Microstructure and tensile property of a BCC-structured high entropy alloy fabricated by laser melting deposition

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Abstract. The microstructure and tensile property of a BCC-structured high entropy alloy fabricated by laser melting deposition was investigated in this paper. The microstructure of as-deposited specimens was equiaxed grain and consisted of BCC phase and Zr rich precipitate. Due to the in-situ aging effect, the precipitate content in the as-deposited specimen increased with the increase of the distance from the last build plane, which can be weakened by decreasing the input power. With a heat treatment at 950℃ for 1h, the precipitate can be completely removed. The strength and ductility of the heat treated specimen were much higher than those of the as-deposited specimen, which may be owing to the increased solution strengthening effect through the dissolution of the precipitates.

1. Introduction

Recently, high entropy alloy (HEA), a new kind of metallic alloys, has attracted much attention due to its good mechanical properties, excellent thermal stability and wear resistance[1]. Up to now, the main fabrication methods of HEA are arc melting[2] and mechanical alloying[3], which have some obvious weakness in the geometry complexity and production efficiency. This limits the practical application of HEA greatly. Laser melting deposition (LMD)[4] is one of the advanced manufacturing technologies which can solve the above problem. LMD is a typical metal additive manufacturing (AM) technology, which directly fabricates 3-dimension (3D) metal structures by depositing the melted powders on the platform layer by layer, reducing the raw material usage and shortening the production period. In addition, LMD can use the mixed powder of pure metals to fabricate HEA with any composition[5], which solves the powder fabrication difficulty of HEA with high melting point or reactivity, and liberates the design freedom for novel HEAs.

At present, there are several reports about the LMD HEA[6], which concentrate on the 3d-transition and refractory HEAs. Haase et al. [7] indicated that the columnar grains were formed in the CoCrFeMnNi fabricated by LMD with the elemental powder blend. Xiang et al. [8] found that the element distribution in LMD CoCrFeMnNi specimen was much more homogeneous than that in the cast counterpart. Joseph et al. [9] indicated that large columnar grain was formed in the LMD AlxCoCrFeNi, and it led to the anisotropy of mechanical properties. More interestingly, the LMD CoCrFeMnNi HEA showed better mechanical properties than the cast counterpart [10], which suggests the enormous application potential of LMD to more HEA systems. Because of the composition complexity of HEA and thermal history complexity of LMD, the relationship among LMD parameters, microstructures and mechanical properties should be investigated further for the novel HEA system to direct the development of HEA suitable for the LMD process.
In this study, a Ti$_{3.6}$Zr$_{1.2}$V$_{0.8}$NbAl$_{0.3}$ (denoted as Ti3.6) HEA with good mechanical property after recrystallization was prepared by LMD. The effect of power and heat treatment (HT) on the microstructure and tensile property were investigated to find a way to obtain the HEA with high mechanical property by LMD.

2. Experiment

Ti3.6 HEA blocks in the size of 38 mm (L) × 23 mm (W) × 14 mm (H) were deposited on the Ti6Al4V alloy substrate by RC-LDM 4030 apparatus with the gas atomized powders ranging from 45 μm to 150 μm, and one of them are shown in Figure 1(a). The main fabrication parameter included the beam diameter of 3 mm, the input power of 1200-1500W, the scanning speed of 600 mm/min and the layer thickness of 0.6 mm. The scanning strategy was bidirectional scanning along the width direction, as shown in Figure 1(b). The fabrication was proceeded in an argon gas protection atmosphere, where the concentration of oxygen and water vapor were lower than 50 ppm. The specimens taken from the middle part of the 1200W deposited block were heat treated at 800℃-1000℃ for 1 hour to find the optimum condition to remove the precipitates. The microstructure on the vertical cross section was investigated by X-ray diffraction (XRD, Bruker AXS D8 Advance) and scanning electron microscope (SEM, FEI Quanta 650F). The tensile specimens with a gauge of 10 mm length, 3 mm width, and 1 mm thickness were cut on the plane approximate 5 mm from the last build plane, and the loading direction and thickness direction were set parallel to the y- and z-axes, respectively, as shown in Figure 1(b). The tensile test was carried out on CMT4305 universal electronic tensile testing machine at room temperature with a strain rate of 1×10$^{-3}$ s$^{-1}$.

Figure 1  (a) Physical picture of the as-deposited specimen; (b) Schematic illustration of the scanning strategy and sample way for the tensile specimen, the black arrows represent the scanning direction of the laser beam.

3. Results and discussion

Figure 2 shows the XRD results of the powder and the as-deposited specimens taken in the middle part of the block. Only the peaks from the BCC phase can be observed, which suggests the Ti3.6 HEA powder and its as-deposited block may be the BCC single phase. However, the microstructure observation for the as-deposited blocks (Figure 3 and Figure 4) suggests there is also precipitate in fact, whose content may be beyond the detect limitation of XRD. Figure 3 shows the SEM images on different heights of the as-deposited block using the power of 1200 W. The precipitates continuously existed in the grain boundaries and were dispersedly distributed in the grain inside with the disk-like morphology. The disk-like precipitate inside the grain was around 3mm and was deduced to be rich in Zr by the phase diagram calculation. The precipitate content inside the grain of middle part was more than that in the top part, which suggests that the precipitate content increased with increasing the distance from the last build plane. This is considered to be caused by the in-situ aging effect [11]. In the process of AM, as the laser moves track by track and layer by layer, the temperature of the early-built part drops in a fluctuating manner and eventually tends to be within a stable range, which can be over 0.5 Tm in LMD [12] and EBM [13]. The stay at such temperature range during AM is like suffering an aging treatment, therefore it is often called “in-situ aging”. The top part goes through shorter cyclic heating time than the middle
part, i.e., shorter in-situ aging process, therefore, its precipitate content was less. The detail microstructure observation suggests that the less precipitate region is only around 3 mm in height, and the microstructure of as-deposited block is dominated by the BCC grain with large amount of Zr rich precipitates in the grain and grain boundary.

