The Effect of Energy Density and Nb Content on the Microstructure and Mechanical Properties of Selective Laser Melted Ti-(10-30 wt.%) Nb

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In this study, Ti-(0-30 wt.%)Nb alloys developed from elemental powders were fabricated by the Selective Laser Melting (SLM) process. Compositional homogeneity, microstructure and mechanical performance were investigated as a function of energy density. The proportion of un-melted Nb particles and isolated pore count reduced with increasing energy density, while Ti allotropic content (i.e. α' , α'' and β) varied with energy density due to in-situ alloying. Increasing the Nb content led to the stabilisation of the α'' and β phases. The mechanical properties were similar to those compositions manufactured using casting methods, without further post processing. The addition of 20Nb (wt.%) and using an energy density of 230 J/mm³ resulted in a Young's Modulus of 65.2 ± 1.8 GPa, a yield strength of 769 ± 36 MPa and a microstructure of predominantly α'' martensite. This strength to stiffness ratio (33% higher than Ti-10Nb and 22% higher than Ti-30Nb), is attributed to in-situ alloying that promotes solid solution strengthening and homogenisation. These alloys are strong contenders as materials suitable for implantable load-bearing orthopaedic applications.

Keywords additive manufacturing, biomedical, Titanium, mechanical testing

1. Introduction

Titanium and its alloys have characteristics, such as low density, corrosion resistance and non-toxicity for in vivo applications, making them ideal materials for use in orthopaedics and tissue engineering. However, titanium has a larger Young's Modulus (100 GPa) compared to cortical bone (10-30 GPa) (Ref 1). A mismatch that can lead to stress-shielding and osteopenia (Ref 2). It is desirable to lower the Young's Modulus of the implant material, close to that of the host tissue, i.e., bone. A proposed approach is to alloy titanium (Ti) with elements, such as niobium (Nb), molybdenum (Mo) or tantalum (Ta). These alloying elements, known as isomorphous β stabilisers, prevent the formation upon cooling of the hexagonal α phase, allowing the retention of the high temperature β phase. The presence of the β phase at room temperature has been found to lower Young's Modulus, in comparison to the α phase

present in pure titanium (Ref 3,4). The addition of these β stabilisers can also lead to the presence of additional phases, including the orthorhombic α'' martensitic phase and the interstitial ω phase. These phases alter the mechanical properties, with α'' leading to a reduction of the Modulus compared with the α phase, and the ω phase leading to an increase (Ref 5). Nb is a β stabilising element with lower cyto-toxicity, in comparison with other β stabilisers, such Mo and Fe (Ref 4,6). Ti-Nb alloys have been found to contain high strength and low Young's Modulus, making them promising for orthopaedic implant applications (Ref 4,7,8).

Selective Laser Melting (SLM), which uses a laser to melt powder in layers to build the required part, can manufacture customised orthopaedic implants of complex geometries, with lowered investment cost and reduced machine time compared to traditional processes such as casting (Ref 9,10). The application of this process has been dominated by industrially attractive alloys, such as Ti-6Al-4V, a $\alpha+\beta$ phase alloy, with few investigating β stabilised titanium alloys, such as Ti-Nb alloys (Ref 11-13).

The limited adoption of Ti-Nb alloys is in part due to the high cost of the pre-alloyed powders, and the difficulty in achieving "in-situ alloying", i.e. when the laser beam not only melts but also homogenises elemental powders in the melt pool (Ref 14,15). Attempts have been made to use in-situ alloying to improve the mechanical properties, including adding yttria-stabilised zirconia to Ti-6Al-4V to increase hardness, rhenium to titanium to improve the corrosive properties and Mo to Ti-6Al-4V to improve strength (Ref 16-18). Owing to the complex nature of the SLM thermal profile, as well as differences in fusion temperature of added alloying elements, achieving compositional homogenisation remains largely unresolved. Several studies have investigated the in-situ alloying of Ti with β -stabilising elements (Ref 14,16,19-21). Fischer et al. showed that increments in energy density improved homogenisation of in-situ alloyed Ti-26Nb (at.%) (Ref 22). Similar

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results have been reported by Chen et al. using a mixture of Ti-37Nb-6Sn (wt.%) from elemental powders (Ref 23). In terms of Nb content, Wang et al. suggests that the quantity of Nb within the alloy affects its homogenisation, with increased Nb content leading to an increased fraction of un-melted Nb (Ref 24). However, as shown in Fig. 1, little work has focused on Ti-Nb alloys, especially at compositions, where α' and α'' are expected (Ref 7,22-29).

