COMPARISON OF IN SITU ALLOYED Ti-6Al-4V+10Mo VIA SELECTIVE LASER MELTING AND DIRECTED ENERGY DEPOSITION

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ABSTRACT

In situ alloying is an important topic for alloy development and improvement of mechanical properties in additive manufacturing. With the scarcity of getting most commercial titanium alloys in powder form, development and qualification of such techniques are essential. This work therefore investigates the microstructural differences and mechanical properties of Ti-6Al-4V+10Mo manufactured by selective laser melting and directed energy deposition. It was found that the alloy manufactured by directed energy deposition exhibited better melting of molybdenum particles and hence a more homogeneous microstructure compared to the high power, high speed selective laser melting process.

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1. INTRODUCTION

In situ alloying is an important topic in terms of alloy development and improvement of mechanical properties in additive manufacturing, as reported by Attar *et al*. [1]. Fischer *et al*. [2] recognized that the scarcity of powder form of most of the commercial titanium alloys, makes the development and qualification of *in situ* alloying techniques essential. Lewandowski *et al* [3] studied both the selective laser melting (SLM) and the directed energy deposition (DED) processes, in a review of mechanical properties of components produced by additive manufacturing. In particular, Shunmugavel *et al* [4] showed that titanium alloys are widely used in aerospace construction as components. Although both processes build parts according to CAD files and in a layer-wise profile, the SLM process is a powder bed technique, while the DED process is a blown powder technique.

The powder bed technique requires the use of a base plate (bed) where a layer of powder is spread using a scraper before the laser melts powder into the desired part shape, whereas the blown powder method utilizes a nozzle mechanism to deliver the powder, the heat source (laser) emanates from the central region between the nozzles and melts the powder at the point of convergence onto the base plate. Collins *et al*. [5] described one DED platform, the Laser Engineered Net Shaping (LENS™) machine, which has the added benefit and flexibility suitable for *in situ* alloy creation by mixing elemental powders through a multi-hopper system. Conversely, the powder bed fusion (PBF) process is not designed for *in situ* alloying, and requires a preliminary powder blending/milling step before processing. Processing from pre-alloyed material yields similar microstructural characteristics from both processes, and the typical microstructure reported by Arthur *et al*. [6] and Xu *et al*. [7] for pre-alloyed Ti-6Al-4V is the alpha martensite “basketweave” microstructure growing within columnar beta grains.

Chlebus *et al*. [8] reported that most investigations aimed at *in situ* alloying using the SLM process include the addition of refractory metals such as rhenium, molybdenum, niobium and tantalum, which are beta stabilisers, to titanium and titanium alloys, and these metals are known for their high melting points, resistance to wear, corrosion and deformation. Fischer *et al*. [2], Chlebus *et al*. [8], Vrancken *et al*. [9] and Madikizela *et al*. [10] all found that when refractory metals were added to titanium alloys, the as-built microstructures had undissolved refractory particles, giving inhomogeneity within the alloy composition, and a composite-like microstructure. This phenomenon is mostly due to the higher powers and speeds used in SLM processing, which leads to insufficient interaction times between the metal powder and the laser. Typical laser powers used on the LENS™ for DED range from about 300 W to 600 W, at speeds of approximately 0.005 m/s to 0.015 m/s, whereas typical laser powers used for SLM range from about 1 kW to 3 kW, at speeds of approximately 2 m/s to 4 m/s. The laser power used for DED is much lower than that used for SLM, although the longer interaction times (due to lower speeds) associated with DED allow for sufficient melting of material. The effect of increasing the hatch spacing in both processes is a decrease in porosity and improved heating due to increased track overlap.
Vrancken *et al*. [9] used the SLM process, adding 10 wt% Mo to Ti-6Al-4V to stabilize the beta phase, which resulted in increased fracture toughness and ductility. Molybdenum is a titanium beta stabilizer, and when added to Ti-6Al-4V, it increases the beta phase fraction, which is more ductile than the alpha phase. Vrancken *et al*. [9] undertook this work in an effort to improve the mechanical properties of Ti-6Al-4V produced via the SLM process, since Xu *et al*. [7] reported the acicular alpha microstructure to give poor ductility (less than 10% elongation). Vrancken *et al*. [9] reported that the hardness of the beta-stabilized composite sample, manufactured at 250 W was lower (338±5 HV) than the hardness of Ti-6Al-4V (360±9 HV) also at 250 W. Madikizela *et al*. [10] produced the same composite at higher power (1.3 kW), with a lower hardness (277±3 HV).

