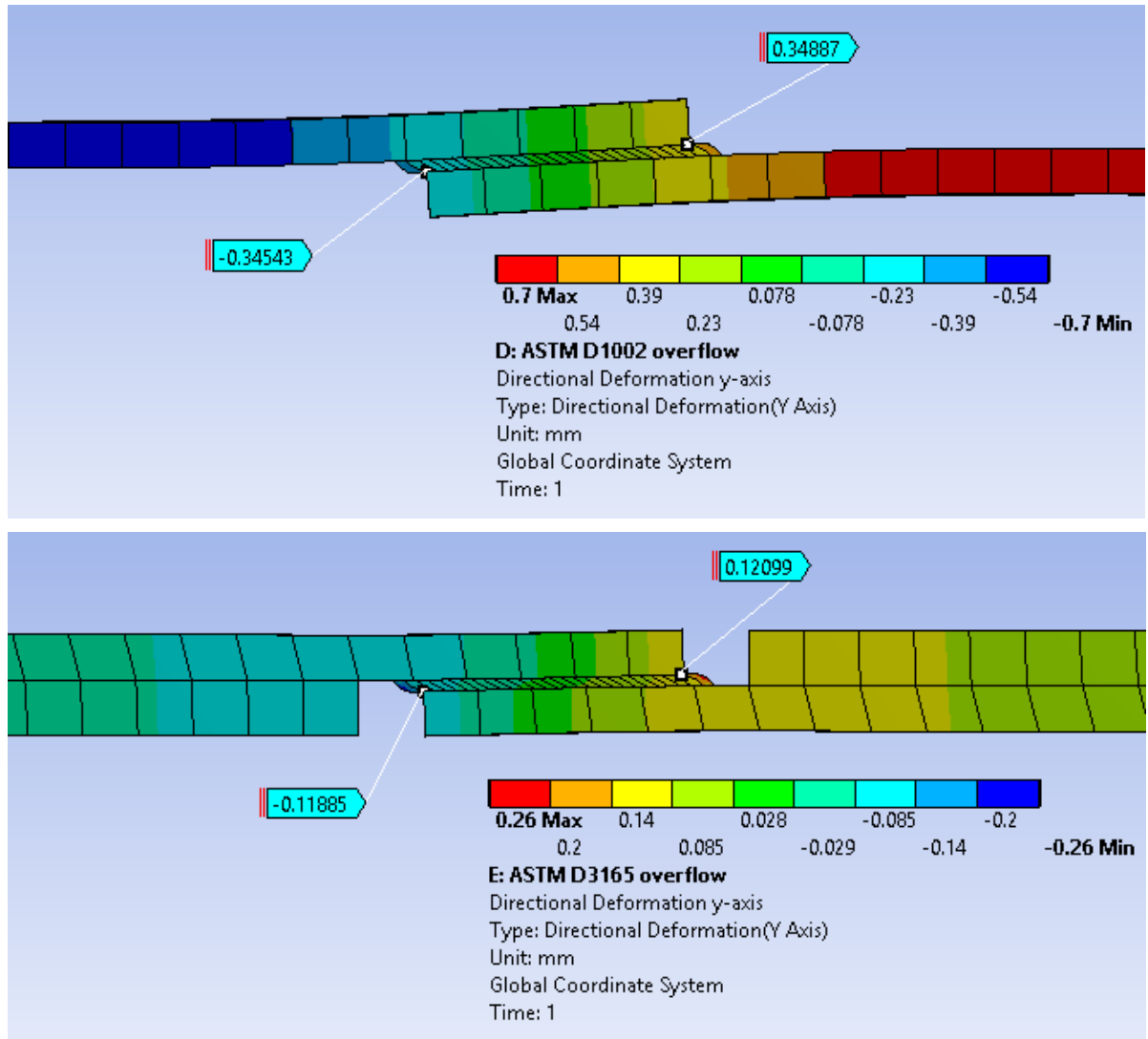


Figure 144: Analytical deformation along the y-axis for both the D1002 and D3165 geometries

As the y-axis deformation was reduced with the D3165 geometry, it is evident that concentric loading reduces the induced bending moments. The next section will investigate the stress distributions along the adhesive bond line, to understand the failure path and the stress that leads to failure.

4.3.2 Failure path and maximum stress location

The failed surfaces of the experimental meshed samples, shown in Figure 145 show that the failure path for all meshed samples was consistent with more adhesive material remaining on the lapping edges of all the samples. This failure path of more adhesive material remaining at the lapping edges was consistent with all samples which showed a mixed or cohesive failure mode, such as the NaTESI anodised samples and some of the vertical samples. However, for visual representation, the meshed samples presented this the clearest.

