Selective laser melting process optimization of Ti-Mo-TiC metal matrix composites

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Selective Laser Melting (SLM) was used to process a powder mixture of CP Ti, 6.5 wt% Mo and 3.5 wt% Mo₂C. The process parameters were optimized to obtain full-density, crack free parts. After the in situ decomposition of Mo₂C in favor of the formation of TiC, the material consisted of a homogeneous dispersion of submicrometer sized TiC platelets in a β -(Ti,Mo) matrix exhibiting a high hardness up to 550 HV and compressive yield stress of 1164 ± 37 MPa. The microstructure and mechanical properties could be tailored by variation of the process parameters within the high-density processing window, as well as through post-process heat treatments.

Selective Laser Melting (SLM), Metal matrix composite, Titanium

1. Introduction

Additive manufacturing (AM) is enabling production of geometrically complex parts that reduce weight, increase productivity, and improve performance. AM has also generated a new path to create novel materials. In Selective Laser Melting (SLM) for example, the powder-based production, localized melting, and high cooling rates are particularly suitable conditions to create homogeneously dispersed metal matrix composites (MMCs) [1]. The small melt pool locally mixes the constituents, rapidly solidifies and limits segregation to the micro-scale if it even occurs at all. The Marangoni flow inside the melt pool provides efficient mixing, and high cooling rates avoid coarsening of the formed secondary phase particles [2]. The in situ reaction leads to a strong interface between the matrix and reinforcing particles [3]. Additionally, supersaturation of alloying elements in the matrix can cause particles to precipitate in the heat-affected zone during deposition of subseq layers or during post-process heat treatment.

In situ alloying during SLM is receiving an increasing amount of attention with the intent to facilitate processing of a material, and/or to induce superior properties. Specifically for Ti-based alloys, Ti6Al4V has been processed from an elemental mixture of Ti, Al and V [4]. Addition of various amounts of Mo to Ti during Directed Energy Deposition (DED) demonstrated that a 100% β phase can be maintained at room temperature upon quenching with 10 wt% Mo [5]. This suppresses the reaction to the hard but less ductile α' martensite. Consequently, SLM of Ti6Al4V+10Mo resulted in a metastable, fully β phase alloy of which the ductility greatly surpassed SLM'ed Ti6Al4V (20% versus 8% [6]), while the strength was higher than that of other β -Ti phase alloys with comparable ductility [7].

D. Gu et al. have performed extensive research on the AM production of MMCs, including Ti matrices [2,8], or TiC reinforcements [2,9]. A maximum hardness of 570 HV was achieved when mixing 12.5 wt% spherical nanosized TiC powder with larger Ti powder, creating a dense dispersion of nano-sized platelet TiC precipitates [2]. Similar TiC platelets were also reported to form during DED of TiC and the TA15 Ti alloy, with the platelets said to originate from the eutectic reaction, while primary TiC was rounder in shape [10]. The mechanical properties deteriorated for TiC additions in excess of 5 wt%. The size of the TiC formed during DED of a Ti6Al4V + TiC mixture could be controlled by variation of the deposition parameters [11].

In this work, the powder mixture consisted of 6.5 wt% Mo, 3.5 wt% Mo₂C, and remainder Grade 1 Cp Ti. Fully dissolved, the 3.5 wt% Mo₂C theoretically results in 1 wt% of reinforcing TiC particles. An additional 6.5 wt% Mo was added for a total of 10 wt% Mo in the final alloy, previously stated to be sufficient to

suppress α' formation and stabilize the β phase [5]. Since TiC was expected to embrittle the material, the intention was to use the more ductile Mo-induced β phase to facilitate SLM processing, with the possibility for further optimization through post-process heat treatments. This work shows that the extent of the $\text{Ti} + \text{Mo} + \text{Mo}_2\text{C} \rightarrow \beta\text{-(Ti,Mo)} + \text{TiC}$ reaction depends on the SLM process parameters as well as the heat treating regime.

2. Materials & Methods

2.1. Material and SLM processing

Grade 1 CP Ti powder (LPW Technology, UK) with a particle size between 15–45 μm was dry mixed for 8 hours in a Turbula mixer with 6.5 wt% Mo (particle size 3–5 μm) and 3.5 wt% Mo₂C (Changsha Langfeng Metal Materials Co. Ltd., China, particle size 3–5 μm). Figure 1 shows the resulting powder mixture, where the smaller irregular shaped Mo and Mo₂C particles (white particles) partially decorate the larger spherical Ti particles (grey), though a majority does not adhere to the Ti as would be desired. This is likely due to the large size of the Mo and Mo₂C powder. Furthermore, hard Mo or Mo₂C starting powder agglomerates were still present that were not de-agglomerated during mixing.