Conversely, Collins *et al*. [5] successfully performed *in situ* alloying of molybdenum with commercially pure (CP) titanium using the DED process and reported no un-melted particles

or inhomogeneity. This was attributed to the increased laser-material interaction time achievable with DED. The microstructure was composed of short alpha precipitates in a beta matrix [5]. With increasing Mo content, Collins *et al*. [5] observed increased beta fraction and decreased proportions of primary alpha laths. The micro-hardness results showed an increase with an increasing Mo content until a peak of 450 HV was reached at a Mo content of 10 at. %, after which the hardness decreased with increased Mo content.

Other authors who have used other materials for *in situ* alloy development via the DED found promising results. Collins *et al*. [11] manufactured samples from an elemental blend of Ti–15Mo–3Al–2.7Nb–0.2Si and found that the microstructure from the blended powders was identical to that obtained from pre-alloyed powder. Banerjee *et al*. [12] was able to successfully *in situ* alloy Ti-6Al-4V-TiB composites via the DED process. Banerjee *et al*. [12] concluded that for the synthesis of discontinuously reinforced metal-matrix composites, DED with LENS™ is a promising technique for producing such materials *in situ* in a near-net shape form.

It is therefore important to further investigate the suitability of the different techniques in producing homogeneous microstructures. This study investigates the additive manufacturing of Ti-6Al-4V+10Mo, employing both the SLM and DED techniques for comparison, and to ascertain the effect of the resultant microstructures on the hardness.

2. EXPERIMENTAL PROCEDURE

Powder samples were prepared and mixed in a tubular mixer for 30 minutes. The mixed samples were analysed and the morphology and the particle size distribution was characterized by SEM and a Microtrac bluewave particle size analyser. The powders were then processed on a SLM machine fitted with a 5 kW Nd:Yag laser at 2 kW power and at a speed of 2 m/s to produce 10x10x10 (mm^3) samples. For comparison, the same mixed powder was also used for processing by the LENS™ fitted with a 1kW IPG laser, at 400 W power and at a speed of 0.008m/s.

The samples from both techniques were metallographically prepared and etched with Kroll's reagent to reveal the microstructures before optical microscopy and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) was performed. Electron backscatter diffraction EBSD was conducted on the Zeiss Cross Beam 540 FIBSEM, at an acceleration voltage of 25kV and a beam current of 10nA. Micro-Vickers hardness testing was done on these samples at a 300g load and a dwelling time of 10 seconds, with the measurements taken from the bottom of the sample to the top in a straight line to ascertain the effect of position within the sample. For comparison, macro-Vickers hardness tests were conducted at a 20 kg load and a dwelling time of 10 seconds and these measurements were taken in a more random approach to ascertain the overall hardness.

3. RESULTS AND DISCUSSION

3.1 Powder analysis

Figure 1 shows the morphology and particle size of the SLM samples. The Ti-6Al-4V particles were spherical and darker in contrast, wheras the molybdenum particles were spherical and lighter in contrast in the backscattered electron mode. Working with spherical shaped powder particles is a precondition as they produce high flow-ability for processing, and promote optimal conditions for powder melting, and ultimately better builds (reduced porosity) of the components as reported by Attar *et al*. [1] . To obtain better melting of the molybdenum particles, molybdenum powder had been sieved beforehand, to obtain a finer distribution than Ti-6Al-4V. From the cumulative particle size analysis graph in Figure 1, Mo had a finer size range of 20-50 μm as required, while Ti-6Al-4V had a coarser size range of 50-100 μm.