![Figure 2](image1.png)

**Figure 2** XRD results of the powder and the as-deposited specimens taken in the middle part of the block.

![Figure 3](image2.png)

**Figure 3** SEM images on different heights of the as-deposited block using the power of 1200 W. 
(a,b,c) Top part; (d,e,f,g) Middle part.

Figure 4 shows the SEM images in the middle part of the as-deposited block using the power of 1500 W. The continuous precipitates can also be observed on the grain boundaries of 1500 W deposited specimen, like the case in 1200 W deposited specimen. However, the content of the precipitates inside the grain of 1500 W deposited specimen was significantly lower than that of 1200 W deposited specimen. This suggests that increasing the input power can weaken the formation of precipitate inside the grain. This may be because the overall in-situ aging temperature of the early built part increases as the laser power increases, exceeding the dissolving temperature of the precipitate.
Figure 4 The SEM images of 1500W as-deposited specimens in the middle of the block

Figure 5 shows the SEM images of the 1200 W deposited specimens after different HT temperatures for 1 hour. With increasing the temperature from 800 °C to 1000 °C, the precipitate in the grains dissolved quickly, and nearly disappeared at 850 °C, while the precipitates on the grain boundary dissolved slowly, and completely disappeared until 1000 °C. The variation of precipitates content with the heat treatment temperature is shown in Table 1. The average grain size was around 45 µm when the HT temperature was below 900 °C. A slightly bigger grain size (~60µm) was observed in the specimen with HT at 950 °C, where there were just a few precipitates left on the grain boundary. However, the average grain size rose to ~270 µm when the HT temperature increased to 1000 °C, where the grain boundary was clean. This suggests that partly residual precipitate at the grain boundary is benefit to prevent the grain growth, and 950 °C is the critical temperature that the grain size of Ti3.6 HEA specimen could remain fine after high temperature HT for 1 hour.

Table 1 The content of precipitates after different heat treatments

| Temperature/℃ | 800 | 850 | 900 | 950 | 1000 |
|---------------|-----|-----|-----|-----|------|
| the content of precipitates (%) | 15.12±0.4 | 14.83±0.6 | 2.13±0.7 | <0.5 | 0 |

Figure 6 (a) shows the typical stress-strain curves of the 1200 W deposited Ti3.6 HEA specimens after different HT conditions under the tensile test. The as-deposited specimen was brittle with fracture occurring during the elastic deformation. After HT at 800°C for 1h, the specimen exhibited the yielding strength of ~870 MPa and the limited elongation of ~6%. When the HT temperature increased to 950°C, the yielding strength and elongation of the specimen increased to ~930 MPa and ~10%, respectively. The precipitate content decreases with increasing the HT temperature (Figure 5 (a, d)), therefore, it is
nature that the plastic deformation ability increases with increasing the HT temperature. However, it is quite peculiar that the yield strength increases in the same way. The effect of grain size can be excluded because the grain size of specimens with HT at 800 ℃ and 950 ℃ for 1 hour are similar (Figure 5 (a, d)). Then, the variation of solution strengthening may be the possible reason. The precipitate is rich in Zr, whose atom radius is much larger than those of the other elements. When the Zr rich precipitate is dissolved into the matrix, the lattice distortion of the matrix may increase greatly, making the effect of solution strengthening stronger than that of precipitate strengthening. Similar results are also observed in TiNbTa0.5ZrAl0.5 HEA [14], which is explained by a competition mechanism between the softening of precipitates dissolving and solution strengthening.

Figure 6 (b, c) show the representative fracture surfaces for the 1200 W deposited specimen and the specimen with HT at 950 ℃ for 1 hour. It showed numerous facet feature on the fracture surface of the as-deposited specimen (Figure 6 (b)), and the size of the facet was near the grain size. This suggests that intergranular fracture occurs in the as-deposited specimen, and the continuous precipitates on the grain boundary reduces the grain boundary strength. The dimple was the main feature for the fracture surface of the specimen with HT at 950 ℃ for 1 hour, which was corresponding to its good ductility. In addition, some groove-like microstructures can be observed, which may be caused by the detaching along the residual disc-like precipitates.

Figure 6 Tensile behavior of the Ti3.6Zr1.2V0.8NbAl0.3 in different condition: (a) Engineering stress-strain curve; (b) fracture surface of as-deposited and (c) 950 ℃-1h heat-treated specimens.

4. Conclusion
In this study, the effects of LMD parameter and HT condition on the microstructure and tensile property of Ti3.6 HEA were investigated and the main conclusions were drawn as follows:

1) The microstructure of the as-deposited specimen was equiaxed grain and consisted of a BCC matrix and Zr rich precipitates. The precipitates appeared preferentially on the grain boundary and formed a precipitate net along the grain boundary.

2) The precipitate content increased with increasing the distance from the last build plane owing to the in-situ aging effect. The precipitate content can be reduced by increasing the input power.

3) The intergranular and intragranular fracture occurred in the as-deposited and heat-treated specimen, respectively. The strength and ductility of the specimen can be improved at the same time by the post-deposited HT at 950 ℃ for 1 hour.

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