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Additive manufacturing of multiple materials by selective laser melting: Ti-alloy to stainless steel via a Cu-alloy interlayer

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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 been typically 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 this work, the selective laser melting (SLM) process was used to manufacture MM parts which feature steep material transitions from 316L stainless steel (SS) to Ti-6Al-4V (TiA) through an interlayer of HOVADUR® K220 Copper-alloy (CuA). The microstructure in both the CuA/SS and TiA/CuA interfaces were examined in detail and the latter was found to be the critical interface as it contained three detrimental phases (i.e. L2₁ ordered phase, amorphous phase, and Ti₂Cu) which limit the mechanical strength of the overall MM part. By making use of the non-homogeneity within the melt pool and limiting the laser energy input, the relatively tough

interfacial α' -Ti phase can be increased at the expense of other brittle phases, forming what is essentially a composite structure at the TiA/CuA interface. During tensile testing, the interfacial α' -Ti phase is capable of deflecting cracks from the relatively brittle TiA/CuA interface towards the ductile CuA interlayer and an overall tensile strength in excess of 500 MPa can be obtained. This method of introducing an interfacial composite structure to improve MM bonding is envisioned to be applicable for the SLM of other metallic combinations as well.

Keywords: Multiple materials, Additive manufacturing, Powder bed fusion, Selective laser melting, Titanium alloy, Stainless steel, Interface

1. Introduction

The defining characteristic of additive manufacturing (AM) is the deposition and fusion of material at selective locations on the exposed component surface. This trait of AM not only allows geometrically complicated shapes to be manufactured, it can also be used to process multiple materials (MM) parts featuring site-specific properties [1]. Due to the relative ease of mixing and/or switching between different material compositions in real-time, directed energy deposition (DED) techniques have been frequently used to process MM parts and functionally graded materials [2-6]. On the other hand, MM processing can also be achieved using powder bed fusion (PBF) techniques such as SLM through the use of a modified powder deposition mechanism which comprises of a series of nozzles that hold and deposit different powders on selective locations within the powder bed [7, 8]. Recently, the incorporation of such a powder deposition mechanism into a conventional SLM system has been demonstrated by Wei et al. [9].

Conventionally, MM parts are obtained through joining processes such as laser welding [10, 11], electron beam welding [12-14], friction stir welding [15], explosive welding [16, 17], diffusion

bonding [18, 19] and so on [20]. By definition, all joining processes revolve around the merger of two surfaces. This imposes certain limitations on the geometrical design of the interface as well as the spatial distribution of different materials. In diffusion bonding and explosion welding planar or near-planar mating surfaces are often required for the application of uniform contact pressure. In other joining processes such as friction stir welding, laser welding and electron beam welding, the location of the MM joint needs to be accessible by the respective tools. These requirements deny material variation within internal features and around tight geometries. However, such constraints are non-existent in AM as the concept of joining is naturally incorporated into the material addition process via a change in feedstock powders [1, 3].

MM combinations have been frequently utilized to vastly expand the functionalities of components beyond the limitations of a single material [1, 3, 20, 21]. Among the numerous MM combinations, the processing of titanium/titanium alloys to steel is one that has attracted much attention. The favorable combination of corrosion resistance from titanium alloys and the wide range of properties from relatively low-cost steels have applications in the nuclear, chemical and aerospace industries [5, 6, 11, 15, 16, 18, 19, 22-24]. However, a direct bond between steel and titanium is often compromised by the formation of detrimental Fe-Ti intermetallic compounds (IMCs). Under the high residual stresses that are known to exist in the DED and SLM processes [25-28], these brittle IMCs could fracture and lead to delamination [22]. Regardless of the type of joining or AM techniques used, the minimization of such Fe-Ti IMCs has always been vital to the integrity of the Fe/Ti bond [5, 6, 11, 14-16, 18, 19, 22-24]. A common approach to circumvent the formation of Fe-Ti IMCs is to introduce interlayer materials such as Cu [29-35], Ni [36, 37], and others [23, 38-40] to partition the Fe and Ti atoms. While these interlayers do prevent the formation of Fe-Ti IMCs and usually do not react with steels to form brittle phases,

they interact with Ti atoms to form Cu-Ti [29-34] or Ni-Ti IMCs [36, 37]. Although such IMCs are commonly regarded to be less detrimental as compared to the Fe-Ti IMCs, its minimization is still necessary for optimal bonding [29-34, 36, 37]. The complete elimination of interfacial IMCs can be achieved using a series of interlayers, which individually do not form brittle IMCs with its immediate neighbors [41, 42]. The use of a series of interlayers with different compositions to avoid brittle phase formation can be generalized under the “gradient path” approach suggested by Hofmann et al. [4]. It was shown that the gradient path connecting the base alloys can be deliberately planned out using multi-component phase diagrams to avoid brittle phase formation. Subsequent studies showed that thermodynamic calculation performed within the appropriate temperature range is, to a certain extent, capable of capturing the phases present within the functional gradient [2, 5, 22]. Due to the continuous variation in composition, such functional gradients generally span across tens of layers and could reach a thickness of several millimeters [2, 4, 5, 22]. While a gentle transition in material properties is favorable for reducing mechanical stress concentrations [43], there may also be scenarios where a steep transition in composition may be useful. Instead of adopting a continuous composition gradient to circumvent brittle phases, a discontinuous composition jump could also be a viable option to avoid or minimize brittle phase formation [5]. Furthermore, the composition gradient, which is chosen to avoid brittle phase formation, may not necessarily offer favorable functional properties pertaining to the operating environment of the component. In these hypothetical scenarios a steep transition in composition and properties, as is the case for most joining processes, may be useful.

In this study, Ti-6Al-4V/HOVADUR® K220 copper alloy/316L stainless steel MM parts, which feature steep composition transition across material interfaces were built using the SLM process. The choice of using the SLM process over the commonly employed DED techniques is due to

the disparity between its potential for MM processing and the lack of associated literature [9, 44, 45]. The CuA interlayer was deliberately added between the TiA and SS alloys to eliminate the formation of detrimental Fe-Ti intermetallic compounds [29-35]. The laser processing parameters for the TiA/CuA interface were intentionally altered to reduce the amount of brittle interfacial phases. The microstructure at the CuA/SS and TiA/CuA interfaces were characterized in detail. The relationships between the laser parameters, melt track dimensions, interfacial phases and fracture morphology were discussed. Accordingly, potential strategies and suggestions to improve interfacial bond properties were proposed.

2. Materials and Methods

2.1 Selective laser melting of single tracks and multiple material parts

The MM parts, which consist of a 316L stainless steel (base), a K220 HOVADUR® copper alloy (interlayer) and a Ti-6Al-4V (top), were built using the SLM250HL machine from SLM Solutions AG (Fig. 1a). The machine is equipped with a 400W laser system with a measured spot diameter of ~0.095 mm and operates in an argon-flushed chamber. All spherical metallic powders (Fig. 1b) were sieved through a 63 μm -sized mesh to remove oversized particles before use. The compositions of the major elements in the powders are stated in atomic percentage as shown in Table 1. All composition values reported in this paper are given in atomic percentage.

Fig. 1. (a) Build configuration of MM part and dimensions of the tensile sample. (b) Morphology of powder used for the builds. (c) Illustration of the chessboard scanning strategy used during the SLM process.

Table 1

Composition of the major elements in the respective powders (at.%).