The in-house developed LM-Q SLM machine (PMA, M.E. Dept., KU Leuven) was used to produce $10 \times 10 \times 7.5 \text{ mm}^3$ cuboids in an Ar atmosphere containing less than 50 ppm O₂. The laser spot size was 60 μm ($1/e^2$). The system is described in detail in [12]. The zigzag scan strategy was rotated 90° between each layer. A wide range of SLM process parameters were employed, varying the laser power P between 40 – 450 W, the scan speed v between 200 – 2000 mm/s, the hatch spacing h between 35 – 100 μm and a layer thickness t of either 30 or 60 μm . This resulted in an energy density $E = P/(v \cdot h \cdot t)$ between 40 – 320 J/mm³. All employed parameter sets are shown in Fig. 2. Some parameter sets are marked in red, indicating that they were unstable and terminated before build completion. For clarity, the discussion will focus on density and microstructure **trends** visible over these ranges. All heat treatment and mechanical property-related results in Fig. 5–7 were obtained on samples built with $P = 235 \text{ W}$, $v = 1400 \text{ mm/s}$, $h = 70 \mu\text{m}$ and $t = 30 \mu\text{m}$ (sample 2L in Fig 3(b)).

Figure 1. Powder mixture of Grade 1 CP Ti (grey spherical particles), 6.5 wt% Mo (white) and 3 wt% Mo₂C (white).

Figure 2. Process parameters used in this work, including two different low and high laser power/scan speed regions. Further parameter sets are mostly located along two different iso- P/v ratio curves.

2.2. Characterization

Heat treatments were performed in a vertical tube furnace for 1 hour in an Ar (3 ppm oxygen) atmosphere. Air cooling was applied after aging (400°C-600°C), and water quenching after annealing (750°C-850°C). Microstructural characterization was carried out using a FEI XL30 FEG scanning electron microscope (SEM). Only SEM BSE contrast imaging was employed on non-etched specimens to reveal microstructural features. Phase identification was carried out using a Siemens D500 diffractometer with Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$). MicroVickers hardness was measured by a Leitz-Durimet microhardness tester with a 1 kg load applied for 15 s. Compression tests were performed on cylindrical samples of 6 mm diameter and 9 mm length using a 250 kN INSTRON universal testing machine at room temperature. Part densities were determined using the Archimedes method in ethanol.

3. Results

3.1. Density

The material being produced is novel with an unknown and difficult to determine theoretical full density (TD). The difficulty arises from the different constituents and even phases of the starting material (α' -Ti, Mo, and Mo₂C) and the final product (β -(Ti,Mo), TiC, and trace α -Ti, Mo and Mo₂C). A simple weighted average of the densities of α -Ti, Mo and Mo₂C results in a density of 5.083 g/cm³, but this results in calculated part densities < 96%. This does not correspond to the cross-section images, in which no pores could be detected for select parameter combinations. Other calculation routes, including determining the mass per unit cell of a β -Ti₁₀Mo alloy based on the lattice parameter found in [13], or a weighted average between α -Ti and Ti₁₅Mo, yielded equally unrealistic values (5.021 g/cm³ and 4.839 g/cm³ resp.). Therefore, 100% TD was equated to 4.822 g/cm³, the highest measured

density (sample 2X in Fig. 3), for which no porosity was detected by SEM.

Figure 3. Density evolution as a function of the process parameters. Notice the scale difference between (a) and (b), (c). Unless indicated otherwise, $t = 30 \text{ }\mu\text{m}$ and $h = 70 \text{ }\mu\text{m}$. Failed samples are marked in red.

In Fig. 3(a), a low v - P regime ('Low v, P ' in Fig. 1) is compared to a high v - P regime ('High v, P ' in Fig. 1), both based around parameter sets that are known to lead to high density for Ti6Al4V [6]. High densities >99% are obtained across the entire high v, P regime. By contrast, using a low v - P combination leads to significantly lower densities, even though the energy density covered by both ranges is similar. A similar conclusion can be drawn from Fig. 3(b), where the density increases with increasing v and P (along the $P/v = 0.17 \text{ J/mm}$ line in Fig. 2), and in Fig. 3(c), where the density increases with increasing v and P (along the $P/v = 0.34 \text{ J/mm}$ line in Fig. 2 for 3A to 3R and along the $P/v = 0.17 \text{ J/mm}$ line in Fig. 2 for 3S to 3X). Note the different scale on the y-axis of Fig. 3(a), (b) and (c). In the low v - P regime, the density does increase with increasing P (1A to 1C, 1D to 1F, 1M to 1O, 1P to 1R).