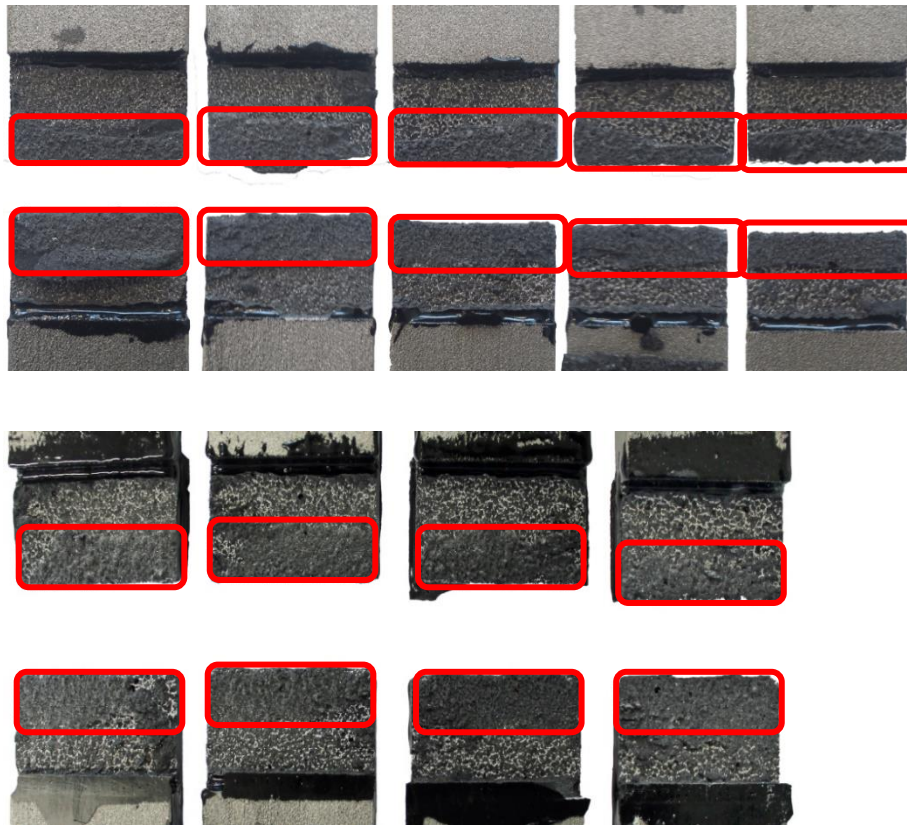


Figure 145: Fracture surface for all D3165 meshed samples

As shown in Figure 146, the fracture paths (in red) began at the lapping edges (the highest stressed points) and moved along the adhesive/substrate interface until midway along the plane. They then shifted their path converging into the bulk of the material. Due to the failure path travelling from both sides, the convergence caused material to be lost from the centre of the sample, as highlighted in red in Figure 146.

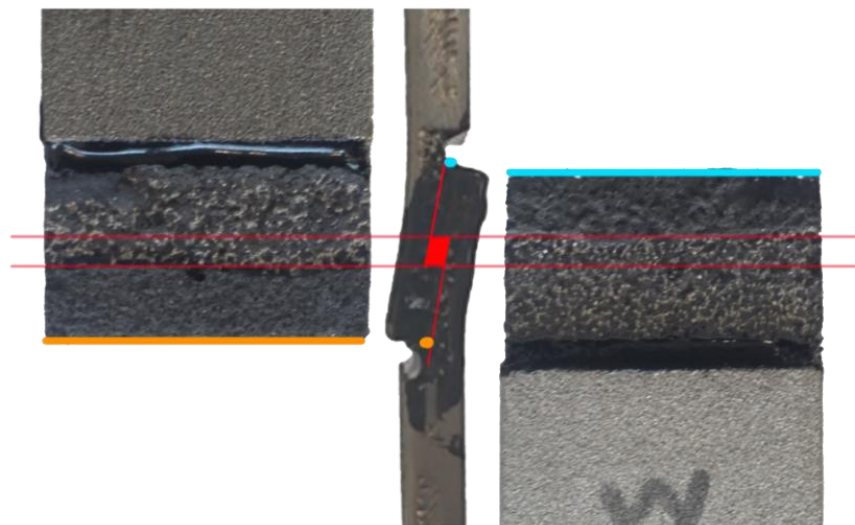


Figure 146: Fracture path for the D3165 meshed samples

The maximum principal and normal y-axis stresses shown below in Figure 147 coincide with the experimental data, confirming that the highest stressed points are in the lapping edges where the adhesive meets the substrate. These points are shown in Figure 147 highlighted in blue and orange.