Ti-6Al-4V Grade 23	Ti(85.9)	Al(10.3)	V(3.8)	-	-	-
HOVADUR® K220	Cu(95.2)	Ni(3.1)	Si(1.3)	Cr(0.4)	-	-
SS316L	Fe(65.3)	Cr(18.9)	Ni(10.6)	Mn(2.1)	Si(1.9)	Mo(1.2)

Prior to building the actual MM part, single track studies were conducted to investigate the effects of laser parameter on melt track dimensions and morphology. Three different parameters were used to deposit single tracks of TiA on CuA substrates while a single parameter was used to deposit CuA tracks on SS substrates (Table 2). Both the SS and CuA substrates were ground and powder blasted with SS and TiA powders respectively to a resultant average roughness (R_a) of $\sim 2 \mu\text{m}$ prior to the deposition of the single tracks. Penetration depth and track width measurements were obtained using optical microscopy from the cross-section and top view of the single tracks respectively. The morphology and stability of the single tracks were qualitatively accessed from the scanning electron microscopy (SEM) images.

Table 2

SLM parameters used to process the single tracks and MM parts. For the single track study, the hatch distance and layer thickness are irrelevant and only the laser scanning velocity pertaining to layer 1 was applied.

Sample	Ti-6Al-4V (TiA)	HOVADUR® K220, Cu-alloy (CuA)	SS316L (SS)
V350	Laser power: 120W Hatch distance: 0.08mm Initial powder thickness: 0.05mm Layer thickness: 0.05mm Scan velocity, layer 1-5: 350mm/s Scan velocity, layer 6-300: 350mm/s	Laser power: 370W Hatch distance: 0.09mm Initial powder thickness: 0.03mm Layer thickness: 0.03mm Scan velocity, layer 1-11: 530mm/s Scan velocity, layer 12-30: 400mm/s	Laser power: 380W Hatch distance: 0.04mm Initial powder thickness: 0.05mm Layer thickness: 0.05mm Scan velocity, layer 1-300: 1750mm/s
V500	Laser power: 120W Hatch distance: 0.08mm Initial powder thickness: 0.05mm Layer thickness: 0.05mm Scan velocity, layer 1-5: 500mm/s Scan velocity, layer 6-300: 350mm/s		
V650	Laser power: 120W Hatch distance: 0.08mm Initial powder thickness: 0.05mm Layer thickness: 0.05mm Scan velocity, layer 1-5: 650mm/s Scan velocity, layer 6-300: 350mm/s		

After the single track investigations, similar parameters were applied to the respective interfaces in the MM parts. The build sequence of the MM parts begins with the SLM of 300 layers (15 mm height) of SS powder over a steel substrate. Subsequently, 30 layers of CuA powder were fused over the SS base to form a 0.9 mm thick interlayer. Finally, another 300 layers (15 mm height) of TiA powder were fused over the CuA interlayer. A 5 mm chessboard laser scanning pattern with 79° rotation across each layer was used throughout the entire build (Fig. 1c). The laser parameters used to process layers 6-300 of the TiA, layers 1-30 of the CuA interlayer and layers 1-300 of the SS base are identical across all three samples as shown in Table 2. The difference between the three sets of parameters lies in the laser scanning speed used in layer 1-5 of the TiA build. The V350, V500 and V650 samples were processed using a laser scanning velocity of 350 mm/s, 500 mm/s, and 650 mm/s respectively during the initial 5 layers of the TiA build. As the SLM250HL is designed for single material storage and deposition, the machine was cleaned before and after each material deposition so as to avoid material cross-contamination. In

addition, the top surface of the SS part and the top 0.4 mm of the CuA interlayer were ground off and power-blasted to a R_a of $\sim 2 \mu\text{m}$ prior to the addition of CuA and TiA respectively. This was done to replicate the surface conditions of the single track studies so that a fair comparison can be made between the single track results and the resultant MM interfaces.

2.2 Analytical Methods

Microstructural characterization of the TiA/CuA and CuA/SS interfaces were performed using SEM on the JEOL 7600F FESEM. Semi-quantitative composition data across the TiA/CuA and CuA/SS interfaces were obtained by energy-dispersive x-ray spectroscopy (EDX) analysis using the X-Max^N spectrometer attached to the FESEM. Interfacial phase maps were obtained via electron backscatter diffraction (EBSD) analysis which was carried out using the NordlysMax³ EBSD detector also attached to the FESEM.

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

X-ray diffraction (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.

Tensile specimens with dimensions stated in Fig. 1a were cut from the MM part using electric discharge machining (EDM) and subsequently ground to 600# before testing. The tensile strength of the MM parts was measured using the Instron 5569 universal testing system under a crosshead movement speed of 0.02 mm/min. Fracture surface imaging and composition analysis were again performed using the JEOL 7600F FESEM equipped with an EDX spectrometer.

3. Results

3.1 Penetration depth and morphology of single tracks

The TiA/CuA/SS MM parts consist of two interfaces, namely the TiA/CuA interface and the CuA/SS interface. As the optimal process parameters associated with these interfaces are likely to be different from those of the bulk material, single track studies were performed to identify a range of feasible parameters. The cross-section and top view of the TiA and CuA tracks deposited over the CuA and SS substrates respectively are shown in Fig. 2a-h. Notably, an increase in laser scanning velocity led to a decrease in penetration depth and track width of the TiA melt tracks (Fig. 2i). The penetration depth of TiA single tracks ranged from 10-18 μm while its track width varied from 99-119 μm . Since the minimum track width is $\sim 99 \mu\text{m}$, the hatch spacing used for the subsequent MM build is selected to be 80 μm (see Table 2) so that the overlapping of adjacent tracks is ensured even for the V650 samples. Under the V650 parameter, the tracks appeared highly irregular (Fig. 2e) and less stable as compared to the V350 and V500 tracks (Fig. 2a & c). Therefore, the laser scanning velocity is capped at a maximum of 650 mm/s to avoid further degradation of melt track stability. On the other hand, the CuA tracks (Fig. 2g-h) deposited using a single parameter had a relatively large penetration depth and track width of 44

and 242 μm respectively (Fig. 2i). As will be seen later, the mechanical strength of the overall MM part is more critically dependent on the TiA/CuA interface than the CuA/SS interface. Hence, the process parameters used to fuse the CuA tracks on the SS substrate were not varied for simplicity. The actual MM parts were built using the parameters employed in the single track study and the microstructures of the resultant TiA/CuA and CuA/SS interfaces are shown in the following sections.

Fig. 2. Top and cross-sectional view of the TiA single tracks deposited over the CuA substrate using (a-b) V350, (c-d) V500, and (e-f) V650 parameters. (g-h) Top and cross-sectional view of the CuA single track deposited over the SS substrate. (i) Plot of melt track dimensions for the various TiA and CuA single tracks.

3.2 Microstructure at CuA/SS interface

Fig. 3a captures the CuA/SS interface with backscatter electron (BSE) imaging to highlight the difference in the atomic number and grain orientation. The overall interfacial thickness,