To the best of the author's knowledge, no study has systematically compared the effect of Nb content with energy density. Therefore, this present work focuses on the influence of energy density and Nb content to produce Ti-Nb alloys (10, 20 and 30Nb (wt.%)). These compositions were chosen as exemplars of different allotropic phases; i.e., Ti-10Nb is expected to display a predominant α' phase, Ti-20Nb containing the α'' phase and Ti-30Nb expected to contain $\alpha'' + \beta$ phases. The chosen compositions are yet to be explored, as shown in Fig. 1. The phases, microstructural evolution, homogeneity, and mechanical properties of these alloys were investigated with respect to those produced using conventional methods, such as vacuum cast re-melting.

2. Materials and Methodology

2.1 Material Preparation

Gas atomised CP-Ti powder (Carpenter Additive Ltd, USA, 99.5%, D50 = 34 μm), and mechanically crushed Nb powder (Alfa Aesar, UK, 99.8%, <45 μm), were mixed to the required composition (i.e. 0 (referred to as CP-Ti), 10, 20 and 30 wt.% Nb). All compositions are provided in wt.%, unless otherwise stated. Mixing was performed on a PM100 (Retsch, Germany),

using a ball to powder mass ratio of 2:1 at 100 RPM for 1 hour. The morphology and size of the powder after mixing, was observed using a Scanning Election Microscope (7800, JEOL, Japan). As shown in Fig. 2, morphology and powder characteristics are consistent with the pre-mixed powder, and no variation was observed as a result of the mixing process. In addition, the Nb particles were found to be evenly distributed in the Ti powder. The average powder size was 34.0, 32.3, 30.1, 29.6 μm for CP Ti, Ti-10Nb, Ti-20Nb and Ti-30Nb, respectively. All compositions had good flowability and printing characteristics, with Ti-30Nb (containing the highest fraction of non-spherical Nb particles), having a powder density 45% and high circularity (0.87), suitable for the SLM process.

2.2 In-situ Alloying of Ti-Nb Alloy by SLM

The SLM process was conducted using a TruPrint 1000 LMF (Trumpf, Germany), equipped with a 200 W Nd:YAG solid-state laser with a spot size of 55 μm . Processing was completed within an argon atmosphere to an oxygen content below 100 ppm to prevent oxidation.

The laser scanning parameters were chosen to control the volumetric energy density supplied to the fabricated part. The Volumetric Energy Density (VED) was calculated using Eq. 1.

$$VED(J/mm^3) = \frac{P}{V \times h \times t} \quad (\text{Eq 1})$$

Where P = laser power (W), V = scanning speed (mm/s), h = hatch distance (mm), t = layer thickness (mm).

Based on initial evaluation of potential parameters available, three different values of energy density were chosen (50 J/mm³, 110 J/mm³ and 230 J/mm³). These energy densities were chosen based on the maximum energy densities achievable within the limits of the machine (i.e. 230 J/mm³), and the lowest energy

Fig. 1 Energy Density vs Nb (wt.%) examined in literature, as well as the predicted phase expected based on Mo equivalence (Ref 7,22-29)

Fig. 2 SEM micrographs of CP-Ti (a), Ti-10Nb (b), Ti-20Nb (c), and Ti-30Nb (d) powder feedstock after mixing

