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SELECTIVE LASER MELTING OF TI ALLOY–CU ALLOY-STAINLESS STEEL MULTIPLE MATERIAL PART

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SELECTIVE LASER MELTING OF TI ALLOY–CU ALLOY-STAINLESS STEEL MULTIPLE MATERIAL PART

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A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
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Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

25 March 2019

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A handwritten signature in black ink, appearing to read 'Tey', written over a horizontal line.

Tey Cher Fu

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Yeong Wai Yee

Authorship Attribution Statement

This thesis contains material from 1 paper published in the following paper accepted at a conference in which I am listed as an author.

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The contributions of the co-authors are as follows:

- I designed the experiment, prepared the samples in the Singapore Centre for 3D Printing and performed the data measurements in NTU School of MAE Materials Laboratory 1.
- Assoc Prof Yeong participated in the discussions, helped to interpret the results, and edited the manuscript draft.

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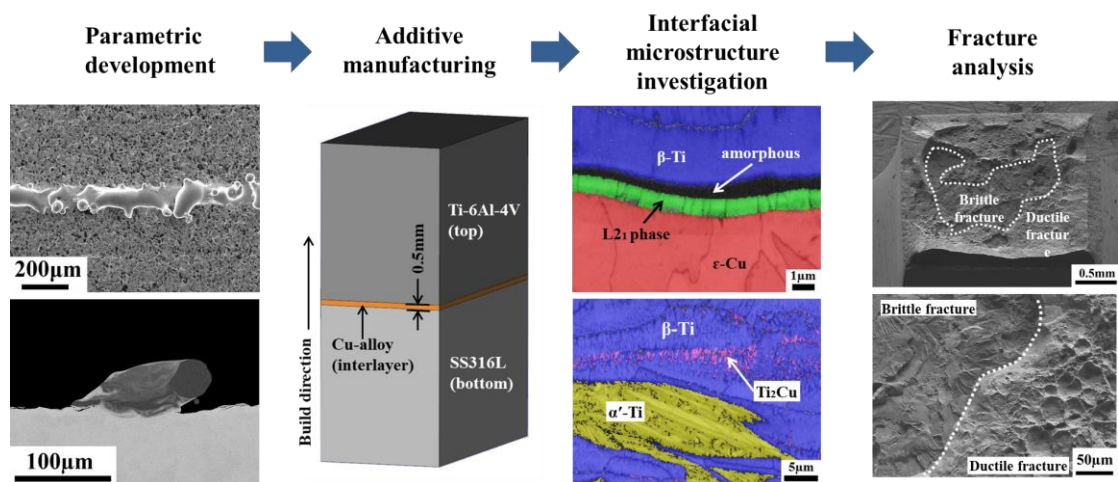
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Tey Cher Fu

Abstract

The ability to combine multiple materials (MM) into a single component to expand its range of functional properties is of tremendous value to the ceaseless optimization of engineering systems. Although fusion and solid-state joining techniques have typically been used to join dissimilar metals, additive manufacturing (AM) has the potential to produce MM parts with a complex spatial distribution of materials and properties that is otherwise unachievable. In particular, powder bed fusion (PBF) processes such as selective laser melting (SLM) possesses certain desirable traits that make it attractive for MM processing. The high build resolution, small melt pool dimensions, and rapid cooling characteristics of SLM can be used to produce MM interfaces with lower dilution (i.e. less intermixing between dissimilar materials) and unique microstructural phases. Despite its potential for MM processing, little is known about its interfacial characteristics. As such, research effort was dedicated to addressing this gap. In this work, the SLM process was used to manufacture Ti alloy (TiA)/ Cu alloy (CuA)/ stainless steel (SS) MM parts which feature material transitions from 316L stainless steel to Ti-6Al-4V through an interlayer of HOVADUR® K220 Copper-alloy.



The SLM of the TiA/CuA/SS MM part begun with the development of appropriate parameters to process the TiA/CuA and CuA/SS interfaces. The process parameters were devised to 1) minimize dilution and 2) maintain stable and continuous melt pools across the interfaces. Due to the composition gradient at the interface, the dimensions and stability of the melt pools varied across the interfacial build layers. To maintain consistent melt pool stability, the laser energy inputs were varied at appropriate build layers across the MM interfaces.

The microstructure in both the CuA/SS and TiA/CuA interfaces were examined in detail and the former was found to contain a non-homogeneous mixture of face-centred-cubic ϵ -Cu and γ -Fe phases. No detrimental phases were detected at the CuA/SS interface. On the other hand, the TiA/CuA interface featured distinct layers of phase/s listed in the following order, starting from the CuA interlayer: Cu_2TiAl phase, amorphous phase, and a composite layer consisting of α' -Ti reinforcements within a matrix of β -Ti+ Ti_2Cu phase mixture. The formation of the composite layer is attributed to the imperfect mixing and non-homogeneous Cu distribution within the melt pools. During solidification and cooling, the Cu-poor (0-5 at.% Cu) and Cu-rich (5-30 at.% Cu) regions transformed into the α' -Ti and β -Ti+ Ti_2Cu phase mixture respectively. The β -Ti+ Ti_2Cu and amorphous phase had a hardness (7.4-7.9 GPa) which exceeded that of the α' -Ti phase in the bulk TiA (4.9 GPa). Using the devised interfacial process parameters, the thickness of the L_{21} layer, amorphous layer, and α' -Ti+(β -Ti+ Ti_2Cu) composite layer can be reduced to $\sim 1\text{ }\mu\text{m}$, $\sim 2\text{ }\mu\text{m}$, and $\sim 52\text{ }\mu\text{m}$ respectively. Such an interface also possessed a high volume fraction of α' -Ti phase ($\sim 30\text{ vol.}\%$) within the composite layer.

Tensile fracture of the TiA/CuA/SS MM part occurred at the TiA/CuA interface. Cracks typically initiated from critically stressed pores that were located in the vicinity

of a brittle phase, which was usually an amorphous region. Once initiated, the crack propagates out of the thin amorphous region and into the much thicker layer of β -Ti+Ti₂Cu phase mixture. During propagation, the crack may encounter a large region of tough α' -Ti phase and, consequently, be majorly deflected towards the underlying CuA interlayer. This resulted in fracture surfaces which consists of distinct dimpled and cleavage regions belonging to the ductile CuA interlayer and the brittle TiA/CuA interface respectively. The TiA/CuA interface which possessed the highest volume fraction of interfacial α' -Ti, therefore, presented a more arduous crack propagation path with several major deflections. This led to increased fracture resistance and tensile strength in excess of 500MPa can be obtained. The reported tensile strength is among the highest for similar interfaces produced by other joining techniques reviewed in this thesis. This method of introducing an interfacial composite structure to improve MM bonding is envisioned to be applicable for the SLM of other metallic combinations.

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List of Abbreviations

3D	– Three dimensional
AM	– Additive manufacturing
BSE	– Backscatter electron
CNC	– Computer numerical control
CP-Ti	– Commercially pure titanium
CuA	– Cu alloy
DED	– Directed energy deposition
DOD	– Drop-on-Demand
DRZ	– Dynamic recrystallization zone
EBM	– Electron beam melting
EBS	– Electron backscatter diffraction
EDM	– Electric discharge machining
EDX	– Energy dispersive x-ray spectroscopy
FIB	– Focussed ion beam
FSW	– Friction stir welding
HAZ	– Heat-affected zone
IMC	– Intermetallic compound
IPF	– Inverse pole figure
MM	– Multiple-material
MMAM	– Multiple-material additive manufacturing
OM	– Optical microscopy
PBF	– Powder bed fusion
SEI	– Secondary electron imaging
SEM	– Scanning electron microscopy
SLM	– Selective laser melting
SS	– Stainless steel
TEM	– Transmission electron microscopy
TiA	– Ti alloy
TLPB	– Transient liquid phase bonding
TMAZ	– Thermomechanical affected zone
UTS	– Ultimate tensile strength
XRD	– X-ray diffraction

List of Symbols

α	– Thermal diffusivity
$\emptyset_c$	– Critical contact angle of the melt pool
γ	– Surface tension
μ	– Dynamic viscosity
ΔT	– Difference between maximum melt pool temperature and solidus temperature
c	– Consolidation ratio
D	– Diameter of segmental cylinder or melt pool
E	– Laser energy density input
h	– Bead height
H	– Hatch spacing
l	– Loss coefficient
ℓ	– Wavelength of axial harmonic disturbance
L	– Characteristic dimension of melt pool
Ma	– Marangoni number
p	– Powder packing density
P	– Laser power
p_c	– Critical penetration depth of melt pool
P_q	– Root-mean-square roughness of the primary profile
R_a	– Arithmetic mean roughness
T	– Temperature
t_{mn}	– Thickness of consolidated build layer
t_{pn}	– Thickness of unconsolidated powder
V	– Laser scanning velocity
z	– Platform displacement

Chapter 1 - Introduction

In this chapter, the research background, motivation and objectives are discussed. The background begins with a description of the unique features of additive manufacturing (AM). Next, the AM of multiple-material (MM) parts using powder bed fusion (PBF) and directed energy deposition (DED) techniques will be discussed. Subsequently, the benefits and complications of metallic MM processing are highlighted along with the typical approaches to circumvent such complications. Finally, the motivation for exploring the MM capability of the SLM process and the objectives of this research are given.

1.1 - Background of Additive Manufacturing and Multi-Material Processing

The defining characteristic of AM, also commonly known as 3D printing, is the successive fusion of layers of material to form a 3-dimensional (3D) part. The process by which each layer is produced through AM is analogous to the inkjet technology. AM processes deposit and/or fuse materials, which could be solid, liquid or suspension-based, onto specific locations within the build envelop to form a desired cross-sectional profile. These cross-sectional layers are sequentially added over each other to form a 3D geometry (Figure 1.1), hence the term additive manufacturing. In contrast, conventional manufacturing processes are often subtractive as they rely on a series of computer numerical control (CNC) cutting, milling, drilling, and joining operations to complete the net-shape object. Even though subtractive operations can produce complex external features with tight tolerance, they are not suitable for the production of internal features which are inaccessible to the cutting tools. Parts with complex internal features may be produced through casting which would require an

equally complex mould to be built. Since moulds can be expensive and time-consuming to produce, this approach is often justifiable only when the production volume of the casting is sufficiently large to normalize the cost of the mould. However, such a concern is irrelevant in AM where geometric complexity comes at little to no additional cost. As such, AM is especially appealing to the production of highly customized, complex, and geometrically optimized parts.

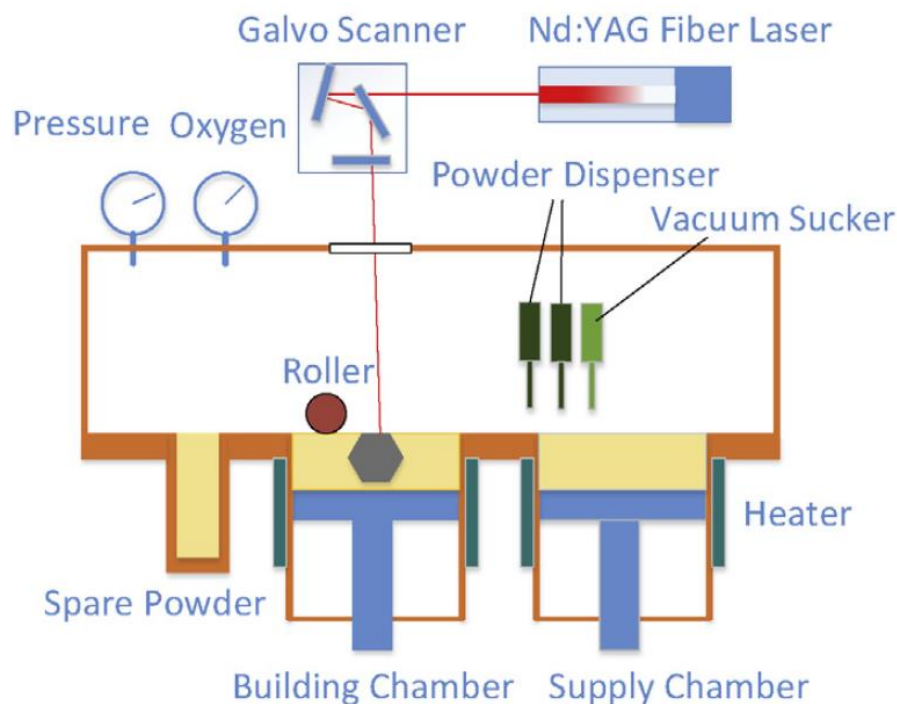


Figure 1.1 SLM process with multiple nozzles for multiple material deposition [1]

In addition to producing complex geometries, AM is also well-suited for the processing of MM components. Much like how inkjet printers selectively deposit different inks at specific locations to form a coloured photograph, different materials can also be deposited onto a single component using AM to expand its range of functional properties. Multiple-material additive manufacturing (MMAM) has been implemented to a relatively good degree of success in polymer-based AM techniques such as fused deposition modelling and Polyjet technology [2]. This success is mostly attributed to the fact that polymers 1) have a low melting temperature, 2) are readily

available in the liquid resin state which makes mixing and dispensing relatively easy, and 3) generally bonds well with dissimilar polymers without forming brittle reaction phases. In comparison, MM processing of metals is often complicated by the formation of intermetallic compounds (IMCs) [3]. These IMCs are often brittle and can cause the MM interface to crack or fracture under the presence of residual and applied stresses. Additionally, the piezoelectric or thermal actuators used in conventional inkjet technology cannot be used to dispense molten metal droplets due to its high melting temperature and viscosity. Metals are most conveniently stored in its solid powder form prior to being deposited and fused into a component using a laser or electron beam energy source.

The method used to dispense dissimilar metal powders varies for different metal AM techniques. In general, the AM of bulk metallic components is achieved either through directed energy deposition (DED) techniques or powder bed fusion techniques (PBF) such as selective laser melting (SLM) and electron beam melting (EBM). In PBF, a uniform layer of powder is spread over the build area before a laser or electron beam is activated to melt and fuse a selective region within each layer (Figure 1.1). After each layer, the build platform is displaced downwards by an amount equal to the layer thickness setting. The powder spreading and fusion process are repeated until the part is completed. The completed part is buried in unconsolidated metal powder which can be recycled for subsequent builds. To make PBF techniques compatible with MMAM, an additional MM deposition mechanism needs to be added. This can be achieved using a multiple nozzle setup which holds different metal powders (Figure 1.1). With a CNC frame, the nozzles can be positioned at any location within the build layer and the dispensing of powder can be achieved through acoustic vibrations. By coordinating the movement of the CNC frame with the powder dispensing mechanism, complex

distribution of dissimilar materials can be achieved in each build layer [4]. Additionally, a vacuum nozzle may also be mounted onto the CNC frame to selectively remove powder from specific locations before dispensing a dissimilar powder [1]. This is done to minimize cross-contamination of different powders within the powder bed.

In DED techniques, material addition is achieved by jetting solid metal powders into the laser beam and melt pool where it is melted and fused onto the part. The part is typically deposited on a 5-axis platform which can be used to tilt, translate and rotate the part into any desired orientation relative to the deposition head. DED is conceptually similar to the laser cladding technique which is commonly used to coat and modify the surface of existing objects with layers of dissimilar material [5, 6]. Unlike PBF, the deposition and fusion of material happen concurrently in DED and the build object is not buried in a powder bed. The absence of a powder bed meant that DED techniques can operate with a lesser volume of powder and material change is relatively simple as it only involves a change in the powder feedstock. MM deposition can be easily achieved in DED by using multiple powder feed tanks. Dissimilar powders from separate feed tanks can be easily mixed in different proportions before being jetted into the melt pool. Due to the ease of material change, the DED process has been commonly employed to produce MM parts or functionally graded materials (FGM) [7].

Even though MM deposition can be easily incorporated into DED techniques, there are considerations which favour PBF techniques for MMAM as well. The smaller laser spot size (0.08-0.1mm), narrower melt pool widths (0.1-0.4mm), and lower layer thickness (0.02-0.1mm) of PBF techniques allow its MM interface to be processed with higher resolution. This leads to superior control over the intermixing of materials

at the MM interface. In comparison, the track width (0.7-2mm) and laser spot diameter (0.3-3mm) in DED are often larger than those of PBF. Multiple sets of lasers and optics can be used to increase the production speed of PBF techniques while maintaining the same build resolution. Employing multiple print heads is, however, not feasible in DED due to the proximity between the deposition head and the build part. PBF generally features a higher yield as most of the powder within the build chamber can be recycled for subsequent builds. In contrast, the powder yield for DED can be as low as 50-80% because a portion of the sprayed powder may not be absorbed into the melt pool especially when larger mm-sized nozzles are used. The powder bed in PBF techniques also acts as a support for the processing of overhanging features such as those found in periodic lattice structures. On the other hand, the printing of complex overhanging features using DED requires a deliberate plan for the tool path as well as the use of additional solid support structures. While DED and PBF techniques each have their own set of advantages and disadvantages with regards to MMAM, both techniques have the potential to produce MM components with a complex spatial distribution of materials.

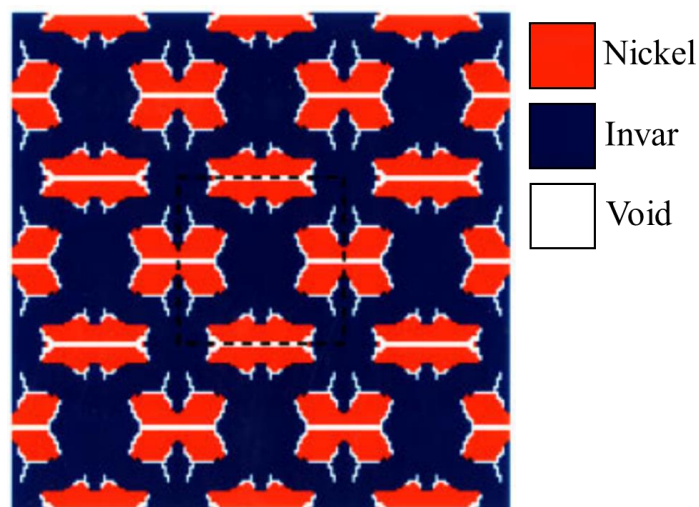


Figure 1.2 2D MM structure topologically optimized to maximize thermal contraction stress in the vertical direction [8]

MM parts can be designed to exhibit various functional properties. For instance, Figure 1.2 shows a 2-dimensional (2D) MM structure, which consists of nickel, Invar and empty spaces [8]. This structure is topologically optimized to exhibit maximum thermal contraction stress in the vertical direction upon heating. Such a unique thermal contraction property can only be realised using MM with different coefficient of thermal expansion. MM combinations have also been commonly used to expand the functional properties of engineering components. For example, yttria-stabilized zirconia coating has been applied to metallic components to allow it to operate in higher environmental temperatures [9]. TiO coatings can be used to enhance wettability, cell-material interactions and lubrication ability of Ti hip prostheses [10]. Copper can be bonded to steel for enhanced heat spreading capability and has potential applications in nuclear reactors [11] and hot forging dies.

While MM structures can be designed to exhibit various interesting and unique properties, parts with complex material variation, such as that shown in Figure 1.2, are challenging to fabricate due to the limitations associated with conventional joining techniques. Since joining involves the merging of two free surfaces, it is constrained by the geometrical complexity of the interfacial joint. For example, in diffusion bonding and explosion welding, the joining interface typically needs to be planar or near planar to facilitate the application of uniform contact pressure. In friction stir welding, laser and electron beam welding the joint needs to either be accessible or within line-of-sight to the respective welding tools. Consequently, complex material variation within internal features and around tight geometries cannot be achieved through joining techniques. The most feasible way to fabricate such optimal and complex structures is through MMAM. In AM there is no merging of surfaces, only the deposition of material on a single exposed surface of the built part. Hence, in AM,

the concept of joining simply translates to the deposition and fusion of a different material. As such, material distributions with higher complexity can be realised through AM.

1.2 - Motivations

There are numerous possible MM combinations. This thesis focuses on the combination of titanium and steel. The favourable combination of corrosion resistance from titanium alloys and the wide range of properties from the relatively low-cost steels have potential applications in the nuclear, chemical and aerospace industries [12-21]. However, the direct bonding of titanium to steel is hindered by the formation of detrimental Fe-Ti IMCs which have hardnesses of over 1000 Hv [22-24]. These IMCs can cause the Fe/Ti interface to crack and delaminate during processing, and/or fracture in a brittle manner under external loading [19, 25, 26].

To minimize the interfacial IMCs and improve the bond properties, the SLM process is used to produce the MM interface. There are two reasons for choosing the SLM process over DED techniques. As previously mentioned, the first reason is due to the smaller laser spot size and layer thickness associated with the SLM process. This improves the build resolution at the interface and allows the dilution to be minimized beyond the limits associated with DED techniques. Second, the high laser scanning velocity and rapid solidification conditions in the SLM process may potentially be used to create a non-homogeneous MM interface featuring a composite-like structure [27]. Such a unique interface will possess properties which differ from those obtained through DED or other joining techniques. In particular, the regions within the non-homogeneous interface which contained a high concentration of base alloy [27] could potentially act as reinforcements for the, otherwise, brittle interface. Furthermore, the

rapid solidification condition may also lead to the formation of metastable phases which would also alter the interfacial properties.

Other methods can also be used in combination with SLM to improve the properties of the MM interface. Interlayer/s with different compositions can be inserted between Ti and steel to replace the Fe-Ti IMCs with less detrimental phases [28-33]. Functional gradients can also be implemented to circumvent the IMCs forming compositions and to induce a gradual change in material properties [7, 34]. Due to all these possibilities and potential benefits, it is believed that an evaluation of the SLM-processed MM interface is an interesting and worthwhile pursuit.

1.3 - Objectives

At present, the literature on the influence of SLM process parameters on the microstructure and properties of the MM interface is severely lacking. Consequently, the interfacial fracture mechanism is not well understood. Furthermore, there are no guidelines for the process parameter optimization at the MM interfaces. Considering that the devised parameter has to balance between the conflicting requirements of minimizing dilution across the MM interface and maintaining melt pool stability, parametric optimization is non-trivial and can be considerably costly. This thesis aims to address these knowledge gaps and the objectives of the present research are listed as follows:

- Produce a TiA and SS MM part that is bonded with a CuA interlayer using the SLM process. The 0.5 mm thick CuA interlayer is introduced to partition the Ti and Fe atoms such that the formation of the highly detrimental Ti-Fe IMCs is eliminated.

- Develop an experimental methodology to select feasible process parameters for the TiA/CuA and CuA/SS MM interfaces such that dilution at the interface is minimized while maintaining sufficient melt pool stability.
- Characterise the microstructure at the TiA/CuA and CuA/SS interfaces under different process conditions.
- Evaluate the fracture mechanism of the TiA/CuA/SS MM part.

1.4 - Scope

The parametric study, microstructural evaluation, and fracture analysis of the SLM-processed TiA/CuA/SS MM parts are investigated through a series of experimental techniques listed as follows:

- Optical microscopy (OM) and scanning electron microscopy (SEM) for imaging.
- X-ray diffraction (XRD), electron backscatter diffraction (EBSD), and transmission electron microscopy (TEM) for phase identification using diffraction analysis.
- Energy dispersive x-ray spectroscopy (EDX) for composition analysis.
- Nano-indentation on different regions within the TiA/CuA and CuA/SS MM interface to evaluate the hardness of different phase/s.
- Tensile testing of the MM part with its interface oriented normally to the loading direction.

1.5 - Organisation of Report

This report consists of 6 chapters. The background of AM as well as MM processing is introduced in chapter 1.

Chapter 2 is dedicated to reviewing the various joining and AM techniques that have been used to process metallic MM parts. The characteristics of the various techniques are discussed and the microstructural features at the respective Ti/steel interfaces are highlighted.

Chapter 3 discusses the methodology used to obtain suitable process parameters at the TiA/CuA and CuA/SS interfaces. The parameters were devised by examining the morphology of the melt pools across the interfacial build layers and identifying the minimum laser energy input needed to maintain marginal melt pool stability.

In chapter 4, the microstructural features of the TiA/CuA and CuA/SS interfaces are characterised in detail through a series of composition analysis as well as electron and x-ray diffraction analysis. The effects of process parameters on the microstructure of the TiA/CuA interface are discussed.

In chapter 5, the tensile fracture characteristics of the MM part are reported. The relationship between the process parameters, interfacial microstructure, and fracture characteristics is highlighted.

Chapter 6 concludes the major findings presented in this thesis. Additionally, the research gaps which are not addressed in this report are highlighted for future investigations.

Chapter 2 - Review of Multiple-Material Joints

This chapter reviews the microstructural features of the Ti/steel joints produced by the various joining and AM techniques. The reviewed techniques include diffusion bonding, brazing, transient liquid phase bonding, friction welding, friction stir welding, explosion welding, laser and electron beam welding, DED, and SLM. From the review, the key characteristics that make a strong MM interface are summarized.

2.1 - Diffusion bonding

Description

In diffusion bonding, a metallurgical bond is established in a vacuum environment by allowing atoms to diffuse across the interface under elevated temperatures and pressures. As the merging surfaces are never perfectly flat, gaps are inherently present between the contacting surfaces in the micro to the nanoscale. Hence, the bonding temperature and pressure should be sufficiently high to plastically collapse the surface asperities such that intimate contact is established for bonding to occur. The temperature needed for active diffusion of atoms is typically 50-80% of the melting point of the respective material. As the dissimilar base alloys have different crystal structures, lattice constants, atomic radius, atomic bond energy, and oxides on the bonding surfaces, the rate of diffusion differs across the MM interface. Therefore, the composition gradient is typically asymmetrical at the interface, i.e. the diffusion distance of atom 'A' in a lattice of atom 'B' differs from the diffusion distance of atom 'B' in a lattice of atom 'A'. If the formation of IMCs is thermodynamically favoured, these ordered phases will form as distinct layers within the interface. IMCs are generally detrimental to the bond properties due to their hard and brittle characteristics. To limit the thickness of the IMCs, the bonding temperature and time are often kept to

a minimum. The main advantage of diffusion bonding lies in the ease of controlling the interfacial thickness within the micrometre range by adjusting its bonding temperature and time. The disadvantage is that it relies on the application of a uniform pressure to close the interfacial gaps. As a result, objects with non-planar joints may experience varying contact pressure and varying bond properties along its irregular interface. Additionally, the IMCs in a diffusion bonded MM interface tend to form continuous and planar layers. This is undesirable as it allows cracks to propagate with relative ease within the IMC layers without much deflection and resistance.

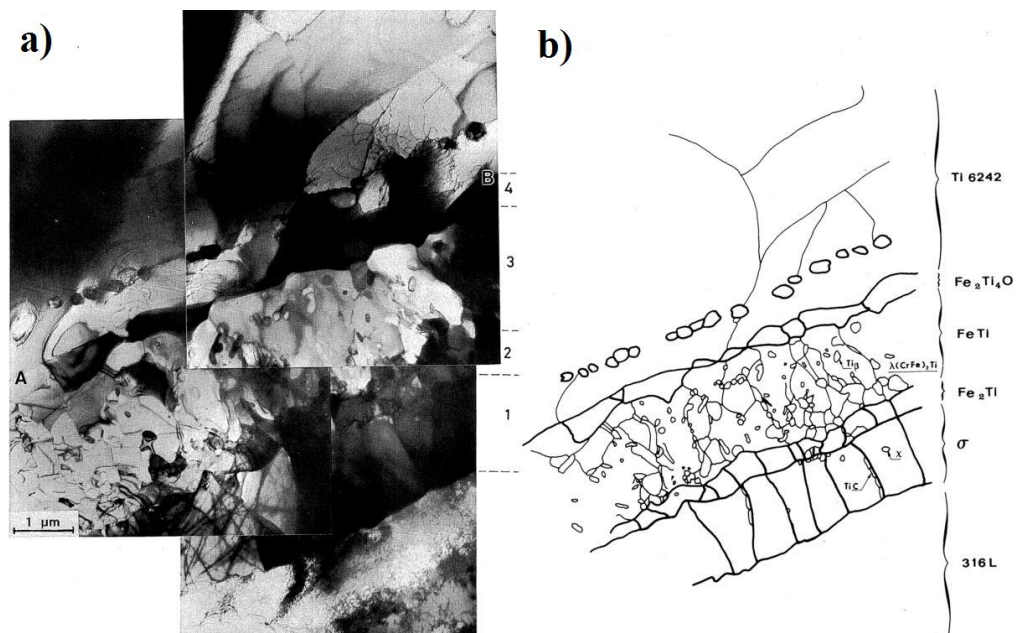


Figure 2.1 a) TEM image of a diffusion bond between Ti6242 and AISI 316L. b) Schematic representation [35]

Microstructure

An example of diffusion bonded TiA/SS interface featuring distinct layers of different phase/s can be seen in Figure 2.1. Using electron diffraction analysis and EDX, Alemán et al. were able to identify the phase/s within each layer based on their crystal structure and composition data [35]. The formation of each phase was strongly dependent on the composition of the major elements such as Ti, Fe, and Cr. The first layer of interfacial product that formed next to the 316L base alloy was the σ -FeCr

phase. The diffusion of Ti atoms into steel decreases the activity of the Cr atoms, resulting in an uphill diffusion of Cr from the adjacent stainless steel base alloy. Once the Cr content is sufficiently high, the brittle σ phase was obtained after bonding. Within the σ grains, a minor amount of χ phase ($\text{Fe}_{17}\text{Cr}_7\text{Ti}_5$) was also detected. As the Ti content continues to increase towards the Ti6242 base alloy and the ratio of Fe to Ti atoms approaches 2:1, the formation of the Fe_2Ti IMC becomes favoured. Thus, a thin layer of Fe_2Ti was observed next to the σ phase. When the ratio of Fe to Ti atoms decreases to 1:1, a layer of FeTi IMC formed. Additionally, other phases such as $\beta\text{-Ti}$ and $\lambda(\text{Fe, Cr})_2\text{Ti}$ also existed in equilibrium within the FeTi layer, which is consistent with the prediction from the Fe-Ti-Cr ternary phase diagram.

Where the Ti content was 2-3 times as high as its Fe content, $\text{Fe}_2\text{Ti}_4\text{O}$ is observed. When the Fe content fell below 10 at.%, $\beta\text{-Ti}$ phase was retained due to the β -stabilizing effect of Fe atoms. Evidently, the diffusion bonded interface between Ti6242 and 316L is comprised of multiple layers of phases which are mostly detrimental to the bond properties. Similar phases were also reported in diffusion bonds involving other combinations of Ti alloys and steels [19, 25, 26]. Fracture strength of the TiA/steel diffusion bonds is typically limited to 217-326 MPa [26, 36-38]. Depending on the type of base alloys used, such an interfacial strength corresponds to ~40-100% and 30-60% of the UTS of the Ti/TiA and steel base, respectively [26, 36-38]. Even though some of the interfacial bond strength seemingly approached the UTS of the Ti base alloy, the interface is, nonetheless, brittle as fracture consistently occurred within the detrimental IMCs. The highest tensile strength of 510 MPa reported by Kundu et al. [23] is by far the only exception that exceeds the typical range of tensile strength. The relatively high tensile strength reported by Kundu et al. [23] is attributed to 1) the intimate bonding between the base

alloys and 2) the low thickness of detrimental phases (4.6 μm). Despite the high strength, fractography revealed that fracture occurred in a brittle manner across the detrimental FeTi and $\lambda(\text{Fe, Cr})_2\text{Ti}$ phases [23].

One of the ways to eliminate the Fe-Ti IMCs is to make use of a TiC diffusion barrier [35, 39]. When the carbon content within the steel is sufficiently high ($\sim 0.1\text{--}0.2\text{ wt.}\%$), a significant amount of C atoms can diffuse ahead of the Fe atoms to form a continuous layer of TiC at the interface. Even though the TiC layer inhibits the interdiffusion of Ti and Fe atoms and eliminates the formation of Fe-Ti IMCs, the TiC layer is also a brittle phase that is prone to fracture under external loading. The tensile strength of an interface which contains a 4-5 μm thick layer of TiC is reported to be 324 MPa [39].

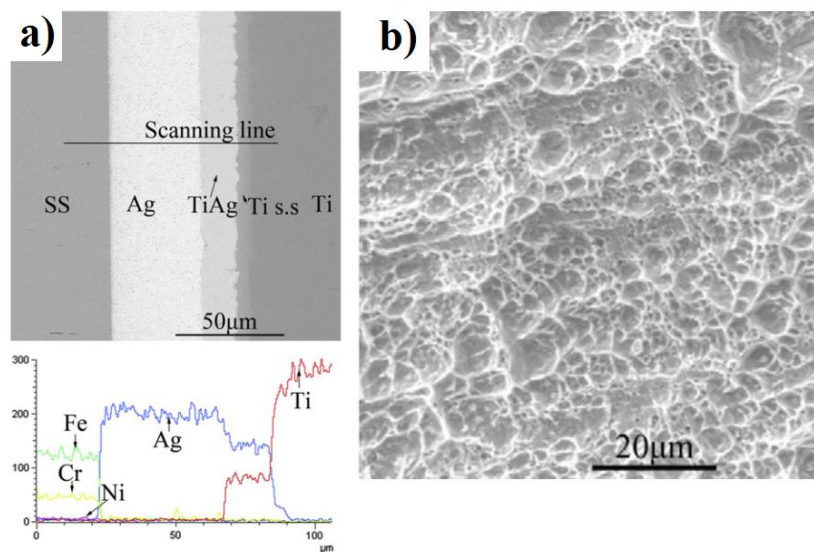


Figure 2.2 a) BSE image of a Ti/Ag/304SS diffusion bond. b) fracture surface of the Ag interlayer [40]

Fe-Ti IMCs can also be eliminated by using interlayer/s to partition the Ti and Fe atoms. Ag, Cu, and Ni are commonly used as interlayer materials due to their compatibility with steel. However, the Cu, Ni and Ag interlayers do form Cu-Ti, Ni-Ti and Ag-Ti IMCs, respectively, with the Ti alloy. As shown in the following examples, these IMCs are regarded to be less detrimental than the Fe-Ti IMCs on account of the

higher bond strength. By applying a Ag interlayer between Ti and 304SS, Deng et al. were able to achieve an interfacial tensile strength of 414 MPa [40]. Although a 14-18 μm layer of TiAg IMC was present at the interface (Figure 2.2a), failure occurred within the Ag interlayer and a dimpled fracture surface was observed (Figure 2.2b). In contrast, a directly bonded Ti/304SS joint failed at a UTS of 242 MPa and fractured in a brittle manner across the Fe-Ti IMCs [25]. It is worth mentioning that the UTS of pure Ag is less than 250MPa when tested in an unconstrained configuration [41, 42]. However, when the faces of the Ag interlayer are bonded to stronger and stiffer materials like the Ti and 304 SS, its faces are restrained from lateral contraction during tensile loading. This creates a triaxial stress state and reduces the effective stress (i.e. Von Mises stress) within the Ag interlayer [43]. Hence, the UTS of the constrained Ag interlayer can be increased by as much as 2-3 times of its unconstrained value [43, 44].

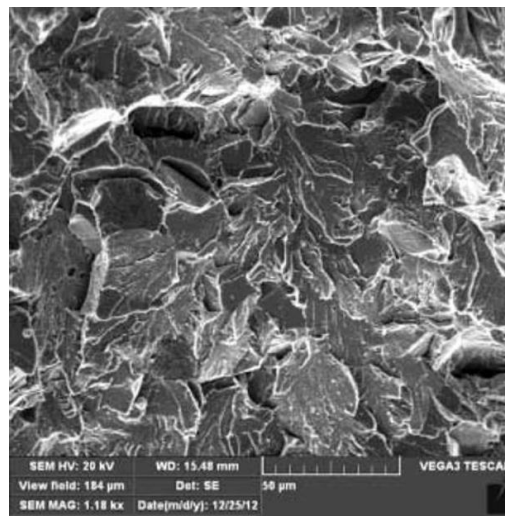


Figure 2.3 Cleavage fracture surface at the Ti/Cu diffusion bonded interface [30]

When Cu was used as an interlayer, Cu-Ti IMCs of various stoichiometric ratios (Ti_2Cu , TiCu , Ti_3Cu_4) formed at the interface. XRD analysis of the fracture surface revealed that failure occurred within these IMCs [30, 45]. The cleavage morphology on the fracture surface indicated the brittle nature of such joints (Figure 2.3). Despite the presence of detrimental Cu-Ti IMCs, the bond strength of the Ti/Cu/304 SS part

(322 MPa) was still greater than that of a directly bonded Ti/304 SS part [46]. When a Ni interlayer is used, similar bond strength of 311 MPa was reported. Failure of the Ti/Ni/304 SS part occurred within the Ni-Ti IMCs and the fracture surface displayed cleavage patterns similar to those in Figure 2.3 [29].

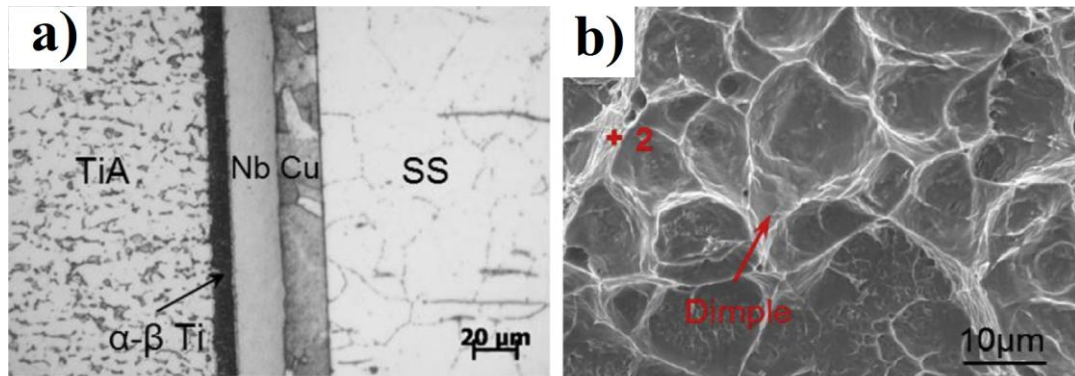


Figure 2.4 a) Cross-sectional image of the TiA/Nb/Cu/316L diffusion bond. b) Fracture surface of the Cu interlayer [47]

The complete elimination of IMCs and brittle phases can be achieved with a series of interlayers which are individually compatible with its adjacent materials. Figure 2.4a shows that Nb and Cu interlayers can be used to join Ti-6Al-4V to 316L SS with no IMC or brittle phase formation. Due to the β -Ti stabilizing effect of Nb, only a layer of $\alpha+\beta$ -Ti phase formed at the Ti/Nb interface. Such an interface is reported to have a tensile strength of 489 MPa and ductile fracture is found to occur within the Cu interlayer (Figure 2.4b). Other reported configurations of diffusion bonds involving multiple interlayers include Ti/V/Cu/steel [48] and Ti/Nb/Cu/Ni/AISI321 SS [49].

2.2 - Brazing

Description

In brazing, a filler metal with a relatively low melting temperature is introduced between the base alloys. Upon heating, the filler metal begins to melt while the base alloys remain solid. Even though the base alloys are not melted during brazing, the atoms from both alloys could still dissolve into the common molten filler and react to

form IMC. As the joint cools and solidifies, a metallurgical bond is established between the filler and the base alloys. There are many variants of the brazing process, each featuring different heat sources, different ways of introducing the filler material and different environments. Heating of the joint can be achieved using a furnace, an induction heater, a torch or via Joule heating. The filler may be plated onto the bonding surfaces of the base alloys, introduced externally into the heated joint using wires, or inserted in the form of a foil or paste. Brazing can also be carried out in a vacuum, inert or normal atmospheric conditions. Much like diffusion bonding, the resultant bond properties are highly dependent on the interaction between the filler material and the base alloys. If the filler reacts with the base alloy to form brittle phases, the bond properties will be poor. In contrast, compatible material combinations could produce joints with strengths higher than those of the base alloys. An important consideration in brazing is the wetting behaviour between the filler and base alloys. Good wettability helps the molten filler to spread quickly between the bonding surfaces through capillary action, thus, producing intimate, leak-tight joints with good mechanical properties. For this reason, the bonding surfaces are usually ground and cleaned to remove the oxide layer, grease, and dirt which could inhibit the wetting of the surfaces. Flux is often applied during brazing to prevent oxidation and improve the wettability of the bonding surfaces. Due to the use of a low melting point filler material, the joint can be processed at a lower temperature as compared to the typical fusion welding processes such as arc, laser and electron beam welding. Consequently, the amount of warping in a brazed joint is also lower. Additionally, the low processing temperature also helps to preserve the original metallurgical characteristics of the base alloys. Since the base alloys are not melted during brazing, the process is also suitable for the joining of dissimilar and incompatible materials. Unlike diffusion bonding,

where pressure is applied to force the materials into intimate contact, in brazing the filler material seeps into the gaps naturally via capillary action and the application of contact pressure is not as critical. As such, brazed joints need not necessarily be planar or near planar for the application of uniform pressure. Hence, more complex geometries may be adopted.