estimated from the local composition gradient in Fig. 3b, is $\sim 284 \mu\text{m}$. Spikes in the composition plot originate from the presence of large steel bands (Fig. 3a) and the microscopic elemental segregation (Fig. 3c-e). The composition of a typical SS globule and the CuA matrix, as measured from points C1 and C2 in Fig. 3g, was found to be 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. All the phases detected by EBSD analysis have a face-centered cubic (fcc) structure, which depending on its composition, belong either to the γ -Fe or ε -Cu phase. The enlarged view of region A1 along with its elemental map and inverse pole figure (IPF) are shown in Fig. 3c-f. Spherical SS globules with sizes varying between $0.1\text{-}5.5 \mu\text{m}$ are present within the Cu-rich matrix (Fig. 3e) while nano-sized CuA globules exist within the Fe-rich SS bands (Fig. 3d). Despite the strong chemical segregation (compare Fig. 3d-e), grain growth can occur across the boundary separating the Cu and Fe-rich regions. This is shown in a comparison between Fig. 3c & f where the Fe-rich region containing small CuA globules (lower part of Fig. 3 c & f) forms a single large grain (colored blue in the IPF of Fig. 3f) which extends across its upper boundary into the Cu-rich region. In region A2 (Fig. 3g-h) a variation of grain sizes can be seen. Fine grains are observed in the upper region of Fig. 3g & h where a high density of finely dispersed nano-sized SS globule is present. Conversely, larger grains are obtained in the lower half of Fig. 3g & h where the SS globules are larger and more widely spaced. In region A3, which is towards the upper end of the CuA/SS interface, alternating bands of equiaxed and columnar grains with a periodicity of $\sim 20\text{-}30 \mu\text{m}$ is observed (Fig. 3i). Each pair of equiaxed and columnar bands correspond to a single build layer of $30 \mu\text{m}$ thickness. The bottom of each build layer is populated by equiaxed grains (Fig. 3j-k) which subsequently emerge as columnar grains as they grow in the upward direction. The layer of equiaxed grains is $\sim 4\text{-}5 \mu\text{m}$ thick in region A4 where

the SS speckles are present in considerable amounts (dark spots in Fig. 3j). Further up the interface in region A5 the SS speckles were further depleted due to the addition of more CuA layers (Fig. 3k) and the thickness of the equiaxed bands decreased to $\sim 2\text{ }\mu\text{m}$. Beyond region A5, the SS content was diluted to a negligible amount and only columnar grains that grew across multiple layers were observed.

Fig. 3. (a) BSE image of the overall CuA/SS interface shows the presence of a non-homogeneous distribution of elongated steel bands. Boxed regions A1 to A3 indicate locations of the magnified views in (c)-(i). The vertical dashed line in (a) indicates the location of the EDX composition line scan. (b) Composition plot across the CuA/SS interface. (c) BSE image of region A1. (d-e) Cu and Fe elemental map of region A1. (f) IPF of region A1. (g) BSE image of region A2. Points C1 and C2 in (g) indicate the locations where the point composition measurements were obtained for the SS globule and Cu-rich matrix respectively. (h) IPF of region A2. (i) IPF of region A3. Boxes in (i) indicate the locations of the magnified views in (j) & (k). (j) BSE image of region A4. (k) BSE image of region A5.

3.3 Microstructure at TiA/CuA interface

Unlike the CuA/SS interface, the TiA/CuA interface is known to contain IMCs as predicted by the Ti-Cu binary phase diagram. This makes it a critical interface as the formation of an excessive amount of brittle phases is detrimental to the bond integrity. As such, three sets of processing parameters (V650, V500 & V350) have been used to create TiA/CuA interfaces with different thicknesses. The cross-sectional view of the TiA/CuA interface processed with the V650 laser parameters is shown in Fig. 4a. The interfacial thickness (Fig. 4b-d), defined here as the distance for Cu content to drop from its parent composition to below 5 at.%, is $55.6 \pm 17.2 \mu\text{m}$, $99.2 \pm 14.4 \mu\text{m}$, and $115.5 \pm 18.8 \mu\text{m}$ for the V650, V500, and V350 TiA/CuA interface respectively. All the TiA/CuA interfaces display similar microstructural features. Hence only the characteristic regions of the V650 TiA/CuA interface are shown in Fig. 4e-j. It should be noted that the input phases used for EBSD analysis shown in Fig. 4f, h & j were validated by XRD and TEM results which will be shown in the subsequent sections.

Fig. 4. (a) BSE image of the V650 TiA/CuA interface shows a composite structure with a high level of composition non-homogeneity. White arrows in (a) indicate regions of α' -Ti phase with limited Cu content. Boxes in (a) indicate locations of magnified views shown in (e-h). EDX composition line plots across the (b) V650, (c) V500, and (d) V350 TiA/CuA interfaces. (e) BSE image and (f) EBSD phase map of region A6 show that a layer of L2₁ ordered phase and a layer of amorphous phase are present immediately above the CuA interlayer. (g) BSE and (h) EBSD phase map of region A7 show the presence of α' -Ti region within the β -Ti + Ti₂Cu phase mixture. (i) BSE image of β -Ti + Ti₂Cu phase mixture shows the Ti₂Cu phase as bright features within the darker β -Ti matrix. (j) IPF of the bulk TiA taken from beyond the TiA/CuA interface shows the presence of α' -Ti phase with columnar prior β -Ti grain boundaries.

The microstructure of the entire V650 TiA/CuA interface can be sub-divided into two regions; the start of the interface is captured by region A6 (Fig. 4e-f) while the bulk of the interface is captured by region A7 (Fig. 4g-h). Region A6 shows that the interface begins with a layer of sub-micron equiaxed grains that have an L2₁ ordered structure identical to that of the Cu₂TiAl Heusler compound (colored green in Fig. 4f). Above that is a thin layer of amorphous phase which is un-indexed during EBSD analysis due to the absence of diffraction patterns (black in Fig. 4f). Beyond the amorphous layer, β -Ti is detected. As shown in Table 3, the measured thickness of the L2₁ ordered phase remains fairly constant across the V350, V500, and V650 samples. On the other hand, the thickness of the amorphous phase increases significantly from $2.4 \pm 2.7 \mu\text{m}$ to $8.8 \pm 4.6 \mu\text{m}$ for the V650 and V350 samples respectively. These thin layers of L2₁ and amorphous phase are consistently present on top of the CuA interlayer and are seemingly never broken at any location by the Marangoni flow that is known to exist within the melt pool [46]. It is believed that the L2₁ and amorphous layers existed within the velocity boundary layer where fluid flow is greatly retarded and conforms to the solid boundary encompassing the melt pool. According to literature, the Cu₂TiAl phase with an L2₁ structure can form on recrystallization of the ternary Cu-Ti-Al amorphous phase [47]. However, the L2₁ phase obtained here is not a product of recrystallization as it is not homogeneously precipitated within the amorphous layer. Instead, the L2₁ phase formed between the CuA interlayer and the amorphous layer. Hence, it is postulated that the 1-1.5 μm uniform layer of L2₁ phase formed as a consequence of inter-diffusion across the boundary of the CuA interlayer and the amorphous layer.

Inter-diffusion is, in turn, influenced by the thermal history experienced during the deposition of the TiA build layers. Although the laser scanning velocity and, consequently, the thermal history

of the V650, V500 and V350 MM parts were different in layer 1-5 of the TiA build, the parameters for the majority of the build (layer 6-300) were identical. Hence, the difference in thermal history and the extent of inter-diffusion is expected to be negligible. Therefore, the L2₁ phase appeared with similar thicknesses across the V650, V500 and V350 samples (Table 3).

Table 3
Interfacial thickness of the phase/s in the TiA/CuA interface (in μm)

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

The bulk of the TiA/CuA interface consists of a non-homogenous mixture of α' -Ti islands (white arrows in Fig. 4a) within the β -Ti + Ti₂Cu phase mixture. A magnified view of this composite structure is shown in region A7 (Fig. 4g-h). The BSE images in Fig. 4g & i reveal that all β -Ti grains are populated by bright lines along the grain boundaries and bright spots at the core. Since BSE imaging produces atomic number contrast, this indicates that the brighter features have a higher Cu content compared to the surrounding matrix. EBSD analysis identifies some of the bright features to be Ti₂Cu IMC while the vast majority of the bright spots within the grains have been indexed as β -Ti phase along with its surrounding matrix (Fig. 4h). As these Ti₂Cu grains have widths that are narrower than 500 nm, not every grain can be indexed successfully in the EBSD analysis due to limitations in spatial resolution and the overlap of Kikuchi patterns with the surrounding β -Ti matrix. Due to the sub-micron sizes of these particles, composition measurements of these Ti₂Cu grains cannot be reliably obtained through EDX analysis of thick samples. This is because the X-ray production volume for Ti elements under a 20 kV electron accelerating voltage is $\sim 2.4 \mu\text{m}$, which is significantly larger than the sub-micron features. EDX measurements of area C3 (α' -Ti phase) and area C4 (β -Ti + Ti₂Cu phase mixture) in Fig. 4g

reveal a composition of Ti(85.1)-Cu(1.8)-Al(9.4)-V(3.7) and Ti(63.9)-Cu(25.5)-Al(6.2)-V(2.7)-Ni(0.8)-Si(0.7)-Cr(0.1) respectively. The composition difference between area C3 and C4 shows that Cu content is not evenly distributed within the interface and is indicative of the non-homogenous mixing within the melt pool. The thickness of the composite layer consisting of α' -Ti + (β -Ti + Ti₂Cu) phase mixture increases significantly from 52.2±17.2 μ m for the V650 sample to 95.2±18.8 μ m for the V350 sample (Table 3).