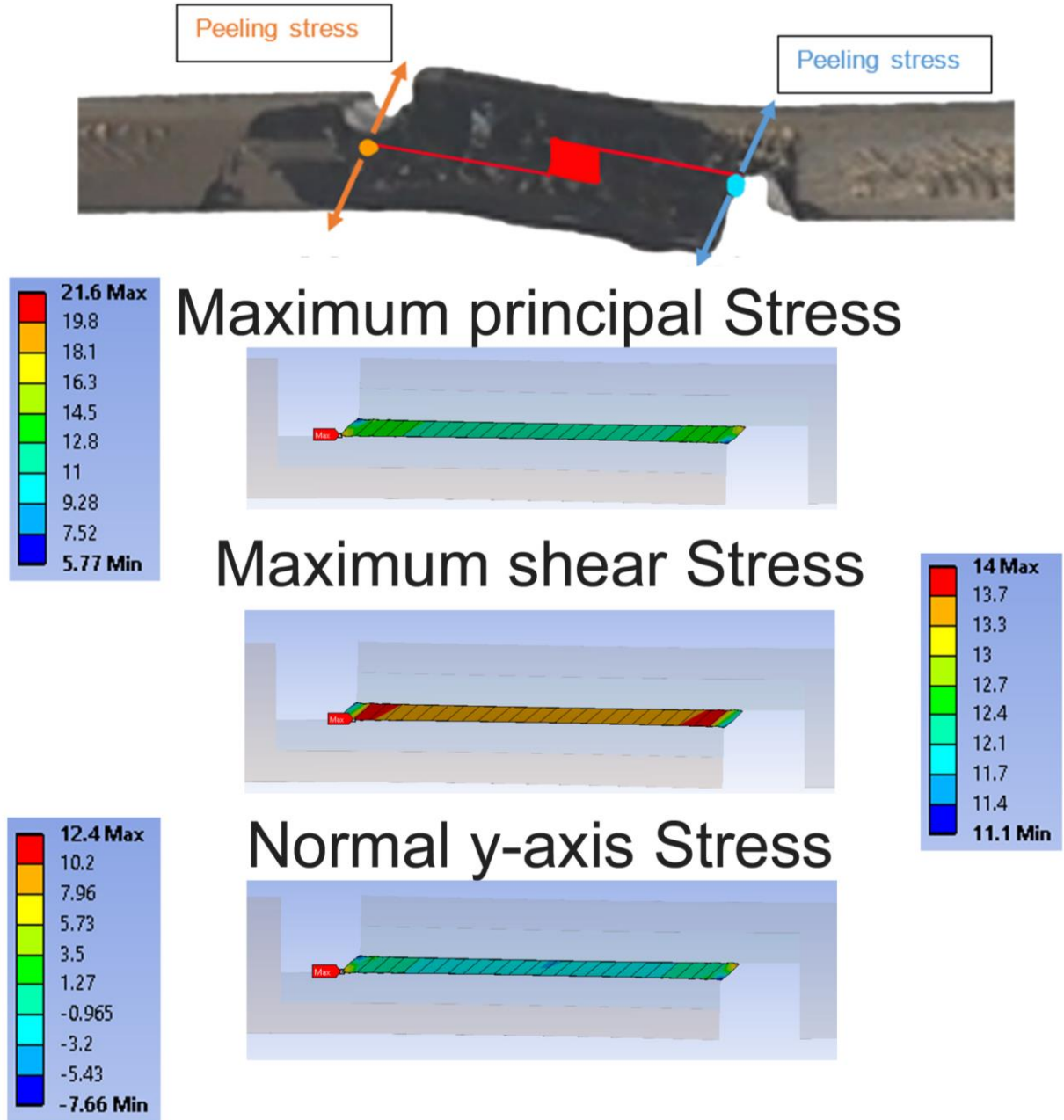


Figure 147: Location of maximum stresses for the D3165 samples

Figure 148 presents the principal stresses in vector form. Here, the lapping edges are shown to be stress concentration points increasing the magnitude of the principal stresses. Further, the direction of these principal stresses is also acting in the peeling direction, placing the adhesive under its weakest loading condition.