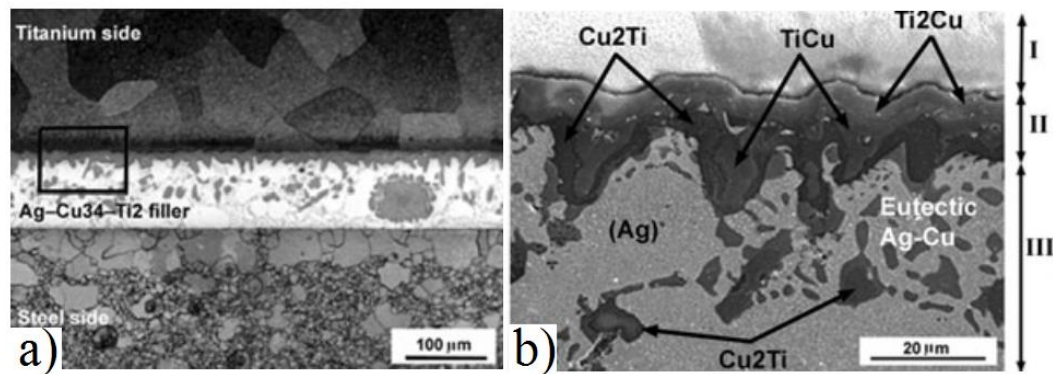


Figure 2.5 a) Interface of the Ti/steel joint brazed using Ag-Cu-Ti filler. b) Magnified view [50]

Microstructure

Most of the brazed joints between TiA and steel are performed using variations of the Ag-28Cu (wt.%) filler material [31, 32, 50-66]. This composition has been used because of 1) the suppressed melting temperature at the eutectic composition (780°C) and 2) the compatibility of Ag and Cu with steel. Brazing of the eutectic Ag-Cu filler can often be achieved at temperatures below 850°C [31, 32, 50, 51, 53, 56, 67]. Such brazing temperatures are lower than the β -transus temperature of most α -Ti and α + β -Ti alloys such as CP-Ti (890-950 °C) and Ti-6Al-4V (975-995 °C) [68]. The relatively low bonding temperature aids in preserving the microstructural properties of the base alloys while also limiting grain coarsening. Due to the dissolution and diffusion of Ti atoms into the molten filler, a Ti composition gradient is present across the interface. Even though the Ag-Cu filler does not react with steels to form brittle phase, its Cu atoms react readily with Ti to form Cu-Ti IMCs [31, 61, 67]. The Cu-Ti IMCs tend to form as continuous layers in the vicinity of the TiA base alloy and break up into

isolated regions towards the centre of the filler material (Figure 2.5a-b). This results in a layered interface which resembles that of diffusion bonding. Even though Ag is the predominant element in the Ag-Cu filler, Ti-Ag IMCs were not detected when the Cu content in the filler was greater than 28 wt.% [31, 50, 53, 54, 56, 62, 66]. Ag-Ti IMCs were only detected when the TiA is in direct contact with a solid solution with less than 5 wt.% Cu [32, 58, 69]. Increased bond temperature, bond time and Cu content in the filler material result in increased Ti dissolution and a greater amount of interfacial Cu-Ti IMCs [62, 66]. Under excessive bonding conditions, Fe-Ti IMCs begin to form next to the steel base alloy due to profuse diffusion of Ti across the filler material [50, 67]. Fracture of such an interface occurred within the thin layer of Fe-Ti IMCs at a shear strength of 96MPa [67]. Optimal brazing conditions should, therefore, allow sufficient time for the filler to wet the mating surfaces and establish an intimate metallurgical bond but not result in excessive Ti dissolution and the formation of Fe-Ti IMCs.

One way to suppress the formation of Fe-Ti IMCs in a brazed joint is to coat/plate the steel surface with a Ni layer before brazing to act as an additional diffusion barrier between the Ti and Fe atoms. Essentially, the Ni layer functions just like the interlayer material used in diffusion bonding. The presence of the Ni coating led to an increased shear strength from 96MPa to 210MPa [67]. Even though the bond properties did improve significantly, the presence of Cu-Ti IMCs was still detrimental to the bond properties as seen by the fracture across such phases (Figure 2.6).

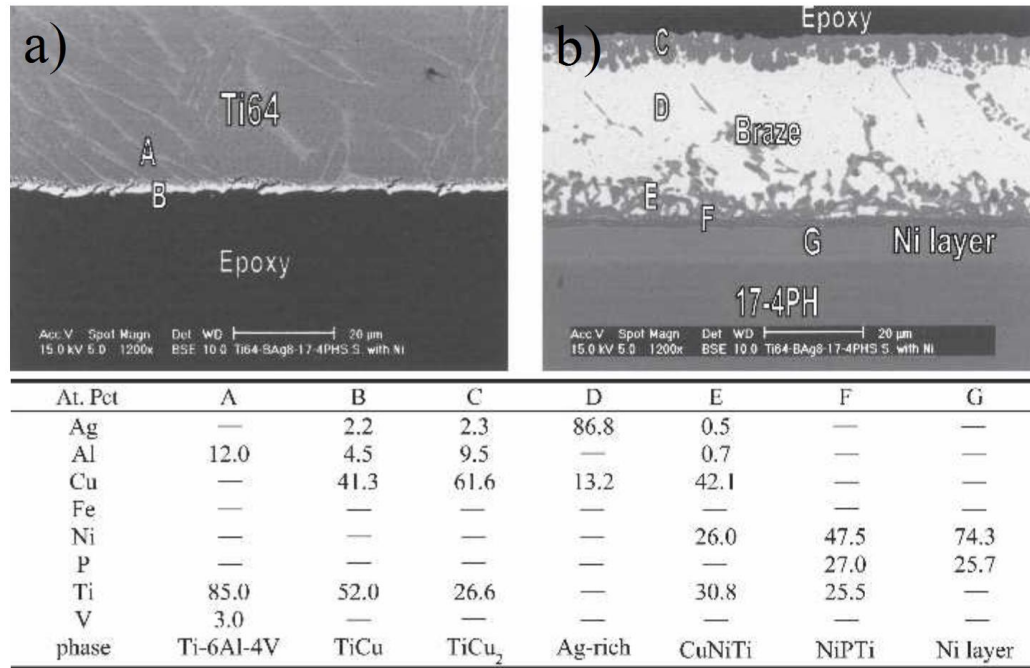


Figure 2.6 Fracture of Ti-Cu IMCs in a TiA/steel joint brazed using a Ni layer and a Ag-Cu filler. a) Ti-alloy side. b) Steel side [67]

Further improvement was observed when the TiA base is sputter-coated with a layer of Ag before brazing. The Ag coating separates the Ti atoms from the Cu atoms that are present in the filler material [32, 53], resulting in an interface which comprised of TiAg and Ag layers (Figure 2.7). Such an interface fractured within the Ag solid solution at a tensile strength of over 400 MPa [32]. Even though a layer of TiAg IMC existed within the interface, it was regarded to be non-detrimental as indicated by its low hardness of 164HV [32].

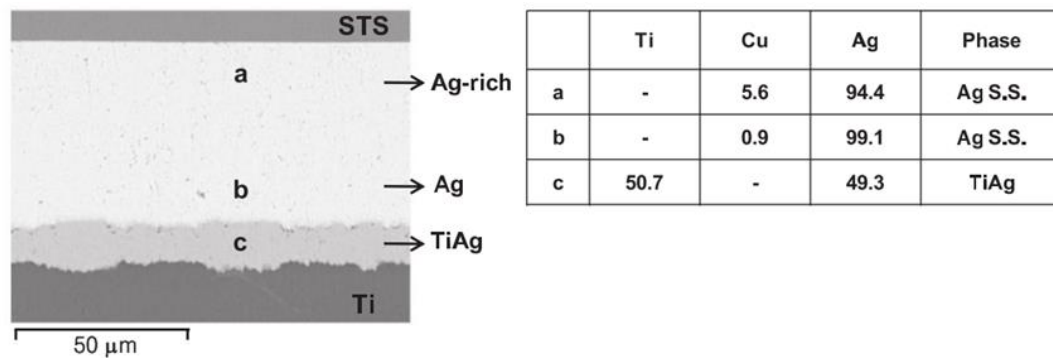


Figure 2.7 Ti/SS joint brazed using a Ag-Cu filler and a Ag interlayer [63]

To eliminate IMC from the interface, the steel base can be coated with a series of interlayers before brazing. By sputtering the steel base alloy with sequential layers of Ni, Cr, and V coatings before the brazing operation, Lee et al. were able to create a joint which is stronger than the Ti base metal (Figure 2.8) [70]. This caused the MM part to fail within the Ti base alloy at a UTS of ~480 MPa. Other filler materials that have been used to braze Ti to steel include Cu-based [71-74], Zr-based [75], and Al-based alloys [76]. However, all of those interfaces were populated with various IMCs and exhibited lower bond strengths.

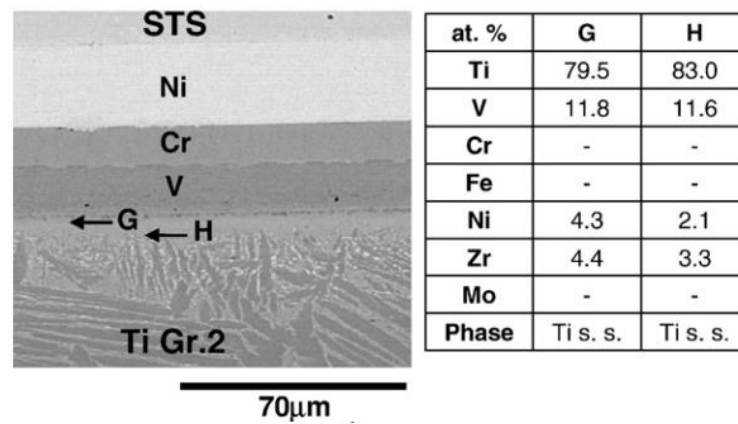


Figure 2.8 Ti/SS joint brazed using a Ti-Zr-Ni filler and V/Cr/Ni interlayers [70]

2.3 - Transient Liquid Phase Bonding

Description

Transient liquid phase bonding (TLPB) employs a similar setup to the brazing process. However, they differ in the solidification mechanism. In brazing, solidification is achieved by cooling the molten filler below its solidus temperature. In TLPB the filler solidifies via isothermal solidification while undergoing a composition change [77]. The filler, which typically has a near eutectic composition or contains a melting point depressing element, melts when the bonding temperature is raised above its liquidus temperature. Once melted, the base alloys begin to dissolve into the molten filler to dilute its composition. As the composition of the filler continues to shift away from its

eutectic point, its liquidus temperature increases until it matches the bonding temperature of the TLPB process. Thereafter, equilibrium conditions are maintained at the solid/liquid interface and isothermal solidification of the molten filler begins. The solid/liquid interface advances into the molten filler until the entire interface is eventually solidified at a constant bonding temperature. After isothermal solidification is completed, the interface may still contain a relatively high concentration of the atom used to suppress the melting point of the filler material. These atoms could precipitate as IMC upon cooling. Therefore, additional heat treatment is usually adopted to allow the interfacial composition to homogenize and approach that of the base alloy so that precipitation of IMC is avoided upon cooling.

Microstructure

The TLPB of TiA and steel is typically carried out using a Cu interlayer due to its ability to form a low melting point eutectic with Ti ($\sim 875^{\circ}\text{C}$). Consequently, the bonding temperature usually lies between 870 and 980°C and the bonding time is 30-90mins. At low bonding temperature and time, the diffusion of Cu into the base alloy and the dissolution of Ti are retarded and isothermal solidification is incomplete. Hence, the interface is populated by a large amount of Cu-Ti IMCs as shown in Figure 2.9a. With an increase in bonding temperature and/or time, the Cu atoms can diffuse faster and further into the TiA base alloy [45, 78] and isothermal solidification approaches completion. As such, the amount of interfacial Cu-Ti IMCs decreased as shown in Figure 2.9b. According to Norouzi et al. [79, 80], this led to decreased peak hardness, increased interfacial strength, and a dimpled fracture at the TLPB interface. While other authors also observed a similar decrease in the amount of interfacial Cu-Ti IMCs, the interfacial strength was, instead, found to decrease with bond temperature and time [81]. This result, which contradicts that of Norouzi et al., was attributed to

the detrimental accumulation of Fe-Ti IMCs adjacent to the steel base alloy at excessive bonding temperature and time. Although the reason behind the discrepancy between the results is unclear, it is certain that the beneficial reduction of Cu-Ti IMCs and the detrimental increase in Fe-Ti IMCs are both expected to occur at elevated bonding temperature and time. Therefore, the optimal bonding condition is likely to be the one which best compromises between both effects.

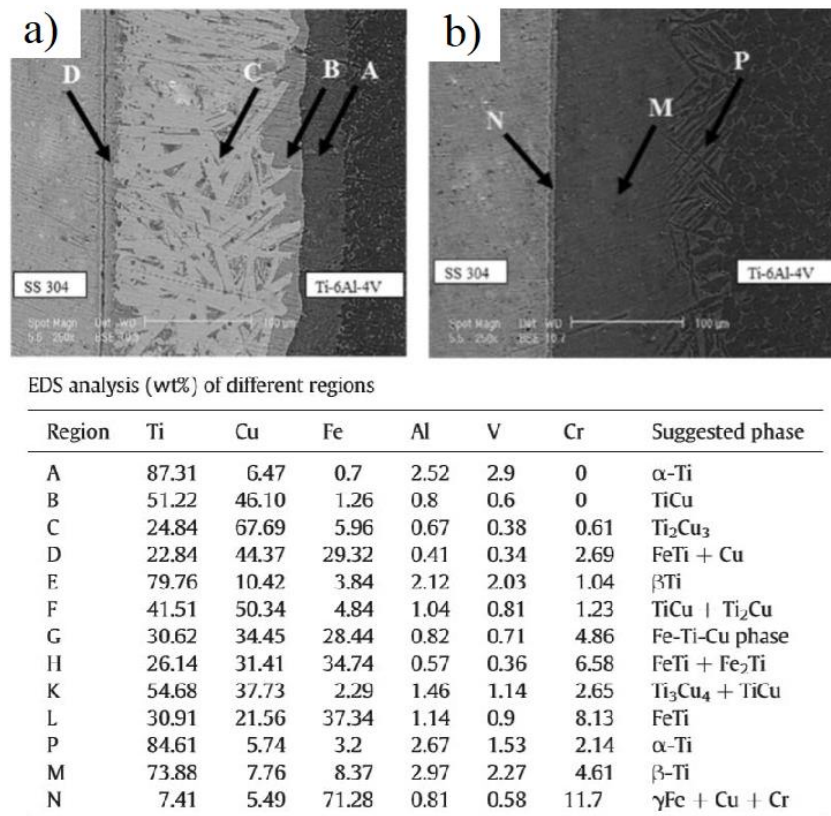


Figure 2.9 SEM images of SS/Cu/TiA interface obtained through TLPB at a) 870°C and b) 960°C for 60min [79]

2.4 - Friction Welding

Description

In friction welding, the energy needed to create a metallurgical bond is generated by rubbing the joining surfaces together under a compressive force. When enough frictional heat is built up at the interface, the solid material begins to soften and flow. Consequently, some of the plasticized material is squeezed out of the interface while

carrying with it some of the residual oxides which may have been initially present on the joint surfaces. Once the interface is sufficiently hot, the rubbing action is stopped, and the base alloys are allowed to bond under a high compressive force while the joint continues to cool. Essentially, the friction welding process consists of two sequential phases; the friction phase and the forging phase. As heat is directly generated at the interface, friction welding is relatively energy efficient, features a narrow heat-affected zone (HAZ) and suffers minimal part distortion. The entire process is, clean, non-hazardous, takes only tens of seconds to complete, and conceptually simple to operate and automate. Since no melting is involved, solidification cracking, elemental segregation, porosity formation, and excessive IMC formation are also greatly suppressed [82, 83]. The limitation of this process is that the joining surfaces must be planar. The two major variants of friction welding are rotary friction welding and linear friction welding. In rotary friction welding, relative motion is achieved by rotating one part along its longitudinal axis while keeping the other part stationary. Due to the rotating motion, at least one of the parts must be cylindrical. As the linear velocity of the rotating part varies from the centre to the periphery, frictional heating also tends to be non-uniform in rotary friction welds. On the other hand, in linear friction welding, one part is made to oscillate linearly with respect to the other to induce rubbing. Hence, the joined parts do not have to be cylindrical and heat generation is also more uniform across the rubbing surfaces compared to rotary friction welding. However, most literature on the friction welding of dissimilar metals is based on rotary friction welding due to its relatively simple design.

Microstructure

The friction welded joint typically features a few distinct regions. The narrow region where a metallurgical bond is established between the two surfaces is called the weld

zone. For dissimilar material welding, this is where the change in composition is observed. Adjacent to the weld zone is a dynamic recrystallization zone (DRZ) where the grains become refined due to severe plastic deformation under high temperature. Next to the DRZ is a thermomechanical affected zone (TMAZ) which contains elongated grains that are oriented in the direction of the material flow. Beyond that is the heat-affected zone (HAZ) which experienced elevated temperatures without any plastic deformation. In general, when TiA is friction welded to steel, TiA will be the one to plasticize and flow out of the interface due to its lower strength at elevated temperatures. This causes the DRZ to form predominantly in TiA side of the joint [84]. Owing to the grain refinement in the DRZ, this region often possesses a higher hardness compared to the base alloy [85]. As the temperatures in the DRZ, TMAZ, and HAZ may exceed the β -transus temperature of common TiA (890-950 °C for CP-Ti and 975-995°C for Ti-6Al-4V) and the austenitization temperature of steels (780-950°C for various steels), these regions may undergo a phase transformation to produce a different microstructure after welding. For instance, the austenite grains in the HAZ could transform into martensite instead of pearlite during cooling to produce a bond with limited ductility [86, 87]. Consequently, a post-weld heat treatment may be required to restore the microstructure and ductility of the joint. The strength of friction welded Ti/steel joint is typically much stronger than those obtained through diffusion bonding, brazing, and TLPB. This is due to the limited heat input and the quick bonding time of tens of seconds, which in turn results in a much narrower weld zone that has a thickness of only 0.5-3 μm [85-92]. As the composition gradient in the weld zone is confined to a narrow thickness of 3 μm or less, the amount of detrimental phases is also minimal. Hence, the strengths of the Ti/steel bonds frequently exceed

that of bulk Ti, causing the fracture to occur within the base alloy at strengths of 375-766 MPa [84, 86, 87, 90, 92-94].

Literature containing reliable microstructure analysis of the friction welded Ti/steel joint is rather limited. Based on the TEM [88, 90], SEM and XRD analysis [85, 87, 91, 94] from various authors, the weld zone of a Ti/steel or TiA/steel joint is likely comprised of FeTi, Fe₂Ti and a minor amount of other phases (Figure 2.10). Under a certain combination of materials and processing conditions, carbon can also accumulate at the weld zone to form detrimental TiC [86-88, 91]. However, the accumulated carbon can be dispersed by employing the appropriate post-weld heat treatment [87]. Instead of a direct bond between TiA and steels, some researchers have also used Cu [93] and Ni [95-97] interlayers which led to the formation of Cu-Ti and Ni-Ti IMCs respectively. Due to the limited literature on the use of interlayers, its benefits over direct friction welding of TiA to steels cannot be evaluated.

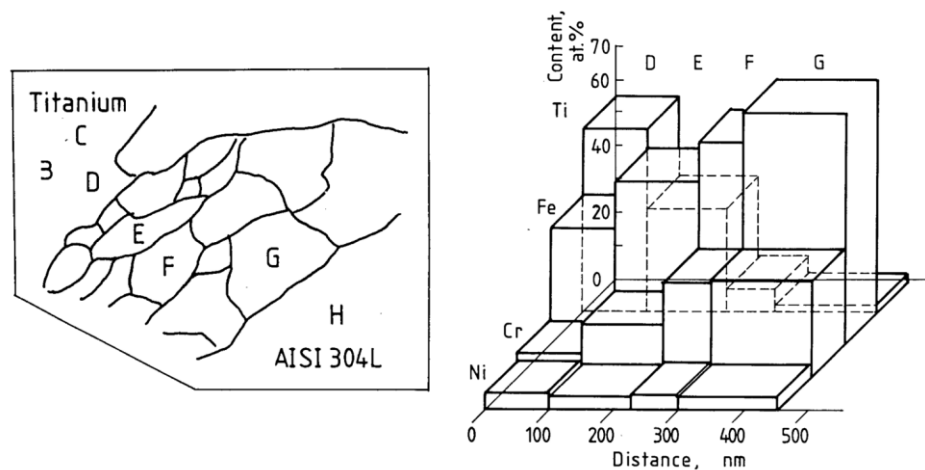


Figure 2.10 Schematic representation and composition of friction welded Ti/304L interface [90]

2.5 - Friction Stir Welding

Description

Another solid-state joining technique which uses frictional heat to establish metallurgical bonds is the friction stir welding (FSW) process. In FSW, the joining parts are kept stationary while a rotating, non-consumable welding tool is plunged into the base alloys and traverses along the joint line. The rotating tool imparts heat to its surroundings and causes the material on both sides of the joint to intermix through hot plasticized flow, resulting in a metallurgical bond. Due to the frictional contact between the welding tool and the base alloys, the material from the tool could also dissolve into the joint under excessive welding temperatures. The advantages of FSW are similar to those of friction welding. It is energy-efficient, environmentally friendly, produces joints with good metallurgical properties, and is suitable for alloys that cannot be fusion welded [98]. As the parts do not have to be oscillating or rotating like in friction welding, joining of large and irregular objects can be done in FSW. Due to the high strain associated with the solid metal flow, the joints produced by FSW also feature similar HAZ, TMAZ, and DRZ (a.k.a. nugget zone or the stirred zone in FSW).

Microstructure

When dissimilar metals such as TiA and steel are joined through FSW, an interface featuring a composition gradient is present in addition to the DRZ, HAZ, and TMAZ. Like the DRZ, the grains within the interface also experience dynamic recrystallization [99, 100] and can be refined to sizes as small as 150-600nm [101]. Depending on the processing condition, the interface can have different morphology and size. When the frictional heat input in FSW is just sufficient to bond the TiA and steel surfaces without inducing any significant mixing, the interface would be planar and have a thickness of $\sim 1 \mu\text{m}$ [16, 21]. The microstructural phases within the planar interface

between the Cp-Ti and 304 SS base alloys are shown in Figure 2.11. Through electron diffraction analysis, the interface was found to contain distinct layers of, Ni-Ti IMC, Fe-Ti IMCs, and σ -FeCr phase [16]. If the frictional heating is increased such that materials across the interface intermix, then vortices with alternating bands of material would be observed as shown in Figure 2.12 [16, 21, 102]. Even though the detrimental phases within the alternating bands are similar to those in the planar interface, such an interface is weaker due to its larger thickness and a greater amount of IMCs [16].

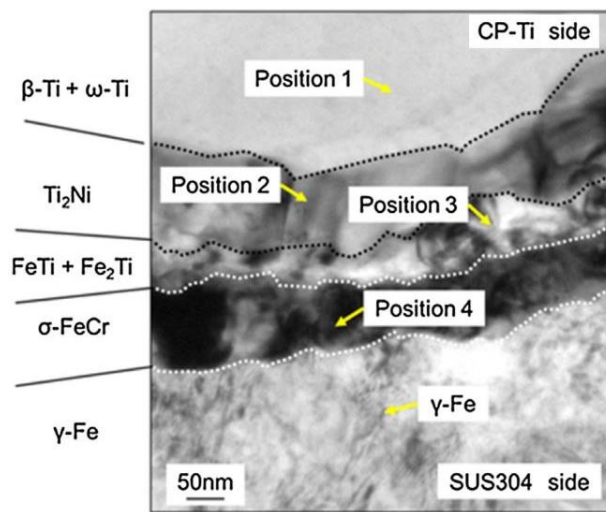


Figure 2.11 TEM image of the Ti/SS interface processed by FSW [16]

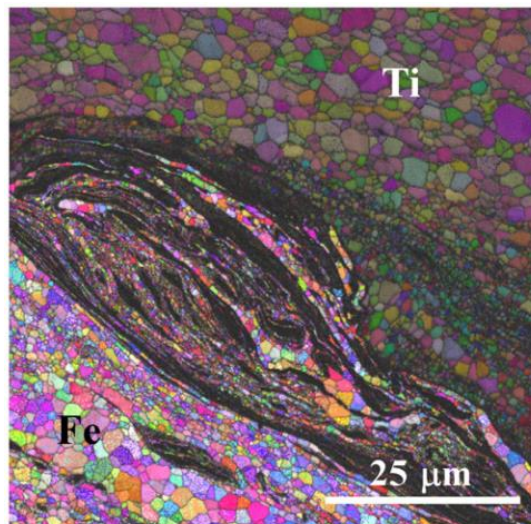


Figure 2.12 EBSD map of the intermixed region of Ti/steel interface processed by FSW [101]

2.6 - Explosion Welding

Description

In explosion welding, a metallurgical bond is established through a high-speed collision of the base alloys. Through an explosion, a thin cladding material is accelerated towards the stationary base material and bonded through a subsonic collision. During the collision between the cladding and the base, a high energy jet is formed at the collision point. The high velocity and high-pressure jet formation is essential to explosion welding and is responsible for 1) removing any surface oxide layer before bonding ensues and 2) deforming the material immediately ahead of the collision point such that the cladding and base are brought into intimate contact [103]. The deformed interface takes on a wavy appearance as shown in Figure 2.13. The vortices at the leading and/or trailing edge of each wave crest are formed due to the trapping of the high energy jet. The kinetic energy of the trapped gas is converted into heat as it continues to swirl in a vortex while thoroughly mixing the cladding and the base material [104]. The temperature in the vortices exceeds the melting point of the materials and so a solidification microstructure is observed in these vortices. Due to the conversion of a large amount of kinetic energy into heat, the size of these melted vortices can reach hundreds of micrometres in length [105-107]. On the other hand, the thickness of the wavy interface in between each pair of vortices is much thinner and ranges from hundreds of nanometre to a couple of micrometres under optimal bonding conditions [17, 105, 108]. As heating of the explosion welded interface is limited to a very narrow region, the bulk of the cladding and base material remains at a low temperature during the brief welding process. Consequently, the melted regions along the interface and vortices experience high cooling rates that are comparable to that of splat quenching (10^4 - 10^7 K/s) [109]. Hence, the interface may comprise of

supersaturated and metastable phases that differ from the predictions of the equilibrium phase diagram.

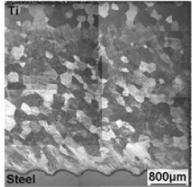
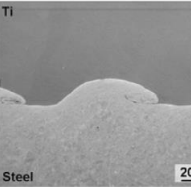
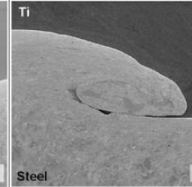
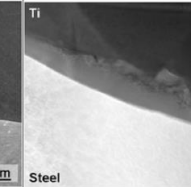
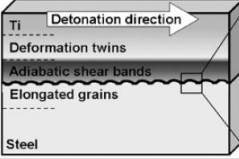
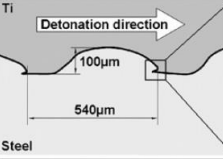
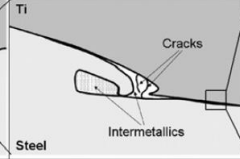
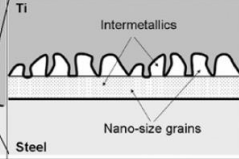
Scale	Macro	Meso	Micro	Nano
Microstructure				
Schematic				
Hierarchical structure unit	Plastically deformed base materials: Different degree of accumulated strain in Ti and elongated steel grains	Wavy interface: wavelength of 540µm and amplitude of 100µm	Wave crest: different intermetallic phases, presence of micro cracks	Thin interface reaction layer: two nano-size grained components

Figure 2.13 Hierarchical structure at the explosion-welded Ti/steel interface [17]

Microstructure

The wavy explosion welded interface may contain different combinations of amorphous phase [108-110], Fe-Ti IMCs [105, 111], TiC [111, 112] or quasicrystalline phase [109] while the vortices along the interface are comprised of Fe_2Ti and/or FeTi IMCs [17, 105]. Due to the congregation of brittle Fe-Ti IMCs in the vortices and the presence of residual stresses, the vortices typically contain cracks of similar lengths [17, 105, 107, 109, 113] (Figure 2.13). As a result, these vortices are the weakest locations along the interface. To preserve the structural integrity of the interface, it is necessary to keep the vortices small and isolated from each other through proper selection of welding parameters. This can be done by lowering the explosive load such that the energy dissipation at the Ti/steel interface is reduced [106, 107, 114, 115]. As the explosive load increases, the morphology of the interface changes in the following sequence: 1) unbonded, 2) planar with no vortex, 3) wavy with isolated vortices, 4) wavy with a continuous layer of melted material. Optimal

interfacial properties are associated with an interface that lies between 2) and 3), where a metallurgical bond is established with minimal melting. One may also lower the amount of energy dissipated at the Ti/steel interface by inserting a suspended piece of steel interlayer between the Ti cladding and the steel base in the welding setup [107, 116]. By changing the thickness of the steel interlayer, it is possible to control and lower the amount of kinetic energy loss during the collision between the Ti cladding and the steel interlayer. Since the kinetic energy lost is directly related to the energy dissipated at the interface, it can be used to effectively control the interface morphology, the volume of melted vortices, and the properties of the Ti/steel interface. As the explosion welding process is completed within a fraction of a second, it is practically diffusionless. Consequently, the amount of detrimental phases in an optimally bonded interface is extremely limited. Hence, the bonded interface can be stronger than the Ti base alloy [108, 110, 117] while also featuring substantial bend ductility [17, 115, 117].

2.7 - Laser Welding and Electron Beam Welding

Description

Most literature on the fusion welding of Ti to steel is based on laser welding and electron beam welding. In both processes, the energy source is focused into an intense spot of hundreds of micrometres on the workpiece. The energy is then absorbed by the materials on both sides of the joint and converted into heat which induces localized melting. Depending on the energy intensity of the focused spot, welding can occur either through conduction or keyhole mode. The former is characterised by a relatively wide and shallow melt pool which is suitable for joining thin pieces of material. In contrast, keyhole mode occurs when the intensity of the focused spot is high enough ($>10^6 \text{ W/m}^2$) to cause extensive vaporisation such that the high-pressure gases above

the melt pool creates a deep and narrow depression into the workpiece, i.e. a keyhole. Due to the large penetration depth of a keyhole weld, it is used to join parts with large thicknesses. Although laser and electron beam welding are conceptually similar, there are some differences between the two techniques. To minimize electron scattering, electron beam welding is usually carried out in a vacuum chamber. The vacuum chamber helps to minimize weld contamination and contain harmful x-ray emissions. However, the combination of a high welding temperature and vacuum environment may lead to the vaporization of volatile elements, thereby affecting the composition of the weld. Additionally, the presence of a chamber also restricts the workpiece dimensions. On the other hand, laser welding uses a shielding gas to prevent the weld from excessive oxidation. Hence, it does not require an enclosure and can be used to weld relatively large parts. However, the associated contamination is higher compared to electron beam welding. Electron beam welding is relatively energy-efficient as ~95% of the kinetic energy of the electrons is being converted into heat to induce melting [118]. In contrast, a significant portion of the incident laser beam is typically reflected off the metallic surface in laser welding [119] and the energy absorption depends on the surface roughness, the absorptivity of the material, and the geometry of the melt pool. As the deflection of the electron beam is controlled by the electromagnetic lens, the beam can traverse across the surface at speeds of 10^3 m/s. In principle, this means that uniform heating and welding can be simultaneously achieved in electron beam welding to tailor the heating and cooling conditions of the weld for optimal bond properties. Compared to electric arc welding and other forms of fusion-based welding techniques, the bond characteristics of laser and electron beam welds are generally superior due to its higher resolution, smaller melt pool, smaller HAZ, and higher

cooling rates [118, 120]. These factors combine to minimize part distortion and the dilution of dissimilar materials across the interface.

Microstructure

During welding of a TiA/steel interface, the high energy beam is usually positioned with an offset towards either of the base alloy. In doing so, the mixing of materials across the interface is minimized. This majorly reduces the amount of Fe-Ti IMCs formed, thus, allowing the TiA/steel joints to remain intact after welding [15]. However, such joints have poor mechanical property [15, 121-123] as the amount of Fe-Ti IMCs is still significantly greater than those associated with friction welding or explosion welding. The only way to achieve a decent bond between fusion-welded TiA and steel is to employ interlayer/s. The interface on either side of the interlayer will have to be welded in separate passes so that the melt zones do not overlap to produce Fe-Ti IMCs. For instance, if Ni is used as an interlayer between TiA and SS, then the TiA/Ni and Ni/SS interfaces will have to be welded separately. The types of interlayers that have been employed for laser and electron beam welding include Cu [122-126], Ni [123], Ag [127], Nb [128], Ta [129], and V [20, 123, 130, 131]. Similar to the observation made in diffusion bonding, the use of interlayers led to improved bond strengths. However, most of these interfaces still fractured in an entirely brittle manner across the IMCs [122, 124-126, 128]. Ductile fracture was observed when Ag and V were separately used as interlayer materials. In the case of the Ag interlayer, the presence of Ag-Ti IMCs was not detrimental to mechanical properties and fracture occurred within the Ag interlayer [127], which is consistent with the literature from diffusion bonding and brazing. In the case of the V interlayer, no IMC or detrimental phases were observed in the TiA/V and V/steel interface (Figure 2.14). Even though the composition at the V/steel interface lies within the brittle σ -FeV phase region in

the equilibrium phase diagram, the formation of σ -FeV phase was suppressed due to the rapid solidification conditions in the melt zone [20, 130]. Instead, Fe-rich and V-rich solid solutions were detected at the V/steel interface while Ti-rich solid solution was detected at the TiA/V interface. Ductile fracture occurred within the V interlayer at a tensile strength of 367MPa [20].

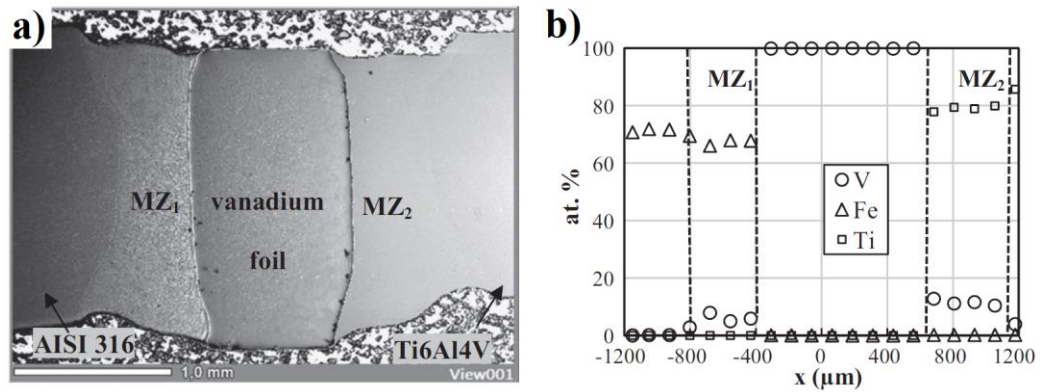


Figure 2.14 Laser welded TiA/V/SS interface (a) SEM image (b) Composition of major elements [20]

2.8 - Directed Energy Deposition

Description

The setup of DED techniques is largely similar to laser welding except that the former features a material feeding mechanism. In DED, the material can be fed into the melt pool either in wire or powder form. The composition of the metal powders or wires introduced into the melt pools can be continuously varied across the build layers by mixing them in various proportions. This allows the MM interfaces processed by DED to have any arbitrary composition gradients. By combining the flexibility of DED with the phase prediction from multi-component phase diagrams, it is possible to design a composition gradient which avoids detrimental phases [7]. Additionally, a smooth and gradual transition in material properties (i.e. a functional gradient) may also be implemented across the interface to minimize stress concentrations arising from property mismatch [34, 132].

Microstructure

Functional gradients have been adopted across the interfaces of TiA/steels MM parts [12, 14]. By linearly varying the mixture of TiA and Invar powders (64wt.% Fe 36wt.% Ni), Bobbio et al. were able to produce a functional gradient which transited from Ti-6Al-4V to Invar (Table 2.1) [12]. Even though the functional gradient was stretched over a relatively large thickness of ~12mm to minimize the mismatch in the thermophysical properties, macroscopic cracks still appeared within the interface. This was due to the detrimental formation of FeTi+Fe₂Ti IMCs within the interface which largely overwhelmed the beneficial effects of the functional gradient.

Table 2.1 Area fraction of different phases within the DED Ti-6Al-4V/Invar interface [12]

	Layer 3	Layer 26	Layer 33	Layer 35	Layer 45	Layer 49	Layer 75
Volume % Invar	0	15	36	42	73	85	100
Phase	Area (vol.) % of phase						
Ti (hcp)	77.9	1.1	—	7.25	1.3	0.1	0.0
FeTi (B2)	0.4	71.4	34.8	7.65	3.4	0.1	0.0
Fe ₂ Ti (C14)	0.1	14.6	60.8	43.3	3.7	1.1	0.0
Ni ₃ Ti (DO ₂₄)	—	0.5	—	19.23	1.4	0.2	0.0
NiTi ₂	0.0	0.1	0.0	0.2	0.1	0.0	3.12
Invar (fcc)	—	1.0	0.5	10.2	89.9	90.1	95.8
Zero solution	21.6	11.3	3.87	12.2	3.4	8.3	1.1

To minimize the amount of interfacial Fe-Ti IMC, Reichardt et al. first produced a gradient from TiA(100%) to TiA(25%)-V(75%) [13]. Next, they proceeded to add the second gradient which varied from SS(25%)-V(75%) to SS(100%). However, as soon as the SS(25%)-V(75%) mixture was deposited onto the underlying layer containing TiA(25%)-V(75%), the Fe and Ti atoms reacted to form Fe-Ti IMCs which caused spontaneous delamination. Hence, Reichardt et al. recommended the following transition sequence: TiA(100%) to V(100%) to Cr(55%)-V(45%) to SS(100%).

The additional step of grading towards Cr(55%)-V(45%) before transiting to SS(100%) was suggested as a means to circumvent the brittle σ -FeCrV phase region that is predicted by the Fe-Cr-V phase diagram. By employing a gradient path similar to that suggested by Reichardt et al., Li et al. showed that it was indeed possible to produce a

crack-free functional gradient using the following sequence: TiA, V, Cr, Fe, SS [133]. While DED is well suited to produce functional gradients with gradual property transition, it can also be used to produce TiA and steel MM parts featuring steep composition changes across the interface. For instance, Sahasrabudhe et al. showed that TiA may be bonded to SS via a Ni-20Cr layer [14]. However, NiTi and Cr₂Ti IMCs were present at the interface and the interfacial bond strength is unknown.

2.9 - Drop-on-Demand Liquid Metal Jetting

Description

Drop-on-Demand (DoD) liquid metal jetting is an AM technique that is conceptually similar to inkjet printing in the way material droplets are assembled to form a 3D part. As shown in Figure 2.15, the metallic feedstock is melted and stored in a nozzle chamber that is subjected to a transient magnetic field. The transient magnetic field, in turn, induces a current flow within the molten metal. Interaction between the magnetic field and the induced current produces a magnetohydrodynamic force which pressurizes the nozzle chamber and forces liquid metal droplets to be ejected through the nozzle. The ejected droplets, which can have a size of 50 – 550 µm [134], is directed towards the underlying substrate and successively stacked to form a 3D object. Good wetting and coalescence of droplets are necessary to minimise the trapped porosity between droplets. The coalescence behaviour is largely influenced by the thermal energy of the droplets and the underlying material. Insufficient thermal energy will lead to lack-of-fusion defects between droplets. The resultant part quality depends on the understanding of conductive heat dissipation from the underlying part, cooling of droplets during flight, droplet ejection frequency, and droplet size [135].