As the Cu content becomes significantly depleted towards the upper end of the TiA/CuA interface, it is no longer possible to retain β -Ti upon cooling and the microstructure becomes mostly α' -Ti with a columnar prior β -Ti grain structure (Fig. 4j).

By obtaining the composition line plots, such as those shown in Fig. 4b-d, at 16 different locations along the V350, V500, and V650 TiA/CuA interfaces, it is possible to estimate the volume fraction of the interfacial phases with different ranges of Cu content. As shown in Fig. 5a-c the V650 TiA/CuA interface is dominated by phases with lower Cu content, while the V500 and V350 TiA/CuA interfaces are dominated by phases containing a greater amount of Cu. To better illustrate the changes across the various TiA/CuA interfaces, the vol.% of the major constituents containing 0-30 at.% Cu has been plotted for the various samples as shown in Fig. 5d. In comparison to the V350 interface, the V650 TiA/CuA interface is found to contain a much higher volume fraction of phases with 0-10 at.% Cu and a lower volume fraction of phases with 10-30 at.% Cu. EBSD and EDX analysis reveal that α' -Ti is the main constituent for ~0-5 at.% Cu, while β -Ti + Ti₂Cu is present for ~5-30 at.% Cu. As such, it can be inferred that the volume fraction of α' -Ti increases from the V350 to the V650 TiA/CuA interface while the amount of β -Ti + Ti₂Cu decreases.

Fig. 5. Volume fraction of phases with the respective ranges of Cu content (at.%) in the (a) V650, (b) V500, and (c) V350 TiA/CuA interfaces. (d) Plot showing the changes in the volume fraction of the major phases at the TiA/CuA interfaces.

TEM analysis has been carried out on three selected regions within the V650 TiA/CuA interface for accurate phase identification using the selected area electron diffraction (SAED) technique as well as to obtain EDX composition data of sub-micron microstructural features. The first TEM sample, as shown in Fig. 6, was extracted from a region similar to that of region A6 in Fig. 4e. The bulk CuA interlayer, which has a composition of Cu(91.4)-Ti(2.4)-Ni(2.7)-Si(3.2)-Cr(0.4), is shown in region A. The start of the TiA/CuA interface begins from region B which consist of a ~500 nm thick layer of equiaxed grains. The SAED pattern of these grains (inset of Fig. 6) consists of distinct strong and weak diffraction spots that match the $\langle 101 \rangle$ zone axis of the Cu_2TiAl Heusler compound which has an ordered L2_1 structure. Additional diffraction patterns from the $\langle 111 \rangle$ and $\langle 102 \rangle$ zone axes also agree with the L2_1 structure of the grains. The measured lattice parameter of the grains ($a=0.608$ nm) is also similar to the reported value of 0.601 nm for the Cu_2TiAl phase [48]. However, EDX analysis on the grains reveals 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 ~2:1 and matches well with that of the Cu₂TiAl phase, the Al content is many times lower than the stoichiometric ratio. According to the isothermal section of the Cu-Ti-Al ternary phase diagram at 500°C, an Al content as low as ~9 at.% is predicted for the Cu₂TiAl phase [49]. As such, it is possible for the Al content of the Cu₂TiAl phase obtained in this study to be well below its stoichiometric ratio, especially under rapid solidification and the presence of other alloying elements. Next to the L2₁ phase is an amorphous area with a composition ranging 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*. Within the amorphous phase is an island of β -Ti phase (region D) 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). The presence of the β -Ti within the amorphous phase is again indicative of the non-homogenous mixing within the melt pool. The inset in Fig. 6 shows the electron diffraction patterns pertaining to regions A to D.

Fig. 6. Bright-field TEM image of ϵ -Cu, Cu_2TiAl , amorphous, and β -Ti phase. Insets show the SAED patterns of the respective phases.

The second TEM sample was extracted from the boundary of an α' -Ti phase and a Cu-rich β -Ti phase (Fig. 7a). Region E, which has a composition of Cu(2.7)-Ti(83.2)-Al(10.1)-V(4.0), does not contain sufficient amount of Cu content to retain the β -Ti phase upon cooling. Consequently, the microstructure consists of α' -Ti phase with internal twins whose length varies from 0.26-1.28 μm . Region G contains a β -Ti phase with a cellular solidification structure whose cell sizes is $\sim 252 \pm 45$ nm. The qualitative composition line scan reveals chemical segregation within the cellular β -Ti phase (Fig. 7b). The average composition of the cell core is determined via EDX to be Cu(24.4)-Ti(62.4)-Al(8.1)-V(3.0)-Ni(0.8)-Si(0.8)-Cr(0.5) while the composition along the cell outline ranges 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). As the composition of the cell outline approaches that of region C and C* in Fig. 6, it vitrifies into an amorphous phase. Hence, a weak diffused ring is observed in the SAED pattern of region G in addition to the β -Ti diffraction

pattern. The average composition of the β -Ti cellular structure is Cu(31.7)-Ti(56.5)-Al(6.8)-V(2.6)-Ni(1.0)-Si(0.9)-Cr(0.5). Region F, which is the bright and narrow area between regions E and G, is a 200-500 nm thick β -Ti phase with a composition of Cu(10.4)-Ti(73.4)-Al(10.3)-V(4.5)-Ni(0.3)-Si(1.0).

Fig. 7. (a) Bright-field TEM image of the α' -Ti phase and the supersaturated β -Ti cells. Insets show the SAED patterns of the respective phases. (b) Qualitative EDX measurement along the dotted line in (a).

The third TEM sample was extracted from a β -Ti grain to identify the phase present in its vein-like patterns (Fig. 8). EDX analysis reveals that the lines decorating the β -Ti grain boundary as well as the spots at the core of the β -Ti grain have a composition of Ti(62.3)-Cu(30.9)-Al(3.7) - V(0.6)-Ni(1.5)-Si(0.7)-Cr(0.3). Additionally, the SAED pattern of these features also matches the $\langle 111 \rangle$ zone axis of the Ti_2Cu phase. This indicates that all the bright features shown in the

BSE image in Fig. 4g & i are indeed Ti_2Cu IMC. The composition of the $\beta\text{-Ti}$ matrix in Fig. 8 ranges between $\text{Ti}(80.5)\text{-Cu}(7.5)\text{-Al}(7.8)\text{-V}(2.6)\text{-Ni}(0.4)\text{-Si}(0.8)\text{-Cr}(0.4)$ and $\text{Ti}(75.8)\text{-Cu}(12.4)\text{-Al}(7.1)\text{-V}(3.0)\text{-Ni}(0.6)\text{-Si}(0.7)\text{-Cr}(0.5)$.

