**Additive manufacturing of a novel alpha titanium alloy from commercially pure
titanium with minor addition of Mo₂C**

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Abstract: In this study, a fully dense and crack-free alpha titanium alloy was fabricated using selective laser melting (SLM) of commercially pure titanium (CP Ti) blended with 1 vol.% micrometre-sized Mo₂C powder. The microstructure and mechanical properties of the fabricated Ti alloy were systematically investigated. It was found that the fabricated Ti alloy consisted of both alpha (α) and beta (β) phases and exhibited a nest-like inhomogeneous

microstructure with graded local phase formation, composition and crystallographic texture. This novel microstructure was formed through melting and rapid solidification of CP Ti and Mo₂C during SLM, assisted by the high laser absorptivity and resultant high temperature rise of the Mo₂C powder. The fabricated Ti alloy exhibited higher tensile strength ($\sim 1250 \pm 50$ MPa) and improved ductility (elongation $\sim 17 \pm 1\%$) when compared to CP Ti fabricated using the same SLM process. The underlying reasons were mainly attributed to (i) the nest-like inhomogeneous microstructure consisting of fine grained α -Ti and β -Ti, (ii) the overall solid solution strengthening of the Ti matrix by interstitial C, and (iii) the high dislocation density in the Ti matrix arising from the mismatch between α -Ti and β -Ti phases. This study not only provides a fundamental knowledge about the modification of CP Ti with minor addition of secondary particles through SLM but also provides insight into the fabrication of inhomogeneous Ti alloys with graded microstructure and local composition through SLM for enhanced mechanical properties.

Key words: Additive manufacturing; Selective laser melting; Titanium alloys; Commercially pure titanium; Graded microstructure.

1. Introduction

Commercially pure titanium (CP-Ti) is an important engineering material with broad applications in various industries, especially in the chemical and petrochemical sectors, due to their excellent fabricability and superior environmental resistance (e.g., corrosion resistance) in service [1]. However, the insufficient strength of CP-Ti severely impedes their implementation for applications where mechanical properties are equally important to corrosion resistance. Unfortunately, the available options for strengthening CP-Ti are relatively few and practically limited to solid solution strengthening (i.e., by interstitials and

substitutional elements), grain boundary strengthening, and dispersing secondary reinforcing particles into CP-Ti. As an example, great efforts have been devoted in the past decades to modifying CP-Ti either through traditional substitutional alloying with trace amount of elements including Pd or Ru ($\leq 2\%$) or designing and fabricating titanium matrix composites (TMCs) by introducing secondary particles or fibres into CP-Ti [1-5]. However, the conventional alloying approach is costly and very limited regarding the enhancement of mechanical properties of CP-Ti, while the conventional processing of TMCs is time-, energy- and material-consuming due to its high melting point ($\sim 1668^\circ\text{C}$) and high affinity to oxygen at elevated temperatures. Moreover, post-processing or machining of the fabricated TMCs is also difficult due to their high strength and high hardness [1].

As an emerging powder-based additive manufacturing technique, selective laser melting (SLM) produces metal components in a layer-wise fabrication manner from a computer-aided design (CAD) model [6, 7]. Apart from its widely-known advantages over conventional processing techniques such as high freedom of custom design, production of complex geometries and no need for post-machining processes, etc. [6, 7], it also features another two unique characteristics. The first characteristic is the cyclic heating and cooling process with very high heating and cooling rate due to the short interaction time and volume between the laser and materials [8]. This high cooling rate in SLM allows the fabrication of very fine microstructure with small grain size in many alloys as well as supersaturated non-equilibrium microstructure with higher concentration of solute elements. The second characteristic is the fabrication of new alloys of varying compositions by SLM of a mixture of two or more powders, arising from the powder metallurgy origin of the SLM manufacturing process. This flexibility of processing powder mixtures by SLM enables the design and fabrication of metal matrix composites (MMCs) reinforced by various secondary particles. As such, by producing very fine and supersaturated microstructure or MMCs, SLM