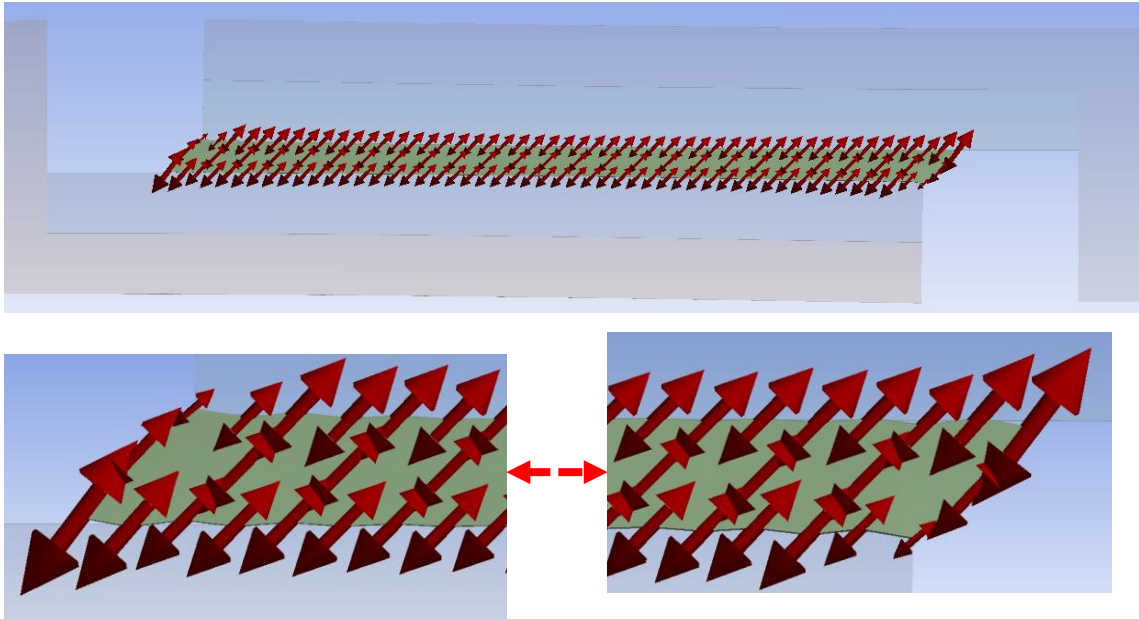


Figure 148: Stress vectors showing the principal stresses acting in the peel direction

The direction of these principal stresses all derive from the bending moment that causes the material at the centre of the coupons to rotate about the neutral axis. This moment can be reduced by:

- Aligning the forces to act concentrically along the joint's neutral axis, as D3165 solves
- Increasing the stiffness by use of a material with a higher torsional modulus
- Increasing the stiffness of the geometry by increasing the amount of material resisting deformation
- Increasing the geometries' second moment of inertia by placing the material as far away from the neutral axis as possible

For the following simulations, two different geometries are used: the standard D3165, the other a D3165 geometry with a reduced thickness. These two geometries were compared for resulting stresses. All materials remained the same. By decreasing the thickness of the titanium substrate, the stiffness was reduced by decreasing the amount of material resisting deformation, and by reducing the second moment of inertia, see Figure 149 and Figure 151. The forces used for these following simulations were 4200N.