Fig. 8. Bright-field TEM image of the $\beta\text{-Ti}+\text{Ti}_2\text{Cu}$ phase mixture. Insets show the SAED patterns of the respective phases.

Table 4 summarizes the EDX compositions of the respective phases measured from the TEM samples as well as the bulk TiA/CuA interface. It should be noted that these EDX composition measurements are semi-quantitative and contain intrinsic uncertainty. Nonetheless, it is clear that the Cu content within the interface has a major influence on the resultant phase formation. While the exact Cu content denoting the phase boundaries cannot be determined precisely, it is useful to assign an approximate range of Cu content to each phase or phase mixture based on the actual composition measurements (Table 4). Evidently, $\alpha'\text{-Ti}$ phase exists only in the narrow range of 0-5 at.% Cu, while $\beta\text{-Ti}+\text{Ti}_2\text{Cu}$ phase mixture exists over a much wider range of 5-35 at.% Cu. Using these approximations, the phases within the fracture surfaces and nano-indentations can be conveniently identified via simple EDX analysis.

Table 4

EDX composition measurements of the various phase/phase mixtures obtained during TEM and FESEM analysis. The resultant phase/s can be associated with the different ranges of Cu content approximated in divisions of 5 at.%.

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

3.4 Overall phase analysis

The XRD patterns corresponding to the bulk TiA, V350, V500, and V650 TiA/CuA interfaces as well as the bulk CuA, CuA/SS interface, and bulk SS phases are shown in Fig. 9. Since XRD analysis surveys a much larger area as compared to EBSD and TEM analysis, it can be used to validate the presence of major phases within the TiA/CuA/SS MM part. The bulk TiA consists of a fully α' -Ti martensitic microstructure without any presence of β -Ti peaks. In the V350, V500 and V650 processed TiA/CuA interfaces, α' -Ti, β -Ti, Ti₂Cu, and ϵ -Cu peaks were detected. The ϵ -Cu peaks originate from the underlying CuA interlayer and indicate that the survey depth of the XRD analysis was sufficient to include the L2₁ and amorphous layer. However, the diffused peak from the amorphous phase and the crystalline peaks from the L2₁ phase are absent in the XRD patterns of all the TiA/CuA interfaces. This suggests that both of these phases are present only in low quantities, which is also supported by the narrow thickness measurements from the FESEM images (Table 3).

Fig. 9. XRD patterns of the various bulk materials and interfaces. α' -Ti, β -Ti, and Ti_2Cu were detected in all TiA/CuA interfaces. In the CuA/SS interface, only γ -Fe and ϵ -Cu phase are detected.

The CuA/SS interface only consists of γ -Fe and ϵ -Cu peaks which are expected since, Cu and Fe are immiscible and do not form any reaction phases upon mixing [50, 51]. The diffraction angles of γ -Fe and ϵ -Cu overlap strongly due to their identical fcc crystal structure and similar lattice constants. All diffraction peaks obtained from the XRD analysis agree with the phases detected via EBSD and TEM analysis thus validating the results of prior analysis.

3.5 Nanohardness at TiA/CuA and CuA/SS interfaces

The hardness versus composition data for the nano-indentations made within the TiA/CuA and CuA/SS interfaces are shown in Fig. 10a & b respectively. As both interfaces feature large composition gradients within the micron to sub-micron scale, hardness measurements on an identical phase could differ depending on its surrounding medium [52]. To ensure that the results are reliable averaged hardness values were obtained from a total of 149 and 79 indents

performed across the TiA/CuA and CuA/SS interfaces respectively. The hardness values within the TiA/CuA interface exceeded those of the parent phases and can be seen to increase with Cu content. When the Cu content is as low as 0-5 at.%, the α' -Ti phase has a hardness of 4.9 ± 0.1 GPa. When the Cu content increased to 5-10 at.% the microstructure changed to β -Ti + Ti_2Cu and the hardness increased slightly to 5.3 ± 0.6 GPa. This is due to the formation of hard Ti_2Cu IMC as well as the solid solution strengthening effect of Cu in the retained β -Ti phase [53]. The contribution to increased hardness from these two effects persists up to ~30 at.% Cu at which the measured hardness is 7.4 ± 1.0 GPa. Further increase of Cu content to 30-35 at.% leads to the formation of amorphous + β -Ti phase mixture with a similar hardness of 7.4 ± 1.2 GPa. When the Cu content lies within the 35-45 at.% range the resultant phase becomes predominantly amorphous and has a peak hardness of 7.9 ± 1.0 GPa. Hardness values for the L_{21} phase, which has a Cu content of ~60 at.%, is unavailable due to the difficulty in performing reliable indents on the $\sim 1.5 \mu\text{m}$ thick phase. The parent CuA (90-95 at.% Cu) has a hardness of 2.3 ± 0.1 GPa which is the lowest of all phases.

Fig. 10. Hardness of phases in the (a) TiA/CuA interface, and (b) CuA/SS interface.

On the other hand, hardness across the CuA/SS interface, which consists entirely of γ -Fe and ϵ -Cu phases, has intermediate values that lie between those of the parent alloy phases. Hardness

data corresponding to 25-40 at.% Fe is absent as such composition ranges were not found within the CuA/SS interface due to the liquid phase miscibility gap in the Cu-Fe system [50, 51].

3.6 Interfacial strength and fracture surface

The profile of the tensile specimens, which is cut using EDM, is shown in Fig. 1a. It should be mentioned that during the EDM process, a significant number of V500 and V350 samples delaminated along the TiA/CuA interface due to the relief of residual stresses. Among the V500 and V350 tensile specimens, only those which did not contain any visible delamination have been selected for tensile testing. As such, tensile strengths pertaining to the V500 and V350 samples should be interpreted with care. On the other hand, the V650 samples have been tested without such bias as all samples remained perfectly intact during and after EDM. The average ultimate tensile strength (UTS) for the V650, V500, and V350 samples are 523 ± 1 , 496 ± 23 , and 473 ± 26 MPa respectively.

Fig. 11. SEM images of the fracture surface corresponding to the (a) V650, (b) V500, and (c) V350 samples. The fracture surfaces belonging to the TiA/CuA interfacial phases are enclosed in dashed lines. All remaining surfaces, which are not outlined, belong to the CuA interlayer.

As shown in Fig. 11a-c, the fracture surfaces of the V650, V500, and V350 samples show different proportions of cleavage and ductile fracture that belong to the TiA/CuA interface and CuA interlayer respectively. Notably, the V650 fracture surface contains the highest proportion

of ductile fracture while the V350 fracture surface is entirely brittle. As the morphological features are similar across the V650, V500, and V350 fracture surfaces, only those corresponding to the V650 fracture surface are shown in Fig. 12.

Fig. 12. (a) SEM image of the cleavage fracture across V650 TiA/CuA interface showing feather patterns converging towards the boxed region. (b) Magnified image of the boxed region in (a) shows the feather patterns terminating at a featureless amorphous fracture site with a neighboring porosity. Dashed line indicates the location of the EDX line scan as shown in (c). (c) Composition data along dashed line shown in (b). (d) Magnified image of the amorphous region boxed up in (b). SEM images of the dimples belonging to the (e) β -Ti + Ti₂Cu phase with 28.1 at.% Cu, (f) β -Ti + Ti₂Cu phase with 16.6 at.% Cu, (g) α' -Ti phase, and (h) ϵ -Cu phase.