Table 1 Chosen laser scanning parameters

Volumetric Energy Density, J/mm ³	Laser power, W	Hatch distance, μm	Layer thickness, μm	Scanning speed, mm/s	Scanning strategy
50	140	110	30	848	bi-directional raster with 90° offset between layers
110	140	110	30	386	bi-directional raster with 90° offset between layers
230	140	110	30	186	bi-directional raster with 90° offset between layers

density able to successfully fabricate the required part (i.e. 50 J/mm³). 110 J/mm³ was chosen as it is recommended manufacturers value for CP-Ti, being 60 J/mm³ higher than the lowest value and 120 J/mm³ lower than the higher energy density achievable. Scanning speed was chosen as the parameter of interest, as it allowed greater flexibility compared to the other parameters in the energy density equation. The scanning speed was altered to achieve the required energy density, while other parameters were maintained as shown in Table 1. For each composition and energy density, two cubic samples (7x7x7mm) were fabricated for microstructural analysis, and three cylindrical samples (6 mm diameter x 12 mm height) were fabricated for mechanical testing. After fabrication, the samples were cut from a build plate along the x-y plane with the use of a high-speed saw (IsoMet High Speed Pro, Buehler, Germany) fitted with a diamond-coated blade (IsoMet Blade, 15HC - 4in, Buehler, Germany). For metallurgical examination, samples were ground with P400 grit SiC abrasive paper, followed by polishing with 9

μm diamond suspension, and 0.02-0.6 μm colloidal silica. Grinding and polishing processes were performed using an automated polishing machine (Automet 250, Buehler, USA).

2.3 Microstructural and Homogeneity Analysis

Homogeneity characterisation was ascertained by calculating the area fraction of un-melted Nb particles within the entire cross-section, obtained from a Scanning Electron Microscope (SEM, 7800, JEOL, Japan). Further SEM micrographs were on chemically etched surfaces (Kroll's reagent, vol. 91% H₂O 6% HNO₃, 3% HF, exposed for 15 seconds) to reveal microstructural features. Optical micrographs (Zeiss Primotech Materials Microscope, USA) were used to measure void content. The area fraction of the voids was calculated from optical micrographs, using MATLAB software (MATLAB ver. R2018b, The MathWorks, inc., USA). The plane of analysis for optical and SEM imaging was offset by 3 mm from the top surface in the build

direction, to avoid transitional effects present in the outermost top layers.

2.4 X-Ray Diffraction

The phase identification was performed using an x-ray Diffractometer (D2, Bruker, USA) with a Cu source, operating with a voltage of 30 kV, and an electron current of 10 mA. The peaks were measured from a 2θ angle of 30° to 80° , with a step of 0.2° .

2.5 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) was performed to assess the phases present in the sample and measure the transformation temperature to give an understanding of the β stabilisation of the fabricated alloy. The DSC measurements were performed on a Shimadzu DSC60 (Kyoto, Japan), with a cooling/heating rate of 10°C , from an initial temperature of 40°C up to a max temperature of 570°C . The second heating/cooling cycle was performed to assess the decomposition of metastable phases within the alloy. The machine was continuously purged with Argon gas, at a rate of 100 ml/min. A baseline scan was performed without any samples present, and used to remove any noise from the scan. The samples used were cut to a mass between 60–80 mg, and cleaned in isopropyl before use.

2.6 Mechanical Testing

The samples were prepared, according to the ASTM E9 standard, having a length-diameter ratio equal to 2 (Ref 30). Top and bottom faces were ground with P800 grit SiC paper to ensure they were flat and parallel. All compression specimens were fabricated with dimensions 12 mm in length and 6 mm in diameter. Compression testing was performed on an Instron universal testing machine (3369, Instron, UK, 20 kN), with a constant strain rate of 0.005 s^{-1} . The Young's Modulus was obtained from the slope of the elastic region formed, when plotting stress vs strain. An extensometer (2601, Instron, UK) was attached to a mechanical testing rig to accurately assess the strain and calibrated before use to the manufacturer's recommendation. Three test samples of each parameter set were assessed, with each sample being loaded in the elastic region 5 times to ensure repeatability. Finally, samples were loaded to plastic deformation to obtain the yield strength. The yield strength was calculated using the 0.2% strain-offset method.