Thinner D3165 sample, only a 1mm thick beam across the bond line

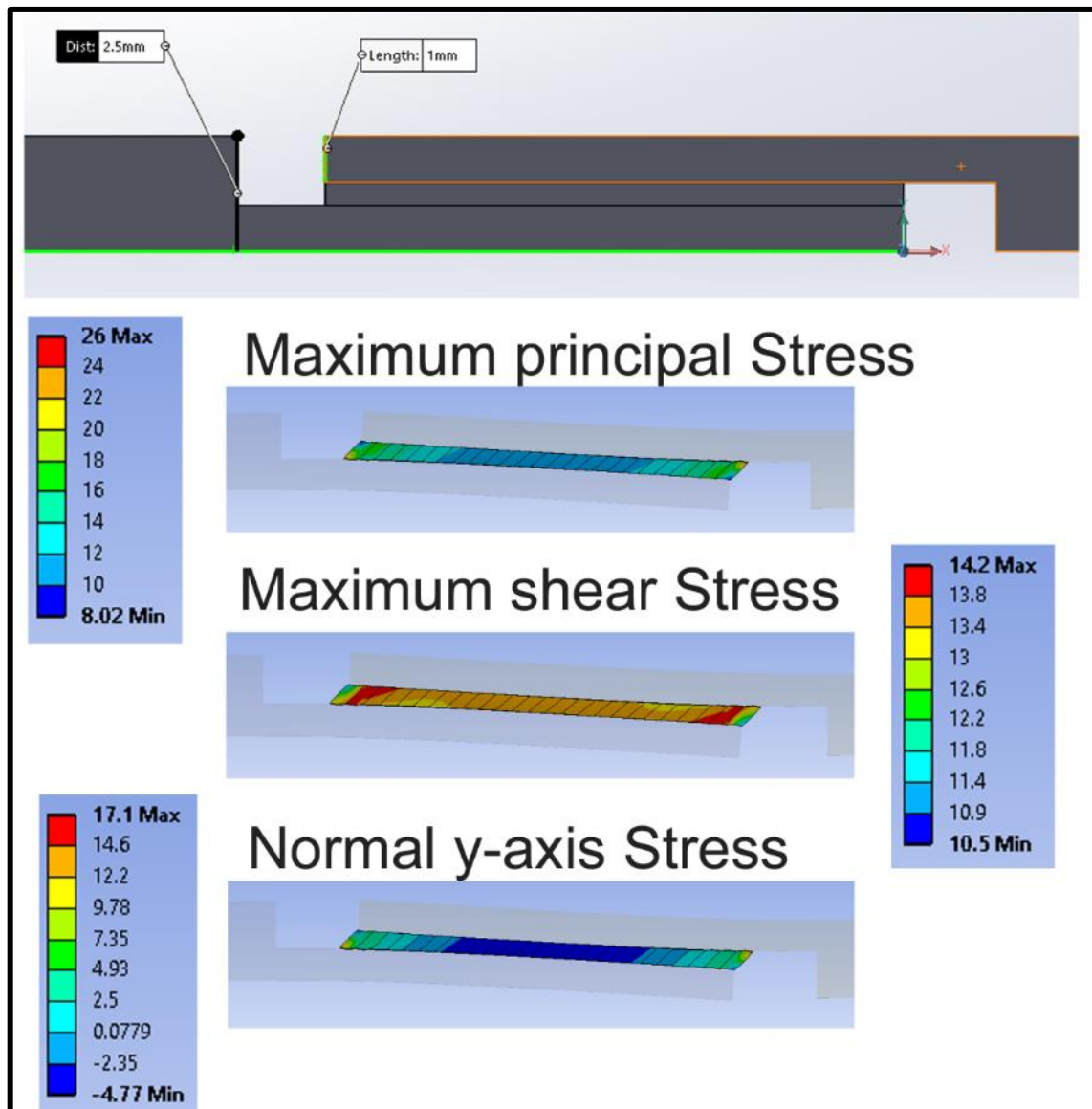


Figure 149: Location and magnitude of maximum stresses for a thinner D3165 sample

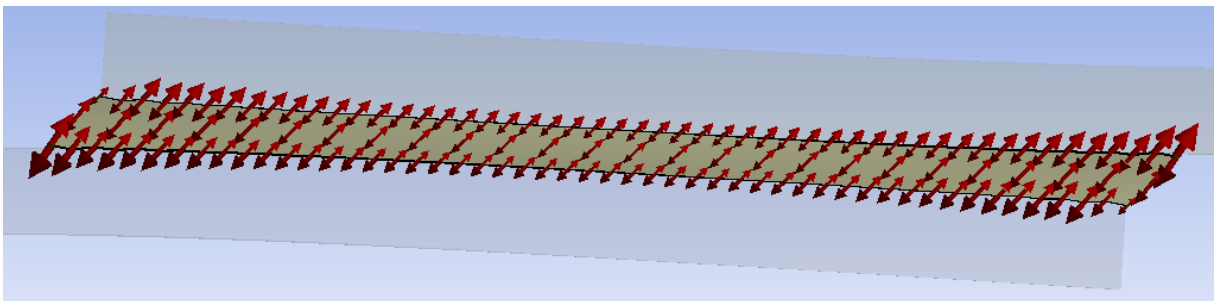


Figure 150: Stress vectors showing the direction of the principal stresses for the thinner D3165 sample