The region of the V650 fracture surface that belongs to the TiA/CuA interface is populated by an abundance of feather patterns which indicates a transgranular cleavage fracture (Fig. 12a). Amidst the cleavage fracture surface, several “radiate core” features can be observed (Fig. 12b). At the center of each radiate core is a relatively smooth region from which the feather patterns on the cleavage surface originate and spread in an outward manner. The EDX line plot shows that the core 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) (Fig. 12b-c). The Cu content and the relatively smooth appearance of the cores (Fig. 12d) indicate that they are amorphous. On the edge of the core, a ~40 μm long porosity is also observed (Fig. 12b). This implies that the presence of a defect around the amorphous core led to stress concentrations

which initiated the fracture. While Cu-based amorphous metals have compressive yield strengths greater than 1 GPa [54, 55], they generally have low fracture toughness and often fail catastrophically in tension through the unrestrained extension of a single dominant shear band [56]. Therefore, it is unsurprising to find fracture initiating from an amorphous phase with a neighboring pore under a tensile load that is lower than its yield strength. The cleavage surfaces surrounding the amorphous core has a Cu content of 9.5-28.7 at.% (Fig. 12c) which corresponds 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 visible on the scale of tens of micrometers. In the sub-micron scale, small and shallow dimples can be observed on the fracture surfaces of the β -Ti+Ti₂Cu phase mixture (Fig. 12e-f). The size of the dimples decrease from 0.1-0.4 μ m (Fig. 12f) to 0.08-0.26 μ m (Fig. 12e) as its Cu content increase from 16.6 at.% to 28.1 at.% Cu. The reduction in dimple size, which corresponds to decreased ductility, is attributed to the solid solution strengthening effect of Cu in β -Ti as well as the increased formation of brittle Ti₂Cu IMC. In contrast, the α' -Ti phase with only 4.0 at.% Cu (Fig. 12g) fractures in a more ductile manner, featuring larger dimples of 1-3 μ m in size. In addition to the TiA/CuA interfacial phases, ~50% of the remaining V650 fracture surface is comprised of the ductile ϵ -Cu phase which featured large dimples of 4-30 μ m in size (Fig. 12h). 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). Notably, this order of decreasing dimple size coincides with the order of increasing hardness as shown in Fig. 10a. This again suggests that the phases in the TiA/CuA interface become more brittle with increased Cu content.

The cross-sectional view of the fracture surface (Fig. 13a) shows that fracture preferentially propagates within the β -Ti + Ti₂Cu phase mixture and is seen to navigate around isolated α' -Ti regions. However, when the fracture is channeled into a cluster of α' -Ti phase it is forced to deflect into the ϵ -Cu phase. These deflections are caused by the difference in toughness between the α' -Ti phase and the brittle β -Ti + Ti₂Cu surroundings. On the fracture surface, the transition between the cleavage dominated TiA/CuA interface and the dimpled CuA interlayer occurs via a step change in height (Fig. 13b). Besides being deflected, Fig. 13c shows that cracks can also bypass the α' -Ti regions or become arrested by it. The multiple cracks found within the amorphous phase (Fig. 13d) indicates that it is a crack initiation site, which is consistent with the observation in Fig. 12b.

Fig. 13. (a) BSE image of the cross-sectional view of the fracture surface showing fracture being directed from the β -Ti + Ti_2Cu phase mixture into the ϵ -Cu phase via a major deflection around an α' -Ti cluster. (b) SEM image of fracture transiting from the TiA/CuA interface to the CuA interlayer. (c) BSE image of a crack propagating around an α' -Ti region before being arrested at another α' -Ti region. (d) BSE image of multiple cracks in the amorphous region.

As shown in Fig. 11a-c, the proportion of the various phases on the V650, V500, and V350 fracture surfaces are different. The area fraction of phases with the different ranges of Cu content was estimated by obtaining 352 regularly spaced, point composition data from each fracture surface and the results are shown in Fig. 14a-c. The lack of ϵ -Cu on the V350 fracture surface and the abundant amount of it on the V650 fracture surface is immediately noticeable. Fracture propagation along the TiA/CuA interface occurs predominantly within phases with 5-25 at.% Cu

(β -Ti + Ti₂Cu). The α' -Ti (0-5 at.% Cu) and amorphous phase (35-45 at.% Cu) constitute only a relatively small area fraction within the fracture surfaces of all the samples.

Fig. 14. Area fraction of phases with different ranges of Cu content on the (a) V650, (b) V500, and (c) V350 fractures surfaces.

4. Discussion

4.1 CuA/SS interface bonding

The microstructure within the CuA/SS interface consists entirely of fcc ϵ -Cu and γ -Fe phase with no reaction products as indicated by XRD and EBSD analysis. As a result, the hardness across the different compositions within the CuA/SS interface has intermediate values between that of the bulk SS and CuA (Fig. 10b). The presence of large steel bands in Fig. 3a is a result of the non-homogenous convective mixing within the laser created melt pool [46, 57-59]. On the other hand, the 0.08-5.5 μ m diameter SS and CuA globules (Fig. 3c & g) are formed by liquid phase separation due to the liquid miscibility gap in the Cu-Fe system [50, 51]. The liquid phase separation between CuA and SS is commonly observed during laser, electron beam and arc welding processes [57, 58] and can be avoided by 1) slow cooling such that the Cu and steel liquid mixture is not undercooled into the miscibility gap [51] and 2) alloying with elements which suppress the miscibility gap [50]. The lattice constants of the γ -Fe and ϵ -Cu phase, determined using XRD, are 0.3596 and 0.3614 nm respectively. Due to their similar crystal

structure and lattice constants, it is possible for the CuA grains to growth epitaxially on the SS phases. As such, the ϵ -Cu and γ -Fe phases can be seen to show the same crystallographic orientation across their phase boundaries as shown in Fig. 3c & f. Such epitaxial growth of CuA on SS and vice versa had also been observed by others [60, 61]. As the melting point of SS ($\sim 1400^\circ\text{C}$) is higher than that of CuA ($\sim 1080^\circ\text{C}$), the liquid-phase-separated SS phase solidifies first within the molten CuA phase. Once the melt pool temperature falls below the liquidus of the CuA, the molten CuA preferentially nucleates and grows epitaxially on the low-energy solid SS globules. The abundance of these SS globules within the interface allows CuA grains to grow ahead of the solidification front, resulting in the formation of equiaxed grains (Fig. 3h). This observation is conceptually similar to the work of Martin et al. who have demonstrated that the equiaxed grains, obtained through the addition of a nucleant phase that has a low lattice mismatch with the bulk material, is capable of suppressing solidification cracking and hot tearing in susceptible materials [62].

Since the SS globules act as low energy nucleation sites, locations with a high density of finely dispersed globules should, therefore, undergo grain refinement. Such a location is shown in the upper half of region A2 (Fig. 3g-h) where an abundance of fine SS globules is accompanied by sub-micron grain sizes. In contrast, bigger grains are obtained where the SS globules are larger and more widely spaced as seen in the lower half of region A2 (Fig. 3g-h). While the SS globules can act as nucleants to promote and refine equiaxed grain formation in CuA, CuA globules do not refine the SS grains because CuA solidifies after SS. Hence, no refinement is observed in SS grains which contains a significant amount of CuA globules (lower half of Fig. 3d-f).

Due to the repeated dilution from the addition of CuA layers, the quantity of SS nucleation sites depletes to moderate amounts at region A3 (Fig. 3i) where it is no longer possible to retain a

fully equiaxed microstructure. Instead, alternating bands of equiaxed and columnar grains with a periodicity of ~20-30 μm , similar to the layer thickness setting, are seen. This observation is similar to the competitive grain growth behavior that is observed in conventional castings. After the deposited powder is melted, the liquid above the relatively cold underlying solid layer experiences a large undercooling. This large undercooling, coupled with a moderate amount of SS nucleation sites, resulted in the formation of fine equiaxed grains. The nucleated grains which have their $\langle 001 \rangle$ preferred growth direction orientated parallel to the direction of heat flow tends to grow faster than grains with a less favorable orientation (i.e. competitive grain growth). This results in the observed equiaxed to columnar grain transition within the build layers that feature a moderate amount of SS nucleation sites.