3. Results and Discussion

3.1 Phase Analysis

Figures 3, 4, 5 and 6 exhibits the XRD scans of the as-fabricated alloy composition at the chosen energy densities. The CP-Ti (Fig. 3) and Ti-10Nb (Fig. 4) alloys all displayed peaks associated with the hcp α (or hcp α' , given that both display the same lattice parameters) phase. When the Nb content was increased to 20% and above, martensitic orthorhombic α'' was the predominant phase present in the alloy (Fig. 5). This phase is developed from the distortions of the Ti lattice, due to the introduction of Nb atoms, and is often found in Ti-Nb alloys with $>13\text{ Nb}$ (Ref 31). In addition to the α'' phase, other peaks present are associated with the cubic β

phase as indicated. This phase is unexpected in a fully homogenised alloy at Ti-20Nb, with the only phase expected being α'' (Ref 31). Therefore, the suspected β phase peaks can be linked to locally enriched Nb regions or un-melted Nb particles in the Ti-Nb matrix. The presence of both phases (β and α''), is an indication that the alloy has not been fully homogenised by the SLM process. However, with increments in the energy density, the intensity of the peaks associated with the β -Nb phase decrease. This highlights the impact of energy density in increasing the homogenisation of the alloy, and reducing the presence of un-melted Nb particles. Ti-30Nb (Fig. 6) also exhibited peaks linked to α'' phase and β phases. However, the increased Nb content led to an increased peak intensity of the β phase, and therefore an indication of a further β stabilised alloy.

All compositions displayed a growth in the preferred crystallographic texture with increasing energy density. The CP-Ti and Ti-10Nb alloys showed increased intensities in peaks, associated with the $\alpha(102)$ and $\alpha(110)$, and a corresponding decrease in $\alpha(101)$ peak. On the contrary, Ti-20Nb and Ti-30Nb alloys exhibited growth in the $\alpha''(022)$ and $\beta(200)$ orientations, as the energy density increased. It is hypothesised that this trend is a result of the re-melting of applied layers with the subsequent laser scans during the SLM process, resulting in elongated grain growth along the thermal gradient. With higher energy density the heat penetration increased, creating a large thermal gradient in the build direction, and increasing crystallographic alignment in this direction. This can be corroborated by the enlarged $\beta(200)$ peak in the Ti-20Nb and Ti-30Nb alloys, suggesting the β prior grains are orientated in the $\{001\} <100>$ direction, corresponding to the build direction (Ref 23). The increase in the $\alpha''(022)$ peak in the Ti-20Nb alloy can be explained by the orthorhombic transformation, undergone during rapid cooling from the $\beta(200)$ textured prior β grains to $\alpha''(022)$ orientation, using the lattice correspondence $\{001\}_\beta \rightarrow 1/2\{011\}_{\alpha''}$ (Ref 32). A comparison between the relative intensities of the peaks of Ti-20Nb and Ti-30Nb alloys manufactured at 230 J/mm^3 showed increased Nb content led to a reduction in the $\alpha''(022)$ peak, and an increase in the $\beta(200)$ peak. This change in relative intensity indicates a link between increased Nb concentration and increased β stabilisation, which leads to the suppression of the martensitic ($\beta \rightarrow \alpha''$) transformation.

3.2 Void Content

The formation of voids was found to be correlated to the Nb content and the energy density used (Fig. 7). At 50 J/mm^3 increasing the Nb content was found to lead to an increase in the area fraction of voids, from 0.045% in Ti-10Nb through 0.6% in Ti-20Nb to 1.67% in Ti-30Nb. This suggests that at the low energy density, the presence of isolated pores is dependent on the Nb content. However, at 230 J/mm^3 all alloys displayed similar levels of porosity, rendering the phenomenon independent of Nb content with sufficient energy density. The increase in the area fraction of void with the increasing Nb content can be correlated to the higher melting temperature of Nb (2447°C), compared with Ti (1668°C). Therefore, at the lower energy density, the energy supplied to the powder appeared insufficient for the complete melting of Nb, resulting in a lack of fusion between the Ti and Nb particles and the presence of isolated pores. There were no pores or cracks linked to β

Fig. 3 XRD patterns of CP-Ti, as-fabricated as a function of energy densities

Fig. 4 XRD patterns of Ti-10Nb alloys, as-fabricated as a function of energy densities

Fig. 5 XRD patterns of Ti-20Nb alloys, as-fabricated as a function of energy densities

Fig. 6 XRD patterns of Ti-30Nb alloys, as-fabricated as a function of energy densities

Fig. 7 Comparison in area fraction of voids with energy density and niobium (Nb) content (inset: optical micrographs of cross-sectional surface of the Ti-30Nb alloy at indicated energy densities)

excessive energy and gas entrapment found in any of the samples.