Normal D3165 sample, with a 2mm thick beam across the bond line

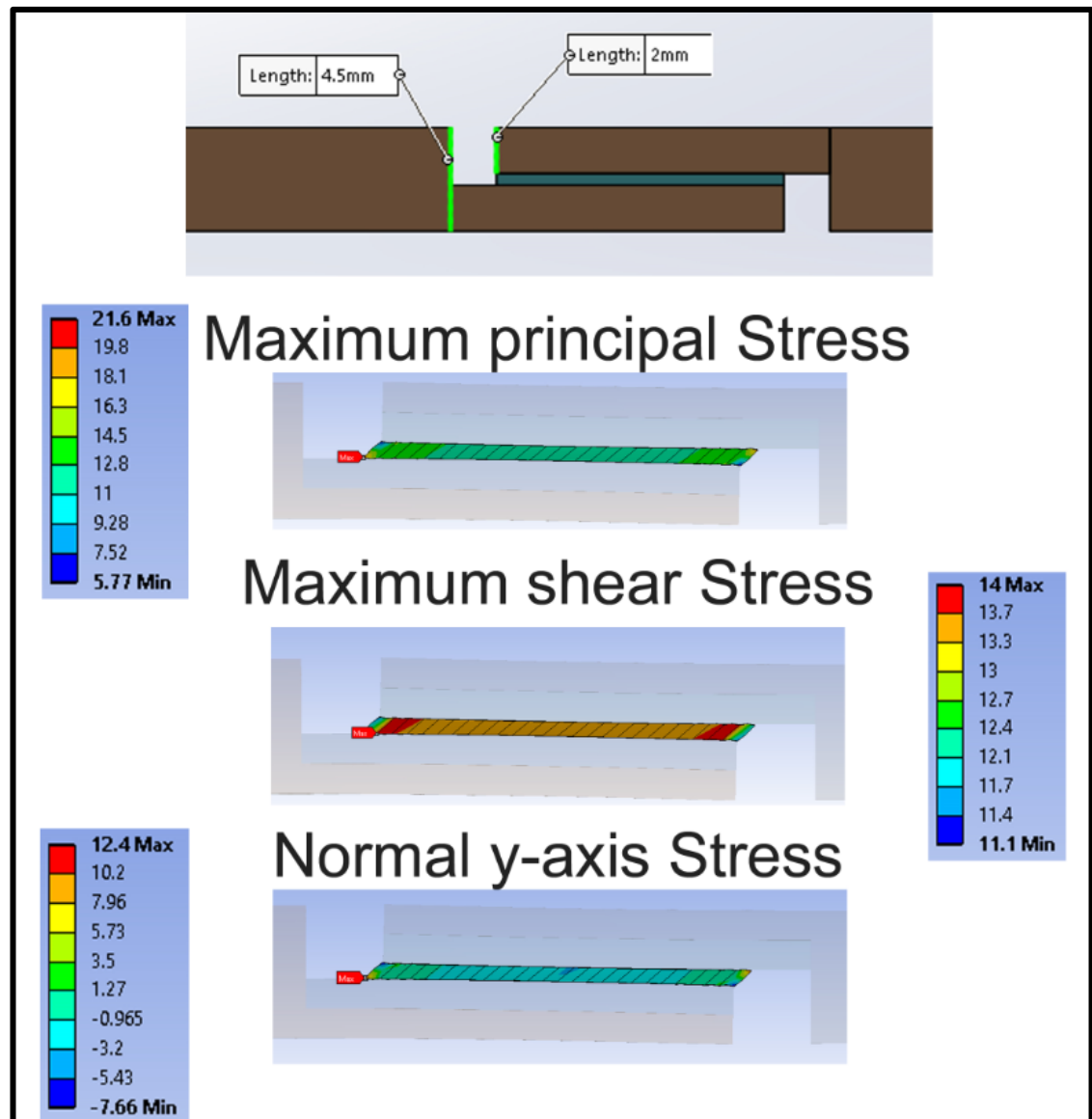


Figure 151: Location and magnitude of maximum stresses for the default D3165 sample

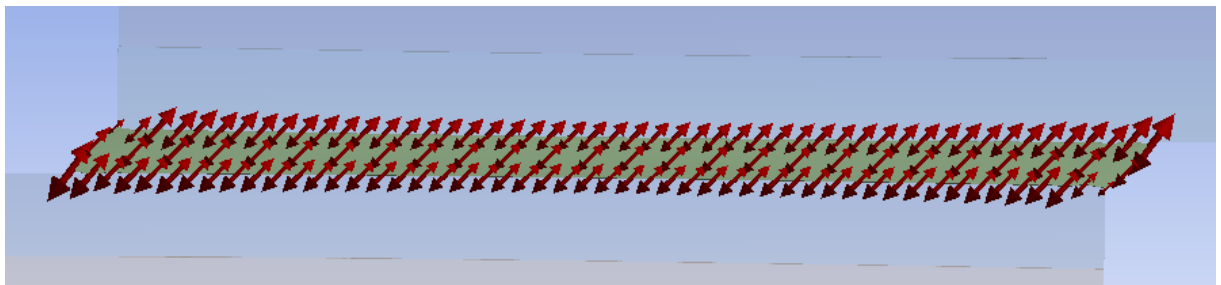


Figure 152: Stress vectors showing the direction of the principal stresses for the standard D3165 sample

From these simulations it was shown that, the maximum shear strength was not significantly affected. However, as the substrate thickness was reduced, both the maximum principal and the normal y-axis stress increased substantially. Therefore, as speculated, reducing the substrate

thickness reduced the induced bending moments confirming the relationship between stiffness, geometry, and rotational deformation.

Figure 153 presents the peak stresses for the different substrate thicknesses. Here, the change in geometry barely affects the shear stresses. However, the thickness is shown to directly impact the joint's ability to resist bending, and thus the thinner substrates exposed the lapping edges to greater principal and peeling stresses. Therefore, for bonding strength purposes, the design of a joint should aim to stiffen the geometry as this reduces the induced bending moments and peeling stresses, which are the stresses the adhesive is most prone to failing from.