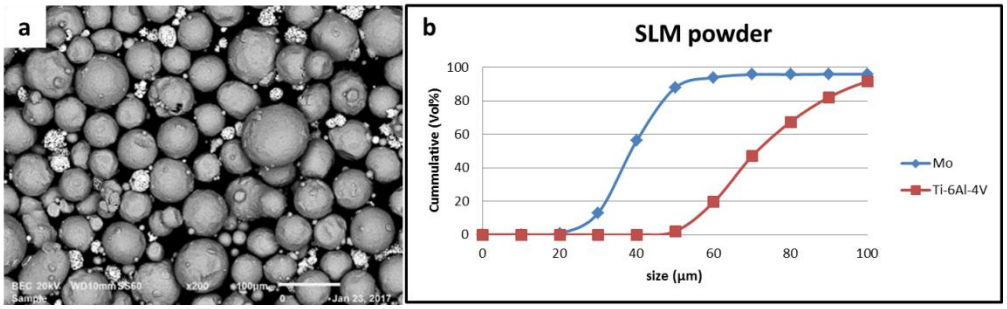

Figure 1: Powder analysis results of SLM powder: (a) a SEM_BSE image, and (b) powder particle size analysis.

The particle size distribution of the SLM powder could not be used for the DED powder due to the machine powder requirements. The DED process requires a powder particle size range of 45-100 µm for efficient flowability, and hence separate powders had to be mixed. Figure 2a indicates that both the Mo and Ti-6Al-4V had spherical powder particles, and the particle size distribution revealed that both powders had a particle size ranging from 50-100 µm, although molybdenum had more powder at a finer size range than Ti-6Al-4V (Figure 2b).

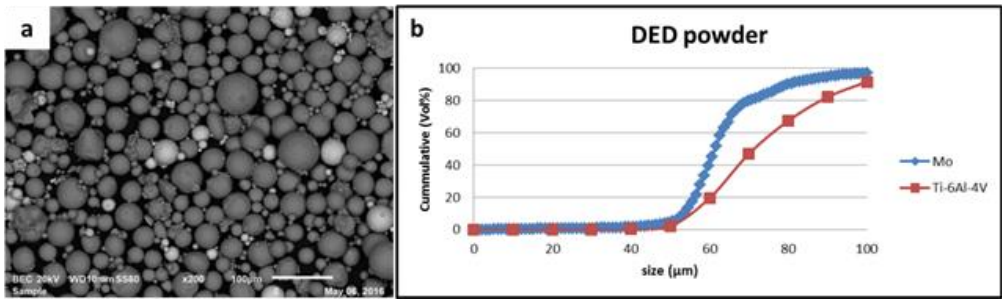

Figure 2: Powder analysis results of DED powder: (a) SEM-BSE image, and (b) powder particle size analysis.

3.2 Microstructure

The micostructure of the SLM sample had unmelted Mo particles, which are seen as the bright particles in Figure 3a, and a flow-like pattern, which showed the elliptic shape of the melt pool. Distinct light and dark bands running from left to right are also evident in the micrograph, indicating variations in the composition. The light contrast bands had more Mo dissolved in the matrix, hence more stabilized beta compared to the dark contrast bands. Figure 3c shows the SLM sample at higher magnification, revealing a fine needle-like structure in areas which were associated with undissolved Mo, and therefore no stabilisation of the beta phase. Madikizela *et al*. [10] noted this previously, whereas Vrancken *et al*. [9] only reported unmelted particles in a fully beta matrix. EDS results revealed that the matrix of the sample had ~5% Mo in it, whereas 10% Mo had been mixed with Ti-6Al-4V.

The DED sample had a more homogeneous mictrostructure with no discernable unmelted Mo particles, Figure 3b. EDS results gave ~9% Mo in the matrix. There were also no flow-like patterns as in the SLM sample, due to the considerably lower speeds used with the DED process (Figure 3b). At higher magnification, Figure 3d, laths in the microstructure were observed, agreeing with Collins *et al* [5].

In the SLM sample, some extremely low values of Mo (e.g. 1%) were found by EDS analysis on different areas in the sample, there were some areas in the. Conversly, the DED sample had consistent EDS results throughout the sample, from the more homogenous microstructure, resulting from the increased material-laser interaction associated with the DED process. Although the same mixing procedure was used in both processes, and the particle morphology/PSD was controlled for the requirements of each process for consistency, the laser processing method greatly influenced the homogeniety of the samples.