has opened up new opportunities to strengthen existing metals and alloys by solid solution strengthening, grain boundary strengthening, and introducing secondary particles to form composites, which are the most important three strengthening methods for CP-Ti. Therefore, SLM has been considered another promising alternative to the modification of CP-Ti and the design and fabrication of various strengthened Ti alloys or TMCs without post-machining. Some pioneering studies have been reported in recent years [9-13]. Fisher et al. reported the fabrication of a binary Ti-26Nb alloy by SLM from elemental Ti and Nb mixed powders. A homogeneous β -Ti alloy with non-columnar but elongated grains was achieved [14]. Gu et al. reported on the fabrication of TMCs by SLM of a mixture of CP Ti and micrometre-sized SiC particles. The microstructure showed a unique network of distributed TiC and a sub-micrometre dendritic morphology, which resulted in high microhardness (980 HV_{0.2}) and a low friction coefficient [15]. Apart from this, similar attempts were also made to fabricate other TMCs via SLM including Ti-TiC nanocomposites, in-situ Ti-TiB₂ composites and TiB reinforced near α -Ti metal composites from CP Ti and micrometre-sized CrB₂ [16-18]. Although these studies result in the fabrication of fully dense and crack-free Ti alloys or TMCs with improved mechanical properties by manipulating the SLM processing parameters, they all introduced a relatively large quantity of secondary particles (≥ 5 vol.%) to either form TMCs or form a substantial amount of β -Ti phase in the CP-Ti for strengthening purposes. For example, the secondary particles in previous studies (e.g., TiC and TiB) either remain intact after SLM or react with CP-Ti to induce the formation of a new compound in the matrix during SLM. As such, the role of solid solution strengthening in these SLMed Ti alloys or TMCs cannot be decoupled from the influence of large amount of β -Ti phase or residual/newly-formed secondary particles. Hence, another important strengthening mechanism in CP-Ti, namely the solid solution strengthening mechanism, has not been systematically investigated and fully understood in SLMed CP-Ti, in particular the influence

of interstitials and substitutional elements. Moreover, most of these fabricated Ti alloys or TMCs have a relatively homogeneous microstructure where the understanding in local tailorable microstructure and composition by adding secondary particles were not provided and are still unclear. Hence, it becomes crucial and necessary to investigate the important role of solid solution strengthening mechanism in CP-Ti through SLM of CP-Ti with a minor addition of secondary particles. Following this, the influence of the minor additions on the local microstructure and composition in the SLMed CP-Ti and hence the resultant mechanical properties can also be investigated and understood.

In this study, since Mo_2C contains both Mo and C and a small amount of Mo_2C is supposed to be fully melted and dissolved into Ti according to equilibrium phase diagram, Mo_2C was chosen as the source of interstitials and substitutional elements to CP-Ti. By optimising the SLM processing parameters, a fully dense and crack-free α -Ti alloy was obtained by SLM of CP-Ti with 1 vol.% Mo_2C particles. The microstructure and mechanical properties of the SLMed Ti alloy were systematically investigated. In contrast to previous studies, most of the Mo_2C particles were fully melted and entered into the Ti matrix as Mo and C to form solid solutions and no TiC was formed. Importantly, the fabricated Ti alloy exhibited a nest-like inhomogeneous microstructure and showed a higher tensile strength (around 1250 ± 50 MPa) and improved ductility (elongation around $17 \pm 1\%$) in comparison with the SLMed CP Ti. The underlying reason for this is discussed in detail. This study provides a promising alternative for strengthening CP-Ti by solid solution strengthening mechanism and fabricating inhomogeneous Ti alloys with graded microstructure and composition through SLM for better mechanical properties.

2. Experimental procedures

2.1 Powder materials and laser absorptivity

Commercially pure titanium powder (CP Ti, Grade 1, LPW, UK) with powder particle size from 15 to 45 μm and molybdenum carbide powder (Mo_2C , Changsha Langfeng, China) with an average powder particle size $\sim 3.5 \mu\text{m}$ were used in this study. Mo_2C powder was added to the CP Ti powder to make up a volume fraction of 1% and the powder was mixed in a multidirectional mixer for 4 h to ensure a homogeneous distribution. The laser absorptivity of the CP Ti powder, Mo_2C powder and the mixed powder were measured using diffuse reflectance spectroscopy (DRS). DRS was carried out in the 250 to 2250 nm wavelength range using an UV-Visible-NIR Lambda 950 Perkin Elmer spectrometer equipped with a 150 mm diameter integrating sphere coated with Spectralon with 1 nm spectral resolution. A Spectralon reference was used to measure the 100% reflectance and internal attenuators were used to determine zero reflectance in order to remove background and noise. The powders were placed in a quartz cuvette, sealed, and mounted on a Teflon sample holder for the DRS measurement.

2.2 Selective laser melting (SLM)

The mixed powder was used to produce Ti alloy specimens (10×10×10 mm) and standard tensile bars on an in-house built selective laser melting machine which is equipped with a fibre laser, with a wavelength of 1.06 μm and maximum power of 300 W on the part bed. An inert, high purity ($\geq 99.99\%$) argon gas atmosphere flow was used during the whole process to minimise oxidation. Optimal laser power and scanning speed were used to fabricate fully dense and crack-free specimens based on previous investigations [19]. The powder layer thickness was fixed at 30 μm , the scan spacing at 60 μm , without pre-heating. For comparison, CP Ti specimens (10×10×10 mm) were also produced using SLM with the

same optimised parameters. A total of 10 specimens were fabricated for both Ti alloy and CP Ti.