Further depletion in the SS nucleation sites towards the upper boundary of the CuA/SS interface caused the equiaxed grain formation to become completely suppressed. Instead, the solidified CuA grains tend to grow epitaxially from the CuA grains in the underlying layer, leading to long columnar grains. As such the thickness of the equiaxed band decreased from region A4 (Fig. 3j) to A5 (Fig. 3k) and vanished beyond the CuA/SS interface where SS globules were practically absent.

4.2 TiA/CuA interface bonding and fracture

Due to the presence of brittle phases, the TiA/CuA interface is more critical compared to the CuA/SS interface. The microstructure at the TiA/CuA interface can be pictured as sequential layers of various phases in the following order: $\epsilon\text{-Cu}$ / $L2_1$ ordered phase/ amorphous phase/ $\alpha'\text{-Ti} + (\beta\text{-Ti} + \text{Ti}_2\text{Cu})$ / $\alpha'\text{-Ti}$. Each of these phases can be identified through their different ranges of Cu content as shown in Table 4. While the phases across the V650, V500, and V350 TiA/CuA

interfaces are similar, the thickness (Table 3) and the volume fraction of the respective phases (Fig. 5) are different. Consequently, the fracture behavior of the respective interfaces also differs (Fig. 11a-c). Fig. 15 illustrates the fracture paths within the V650 and V500 TiA/CuA interfaces. Although the amorphous phase (35-45 at.% Cu) occupies less than 3% of the fracture surfaces, they are often found to be the crack initiation site as indicated by the presence of multiple cracks (Fig. 13d) and the convergence of river patterns around the featureless amorphous cores (Fig. 12b). While the amorphous layer is present throughout the entire TiA/CuA interface (Fig. 4f), only the amorphous regions with neighboring porosity and/or cracks are found on the fracture surfaces (Fig. 12b). This indicates that the fracture of the amorphous phase is initiated by the stress concentrations around the defects. Once initiated, the crack propagates into the surrounding β -Ti + Ti₂Cu phase mixture and preferentially remains within it. Hence, a large area fraction of the fracture surface consists of the β -Ti + Ti₂Cu phase mixture which contains 5-25 at.% Cu (Fig. 14a-c). When the crack propagates into an isolated region of α' -Ti phase, it may undergo minor deflection, bypass the α' -Ti phase or become arrested by it (Fig. 13a & c). However, when a cluster of α' -Ti phase is encountered, the fracture path is forced to take a major deflection which is often in the downward direction towards the CuA interlayer (Fig. 13a). The preference for a downward deflection is due to its higher Cu content and, consequently, increased amount of brittle phases at the bottom of the TiA/CuA interface. As the fracture continues in its downward deflection, it may propagate pass the thin layers of amorphous and L2₁ phase and enter the CuA interlayer, leading to the presence of ductile ϵ -Cu regions on the V650 and V500 fracture surfaces (Fig. 11a-c). When fracture transits into the CuA interlayer, the fracture mechanism changes from that of crack propagation to micro void coalescence. This transition is shown in Fig. 13b where the cleavage fracture surface at the TiA/CuA interface

changed to a dimpled fracture surface at the CuA interlayer. Since the interfacial α' -Ti phase is tougher than the other interfacial phases, as suggested by its lower hardness (Fig. 10a), it does not fracture easily and is only present in minor amounts across all the fracture surfaces. The V650, V500, and V350 fracture surface consist of 58%, 24% and 1% of ϵ -Cu phase respectively (Fig. 14a-c). The high amount of ϵ -Cu on the V650 fracture surface is attributed to its high volume fraction of interfacial α' -Ti phase (30 vol.%) which resulted in frequent fracture deflections into the CuA interlayer. In contrast, when the amount of interfacial α' -Ti decreased to 10 vol.% in the V350 interface, it is no longer present in sufficient amount to significantly hinder crack propagation. Hence, the fracture remained entirely within the β -Ti + Ti₂Cu phase mixture, leading to the absence of ϵ -Cu phase on the V350 fracture surface. From the fracture toughness consideration, the cleavage dominated fracture surface of the V350 and V500 samples are unfavorable since they present a lower resistance to crack propagation. As a result, several V350 and V500 samples delaminated spontaneously during the EDM process. In comparison, the V650 sample, which contained the highest volume fraction of interfacial α' -Ti phase, is much tougher and was not observed to undergo any delamination during EDM.

Fig. 15. Illustration of fracture paths within the TiA/CuA interface.

4.3 TiA/CuA interface strengthening through maximizing interfacial α' -Ti

Based on all the experimental evidence, it is clear that the optimization of bond properties across the critical TiA/CuA interface relies on maximizing the amount of tough α' -Ti reinforcement phase within the β -Ti+Ti₂Cu phase mixture. This can be achieved in two ways: 1) minimize the interfacial Cu content such that the formation of brittle β -Ti + Ti₂Cu phase mixture and amorphous phase is reduced and 2) adopt a laser processing parameter which favors melt pool non-homogeneities such that majority of the molten TiA solidifies and transforms into the tough α' -Ti without being diluted with significant amounts of Cu.

In order to minimize the interfacial Cu content, it is important to first recognize that Cu is introduced into the TiA/CuA interface through the remelting of the underlying CuA interlayer

(i.e. penetration depth) in the first TiA build layer. The molten CuA is mixed into the TiA build layer through the Marangoni effect [46]. During subsequent layer depositions, the remelting and mixing processes repeat to spread the Cu content across multiple layers. As such, the objective of minimizing interfacial Cu content translates to the minimization of melt pool penetration depth in the first TiA build layer. To show that the penetration depth of the first TiA build layer controls the interfacial Cu content, the Cu composition line plots (Fig. 4b-d) can be converted to an equivalent thickness of melted CuA and compared against the single track penetration depth measurements in Fig. 2i. This conversion is done by integrating the Cu vs displacement plot within the composition gradient and normalizing the result by the Cu content within the bulk CuA. A qualitative comparison between the measured melt pool penetration depth and the equivalent thickness of melted CuA for the respective samples (Fig. 16) shows that the objective of limiting the interfacial Cu content is similar to reducing the melt pool penetration depth in the first TiA build layer. Accordingly, the V650 samples, which have the lowest penetration depth due to its lowest interfacial laser energy input, also have the thinnest TiA/CuA interface, the largest amount of interfacial α' -Ti, the largest area fraction of ϵ -Cu fracture surface, and the highest tensile strength.

Fig. 16. Plot of the equivalent melted CuA thickness and the measured penetration depth of the TiA single tracks for the various samples.

The reduction of interfacial Cu content and brittle phases through a simple increase in laser scanning velocity is seemingly valid for the limited range of scanning velocities investigated in this study. However, this increase in scanning velocity cannot be abused without limit. There is a minimum energy input that should be maintained in the SLM process before detrimental melt pool instability such as “balling” occurs [63]. As seen in Fig. 2e, the V650-processed melt track appeared irregular and is prone to “balling” if the laser energy input is further reduced via an increase in laser scanning velocity. As such the minimization of penetration depth should be considered in parallel with the stability of the melt pool. According to the stability criteria proposed by Yadroitsev et al. the critical contact angle that is needed to ensure the marginal stability of a liquid segmental cylinder under axial harmonic disturbance can be implicitly defined as [63]:

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

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 (Fig. 17) which must not be exceeded for the melt pool to remain stable. The critical contact angle can be equivalently converted to the critical penetration depth using the following geometrical relationship:

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

Where p_c is the critical penetration depth that is minimally needed to maintain marginal melt pool stability and h is the height of the liquid cylinder above the substrate, which depends on the layer thickness setting in the SLM process.