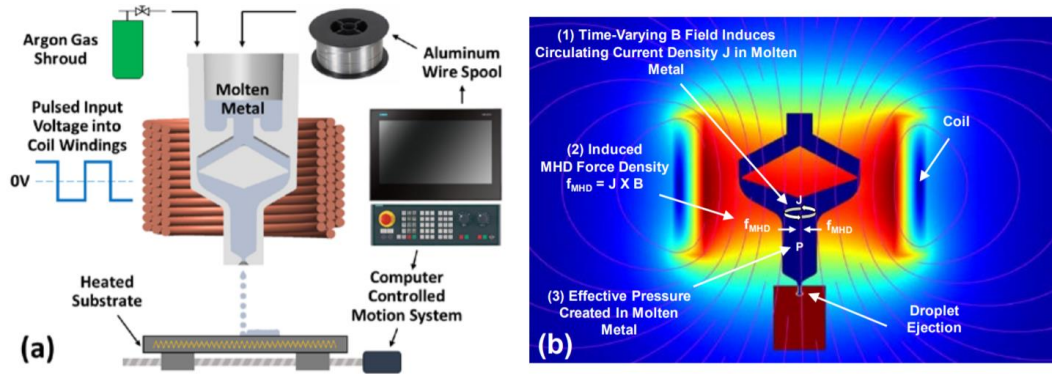


Figure 2.15 a) Schematic of Drop-on-Demand metal jetting process. b) Magnetohydrodynamic interactions within nozzle chamber [135]

Substrate heating is commonly employed in metal DOD processes to minimize thermal dissipation and improve the coalescence of the deposited droplets [135, 136]. To date, DOD metal jetting has mostly been used to process materials with low melting temperatures such as Al [135] and Sn alloy [137, 138]. Recently, Ag has also been deposited using DOD metal jetting using droplet temperatures of over 1000 °C [136]. However, due to the rapid cooling during flight, the droplets ejected at 1015-1025 °C did not fuse well on the 500 °C preheated substrate, resulting in ~8% part porosity. It was estimated that the fusion of the droplets can be achieved by further raising either the droplet temperature to ~1400 °C or the substrate temperature to ~900 °C [136].

There are several advantages associated with the DOD metal jetting process. The material feedstock can be supplied in the form of wire, rod or shots which is cheaper compared to micron-sized powder that is used in typical metal AM techniques. Additionally, multiple deposition heads can be incorporated to increase the deposition rate. Furthermore, multiple material deposition on a single part can potentially be achieved using separate deposition heads for different materials [136].

However, several challenges remain to be resolved in DOD metal jetting as well. In particular, the technology has not matured to the point of producing high melting point alloys ($>1000\text{ }^{\circ}\text{C}$) with low porosity. Consequently, DOD metal jetting is, currently, unable to process steel and titanium alloys. Although it has been shown that overhangs of $\sim 45^{\circ}$ can be produced by DOD metal jetting [134], it is not certain whether the process is capable of printing lower overhanging angles. In comparison, overhanging angles as low as $0\text{--}10^{\circ}$ can be produced by PBF techniques due to the support from the surrounding powder bed [139].

Although DOD metal jetting is conceptually viable for MM deposition, the material choice, at present, is limited to Al alloys and low melting temperature alloys [140]. Additionally, the mechanical properties and microstructure of the produced metallic samples remain to be evaluated in future studies. Considering the current state of the DOD metal jetting technology, an in-depth and fair evaluation of its MM printing capability is deemed to be premature. Hence, DOD metal jetting is not discussed beyond this literature review chapter.

2.10 - Selective Laser Melting

In SLM, the powder is spread over a build platform before a laser beam is activated to melt and consolidate selective regions within each layer. A 3D part is formed by sequentially stacking the consolidated layers. Currently, the default set up of SLM does not possess the same level flexibility as DED for MM processing. This is due to the lack of a commercial MM deposition mechanism for the PBF techniques. Hence, MM research based on the SLM process is presently limited. However, this is starting to change as new powder deposition mechanisms are being developed for the SLM process. By introducing a simple partition in the powder recoating mechanism (i.e.

recoater), Liu et al. partitioned two different metal powders within the same recoater so that either material may be deposited at any build layer to produce a MM part [141]. However, such a method only allows the materials to be varied across the layers and not within each layer. Additionally, the unconsolidated powder from both materials cannot be easily recycled as they are both mixed within the common powder bed. To realize intra-layer material variation, Yang et al. developed a nozzle based system to store and deposit different powders at selective locations within each build layer [4]. Later on, Al-Jamal et al. incorporated the nozzle based mechanism into the SLM process and produced parts with intra-layer material variation [142]. This was improved by Wei et al. who further included a vacuum system to remove loose powders from selective regions on the powder bed [1]. In doing so Wei et al. avoided cross-contamination in the powder bed, thus allowing the unconsolidated powders to be recycled. Besides the nozzle based approach, Aerosint recently demonstrated that MM deposition can also be achieved using multiple patterning drums [143]. Each patterning drum deposits its specific material selectively onto the substrate as the recoating unit sweeps across the powder bed. The combined depositions from the multiple patterning drums result in layers featuring intra-layer composition variation.

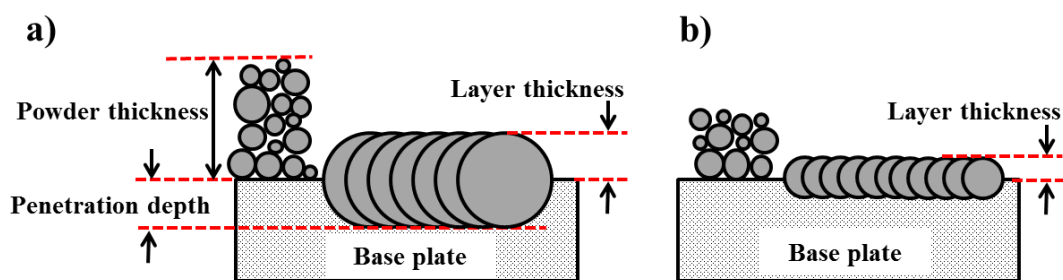


Figure 2.16 Illustration of Ni powders melted over Ti substrate with a) large layer thickness and b) low layer thickness

Compared to DED, PBF techniques such as SLM is better suited to print parts with complex overhanging features such as those found in lattice structures [144-146]. This

is due to the presence of a powder bed which acts as structural support for the overhangs. The in-plane build resolution of SLM is also superior to that of DED due to its smaller laser spot diameter of $\sim 0.08 - 0.1$ mm. In contrast, the laser spot diameter of DED is typically 0.3-3 mm. More importantly, the resolution in the build direction (i.e. layer thickness) for SLM can be as fine as 0.02 mm. The layer thickness setting is one of the key parameters used in MM processing via SLM. To illustrate its importance, consider a scenario where Ni powder is melted over a Ti substrate using two different layer thickness settings (Figure 2.16). Assuming the melt pools in both cases are half embedded in the substrate for stability considerations, a larger layer thickness typically leads to increased penetration depth. Due to the larger penetration, the build layer in Figure 2.16a is expected to contain a greater amount of Ni-Ti IMCs and, thus, possess lower mechanical strength than that of Figure 2.16b. To minimize detrimental phase formation, the layer thickness or, equivalently, the powder thickness should be kept to a minimum.

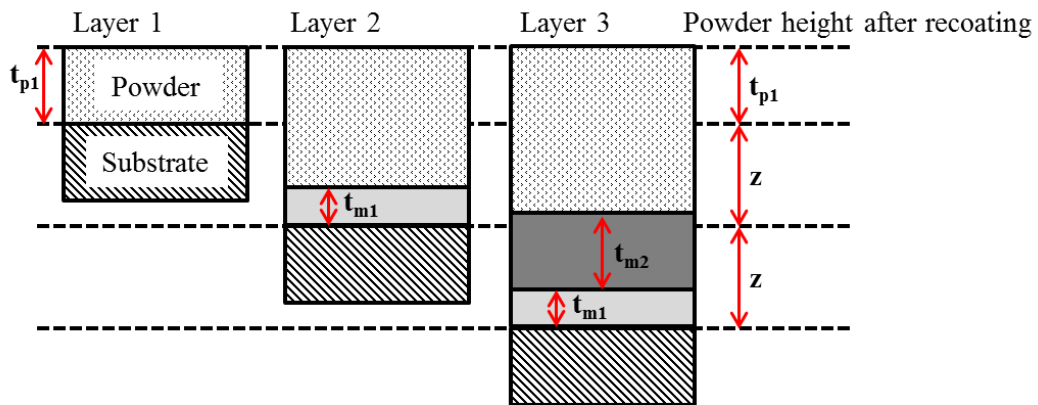


Figure 2.17 Illustration of layer thickness variation

The layer and powder thickness can, however, vary significantly in the initial build layers when they are not at the steady-state thicknesses. To understand how the powder thickness varies across the initial build layers, consider the schematic as shown in Figure 2.17. When the powder is deposited in layer 1, it has a thickness of t_{p1}

which is also equivalent to the physical gap between the substrate and the lower tip of the recoater blade. After the loose powder layer in layer 1 is melted, it consolidates into a dense layer with a thickness of t_{m1} . Thereafter, the entire substrate is lowered by a fixed displacement, z , and a new powder layer is deposited. If the thickness of the consolidated build layer (t_{m1}) is smaller than the substrate displacement (z), then the thickness of the unconsolidated powder ($t_{p2}, t_{p3} \dots t_{pn}$) and layer thickness ($t_{m2}, t_{m3} \dots t_{mn}$) will continue to increase in the next layer until the steady-state value is reached. The powder thickness (t_{pn}) and layer thickness (t_{mn}) for each build layer can be calculated using the following formula [147]:

$$t_{pn} = t_{p1} + (z - c \cdot t_{p1}) \sum_{i=0}^{n-2} (1 - c)^i \quad (1)$$

$$t_{mn} = c \cdot t_{pn} \quad (2)$$

where c is the consolidation ratio defined in equation (2). Given that the initial powder thickness (t_{p1}) and platform displacement (z) are known, one only needs to take experimental measurements of the layer thickness (t_{mn}) to obtain the consolidation ratio, c , using equations (1) & (2). Equivalently, the consolidation ratio may also be defined as the product of the powder packing density (p) and a material loss coefficient (l) as shown in equation (3).

$$c = t_{mn} / t_{pn} = p \cdot (1 - l) \quad (3)$$

Under ideal conditions where no material is lost during melting, the consolidation ratio, c , should be identical to the powder packing density, p . In reality, some material is ejected during the melting process. Hence, a loss term is added to account for powder particles ejected due to spattering. The works of various authors [148-151] showed that the momentum imparted to the spattered particles comes from 1) an intense metal vapour jet above the melt pool and 2) an induced gas flow that converges towards the

melt pool. The induced gas flow carries the powder particles towards the melt pool while the intense metal vapour jet imparts upward momentum to eject the particles away from the melt pool. Since the powder density typically ranges between 0.4 - 0.6 and the consolidation ratio (c) is ~ 0.3 [147], powder lost due to spattering is estimated to be 0.25 - 0.5.

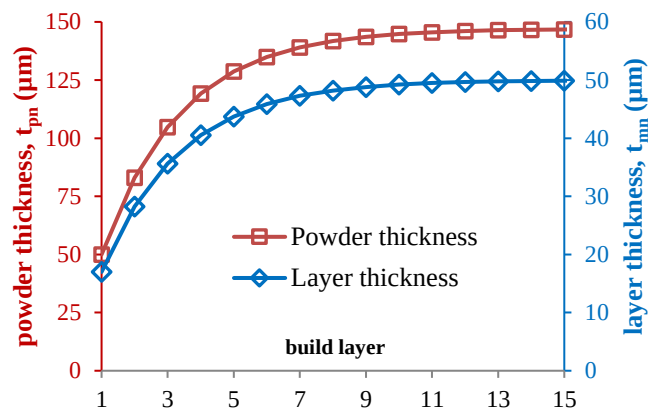


Figure 2.18 Powder and layer thickness variation across the initial build layers

Figure 2.18 shows the layer thickness variation calculated using equation (1) & (2) for an initial powder thickness (t_{p1}) of 50 μm , constant platform displacement (z) of 50 μm , and a consolidation ratio (c) of 0.34. It can be seen that the layer and powder thickness increase gradually and reach $\sim 90\%$ of its steady-state value within 6 build layers. This increase in layer thickness can be advantageous to the processing of MM interfaces. In particular, low layer thickness and low laser energy input can be used in the first build layer to minimize the melt pool penetration depth and limit dilution between dissimilar materials. After several layers of dissimilar material has been fused over the substrate, the composition of the top layer shifts towards that of the deposited material. Thereafter, dilution control is no longer a critical consideration. Thus the layer thickness and penetration depth can be increased to improve productivity.

The MM literature related to the SLM process is very limited. By far, the only MM combinations printed using SLM are Cu alloy/steel [1, 141, 142], Cu alloy/aluminium alloy [152], steel/aluminium alloy [153], and Ni alloy/SS [1]. The above literature mostly focussed on the powder deposition mechanism with limited microstructural analysis at the MM interfaces. The effects of process parameters on interfacial microstructure and mechanical properties are also unavailable. Additionally, the effects of rapid cooling and residual stresses on the integrity of the MM interfaces also remains to be investigated. Due to the lack of literature, an accurate review of the MM capabilities of the SLM process cannot be made.

2.11 - Factors Affecting the Mechanical Property of MM Interfaces

2.11.1 – Intrinsic Properties of Interfacial Phases

The review of the various joining and AM techniques shows that the structural properties of the MM interface are generally dependent on 1) the properties of the constituent phase/s, 2) the thickness or amount of detrimental phases, and 3) the morphology of the interfacial phase/s.

Interfaces that contain thick layers of detrimental IMCs typically fracture in a brittle manner. Regardless of the type of joining and AM techniques used, Fe-Ti IMCs are consistently found to be most detrimental to bond properties. The presence of such IMCs caused the interface to crack during solidification and cooling [12, 14, 123]. To suppress or eliminate the formation of Fe-Ti IMCs, Cu [28, 126], Ni [95, 154], and Ag-based [32, 40] interlayers have been commonly used to partition the Ti and steel base alloys. Even though the bond strength improved with the use of interlayers, interfaces containing Cu-Ti and Ni-Ti IMCs still failed in a brittle manner across the IMCs. AgTi is the only IMC which did not adversely affect the bond strength. Fracture

of a Ti/AgTi/Ag/SS interface occurred within the ductile Ag interlayer instead of the adjacent AgTi IMC layer [32, 40]. Furthermore, the hardness of the AgTi IMC (164HV) [32] is also much lower compared to hardness of the Cu-Ti (530-670HV) [122], Ni-Ti (~662HV) [96, 154], and Fe-Ti IMCs (>1000HV) [22]. Other commonly reported detrimental phases include σ -FeCrV phase (forms when SS is excessively enriched with V and/or Cr content [13, 16]), TiC (forms when Ti is bonded directly to steels with more than ~0.16wt.% C) [39, 110], and λ (Cr, Fe)₂Ti [35].

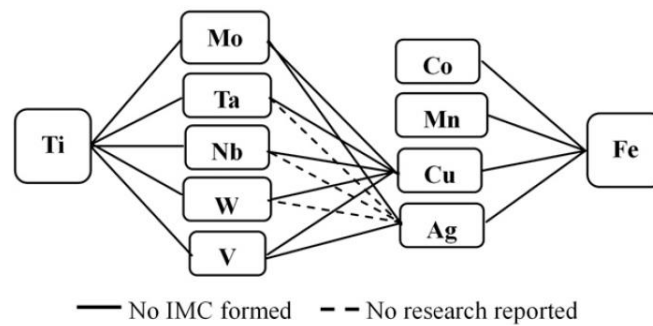


Figure 2.19 Binary combinations of elements with no intermetallic compounds [131]

The complete elimination of brittle phases at the MM interface can be achieved using a series of compatible interlayers (Figure 2.19). The binary phase diagrams of all the connected pairs of elements in Figure 2.19 are free of brittle phases. With the appropriate choice of interlayers, it is possible to achieve ductile fracture either within the interface or the weaker base alloy [47, 49]. The pairing shown in Figure 2.19 is only a fraction of all possible combinations of interlayers. In general, the number of interlayers used and the composition of each interlayer are both arbitrary. Alloys may also be used as interlayers. This leads to countless ways to sequence the interlayers between the Ti and steel base alloys. Using a large number of interlayers is, however, impractical for most joining processes as a large number of alloys compositions will have to be prepared. The most practical way to achieve a wide range of compositions across the MM interface is to through DED. DED allows elemental and pre-alloyed

powders to be arbitrarily mixed and deposition in real-time to achieve a continuously varying composition gradient at the interface [7, 12, 13].

2.11.2 - Quantity of Detrimental Phase

Other than the intrinsic properties of the interfacial phases, the quantity of those phases also has a drastic effect on the bond properties. When a large amount of detrimental phases is formed due to excessive dilution between the interlayer/s and base alloys, the structural properties of the interface become severely compromised. Consequently, the tensile strength of diffusion bonded interfaces decreases with an increase in IMC thickness [37, 154]. If the quantity of IMCs is greatly suppressed, then even the Ti/steel interface which contains detrimental Fe-Ti IMCs can possess a high bond strength. Therefore, the friction welded and explosion welded Ti/steel interfaces are typically stronger than those associated with other joining techniques. Fracture tends to occur within the base alloy instead of the friction welded and explosion welded Ti/steel interface [16, 101, 108, 110, 117].

2.11.3 - Interfacial Morphology

Another factor that influences the interfacial properties is the morphology of the detrimental phases. In diffusion bonding, brazing and TLPB, the IMCs often form as continuous layers within the interface. Such a morphology is undesirable as it allows cracks to propagate without much deflection. The fracture path of such joints is often confined to a specific layer/s of brittle IMCs [50, 71, 74] and a cleavage morphology is typically observed over the entire fracture surface. In explosion welded interfaces, the Fe-Ti IMCs which exist within the vortices are isolated by the surrounding ductile regions (see Figure 2.13). The ductile surroundings help to contain the cracks within the vortices, thus, preventing spontaneous delamination. Due to the isolation of the Fe-Ti IMCs, the interfacial fracture was also forced to propagate through both the ductile

and brittle regions [17, 112]. Hence, the explosion-welded interface features improved strength over the other interfaces that contain continuous layers of IMCs. Another morphological advantage of the explosion-welded interface is its microscale waviness. Compared to the planar interfaces obtained in diffusion bonding, the wavy appearance of the explosion-welded interface presents a more arduous path for crack propagation. The fracture toughness associated with a wavy interface is also higher than that of a planar interface [155-157].

2.12 - Multiple-Material Processing: Additive Manufacturing versus Joining Techniques

A summary of the characteristics of the various joining and AM techniques is shown in Table 2.2. Compared to joining techniques, AM has its own set of disadvantages as well as the unique potential for MM processing. The major disadvantage of AM in MM processing stems from the fact that it is a fusion-based process. Due to the simultaneous melting of the base alloys at the Ti/steel interface, the Ti and Fe atoms can mix readily in the molten state to form a relatively large amount of detrimental Fe-Ti IMCs during solidification. When coupled with the misfit strains incurred during cooling, cracks could form easily at the Ti/steel interface. Therefore, the AM of Ti/steel interface is not feasible even with the use of a functional gradient [12]. The strength of similar laser and electron beam welded Ti/steel interface is also very low. On the other hand, solid-state joining techniques such as friction welding and explosion welding are capable of producing Ti/steel interfaces with high bond strength due to its low interfacial dilution [16, 101, 108, 110, 117]. To compensate for the large dilution associated with fusion-based processes, interlayer/s can be used. With interlayer/s the Fe-Ti IMCs can be eliminated at the expense of other phases and the interfacial bonding can be greatly improved [7, 14, 20, 122-127, 130, 131, 133].

Table 2.2 Features of the various joining and additive manufacturing techniques used for multiple material processing

Process	Interfacial thickness (μm)	Bond strength	Bond time	Material distribution	Remarks
<u>Solid state joining</u>					
Diffusion bonding, brazing, transient liquid phase bonding	$10^0 - 10^1$	Moderate	10 min	2D	• microstructures of base alloys are altered due to uniform heating • surface preparation is critical • bond time is independent of surface area • inert or vacuum environment required
Friction stir welding	$10^0 - 10^2$ ***	Moderate	10 min **	2D	• relatively long bonding time • microstructure of base alloys are preserved • inert environment not required
Friction welding	$10^{-1} - 10^1$	High	10 sec	1D	• rotating parts need to have axial symmetry • narrow HAZ, TMAZ, and DRZ • special fixtures needed for the securing of irregular parts • inert environment not required
Explosion welding	$10^{-1} - 10^1$	High	< 1 sec	1D	• narrow HAZ, TMAZ, and DRZ • wavy interface • extremely high cooling rate • can be used to weld extremely large areas • inert environment not required
<u>Fusion-based joining</u>					
Laser welding, electron beam welding	$10^2 - 10^3$	Low (no interlayer) Moderate (with interlayer/s)	1 min **	2D	• large dilution • susceptible to solidification cracking • high cooling rate • inert or vacuum environment required
<u>Fusion-based additive manufacturing</u>					
Directed energy deposition	$10^1 - 10^4$ *	Unknown	Variable	3D	• capable of producing functionally graded materials • high cooling rate • susceptible to solidification cracking • inert environment required
Selective laser melting	$10^1 - 10^2$ *	Unknown	Variable	3D	• capable of producing MM parts with complex and intricate geometrical features • susceptible to solidification cracking • high cooling rate • inert environment required

* Depends on the material deposited and laser parameters

** Estimated based on a weld length of 1m

*** Varies depending on joint and welding configuration

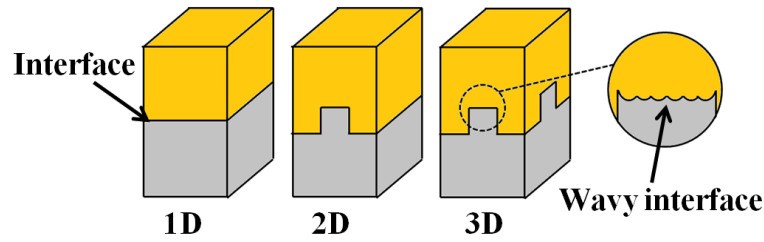


Figure 2.20 Illustration of interfaces with 1D, 2D and 3D material variations

Unlike conventional joining techniques, AM features unique capabilities which make it attractive for MM processing. Firstly, with the appropriate MM dispensing mechanism, the material composition can be varied across the build layers by mixing different powders in various proportions. This allows the user to introduce any arbitrary number of interlayers between the base alloys. This makes it is possible to manipulate the composition, microstructure, and properties across the interface during the build process.

Secondly, by varying the material distribution within and across each build layer, MM interfaces with a complex geometrical design and material variation in 3D can potentially be created (Figure 2.20). This could allow interlocking mechanisms to be incorporated at the MM interface for improved interfacial fracture toughness [155-157]. In comparison, friction welding and explosion welding are restricted to the bonding of near-planar and/or planar surfaces. As a result, the distribution of material can only be varied in one-dimension (1D). Other joining techniques like laser welding, electron beam welding, diffusion bonding, brazing, transient liquid phase bonding, and friction stir welding can process non-planar surfaces featuring material variations in 2D.

Thirdly, the repeated stacking of melt pools within and across the build layers naturally induces microscale waviness (see Figure 2.20). This waviness could potentially increase the resistance to crack propagation and enhance fracture toughness

[155-157]. In contrast, joining processes such as diffusion bonding, brazing, and transient liquid phase bonding produce joints with continuous and planar layers of IMCs which makes crack propagation relatively easy.

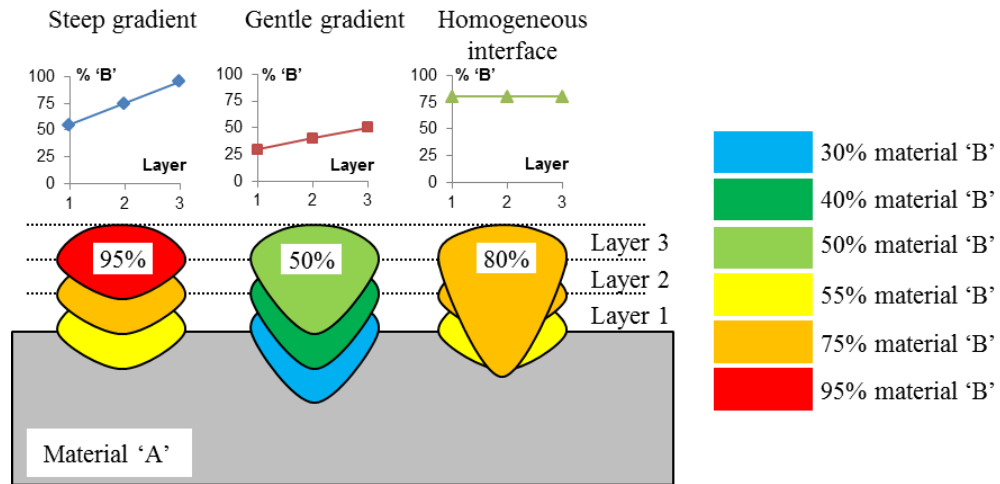


Figure 2.21 Effect of melt pool dimension on composition gradient

Lastly, the layer thickness and penetration depth of the melt pool in AM techniques can be varied to control the interfacial composition gradient (Figure 2.21). Low layer thickness and shallow penetration depth can be used to produce a narrow interface with limited dilution while a large layer thickness and penetration depth can be used to produce a thicker interface with a relatively gradual transition in properties. By dynamically changing the penetration depth at selected layers, it is also possible to homogenize or create an arbitrary functional gradient across the interface (see Figure 2.21). Such control over the interfacial gradient is not available to other joining techniques.

Even though the four unique features discussed above are available to both the DED and SLM processes, each excels in respective areas. DED excels in varying the material across and within each build layer while the SLM process requires an additional MM dispensing mechanism to realise such benefits [1, 4, 142]. However, the better resolution of the SLM process makes it superior in limiting interfacial

dilution. Additionally, the SLM process also features higher cooling rates (10^6 - 10^7 K/s [158]) than DED due to its smaller laser spot diameter (~ 80 - $100\text{ }\mu\text{m}$), lower layer thickness (20 - $100\text{ }\mu\text{m}$), and higher laser scanning velocities (10^2 - 10^3 mm/s). Hence, the microstructure of SLM interfaces is likely to be finer and may contain metastable phase/s which differs from DED interfaces. Furthermore, the SLM process may also produce a unique composite-like interface due to imperfect mixing within the rapidly solidified melt pools [27]. The composite-like interface may contain ductile regions belonging to the base alloy that could potentially act as a ductile reinforcement for the brittle interface. This, however, needs to be verified through further research.

Due to the lack of tensile test data for additively manufactured MM parts, little is known about its capabilities and bond strength. The MM processing potential of PBF techniques such as SLM has been largely overlooked. Nevertheless, AM techniques possess a unique combination of characteristics that could make them competitive for MM processing.

2.13 - Summary

The characteristics of the various joining and AM techniques as well as the microstructural features at the respective Ti/steel interfaces have been reviewed and the key findings are as follows:

- The mechanical properties (toughness, tensile properties, fatigue properties etc.) of the MM interface are affected by the type, quantity, and morphology of its constituent phases. With the use of appropriate interlayer/s, the type and quantity of the interfacial phases can be altered for improved bond properties.
- Explosion welding and friction welding feature extremely low dilution, hence, they can produce Ti/steel joints with high bond strengths. Similar Ti/steel

joints produced through other joining or AM techniques are relatively weak and brittle due to large amounts of Fe-Ti IMCs. Therefore, interlayer/s are typically introduced between the Ti and steel base alloys to minimize the amount of detrimental phases.

- AM techniques such as DED and SLM have the unique capability to manipulate the composition gradient at the MM interface either by introducing different materials at the interface or by controlling the layer thickness and penetration depth of each layer to achieve the desired functional gradient. Complex material variations in 3D can be achieved using AM techniques to either induce interlocking mechanisms at the MM interfaces or to create MM parts with a unique range of functional properties.
- The MM processing capability of PBF techniques such as SLM has been overlooked. The microstructure and fracture characteristics of SLM MM interfaces are not well understood.

In this research, the SLM process is used to build a TiA/CuA/SS MM part out of Ti-6Al-4V, HOVADUR® K220 Cu alloy, and 316L SS.

It is worth noting that SLM of pure Cu is often challenging because of its 1) high reflectivity for fibre laser with a wavelength of 1070 nm and 2) its high thermal conductivity [159, 160]. The former reduces the laser energy absorbed by the Cu powder while the latter leads to rapid conductive heat loss from the melt pool. These effects lead to lack-of-fusion defects within and between build layers. Hence, the density of SLM Cu is often lower than 98 % [161, 162]. These challenges can be overcome either by 1) alloying to reduce the thermal conductivity and reflectivity of Cu or 2) using lasers with a shorter wavelength to increase energy absorption of Cu [159, 163]. In this research, the alloying approach is adopted. This led to the choice of

HOVADUR® K220 Cu-alloy as the interlayer material in this study [164]. Other viable Cu-alloys that had been processed by SLM to densities exceeding 99.5 % include CuCrZr [160, 165], Cu-10Sn [166], and Cu-10Zn [167].

The Cu-alloy interlayer is used to replace the highly deleterious Fe-Ti IMCs in the original Ti/steel interface with the less detrimental Cu-Ti IMCs in the TiA/CuA interface. Although the Ti-Cu IMCs are still detrimental and the SLM of such a brittle interface is expected to be challenging, this challenge will serve as a valuable benchmark to evaluate the MM potential of the SLM process. Moreover, brittle IMCs are commonly formed in most binary metallic combinations. Hence, the investigation of the TiA/CuA interface is believed to be relevant for the SLM of other IMC-forming metallic combinations. In contrast, the CuA/SS interface does not contain any detrimental phases or IMC. Hence, this interface is representative of metallic combinations that are compatible with each other.

The morphology of both MM interfaces will be kept planar to eliminate the interlocking and surface roughness effects so that a fair comparison of bond strength can be made with the planar interfaces obtained through other joining techniques. Furthermore, a planar MM interface can be readily produced using any default SLM machine without incorporating any MM dispensing mechanism. A MM part with a planar interface can be produced by simply printing over a substrate or an existing part of dissimilar composition. Hence, the results presented in this study are also relevant to all default SLM machines.

Chapter 3 - Parameter Development for Multiple-Material Interfaces: Single-Track Studies

This chapter describes the methodology used to devise suitable process parameters for the respective MM interfaces. Building a TiA/CuA/SS MM part with planar interfaces requires five sets of parameters; three for the respective bulk materials and the two for the CuA/SS and TiA/CuA interfaces. Process parameters capable of producing high-density SS, CuA, and TiA parts are available either in the literature [168-172] or known from prior experience on working with the material. However, parameters capable of producing CuA/SS and TiA/CuA interfaces with low porosity is unavailable and need to be developed. The criteria for maximising part density are 1) maintain stable and continuous melt pools across all build layers and 2) ensure sufficient overlap between neighbouring melt pools to minimize trapped porosity and lack of fusion defects. Both criteria rely on the understanding of the melt pool morphology and dimension under different process conditions. To obtain such information, the SLM process was used to deposit singular melt tracks (i.e. single-tracks) of TiA and CuA onto CuA substrates and SS substrates respectively. By varying the process parameters and observing its effects on the single-tracks, parameters capable of producing dense MM interfaces can be devised. In the following section, the experimental setup for the single-track studies will be presented. Next, the dimension and morphology of the single-tracks will be discussed. Finally, a generalized methodology to obtain suitable process parameters for MM interfaces is suggested.

3.1 - Experimental Setup

Single-track of TiA deposited on CuA substrates

The experimental setup used to deposit single-tracks of CuA on SS substrates (CuA-on-SS) and single-tracks of TiA on CuA substrates (TiA-on-CuA) are similar. Hence, only the latter is described in detail below.

- Firstly, multiple CuA substrates with dimensions of 12x12x6 mm (width x length x height) were built on the base plate (Figure 3.1a) using the parameters in Table 3.1. The listed parameters were chosen, based on prior experience, to maximise the TiA and CuA part density.
- Secondly, the printed CuA substrates, along with the attached base plate, were removed from the SLM machine. The top surfaces of the CuA substrates were ground flat and sandblasted to resultant surface roughness, R_a , of $\sim 2 \mu\text{m}$ (Figure 3.1b).
- Thirdly, the substrates were put back into the SLM machine that was cleaned and loaded with TiA powder. Thereafter, 12 mm long TiA-on-CuA single-tracks were deposited on layers 1, 3, 5, 7, 9, 11, 15, 25, and 45 (Figure 3.1c-d) using 4 different sets of parameters as shown in Table 3.1. A bi-directional scanning strategy with a 90° rotation between build layers was used throughout the entire SLM process.
- Lastly, the completed TiA-on-CuA parts were removed from the SLM machine and cut off from the base plate using wire-cut Electric Discharge Machining (EDM). Single-track imaging and measurements were performed using OM and SEM.

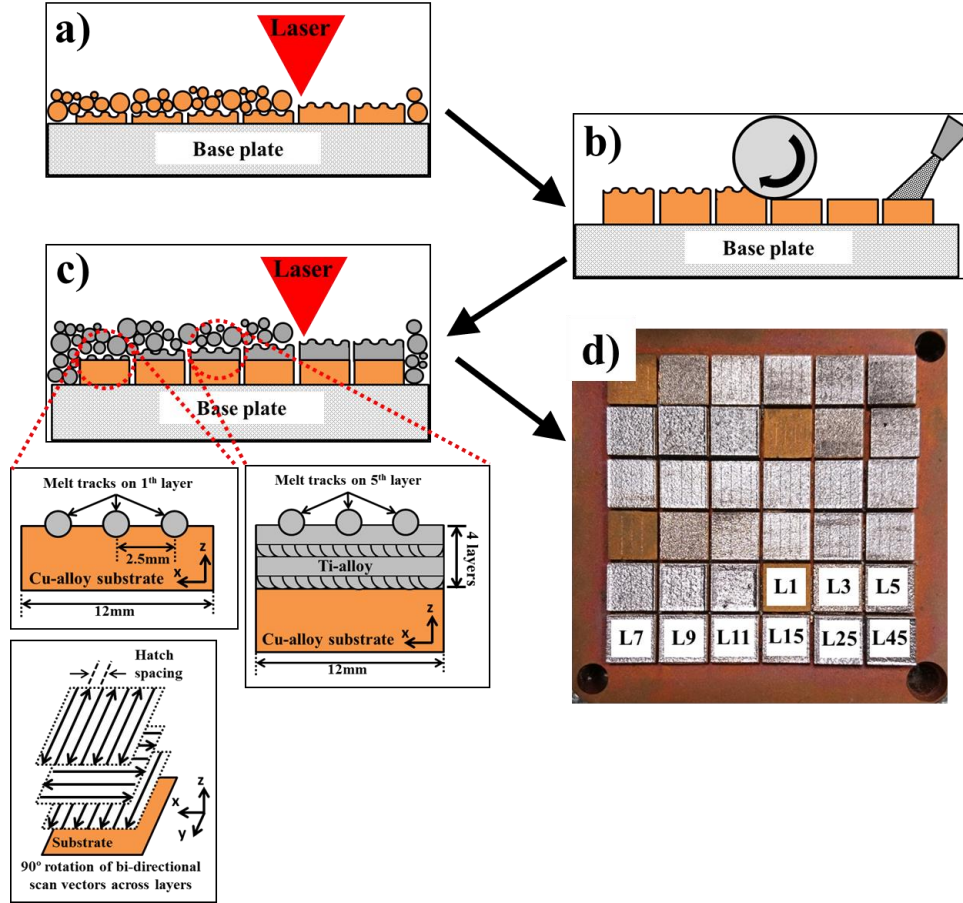


Figure 3.1 Experiment setup of TiA-on-CuA single-tracks. a) Additive manufacturing of CuA substrates on the base plate. b) Grinding and sandblasting of the CuA substrates. c) Deposition of TiA single-tracks on CuA substrates. d) Actual Ti-on-CuA samples

Table 3.1 Process parameters of the TiA-on-CuA single-tracks

Sample	Ti-6Al-4V single tracks	K220 substrate
TC350	Power: 120W	Power: 370W
	Hatch distance: 80 μ m	Hatch distance: 90 μ m
	Steady-state layer thickness: 50 μ m	Layer thickness: 30 μ m
	Initial powder thickness: 50 μ m	Scanning velocity: 400mm/s
	Scanning velocity: 350mm/s	
TC500	Power: 120W	
	Hatch distance: 80 μ m	
	Steady-state layer thickness: 50 μ m	
	Initial powder thickness: 50 μ m	
	Scanning velocity: 500mm/s	
TC650	Power: 120W	
	Hatch distance: 80 μ m	
	Steady-state layer thickness: 50 μ m	
	Initial powder thickness: 50 μ m	
	Scanning velocity: 650mm/s	
TC650-350	Power: 120W	
	Hatch distance: 80 μ m	
	Steady-state layer thickness: 50 μ m	
	Initial powder thickness: 50 μ m	
	Scanning velocity, layer 1-5: 650mm/s	
	Scanning velocity, layer 6-45: 350mm/s	

In the experiments carried out in this thesis, only the laser scanning velocity was varied across the different parameters shown in Table 3.1, Table 3.3, Table 3.4, and Table 4.1. Other parameters such as laser power, hatch spacing, and layer thickness were not varied to keep the sample size of the parametric study manageable. The choice of varying only the scanning speed is, however, not deemed to jeopardize the effectiveness of the parametric study. Part density is often maximized when the appropriate laser energy density input is used during the SLM process [168, 173]. Therefore, the combined effect of laser power, scanning speed, layer thickness, and hatch spacing in the form of laser energy density input (see equation 4 in Section 3.2.1) is more important than the individual parameter that was varied. The laser energy density input can be increased either by increasing the laser power or by decreasing the scanning speed, layer thickness, and hatch spacing. If the hatch spacing and layer thickness are fixed, the laser energy density input simply reduces to a ratio of laser power to scanning speed. Since the laser energy density input can be changed by any of its parameters, only the laser scanning velocity was varied during the parametric development process. Nonetheless, a detailed parametric optimization involving more process parameters could be performed in future investigations.

All parts were produced using the SLM250HL machine from SLM Solutions. The machine is equipped with a 400 W laser that has a measured spot diameter of $\sim 98 \mu\text{m}$. The metal powders used for all the experiments described in this report had diameters in the range of 20-63 μm . All powders were sieved using stainless steel meshes to ensure that the powder diameters were smaller than 63 μm . The TiA, CuA, and SS powders had a spherical morphology (Figure 3.2) and the compositions of its major elements are given in Table 3.2.

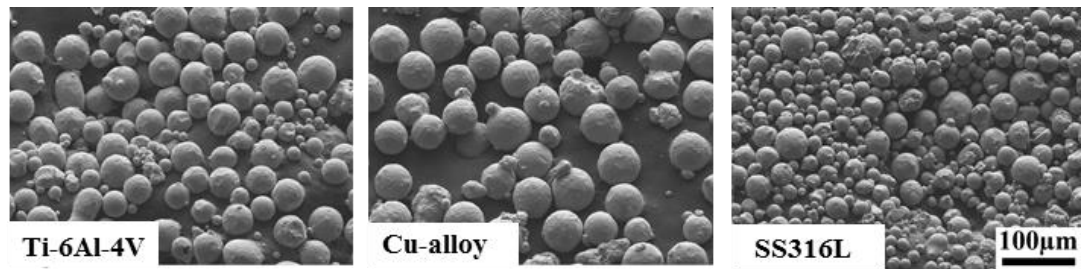


Figure 3.2 Morphology of metal powders

Table 3.2 Composition of metal powders (at.%)

Ti-6Al-4V Grade 23	Ti(86.2)	Al(10.2)	V(3.6)	-	-	-
HOVADUR® K220	Cu(95.3)	Ni(2.6)	Si(1.6)	Cr(0.5)	-	-
SS316L	Fe(65.5)	Cr(18.2)	Ni(11.4)	Mn(2.0)	Si(1.5)	Mo(1.4)

Single-track of CuA deposited on SS substrates

The setup for depositing CuA-on-SS single-tracks follows a similar procedure but uses a different set of materials and process parameters. The parameters used to build the SS substrates as well as to deposit the CuA-on-SS single-tracks are stated in Table 3.3. The single-tracks were deposited on layers 1, 3, 5, 7, 9, 11, 15, 25, and 45 for each set of parameters. A similar bi-directional scanning strategy with a 90° rotation between build layers was used throughout the entire SLM process.