2.3 Microstructure characterisation

The microstructure of the powder materials and SLMed Ti alloy was characterised using a FEI-Nova NanoSEM 450 scanning electron microscope (SEM, acceleration voltage 10 kV, working distance 5 mm) and a FEI Tecnai G2 transmission electron microscope (TEM, operated at 200 kV). A state-of-the-art FEI Titan Themis 300 TEM, equipped with a probe aberration corrector and a highly efficient (4 quadrant) energy dispersive X-ray (EDX) system and operated at 200 kV, was further used for atomic and nanoscale characterization in the scanning TEM mode. The TEM 3 mm disc samples from the SLMed Ti alloy were mechanically polished and finally thinned by a Precision Ion Polishing System (Gatan PIPSTM) where low-angle and low-current polishing conditions were used in conjunction with a liquid nitrogen cold stage. Texture and grain size of SLMed Ti alloy were characterised by electron backscattered diffraction (EBSD) using a TSL orientation imaging microscope system mounted on a FEI-Nova NanoSEM 450 SEM (step size of 0.1 μm), and also by nano-beam diffraction using a Nanomages Astar system on a Tecnai G2 TEM (beam size of around 2 nm and step size of 10 nm). TEM Astar data was post treated using ATOM software [20].

Atom probe tomography (APT) was carried out on the SLMed Ti alloy. For specimen preparation, the samples were dissected into 0.5 mm $\times$ 0.5 mm square rods, which were then sharpened via electropolishing to create the needle shaped specimens required for APT analysis. Electropolishing was conducted at 38 V, with an electrolyte of 5 % perchloric acid in 30 % n-butoxyethanol and 65 % methanol cooled down to -31°C. The obtained tips were then sharpened in a Zeiss Auriga FIB-SEM to ensure that the needles had a tip diameter of less than 80 nm and that the surface was free of protrusions and dimples. The atom probe

experiments were carried out on a Cameca LEAP 4000X Si in laser pulsing mode at a specimen temperature of ~50 K, a pulse rate of 250 kHz, a pulse energy of 80 pJ and a target evaporation between 0.5-1 %. IVAS 3.6.8 software was used to reconstruct and visualise the APT data.

The phase formation in the powder and SLMed Ti alloy was characterised using X-ray diffraction (XRD, Siemens D500 powder diffractometer, Cu K α target, operated at 40 kV and 40 mA with a step size of 0.02° and scanning speed 2°/min, all XRD scans were done on the plane parallel to the SLM building direction). Since the oxygen and nitrogen pick-up during SLM can possibly influence the mechanical properties of the SLMed alloys, an inert gas fusion technique using a commercial analyser of the type Leco ONH836 was applied for quantitative analysis of the oxygen and nitrogen contents of the SLMed Ti alloy and the starting powder.

2.4 Mechanical properties

Standard tensile tests were carried out on SLMed and machined Ti alloy specimens (gauge length ~4×2×16 mm, prepared by electrical discharge machining, EDM), using an Instron 5982 machine at a constant strain rate of 1 mm/min. Strain was measured with a 12.5 mm gauge length extensometer. Samples were aligned perpendicular to the build direction and a total of 5 samples were tested. In addition, in order to in situ observe the tensile behaviour (e.g., slip bands) of the samples, SLMed CP Ti and Ti alloy micro-tensile specimens were prepared by EDM from the fabricated 10×10×10 mm cubes, followed by careful polishing. In-situ micro-tensile tests were carried out on the SLMed and machined specimens (gauge length ~2×0.5×6 mm) using Deben MICROTTEST 200N modules at a constant extension rate of 0.05 mm/min in a FEI-Nova NanoSEM 450 SEM. Samples were aligned perpendicular to the build direction and a total of 10 samples were tested.

3. Results

3.1 Mixed powder and laser absorptivity

The morphology of the CP Ti, Mo₂C and the mixed powder with 1 vol.% Mo₂C is shown in Figure 1. The CP Ti powder has a spherical shape, which is the typical gas-atomised powder morphology while the Mo₂C powder has an irregular shape. After mechanical mixing for 4 h, the micrometre-sized Mo₂C powder distributes relatively homogeneously. Although the majority of the Mo₂C particles are attached to the surface of the CP Ti powder, due to the fact that only 1 vol.% Mo₂C was added, no deterioration in the flowability of the CP Ti powder was expected. The laser reflectivity and K-M absorption factor were used to assess the laser absorptivity of the CP Ti, Mo₂C and the mixed powders (for comparison, CP Ti powder with 5 and 10 vol.% of Mo₂C were also prepared and measured). As shown in Figure 2, the laser reflectivity of Mo₂C powder and CP Ti powder at 1.06 μ m laser wavelength was measured to be ~22% and ~30%, respectively. With increasing the amount of Mo₂C powder, the laser reflectivity of the mixed powder decreased. Specifically for the addition of 1 vol.% Mo₂C powder in this study, the laser reflectivity of the mixed powder was reduced to ~27%. This indicates that even a small addition of Mo₂C (1 vol.%) can result in an improved laser absorptivity.