The back-and-forth scraping mechanism used in the PBF process changed the homogeneity of the powder, as it acted as a secondary mixing stage, further spreading the particles and causing an uneven distribution of Mo in the sample. The incomplete melting of the Mo powder (which has a high melting point of 2623°C compared to Ti-6Al-4V (1660°C)) also caused inhomogeneity, as inadequate heating and short interaction times were unfavourable to melt the Mo. Although the homogeniety of the powder mixture could have been changed when the powder travelled from the hoppers to the nozzles, the slower speeds of the DED process acted as a corrective measure by melting all the Mo powder and providing enough heat for Mo to diffuse more evenly throughout the sample.

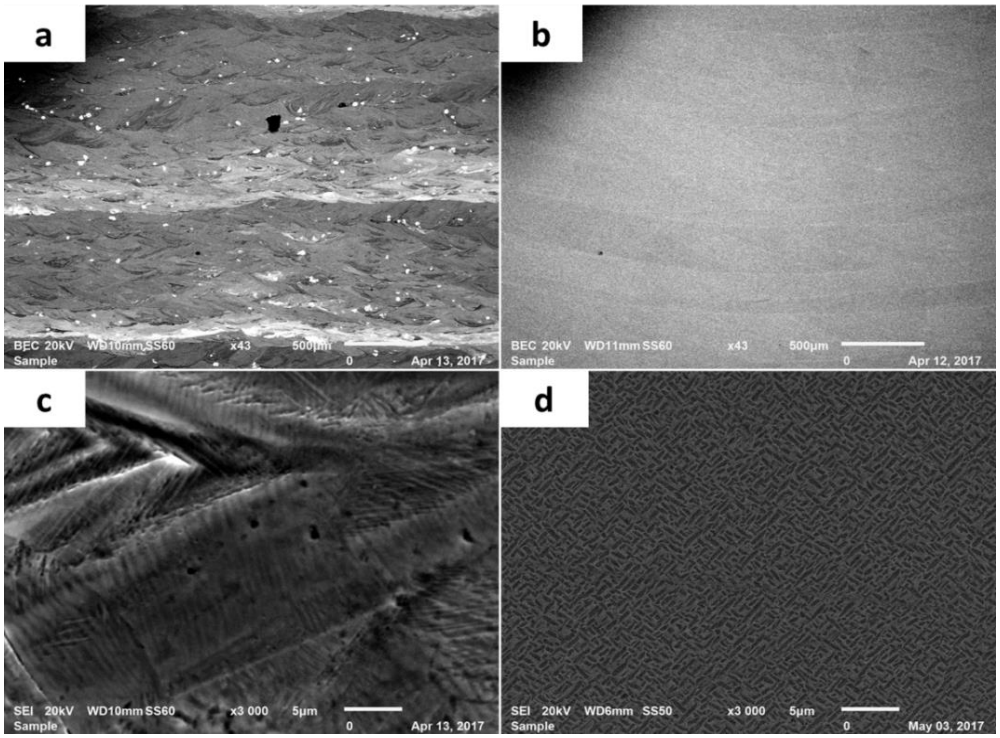

Figure 3: SEM micrographs in BSE (a and b) and SE (c and d) modes: (a) and (c) show the SLM sample, and (b) and (d) show the microstructure of the DED sample.

EBSD analyses done on the SLM sample confirmed the observations from SEM and EDS, as shown in Figure 3a and Figure 3c. Figure 4 shows the EBSD images of a SLM sample, and although some of the beta phase whas stabilized, there was still considerable proportions of alpha in the microstructure. The alpha phase was more prominent in the crevice-like areas of the microstructure.