3.3 Un-Melted Nb Particles

Figure 8 shows the measured un-melted Nb area fraction, normalised against the added Nb content, of the Ti-Nb alloys fabricated in this study, and the values are provided in Table 2. The inset micrographs show the chemical inhomogeneity present, depicting colour contrast as a result of the elemental atomic contrast, i.e. lighter areas linked to increased Nb content, and darker areas having a higher Ti content, and the white particles visible being the un-melted Nb particles. The presence of the un-melted Nb particles in the melt pool suggest that the temperature in the melt-pool is insufficient to melt some

of the larger Nb particles, which is exacerbated at lower energy densities. As shown, the area fraction of un-melted Nb particles is linked to the energy density used, as with increasing energy density, the fraction of un-melted Nb particles decreases at all Nb contents. Increasing the added Nb content also increased in the un-melted fraction, with Ti-30Nb displaying the highest ratio, compared with Ti-20Nb and Ti-10Nb. It is likely due to the increased added Nb content, and therefore, the increased heat of fusion in the melt pool (Ref 33).

3.4 Microstructural Analysis

For the Ti-(10-30)Nb alloys, the samples fabricated at 50 and 110 J/mm³ displayed large variation in composition due to the elemental inhomogeneity, resulting in no clear and pre-

Fig. 8 Comparison in area fraction of un-melted Nb particles to added Nb content with energy density and niobium (Nb) content (inset: SEM micrographs of cross-sectional surface of the Ti-30Nb alloy at indicated energy densities)

Table 2 Area fraction of un-melted Nb particles to added Nb content with energy density and niobium (Nb) content

	Area fraction of un-melted Nb particles to added Nb content (% ± SD)		
	Ti-10Nb	Ti-20Nb	Ti-30Nb
50 J/mm ³	13.9 ± 5.8	29.6 ± 5.1	46.5 ± 4.8
110 J/mm ³	5.5 ± 2.8	12.9 ± 3.3	30.5 ± 2.7
230 J/mm ³	1.7 ± 1.6	2.0 ± 1.1	4.1 ± 1.2

dominate microstructure. However, at the highest energy density (230 J/mm³) a more homogenous microstructure was present. SEM (backscatter) micrographs of the etched microstructure of the alloys fabricated at this energy density are displayed in Fig. 9. At the highest energy density, the Ti-10Nb alloy (Figs. 9a-b) predominantly displayed a Widmanstätten α' microstructure, similar to cast alloys of the same composition (Ref 31). The Ti-20Nb alloy displayed a martensite α'' microstructure with evident un-melted Nb particles. Melt pool boundaries and cellular structures were also present. Within the bulk sample (Figs. 9c-d), away from un-melted Nb particles, the α'' martensite is present, and propagating from the edges of the prior β grains. In addition to the primary martensite needles, in the range of 10 μ m in length (Fig. 9d), small needles are present orientated perpendicular to the primary needles. This morphology was described previously by Yang et al. (Ref

34) in the α phase of Ti-6Al-4V, who classified the martensitic needles into size categories (i.e. primary, secondary, tertiary etc) with decreasing size. This microstructure, not present in traditional manufactured alloys, is the result of the rapid heating and cooling of previously deposited layers. It is proposed that primary needles were formed in the initial heating cycles, with the subsequent heating cycles, forming the secondary, tertiary needles and the growth of the subsequent needles, being constrained by the presence of previous needles. This microstructure results in an increased density of dislocations, which impedes movements of the dislocations, and is the most plausible reason to explain the increased strength and reduced ductility present in the Ti-20Nb alloy, fabricated at 230 J/mm³.