3.2 Microstructure of the SLMed Ti alloy

The phase formation in the CP Ti and Mo₂C powder as well as the SLMed Ti alloy specimens is shown in Figure 3. Both CP Ti powder and the Mo₂C powder have a hexagonal close packed (*hcp*) crystal structure. Only α -Ti was detected in the CP Ti powder while no β -Ti (body centred cubic, *bcc* Ti) was observed. In the SLMed Ti alloy, along with the peaks from α -Ti a tiny peak corresponding to β -Ti appeared, signifying the formation of a small amount of β -Ti in the SLMed Ti alloy. In addition, the relative peak intensity in the SLMed

Ti alloy and the CP Ti remains identical. This implies that no strong crystallographic texture was formed after SLM.

The microstructure of the SLMed Ti alloy in the cross-section parallel to the building direction is shown in the back-scattered SEM (BSE) image in Figure 4a. No cracks have been observed. An inhomogeneous microstructure consisting of three distinct areas with different contrast, i.e. dark area, light grey area and bright grey area can be readily seen. The SEM energy dispersive X-ray spectroscopy (EDX) results corresponding to these areas are shown in Figure 4b. The dark area mainly contains Ti without any Mo being detected, while the light grey and bright grey areas contain a lower amount and higher amount of Mo apart from Ti, respectively. This indicates that most of the Mo₂C particles were melted and dissolved into Ti during SLM. However, it is noteworthy that very few Mo₂C powder particles were also observed embedded in the Ti alloy matrix, as shown in the inset image in Figure 4a. From the spherical morphology of the residual Mo₂C powder particles which was different from its starting irregular morphology, it can be speculated that these Mo₂C particles also underwent a melting process during SLM.

The EBSD results of the SLMed Ti alloy in the cross-section parallel to the building direction are shown in Figure 5. From the inverse pole figure (IPF) image as shown in Figure 5a, two different regions can be observed. Both regions contain fine grains but one with elongated grains and the other with equiaxed grains. The two regions also showed a nest-like distribution where the regions with elongated grains were surrounded by the regions with equiaxed grains. The corresponding phase map shown in Figure 5b showed that the regions with elongated grains were α -Ti while the regions with equiaxed grains were β -Ti and no martensitic α' phase has been observed. According to the random colour in the IPF image, no strong crystallographic texture was formed in the SLMed Ti alloy, consistent with the XRD

result in Figure 3. However, as shown in the pole figures in Figure 5c, a strong local crystallographic texture developed in the α -Ti region while a relatively weak crystallographic texture was formed in the β -Ti region.

To further reveal the inhomogeneous microstructure in the SLMed Ti alloy, a detailed investigation was conducted using TEM. It can be seen from Figure 6a that the elongated lath-like grains were surrounded by very fine equiaxed grains. According to the electron diffraction patterns shown in Figure 6b, the elongated grains are α -Ti and the equiaxed grains are β -Ti, consistent with the SEM EBSD results shown in Figure 5. TEM nano-beam diffraction was also conducted on the SLMed Ti alloy which provided more detailed information about the local grain structure and phase formation, as shown in Figure 7. Both α -Ti and β -Ti exhibited very fine grain structures and distributed inhomogeneously in the Ti matrix. Interestingly, in contrast to previously reported SLMed metals with very low dislocation density [21], a large dislocation density exhibited in the SLMed Ti alloy in both α -Ti and β -Ti grains as shown in Figure 7d, implying that the heat dissipated from subsequent deposited and scanned layers cannot fully anneal out the dislocations formed during SLM. Since Mo is known as a β -Ti phase stabiliser, the distribution of the Mo in the β -Ti grain clusters was investigated using STEM EDX, as shown in Figure 8. It can be seen that the β -Ti grain boundaries were enriched with Mo while Mo was also detected inside the β -Ti grains, indicating that the distribution of Mo was inhomogeneous even at the nanoscale. To reveal the distribution of light elements, especially C, atom probe tomography (APT) was used. Figure 9a shows a reconstruction of the SLMed Ti alloy, containing only 5 % of the Ti ions and 100 % of the Mo and C ions. The remaining ions (e.g., O and N) detected during the analysis are very low and are not shown here, in order to improve the visibility of the other ions. An inhomogeneous distribution of Mo and C within the dataset was found. To better highlight the distribution of C and Mo within the dataset, iso-concentration surfaces of C