Fig. 17. Illustration of a melt track. The definitions of critical contact angle (ϕ_c), critical penetration depth (p_c), melt track height (h), melt pool diameter (D), and melt pool length (L) are shown.

Based on equations (1) & (2), the critical penetration depth can be lowered by two different approaches. The first approach is to increase the melt pool aspect ratio D/L so that the critical contact angle and critical penetration depth is increased and decreased respectively. In this experimental study, the simplistic way of reducing the penetration depth by simply increasing the laser scanning velocity is probably inept as doing so produces a slender melt pool with a lower

D/L [64] and, consequently, a higher critical penetration depth. Since the length of the melt pool, L , cannot be measured experimentally, a more systematic way to obtain a low aspect ratio melt pool is to rely on numerical simulations or mathematical modeling [46, 65]. The second approach to reducing the critical penetration depth is to lower the height of the melt track, h , such that for any given values of $\emptyset_c$, p_c is also reduced in a geometrically similar manner according to equation (2). Conversely, given a fixed penetration depth, the reduction of h may help to improve the stability of an irregular melt pool by lowering the contact angle to within the critical limit of $\emptyset_c$. Between these two approaches, the lowering of the height of the melt track is more readily implemented since it involves only a simple reduction in layer thickness. Given that the height and penetration depth of the V650 melt tracks are $\sim 41 \mu\text{m}$ and $\sim 10 \mu\text{m}$ respectively, a reduction in layer thickness and, consequently, the height of the melt tracks to, say, $12 \mu\text{m}$ could lead to a half embedded melt pool with enhanced stability. In comparison, the CuA melt tracks deposited over the 316L substrate have a height and penetration depth of $\sim 21 \pm 6 \mu\text{m}$ and $44 \pm 10 \mu\text{m}$ respectively. Hence, the melt tracks appear regular and stable (Fig. 2g-h). Since the porosity of the untapped TiA powder is measured to be $49.5 \pm 0.5\%$, a layer thickness of $12 \mu\text{m}$ would correspond to an unconsolidated powder thickness of $\sim 24 \mu\text{m}$. In this study, the powder used have sizes between $20\text{-}63 \mu\text{m}$. While it may be possible to use a $24 \mu\text{m}$ powder thickness on the first TiA build, the powder may not be evenly distributed over the CuA substrate due to the low yield of small-sized powders. The issue can be mitigated by using powder with smaller sizes. Although the low layer thickness setting majorly reduces the build rate, it only needs to be implemented across the TiA/CuA interface. After which, the layer thickness can be readily increased to hasten the build process.

While the minimization of melt pool penetration depth in the first TiA build layer to reduce interfacial Cu content is vital to bond properties, the presence of melt pool non-homogeneities is equally important. If the 10 μm of melted CuA had been homogeneously mixed within the V650 TiA/CuA interface, the interface would have a uniform composition of ~ 15 at.% Cu across an interfacial thickness of 93 μm . This would lead to a microstructure which consists entirely of $\beta\text{-Ti} + \text{Ti}_2\text{Cu}$ without any interfacial $\alpha'\text{-Ti}$ regions to obstruct fracture propagation. Therefore, it is important to also select laser processing parameters which promote such melt pool non-homogeneities. During laser melting of dissimilar materials, the use of lower scanning velocity has been associated with better homogeneity due to the extended laser residence time of the melt pool (i.e. duration when the laser illuminates the melt pool) [66]. Accordingly, it is imperative that the V650 melt pool, which experiences a shorter laser residence time, has a shorter molten duration as compared to the V500 and V350 melt pools. The shorter molten duration causes the melt pool to become kinetically frozen before a greater amount of liquid TiA can be diluted with Cu through Marangoni forces. Hence a larger fraction of $\alpha'\text{-Ti}$ is retained upon solidification and cooling. While melt pool non-homogeneity can also be caused by a positive enthalpy of mixing between the major elements [67], as is the case for the CuA/SS interface, the enthalpy of mixing of the Ti-Cu liquid alloy and the enthalpy of formation of Ti-Cu IMCs are both negative, thus favoring mixing [68, 69]. Therefore, the melt pool non-homogeneity in the V650 TiA/CuA interface is only attributed to the limited laser energy input and shorter molten duration of the melt pool. As such the use of minimal energy input during the processing of the TiA/CuA interface is recommended.

The 523 ± 1 MPa tensile strength of the V650 TiA/CuA/SS MM part, which is primarily limited by the TiA/CuA interface, is among the highest considering all other joining or AM techniques

used to bond TiA to steel either with or without the use of an interlayer material [5, 6, 10, 11, 13-16, 18, 19, 22-24, 29-34, 36-42]. However, it is believed that the V650 TiA/CuA interface, obtained through a simplistic increase in scanning velocity, is by no means optimal. Variations in laser power, scanning velocity, layer thickness, and substrate pre-heating can all be utilized to engineer the ideal melt pool geometry to further reduce the penetration depth of the first TiA build layer, improve melt pool stability and introduce a greater amount of tough interfacial α' -Ti phase. The ability to limit dilution, disperse brittle phases over a significant interfacial thickness, and introduce tough reinforcement phase into a relatively brittle matrix through melt pool non-homogeneity are beneficial characteristics of the SLM process. This makes SLM competitive for MM processing despite its relatively low utilization for such a purpose. The methodologies described herein to strengthen the TiA/CuA interface are postulated to be applicable for other metallic combinations and, perhaps, other AM techniques such as EBM and DED processes as well.

5. Conclusions

The SLM of Ti-6Al-4V to SS316L has been achieved through the use of a Cu-alloy interlayer and the key findings are as follows:

- The microstructure at the CuA/SS interface is comprised of a Cu-rich matrix which contains a non-homogenous distribution of SS bands. Owing to the miscibility gap in the Cu-Fe system, numerous micron-sized SS globules, and sub-micron CuA globules can be found within the Cu-rich matrix and the SS bands respectively. All Cu-rich regions (i.e. matrix and globules) correspond to the ϵ -Cu phase while the Fe-rich regions (i.e. SS bands and globules) belong to the γ -Fe phase. The SS globules, which solidify before the

surrounding CuA matrix, act as low energy nucleation sites to support the formation of equiaxed ϵ -Cu grains. A high density of finely dispersed SS globules is capable of refining the ϵ -Cu grains to sizes as small as 1-2 μm .

- The microstructure at the TiA/CuA interface comprised of layers of phases with distinct ranges of Cu content in the following order: ϵ -Cu (interlayer) /L2₁ phase/amorphous phase/ α' -Ti + (β -Ti + Ti₂Cu)/ α' -Ti (bulk TiA). The L2₁ phase is identified as the Cu₂TiAl Heusler compound with a low Al content. The beneficial presence of the α' -Ti phase within the brittle matrix of β -Ti + Ti₂Cu is attributed to the non-homogeneous mixing within the melt pool. The volume fraction of the interfacial α' -Ti phase can be increased through a reduction in laser energy input in the initial layers of the TiA build.
- Fracture of the TiA/CuA interface often initiated as cracks from the amorphous phase with neighboring porosities. After initiation, cracks propagated preferentially within the β -Ti + Ti₂Cu phase mixture but can be diverted towards the ductile CuA interlayer through a deflection around the relatively tough α' -Ti phase. As fracture transits into the CuA interlayer, the cleavage surface caused by crack propagation changes to a dimpled fracture surface caused by micro void coalescence. Raising the interfacial volume fraction of α' -Ti leads to an increase in the area fraction of the ϵ -Cu fracture surface. Tensile strength in excess of 500 MPa was obtained for the V650 MM samples which contained the highest volume fraction of interfacial α' -Ti phase.

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