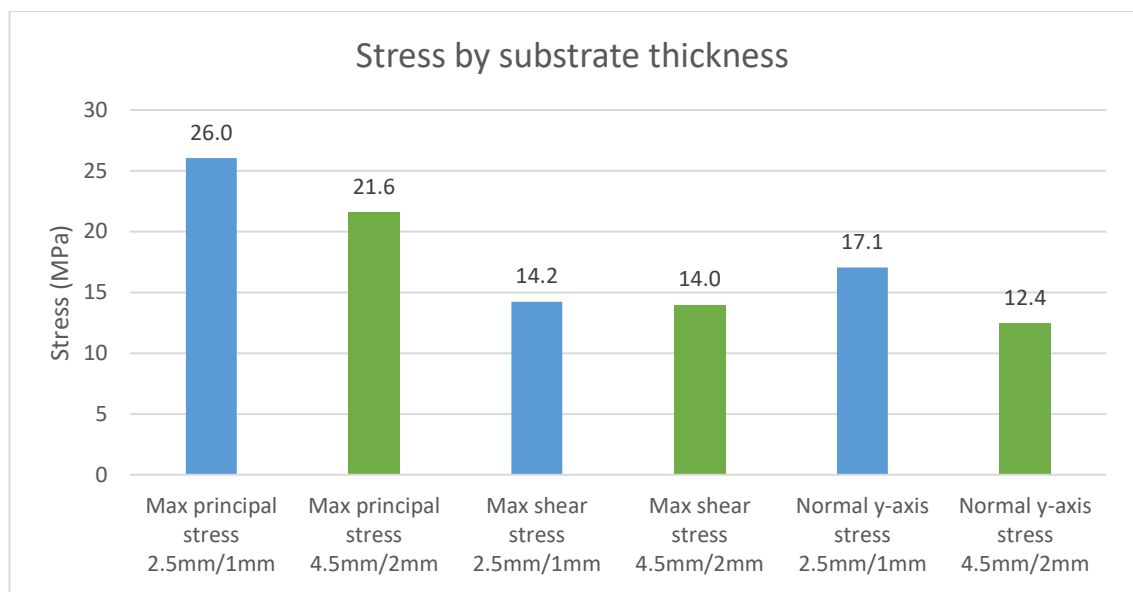


Figure 153: Maximum stress and type for different substrate thicknesses

4.3.3 Summary of analytical simulations

- The material values chosen for the simulation matched the experimental data well for both the D1002 and D3165 geometries, giving confidence that the mechanical properties used for the simulation are reflective of the materials used in the experiment
- Failure for both the D1002 and D3165 samples began at the adhesive/substrate interface at the edge of the adhesive lap. It was shown that the failure was due largely to peeling stresses
- The D3165 geometry was exposed to less peeling stresses than the D1002 due to its loading acting concentrically through the bond line
- For both the D1002 and D3165 samples, bending moments were present but by increasing the substrate thickness the effect these had on the principal and peeling stresses were reduced. Therefore, a stronger joint can be achieved by simply increasing the substrate thickness

Chapter 5: CONCLUSION AND FUTURE WORK

The objective of this thesis was to understand the relationship between different as-built surface morphologies producible by EBM AM and the resulting adhesive bonding shear strength of each surface.

The conclusions of the study are:

- The vertical surfaces, through possessing high degrees of micro-roughness, were strong bonding surfaces (17.9 MPa), which failed through a mixed mode of failure;
- The NaTESI anodised surface had the highest fractal roughness and was the most effective for epoxy adhesive bonding (18.7 MPa), with failure occurring through cohesion failure of the adhesive;
- The trabecular meshed surfaces had high macro-roughness and porosity, with its struts having a similar micro-roughness to the vertical surfaces. Thus, the bond was equivalent to the epoxy's rated strength (15.6 MPa) and failed through a mixed mode of failure;
- The specific adhesion forces of the smooth and horizontal surfaces were not strong enough to provide adequate bonding strength (3 & 12.9 MPa), and failed through complete adhesion failure;
- Finally, a stronger joint could be achieved by increasing the substrate thickness through the reduction of peeling stresses at the lapping edges.

These conclusions will now respectively be discussed in greater detail, followed by a discussion of potential future studies.

5.1 The effect surface morphology has on adhesive bonding strength

From the results of this study it was verified that the cohesion forces of the adhesive were stronger than the specific adhesion forces between the adhesive and the titanium substrate. However, it was observed that by introducing micro and nano surface roughness, the interface adhesion forces could be made to outperform the internal cohesion forces. It was suggested that this occurred through the surface roughness impeding the adhesive's deformation motion at the interface, which would then stress relieve the adhesion forces, diverting the loading forces into the bulk of the epoxy adhesive. It was also proposed that surface roughness and mechanical interlocking provide more contact area between the epoxy polymer chains and the titanium substrate for specific adhesion to act, thus increasing the amount of adhesion force interactions. This explanation is based on the empirical evidence which showed that by

increasing the fractal roughness of a surface, both the cohesion failure amount and the adhesive bonding strength increased.