(blue), and iso-density surfaces of Mo (red) were created in Figure 9b, with a C concentration of 0.75 at% and an atomic density of 0.44 Mo/nm³. It can be seen that C and Mo are not located in the same areas. This is the case for all analysed datasets both in the matrix and along grain boundaries. A proxigram of all Mo iso-surfaces contained within the dataset is shown in Figure 9c, which further emphasises that the location of C and Mo is not correlated. Proxigrams are a 3D concentration distribution profile, which show the composition in the vicinity of an interface, and are generated by calculating a composition profile of all elements present within an iso-surface, with respect to their distance from the local normal of the interface [22]. This indicates that upon the melting and solidification of CP Ti and Mo₂C, C as an interstitial element can diffuse into the Ti matrix and then freezes inside the grains, probably as a result of the rapid cooling process during SLM. Analyses of the oxygen and nitrogen contents of the SLMed Ti alloys and the starting powders are listed in Table 1 which demonstrates that the oxygen and nitrogen pick-up during SLM is negligible.

3.3 Mechanical properties of the SLMed Ti alloy

Both standard tensile tests and in-situ micro-tensile tests were carried out to investigate the tensile behaviour of the SLMed Ti alloy and SLMed CP Ti as a comparison. The stress-strain curves of the standard and micro-tensile tests are shown in Figure 10. The SLMed CP Ti showed a tensile strength and elongation $\sim 760 \pm 30$ MPa and $15 \pm 1\%$, respectively. In contrast, the SLMed Ti alloy exhibited a much higher tensile strength and slightly higher elongation of $\sim 1250 \pm 50$ MPa and $17 \pm 1\%$, respectively (it should be pointed out that the relatively lower deformation strain in the micro-tensile specimens is mainly due to the fact that no physical extensometer was used for micro-tensile tests in this study. Therefore, the observed strain in the stress-strain curves (Figure 10b) is a combined result of the deformation from both the tensile testing stage (Deben MICROTTEST 200N modules) and the micro-tensile specimens). The fracture surfaces of the SLMed Ti alloy and SLMed CP Ti

from the micro-tensile tests are given in Figures 11a and 11b. It is clear that the SLMed CP Ti failed with a 45° angle relative to the loading direction while the SLMed Ti alloy failed perpendicular to the loading direction. Both have apparent necking, i.e., a typical ductile fracture behaviour. Some large voids can be readily seen on the fracture surface of the SLMed CP Ti. In addition, a higher number of slip bands can be seen near the fracture surface of the SLMed Ti alloy while very limited slip bands can be observed in the SLMed CP Ti. This again demonstrates the better ductility in SLMed Ti alloy than the SLMed CP Ti. Another close look at the fracture surfaces of the SLMed Ti alloy as shown in the BSE images in Figure 11c reveals that a high amount of micro-cracks formed in the dark area, which contained none or a low content of Mo. These micro-cracks were parallel to each other and perpendicular to the direction of the elongated grains which also had a small angle (mostly $\leq 10^\circ$) with the loading direction. This indicates that the failure in SLMed Ti alloy probably started in the elongated lath-like α -Ti grains which aligned along or close to the loading direction.

4. Discussion

4.1 Microstructure of the SLMed Ti alloy

Recently, manipulation of microstructures in SLMed metal components for improved mechanical properties has been realised through controlling the processing parameters in SLM including laser power, scan speed, hatch spacing and preheating temperature. As a result of the directional global heat flux and local high cooling rates, a characteristic microstructure consisting of ultrafine grains with or without strong crystallographic texture can be achieved in steel, Al-, Ti-, Ni- alloys, and high entropy alloys [23-29]. Although some inhomogeneous microstructures with different phases and grain sizes can be obtained, site-

specific tailoring of the local microstructure, composition, phase formation and crystallographic texture is still challenging by simply manipulating the SLM parameters. The main reason for this is that there is little to no control over the local thermal profiles. Introduction of secondary particles provides an effective way of altering local thermal profiles as the secondary particles normally have a different laser absorptivity compared to the matrix. This will result in a different temperature rise in the secondary particles and the matrix, which can be potentially utilised to tailor the local microstructure during SLM.

In this study, Mo_2C shows higher laser absorptivity than CP Ti, as shown in Figure 2. This will induce a much higher temperature rise in Mo_2C particles, similar to previous studies on SLM of ceramic particles reinforced Al-Si alloys [21, 30-32]. Based on these studies, this higher temperature rise in the Mo_2C is also expected to promote the melting and dissolving of the Mo_2C particles into Ti, as evidenced by the three distinct areas in the SLMed Ti alloy matrix (Figure 4a) and the spherical morphology of the residual Mo_2C particles. However, due to the low content of Mo_2C (1 vol.%) which is lower than the concentration required for the formation of TiC [33], no TiC was formed during SLM while Mo and C dissolved in the Ti matrix. It is noteworthy that apart from fully melting the Mo_2C particles might also be partially dissolved into the melt pool during SLM. However, further investigations will be needed to uncover this effect. Mo is a well-known β -Ti stabiliser and this is why β -Ti formed in the SLMed Ti alloy [1]. In addition, since SLM has a very high local cooling rate and the interaction time between laser and materials is very short (a few milliseconds), Mo does not have enough time to diffuse for a long distance within the melt pool which normally has a width and depth around 100 and 150 μm , respectively [34]. This is consistent with our previous study on SLM of metallic glasses where heavy elements tend to diffuse over a shorter distance compared to light elements [35]. It is worth pointing out that the convection flow in the melt pool can push the Mo_2C as well as Mo to the edge and bottom of the melt