Increasing h from 70 μm to 100 μm did not lead to significant differences, except for the $v = 1600 \text{ mm/s}$ and $P = 250 \text{ W}$ combination (sample 1V) that produced a narrow melt pool and consequently lack of fusion between adjacent scan tracks. On the other hand, reducing the hatch spacing from 70 μm to 35 μm (Fig. 3(c)), effectively doubling the energy density E , increased the density for low P and v (sample 3G vs 3M), but led to instabilities and premature build failure when using higher P and v (3Q and 3R). Also visible in Fig. 3(c), the layer thickness could be doubled from 30 μm to 60 μm (compare samples 3A-3F with 3G-3L) without a significant loss in density. It even allowed the highest P - v combination to build successfully while it failed for a 30 μm layer thickness (3F vs 3L).

From Fig. 3(b), remelting each layer with $P = 50 \text{ W}$, $v = 250 \text{ mm/s}$ and $h = 105 \text{ }\mu\text{m}$ parameters increased the density for low v - P parts, of which the density without remelting was <99%. If remelting had

a significant effect on the density >99% as in [14], it was outside the accuracy of the Archimedes method.

3.2. Microstructure

Fig. 4 represents the microstructural control that can be exercised through variation of the process parameters during SLM of Ti+6.5Mo+3.5Mo₂C. On the mesoscale, using a low P - v combination leaves residual unmolten or partially molten Mo and Mo₂C particles (white regions in Fig. 4(a)) since Mo and Mo₂C respectively melt at 2623°C and 2687°C, compared to 1668°C for Ti. Moreover, the dissolved Mo is unevenly distributed in the matrix, evident from the darker (Mo poor/C rich) and lighter (Mo rich) streaks in the side view, a solidified remnant of the melt pool flow. These parameter sets were also prone to more porosity, as discussed earlier. This microstructure corresponds to the diffraction spectrum in Fig. 5(a). The spectrum shows that there is a significant amount of α phase present. By contrast, a higher P - v combination as in Fig. 4(b) almost completely dissolves all Mo and Mo₂C particles. This corresponds to the XRD spectrum in Fig. 5(b). Compared to spectrum 5(a), the α peaks are much smaller, the β phase is dominant, and a more pronounced TiC peak at $2\theta = 61^\circ$.

Figure 4. Microstructures obtained after SLM of Ti+6.5Mo+3.5Mo₂C. (a) Inhomogeneous distribution and incomplete dissolution of Mo/Mo₂C using low powers. (b) Homogeneous matrix using higher powers. (c) Fine, homogeneously dispersed precipitates using moderate energy inputs. (d) Coarsened TiC precipitates (black) using high energy inputs.

On the microscale, the desired homogeneous dispersion of fine TiC precipitates is the result of using a moderate to high energy input in the high P - v region. This is shown in Fig. 4(c) where a very high laser power is balanced by doubling the layer thickness. All precipitates are submicrometer in size. They form necklaces along the grain boundaries and are dispersed throughout the interior of the grains. Lastly, as Fig. 4(d) illustrates, the TiC is severely coarsened when using an excessive amount of energy, here achieved by reducing h from 70 μm to 35 μm. The TiC in this work resembles a whisker shape rather than a platelet, as was previously reported in literature [2,10,11]. With widths < 200 nm but up to several micrometers in length, the origin of the whisker shape found in this work is unclear but subject of future work. A coarser TiC size for higher energy inputs was also reported in [9], though not to this extent.

3.3. Heat Treatment

Quenching during the SLM process results in a near fully β phase metastable matrix. Upon heat treatment, alloy elements trapped in

supersaturation will diffuse and be redistributed among both α and β phase. This is evident from the diffraction spectra in Fig. 5(c) to 5(e). Aging at 400°C (Fig. 5(c)) and 500°C (Fig. 5(d)) did not lead to significant changes in the microstructure or phase composition, but there is a significant formation of α phase when aging at 600°C (Fig. 5(e)). Thermomechanical Analysis, not shown here, indicate that this happens at 520°C. Not only do the α peaks become much more prominent after aging at 600°C, there is also a small shift in all peak locations due to the solute element redistribution between the α and β phase.

The α phase fraction evolves towards equilibrium during aging but declines again at higher temperatures since β is the high temperature stable phase. This decline is visible comparing Fig. 6(a) to 6(b), and quantified based on pixel greyscale value in Fig. 6(c), showing a clear decrease in α phase content and coarsening of the microstructure with increasing temperature reached during heat treatment between 750°C and 850°C. At 750°C, the microstructure consists of a fine lamellar mixture of α and β phase. At higher temperatures, the α phase, decreasing in content, becomes a dispersion of coarser plates. With increasing temperature, the TiC fraction increases from 0.15 vol% ($\approx$ wt% for this material) at 750°C to 0.78 vol% at 850°C, close to the 1.03 wt% theoretically obtained at 100% completion of the intended in situ reaction. Comparing Fig. 6(b) with Fig. 4(c), the TiC particles are fewer in number but larger.