Table 3.3 Process parameters of the CuA-on-SS single-tracks

Sample	K220 single tracks	SS316L substrate
CS400	Power: 370W Hatch distance: 90µm Steady-state layer thickness: 30µm Initial powder thickness: 30µm Scanning velocity: 400mm/s	Power: 380W Hatch distance: 40µm Layer thickness: 50µm Scanning velocity: 1750mm/s
CS530	Power: 370W Hatch distance: 90µm Steady-state layer thickness: 30µm Initial powder thickness: 30µm Scanning velocity: 530mm/s	
CS800	Power: 370W Hatch distance: 90µm Steady-state layer thickness: 30µm Initial powder thickness: 30µm Scanning velocity: 800mm/s	
CS530-400	Power: 370W Hatch distance: 90µm Steady-state layer thickness: 30µm Initial powder thickness: 30µm Scanning velocity, layer 1-11: 530mm/s Scanning velocity, layer 12-45: 400mm/s	

Single-track of TiA deposited on TiA substrates

A control experiment involving the deposition of single-tracks of TiA on compositionally similar TiA substrates (TiA-on-TiA) was also conducted (Figure 3.3a). Results from the control experiment were compared against those of the TiA-on-CuA experiment to investigate the effects of the composition gradient on the morphological and dimensional behaviour of the TiA single-tracks. Parameters used for the control experiment are listed in Table 3.4. The only difference between the TiA-on-TiA and TiA-on-CuA parameters (Table 3.1) is the initial powder thickness of 25 µm used for the control experiment. As discussed in Section 2.10, using a low initial powder thickness creates an increasing layer thickness for the initial 7-9 build layers before reaching steady-state values thereafter. To measure the layer thickness variation across the build layers, raster regions were also deposited along with the single-tracks in layers 1, 3, 5, 7, 9, 11, 15, 25, and 45 (Figure 3.3b-c). As illustrated in Figure 3.3c, the layer thickness was measured by comparing the average height difference between the

raster region and the underlying layer. The surface profile in Figure 3.3c is measured using the VK-X200 3D laser confocal microscope by Keyence. All imaging of the tracks was performed using either OM or SEM.

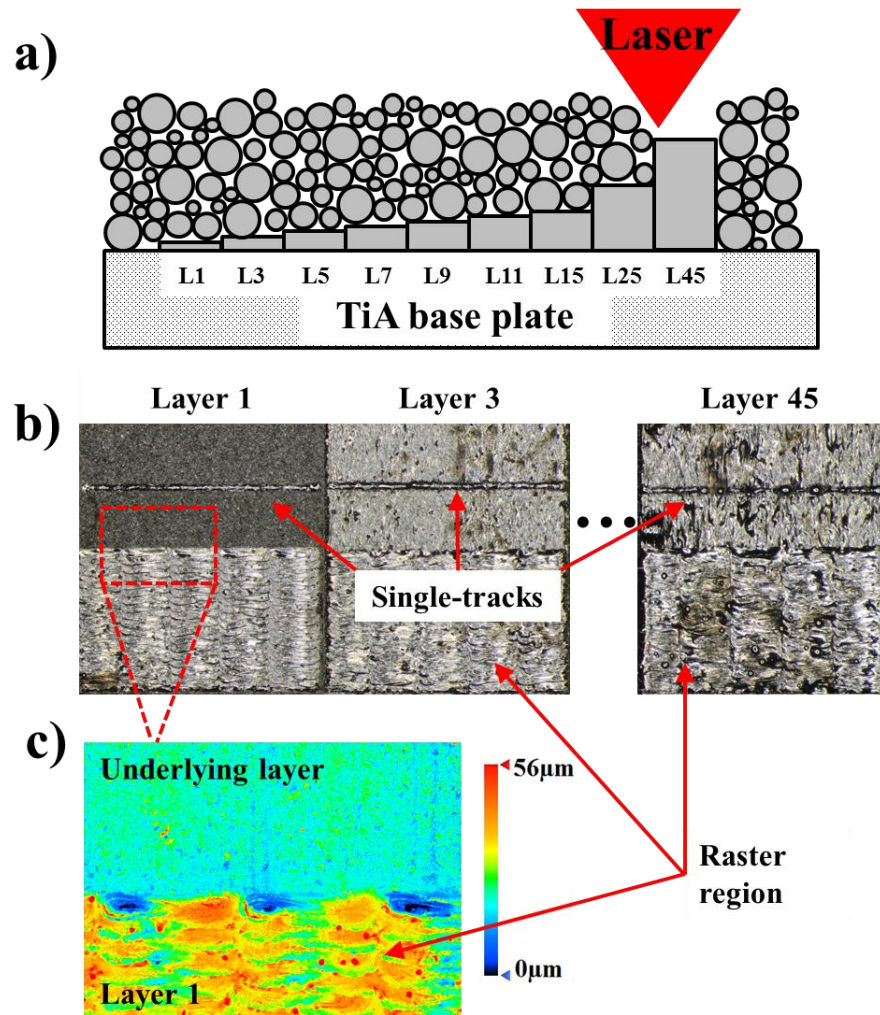


Figure 3.3 a) Experiment setup for TiA-on-TiA single-tracks. b) Appearance of single-tracks and raster regions. c) Surface profile of each build layer

Table 3.4 Process parameters of the TiA-on-TiA single-tracks

Sample	Ti-6Al-4V single tracks
TT350	Power: 120W Hatch distance: 80µm Steady-state layer thickness: 50µm Initial powder thickness: 25µm Scanning velocity: 350mm/s
TT500	Power: 120W Hatch distance: 80µm Steady-state layer thickness: 50µm Initial powder thickness: 25µm Scanning velocity: 500mm/s
TT650	Power: 120W Hatch distance: 80µm Steady-state layer thickness: 50µm Initial powder thickness: 25µm Scanning velocity: 650mm/s

3.2 - Morphology and Dimension of Single-Tracks

3.2.1 – CuA-on-SS Single-Tracks

The morphology of the CuA-on-SS single-tracks deposited using the four sets of parameters on layers 1, 5, and 45 are shown in Figure 3.4. The single-tracks remained continuous and stable within the range of parameters investigated. Track widths were observed to become narrower with higher laser scanning velocity and higher build layer. Figure 3.5 shows the track widths decreased gradually in the initial layers before approaching steady-state values towards the upper layers. Notably, the widths in layer 45 are 65-88 µm narrower than those in layer 1. If unaccounted for, this decrease in track width could result in gaps between adjacent melt pools and increased part porosity. Since the chosen hatch spacing of 90 µm (i.e. the perpendicular distance between adjacent laser scan vectors) is significantly lower than the narrowest track width of 142 µm, the overlap between adjacent tracks was sufficient for all parameters.

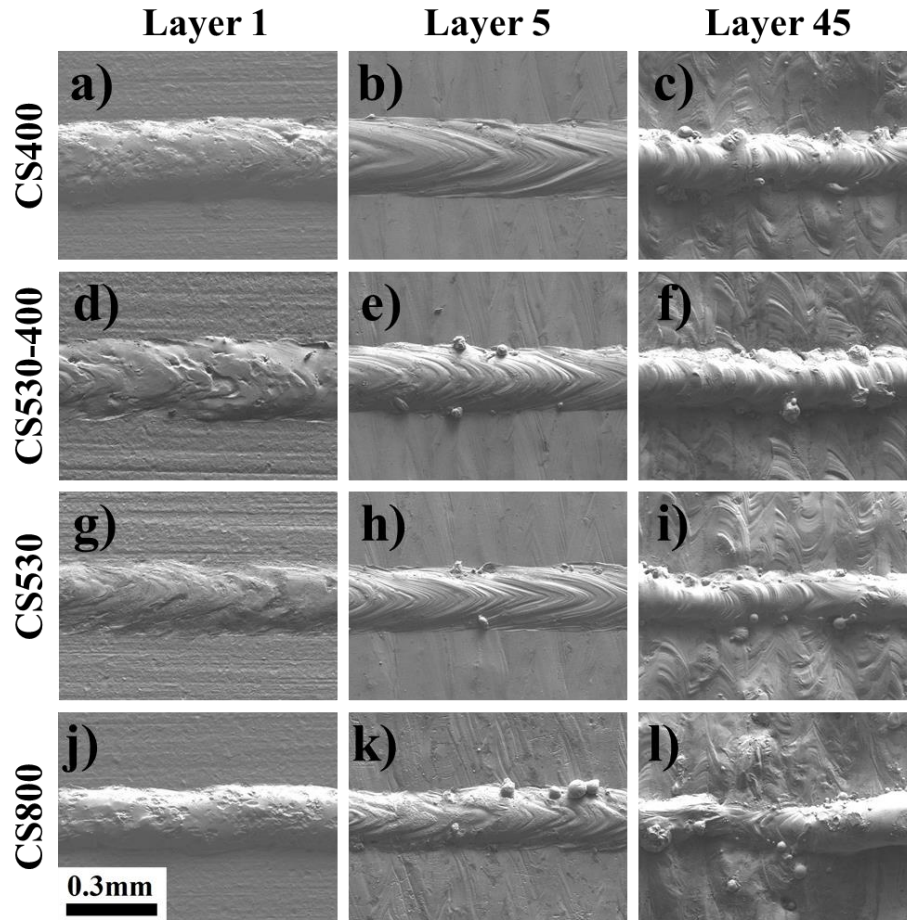


Figure 3.4 Top-view of the CuA-on-SS single-tracks deposited on the different build layers

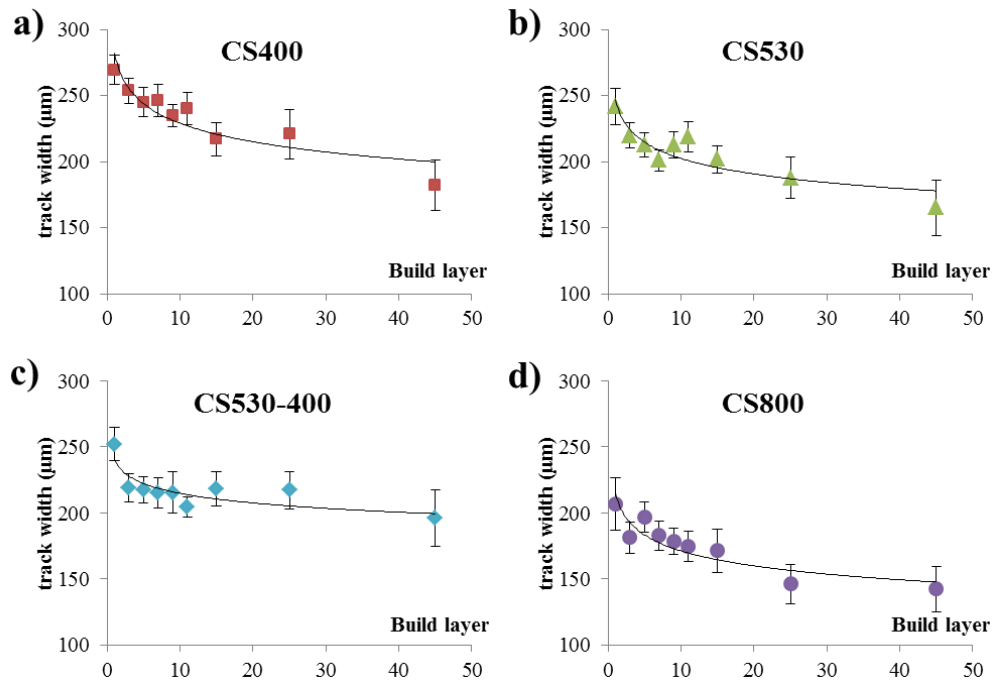


Figure 3.5 Widths of the CuA-on-SS single-tracks across the build layers for the (a) CS400 (b) CS530 (c) CS530-400 (d) CS800 parameters

A switch in the laser parameter during the build process caused the track widths to change dynamically across the build layers. This was demonstrated through the CS530-400 parameter, which featured a change in the scanning velocity from 530 mm/s in layer 11 to 400 mm/s in layer 12 (see Table 3.3). Due to the switch in laser scanning velocity, the widths of the CS530-400 single tracks before layer 12 resembled those of the CS530 parameter while the widths after layer 12 resembled those of the CS400 parameter.

The reason for the decrease in track widths with build layer is due to the presence of a composition gradient. This composition gradient changes the thermo-physical property across the CuA/SS interface. Since CuA and SS have different thermal conductivity, heat capacity, and absorptivity for fibre laser [174], the parameters that are optimized to process CuA and SS are different. The laser energy density input needed to melt bulk SS is often between 70 - 110 J/mm³ [168-170], which is significantly lower than the energy input of ~170 J/mm³ that was used in this study to process the bulk CuA. The laser energy density input, E , is defined as follows:

$$E = P/(V.H.t_m) \quad (4)$$

where P is the laser power, V is the laser scanning velocity, H is the hatch distance, and t_m is the layer thickness. When the first layer of CuA powder was deposited over the SS substrate and melted with a high laser energy input, the melt pools were relatively large due to the melting of large amounts of SS in the underlying substrate. With the repeated addition of CuA layers, the SS content in the underlying layer was gradually replaced by CuA which has a higher laser energy input requirement. Since the laser parameters were kept constant across the build layers, the increased CuA content in the underlying layer led to a corresponding decrease in the track widths.

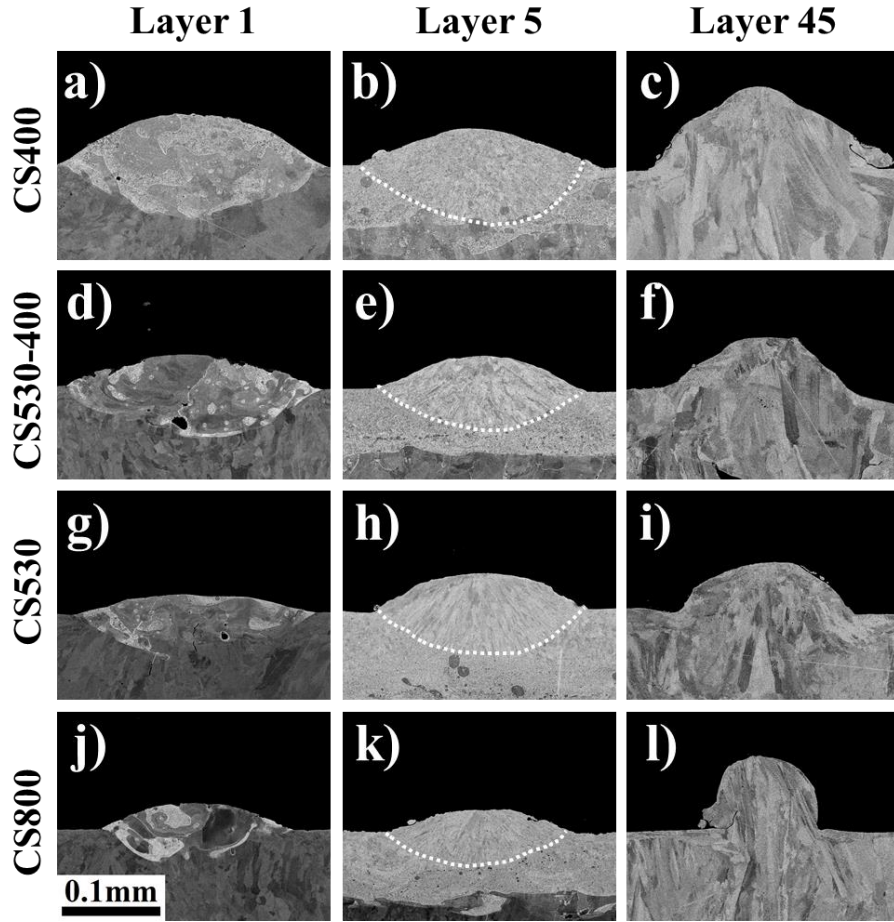


Figure 3.6 Cross-sectional images of the CuA-on-SS single-tracks deposited on the different build layers

Additionally, variations in surface tension, viscosity, and temperature gradient of the melt pools are also expected to accompany the composition variation across the build layers. These factors combine to change the magnitude of the Marangoni flow and, consequently, the shape and dimension of the melt pools [175, 176]. In particular, the gradient of the surface tension to temperature plays a major role in determining the shape and dimensions of the melt pool. Pure metals typically possess a negative surface-tension-to-temperature gradient which induces a radially outward surface flow. Such a flow leads to the formation of a wide melt pool with a shallow penetration depth [176]. In contrast, a positive surface-tension-to-temperature gradient is known to induce a radially inward surface flow which promotes the formation of narrow and deep melt pools. The cross-sectional images of the melt pool in Figure 3.6 have a wide

and shallow shape which indicates that the surface-tension-to-temperature gradient is negative. This is also supported by experimental measurements which indicated that Cu-Fe binary alloys and Cu both have negative surface-tension-to-temperature gradients [175]. In summary, the track width variation is caused by the combined influence from changes in thermal conductivity (SS: 15 W/m/K, CuA: 220 W/m/K), heat capacity (SS: 500 J/kg/K, Cu: 385 J/kg/K), laser absorption characteristics, latent heat of fusion (SS: 270 J/kg/K, Cu: 205 J/kg/K), surface tension (Fe at 1550°C: 1.87 N/m, Cu at 1550°C: ~1.2 N/m [177]), viscosity, and temperature gradient. The assessment of the individual contribution to track width variation is beyond the interest of this parametric optimization.

When the interfacial composition approached 100% CuA, the effect of the composition gradient diminishes and so the track widths begin to level off towards steady-state values. Unsurprisingly, the steady-state track widths increase with the laser energy input and are highest for the CS400 parameter.

3.2.2 – TiA-on-CuA & TiA-on-TiA Single-Tracks

The widths of the TiA-on-CuA and TiA-on-TiA single-tracks are shown in Figure 3.7a-d. In the absence of a composition gradient, the TiA-on-TiA single-tracks retained a consistent width across all build layers. However, when a composition gradient is present, the widths of the TiA-on-CuA single-tracks deviated significantly from those of the control. Specifically, the track widths of the TiA-on-CuA samples were always narrowest in layer 1 and go through a maximum in layer 3-5 before converging towards steady-state values thereafter. The reason for the suppressed track widths in layer 1 is mainly attributed to the presence of the underlying CuA substrate and the difference in the laser energy input requirement of TiA and CuA. Given that CuA has a low absorptivity for fibre laser and the thermal conductivity of CuA and

TiA is ~ 220 W/m/K [178] and 7 W/m/K [68], respectively, a higher laser energy input is needed to process CuA. When the laser beam traverses over the first layer of TiA powder, a part of its energy is dissipated in the CuA substrate. Since the energy required to melt bulk CuA is higher than the energy supplied to process the TiA-on-CuA single-tracks, only a limited amount of CuA is melted. Hence, the TiA-on-CuA track width in layer 1 is the narrowest. After two layers of TiA were fused over the CuA substrate, the composition of the underlying layer shifted towards that of the TiA. Consequently, the laser absorption characteristic of the underlying layer improved, and the conduction heat loss is reduced. As a result, the track width increased. Variations in surface tension (Cu at 1670 °C: ~ 1.2 N/m, Ti at 1670 °C: ~ 1.5 N/m, Ti-20 at.% Cu: ~ 1.4 N/m [179]), viscosity, and the temperature gradient across the build layers also contributed to the change in the magnitude of the Marangoni flow which subsequently affected the melt pool dimensions [179].

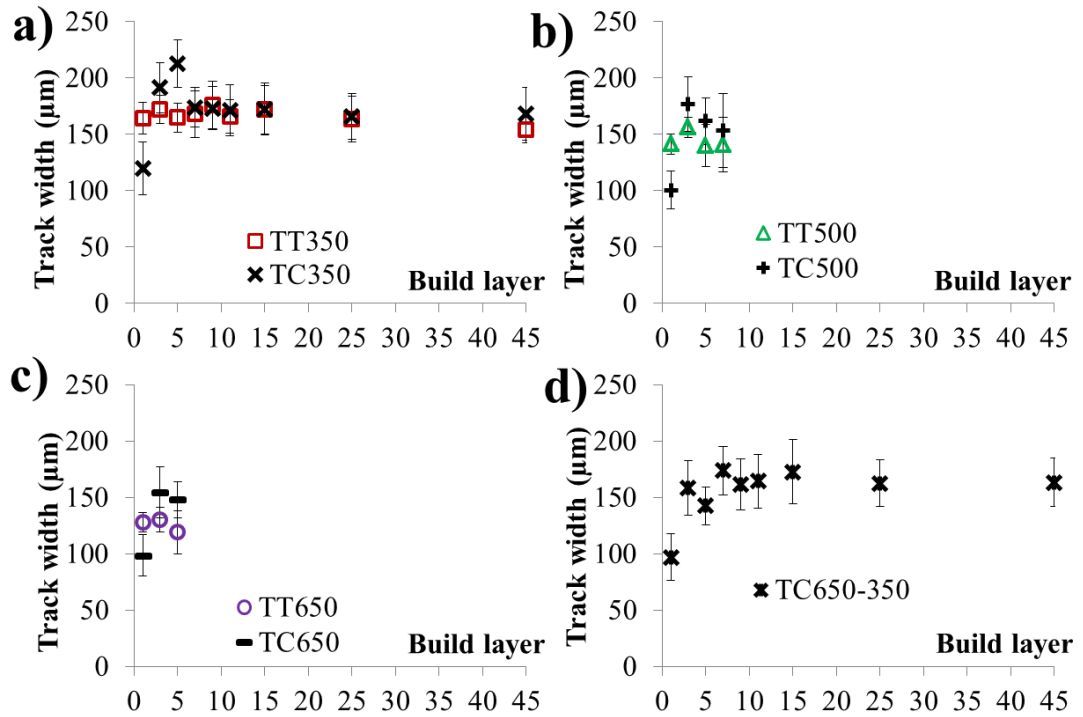


Figure 3.7 Widths of the TiA-on-CuA and TiA-on-TiA single-tracks across the build layers (a) TC350 and TT350 (b) TC500 and TT500 (c) TC650 and TT650 (d) TC650-350

The intermixing of Cu and Ti atoms also led to the formation of Ti-Cu IMCs which has a negative heat of formation [180]. This exothermic reaction process supplies additional heat to cause the melt pool to swell, increasing the track widths. The XRD pattern obtained from the interface of the TC350 sample (Figure 3.8) indicates the presence of Ti_2Cu , α' -Ti and β -Ti phases. The presence of β -Ti is due to the β -stabilizing effect of Cu while the α' -Ti peaks originate from the TiA regions that were diluted with an insufficient amount of β -stabilizing Cu content. A detailed microstructural characterisation of the interface is discussed in Section 4.2 and 4.3.

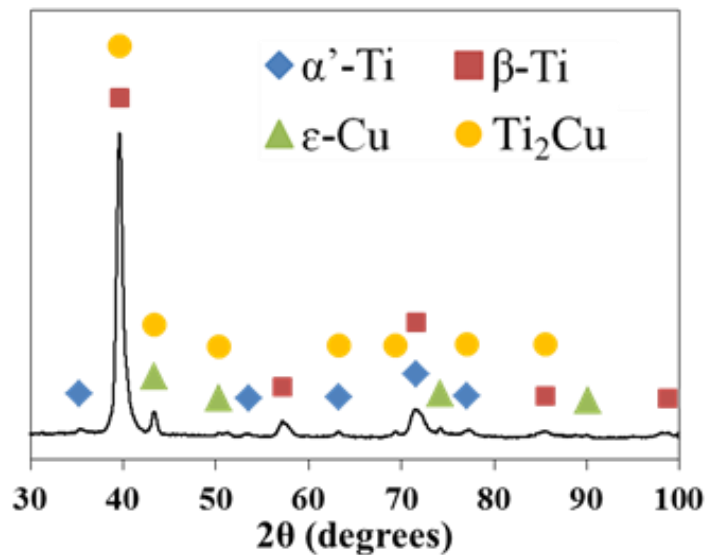


Figure 3.8 XRD pattern of the TiA/CuA interface processed by TC350 parameter

Due to the onset of melt pool “balling”, width measurements are not available beyond layer 7 for the TC500 samples (Figure 3.9f and Figure 3.10f) and layer 5 for the TC650 samples (Figure 3.9i and Figure 3.10i). As seen from the top-view images of the single-tracks, the balling instabilities occurred on similar layers for both the TiA-on-TiA (Figure 3.11f & i) and the TiA-on-CuA melt pools (Figure 3.9f & i). This indicates that the composition gradient is irrelevant to the onset of such instabilities. In this case, the melt pool instability is likely caused by the variation in layer thickness across the initial build layers. Figure 3.12 shows that the average layer thickness of the

TiA-on-TiA samples changed from 12 μm in layer 1 to 42 μm in layer 5 and stabilizes at $\sim 50 \mu\text{m}$ from layer 7 onwards. The reason behind the observed increase in layer thickness is due to the difference between the initial and steady-state powder thickness (see Section 2.10 for explanation).

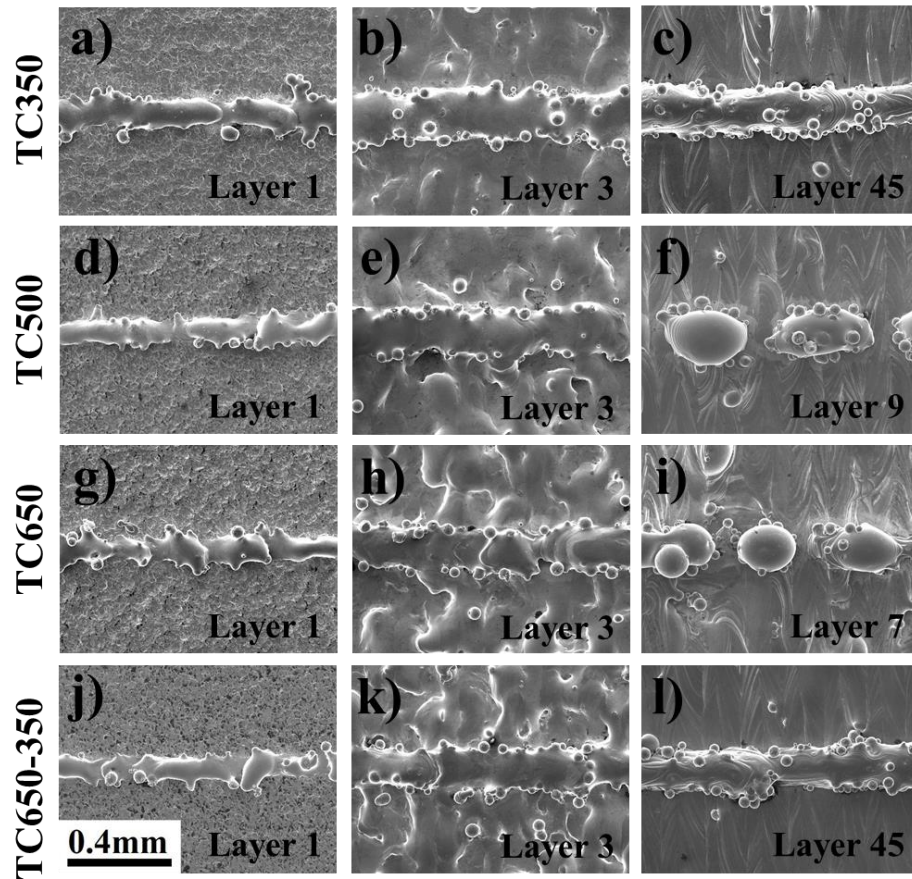


Figure 3.9 Top-view of the TiA-on-CuA single-tracks deposited on the different build layers

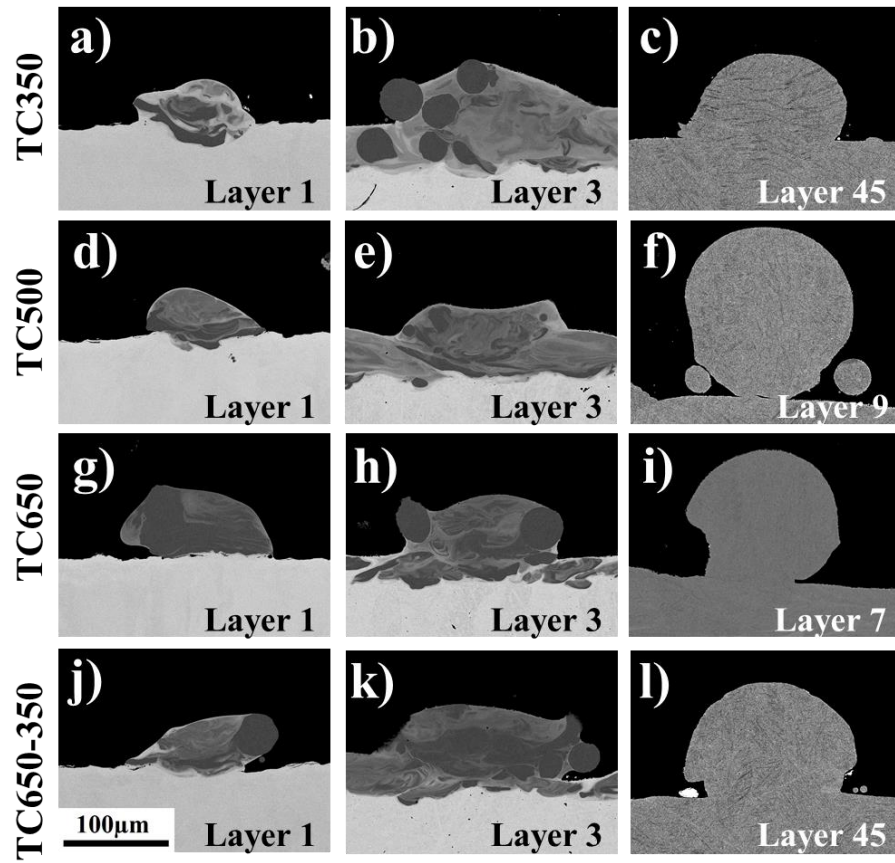


Figure 3.10 Cross-sectional images of the TiA-on-CuA single-tracks deposited on the different build layers

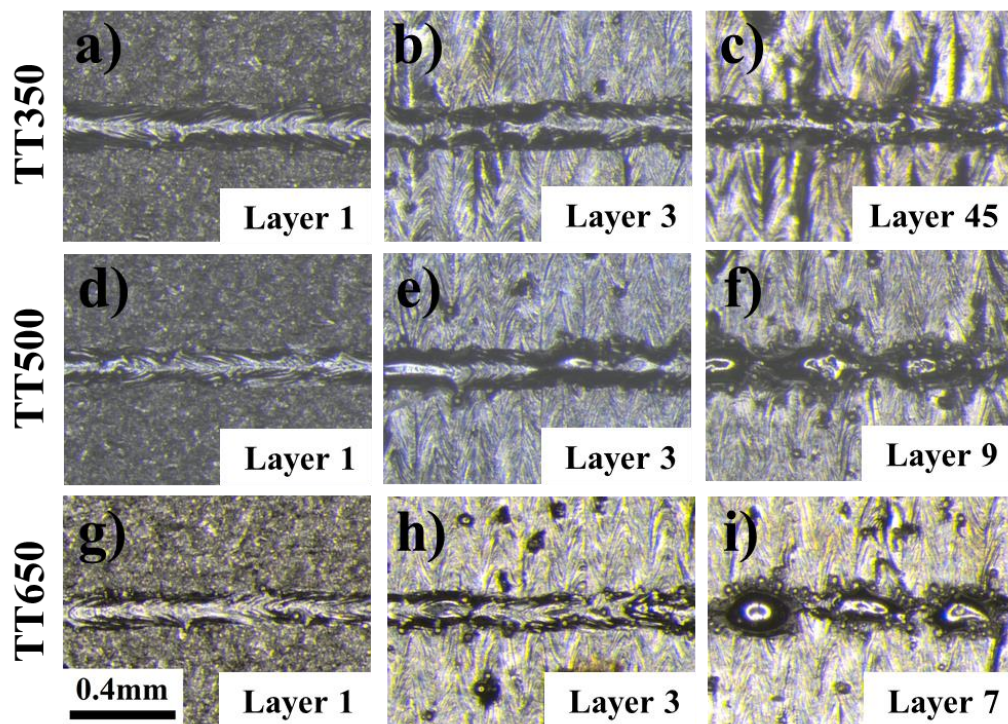


Figure 3.11 Top-view of the TiA-on-TiA single-tracks deposited on the different build layers

Since the laser parameter is fixed across the build layers, an increase in layer thickness necessarily decreases the melt pool penetration into the underlying substrate. Consequently, the contact area between the melt pool and the underlying substrate reduces with increased layer thickness. Once the contact area is reduced beyond the critical limit, melt pool instabilities such as ‘balling’ occur [181]. Considering that the instabilities occurred in layer 7 and 9 for the TT650 and TT500 parameters respectively, the maximum permissible layer thickness for maintaining stable TiA-on-TiA melt pools is estimated to be in the range of 42-50 μm for the TT650 and TT500 parameters. In contrast, the maximum permissible layer thickness of the TT350 parameter is well beyond 50 μm since its melt pools remain stable under a layer thickness of 52 ± 20 μm . Unsurprisingly, the TT350 melt pools have enhanced stability over the TT500 and TT650 melt pools because of its higher energy input which leads to higher penetration depth and larger contact area with the underlying substrate.

The surface roughness (P_q) associated with each build layer is reflected as the error bars in Figure 3.12. P_q is found to have an average value of 10 μm on layer 1 and stabilizes at ~ 20 μm from layer 11 onwards. Interestingly, the increase in layer thickness and surface roughness did not have a significant effect on the widths of the TiA-on-TiA single-tracks (compare Figure 3.7 & Figure 3.12).

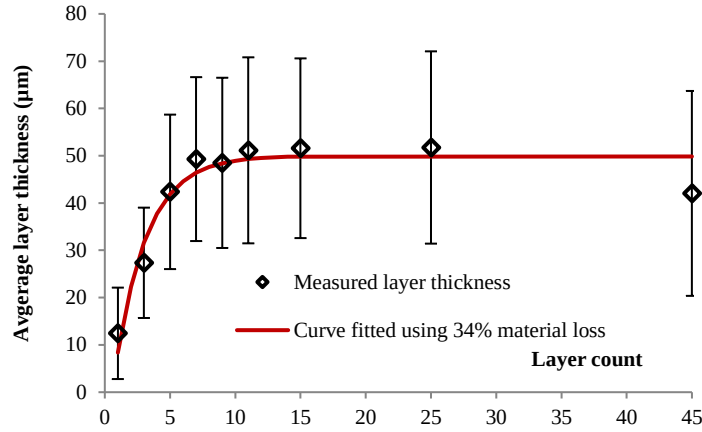


Figure 3.12 Layer thickness variation across the build layers of the TiA-on-TiA single-tracks

The layer thickness variation in Figure 3.12 can be captured using equations (1) & (2) by using the material loss coefficient (l) as a fitting parameter and taking the initial powder thickness (t_{p1}) and powder packing density (p) to be $\sim 25 \mu\text{m}$ and $50.5 \pm 0.5 \%$, respectively. By the least-squares analysis, the best fit is obtained when l is set to 0.34, resulting in the solid line as shown in Figure 3.12. This implies that the net material loss, caused by particle spattering [148, 151, 182], is $\sim 34 \%$ during the SLM process. The consolidation ratio, also known as the ratio between the layer thickness to powder thickness, is calculated using equation (3) and is found to be 0.33. This is comparable to the value of 0.3 reported by Bidare et al. [147]. Based on the consolidation ratio and a layer thickness of $50 \mu\text{m}$, the steady-state powder thickness is estimated to be $150 \mu\text{m}$, which is three times the layer thickness. Hence, if one wishes to maintain a consistent layer thickness of $50 \mu\text{m}$ from the first layer to the last, the initial powder thickness should be set to $150 \mu\text{m}$. However, using such a large layer thickness during the deposition of the first TiA layer would require a corresponding increase in the melt pool penetration depth for stability considerations. A higher penetration into the underlying CuA substrate would, however, lead to an increase in dilution and greater amounts of Ti-Cu IMCs.

3.3 - Stability of the TiA-on-CuA Melt Pools

To maintain a stable melt pool while minimizing dilution, the stability criteria will have to be considered. According to Yadroitsev et al. the critical contact angle, ϕ_c , that is needed to ensure marginal stability of a liquid segmental cylinder under axial harmonic disturbance to its radius can be implicitly defined as [181]:

$$\frac{\pi D}{\ell} = \sqrt{2} \sqrt{\frac{\phi_c(1+\cos 2\phi_c) - \sin 2\phi_c}{2\phi_c(2+\cos 2\phi_c) - 3\sin 2\phi_c}} \quad \text{for} \quad \frac{\pi}{2} < \phi_c \leq \pi \quad (5)$$

Where D is the diameter of the segmental cylinder, ℓ is the wavelength of the axial harmonic disturbance, which can be taken to be the length of the melt pool, and ϕ_c is the critical contact angle needed to maintain marginal melt pool stability as depicted in Figure 3.13. Equation (5) is derived based on the following assumptions: 1) the melt pool can be modelled as a liquid segmented cylinder with an exposed surface above the substrate (Figure 3.13), 2) the liquid segmented cylinder is stable against axial harmonic disturbance to its radius if the disturbance increases its exposed surface area, 3) the liquid is non-viscous, and 4) the contact area of the segmented cylinder with the substrate is unaffected by small disturbances.

The stability of the melt pool is ensured by keeping the contact angle below the critical value of ϕ_c , i.e. maintain a minimum contact area between the segmented cylinder and the substrate. By geometrical considerations ϕ_c is related to the critical penetration depth through the following relationship:

$$\phi_c = \frac{\pi}{2} + \sin^{-1}\left(\frac{h-p_c}{h+p_c}\right) \quad (6)$$

where p_c is the critical penetration depth that is minimally needed to maintain marginal melt pool stability and h is the bead height (see Figure 3.13). Based on

equations (5) & (6), two approaches can be used to lower the critical penetration depth for enhanced melt pool stability. The first is to reduce the melt pool aspect ratio D/ℓ in equation (5) so that the critical contact angle is increased (i.e. the critical penetration depth is decreased). In this experimental study, the simplistic way of reducing the penetration depth by increasing the laser scanning velocity is probably inept as doing so produces a slender melt pool with a higher aspect ratio [183]. Since the length of the melt pool (ℓ) is difficult to measure experimentally, numerical simulations or mathematical modelling [158, 184] will be needed to optimize the aspect ratio. The second approach to lower the critical penetration depth (p_c) is to simply lower the layer thickness such that the bead height (h) is correspondingly reduced. According to equation (6), lower h results in lower p_c for any given value of ϕ_c .

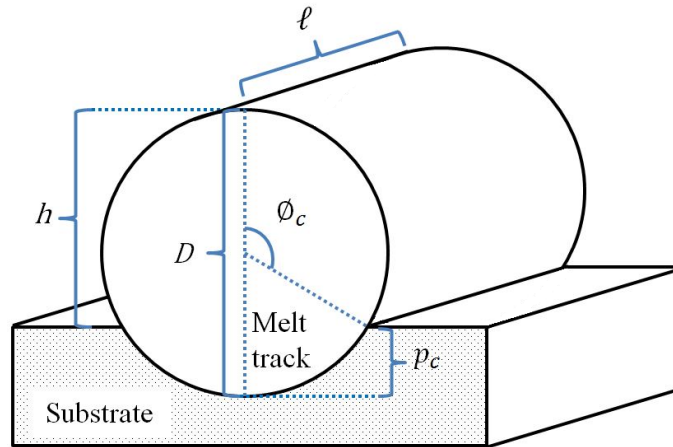


Figure 3.13 Illustration of the liquid segmental cylinder

In the TiA-on-CuA experiment, the initial layer thickness is reduced to a third of its steady-state value. Hence, the critical penetration depth in the first build layer is expected to be much lower compared to those in the subsequent layers. This allows the single-tracks to remain stable and continuous while the penetration depth into the underlying CuA is reduced to minimize dilution between. The cross-sectional images of the TiA-on-CuA single-tracks (Figure 3.10) show that the penetration depth in layer

1 is only a small fraction of the bead height. Measurements indicate the penetration depth of the TiA-on-CuA single-tracks in layer 1 is $10 \pm 4 \mu\text{m}$ and $18 \pm 4 \mu\text{m}$ for the TC650 and TC350 samples, respectively (Figure 3.14).