The Ti-30Nb alloy (Fig. 9e-f) showed a primarily cellular β microstructure, with the presence of martensitic α'' phase also

Fig. 9 SEM (Backscatter) micrographs (X-Y cross-sectional plane) of Ti-10Nb (a,b), Ti-20Nb (c,d) and Ti-30Nb (e,f) alloys, as-fabricated at an energy density of 230 J/mm³

detected. Although the cooling rate was not directly measured, the presence of the martensite phase gives an indication of the high cooling rate of the SLM process. This assumption can be made, as this phase has been reported elsewhere, when a high cooling rate occurs (Ref 7,31). Other studies have measured the cooling rate of the SLM process, with P.A. Hooper (Ref 35) measuring the cooling rate in the range of 1E5-1E6 °C/s. A similar cooling rate would give rise to a martensitic microstructure similar to the one obtained in this study. The increased Nb content led to increased β stabilisation and β phase fraction, compared against the Ti-20Nb alloy. The dendritic formations are a result of the presence of large Nb (solute) content, and the rapid cooling of the SLM process. These two factors contribute to constitutional undercooling, destabilisation of the solidifica-

tion front and the formation of dendritic structures within the larger prior β grains. As shown by Dargusch et al. (Ref 36) these dendritic needles form in the build direction, which when viewed from the normal direction, as in Fig. 9f, are visible as a cellular structure. A result of the concentration of Nb within the initially solidifying dendritic structures, leaves the surroundings with a reduced Nb content. This leads to the dual α'' and β phase composition, with inner dendrites forming the β phase, while the surrounding regions forming the α'' phase due to the depleted Nb content and reduced β stabilisation (Ref 19,22,37-39). The reduced solute content in the Ti-10Nb and Ti-20Nb alloys meant the solidification front was stable and planar, with no dendritic structures visible within the bulk of the alloys. However, some dendritic solidification was present in the Ti-

Fig. 10 DSC heating curves of the Ti-Nb alloys as-fabricated at an energy density of 230 J/mm³ (dotted line represents 2nd heating run)

20Nb alloys in the areas of elevated Nb content surrounding un-alloyed Nb particles.

3.5 Thermal Analysis

Figure 10 shows the heating curves of Ti-(10-30)Nb compositions fabricated using 230 J/mm³. The cooling curves of the sample composition are shown in Fig. 11. The dotted line is the 2nd run of the same sample performed to assess the presence of metastable phases in the first thermal cycle. The Ti-10Nb alloys expressed no peaks related to the martensitic phase transformation in the temperature range, assessed during the heating run nor the cooling run. The low Nb content of this alloy results in an expected transformation temperature above the maximum temperature of the DSC equipment used. The martensitic transformation of Ti-10Nb is expected at around 713 °C, above the scanned range (Ref 25). The Ti-20Nb alloy expressed an exothermic peak at the top of the heating curve from 470 °C. This transformation matches exothermic peaks, linked to the martensitic α'' phase transformations in similar compositions at similar temperatures seen elsewhere (Ref 31,40). However, it is unclear, if this transformation is related to α'' to $\alpha+\beta$ or α'' to β dissolutions. During the second heating run this peak is not present, suggesting the metastable nature of the transformation, and confirming it is most likely associated with the α'' dissolution. No peaks were identified in the cooling curve that could be linked to phase transformations. The Ti-30Nb alloy, fabricated at 230 J/mm³, exhibited large variations in the heat flow during the heating run. An exothermic peak is present between 300 and 450 °C, followed by the endothermic peak between 460 and 530 °C, and finally an exothermic peak at 540 °C. Bonisch et al. and Kent et al. linked this transformation to an isothermal ω phase transformation in similar compositions (Ref 41,42). The first exothermic peak is linked to the β to ω transformation, the endothermic peak linked to the ω to $\alpha+\beta$ transformation, and the final exothermic peak being β to α transformation. In addition, the heat flow moves to an endothermic peak above the max temperature of the DSC scan. This is likely the β transus, matching the expected temperature based on the composition. In this composition, no α'' to β transformation can be detected, despite the α'' phase being detected in the XRD patterns

Fig. 11 DSC cooling curves of the Ti-Nb alloys as-fabricated at an energy density of 230 J/mm³ (dotted line represents 2nd cooling run)

(Fig. 5) of the as-fabricated part. It is likely as the β to ω transformation and α'' to β transformation occur at concurrent temperatures, therefore it is hard to distinguish these transformations and this peak contains both transformations. The cooling curve shows part of an exothermic transformation at the start, and is most likely linked to the β to α transformations.