pool during SLM. Therefore, the distribution of dissolved Mo in the SLMed Ti alloy is inhomogeneous, with most of the dissolved Mo distributed along the edge and bottom of the melt pool. This results in a local graded microstructure with graded composition where the concentration of Mo gradually changes from the centre to the edge of the melt pool. Since no or less Mo was distributed around the core region of the melt pool, mainly α -Ti was formed. This is why a nest-like microstructure consisting of α -Ti and β -Ti was observed in the SLMed Ti alloy and regions with different Mo content (Figure 5).

No martensitic α' phase has been observed in the SLMed Ti alloy. The formation of α' phase is well known in SLM of CP Ti or Ti alloys due to the high cooling rates [36, 37]. Our previous studies have shown the critical role of cooling rate in martensitic transformation in SLM of CP Ti [19]. Considering that identical SLM processing parameters were used in this study compared to our previous studies and only 1 vol.% of Mo_2C was added into the CP Ti matrix, a similar global heat flux can be assumed. Therefore, the underlying cause for the absence of α' phase in SLMed Ti alloy would be related to the local heat profiles which have been modified by the higher temperature rise in Mo_2C as mentioned above. This is why only lath-like elongated α -Ti was observed inside the melt pool, surrounded by β -Ti formed by the melting and dissolving of Mo_2C into CP Ti. According to the TEM results, Mo was distributed inhomogeneously in the β -Ti regions, enriched at the β -Ti grain boundaries. These Mo-enriched grain boundaries can impede the grain growth during solidification during SLM. This is why the size of the β -Ti grains is much smaller than for the α -Ti grains.

In general, SLMed metal components show a strong textured microstructure due to the directional global heat flux and large thermal gradient that exist during the SLM process. The crystallographic texture can be altered or modified by varying the scanning patterns [28, 29]. The underlying mechanism lies in the manipulation of the global heat flux behaviour

during SLM. In addition, there are a few other factors which can influence the crystallographic texture formation including stresses generated by volume change as well as some characteristic grain boundaries which favour nucleation of certain orientation, phase formation, etc. [38]. In this study, although the global heat flux during SLM of Ti alloy cannot be severely altered by addition of this small amount of Mo₂C, the local thermal profile around the Mo₂C can be influenced due to its higher laser absorptivity and higher temperature rise during SLM, especially in the region where the β -Ti formed. As a result, a relatively weak crystallographic texture formed inside the β -Ti region while a strong crystallographic texture formed in the α -Ti region which is less influenced by Mo₂C (Figure 5), which is in contrast to the strong crystallographic texture in the SLMed CP Ti [22]. Therefore, the formation of texture during SLM of Ti alloy in this study is actually a combined mechanism consisting of both global heat flux and local thermal profile. In contrast to previously reported SLM of aluminium nanocomposites where no high dislocation densities were observed due to the dislocations being annealed out by the heat dissipated during SLM [21], high dislocation densities were detected in this study in the SLMed Ti alloy. The reason for this is attributed to the diffusion of Mo into CP Ti matrix to form β -Ti phases where a strong mismatch exists between α -Ti and β -Ti phases.

4.2 Mechanical properties of the SLMed Ti alloy in comparison with SLMed CP Ti

It is known that there are several key mechanisms for enhancing the mechanical properties (e.g., strength and ductility) of a metallic material. These mechanisms include grain boundary strengthening, Orowan and loading-bearing strengthening via secondary particles, increased dislocation density strengthening, bimodal grain structure and non-equilibrium grain boundaries, etc. In this study, since only very few Mo₂C particles were left and no TiC was formed in the SLMed Ti alloy, the observed strengthening of SLMed Ti alloy compared to SLMed CP Ti is probably due to solid solution hardening, strengthening by high