To provide an example, the EBM AM vertical surfaces were good bonding surfaces, and outperformed the results of the epoxy's rated strength by 11.2% (17.9 MPa) in the ASTM D3165 experiments. This strong bonding strength was related to the high degree of micro-roughness (R_a 15.4 μm), which was due to powder particles outside of the build contour overlapping with the melt pool. When bonded, the adhesive was able to wet into the asperities and crevices between these powder particles, creating a mechanically interlocked system. Failure was through a mixed mode, though the exact amounts of cohesion and adhesion failure were not investigated.

The NaTESI anodised surfaces were even stronger than the vertical surfaces, reaching 18.7 MPa. They were fractal in nature, having both micro and nano surface roughness and porosity. Being derived from vertical surface samples, the micro-roughness of the NaTESI samples were unchanged (15 μm). However, unlike the vertical samples, the NaTESI anodised samples had a surface with nano-roughness. This nano-roughness was made up of a porous coral-like meshed structure consisting of ~50nm struts and ~100nm pores. The adhesive was able to wet out into these nano pores, creating a high degree of mechanical interlocking between the epoxy adhesive and the titanium substrate. Therefore, the interface was strengthened, diverting failure into the bulk of the adhesive, where the strength of the system was the weakest, unlike the vertical samples which showed a mixed failure mode. The anodised surfaces failed through complete cohesion failure of the adhesive. Therefore, if combined with a stronger adhesive, the resisted force should be even higher.

The meshed samples, which had macro and micro surface roughness, although weaker than the vertical and anodised surfaces, still provided a good surface for bonding, reaching 15.6 MPa. However, unlike the other surfaces, the mechanical properties of these meshes were more affected by processing defects such as air bubbles.

The horizontal and smooth samples both possessed low amounts of surface roughness (R_a 5.6 & 0.4 μm). These surfaces were significantly weaker than the rougher samples (12.9 & 3 MPa). In particular, the smooth samples failed in some cases under no loading. This proved that the specific adhesion between the titanium substrate and epoxy adhesive alone was unable to produce a strong bond. Thus, for strong epoxy adhesive bonding between EBM produced Grade 5 titanium substrates, the surface morphologies must exhibit high degrees of micro and nano surface roughness.

5.2 The mechanics of failure in single-lap-joints

From this study it was shown that, for the same bonding area, the concentrically loaded D3165 SLJ resisted greater forces than the eccentrically loaded D1002 SLJ. The simulations showed that this was due to the eccentric loading causing larger bending moments than the concentric loading. These bending moments were detrimental to bonding strength, because they caused rotational deformation of the titanium substrate across the adhesive bond line. This produced forces which acted normal to the substrate's surface, inducing peeling stresses which concentrated in the lapping edges, causing failure.

From the simulations, it was found that increasing the thickness of the substrates increased the stiffness of the system. This reduced the induced bending moments and peeling stresses, meaning the stresses acting on the stress concentration points of the lapping edges were lower. This was proven in the thickened mesh experiments, where the thicker samples had less rotational deformation, and higher failure forces than the thinner meshed samples.

5.3 Future work

The aim of this study was achieved, as a range of Grade 5 EBM AM surface morphologies were characterised, with the adhesive bonding strength of each now being better understood. Further, it showed that surface roughness, especially in the micro and nano ranges, is essential for a strong bond. It is acknowledged that some limitations were present in this study. Therefore, future studies that could overcome these limitations are:

- For the smooth surfaces, it is suggested that future work be carried out, where, prior to bonding, the surface is confirmed to be free of contamination. This would confirm whether contamination of the surface produced the low performing bond.
- Image processing is recommended to be used on samples with a mixed failure mode to identify the amount of adhesion and cohesion failure. This would investigate how the distribution of adhesion and cohesion failure impacts the resulting bonding strength. It is speculated that a higher degree of cohesion failure would relate to a higher overall bonding strength.
- Repeating the study using an autoclave to remove air bubbles from the adhesive bond would ensure a uniform bond line is achieved for all samples, producing a more controlled experiment.
- A future study of interest would be testing the different samples under tension and under faster loading conditions. It is proposed that due to the increased macro surface

roughness of the meshed samples that they should perform better than the other surfaces under tensile and fast loading conditions.

- The effect NaTESI anodising has on adhesive bonding strength, when applied as a pre-treatment to the horizontal and smooth surfaces, could be examined. Perhaps a combination of low micro-roughness but high nano-roughness is stronger than the present work's strongest surface, being one of high micro and nano-roughness.
- An experiment using a stronger adhesive could be conducted to discover the ultimate failure strength of the NaTESI interface.
- An experiment could be conducted to see whether the actual fractal dimensions of the surfaces can be used to predict the adhesive bonding strength.
- Investigating whether non-chemical, laser-induced nano-structuring pre-treatments produce results similar to the NaTESI anodising method would be a useful further study.
- Finally, the understandings from this research could be applied towards the designing of a large structure produced from titanium nodes, adhesively bonded to carbon fibre tubing.

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