3.6 Mechanical Properties

3.6.1 Young's Modulus. Figure 12 shows the compressive stress-strain curves of the alloys loaded until yield. These compression tests were performed on samples with dimensions 12 mm in length and 6 mm in diameter. With increasing Nb content there is a change in yield behaviour, with a reduction in the sharpness of the yield points. This change corresponds with an increasing martensitic structure present within the alloy, α' in Ti-10Nb and α'' in Ti-20Nb. This yield behaviour could be the result of micro-yielding caused by high local internal stress that resulted from the martensitic phase transformation (Ref 43). In addition, there is an increase in strain at yield with the addition of Nb. A more defined yield point can be seen in Ti-30Nb alloys, as the α'' phase fraction decreased with increasing Nb content.

The Young's Modulus (Fig. 13) decreased with increasing Nb content, reaching its lowest values of 61-65 GPa with the addition of 20Nb, before increasing to 70-84 GPa, when the Nb content increases to 30Nb. Young's Modulus values of the developed alloys follow a similar pattern to those fabricated using casting techniques, with the addition of Nb leading to an initial decrease in the Young's Modulus. A decrease with the addition of 20Nb fraction in SLM samples measured between 34 and 36 GPa. This trend follows those described in literature for cast samples, e.g. Lee et al. found that the modulus decreased by 30 GPa with the formation of α'' (Ref 7). A minimum has been suggested to be around Ti-15Nb, linked to the point, where the α phase loses its hexagonality, and starts to form the orthorhombic phase (Ref 5,44). Similar conclusions have been drawn by Wang et al. (Ref 24). The increased modulus of the Ti-30Nb samples is unexpected due the lower modulus of the β phase, compared to the α'' phase (Ref 45).

Fig. 12 Compressive Stress-Strain graphs for CP-Ti (a), Ti-10Nb (b), Ti-20Nb (c), and Ti-30Nb (d) alloys fabricated at the chosen energy densities

Fig. 13 Young's Moduli of the CP-Ti and Ti-Nb alloys fabricated at the chosen energy densities

However, the increase has been linked to the presence of the brittle ω phase, with similar increases in Moduli being found in cast samples and linked to the ω phase in literature (Ref 42,46). Therefore, the increase in the Young's Modulus cannot be associated with the increased β phase fraction, and must be linked to the precipitation of the ω phase (Ref 7). However, its

small size makes it hard to detect using x-ray diffraction (Ref 47). The ω phase can be formed either from rapid cooling (athermal), or upon ageing (isothermal), with both occurring at similar Nb contents (Ref 31). Therefore, the isothermal ω transformations detected in the DSC scans (Fig. 10) suggests the addition of 30Nb has the potential for athermal ω phase formation during the rapid cooling of the SLM process. This is also suggested by the increase in the Young's Modulus seen. However, the presence of the athermal ω phase in the as-fabricated samples is not confirmed, and further investigations are needed.

The variation with energy density was also found to influence the Young's Modulus. In CP-Ti samples, the Young's Modulus increased from 99 to 102 GPa with increasing energy density. This can be linked to the increased densification and reduction in porosity at higher energy densities. In the Ti-Nb alloys, as well as the reduced porosity, the variations in the Moduli can be the result from variations such in phases present, homogeneity, as well as the fraction of un-melted Nb particles. As all of these phenomena are influenced by the energy density and occur concurrently, the exact mechanism behind the variation with energy density, is yet to be isolated.

Table 3 shows a comparison between cast and SLM titanium alloys for biomedical applications extracted from literature against the alloys reporting the lowest Young's Modulus developed in this study. The Young's Modulus of the alloys developed in this study compare favourably to the un-alloyed

Table 3 Comparison between mechanical properties of SLM and Cast titanium alloys developed for biomedical applications studied in literature and alloys developed in this study