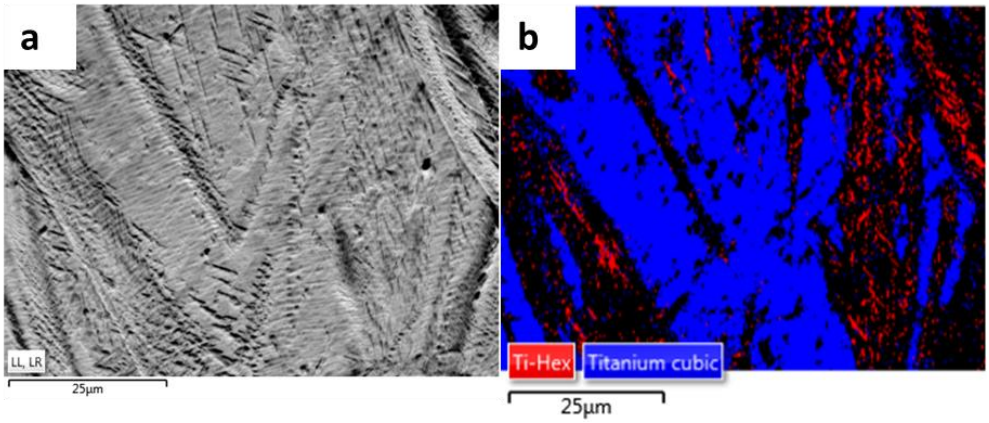

Figure 4: EBSD results of SLM sample: (a) area of analysis, and (b) phases present: alpha (Ti-Hex) and beta (Titanium cubic).

Figure 5 shows the EBSD results of a DED sample. In agreement with Collins *et al*. [5], the laths consisted of the alpha phase, and there was no beta phase identified.

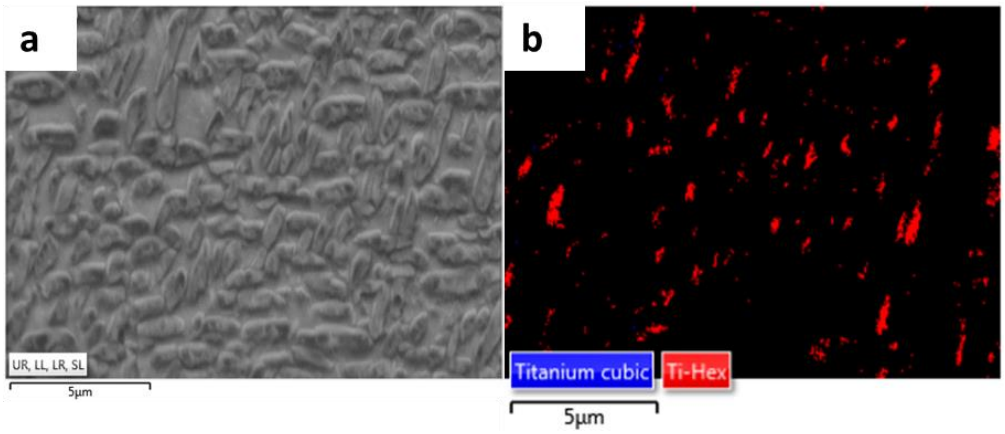

Figure 5: EBSD results of DED sample: (a) area of analysis, and (b) phases present: alpha (Ti-Hex).

Comparing the Ti-6Al-4V (Figure 6a) and Ti-6Al-4V + 10Mo (Figure 6b) microstructures built at the same processing parameters (2 kW power and 2 m/s speed) via the SLM process, significant differences were evident. There was acicular alpha in Figure 6a, and a more beta stabilized microstructure in Figure 6b, with some unmelted Mo particles. The acicular alpha microstructure is known to be very hard as reported by Arthur *et al*. [6], and the addition of Mo stabilizes the beta phase. This results in less alpha microstructure, and the increased beta microstructure gives a softer alloy than conventional Ti-6Al-4V, due to the addition of Mo.