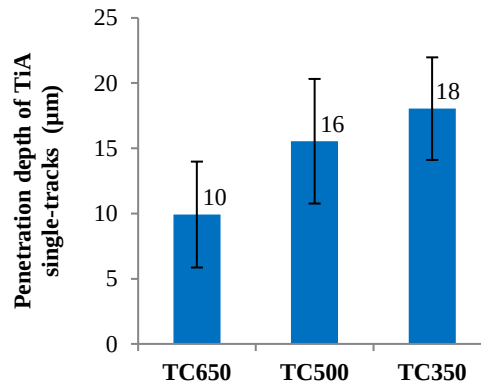


Figure 3.14 Penetration depth of TiA-on-CuA single-tracks on the first TiA build layer

After several layers of TiA have been fused onto the CuA substrate, the melt pools may no longer penetrate the underlying CuA substrate to further dilute the TiA/CuA interface with more Cu content. Hence, it is no longer necessary to limit the layer thickness and penetration depth. Instead, the layer thickness is increased in favour of higher productivity. Since the TC650 parameter is only capable of sustaining a stable melt pool up to layer 5 where the layer thickness is $\sim 42 \mu\text{m}$, a switch to TC350 from layer 6 onwards (i.e. TC650-350) is necessary to maintain melt pool stability. As shown in Figure 3.9, the TC650-350 parameter can indeed maintain continuous melt pools across all build layers while minimizing dilution in layer 1. This change in the laser parameter leads to a corresponding change in track width. Figure 3.7 shows that the widths of the TC650-350 single-tracks from layer 1 to 5 resemble those processed using the TC650 parameter while the widths from layer 7 resemble those of the TC350 parameter. Except for the layer 1, the track widths associated with the TC650-350 parameter remains at a consistent value of $\sim 163 \mu\text{m}$ across the build layers.

3.4 - Generalized Methodology for Parametric Optimization

In this TiA-on-CuA study, only the laser scanning velocity has been varied across the samples while other parameters such as laser power, initial powder thickness, layer thickness, and hatch spacing were kept constant. The laser power versus scanning velocity diagrams for various SLM materials indicate that the processing window for each material is associated with a suitable ratio of laser power to scanning velocity (P/V) [185-187]. In general, excessive P/V can lead to distorted melt tracks [181] and keyholes which contain a greater amount of trapped porosity [188]. On the other hand, insufficient P/V can lead to balling and lack-of-fusion defects. Given a fixed laser power, a suitable P/V can be obtained by varying the laser scanning velocity until stable and continuous melt tracks are obtained, as is the case in this work.

Regardless of the parameter being varied, the behaviour of the track width and the approach to selecting optimal laser parameters for MM interfaces are expected to remain similar. The track width versus build layer plot is expected to have a general appearance as illustrated in Figure 3.15a.

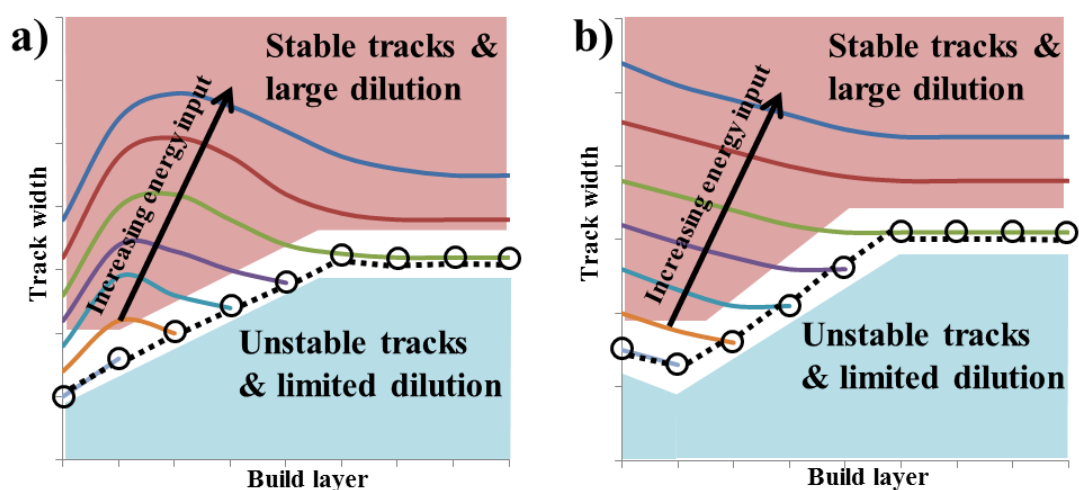


Figure 3.15 Generalized behaviour of track width across the build layers for (a) TiA-on-CuA single-tracks (b) CuA-on-SS single-tracks

Each curve in Figure 3.15a corresponds to a unique set of process parameters. Increasing the laser energy input causes the curves to be displaced upwards. The upper region of Figure 3.15a corresponds to parameters that produce stable melt pools across all build layers but suffers from large dilution at the MM interface. On the other hand, the lower region in Figure 3.15a corresponds to the parameters which produce a MM interface with limited dilution but can only sustain a stable melt pool up to a certain build layer. The approach to select optimal parameters across all build layers is to keep the combination of laser energy density and build layer just above the unstable region as depicted by the dashed curve in Figure 3.15a. This way the penetration depth in the initial build layers is minimized while the stability of the melt pools is marginally maintained by gradually increasing the laser energy input across the build layers. The dashed curve in Figure 3.15a can also be used to predict the variation in the track width across the build layers. To maintain a consistent amount of overlap between adjacent melt tracks, the hatch spacing can either be set to a fraction of the varying track widths or set to a value that is lower than the minimum width. For simplicity, a constant hatch spacing of 80 μm is adopted in the TC650-350 parameter. This hatch spacing is deemed to be appropriate as it is lower than the minimum track width of 97 μm in layer 1.

Depending on the material combination, the track width versus build layer plot may have a different curvature. For instance, if a wider range of laser scanning velocity has been investigated for the CuA-on-SS experiment, the track widths would be expected to behave according to the illustration in Figure 3.15b. Even though the track width variation is different compared to the TiA-on-CuA samples, the selection of appropriate laser parameters for minimal dilution and marginal melt pool stability remains similar and is denoted by the dash cure in Figure 3.15b. Minimizing dilution

for the CuA-on-SS single-tracks is, however, not a critical consideration as IMCs are absent in the Cu-Fe system. In this case, maintaining melt pool stability will be the sole priority.

The methodology described here offers a fast and simple way to optimize the process parameters on every build layer across the MM interface. The only parameters which are not determined in this method are the initial and steady-state powder thicknesses. The powder thickness in layer 1 should, ideally, be as low as possible to limit dilution and enhance melt pool stability. However, the powder thickness needs to be larger than the minimum powder size to ensure a uniform spread of powder. The diameter of the powder particles used in these experiments lies in the range of 20-63 μm . Hence, the ~ 50 μm initial powder thickness used in the TiA-on-CuA experiments is deemed to be suitable. On the other hand, the ~ 25 μm powder thickness used for the TiA-on-TiA control samples may have been too low considering the low yield of small-sized powder particles. The selection of the steady-state layer thickness, which is synonymous with the platform displacement after each layer, is mainly determined by the build rate and part resolution requirements. If a high build rate is desired and part resolution is not a major concern, a larger layer thickness of 50 - 100 μm may be adopted.

3.5 - Summary

Through a systematic study of the single-track morphology across the build layers, feasible process parameters have been obtained for the SLM of the TiA/CuA and CuA/SS interfaces. The key findings are as follows:

- The widths of the CuA-on-SS tracks decrease gradually towards steady-state values with increased build layers. Track width reduction of up to 48% is

attributed to the change in thermophysical properties such as surface tension, viscosity, thermal conductivity, heat capacity etc. across the composition gradient. Balling and melt pool discontinuity are not observed within the range of process parameter investigated. Due to the absence of detrimental reaction products in the Cu-Fe binary system, dilution control at the CuA/SS interface is not a critical consideration. Therefore, the CS530-400 parameter was selected for its stable melt pools and consistent track width.

- The widths of the TiA-on-CuA single-tracks changed from a minimum in layer 1 (100 %) to a maximum in layer 3-5 (~170 %) before stabilizing to steady-state values (~150 %) from layer 7 onwards. The minimum width in layer 1 is caused by limited melting of the underlying CuA substrate. On the other hand, the peaking of track width in layer 3-5 is caused by the exothermic formation of Ti_2Cu IMC as well as changes in surface tension and other thermophysical properties across the composition gradient.
- Minimum dilution and marginal melt pool stability can be simultaneously achieved in layer 1 of the TiA-on-CuA build by adopting a low layer thickness and minimum laser energy input. From layer 2 onwards, the layer thickness can be gradually increased in favour of higher build rates. As the melt pools start to become unstable with increased layer thickness, a dynamic switch to higher laser energy input can be used to increase the penetration depth and improve the stability of the melt pools. The optimal parameter devised to process the TiA/CuA interface is the TC650-350 parameter.

Chapter 4 – Interfacial Microstructure Characterisation

The previous chapter focused on parametric optimization to minimize interfacial dilution while maintaining marginal melt pool stability. In this chapter, the interfacial microstructure of the MM parts produced using the devised parameters is examined in detail using a series of techniques which include SEM, EDX, EBSD, TEM, XRD, and nano-indentation.

4.1 - Experimental Methods

Manufacturing of MM parts

TiA/CuA/SS MM samples (Figure 4.1a) with an overall dimension of 30.5 x 25 x 12 mm (height x length x width) were built using the SLM250HL in sequential steps listed as follows:

- 1) 300 layers (15 mm) of 316L SS were built on a base plate using SLM.
- 2) The completed SS parts along with the base plate were removed from the SLM machine and the top surfaces of the SS parts were ground flat and blasted with SS powders to a roughness (R_a) of $\sim 2 \mu\text{m}$.
- 3) The SS parts were loaded back into the cleaned SLM machine and 30 layers (0.9 mm) of CuA were fused on top of the SS.
- 4) The completed CuA/SS parts were removed from the machine and the CuA material was ground to a thickness of 0.5 mm and blasted with TiA powders to a roughness (R_a) of $\sim 2 \mu\text{m}$.
- 5) The CuA/SS parts were loaded into a cleaned SLM machine and 300 layers (15 mm) of Ti-6Al-4V material were fused on top of the CuA surface.

- 6) The completed TiA/CuA/SS parts were removed from the machine and cut into tensile bars (Figure 4.1a) using wire-cut EDM. These cut-outs were used for microstructural examination.

The top surfaces of the SS and CuA parts were deliberately ground flat and powder blasted in steps 2 and 4 to replicate the conditions of the single-track study from which the process parameters were derived. The TiA/CuA/SS MM parts were processed using the parameters listed in Table 4.1. A 5 mm chessboard scanning strategy, whose scan vectors were rotated by 79° across each layer, was used throughout the build (Figure 4.1b).

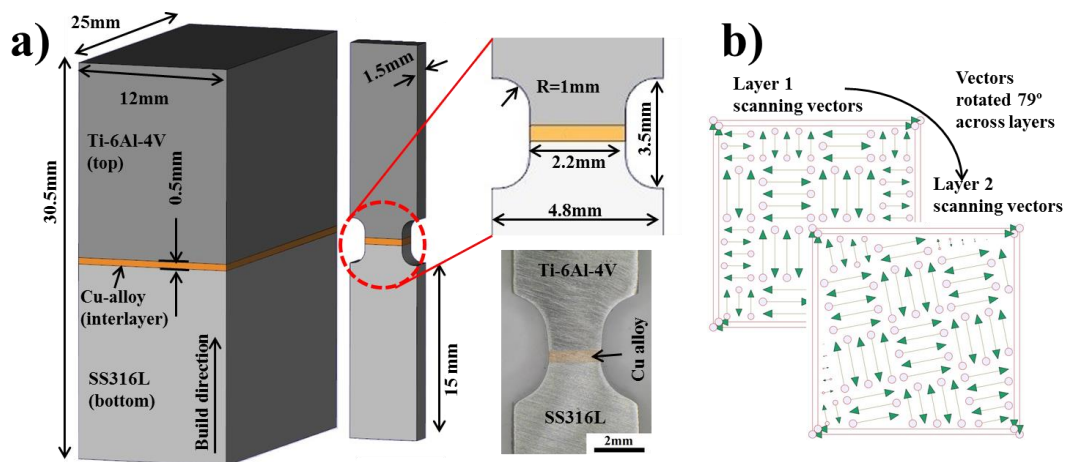


Figure 4.1 (a) Build configuration of MM part and dimensions of the tensile sample. (b) Chessboard scanning strategy used during the SLM process.

Table 4.1 Process parameters used to build the TiA/CuA/SS MM parts.

Sample	Ti-6Al-4V	Cu-alloy	SS316L
V350	Laser power: 120W Hatch distance: 0.08mm Initial powder thickness: 0.05mm Steady-state layer thickness: 0.05mm Scanning velocity, layer 1-5: 350mm/s Scanning velocity, layer 6-300: 350mm/s	Laser power: 370W Hatch distance: 0.09mm Initial powder thickness: 0.03mm Steady-state layer thickness: 0.03mm Scanning velocity, layer 1-11: 530mm/s Scanning velocity, layer 12-30: 400mm/s	Laser power: 380W Hatch distance: 0.04mm Initial powder thickness: 0.05mm Layer thickness: 0.05mm Scanning velocity, layer 1-300: 1750mm/s
V500-350	Laser power: 120W Hatch distance: 0.08mm Initial powder thickness: 0.05mm Steady-state layer thickness: 0.05mm Scanning velocity, layer 1-5: 500mm/s Scanning velocity, layer 6-300: 350mm/s		
V650-350	Laser power: 120W Hatch distance: 0.08mm Initial powder thickness: 0.05mm Steady-state layer thickness: 0.05mm Scanning velocity, layer 1-5: 650mm/s Scanning velocity, layer 6-300: 350mm/s		

Analytical methods

Microstructural characterization of the TiA/CuA and CuA/SS interfaces were performed using SEM on the JEOL 7600F FESEM. Semi-quantitative composition measurements across the TiA/CuA and CuA/SS interfaces were performed by EDX analysis using the X-Max^N spectrometer that is incorporated with the FESEM. Interfacial phase maps and inverse pole figures (IPFs) were obtained through EBSD analysis using the NordlysMax³ EBSD detector which is also attached to the FESEM.

High-resolution imaging, composition measurements and electron diffraction of sub-micron features were carried out using TEM on the JEOL 2010UHR while qualitative composition line scans were carried out on the JEOL 2100F. Samples used for TEM analysis were extracted with a focused ion beam (FIB) using the FEI Nova 200 Nanolab.

XRD analysis was performed using the PANalytical Empyrean X-ray diffractometer using Cu K_α radiation at 40 kV and 40 mA.

Nano hardness measurements at an indentation depth of 0.9 - 1 μm across the MM interfaces were obtained using the Agilent G200 nanoindenter.

4.2 - CuA/SS Interface

4.2.1 - Microstructure

The CuA/SS interface shown in Figure 4.2a was imaged using backscatter electron (BSE) to highlight the variation in the atomic number and grain orientation across the interface. The thickness of the interface is ~284 μm as seen from the composition line plot in Figure 4.2b. Local fluctuations in the composition plot are caused by the presence of micron-sized SS globules (Figure 4.3a, c, d) and elongated SS bands with lengths of ~100 μm (Figure 4.2a). The SS bands were formed by non-homogeneous

mixing within the rapidly solidified melt pools [189, 190] while the SS globules were formed by liquid phase separation due to the miscibility gap in the Cu-Fe system [191, 192]. Liquid phase separation is also commonly observed in other Cu-steel interfaces joined via arc, laser, and electron beam welding processes [189, 190]. The segregation of Cu and Fe atoms can be reduced by alloying to suppress the miscibility gap to lower temperatures [192] or by slow cooling such that the Cu-Fe liquid is not undercooled into the miscibility gap [191]. The composition of the segregated Fe-rich phase (point C1 in Figure 4.4a) and Cu-rich phase (point C2 in Figure 4.4a) are Fe(59.0)-Cu(9.2)-Cr(16.2)-Ni(10.5)-Si(3.4)-Mo(1.5)-Mn(0.2) and Fe(10.1)-Cu(82.0)-Cr(2.6)-Ni(3.9)-Si(0.8)-Mn(0.6), respectively.

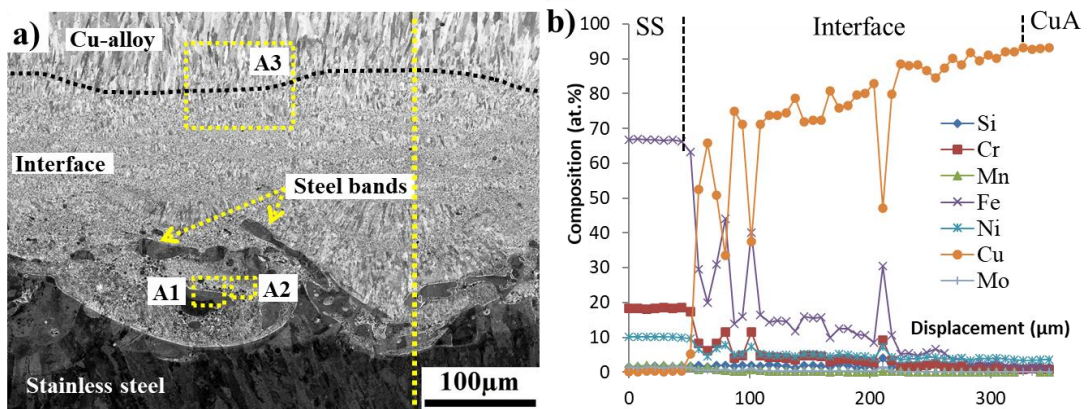


Figure 4.2 CuA/SS interface (a) BSE image (b) EDS composition plot across the interface

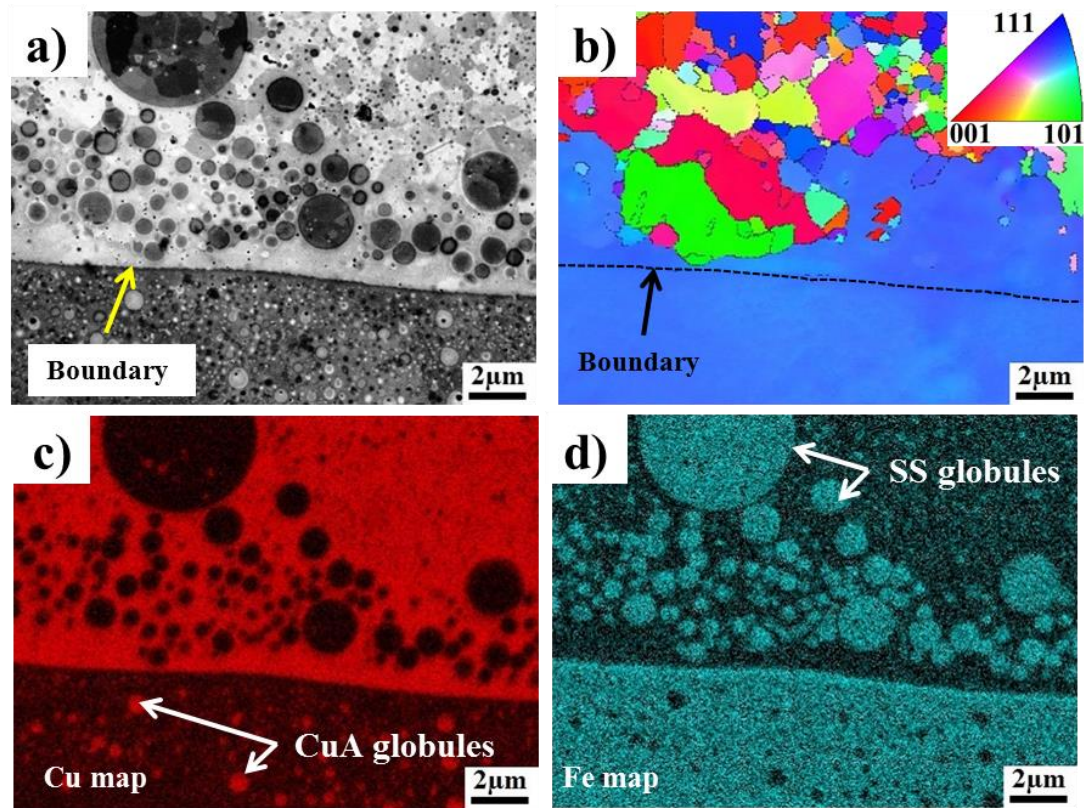


Figure 4.3 Magnified views of region A1 in Figure 4.0a (a) BSE image (b) IPF (c) Cu-K α map (d) Fe-K α map

The magnified view of region A1 in Figure 4.2 is shown in Figure 4.3. The elemental maps (Figure 4.3a, c & d) show that SS globules of 0.1-5.5 μm diameter exist within the Cu-rich matrix. In contrast, the CuA globules that exist within the SS bands are typically sub-micron in size. A comparison between the BSE image (Figure 4.3a) and the IPF (Figure 4.3b) shows that the Cu-rich and Fe-rich phases can share a common crystallographic orientation across the composition boundary that is denoted by a dashed line in the lower half of Figure 4.3b. This indicates that epitaxial growth occurred during solidification. Given that SS has a higher melting point ($\sim 1400^\circ\text{C}$) than CuA ($\sim 1080^\circ\text{C}$), the SS bands and SS globules necessarily solidify first as the liquid mixture begins to cool. Once the temperature is sufficiently low, the surrounding CuA matrix begins to solidify in the presence of the solid SS phases. As the Cu-rich ($\epsilon\text{-Cu}$) and Fe-rich phases ($\gamma\text{-Fe}$) both have an f.c.c crystal structure with a lattice constant of 0.360-0.361 nm, the lattice mismatch is minimal. Hence, the CuA

tends to grow epitaxially from the existing solid SS particles. As a result, the grain boundaries and composition boundaries do not coincide in Figure 4.3a & b, and the spherical appearance of the SS and CuA globules cannot be observed in the IPF (Figure 4.3b).

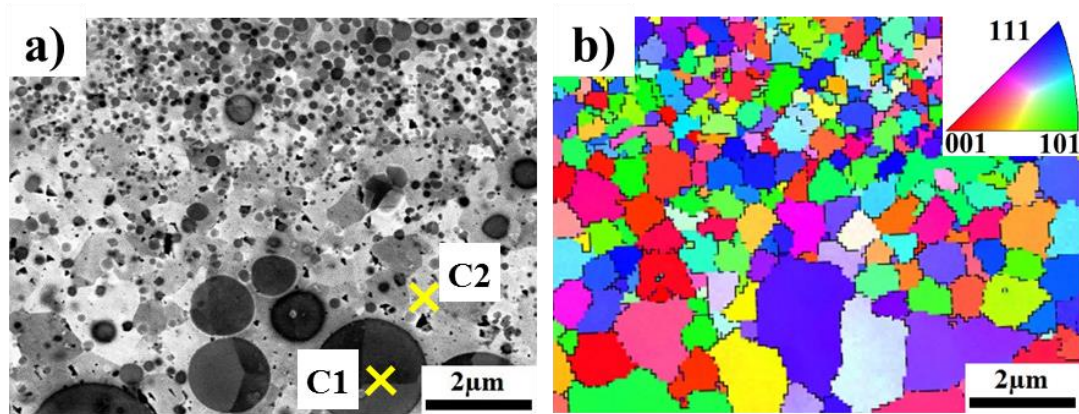


Figure 4.4 Magnified view of region A2 in Figure 4.0a (a) BSE image (b) IPF

Since the SS globules act as a low energy nucleation site for the molten CuA, locations with a high density of finely dispersed SS globules should, therefore, feature smaller grain sizes. A comparison between the BSE image (Figure 4.4a) and the IPF (Figure 4.4b) shows that a high density of small SS globules results in sub-micron grain sizes (upper half of Figure 4.4a-b). In contrast, the large SS globules in the lower half of Figure 4.4a-b led to micron-sized grains. Although SS globules can be used to refine the CuA grains, the reverse is not possible because SS solidifies before CuA. Therefore, grain refinement was not observed in the γ -Fe grain located in the lower half of Figure 4.3a-b despite the presence of sub-micron CuA globules.

The SS globules also promote heterogeneous nucleation of ϵ -Cu grains ahead of the solidification front [193]. Hence, the grains in regions A1, A2 and the majority of the CuA/SS interface have an equiaxed morphology. This approach of using a nucleating phase to promote fine equiaxed grains in SLM is conceptually similar to the works of

Martin et al. who demonstrated that the resultant equiaxed microstructure is favourable in suppressing solidification cracking in, otherwise, susceptible materials [194].

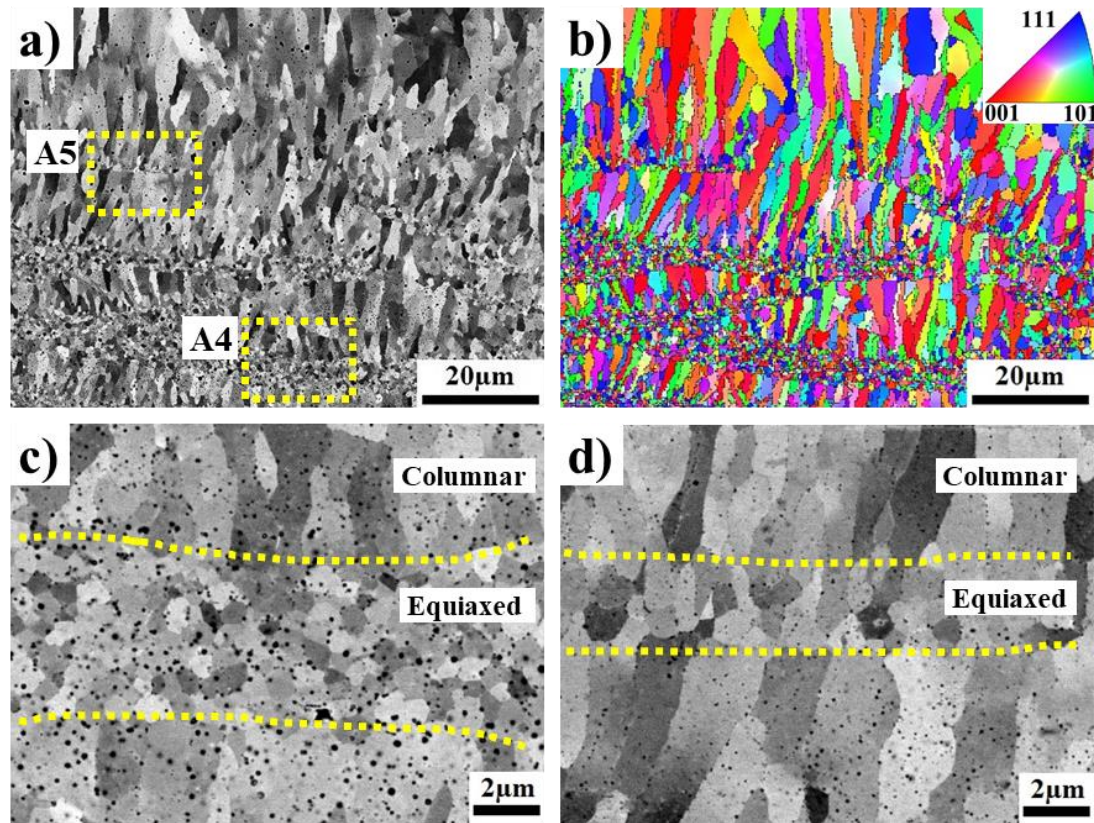


Figure 4.5 (a) BSE image and (b) IPF of region A3 in Figure 4.0a. (c) Region A4 with substantial amount of SS speckles and a $\sim 4 \mu\text{m}$ equiaxed band. (d) Region A5 with minor amount of SS speckles and a $\sim 2 \mu\text{m}$ equiaxed band.

The magnified view of region A3 in Figure 4.2 is shown in Figure 4.5a-b. In this region that is located towards the upper boundary of the CuA/SS interface, alternating layers of equiaxed and columnar grains can be observed. The layers of equiaxed grains repeat in the build direction with a periodicity of 20-30 μm . Hence, each pair of equiaxed and columnar bands correspond to the different build layers that were fused on top of each other with a layer thickness of 30 μm . During the initial stages of melt pool solidification, equiaxed grains formed along the edge of the melt pool due to the presence of a high density of SS nucleants. As the melt pool continues to solidify, the equiaxed grains undergo competitive grain growth to eventually emerge as columnar grains as shown in regions A4 (Figure 4.5c) and A5 (Figure 4.5d). The equiaxed layer

in region A4 is 4-5 μm thick while the one in A5 is only $\sim 2 \mu\text{m}$ thick. This difference in thickness is attributed to the different amount of SS nucleants present in the two locations. As region A4 is located closer to the underlying SS alloy, it contained a greater amount of SS nucleants as shown by the black speckles in Figure 4.5c. Hence, a thicker equiaxed layer formed in region A4. In comparison, the SS nucleants were significantly depleted in region A5 (compare the dark SS speckles in Figure 4.5c & d) so a thinner equiaxed layer is obtained. Beyond the CuA/SS interface, where the SS nucleants were no longer present in any significant amount, solidification occurs in an epitaxial manner. This results in long columnar grains which extend in the vertical build direction, opposite to the general direction of conduction heat loss.

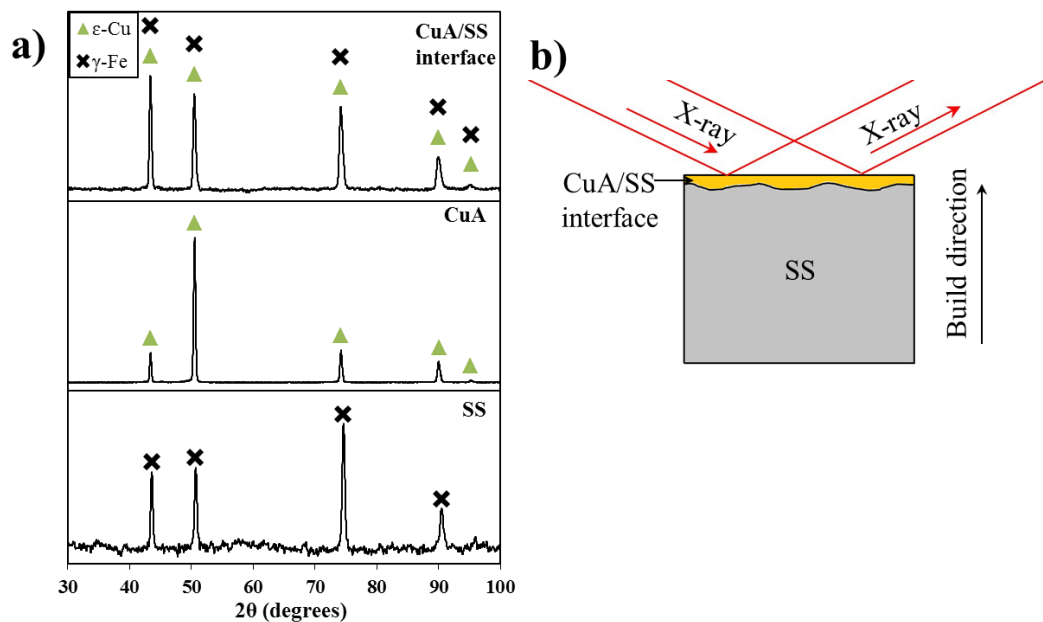


Figure 4.6 (a) XRD pattern of CuA, SS, and CuA/SS interface. (b) Setup of XRD measurement

XRD analysis was performed on the SS, CuA, and the CuA/SS interface to verify its constituent phases. Before performing the XRD analysis, the excess CuA above the interface had to be removed until the CuA/SS interface is exposed. This is done by grinding the top surface of the CuA until a small fraction of the underlying SS becomes visible.

The XRD pattern of the CuA/SS interface (Figure 4.6) only contained γ -Fe and ϵ -Cu peaks, thus, verifying the results of prior EBSD analysis. Due to their similar crystal structures and lattice constants, the γ -Fe and ϵ -Cu peaks overlap strongly and cannot be differentiated. The lattice constants of bulk γ -Fe phase and bulk ϵ -Cu phase are 0.3596 nm and 0.3614 nm respectively.

4.2.2 - Hardness

A total of 79 nano-indentations with an indentation depth of 1 μm were performed on the CuA/SS interface in the manner depicted in Figure 4.7b. To identify the phases associated with each indent, the composition of each indent was also measured using EDX. The variation in hardness with different Fe content is shown in Figure 4.7. Fe content of 0 at.% and 67 at.% corresponds to that of bulk CuA and SS, respectively. The hardness within the CuA/SS interface increases with Fe content and has intermediate values that lie between that of bulk CuA (2.3 ± 0.1 GPa) and SS (3.9 ± 0.3 GPa). Indentations made on regions with 0-25 at.% Fe survey a microstructure that comprises of SS globules in a CuA matrix (e.g. see the upper half of Figure 4.3). On the other hand, indents on regions with 40-67 at.% Fe survey a microstructure that contains CuA globules in a SS matrix (e.g. see the lower half of Figure 4.3). Due to the higher SS content, indents made on regions with 40-67 at.% Fe register higher hardnesses compared to those made on regions with 0-25 at.% Fe. Indents with an average Fe content of 25-40 at.% were not available because such a composition range is not present within the immiscible CuA-SS mixture. Among the indentations made, none featured an exceptionally high hardness. This indicates that the CuA/SS interface is free of detrimental phase.

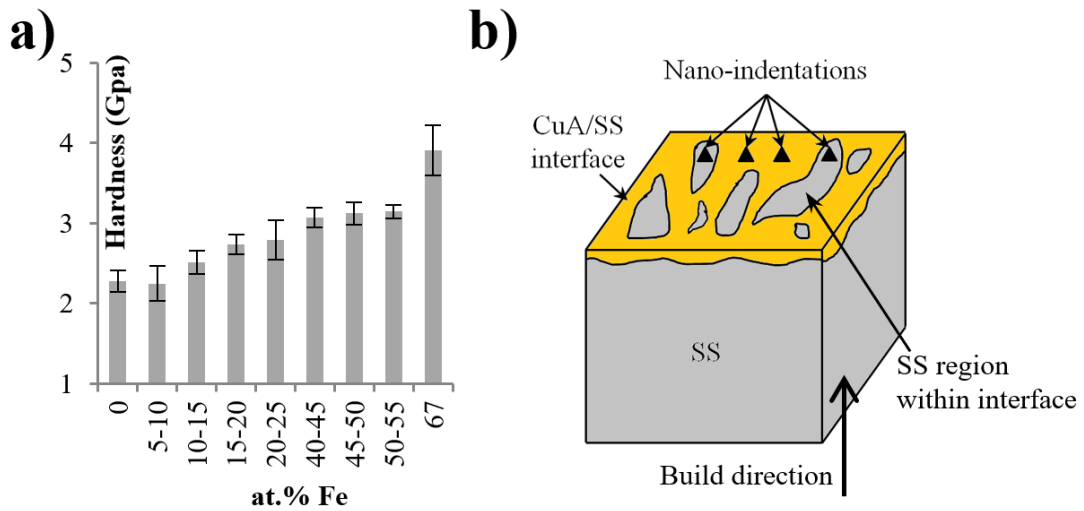


Figure 4.7 (a) Hardness of phases at the CuA/SS interface. (b) Setup of nanoindentation measurements

4.3 - TiA/CuA Interface

4.3.1 - Microstructure

Unlike the CuA/SS interface, the TiA/CuA interface is expected to contain detrimental IMCs as predicted by the Ti-Cu binary phase diagram. This makes the TiA/CuA interface a critical location within the MM part where dilution control and minimisation of detrimental phases become importance. To investigate the effects of the process parameters on the dilution and the distribution of the various phases, the TiA/CuA interfaces were processed using three sets of laser parameters as previously shown in Table 4.1. The difference between the parameters lies in the laser scanning velocity used for the initial TiA build layers; the scanning velocity used in layer 1-5 of the TiA build is 650mm/s, 500mm/s and 350mm/s for the V650-350, V500-350 and V350 parameters respectively. As verified in the single-track study (Section 3.2), these parameters can produce stable melt pools with sufficient overlap between adjacent tracks throughout the entire build process.

All TiA/CuA interfaces display similar microstructural features, hence, only the characteristic regions of the V650-350 TiA/CuA interface is shown in this section. Images of the V350 TiA/CuA interface can be found in Appendix A. The cross-

sectional view of the V650-350 TiA/CuA interface, imaged with BSE, is shown in Figure 4.8. The dark region at the top and the bright region at the bottom of Figure 4.8 belong to the bulk TiA and CuA respectively. The composite-like structure that exists in the middle corresponds to the TiA/CuA interface. The microstructure of the entire V650-350 TiA/CuA interface can be represented by two characteristic regions; region A6 in Figure 4.8 captures the microstructure at the start of the interface while region A7 (Figure 4.8) characterises the bulk of the TiA/CuA interface.

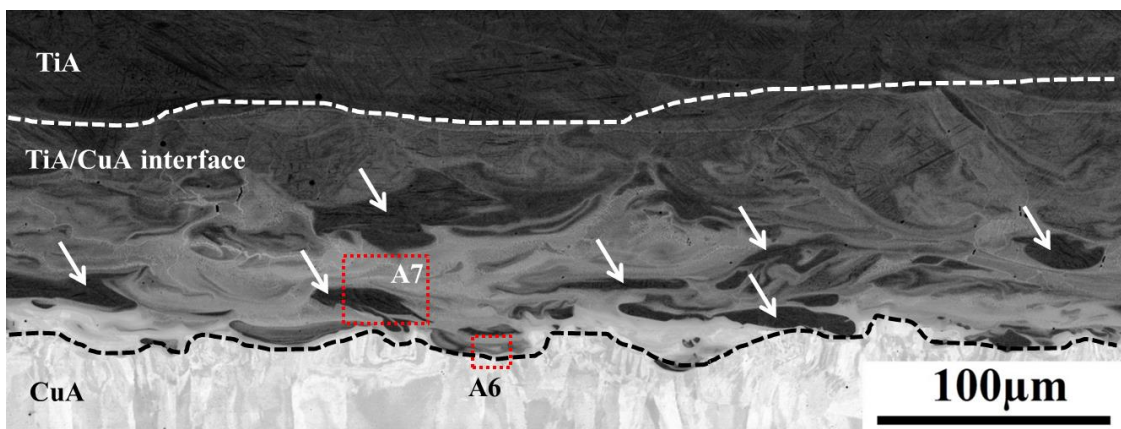


Figure 4.8 BSE image of the cross-sectional view of V650-350 TiA/CuA interface

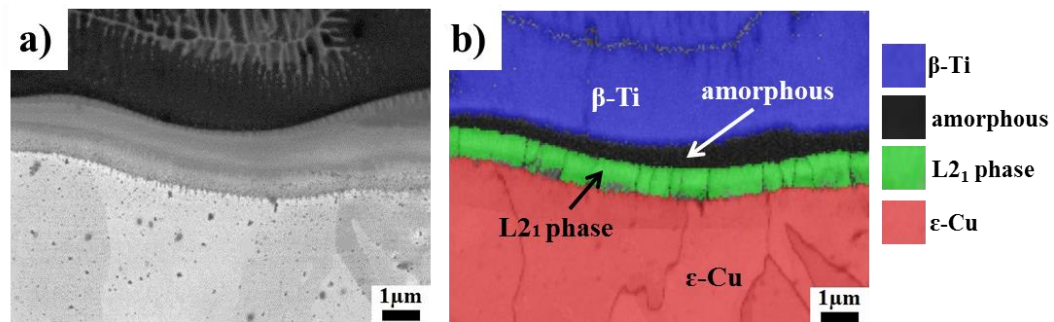


Figure 4.9 Microstructure in region A6 featuring continuous layers of amorphous and L_{21} ordered phase. (a) BSE image, (b) overlay of EBSD phase map and band contrast image.

The magnified view of region A6 is shown in Figure 4.9a while Figure 4.9b shows the overlay of the phase map and band contrast image obtained from EBSD analysis. The TiA/CuA interface began with a thin and continuous layer of L_{21} ordered phase that is identical to the Cu_2TiAl Heusler compound (coloured green in Figure 4.9b). Above the L_{21} phase, a continuous layer of amorphous material was detected (black in Figure

4.9b). The amorphous phase was unindexed during EBSD analysis due to the absence of diffraction patterns. Confirmation of the amorphous phase was obtained through TEM analysis which will be shown later in this section. Beyond the amorphous layer, β -Ti was detected.