Composition, wt. %	Method	Young's Modulus	Yield Strength	Reference
CP-Ti	Cast	100 GPa	240 MPa	Geetha et al. (Ref 2)
Ti-20Nb	Cast	61 GPa	...	Lee et al. (Ref 7)
TNTZ(Ti-29Nb-13Ta-4.6Zr)	Cast	63 GPa	...	Niinomi et al. (Ref 49)
Ti-38Nb	Cast	56 GPa	850 MPa	Guo et al. (Ref 50)
Ti-42Nb	SLM	61 GPa	674 MPa	Schulze et al. (Ref 29)
Ti-26Nb	SLM	70 GPa	...	Fischer et al. (Ref 22)
Ti-13Nb-13Zr	SLM	65 GPa	794 MPa	Zhou et al. (Ref 51)
Ti-25Ta	SLM	75 GPa	882 MPa	Zhao et al. (Ref 37)
Ti-20Nb (110 J/mm ³)	SLM	61.0 ± 0.6 GPa	675 ± 29 MPa	This study
Ti-20Nb (230 J/mm ³)	SLM	65.2 ± 1.8 GPa	769 ± 36 MPa	This study

Fig. 14 Yield Strength of the CP-Ti and Ti-Nb alloys fabricated at the chosen energy densities

titanium (reduction of 34-36 GPa), and are comparable to the properties found in cast and SLM β -stabilised Ti alloys of similar compositions.

3.6.2 Yield Strength. The yield strength (Fig. 14) was found to increase with the addition of Nb and energy density. Increasing Nb content between 0 and 20Nb, increased the yield strength, resulting from solid solution strengthening with the addition of Nb into the Ti matrix. Although studies on SLM manufactured Ti alloys are scarce, a similar effect has been reported with the introduction of β stabilisers, using other fabrication techniques (Ref 7,48). Increasing the energy density in the Ti-10Nb and Ti-20Nb also led to an increased yield strength, due to increased homogenisation, and therefore, increased solid solution strengthening effect. In addition, the extended β stabilisation led to the stabilisation of the orthorhombic α'' phase. Due to the increased dislocation density and small crystal spacing of the martensite phase, which hinders the motion of dislocations, increasing the fraction of this phase led to an increase in the yield strength. However, as indicated by the increase in yield strength in the un-alloyed Ti, from 548 to 618 MPa, the reduction in void content and preferred orientation in the build direction (corresponding to the direction of loading during the test) also causes an increase in the yield strength. At Ti-30Nb there is a reduction in the yield

strength from samples manufactured with 230 J/mm³ compared to samples manufactured with 110 J/mm³, from 800 to 760 MPa. This is likely the result of increased homogenisation at the higher energy density, increasing the stabilisation of the β phase. This leads to a reduction in the α'' phase fraction, and a corresponding increase of the β phase fraction. Therefore, the strengthening effect of the martensite phase is reduced and yield strength decreases. Similar findings are reported by Vrancken et al., with the introduction of 10Mo (wt.%) into Ti-6Al-4V, resulting in the change from α' to β phases, and a corresponding reduction in yield strength (Ref 16).

4. Conclusions

The effect of energy density and Nb content on Ti-Nb alloys manufactured using SLM was investigated by studying their mechanical and microstructural properties. The results are summarised as follows:

- (1) It was possible to achieve exemplars of Ti allotropes by increasing the amount of Nb in the alloy; Ti-10Nb processed at any of the energy densities displayed an α' phase. At Ti-20Nb and above 110 J/mm³ orthorhombic α'' phase appeared. In Ti-30Nb fabricated at 230 J/mm³, the martensite transformation was suppressed, and the alloy exhibited a primarily β microstructure.
- (2) Across all Nb content, increasing the energy density, reduced the presence of voids, and increased the homogenisation in the sample. The energy density of 230 J/mm³ created a homogenised microstructure, showing a small number of un-melted Nb particles, and presenting low void content.
- (3) The Ti-20Nb samples produced using 230 J/mm³ displayed the largest strength-to-stiffness ratio amongst the entire set, with a Young's Modulus of 65.2 ± 1.8 GPa and a Yield Strength of 769 ± 36 MPa, ascribed to the stabilisation of the fine-grained α'' martensite, sufficient solid solution strengthening and adequate chemical homogenisation.
- (4) This study demonstrates that the SLM process promotes in-situ alloying for the fabrication of Ti-Nb alloys, which display a low Young's modulus, comparable to properties of samples manufactured via conventional

methods, such as casting, and without the requirement for pre-alloyed powders. This represents a great advantage in the manufacture of low stiffness, high strength Ti alloys in a more simplified process.

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