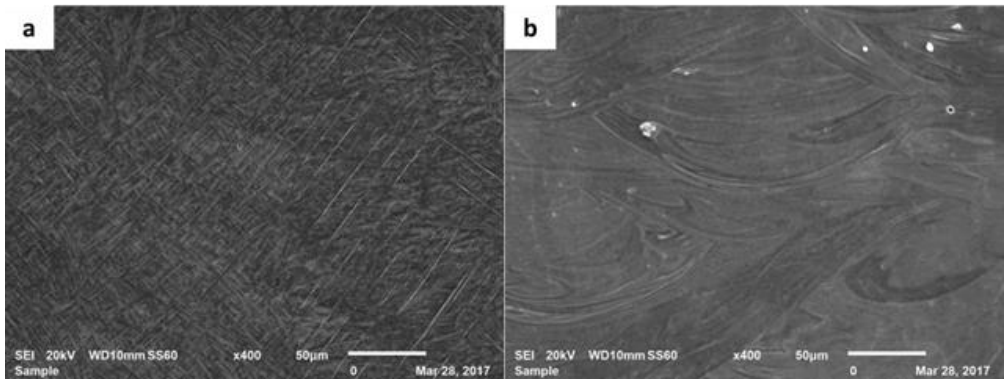

Figure 6: SEM micrographs in SE mode: (a) Ti-6Al-4V and (b) Ti-6Al-4V + 10Mo, built at a power of 2kW and a speed of 2 m/s via the SLM process.

Compared to the work of Arthur *et al*. [6], where Ti-6Al-4V was produced from the DED process, at the same power (400 W) and speed (0.008 m/s) used in this work for Ti-6Al-4V+10Mo, there was a large difference in microstructure. Figure 7a shows the Ti-6Al-4V sample of Arthur *et al*. [6] with a Widmanstätten microstructure, which is has long alpha needles in a "basket-weave" pattern. With the addition of 10 wt% Mo, Figure 7b, the resultant microstructure had shorter, but thicker, alpha needles in a beta matrix.

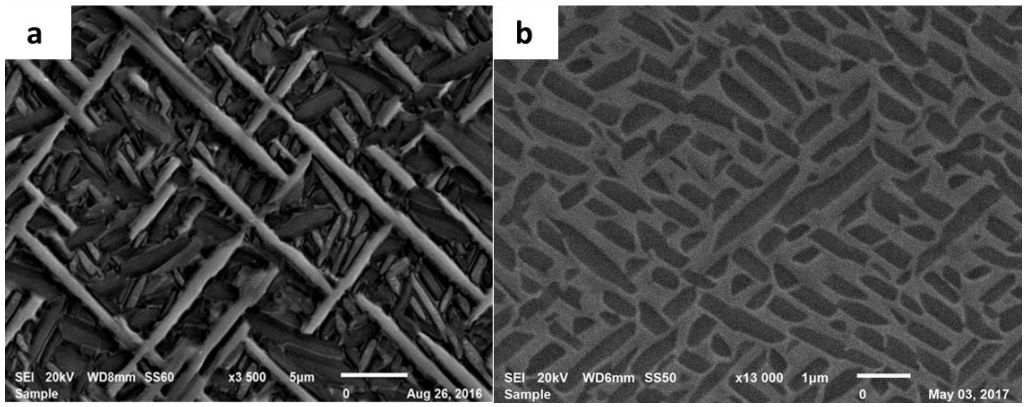

Figure 7: SEM micrographs in SE mode: (a) Ti-6Al-4V (Arthur *et al*. [6]) and (b) Ti-6Al-4V+10Mo, built at a power of 400 W and a speed of 0.008 m/s using the DED process.

3.3 Hardness

The average micro-hardness results for the DED sample were found to be 407±36 HV which is higher than that found for the SLM sample (207±33 HV) (**Error! Reference source not found.**). The hardness profile in Figure 8a, for the DED sample, increased from the bottom of the sample to the middle, and then decreased near the top. This is attributed to material closer to the top of the sample having been exposed to the heat from the laser for a shorter period of time than the lower regions. The hardness profile for the SLM sample was uniform from the bottom of the sample to the middle, and increased at the top (Figure 8b). The large differences in hardness was due to the differences in the process parameters (higher energy densities in the DED process (281.30 J/mm^3) than the SLM process (160.26 J/mm^3)) used and the microstructure which resulted from this. The energy density defined by Attar *et al*. [1] is:

$$E = \frac{P}{v \times h \times t}$$

where P = laser power (W), v = laser scanning speed (mm s^{-1}), h = hatch spacing (mm) and t = layer thickness (mm).