It is worth emphasizing that the L2₁ and amorphous phase were present as distinct and continuous layers on top of the CuA interlayer. These layers were not broken by the vigorous Marangoni flow that is known to exist within the melt pools [184]. Although the continuous L2₁ and amorphous layers seemed to resemble diffusion layers, the amorphous phase is unlikely to be a product of diffusion. Rather, the Ti-Cu amorphous phase is likely to have formed via rapid solidification [195, 196]. Besides, the thickness of the amorphous layer in the V650-350 TiA/CuA interface ($2.4 \pm 2.7 \mu\text{m}$) featured large fluctuation which is uncharacteristic of a diffusion layer. Instead, the continuous amorphous layer is postulated to have formed within the velocity boundary layer of the melt pool where fluid flow conforms to the melt pool boundary. Since the flow within the boundary layer is retarded, it also experienced less mixing and has a different composition compared to the interior of the melt pool. If the composition favours vitrification, then the liquid in the velocity boundary layer would be quenched into an amorphous layer during rapid cooling.

The EDX composition of the amorphous phase (at.%) lies between Ti(45.4)-Cu(45.8)-Ni(1.8)-Al(3.7)-V(1.7)-Cr(0.4)-Si(1.3) and Ti(52.1)-Cu(37.8)-Ni(1.5)-Al(4.4)-V(2.5)-Cr(0.4)-Si(1.3). According to literature, amorphous metals with similar but non-identical compositions could typically vitrify into rods with a critical diameter of $\sim 1\text{-}4 \text{ mm}$ using the copper mould casting technique [197-199]. The associated critical cooling rate of these $1\text{-}4 \text{ mm}$ diameter castings can be estimated to be $\sim 10^2\text{-}10^3 \text{ K/s}$ [200]. Given that the cooling rates in the SLM process typically range from $\sim 10^3\text{-}10^7$

K/s [158, 201, 202], the formation of an amorphous phase is possible. Similar amorphous metals typically crystallize upon reaching a temperature of 361-453 °C [197-199]. Since the amorphous layer did not crystallize, this signifies that it was not exposed to prolonged periods of elevated temperatures during the build process.

The thin layer of L2₁ phase (1.0±0.6 μm) that is sandwiched between the amorphous layer and the CuA interlayer is postulated to be a product of interdiffusion. As the melt pool and the amorphous layer cools from elevated temperatures, some amount of interdiffusion, inevitably, occurs across the boundary separating the amorphous phase and the CuA interlayer. The higher Cu content in the interdiffusion layer likely stabilized the Cu₂TiAl phase which has an L2₁ structure. Thus, the interdiffusion region transformed into a layer of L2₁ phase. Although Cu₂TiAl can also crystallize from the ternary Cu-Ti-Al amorphous phase under elevated temperatures [203], the L2₁ phase seen in Figure 4.9 is unlikely to be a product of crystallization because as it was not homogeneously precipitated within the amorphous layer.

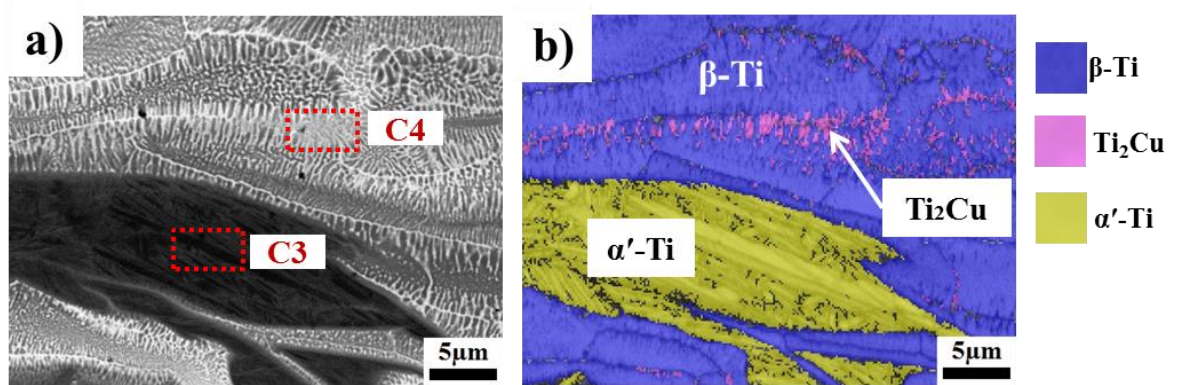


Figure 4.10 Microstructure in region A7 featuring α' -Ti phase within a matrix of β -Ti+Ti₂Cu. (a) BSE image, (b) overlap of EBSD phase map and band contrast image.

The bulk of the TiA/CuA interface is made up of α' -Ti islands (indicated by the white arrows in Figure 4.8) which exist within a matrix of β -Ti+Ti₂Cu phase mixture. This composite structure is represented in region A7 (Figure 4.10a-b). The shaded patch in Figure 4.10a corresponds to the α' -Ti phase while the brighter region belongs to the β -

Ti+Ti₂Cu matrix. Marangoni flow within the melt pools caused the interfacial α' -Ti regions to stretch, resulting in an elongated morphology (see Figure 4.8 and Figure 4.10). EDX measurements showed that the composition of the α' -Ti region (area C3 in Figure 4.10) is Ti(85.1)-Cu(1.8)-Al(9.4)-V(3.7) while the composition of the β -Ti+Ti₂Cu matrix (area C4) is Ti(63.9)-Cu(25.5)-Al(6.2)-V(2.7)-Ni(0.8)-Si(0.7)-Cr(0.1). Notably, the α' -Ti phase has a much lower Cu-content compared to the surrounding β -Ti+Ti₂Cu phase mixture. Hence, α' -Ti appeared darker in the BSE image in Figure 4.10a. The existence of α' -Ti is attributed to 1) the non-homogeneous mixing within the melt pool and 2) the rapid cooling conditions in SLM. Imperfect mixing results in a spatial variation of Cu content. Since Cu is both a β -Ti stabilizer and a component of the Ti₂Cu IMC, Cu-rich regions tend to solidify into the β -Ti+Ti₂Cu phase mixture while Cu-poor regions transform into the α' -Ti phase during cooling. Rapid cooling favours the formation of metastable α' -Ti in the as-built TiA instead of the equilibrium α -Ti phase [171, 172, 204]. During solidification, molten TiA first nucleates as β -Ti grains. As the β -Ti grains cool to the β -transus temperature it can either transform into α -Ti or the martensitic α' -Ti if the cooling rate is >410 K/s [205]. Since the cooling rate of the SLM process is undoubtedly higher than 410 K/s, α' -Ti is typically obtained. Given that the interfacial α' -Ti regions are diluted with ~0-5 at.% of Cu, which is a β -stabilizing element, its β -transus temperature is expected to be lower compared to the original Ti-6Al-4V alloy (975-995 °C).

The BSE image in Figure 4.10a shows that the β -Ti grains are populated by bright lines along its boundaries and bright spots at its core. The bright features correspond to the Ti₂Cu IMC. Even though the BSE image in Figure 4.10a captures an abundance of Ti₂Cu within the β -Ti grains, EBSD analysis only indexed a minor portion of these bright features as the Ti₂Cu IMC (compare Figure 4.10a & b). This disparity is caused

by the limitation in the spatial resolution associated with the EBSD analysis of bulk samples. The width of the Ti_2Cu phase, which is estimated to be less than 400 nm, is comparable to the interaction volume of the EBSD analysis. Hence, the diffraction patterns belonging to the Ti_2Cu and the surrounding $\beta\text{-Ti}$ phase tend to overlap, causing the analysis software to erroneously index the small Ti_2Cu particles as the surrounding $\beta\text{-Ti}$ phase. Similarly, EDX analysis also cannot be used to obtain reliable composition measurements for the Ti_2Cu phase as the associated interaction volume is $\sim 2\text{ }\mu\text{m}$ for bulk samples.

As the Cu content becomes significantly depleted towards the upper end of the TiA/CuA interface, $\beta\text{-Ti}$ can no longer be retained during cooling and the microstructure becomes fully $\alpha'\text{-Ti}$ with a columnar prior $\beta\text{-Ti}$ grain structure (Figure 4.11).

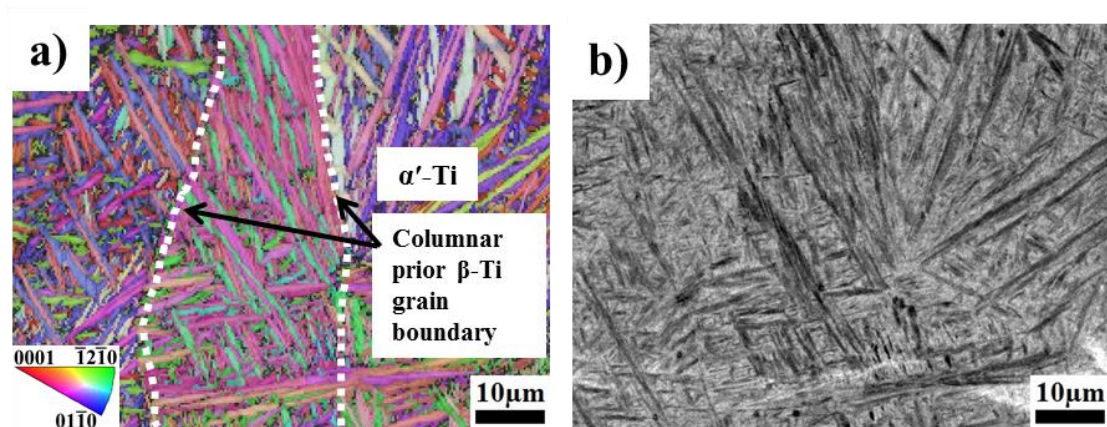


Figure 4.11 Microstructure of bulk TiA. (a) Overlap of IPF and band contrast image, (b) BSE image

To circumvent the spatial resolution limit associated with the EBSD and EDX analysis of bulk samples, TEM analysis was performed on thin lamellae samples. This allows electron diffraction and EDX analysis to be carried out with a higher spatial resolution so the different phases can be accurately identified and validated against the results of the EBSD analysis.

The first TEM sample was extracted from a region similar to that of A6 and the bright field image is shown in Figure 4.12. Region A has a composition of Cu(91.4)-Ti(2.4)-Ni(2.7)-Si(3.2)-Cr(0.4) and a SAED pattern which matches the $\langle 111 \rangle$ zone axis of the ϵ -Cu phase (inset of Figure 4.12). Hence, it belongs to the CuA interlayer. Region B consists of a ~ 500 nm thick layer of equiaxed grains. The SAED pattern of these grains features strong and weak diffraction spots (inset of Figure 4.12) that match the $\langle 101 \rangle$ zone axis of the Cu_2TiAl Heusler compound. Additionally, two other SAED patterns which match the $\langle 111 \rangle$ and $\langle 102 \rangle$ zone axis of the Cu_2TiAl phase have also been obtained to confirm the L_{21} structure of the grains. The measured lattice constant of the L_{21} phase (0.608 nm) is similar to the reported value of 6.01 nm for the Cu_2TiAl phase [33]. EDX measurements show that L_{21} grains have compositions ranging between Cu(56.0)-Ti(32.5)-Al(4.1)-V(1.4)-Ni(2.1)-Si(3.3)-Cr(0.6) and Cu(63.1)-Ti(28.8)-Al(2.6)-V(1.0)-Ni(2.3)-Si(1.7)-Cr(0.5). Even though the ratio of Cu to Ti content is $\sim 2:1$ and matches well with that of the Cu_2TiAl phase, its Al content is several times lower than its stoichiometric ratio. According to the isothermal section of the Cu-Ti-Al ternary phase diagram at 500°C , the Al content of the Cu_2TiAl phase can be as low as ~ 9 at.% [206]. As such, it may be possible for the Cu_2TiAl phase in this study to have an Al content that is well below its stoichiometric ratio, especially under the influence of rapid solidification and the presence of other alloying elements.

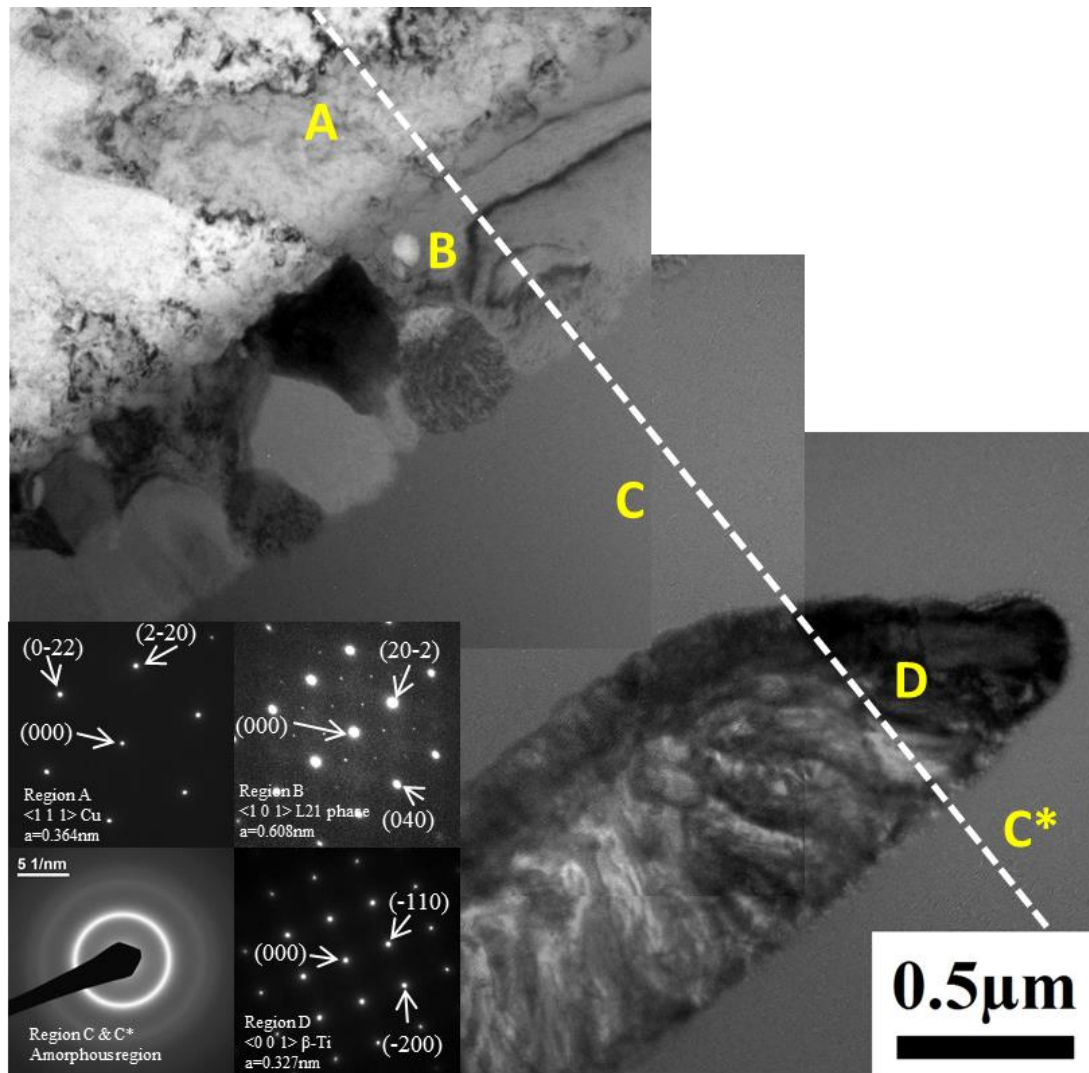


Figure 4.12 Bright-field TEM image of ϵ -Cu, Cu_2TiAl , amorphous, and β -Ti phase

Region C is amorphous as shown by the diffused rings in its SAED pattern (inset of Figure 4.12). The composition of the amorphous phase ranges from Cu(45.8)-Ti(45.4)-Al(3.7)-V(1.7)-Ni(1.8)-Si(1.3)-Cr(0.4) in region C to Cu(37.8)-Ti(52.1)-Al(4.4)-V(2.5)-Ni(1.5)-Si(1.3)-Cr(0.4) in region C*. A β -Ti island which has a core composition of Cu(17.9)-Ti(68.0)-Al(8.0)-V(4.0)-Ni(0.7)-Si(1.2)-Cr(0.3) exists within the amorphous region. The presence of the β -Ti island is caused by the non-homogeneous mixing within a rapidly solidified melt pool. Since the β -Ti island is embedded within the amorphous phase, the solidification and cooling conditions experienced by both phases are likely to be similar. Despite similar cooling conditions, β -Ti crystallized while its surroundings vitrified into an amorphous phase. This

indicates that the resultant phase is highly composition dependent. Notably, the Cu content of the amorphous phase in region C (37.8-45.8 at.%) coincides with the amorphous-forming range of 30-75 at.% found in the binary Cu-Ti system [207]. In contrast, the Cu content of the β -Ti island lies outside this range.

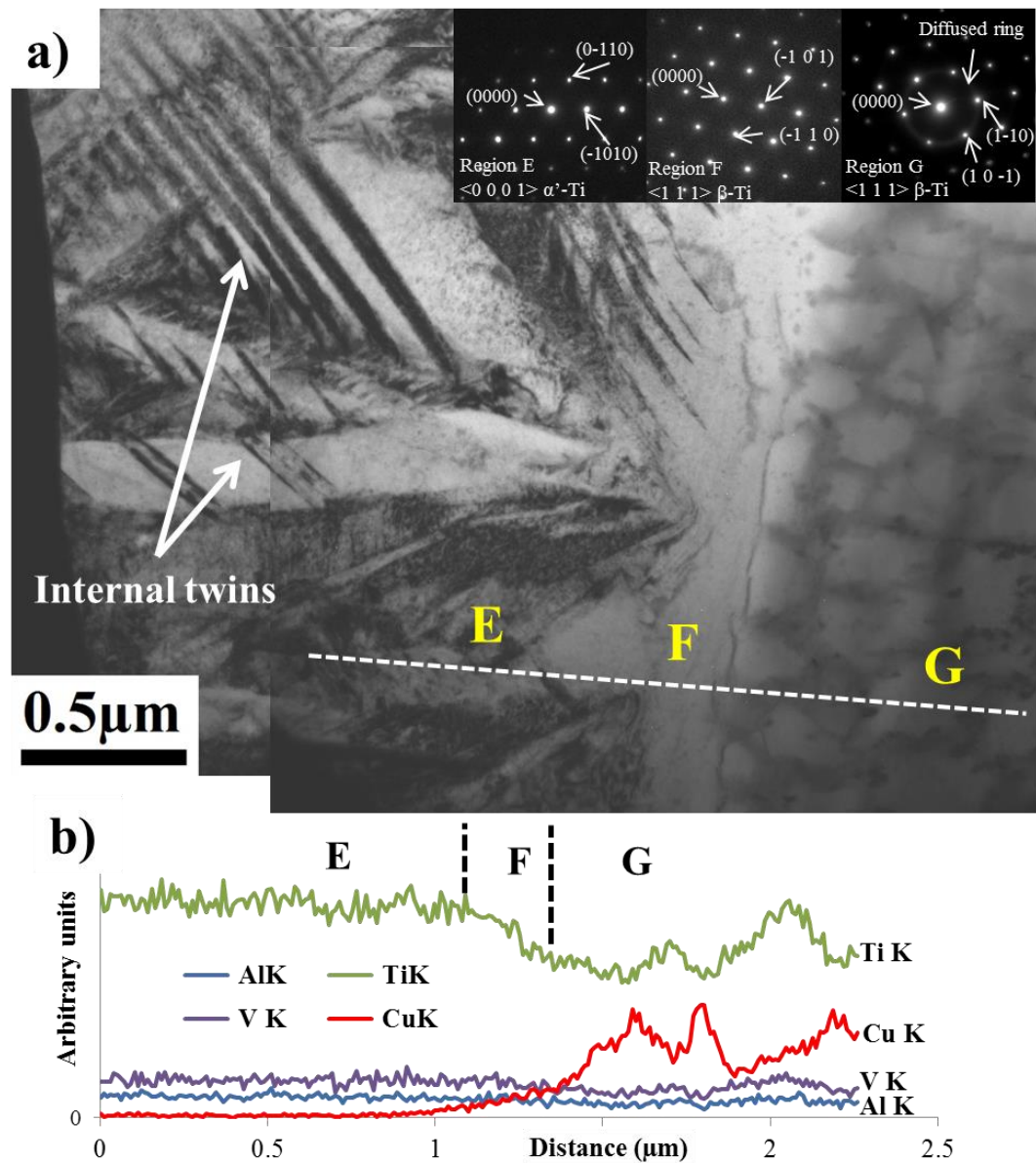


Figure 4.13 (a) Bright-field TEM image of an α' -Ti phase and supersaturated β -Ti cells. (b) Qualitative EDX measurement along the dotted line in (a).

The second TEM sample was extracted from the boundary between an α' -Ti island and its surrounding β -Ti matrix. Region E is identified as the α' -Ti phase based on the SAED pattern as shown in the inset of Figure 4.13a. Due to an insufficient number of

easy slip systems in the HCP structure, plastic deformation in α' -Ti frequently occurs via twinning. Thus, internal twins (white arrows in Figure 4.13a) can be found within the α' -Ti phase. The composition of the α' -Ti phase is Cu(2.7)-Ti(83.2)-Al(10.1)-V(4.0). As expected, the Cu content in the α' -Ti phase is low and insufficient to retain the prior β -Ti phase upon cooling. Region F, which is the bright and narrow region between region E and G, is comprised of β -Ti phase and has a composition of Cu(10.4)-Ti(73.4)-Al(10.3)-V(4.5)-Ni(0.3)-Si(1.0).

In region G, a cellular β -Ti structure with a cell size of 252 ± 45 nm is observed. Qualitative composition line scan (Figure 4.13b) showed that elemental segregation occurred long the cell outlines. EDX measurements revealed that the cell cores have a fairly consistent average composition of Cu(24.4)-Ti(62.4)-Al(8.1)-V(3.0)-Ni(0.8)-Si(0.8)-Cr(0.5) while the cell outlines have compositions ranging between Cu(34.6)-Ti(55.3)-Al(5.9)-V(1.6)-Ni(1.4)-Si(0.8)-Cr(0.4) and Cu(44.0)-Ti(47.6)-Al(4.9)-V(1.0)-Ni(1.4)-Si(0.8)-Cr(0.3). Compared to the cell cores, the outlines have a higher Cu content (34.6-44.0 at.%) which coincides with that of the amorphous phase in region C of Figure 4.12. The SAED pattern of region G features strong β -Ti diffraction spots as well as a faint diffused ring which is indicative of an amorphous phase. Based on the composition and diffraction results, region G likely comprised of β -Ti cells which are outlined by a minor amount of amorphous phase. The average composition of region G, cell core and cell outline combined, is Cu(31.7)-Ti(56.5)-Al(6.8)-V(2.6)-Ni(1.0)-Si(0.9)-Cr(0.5). Based on the composition of the β -Ti core, the maximum solubility of Cu in β -Ti is estimated to be ~ 24 at.%. This is significantly higher than the maximum solubility indicated in the Cu-Ti binary phase diagram (15.9 at.% Cu). The increased solubility of Cu in β -Ti is attributed to the combined effects of rapid solidification and the presence of other alloying elements.

The last TEM sample is extracted from the β -Ti+Ti₂Cu phase mixture and the bright field image is shown in Figure 4.14. SAED patterns (inset of Figure 4.14) affirm that the phase with the darker contrast is Ti₂Cu while the brighter matrix phase belongs to a single β -Ti grain. EDX analysis shows that the Ti₂Cu phase has a consistent composition of Cu(30.9)-Ti(62.3)-Al(3.7)-Ni(1.5)-Si(0.5)-V(0.6)-Cr(0.3). In contrast, the surrounding β -Ti has compositions ranging from Cu(7.5)-Ti(80.5)-Al(7.8)-Ni(0.4)-Si(0.8)-V(2.6)-Cr(0.4) to Cu(12.4)-Ti(75.8)-Al(7.1)-Ni(0.6)-Si(0.7)-V(3.0)-Cr(0.5).

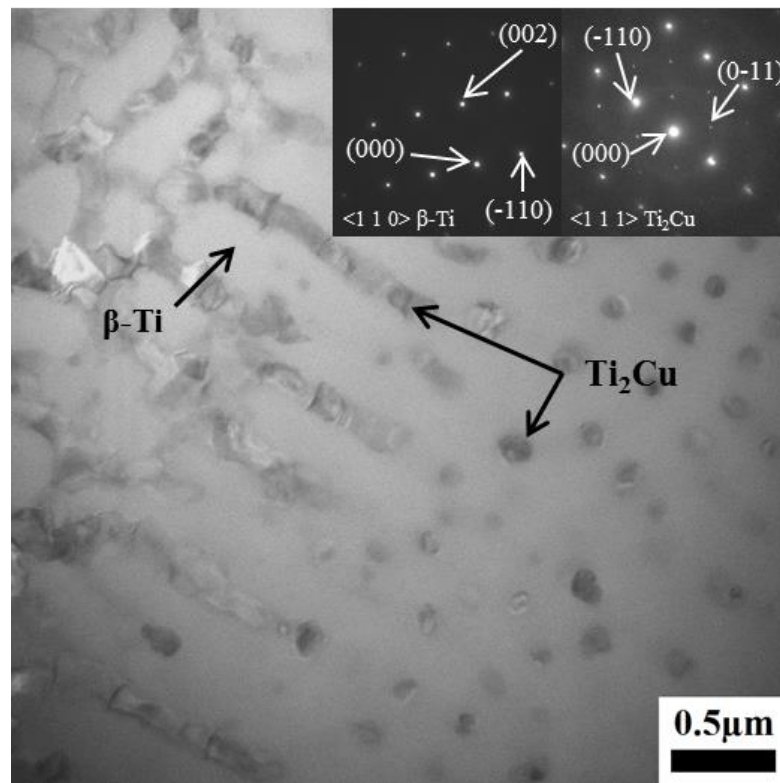


Figure 4.14 Bright-field TEM image of the β -Ti+Ti₂Cu phase mixture.

XRD analysis was performed on the bulk TiA as well as the various TiA/CuA interfaces to survey its microstructural phases. The TiA/CuA interfaces used for the analysis were prepared by carefully grinding away the bulk TiA until the TiA/CuA interface is exposed. The XRD results are shown in Figure 4.15. The bulk TiA consists of α' -Ti peaks with no evidence of retained β -Ti phase. All the TiA/CuA interfaces showed similar diffraction peaks which correspond to that of α' -Ti, β -Ti, Ti₂Cu, and ϵ -

Cu phases. The diffraction angles are listed in Appendix B. The presence of the ϵ -Cu peaks indicates that the survey depth of the XRD analysis was sufficient to reach the underlying CuA interlayer. Since the L2₁ and amorphous layers form on top of the CuA interlayer, they are also within the survey depth of the XRD analysis. However, the crystalline peaks of L2₁ phase and the diffuse peaks associated with the amorphous phase were not explicitly detected. This indicates that the L2₁ and amorphous phase were only present in minor amounts, which is consistent with their low thicknesses as seen in Figure 4.9 and Figure 4.12. The absence of unidentified peaks in the XRD patterns signifies that the major constituent phases within the TiA/CuA interface have been identified.

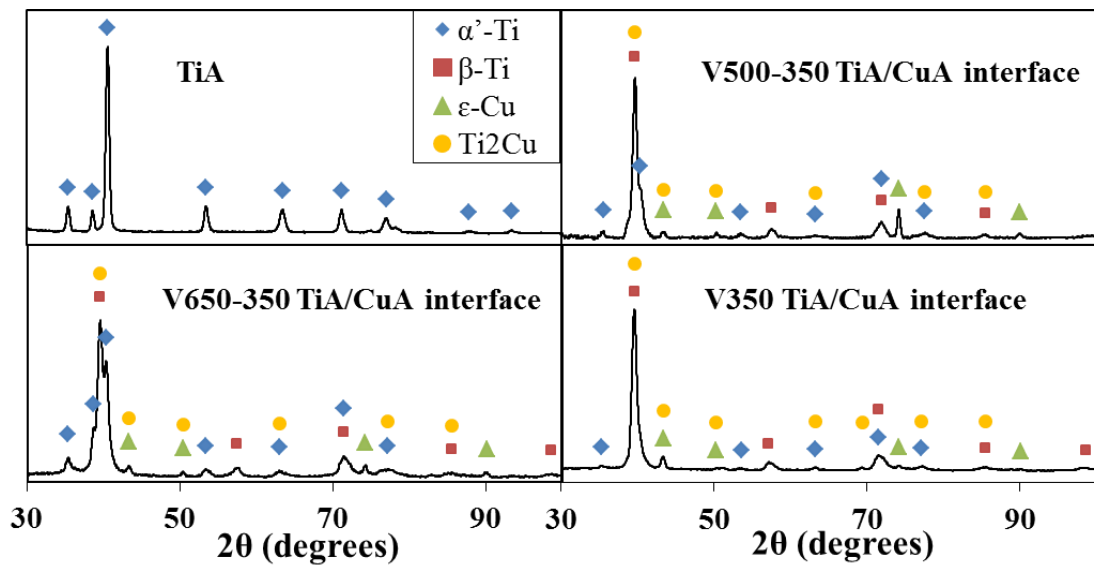


Figure 4.15 XRD pattern of the bulk TiA and the various TiA/CuA interfaces

The phases identified through TEM and XRD analysis serve as important validations for the phase maps obtained through EBSD analysis (Figure 4.9 and Figure 4.10). Understandably, the only phase that cannot be directly captured in the EBSD analysis is the amorphous phase due to its lack of diffraction pattern. Specifically, regions such as the cell outlines in region G (Figure 4.13) as well as the amorphous layer in region C (Figure 4.12) cannot be indexed during EBSD analysis. However, the presence of

these amorphous phases can be inferred from its composition. A uniform amorphous layer is present when the unindexed region has a Cu content of 37.8-45.8 at.%. On the other hand, the presence of amorphous cell outlines can be inferred when the average composition of the β -Ti phase has ~ 32 at.% Cu.

4.3.2 - Composition of Phases

The average composition of the respective phase/s obtained from the EDX analysis is listed in Table 4.2. Each phase/s is associated with a unique range of Cu content. Even though the exact composition boundaries separating the respective phases cannot be determined precisely, an approximate range of Cu content can be assigned to the respective phases based on actual composition measurements (see right column of Table 4.2). In general, α' -Ti can be expected to form at 0-5 at.% Cu, β -Ti+Ti₂Cu is present at 5-30 at.% Cu, the amorphous phase forms at 35-45 at.% Cu and the L2₁ phase is found at 55-65 at.% Cu. Using these approximations, the volume fraction of the respective phases within the TiA/CuA interfaces can be estimated through simple EDX measurements. Additionally, the phase/s associated with each nano-indent can also be estimated by measuring and comparing its Cu content to the approximated values in Table 4.2.

Table 4.2 EDX composition of the different phases in the TiA/CuA interface

Phase/s	Cu	Ni	Si	Cr	Ti	Al	V	Total	Approx Cu content
α' -Ti (min Cu)	0.2	-	-	-	86.9	9.1	3.8	100.0	0-5
α' -Ti (max Cu)	4.9	0.1	0.2	0.3	80.2	10.4	4.1	100.0	
β -Ti + Ti ₂ Cu (min Cu)	8.5	0.3	0.2	0.0	78.9	8.5	3.6	100.0	5-30
β -Ti + Ti ₂ Cu (max Cu)	25.5	0.8	0.7	0.1	64.0	6.2	2.7	100.0	
β -Ti+Amorph (min Cu)	31.7	1.0	0.9	0.5	56.5	6.8	2.6	100.0	30-35
β -Ti+Amorph (max Cu)	32.5	1.0	0.7	0.5	56.2	6.0	3.3	100.0	
Amorph (min Cu)	37.8	1.5	1.3	0.4	52.1	4.4	2.5	100.0	35-45
Amorph (max Cu)	45.8	1.8	1.3	0.4	45.4	3.7	1.7	100.0	
L2 ₁ (min Cu)	56.0	2.1	3.3	0.6	32.5	4.1	1.4	100.0	55-65
L2 ₁ (max Cu)	63.1	2.3	1.7	0.5	28.8	2.6	1.0	100.0	
ϵ -Cu	91.4	2.7	3.2	0.4	2.4	0.0	0.0	100.0	>90

4.3.3 - Hardness

The hardness of the different phases was obtained by placing 148 nano-indentations with a depth of 1 μm on the TiA/CuA interface in a similar manner as previously illustrated in Figure 4.7b. The composition of each indent is then measured using EDX and the average hardness associated with the different Cu content is shown in Figure 4.16.

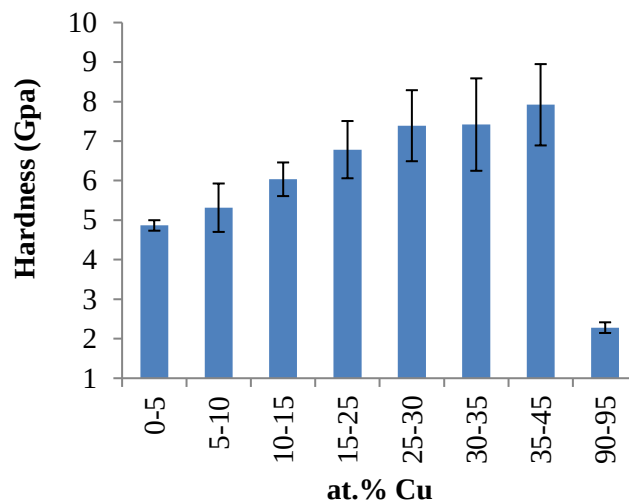


Figure 4.16 Hardness of various phases in the TiA/CuA interface

The hardness of the TiA/CuA interfacial phases exceeds those of the bulk TiA (4.9 GPa) and CuA (2.3 GPa). Regions with 5-10 at.% Cu feature increased hardness of 5.3 GPa compared to the bulk TiA. This region corresponds to the β -Ti+Ti₂Cu phase mixture and its increased hardness is attributed to the solid solution strengthening effect of Cu in β -Ti as well as the formation of a small amount of Ti₂Cu IMC. As the Cu content continues to increase up to 30 at.%, these two effects persist to increase the hardness to 7.4 GPa. A peak hardness of 7.9 GPa is obtained when the resultant phase becomes amorphous at 35-45 at.% Cu. Hardness data for the L₂₁ phase which has a Cu content of 55-65 at.% could not be reliably obtained due to its limited thickness of $\sim 1.5 \mu\text{m}$. Since increased hardness is typically an indication of a brittle material, phases with higher Cu content and hardness are implied to be more detrimental.

Compared to the CuA/SS interface which does not contain detrimental phases and has a low hardness, the TiA/CuA interface is the critical location where brittle fracture is expected to occur.

4.3.4 - Interface Thickness & Cu content

Although the constituent phases in the various TiA/CuA interfaces are the same, the dilution, thickness, and Cu content vary across the V650-350, V500-350, and V350 interfaces. Owing to the higher laser energy density and deeper penetration depth of the V350 melt pool (see Figure 3.14), a larger amount of CuA was melted in the first TiA build layer. Hence, the V350 TiA/CuA interface contained the highest Cu content and is consequently thicker than the other interfaces as shown in Figure 4.17a-c. The interfacial thickness, defined here as the distance required for the Cu content to drop from its parent composition to below 5 at.%, increased from $55.6 \pm 17.2 \mu\text{m}$ for the V650-350 interface to $115.5 \pm 18.8 \mu\text{m}$ for the V350 TiA/CuA interface (Table 4.3). In addition to the larger overall thickness, the amorphous layer in the V350 interface is also ~3 times as thick as that of the V650-350 interface. On the other hand, the thickness of the L2₁ layer is comparable across the various TiA/CuA interfaces.

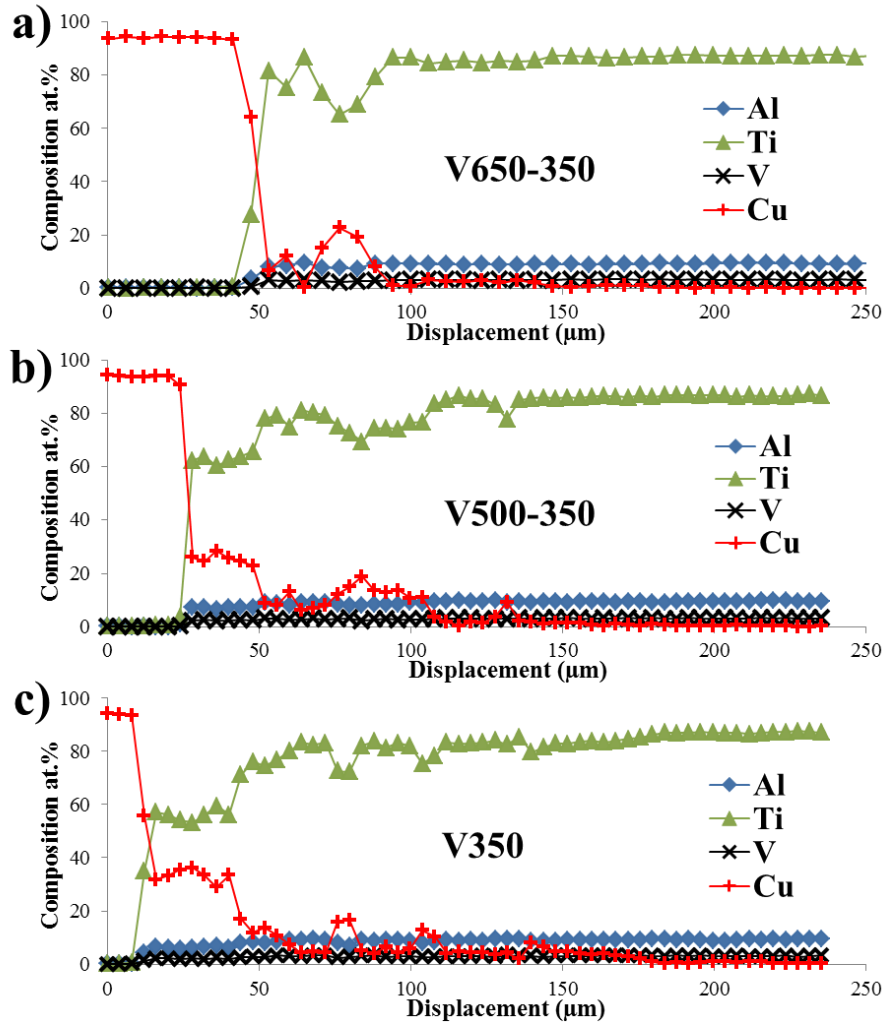


Figure 4.17 EDX composition line plots of the (a) V650-350, (b) V500-350, and (c) V350 TiA/CuA interfaces

Table 4.3 Thickness of the different phase/s in the TiA/CuA interface

Sample \ Phase	L2 ₁	Amorphous	α' -Ti + (β -Ti + Ti ₂ Cu)	Total thickness
V650-350	1.0±0.6	2.4±2.7	52.2±17.2	55.6±17.2
V500-350	1.1±1.0	3.1±3.0	95.0±14.4	99.2±14.4
V350	1.5±0.7	8.8±4.6	95.2±18.8	115.5±18.8

The interfacial Cu content of the various TiA/CuA interfaces can be qualitatively compared by integrating the Cu-displacement plots (Figure 4.17) within the limits of the interface. The integral is first averaged by taking seven measurements across each interface and, subsequently, normalized against the Cu content in the bulk CuA to obtain an equivalent thickness (see illustration in Figure 4.18). Figure 4.19 shows the equivalent thickness of the respective interfaces plotted along with the penetration depth taken from the earlier TiA-on-CuA single-track study. Notably, the V650-350

TiA/CuA interface that featured the lowest penetration depth in the first TiA build layer also had the lowest equivalent thickness. Given that the Cu content in the interface originates from the CuA that was melted in the first TiA build layer, the objective of minimizing interfacial Cu content is, thus, equivalent to minimizing the penetration depth of the first TiA build layer. Since the interfacial hardness and the amount of detrimental phases scale with the Cu content, it is imperative that the V650-350 TiA/CuA interface, which has the lowest Cu content, also contains the least amount of detrimental phases.