dislocation density and grain boundary hardening rather than precipitation hardening. In details, the tensile properties enhancement of SLMed Ti alloys in this study is mainly attributed to: (1) the solid solution strengthening due to interstitial C which is distributed inside the α -Ti phase; (2) the high dislocation density arising from the mismatch between α -Ti and β -Ti phases; and (3) the graded and inhomogeneous microstructure consisting of nest-like fine α -Ti and β -Ti with Mo enriched grain boundaries. As for solid solution hardening, it has been shown that Mo mainly distributed in the β -Ti phase while C was found mainly in the α -Ti phase (Figures 8 and 9). Considering that Mo has a small effect on the lattice parameter of β -Ti and only 1 vol.% Mo_2C was added into CP Ti in this study, the solid solution hardening effect from Mo is trivial. In contrast, the interstitial C is reported to have a significant strengthening effect in the α -Ti phase even at very low concentration, similar to other interstitial elements such as N and O [1, 39]. Therefore, interstitial C plays a critical role in solid solution strengthening of the SLMed Ti alloy. As abovementioned, a high dislocation density was observed in the SLMed Ti alloy mainly arising from the mismatch between α -Ti and β -Ti phases. This high dislocation density means that there is only a short distance between dislocations which can block the motion of each one during deformation, further contributing to the strengthening of the SLMed Ti alloy. In addition, the SLMed Ti alloy has a graded and inhomogeneous microstructure consisting of nest-like fine α -Ti and β -Ti. The fine grained α -Ti and β -Ti can also contribute to the enhanced strength in the SLMed Ti alloy, especially in the β -Ti where the grain boundaries are enriched with Mo which can impede the movement of dislocations. As a result, it can be seen that the enhancement in strength in the SLMed Ti alloy compared to SLMed CP Ti is mainly caused by the solid solution strengthening from interstitial C in α -Ti, high dislocation density and the fine grained α -Ti and β -Ti with Mo enriched grain boundaries. A similar result was also reported

recently on SLM of stainless steel 316L with significantly enhanced mechanical properties due to high dislocation densities, novel microstructures, etc.[40].

It is known that CP Ti can deform through both dislocation activated slip and deformation twinning and the fracture mechanism of CP Ti can be void nucleation and coalescence and/or cleavage fracture [1]. The plastic deformation and fracture mechanisms of CP Ti both depend on various factors including composition, grain size, and crystallographic texture and loading conditions [1, 41]. In SLMed CP Ti, since the grain size is much smaller than the conventionally fabricated CP Ti, the operation of deformation twinning is restricted and the deformation in SLMed CP Ti is mainly activated through slip modes [1]. This reduces the plasticity of SLMed CP Ti and is why only a small number of slip bands can be seen in the deformed SLMed CP Ti. The large void at the fracture surface shows that a void mechanism is in operation and voids are mainly nucleated at α/α grain boundaries. As for the 45° angle between the fracture surface and the loading direction, the main reason for this is attributed to the well-known fact that the maximum shear stress exists along the plane with a 45° angle to the loading direction. Although void nucleation and coalescence mechanism dictates the fracture of SLMed CP Ti, it is worth pointing out that due to the *hcp* crystal structure of α -Ti the crystallographic texture can also increase the propensity for cleavage fracture along the basal plan in α -Ti, especially in the SLMed CP Ti where strong crystallographic texture can exist locally [1, 42]. This can also influence the angle between the fracture surface and loading axis. Further investigations will be needed in the future to uncover the exact fracture mechanism. In the SLMed Ti alloy, α -Ti has a lower strength than β -Ti, and therefore the cracks are expected to initiate in the α -Ti regions when an external load applies. This is why cracks are mainly formed in the α -Ti region. Although the propensity for cleavage fracture in α -Ti decreases with decreasing grain size, the existence of interstitial C will increase the propensity for cleavage fracture in α -Ti [1, 42]. This cleavage

fracture differs from the void nucleation mechanism induced fracture and depends on the stress along the basal plane of α -Ti, which can be influenced by the crystallographic texture of the α -Ti [1, 42]. This can be the reason why multiple parallel cracks in the α -Ti were aligned perpendicular to the elongated α -Ti grain (Figure 11). Upon further loading, these cracks in the α -Ti region will propagate towards the β -Ti grains where α/β interfaces will act as a barrier to stop its further propagation and release the strain energy by initiating slip bands around the interface. As a result, a high density of slip bands can be observed in the deformed SLMed Ti alloy. Due to this slip transmission across the α/β interfaces and the relatively weak crystallographic texture in β -Ti the crack propagation direction will be perpendicular to the loading direction and this is why the fracture surface is perpendicular to the loading direction. As a result of this, the strength and ductility of the SLMed Ti alloys were both enhanced compared to the SLMed CP Ti.