The inhomogeneous microstructure of the SLM process produced local variation in micro-hardness. Where the indention was on an area with less Mo dissolution, the hardness was higher, e.g. 340 HV (Figure 8a), whereas when the indention was on an area with higher Mo dissolution, the hardness decreased to around 200 HV. For the more homogeneous microstructure (DED sample) of a beta matrix with alpha precipitates, the hardness showed less variation (Figure 8a). This was also evident when comparing the micro-hardness results with the macro-hardness results. The average micro-hardness and macro hardness results for the DED sample were almost identical, 407±36 HV and 398±25 HV respectively, whereas the SLM process showed greater variation: 207±33 HV and 301±29 HV respectively.

Table 1: Comparison of average Vickers hardness results

	PBF process	DED process
Average Micro-Vickers hardness (300g load)	207±33 HV	407±36 HV
Average Macro-Vickers hardness (20kg load)	301±29 HV	398±25 HV

The hardness was significantly higher for the DED sample due to the microstructure resulting from the higher energy density used during processing (Figure 3d). Collins *et al.* [5] explained that the decrease in alpha laths refines the microstructure, therefore having a strengthening effect, as well as a fine dispersion of ω precipitates in the beta matrix, further increasing the hardness. Collins et al. [5] suggested the use of TEM to resolve the ω precipitates which cannot be resolved in SEM. Arthur *et al.* [6] found a hardness of 346 HV for the Ti-6Al-4V shown in Figure 7a. The addition of 10 wt % Mo in this work gave an average hardness value of 407±36 HV, and to obtain the same softening effect that Vrancken *et al.* [9] and Madikizela *et al.* [10] found with the PBF process, more Mo would be needed for the DED process. Collins *et al.* [5] found that 10 at.% Mo (18.21 wt % Mo) gave the peak hardness of 450 HV, whereas the lowest hardness value of 280 HV was obtained for 20 at.% Mo (33.4 wt % Mo) addition to CP-Ti.

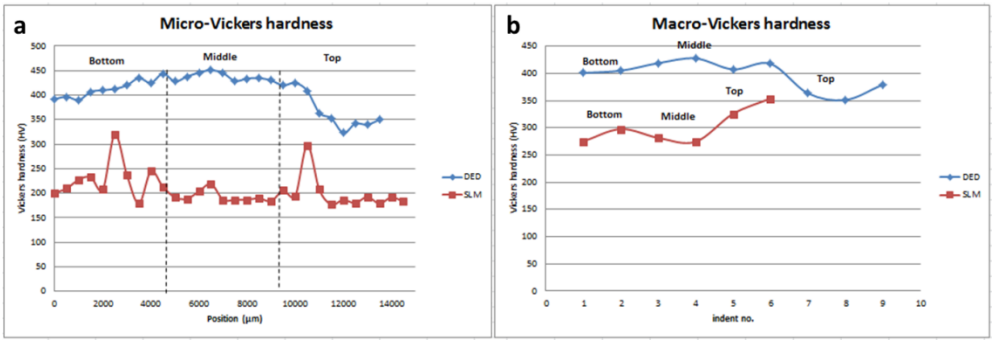

Figure 8: Comparison of hardness results for the DED and SLM processes: (a) micro-hardness, and (b) macro-hardness.

4. CONCLUSIONS

This work revealed that the differences in the process parameters of the SLM and the DED processes, such as speed and laser power, influence the interaction time between the powder and the laser, producing different microstructures. The DED process produced a homogeneous microstructure, whereas the SLM process produced an inhomogenous microstructure with 5 wt% Mo dissolved into the matrix while the latter had 9 wt% Mo dissolved into the matrix. The addition of 10 wt% Mo to Ti-6Al-4V in the the DED process had a hardening effect, giving 407 HV compared to Ti-6Al-4V (346.3 HV). Conversely, the addition of 10 wt% Mo to Ti-6Al-4V produced with the SLM process had a softening effect on the microstructure, giving a lower macro hardness value of 301 HV than Ti-6Al-4V (360 HV). A higher amount of Mo would have had to be added for the DED process to obtain the same softening effect found in the PBF process.The DED process is therefore more suitable for *in situ* alloying of Ti-6Al-4V+10Mo than the PBF process due to the increased material-laser interaction times.

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