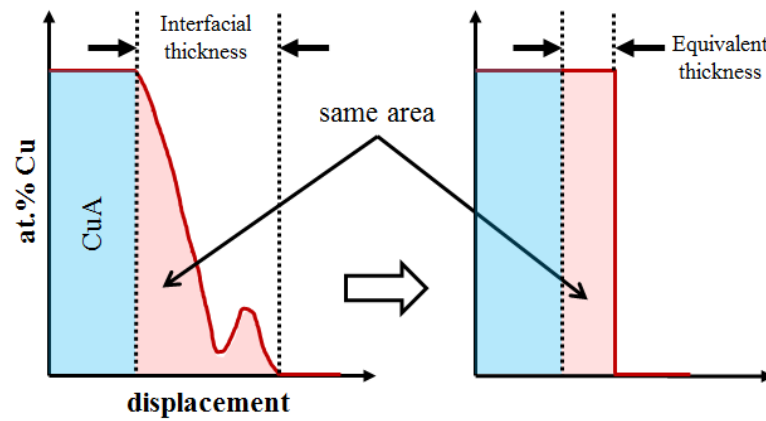


Figure 4.18 Illustration of equivalent thickness

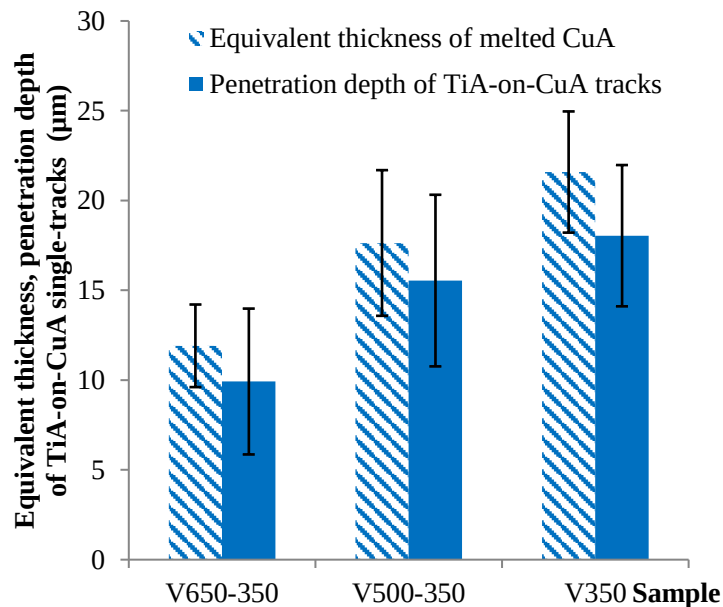


Figure 4.19 Equivalent thickness of the various TiA/CuA interface and the penetration depth of the TiA-on-CuA single-tracks

4.3.5 - Volume Fraction of Phases

To estimate the volume fraction of various phases in the respective TiA/CuA interface, composition line plots, such as those shown in Figure 4.17, were obtained at sixteen different locations for each interface. The data points in the composition plots were then sorted according to their Cu content and presented as distribution plots in Figure 4.20a-c. To better illustrate the difference between the interfaces, the volume fraction of the major constituents containing 0-30 at.% Cu is alternatively represented in Figure 4.20d.

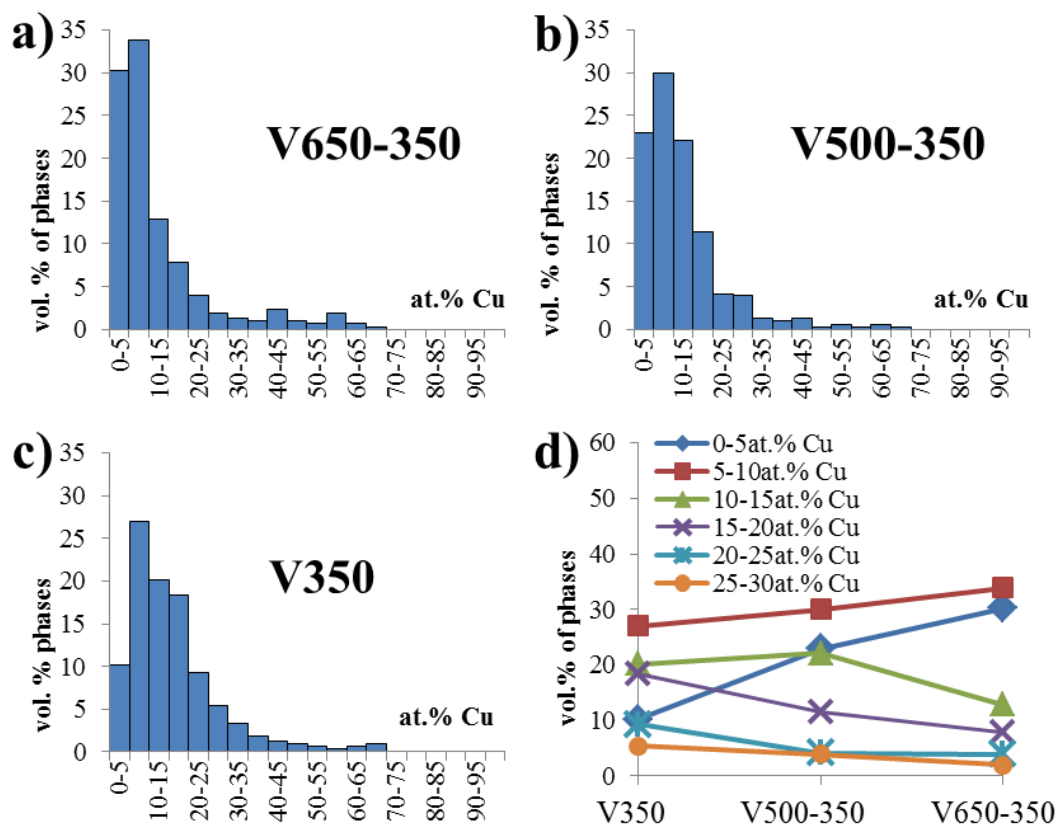


Figure 4.20 Volume fraction of different phases in the (a) V650-350, (b) V500-350, and (c) V350 TiA/CuA interfaces. (d) Changes in the volume fraction of major constituent across the various TiA/CuA interfaces.

A comparison between the distribution plots shows that the V650-350 TiA/CuA interface is dominated by phases with lower Cu content, while the V500-350 and V350 TiA/CuA interfaces are dominated by phases with greater amounts of Cu content. Notably, 30 vol.% of the V650-350 TiA/CuA interface is comprised of α' -Ti

(0-5 at.% Cu). In contrast, the V500-350 and V350 interfaces only contained 23 vol.% and 10 vol.% of α' -Ti, respectively. Besides a high volume fraction of α' -Ti, the V650-350 interface also contained 33 vol.% of phases that has relatively low Cu content of 5-10 at.% (i.e. β -Ti+Ti₂Cu). Since the V650-350 interface is dominated by phases with low Cu content (0-10 at.%), this also implies that it contained the lowest volume fraction of phases with 10-30 at.% Cu (β -Ti+Ti₂Cu).

The large volume fraction of α' -Ti in the V650-350 TiA/CuA interface is caused by the imperfect mixing within the melt pool. Rapid solidification caused the non-homogeneous melt pools to become kinetically frozen before the α' -forming regions can be diluted with more Cu atoms to become β -Ti+Ti₂Cu. If the distribution plots for the V650-350, V500-350 and V350 TiA/CuA interfaces (Figure 4.20a-c) were homogeneous, they would have a uniform Cu content of ~12 at.%, ~12 at.% and ~16 at.%, respectively, and interfacial α' -Ti would have been absent. Mixing within the melt pool can be restricted by lowering the magnitude of the convective flow. The intensity of the flow is captured by the Marangoni number which is expressed as:

$$Ma = - \frac{d\gamma}{dT} \frac{\Delta T}{\alpha} \frac{L}{\mu} \quad (7)$$

Where γ is the surface tension, T is the temperature, ΔT is the difference between the maximum melt pool temperature and the solidus temperature, α is the thermal diffusivity, L is the characteristic length of the melt pool which is taken to be its width, and μ is the dynamic viscosity. Since the V650-350 parameter has the lowest laser energy input, the associated melt pool width, L , and the temperature difference, ΔT , are also expected to be the lowest. The lower temperatures in the V650-350 melt pools result in higher dynamic viscosity, μ . For reference, the dynamic viscosity of liquid Ti increases by ~17 % as its temperature decreases from 2043 K towards its melting point

of 1943 K [208]. The lower penetration depth of the V650-350 melt pools also leads to a lower Cu content which decreases the magnitude of $d\gamma/dT$ [179]. The accumulation of the above factors reduces the magnitude of the Marangoni number which implies that mixing is less intense in the V650-350 melt pools. Since the V650-350 parameter uses a higher laser scanning velocity in layer 1-5 of the TiA build, it is imperative that its melt pools cool and solidify within a shorter time. The reduced molten duration of the V650-350 melt pools restricts mixing, leading to a higher volume fraction of interfacial α' -Ti phase. Conversely, the lower scanning velocity used in the V350 parameter creates a hotter melt pool with lower liquid viscosities and offers a longer mixing time to create a more homogeneous melt pool [27]. Therefore, the V350 TiA/CuA interface has a lower volume fraction of interfacial α' -Ti phase. Even though melt pool non-homogeneities can also be caused by a positive enthalpy of mixing [209], as is the case for the CuA-SS molten mixture, it is not applicable for the Cu-Ti system as Cu and Ti atoms mix favourably with a negative enthalpy of mixing [180, 210].

4.4 - Summary

The TiA/CuA/SS MM part was manufactured using the SLM process and the microstructures and characteristics of the CuA/SS and TiA/CuA interface were characterised in detail. The key findings are:

- 1) The CuA/SS interface comprised of ϵ -Cu and γ -Fe phases with no reaction product. Due to the miscibility gap in the Cu-Fe system, the CuA-SS molten mixture underwent liquid phase separation to form SS globules and CuA globules in a Cu-rich and Fe-rich matrix respectively. The SS globules acted as low energy nucleation sites for the subsequent growth of CuA grains.

Locations with a high density of finely dispersed SS globules featured refined equiaxed CuA grains. The morphology of the CuA grains changed from equiaxed to columnar when the SS globules are depleted towards the end of the interface. The hardness of the CuA/SS interface had intermediate values that lie between its base alloys.

- 2) The microstructure of the TiA/CuA interface, listed from bottom to top, comprised of 1) a 1-2 μm thick layer of L_{21} ordered phase, 2) a 3-9 μm thick amorphous layer, and 3) a 52-95 μm thick composite layer that contains elongated α' -Ti regions within a matrix of β -Ti+Ti₂Cu. The L_{21} ordered phase has a similar crystal structure and lattice constant as the Cu₂TiAl Heusler compound. Each of these phases can be identified from its unique range of Cu content. The hardness of the interfacial phases increases with Cu content and exceeds the hardness of the TiA and CuA base material.
- 3) The Cu content of TiA/CuA interface increases with the penetration depth of the first TiA build layer. The V650-350 parameter, which had the lowest penetration depth, produced the lowest interfacial thickness (~56 μm) and the highest volume fraction of α' -Ti (30 vol.%) at the TiA/CuA interface. The presence of interfacial α' -Ti is attributed to the imperfect mixing within the melt pool.

Chapter 5 - Fracture of TiA/CuA/SS Multiple Material Part

In this chapter, the TiA/CuA/SS MM parts were subjected to tensile loading and the fracture surfaces of the samples were analysed using SEM and EDX. The characteristic features on the fracture surfaces and the crack propagation paths are rationalized based on the microstructural characteristics of each interface.

5.1 - Experimental Setup

The profile of the tensile samples is shown in Figure 4.1a. The V650-350, V500-350, and V350 tensile samples were excised from their respective MM blocks using wire-cut EDM. During EDM a portion of the V500-350 and V350 samples experienced partial delamination at the TiA/CuA interface due to the relief of residual stress and had to be excluded from the tensile test. Therefore, the tensile strength of the V500-350 and V350 TiA/CuA interface should be interpreted with the appropriate care. On the other hand, none of the V650-350 samples underwent delamination during EDM. Therefore, the tensile tested V650-350 samples were not selected with such bias. Even though the V650-350 samples did not delaminate after EDM, it should be emphasized that residual stresses are, nonetheless, present within the MM part. The V650-350 TiA/CuA interface remained intact because the magnitude of the residual stress was insufficient to cause spontaneous delamination. The sources of residual stress come from 1) rapid quenching of the melt pools and 2) different thermal expansion coefficients of the base alloys. For reference, the average thermal expansion coefficients of TiA and CuA are $\sim 11 \times 10^{-6} \text{ K}^{-1}$ [211] and $\sim 19 \times 10^{-6} \text{ K}^{-1}$ [212], respectively.

Tensile tests were performed using the Instron 5569 universal testing machine under a crosshead extension speed of 0.02 mm/min. The fracture surfaces of the samples were examined using SEM. Local composition measurements were obtained using EDX.

5.2 Fracture Surface Characteristics

5.2.1 - Morphology

The stress vs crosshead extension curves for the various samples are shown in Figure 5.1. The ultimate tensile strength (UTS) of the V650-350, V500-350 and V350 samples are 523 ± 1 MPa, 496 ± 23 MPa and 473 ± 26 MPa, respectively.

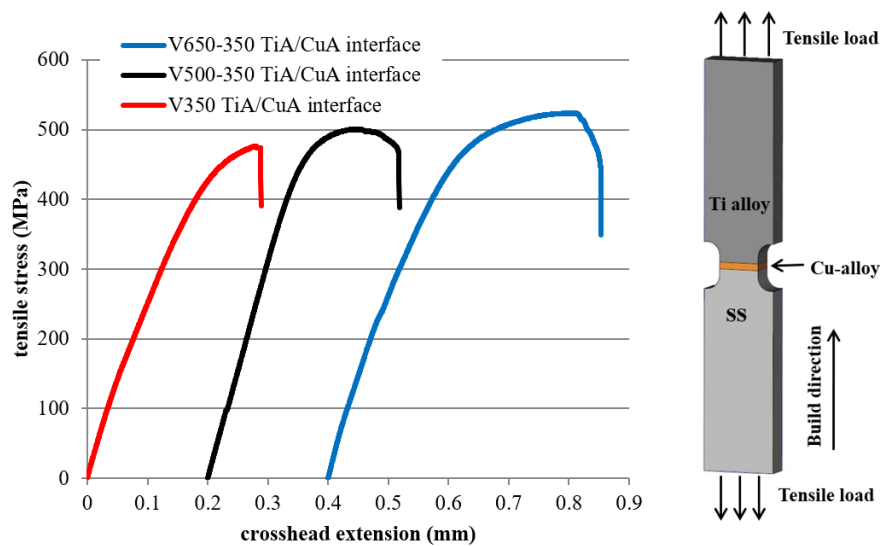


Figure 5.1 Stress versus crosshead extension of TiA/CuA/SS MM parts

The fracture planes of the MM samples were oriented perpendicularly to the tensile loading direction. All fractures initiated from the TiA/CuA interface. Similar features are found on the fracture surfaces of the V650-350, V500-350 and V350 samples. Therefore, only those corresponding to the V650-350 samples are shown in Figure 5.2a-f. Pictures of the V500-350 and V350 fracture surfaces are provided in Appendix C and D, respectively. Figure 5.2a-b shows that the fracture surface is comprised of distinct ductile and brittle regions. The ductile region (Figure 5.2d) is populated by large dimples of 10-40 μm in size and has a composition of Cu(91.7)-Ti(2.5)- Al(0.8)-

Ni(3.3)-Si(1.3)-V(0.1)-Cr(0.4). Therefore, these dimples belong to the ductile CuA interlayer.

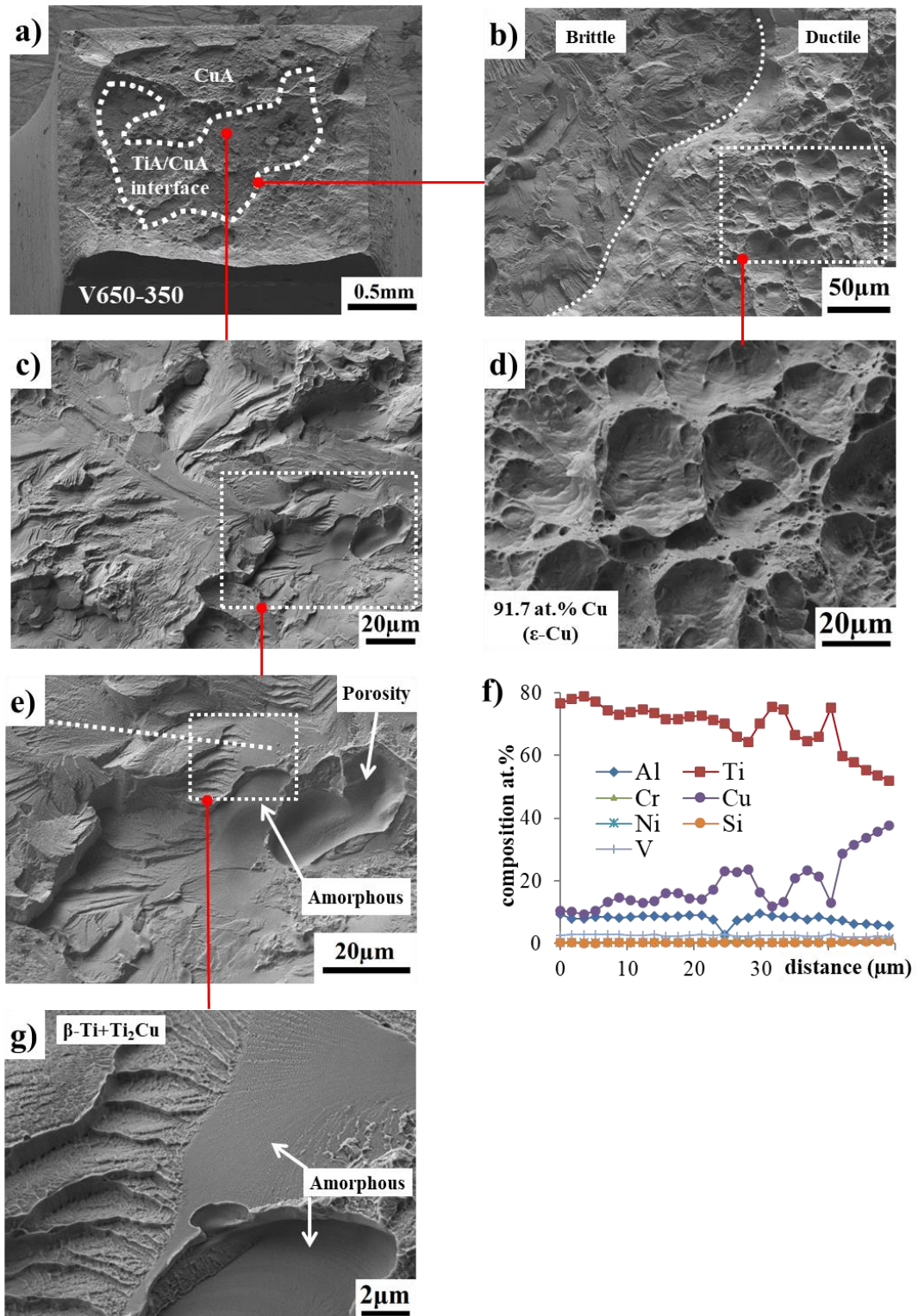


Figure 5.2 Fracture surface of the V650-350 TiA/CuA interface. (a) overview, (b) transition between brittle and ductile fracture surface, (c) cleavage fracture surface of TiA/CuA interface, (d) ductile fracture surface of CuA interlayer, (e) fractured amorphous region with neighbouring porosity, (f) EDX composition plot along the dashed line in (e), (g) magnified view of the amorphous and β -Ti+Ti₂Cu fracture surface

The brittle region in Figure 5.2c has a Cu content ranging from 10-38 at.%, hence, it corresponds to the TiA/CuA interface. This brittle region features a cleavage fracture morphology that is decorated with characteristic river patterns. As shown in Figure 5.2c, e & g, the river patterns typically converge towards a seemingly “featureless” region when viewed under relatively low magnifications. EDX measurements taken along the dotted line in Figure 5.2e shows that the featureless region has a composition of Cu(37.6)-Ti(52.0)-Al(5.6)-V(2.0)-Ni(1.5)-Si(0.9)-Cr(0.4) (see Figure 5.2f). High magnification views of the featureless region show that its surface consists of 1) smooth areas with minute perturbations (Figure 5.3a) and 2) areas decorated with a fine dimple-like feature that has a diameter of ~80 nm (Figure 5.3b). The combined evidence from the fracture surface morphology and the ~37.6 at.% Cu content indicates that the featureless region is amorphous.

The dimple-like feature on the amorphous phase is believed to be caused by a combination of 1) localized softening of material ahead of the crack tip, 2) adiabatic heating of material within the shear band, and 3) coalescence of free volume and microvoid nucleation ahead of the crack tip [213, 214]. The combination of these factors led to locally viscous flow ahead of the crack tip which caused the material between the voids to neck down and produce the dimple-like feature on the fracture surface [214]. Given that the size of the dimples scales with the toughness of amorphous metals [213, 214], the amorphous fracture surface with ~80 nm dimples is estimated to have a notched fracture toughness in the order of $\sim 10^0 \text{ MPa}\cdot\text{m}^{1/2}$.

As shown in Figure 5.2e, a ~40 μm porosity is present next to the amorphous region. Since amorphous metals are generally brittle and known to exhibit limited ductility under tensile loads [215], the stress concentration around the porosity likely caused the

amorphous phase to fracture prematurely at a relatively low remote tensile stress of ~500 MPa.

EDX measurements along the dotted line in Figure 5.2e shows that the cleavage fracture surface surrounding the amorphous region has Cu content ranging between 9.5 and 28.7 at.% (Figure 5.2f). Hence, the cleavage surfaces belong to the β -Ti+Ti₂Cu phase mixture. Unlike the smooth amorphous region, the β -Ti+Ti₂Cu fracture surface is extensively decorated by river patterns which are observable in the scale of 10⁰-10¹ μ m (Figure 5.2g). In the 10⁻¹ μ m scale, small and shallow dimples can be observed on the fracture surfaces of the β -Ti+Ti₂Cu phase mixture (Figure 5.3c & d). Compared to the dimples on the amorphous region (Figure 5.3b), those on the β -Ti+Ti₂Cu fracture surface are significantly larger.

The dimple size on the β -Ti+Ti₂Cu fracture surface decreased from 0.1-0.4 μ m to 0.08-0.26 μ m as its Cu content increased from 16.6 at.% (Figure 5.3d) to 28.1 at.% (Figure 5.3c). The observed change in dimples size is likely related to the microstructure of the β -Ti+Ti₂Cu phase. Specifically, these dimple sizes are comparable to the ~0.2-0.5 μ m spacing between the Ti₂Cu particles (see Figure 4.14). Therefore, the dimples likely nucleated from the Ti₂Cu second phase particles [216]. The higher Cu content led to 1) an increased density of Ti₂Cu particles, 2) an increased frequency of void nucleation at the Ti₂Cu particles, and 3) reduced dimple sizes. Even though the β -Ti+Ti₂Cu fracture surface is populated by sub-micron dimples, these dimples only represent localized plasticity and have limited contribution to the overall ductility. Hence, the β -Ti+Ti₂Cu phase mixture remains brittle as shown by its extensive river patterns and cleavage fracture surfaces (Figure 5.2c & e).

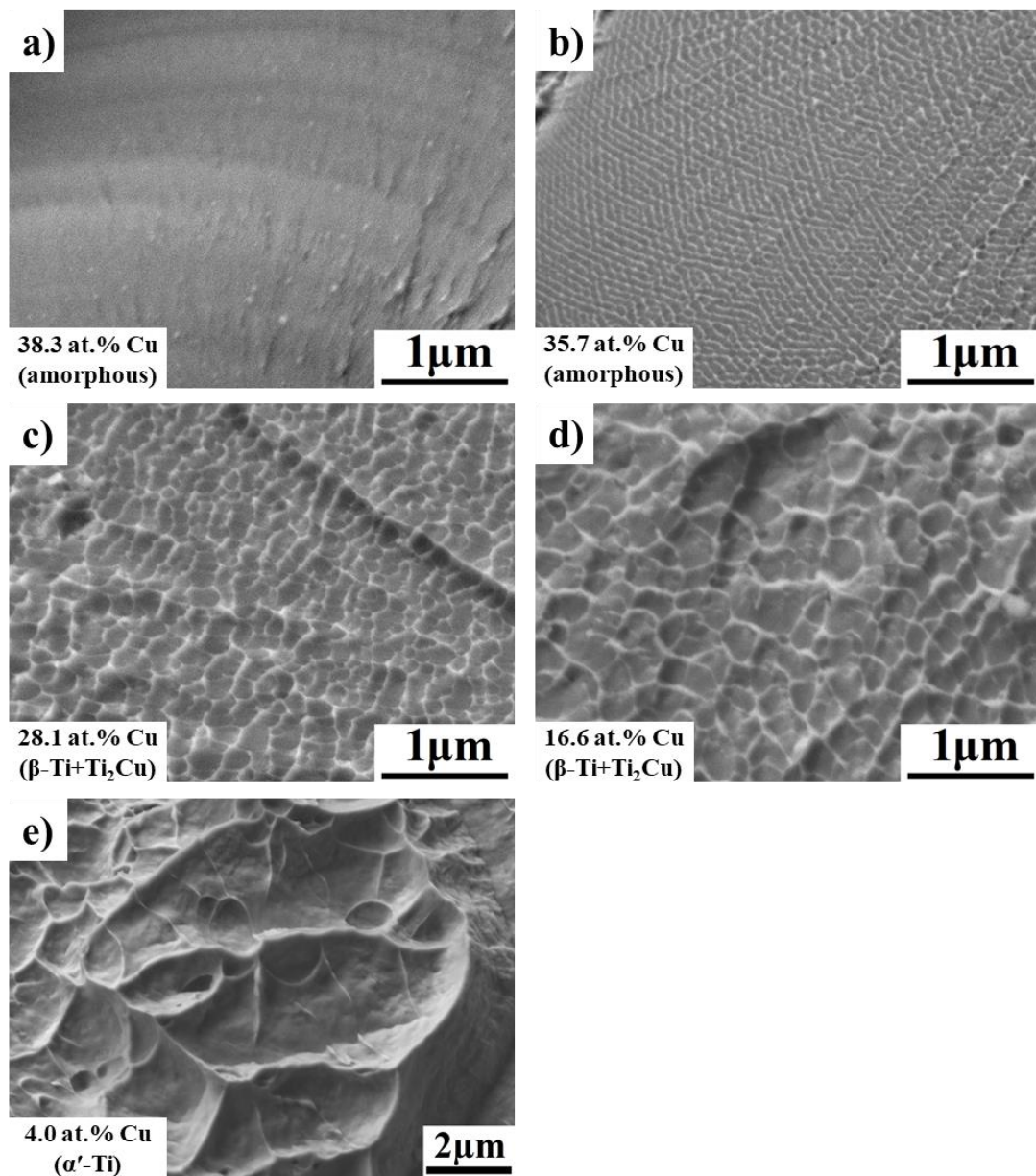


Figure 5.3 SEM images of fracture surfaces containing (a) 38.3 at.% Cu, (b) 35.7 at.% Cu, (c) 28.1 at.% Cu, (d) 16.6 at.% Cu, and (e) 4.0 at.% Cu.

In contrast, the α' -Ti phase with only 4.0 at.% Cu (Figure 5.3e) fractures in a more ductile manner, featuring larger dimples of 1-3 μm in size. The phase/s ranked in the order of decreasing dimple sizes is as follows: ϵ -Cu (91.7 at.% Cu), α' -Ti (4.0 at.% Cu), β -Ti+Ti₂Cu (16.6 at.% Cu), β -Ti+Ti₂Cu (28.1 at.% Cu), and amorphous phase (38.3 at.% Cu). This order of decreasing dimple size coincides with the increase in hardness from 2.3 GPa for the ϵ -Cu phase to 7.9 GPa for the amorphous phase. This suggests

that the brittleness of the constituent phases at the TiA/CuA interface increases with its Cu content.

As shown in Figure 5.2b, the transition between the brittle and ductile fracture surfaces occurs via a step change in height. This suggests that the fracture path experienced an abrupt deflection during its transition. To identify the cause of this deflection, the cross-sectional view of the fractured sample was investigated.

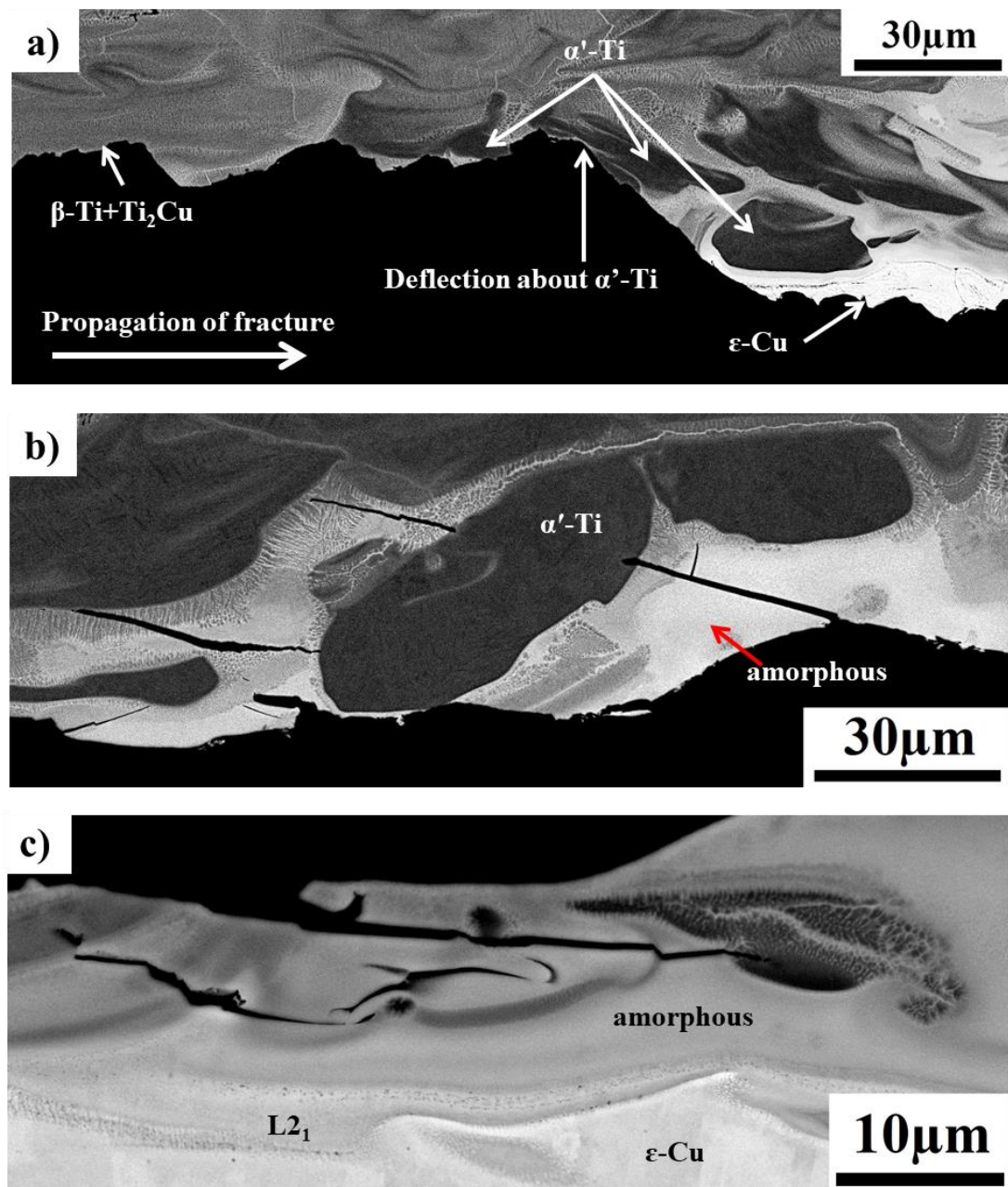


Figure 5.4 Cross-sectional view of fracture surfaces showing (a) a major crack deflection at an α' -Ti region, (b) crack propagating around an α' -Ti region, and (c) multiple cracks in the amorphous region

Figure 5.4a shows the cross-sectional view of the fractured sample at the transition point. Before transiting into the ductile region, the crack propagated within the β -Ti+Ti₂Cu phase mixture. During which, the crack may encounter small and isolated regions of α' -Ti phase which caused it to undergo minor deflection while remaining within the β -Ti+Ti₂Cu phase mixture. The relatively high toughness of the α' -Ti phase makes it more fracture-resistant than the β -Ti+Ti₂Cu phase mixture, hence, the crack is deflected by the small and isolated α' -Ti region. However, when the crack is channelled into a large cluster of α' -Ti, it is forced to take a major deflection in the downward direction, towards the CuA interlayer (Figure 5.4a). In its downward deflection, the crack penetrates the thin layers of L2₁ and amorphous phase and enters the CuA interlayer. As a result, a portion of the fracture surface featured large dimples belonging to the ϵ -Cu phase (Figure 5.2d). The crack generally favours a downward deflection, towards hard and brittle phases with higher Cu content. Conversely, an upward deflection is energetically unfavourable as it leads towards tougher phases which have a lower Cu content.

In addition to being deflected, the cross-sectional image from the V350 fracture surface (Figure 5.4b) showed that cracks may also 1) propagate around the α' -Ti region without deflection and 2) be arrested at an α' -Ti region. The multiple cracks found within the amorphous region (Figure 5.4c) indicates that it is a fracture initiation site, which is consistent with the observations in Figure 5.2c, e & g.

5.2.2 Area Fraction of Constituent Phases on Fracture Surfaces

Even though similar characteristic features are observed on the V650-350, V500-350 and V350 fracture surfaces, the area fraction of the ductile and brittle fracture surfaces are different. Figure 5.5a-c shows qualitatively that the area fraction of ductile ϵ -Cu surfaces decreased significantly from the V650-350 sample to the V350 sample.

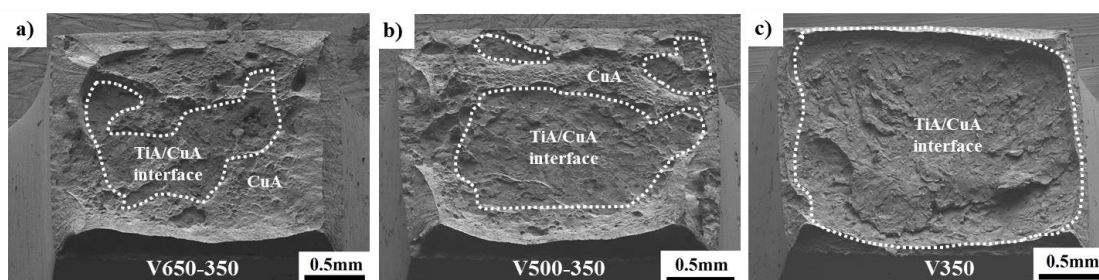


Figure 5.5 Fracture surface of the MM parts processed by (a) V650-350, (b) V500-350 and (c) V350 parameter

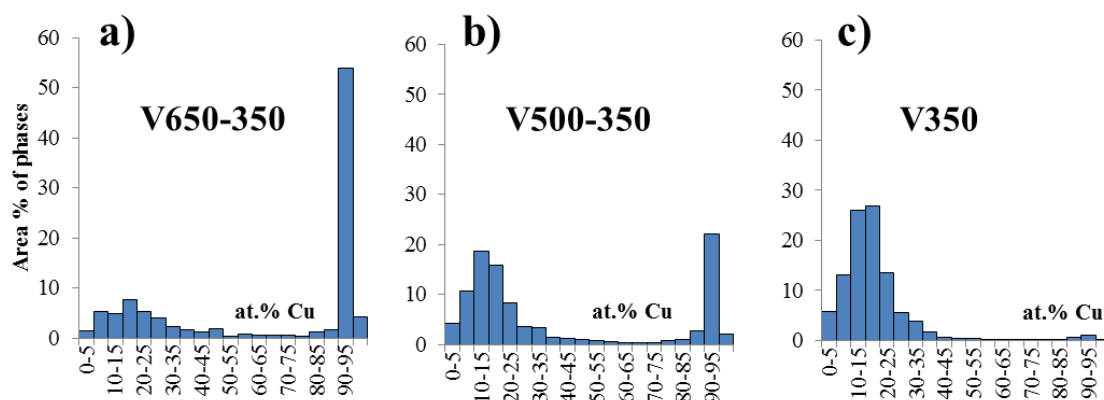


Figure 5.6 Area fraction of phases on the (a) V650-350, (b) V500-350, and (c) V350 fractures surfaces

The area fraction of various phases was estimated by taking 352 evenly spaced point EDX measurements from each fracture surface. The data points for all the fracture surfaces were accumulated, sorted according to their Cu content, and then displayed as distribution plots in Figure 5.6a-c. Notably, ~58 % of the V650-350 fracture surface is comprised of ϵ -Cu phase (>90at.% Cu) while the V500-350 and V350 interfaces contained only ~20% and ~1% of the ϵ -Cu fracture surface, respectively. The large difference in the proportion of ϵ -Cu fracture surface is again attributed to the different volume fractions of α' -Ti within the respective interfaces. Since the V650-350 TiA/CuA interface contains the highest volume fraction of α' -Ti (see Figure 4.20), a crack propagating in such an interface is more likely to encounter an α' -Ti region and be deflected into the underlying CuA. Hence, the V650-350 fracture surface contains a higher area fraction of ϵ -Cu phase. As the α' -Ti phase is relatively tough and does not fracture easily, the area fraction of α' -Ti phase (0-5 at.% Cu) is low across all fracture

surfaces. All of the distribution plots in Figure 5.6 feature a local peak in the range of 10-20 at.% Cu. This again indicates that fracture prefers to propagate within the β -Ti+Ti₂Cu phase, which is consistent with prior observations. Even though the amorphous phase (35-45at.% Cu) is often the fracture initiation site, it comprises only a small area fraction within the fracture surfaces.

5.3 - Discussion

The fracture paths of the V650-350 and V350 TiA/CuA interfaces are illustrated in Figure 5.7. When the MM sample is loaded in tension, stress concentrations start to build up around defects. Once a brittle region with a neighbouring stress concentrator is loaded beyond its critical limit, it begins to seed cracks into the surrounding β -Ti+Ti₂Cu phase mixture. When the crack encounters relatively small and isolated regions of α' -Ti within the interface, it could either be pinned or deflected by the reinforcement phase. Crack deflections result in a non-planar crack that tilts around the interfacial α' -Ti regions (Figure 5.4a) while crack pinning results in a non-linear crack front but without crack deflection (Figure 5.4b). The low area fraction of α' -Ti on the fracture surfaces (Figure 5.6) indicates that crack bridging by the plastic deformation of α' -Ti is insignificant. On encountering a large region of α' -Ti phase, the crack is forced to take a major deflection towards the underlying CuA interlayer, leading to a dimpled fracture surface.

Fracture within the V350 TiA/CuA interface occurs in a similar manner. However, due to its larger interfacial thickness and lower volume fraction of α' -Ti (~10 vol.%), the crack can easily deflect around the α' -Ti regions without being forced into the underlying CuA. Hence, the ϵ -Cu phase is absent on the V350 fracture surfaces.

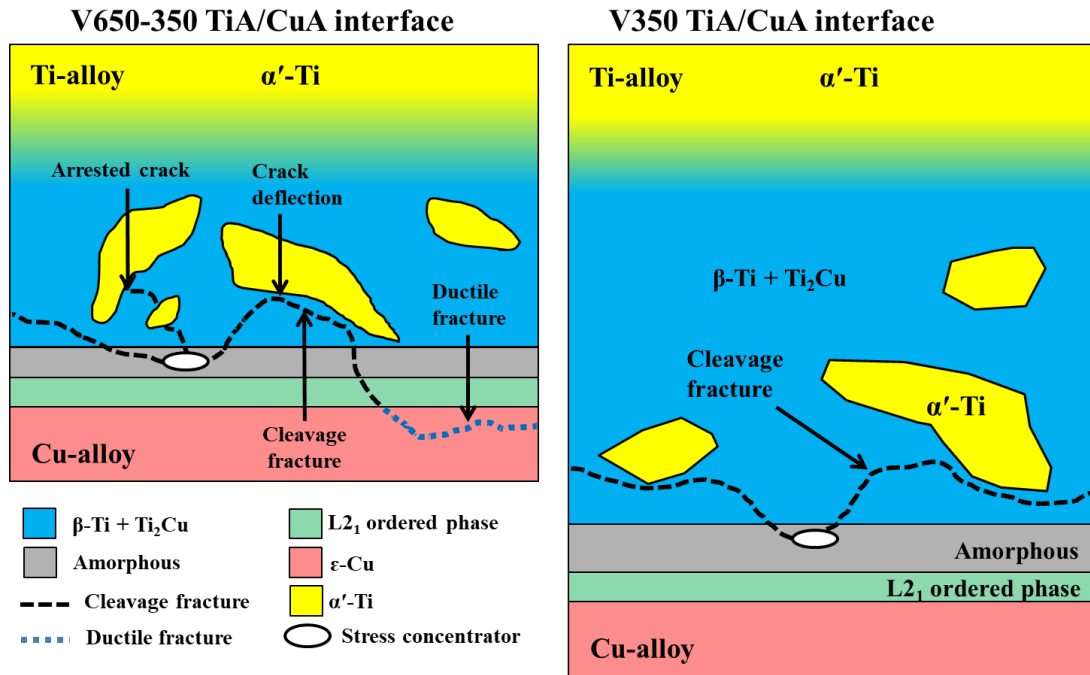


Figure 5.7 Illustration of fracture paths within the TiA/CuA interface.