Figure 5. Diffraction spectra for (a) 2A, built with low power and speed, (b) 2L, built with higher power and speed, and the aging response (1h, air cooling) at (c) 400°C, (d) 500°C and (e) 600°C. The heat treatments were applied to samples built with the same parameters as 2L.

3.4. Mechanical Properties

The microstructural control that could be enforced through variation of the process parameters as well as post-process heat treatment also leads to a range in obtainable hardness between 350 HV and 550 HV. In the as-built state, low P - v combinations that lead to an incomplete dissolution of Mo and Mo₂C also lead to a lower hardness around 350 HV, compared to 450 HV or above for higher P - v combinations with the same P/v ratio. The maximum hardness of 555 ± 11 HV was achieved using $P = 300$ W, $v = 1300$ mm/s, $h = 50$ μm, $t = 30$ μm, $E = 154$ J/mm³. Even though the maximum theoretical TiC content in this work is only 1.03 wt%, this is similar to the 570 HV obtained in [2] by adding 12.5 wt% TiC. Using an excessive energy input by using a small h , such as for sample 3P shown in Fig. 4(d), leads to a significantly softer material than that produced with similar P and v but a larger h .

Aging at 400°C or 500°C does not significantly change the hardness, but the precipitation of α phase during aging at 600°C significantly softens the material (Fig 7(a)). Typically, the α phase is stronger than the β phase and a homogeneous dispersion of small α laths has been shown to increase the hardness in aged

Ti6Al4V+10Mo from 338 HV to 468 HV [7]. The hardness decrease in this work indicates that solid solution hardening contributes significantly to the strengthening, in addition to the TiC precipitates. Annealing treatments between 750°C and 850°C further softened the material to 340 ± 5 HV, similar to heat treated Ti6Al4V+10Mo (338 ± 6 HV) [7].

Figure 6. Microstructure coarsening during subtransus heat treatment (1h, water quench) at (a) 750°C to (b) 850°C. (c): based on the grey-scale value (d), the α fraction (vol%) decreases while more TiC is formed.

Figure 7. (a) Hardness vs. heat treatment temperature. The hardness drop between 500°C and 600°C corresponds to the formation of α phase. (b) Compressive stress-strain curves for as-built material (AB) and material annealed at 750°C and 850°C followed by water quenching (WQ).

Although the compressive stress-strain curves in Fig 7(b) were obtained without an extensometer thus resulting in inaccurate strain data, it is clear that the ductility of the as-built (AB) material can be greatly improved by an annealing heat treatment. A relative improvement of 85% was obtained when annealing at 750°C at a minor reduction in compressive yield stress ($\sigma_{0.2,750^\circ\text{C}} = 1075 \pm 14$ MPa) compared to the as-built state ($\sigma_{0.2,AB} = 1164 \pm 37$ MPa). Heat treating at 850°C resulted in the lowest yield stress ($\sigma_{0.2,850^\circ\text{C}} = 812 \pm 59$ MPa) and a higher ductility than the AB material, but lower than that of material annealed at 750°C. It is possible that the coarsened, undeformable TiC precipitates in the material annealed at 850°C impede plastic flow of the surrounding matrix, causing voids to initiate at the matrix-particle interface that eventually lead to failure. This however is still unclear and subject of future work. The ultimate compressive stress did not change greatly after heat treatment with $\sigma_{UCS,AB} = 1392 \pm 21$ MPa, $\sigma_{UCS,750^\circ\text{C}} = 1313 \pm 10$ MPa, and $\sigma_{UCS,850^\circ\text{C}} = 1362 \pm 22$ MPa.

4. Conclusions

After dissolving Mo and Mo₂C particles, density increases and full density is obtained with increasing laser power P and scan speed v , eventually resulting in a homogenously alloyed β -(Ti,Mo) matrix with a fine dispersion of TiC whiskers. In contrast, there are more

unmelted particles and a heterogeneous distribution of Mo in the Ti matrix when using low P - v combinations. In the as-built condition, the hardness of up to 550 HV exceeds that of SLM'd Ti6Al4V (400 HV). Due to supersaturation of C in the matrix, the material is strong ($\sigma_{0.2,AB} = 1164 \pm 37$ MPa) but has a limited deformability. During post-process heat treatment, the TiC plates coarsen while α laths form. This leads to a slightly lower strength but can nearly double the ductility.

This work demonstrates that the microstructure and mechanical properties of in situ formed metal matrix composites can be controlled by variation of the SLM process parameters and post-process heat treatment. The conclusions are generally applicable to similar material systems in which a powder is alloyed with particles with a higher melting point.

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