5. Conclusions

In this study, a fully dense and crack-free α -Ti alloy was obtained by SLM of CP Ti with 1 vol.% micrometre-sized Mo_2C . The microstructure and mechanical properties of the SLMed Ti alloy were characterised and investigated in comparison with the SLMed CP Ti. The following conclusions can be drawn from this study:

(1) The minor addition of Mo_2C can increase the laser absorptivity of the mixed CP-Ti and Mo_2C powders. Most of the Mo_2C particles were fully melted and entered into the Ti matrix as Mo and C to form solid solutions, facilitated by the high temperature rise in Mo_2C . This results in the formation of three distinct areas with different concentrations of Mo in the SLMed Ti alloy. No TiC was detected, which was probably due to the fact that only a small amount of Mo_2C was added to CP Ti.

(2) The SLMed Ti alloy showed a nest-like inhomogeneous microstructure with graded local microstructure and local composition. Equiaxed β -Ti which was stabilised by Mo formed together with elongated α -Ti in the SLMed Ti alloy. Mo was found enriched along the β -Ti grain boundaries while C was found as an interstitial in the Ti matrix and distributed inside the grains with some high concentrated areas. In addition, α -Ti showed a strong crystallographic texture while β -Ti showed a relatively weak crystallographic texture. The formation of this microstructure was mainly attributed to the convection flow in the melt pool and the modified local thermal profiles during the SLM process.

(3) The fabricated Ti alloy exhibited a higher tensile strength ($\sim 1250 \pm 50$ MPa) and slightly improved ductility ($\sim 17 \pm 1\%$ elongation) when compared to CP Ti fabricated using SLM. The underlying reason was attributed to the fine nest-like α/β microstructure, the solid solution strengthening by interstitial C, and the high dislocation density in the matrix.

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Table 1 Chemical analysis for the SLMed Ti alloys and the starting powders

Sample names	O₂ (ppm)	N₂ (ppm)
Starting powders	485	127
SLMed Ti alloys	517	135

Figure captions

Fig. 1 SEM images of the morphology of (a) CP Ti powder, (b) Mo₂C powder and (c) CP Ti with 1 vol.% Mo₂C powder after mechanical mixing for 4h.

Fig. 2 The laser reflectivity of the CP Ti powder, the Mo₂C powder and the mixed powders with different amounts (1, 5 and 10 vol.%) of Mo₂C powder. The dotted lines in black shows the laser wavelength used in the SLM machine in this study.

Fig. 3 XRD patterns of the Mo₂C powder, the CP Ti powder, SLMed CP Ti and the SLMed Ti alloy. Red arrow points to the XRD peak which belongs to the *bcc* β -Ti and all other XRD peaks belong to *hcp* α -Ti or Mo₂C.

Fig. 4 (a) Back-scattered electron (BSE) SEM images of the SLMed Ti alloy showing three distinct areas: dark area, light grey area and bright grey area. Inset shows the residual Mo₂C powder in the SLMed Ti alloy. (b) SEM EDX point analysis spectra (from bottom to top) corresponding to the dark area, light grey area and bright grey area in (a), respectively.

Fig. 5 (a) EBSD orientation map of the SLMed Ti alloy measured in a section plane along the building direction (BD). The colour code representing the crystal orientation is included. (b) Corresponding phase map of the SLMed Ti alloy. (c) Pole figures showing the local crystallographic texture in the α -Ti and β -Ti regions. Dotted squares in black in (a) and (b) show the α -Ti region, acting as guidance for eyes for the nest-like microstructure.

Fig. 6 (a) TEM BF image of the SLMed Ti alloy. (b) Experimental and (c) Corresponding theoretical electron diffraction patterns of the α -Ti and β -Ti phases. Black and red arrows point to the *hcp* α -Ti and *bcc* β -Ti, respectively.

Fig. 7 TEM Astar results of the SLMed Ti alloy: (a) Index map; (b) orientation map for α -Ti phase; (c) orientation map for β -Ti phase; and (d) geometrically necessary dislocations map. Colour codes for α -Ti and β -Ti are included, respectively.

Fig. 8 (a) STEM HAADF image of the SLMed Ti alloy and the corresponding STEM EDX maps showing the distribution of elements (b) Ti, (c) C and (d) Mo.

Fig. 9 (a) APT reconstruction containing Ti (5 %), Mo (100 %) and C (100 %). (b) APT reconstruction showing the iso-concentration surface of C ions in blue), and the iso-density surface of Mo ions in red. (c) Proxigram of all Mo iso-surfaces.

Fig. 10 Stress-strain curves for (a) the standard tensile tests of the SLMed Ti alloy and (b) the micro-tensile tests of the SLMed Ti alloy and SLMed CP Ti. Insets show the standard tensile specimens and micro-tensile specimens prepared using EDM from the SLMed Ti alloy (bottom inset in b is the micro-tensile specimen in SEM).

Fig. 11 The fracture surfaces of (a) the SLMed CP Ti, (b) the SLMed Ti alloy at low magnification and (c) the SLMed Ti alloy at high magnification. Black arrows in (b) and (c) point to the slip bands and micro-cracks, respectively.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11