Effect of thermal treatment on the structure and hardness of the laser powder bed-fused Ti-Zr-Nb shape memory alloy

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Abstract. A new biomedical Ti-18Zr-14Nb (at.%) alloy was processed using the laser powder bed fusion additive manufacturing technology and subjected to post-fusion annealing in the 400 to 900 °C temperature range. The melt pool and grain structure features, the phase composition and hardness of samples fabricated using different laser energy densities and build rates, while having identical printed material densities, were analyzed. It was shown that the microstructure of the alloy differs depending on the printing parameters used. The higher the energy density, the coarser in size and the more elongated towards the build plate grains are formed during the process. Subsequent annealing results in the formation of different structures depending on the printing conditions, and the smaller the as-built grain size, the lower the onset temperature of recrystallization, which starts up to 100 °C lower for the finer grain structure than for the coarser grain structure of this study.

1. Introduction

The development of novel materials and complex parts with a controlled structure using the 3D and 4D additive manufacturing technologies represents a global trend in modern materials science [1-2]. 4D-technologies are considered a breakthrough, since they combine the potential of digital additive technologies with that of functional materials, such as shape memory alloys (SMA). These technologies allow printing intricate parts capable of modifying their geometry and properties in response to some external stimuli, such as temperature or stress [1].

Special interest represents the use of layer-by-layer material consolidation technologies, in particular laser powder bed fusion (LPBF), to manufacture personalized implants, since this technology allows an easy scaling up from a medical image to a prototype, and then to a product of mass customization [3]. Owing to their unique functional properties, Ti-Zr-Nb SMAs belong to the group of especially promising materials for bone implants [3-5]. These alloys exhibit a unique combination of biomechanical compatibility (low elastic modulus and superelastic behavior) with excellent corrosion resistance and non-toxicity of all the constitutive elements. Furthermore, the functional properties of these alloys can be additionally improved by optimizing their microstructure and phase state using thermal and/or thermomechanical treatments [6-7].

To guarantee adequate mechanical properties of printed parts, modern research in the field of additive technologies is primarily aimed at the fabrication of these parts with densities approaching those of their wrought equivalents [3, 8-9]. However, it is known that different microstructures and textures can intentionally be formed in as-printed parts of the same porosity [9], and these structure features can further
be modified using post-fusion thermal treatments. Such an approach appears to be especially promising for the improvement of functional properties of such structure-sensitive materials as SMAs [10]. Given the importance to study the effect of post-fusion thermal treatment conditions on the structure and phase state and therefore, on the mechanical properties of laser powder bed-fused Ti-18Zr-14Nb alloys, the present study endeavors to provide a preliminary understanding of this relationship.

2. Experimental Procedure
As a precursor material, a 50 mm-diameter, 600 mm-long ingot of the Ti-18Zr-14Nb alloy supplied by Flowserve Corp. Comp (USA) was used. The ingot was gas-atomized by TLS Technik GmbH (Germany). Next, a TruPrint1000 (TRUMPF, Germany) LPBF system equipped with a 200 W ytterbium fiber laser (spot diameter 30 μm) was employed to build a series of samples. Among them, two 10x10x10 (mm³) cube samples, #1 and #2, with identical densities (99.7%), but printed using different laser exposure conditions, were selected (Table 1). For the density measurements, the Archimedes’ method (ASTM B962) was used. The chemical composition of major elements and their distributions were measured using a TESCAN VEGA LMH scanning electron microscope equipped with an energy-dispersive X-ray microanalyzer. The oxygen and nitrogen contents were determined using LECO TC600 infrared cells. Chemical analysis showed that the LPBF process alters the chemical composition of the feedstock powder by decreasing its content in titanium and increasing in oxygen, and the higher the laser energy density, the greater the oxygen intake during the fusion process (Table 1).

Table 1. Printing conditions of sample #1 and #2 and chemical composition.

| Sample | Power, W | Speed, m/s | Hatch distance, mm | Energy density, J/mm³ | Building rate, cm/h | Measured density, % | Chemical composition |
|--------|---------|-------------|-------------------|----------------------|-------------------|-------------------|---------------------|
|        |         |             |                   |                      |                   |                   | in atomic, %        |
|        |         |             |                   |                      |                   |                   | Ti       | Zr       | Nb       | O       | N       |
| 1      | 175     | 1420        | 0.06              | 68.5                 | 9.2               | 99.7              | 65.6     | 18.8     | 15.5     | 0.218   | 0.019   |
| 2      | 130     | 985         | 0.11              | 40.0                 | 11.7              | 99.7              | 65.6     | 19.0     | 15.4     | 0.200   | 0.010   |
| Powder |         |             |                   |                      |                   |                   | 68.6     | 17.8     | 13.6     | 0.121   | 0.012   |

Samples for structural characterization and hardness measurements were cut from the printed cubes and subjected to post-fusion annealing (PFA) for 0.5 h at 400–900 °C in argon atmosphere, and then quenched in water. A Union Versamet-2 optical microscope (OM) equipped with a Nikon D90 camera and a TESCAN VEGA LMH scanning electron microscope equipped with an electron backscatter diffraction (EBSD) unit were used for microstructural analysis. X-ray diffraction phase analysis of the selected samples was performed using an Ultima IV Rigaku diffractometer (monochromatic CuKa-radiation). The Vickers hardness was measured using a Metkon microhardness tester with an applied load of 1 kg and a holding time of 10 sec.