Assuming the elongated interfacial α' -Ti regions may be approximated as disk-shaped reinforcements with a diameter to thickness ratio of ~ 3 , Faber and Evans showed that crack deflections caused by ~ 20 vol.% of such reinforcements could double the material toughness [217]. Additionally, Faber and Evans indicated that the material toughness approaches an asymptotic limit as the crack-deflecting reinforcements increases to ~ 20 vol.% and beyond [217].

The toughness of the TiA/CuA interfaces investigated in this study, however, seemed to improve even as the interfacial α' -Ti increased to 30 vol.% in the V650-350 samples. This is inferred from the fact that the V650-350 TiA/CuA interface, which contained ~ 30 vol.% of α' -Ti, did not delaminate during EDM. In comparison, some of the V500-350 TiA/CuA interfaces containing 23 vol.% of α' -Ti underwent partial delamination. The inferred toughening of the TiA/CuA interface beyond 20 vol.% of α' -Ti indicates that factors other than crack deflection could be at work. One reason could be due to the reduced thickness of the intermetallic and amorphous layers at the

V650-350 TiA/CuA interface (see Table 4.3). The narrower interface combined with the higher volume fraction of α' -Ti could have further restricted the crack propagation path, leading to improved toughness. Additionally, the toughness contribution from crack pinning, which had not been accounted for, could have led to continued toughening of the TiA/CuA interface as the amount of reinforcement increased beyond 20 vol.% [217, 218]. Although the percolation threshold of the interfacial α' -Ti needed to suppress delamination cannot be determined precisely, it is estimated to be ~30 vol.% for the interfaces investigated in this study.

Given that 1) toughness obtained from crack deflection is invariant with reinforcement size [217] and 2) reinforcement size only has a secondary effect on toughness obtained from crack pinning [218], the toughness of the TiA/CuA interface should, therefore, be a weak function of reinforcement size. However, this weak dependence may no longer be true when the reinforcement size becomes comparable to the interfacial thickness. As observed in the V650-350 TiA/CuA interface, cracks could not propagate around the large α' -Ti reinforcements without being diverted into the CuA interlayer. Hence, ductile CuA fracture surfaces were observed. Although the interfacial fracture toughness was not evaluated, the partially ductile V650-350 fracture surface likely possessed higher toughness compared to the cleavage dominated V500-350 and V350 fracture surfaces. Therefore, the influence of reinforcement size on interfacial toughness is likely more pronounced when the reinforcement size becomes comparable to the interfacial thickness. Otherwise, the dependence is expected to be weak.

The beneficial presence of α' -Ti phase at the TiA/CuA interface is attributed to 1) the low interfacial Cu content and 2) non-homogeneous mixing within the melt pools. Interfacial Cu content is minimized by using a low laser energy input and low layer

thickness in the first TiA build layer. This minimizes the melt pool penetration depth into the CuA interlayer while maintaining marginal melt pool stability.

By processing the TiA/CuA interface with a low laser energy input, the magnitude of the convective flow in the melt pools is reduced. This results in greater composition non-homogeneity within the melt pool and leads to a larger volume fraction of Cu-poor regions (<5 at.%) within the interface. During solidification and cooling, the Cu-poor regions, in turn, transform into the α' -Ti phase which toughens the interface through crack deflection and pinning.

Since the V650-350 parameter features the lowest dilution at the TiA/CuA interface, it has the lowest interfacial thickness and the highest amount of interfacial α' -Ti phase. As a result, it featured frequent crack deflections into the CuA interlayer, has improved toughness, and possessed the highest tensile strength among the MM parts.

During the parametric optimization process, only the laser scanning velocity has been varied across the different parameters. Other parameters such as laser power and laser spot size can also be varied to further minimize the melt pool penetration depth and dilution at the TiA/CuA interface. Although the V650-350 parameter obtained through a simple variation in laser scanning velocity is unlikely to be optimal, the tensile strength of the additively manufactured TiA/CuA/SS MM part is already among the highest considering all other joining and AM techniques used to bond TiA to steel with or without the use of interlayer/s [12-21, 28, 32, 40, 45, 49, 53, 70, 121, 124-127, 154, 219-221]. Furthermore, the active deflection of the fracture path from the brittle phases to the ductile interlayer is deemed to be a desirable and unique characteristic which is rarely reported for MM combinations containing brittle reaction products. The ability to limit dilution, control the interfacial thickness, and introduce tough

reinforcement phase through melt pool non-homogeneity are beneficial characteristics of the SLM process. This makes the SLM process potentially viable for MM processing despite its relatively low utilization for such a purpose.

5.4 - Summary

The morphology and constituent phases on the fracture surfaces have been investigated and the key findings are:

- Cracks initiate from the brittle amorphous phase due to stress concentrations from neighbouring porosities. After initiation, the cracks were observed to extend into the β -Ti+Ti₂Cu phase mixture.
- A crack propagating in the β -Ti+Ti₂Cu phase would encounter isolated regions of relatively tough α' -Ti phase that could either deflect or pin the crack. In the event where a large cluster of α' -Ti is encountered, the crack would be forced to deflect towards the underlying CuA interlayer. As a result, ductile CuA dimples are present on the fracture surfaces.
- The V650-350 TiA/CuA interface featured the highest tensile strength of 523 MPa. The high strength is attributed to its low interfacial thickness, thin amorphous layer, and high volume fraction of tough interfacial α' -Ti (~30 vol.%). Frequent crack deflections from the TiA/CuA interface to the CuA interlayer resulted in 58 % of ϵ -Cu phase on the V650-350 fracture surface. In contrast, the V350 TiA/CuA interface, which contains only 10 vol.% of α' -Ti, fractured with a negligible amount of ϵ -Cu on its fracture surface.

Chapter 6 – Conclusions and Future Work

6.1 - Conclusion

A multiple-material part consisting of Ti-6Al-4V, HOVADUR® K220 Cu alloy and 316L stainless steel was uniquely produced using the SLM process. The exclusive interfacial microstructure and fracture characteristic of the MM part showed that SLM has a unique potential for MM processing. The novel findings and contributions in this thesis are divided into three chapters. In chapter 3, an experimental methodology was developed to derive optimal process parameters for the TiA/CuA and CuA/SS interfaces. The parameter is defined to be optimal if 1) the processed melt pools are stable and continuous across the build layers and 2) the penetration depth of the melt pool is minimized to achieve the lowest interfacial dilution. These conflicting requirements were simultaneously achieved by 1) suppressing the layer thickness in the interfacial build layers to enhance melt pool stability and 2) using a low laser energy input to limit dilution at the interface. As the chemical composition and thermophysical properties changed across the interface, the laser energy input was correspondingly varied to maintain consistent melt pools.

In chapter 4, TiA/CuA/SS MM parts were produced using the devised parameters and the microstructure of the respective interfaces was studied in detail. The CuA/SS interface contained a non-homogeneous mixture of liquid-phase-separated ϵ -Cu and γ -Fe phases. No detrimental phase was detected. The γ -Fe phase existed as micron-sized SS globules and elongated SS bands within a matrix of ϵ -Cu phase. The hardness of the interface had intermediate values that lie between the bulk SS and CuA. The γ -Fe phase, due to its higher melting temperature, solidify before the surrounding CuA matrix. As the ϵ -Cu and γ -Fe phases have identical crystal structures and similar lattice

constants, the pre-solidified SS globules became low energy nucleation sites for the solidification and growth of CuA grains. As a result, CuA grain refinement was observed at locations containing a high density of finely dispersed SS globules. The morphology of the CuA grains changed from equiaxed to columnar when the SS nucleation sites become sufficiently depleted towards the end of the interface.

The microstructure at the TiA/CuA interface was found to consist of different layers of phase/s arranged in the following order starting from the CuA interlayer: L2₁ order phased, amorphous phase, and a composite layer of α' -Ti islands within a matrix of β -Ti+Ti₂Cu. The L2₁ ordered phase has a similar crystal structure and lattice constant as the Cu₂TiAl Heusler compound. Each of these phase/s can be uniquely identified from its range of Cu content. Specifically, the L2₁ ordered phase forms at 55-65 at.% Cu, the amorphous phase at 35-45 at.% Cu, the β -Ti+Ti₂Cu phase mixture at 5-30 at.% Cu, and the α' -Ti phase at 0-5 at.% Cu. The hardness of the phase/s increases with Cu content and changes from 4.9 GPa for the α' -Ti phase (0-5 at.% Cu) to 7.9 GPa for the amorphous phase (35-45 at.% Cu). The thickness of these hard and brittle phases can be reduced by lowering the Cu dilution at the interface. Under the V650-350 parameter, the thickness of the L2₁, amorphous, and α' -Ti+(β -Ti+Ti₂Cu) composite layer can be reduced to ~1 μ m, ~2 μ m, and ~52 μ m, respectively. Non-optimal parameters led to thicker layers of detrimental phases. Additionally, the volume fraction of interfacial α' -Ti is also the highest for the V650-350 TiA/CuA interface (~30 vol.%). The presence of interfacial α' -Ti is attributed to the rapid solidification and non-homogeneous mixing within the melt pools.

In chapter 5, the tensile fracture behaviour of the TiA/CuA/SS MM part was investigated. Fracture of the MM part initiated from the brittle phases at the TiA/CuA interface. When the interface is critically loaded, cracks begin to grow from pores that

are located next to a brittle phase, which is typically an amorphous region. As the crack grows, it propagates out of the thin amorphous region into the thicker layer of β -Ti+Ti₂Cu. During propagation, the crack may encounter small regions of α' -Ti phase which could cause it to undergo a minor deflection while remaining within the β -Ti+Ti₂Cu phase. However, when the crack encountered a large cluster of α' -Ti, it was forced to take a major deflection towards the CuA interlayer. Consequently, the fracture path intersected both the TiA/CuA interface and the CuA interlayer and contained a mixture of ductile and brittle areas. The ductile areas belonged to the CuA interlayer and featured large dimples of 10-40 μ m in diameter. In contrast, the brittle areas belonging to the TiA/CuA interface featured a cleavage morphology and was decorated with extensive river patterns. The fracture surfaces of the amorphous, β -Ti+Ti₂Cu, and α' -Ti phases can be differentiated through their fracture surface morphology. The fracture surface of the α' -Ti and β -Ti+Ti₂Cu phases featured dimples of 1-3 μ m and 0.1-0.4 μ m, respectively. In comparison, the amorphous region was either featureless or contained small and shallow dimples of ~80 nm in diameter. The proportion of fracture surface belonging to the CuA interlayer and the TiA/CuA interface varied with the process parameters and interfacial microstructure. The V650-350 TiA/CuA interface contained the highest volume fraction of α' -Ti (~30 vol.%). Therefore, cracks propagating in such an interface were more frequently deflected into the CuA interlayer, resulting in ~58 % of ductile fracture surface. The tensile strength of the V650-350 MM part is over 500 MPa, which is among the highest values reported for similar joints produced by other joining techniques.

The ability to produce a composite-like interface through rapid solidification and non-homogeneous mixing within the melt pool is a unique capability of SLM. Such an

interface has improved toughness due to frequent crack deflections. The findings in this thesis are believed to be relevant for other MM combinations.

6.2 - Future Work

The work presented in this thesis shows SLM has the potential for MM processing. However, further research can be done to expand the knowledge and understanding of the interfacial properties. The proposed future works are:

- Further reduction in the amount of detrimental phase at the TiA/CuA interface. This can be done by diluting the total Cu content in the original V650-350 TiA/CuA interface over a larger thickness such that its average Cu content decreases to less than 5 at.%. In principle, this will suppress the formation of Ti_2Cu and improve the interfacial toughness. Dilution of the interfacial Cu content can be achieved by allowing the melt pools in the upper build layers to penetrate up to the TiA/CuA interface. This spreads the Cu atoms to the upper layers through Marangoni flow.
- Evaluation and reduction of residual stresses at the MM interface. Quenching stresses and differential thermal contraction stresses within the interface makes it prone to delamination. In-process and post-process stress reduction methods can be adopted to minimize the risk of delamination. Such methods may involve a variation in scanning strategy, layer thickness, energy input, substrate preheating, and heat treatment [222-227].
- Investigate the effects of heat treatment on the microstructure at the MM interface. Besides changing the residual stresses, post-process heat treatment can also alter the interfacial microstructure in a few ways. Firstly, interdiffusion between the CuA interlayer and the TiA/CuA interface could

lead to the formation of new phases and/or the thickening of existing ones. Secondly, at heat treatment temperatures of 350-507°C or more, the amorphous layer is expected to crystallize into IMCs such as Ti₂Cu, TiCu and Cu₂TiAl [203, 228]. Thirdly, martensitic α' -Ti regions may start to decompose into relatively ductile α -Ti and β -Ti phases at temperatures above 650°C [229]. Lastly, more Ti₂Cu may precipitate from the saturated β -Ti matrix. All of the above will affect the interfacial properties and should, therefore, be investigated.

- Evaluate the properties of MM interfaces produced by other AM techniques such as DED and EBM. As each technique presents its own unique set of characteristics, its advantages could be investigated and compared in future studies. In DED, the relatively large melt pools could potentially be used to dilute the interfacial Cu content over a sufficiently large thickness to suppress the detrimental formation of Ti₂Cu. In EBM, the 700-900 °C heated powder bed could be used to 1) lower the cooling rates and quenching stresses within the melt pools and 2) reduce the differential thermal contraction stresses in the MM part by stress relieve and slow cooling from the elevated preheat temperature. Additionally, the high-temperature powder bed in EBM also results in different interfacial microstructure and mechanical properties.
- Quantify the toughness of the TiA/CuA interface. Impact tests and fatigue crack growth studies can be conducted to evaluate the toughness of the various interfaces. Pre-cracked samples that are progressively loaded up to the point of fracture can be used to easily monitor the crack propagation path within each interface. Additionally, pre-cracks can be seeded in the different

layers, like the TiA, CuA, SS, and CuA/SS interface, to understand how the crack would propagate under various conditions.

- Evaluate the validity of the proposed methodology on other MM combinations. The ability to control dilution and introduce tough phases from the base alloy into the MM interface are features of the SLM process and are not unique to the TiA/CuA interface. Hence, other MM combinations can also be processed using SLM to investigate the properties of the composite-like interfacial microstructure.

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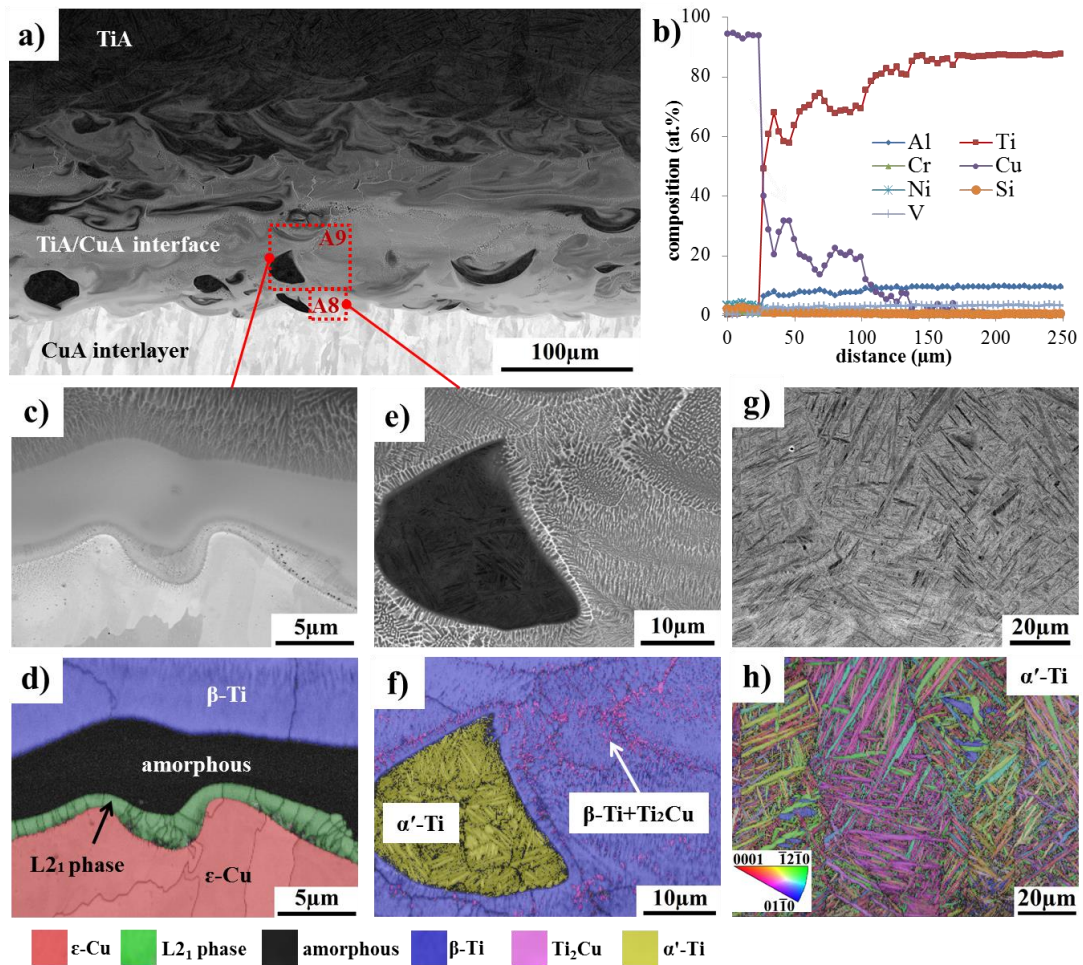
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Appendix A – Cross-sectional images of V350 TiA/CuA interface

This appendix contains the BSE images, phase maps, and IPF of the TiA/CuA interface processed by the V350 parameter.



a) BSE image of the V350 TiA/CuA interface. b) EDX composition measurement across TiA/CuA interface. c) BSE image of region A8. d) Overlay of phase map and band contrast image of region A8. e) BSE image of region A9. f) Overlay of phase map and band contrast image of region A9. g) BSE image of TiA. h) Overlay of IPF and band contrast image of TiA.

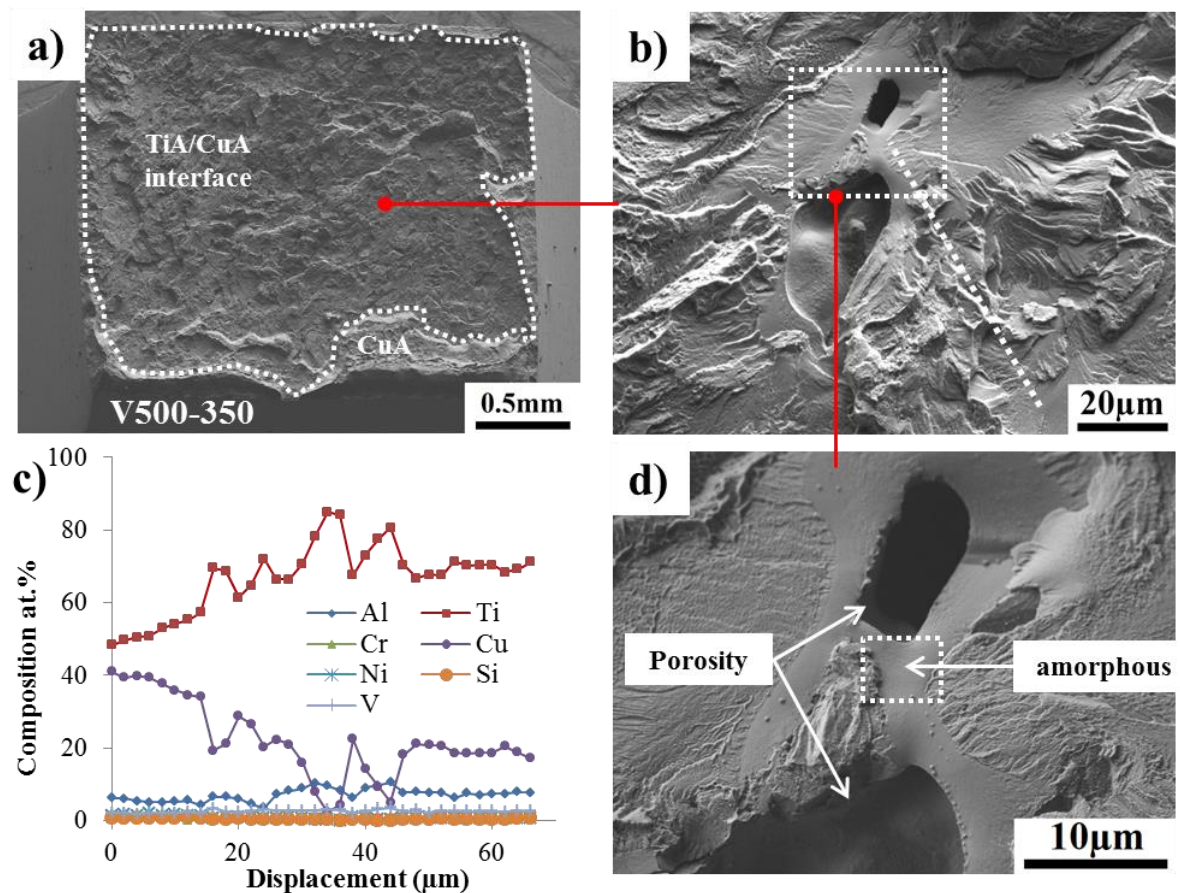
Appendix B – XRD angles of the TiA/CuA interfaces

This appendix contains the diffraction angles obtained from the XRD patterns of the TiA/CuA interfaces processed by the V650-350, V500-350 and V350 parameters. The diffraction angles are obtained using Cu K α radiation at 40 kV and 40 mA.

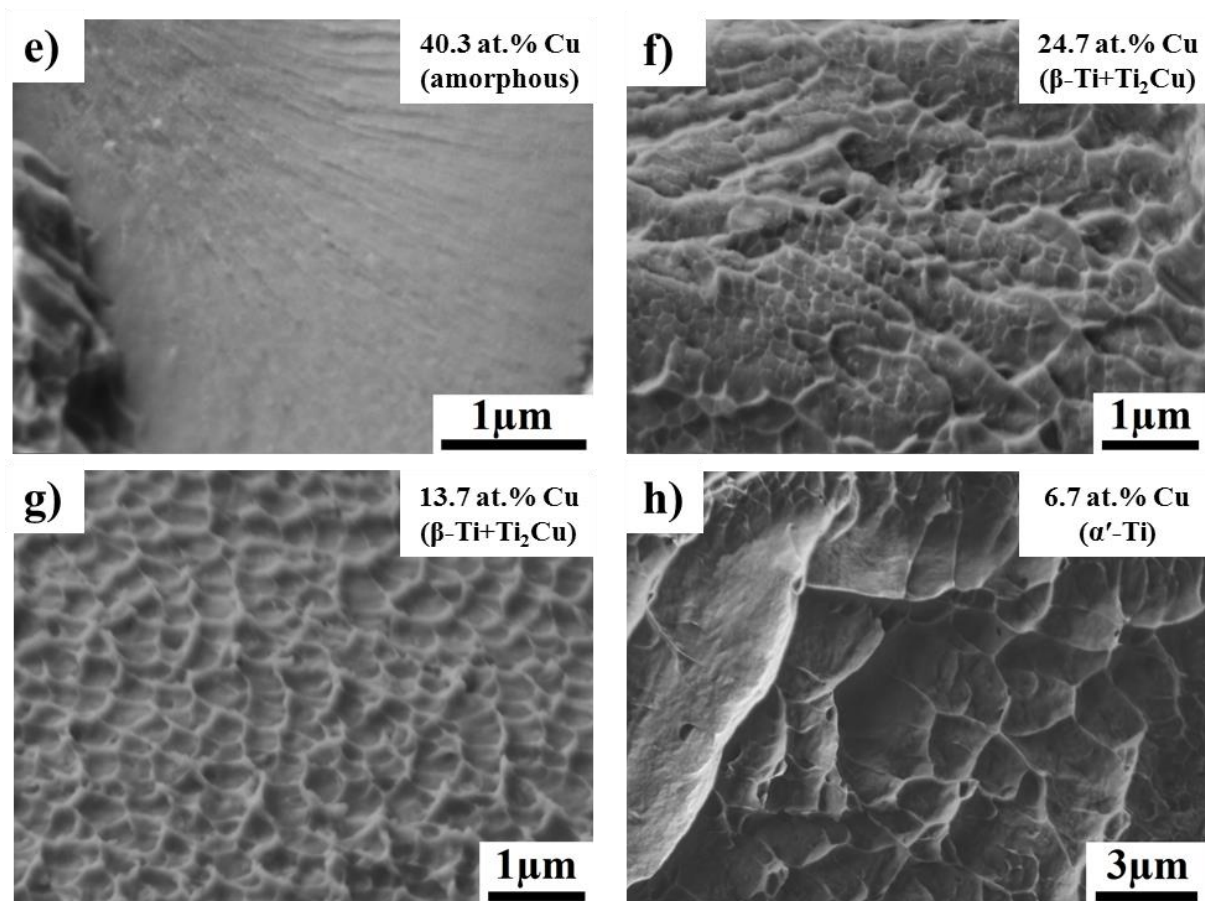
TiA		V650-350		V500-350		V350	
35.46 °	α' -Ti (1 0 -1 0)	35.34 °	α' -Ti (1 0 -1 0)	35.54 °	α' -Ti (1 0 -1 0)	35.31 °	α' -Ti (1 0 -1 0)
38.64 °	α' -Ti (0 0 0 2)	38.74 °	α' -Ti (0 0 0 2)	39.64 °	Ti ₂ Cu (1 0 3), β -Ti (1 1 0)	39.63 °	Ti ₂ Cu (1 0 3), β -Ti (1 1 0)
40.62 °	α' -Ti (1 0 -1 1)	39.55 °	Ti ₂ Cu (1 0 3), β -Ti (1 1 0)	40.24 °	α' -Ti (1 0 -1 1)	43.41 °	Ti ₂ Cu (1 1 0), ϵ -Cu (1 1 1)
53.49 °	α' -Ti (1 0 -1 2)	40.29 °	α' -Ti (1 0 -1 1)	43.43 °	Ti ₂ Cu (1 1 0), ϵ -Cu (1 1 1)	50.27 °	Ti ₂ Cu (0 0 6), ϵ -Cu (2 0 0)
63.51 °	α' -Ti (2 -1 -1 0)	43.33 °	Ti ₂ Cu (1 1 0), ϵ -Cu (1 1 1)	50.26 °	Ti ₂ Cu (0 0 6), ϵ -Cu (2 0 0)	53.60 °	α' -Ti (1 0 -1 2)
71.22 °	α' -Ti (1 0 -1 3)	50.42 °	Ti ₂ Cu (0 0 6), ϵ -Cu (2 0 0)	53.44 °	α' -Ti (1 0 -1 2)	57.17 °	β -Ti (2 0 0)
77.12 °	α' -Ti (2 -1 -1 2)	53.38 °	α' -Ti (1 0 -1 2)	57.53 °	β -Ti (2 0 0)	63.25 °	Ti ₂ Cu (2 0 0), α' -Ti (2 -1 -1 0)
87.90 °	α' -Ti (2 0 -2 2)	57.48 °	β -Ti (2 0 0)	63.21 °	Ti ₂ Cu (2 0 0), α' -Ti (2 -1 -1 0)	69.38 °	Ti ₂ Cu (1 1 6)
93.50 °	α' -Ti (1 0 -1 4)	63.00 °	Ti ₂ Cu (2 0 0), α' -Ti (2 -1 -1 0)	71.93 °	α' -Ti (1 0 -1 3), β -Ti (2 1 1)	71.54 °	α' -Ti (1 0 -1 3), β -Ti (2 1 1)
		71.45 °	α' -Ti (1 0 -1 3), β -Ti (2 1 1)	74.15 °	ϵ -Cu (2 2 0)	74.20 °	ϵ -Cu (2 2 0)
		74.20 °	ϵ -Cu (2 2 0)	77.60 °	Ti ₂ Cu (2 1 3), α' -Ti (2 -1 -1 2)	77.12 °	Ti ₂ Cu (2 1 3), α' -Ti (2 -1 -1 2)
		77.12 °	Ti ₂ Cu (2 1 3), α' -Ti (2 -1 -1 2)	85.52 °	Ti ₂ Cu (2 0 6), β -Ti (2 2 0)	85.51 °	Ti ₂ Cu (2 0 6), β -Ti (2 2 0)
		85.56 °	Ti ₂ Cu (2 0 6), β -Ti (2 2 0)	89.95 °	ϵ -Cu (3 1 1)	90.10 °	ϵ -Cu (3 1 1)
		90.10 °	ϵ -Cu (3 1 1)			98.69 °	β -Ti (3 1 0)
		98.61 °	β -Ti (3 1 0)				

Appendix C – Fracture surface of V500-350 MM part

This appendix contains the images of the fracture surface features belonging to the TiA/CuA interfaces processed by the V500-350 parameter



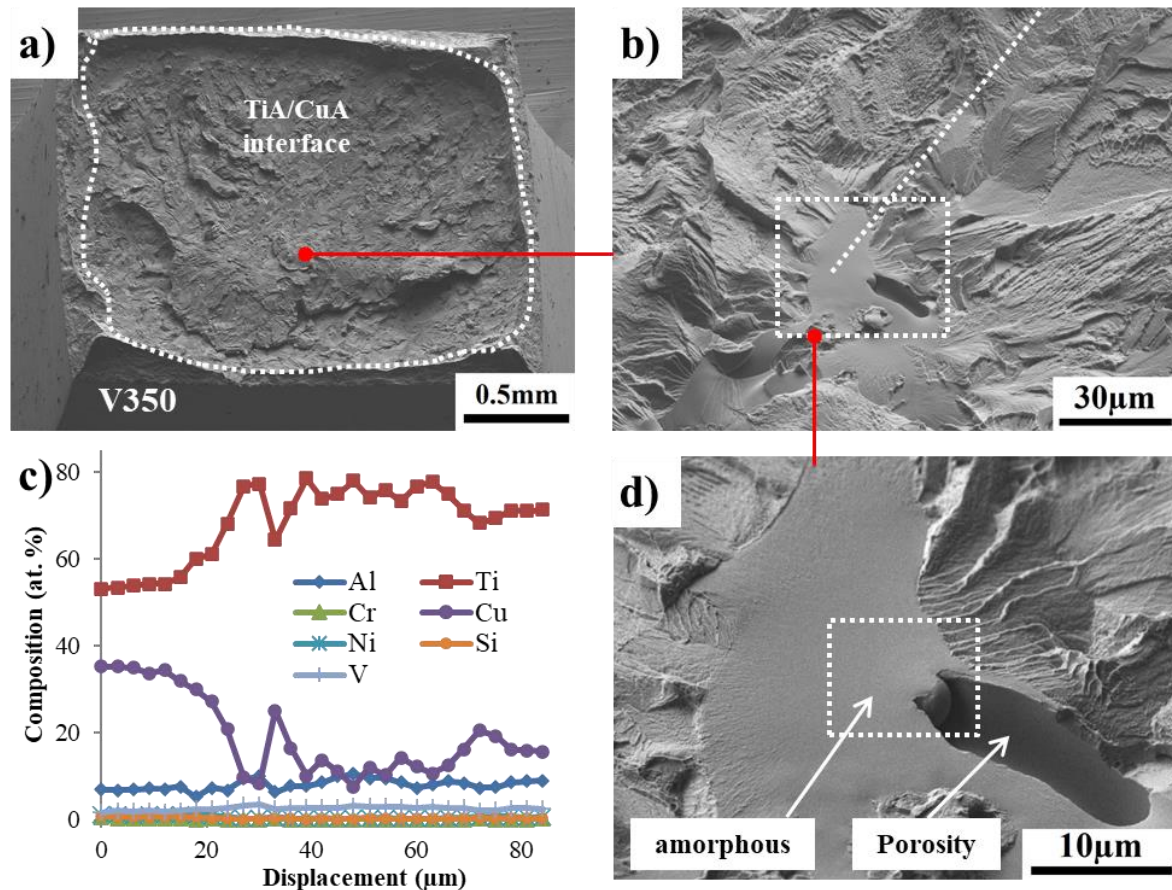
a) SEI image of a fracture surface belonging to the MM part processed using the V500-350 parameter. The area enclosed by dashed line belongs to the TiA/CuA interface. b) Magnified view shows the convergence of river patterns around porosities. c) EDX composition line scan along the dashed line in b). Magnified view of the boxed region in b) shows the presence of porosity in the amorphous phase.



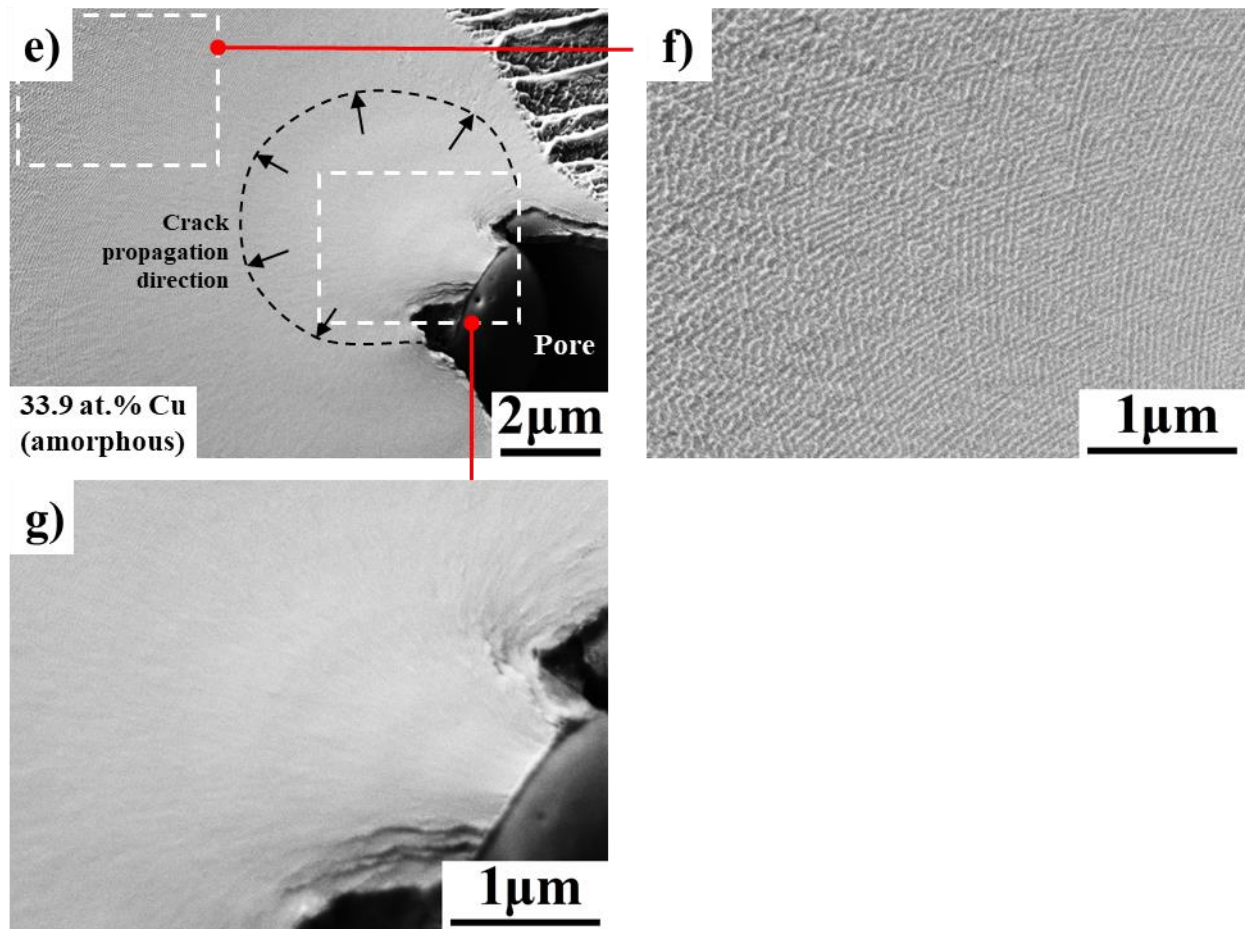
e) Magnified view of the boxed region in d) shows the smooth surface of the amorphous region containing 40.6 at.% Cu. f-g) Sub-micron dimples on the β -Ti+Ti₂Cu fracture surfaces containing 13.7-24.7 at.% Cu. g) Micro-scale dimples on the fracture surface containing 6.7 at.% Cu.

Appendix D – Fracture surface of V350 MM part

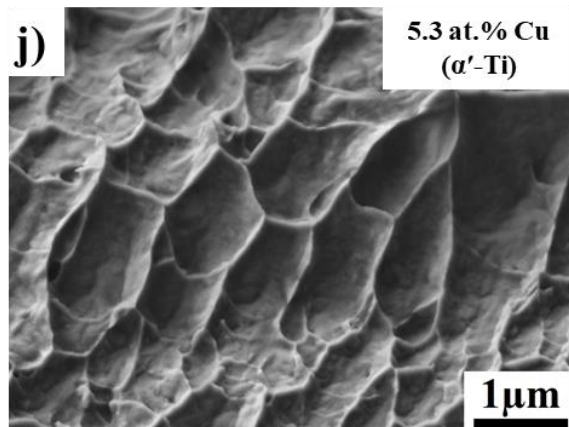
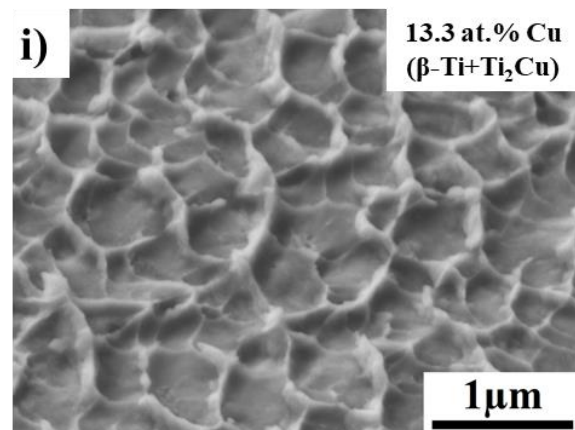
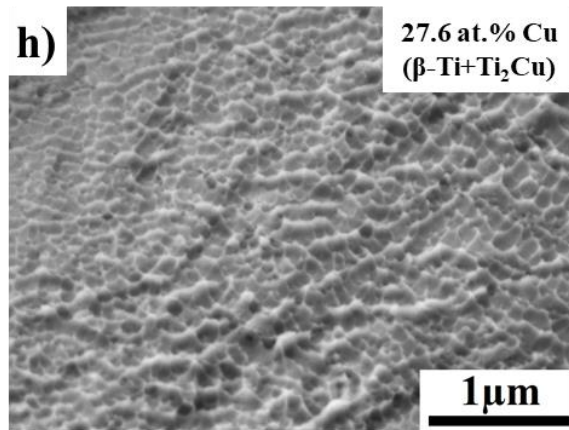
This appendix contains the images of the fracture surface features belonging to the TiA/CuA interfaces processed by the V350 parameter



a) SEI image of a fracture surface belonging to the MM part processed using the 350 parameter. The area enclosed by dashed line belongs to the TiA/CuA interface. b) Magnified view shows the convergence of river patterns around a featureless region. c) EDX composition line scan along the dashed line in b). d) Magnified view of the boxed region in b) shows a pore next to the amorphous region.



e) Magnified view of the boxed region in d) shows the featureless surface of the amorphous region containing 33.9 at.% Cu. f) Localized plasticity on the amorphous fracture surface. g) Featureless amorphous fracture surface next to a pore.



h-i) Sub-micron dimples on the β -Ti+Ti₂Cu fracture surfaces containing 13.3-27.6 at.% Cu. j) Micro-scale dimples on the fracture surface containing 5.3 at.% Cu.