3. Results and Discussion
Figure 1 shows the grain structure images from faces parallel to the build direction (vertical planes) just after LPBF (as-built) and after post-fusion annealing at different temperatures. These images are obtained using optical microscopy and EBSD techniques. It can be seen from Figure 1a-d, that the as-built samples, depending on the LPBF parameters, manifest differences in the melt pool morphologies, grain sizes and elongations: the higher the laser energy density, and the lower the build rate, the larger the melt pools, the coarser the grains and the more pronounced the elongations: grains of sample #1 are bigger and more elongated than those of sample #2 (see Table 1 for the values of energy density and building rate). The LPBF process results therefore in the formation of a columnar microstructure with average grain sizes in the vertical direction of ~98 μm for sample #1 and ~66 μm, for sample #2. The grains grow epitaxially with the continuation of their crystallographic orientations across the meltpool boundaries [10].

Regarding sample #2, PFA at 700 °C of this sample leads to an increase in the average grain size from 66 to 89 μm, and to a weakening of the meltpool boundaries (Figure 1e-f). It is assumed that PFA of sample #2 at this temperature corresponds to the initial stage of the local recrystallization process, while PFA of this sample at 800 °C leads to an active phase of recrystallization and the formation of a microstructure containing a large number of 50-150 μm-sized equiaxed grains (Figure 1j). Regarding sample #1, the
active phase of recrystallization of this sample does not start even after PFA at 800 °C, and the grain structure preserves its columnar morphology. These differences can be explained by the fact that the building rate of sample #2 is higher than that of the sample #1, and therefore, the solidification cooling rate is also higher, which results in finer and more stressed as-built microstructure. It has a cumulative effect that starts the processes of recrystallization of sample #2 at a lower temperature than that of sample #1.

**Figure 1.** Images (vertical planes) of the Ti-Zr-Nb alloy microstructure after LPBF (a-d) and after LPBF +PFA at 700 °C (e-h), 800 °C (i, j): sample #1 (a, c, e, g, i) and sample #2 (b, d, f, h, j).

The X-ray diffractograms obtained for the samples in the as-built state and annealed at different temperatures are shown in Figure 2. The main phase constituent in all the cases is the BCC β-phase. After PFA at 400 °C, some amounts of cooling- or annealing-induced α″- and α-phases are also observed. It is worth noting the presence of TiO₂ (rutile) peaks in all diffractograms. It can be assumed that TiO₂ (rutile) is formed as particles or in the form of oxide on the surface of nano- or micropores. This assumption requires additional study using electron microscopy methods.

**Figure 2.** Results of X-ray diffraction analysis of Ti-Zr-Nb alloy after LPBF and LPBF+PFA: sample #1 (a) and sample #2 (b).

In the initial, as-built, state, the alloy hardness of both samples is ~280 HV (Figure 3). Annealing at 400 °C leads to a sharp increase in hardness up to 290-300 HV, which is associated with the formation of α- and α″-phases in the alloy [6]. An increase in the PFA temperature to 500-600 °C gradually reduces the hardness to ~250 HV. The lowest hardness, associated with the α″↔β transformation-related phenomena [3, 6], is achieved after PFA at 550-600 °C for sample #2 and after PFA at 600-700 °C, for sample #1. Then followed a slight increase in hardness, which is explained by a decrease in the softening contribution of β-phase with increased PFA temperature. Finally, hardness in both samples decreases again, which is
caused by the onset of the recrystallization process. Note that ~100 °C difference between the temperatures corresponding to the lowest hardness (550 °C for sample #2 and 650 °C for sample #1) and between the onset temperatures corresponding to the last decrease in hardness (700 °C for sample #2 and 800 °C for sample #1), indicate that all the processes occurring during PFA of the fine-grained sample #2 occur at temperatures ~100 °C lower than for the coarse-grained sample #1, which correlates with the results of the microstructure analysis (Figure 1).

![Graph showing hardness measurements](Image)

**Figure 3.** Results of hardness measurements of Ti-Zr-Nb alloy after LPBF and LPBF+PFA.

**Summary**

The effect of the laser powder bed-fusion (LPBF) process with two different sets of printing parameters and subsequent annealing at 400-900 °C on the structure and hardness of a new biomedical Ti-18Zr-14Nb shape memory alloy is studied. The morphology of the grain structure depends on the energy density and the building rate. Sample #1 printed with higher energy density and lower building rate contains a columnar microstructure with an average grain size in the vertical directions of ~98 μm. On the contrary, sample #2 printed with lower energy density and higher building rate contains less elongate grains with an average grain size of ~66 μm. The onset of the recrystallization process in sample #2 with a finer microstructure occurs at ~700 °C, and its active phase, at 800 °C, which is ~100 °C lower than for sample #1. The results of the hardness measurements correlate well with the results of the microstructural analysis.

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