Microstructure and mechanical properties of Ni$_{50.7}$Ti$_{49.3}$ shape memory alloy fabricated by selective laser melting

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Abstract. In this work, dense NiTi shape memory alloy (SMA) was fabricated by selective laser melting (SLM) under different laser powers (150 W, 210 W and 270 W). The effect of altered laser power on the microstructure and mechanical properties of NiTi SMA was studied by X-ray diffraction, differential scan calorimetry, optical microscopy and compressive test. The results indicated that the grains of SLM NiTi SMA changed from the uniform and fine honeycomb crystals to large square crystals with the increase of laser power. Meanwhile, the phase transformation temperature of SLM NiTi SMA increased with the increase of laser power, which resulted in the volume fraction of B19' phase in the matrix increased at room temperature. More importantly, when the laser power was 150 W, the SLM NiTi SMA had best compressive strength of 3302.7 MPa and fracture strain of 34.5%, which were better than most of the reported compressive properties in SLM NiTi SMA. This is mainly attributed to the fine and uniform honeycomb crystals in SLM NiTi SMA by 150 W.

1. Introduction
NiTi SMA has received much attention in medical and industrial fields due to its unique functional properties, such as excellent corrosion resistance, biocompatibility, shape memory effect, and superelasticity[1]. Although NiTi SMA has many excellent properties, its poor machinability makes it difficult to manufacture complex NiTi parts[2], which limits its potential applications. In recent years, selective laser melting (SLM) has been found to be an effective way to solve the poor machinability of NiTi SMA. SLM has attracted a lot of attention in manufacturing NiTi parts with complex shape[3]. However, the research on functional properties of SLM NiTi SMA is still in the early stage. Undoubtedly, the primary task in SLM NiTi SMA is to produce NiTi parts with good mechanical properties.

Ma et al.[4] studied the influence of hatch spacing on mechanical properties of Ni50.9Ti49.1 SMA, and they found that when hatch spacing was in the range of 35-120 μm, it had an insignificant effect on the mechanical properties of NiTi SMA. Dadbakhsh et al.[5] produced NiTi SMA in the same energy density range, composed of high laser parameters (HP: high laser power adjusted to high scanning speed) and low laser parameters (LP: low laser power adjusted to low scanning speed), to investigate its influence on the microstructure and mechanical properties of SLM NiTi SMA. The results showed that the HP SLM part was austenite at room temperature, while LP was martensite. Compared with LP, HP had higher compressive yield strength, but its compressive strength was slightly lower. Andani M T et al.[6] used optimized SLM parameters (P=250 W, t=30 μm, v=1250 mm/s,
and h=120 μm, where P is the laser power, t is the powder layer thickness, v is the scanning speed and h is the hatch spacing) to produce NiTi SMA, and the compressive strength and compressive fracture strain of SLM NiTi SMA at room temperature were 1600 MPa and 30%, respectively.

From the previous works, it can be seen that laser scanning speed and laser power (P) have the greatest influence on the microstructure and properties of SLM NiTi SMA. It also can be found that few related studies were exploring the influence of laser power on the microstructure and properties of SLM NiTi SMA. Therefore, in this study, the effect of different laser power on the microstructure and mechanical properties of SLM NiTi SMA was studied. The excellent mechanical properties were obtained in the SLM NiTi SMA fabricated by relatively low laser power. The results in this work could accelerate the industrial applications of SLM NiTi SMA.

2. Materials and Methods

In this study, the near-equiatomic ratio NiTi SMA powders produced by electrode induction-melting gas atomization were used as raw materials. They had a spherical morphology (as shown in Fig. 1a), together with the particle size distribution of D10 = 19 μm, D50 = 33 μm and D90 = 53 μm (Fig. 1b), which was analyzed by the laser particle size analyzer (HORIBA LA960S). They were determined to be Ni-rich Ni50.7Ti49.3(at. %) SMA powders by inductively coupled plasma-atomic emission spectroscopy. Before printing, the powders were sieved and then dried under vacuum at 80 °C for 12 h.

Dense NiTi samples were fabricated on a NiTi base plate using a commercial Selective Laser Melting (SLM) machine (EOSINT, M280) equipped with a fiber laser with maximum power of 400 W and beam size of 80 μm. Before printing, the substrate was preheated to 180 °C. The parameters selected for printing process were as follows: v=1200 mm·s⁻¹, t=30 μm and h=80 μm, while P=150 W, 210 W and 270 W, respectively. The laser scanning strategy was to rotate the scanning direction between layers by 67° and scan in both directions. The 8×8×8 mm cubic SMA samples were print out, their phase composition, microstructure, phase transformation behavior and mechanical properties were chosen as the indicators.

The samples were wet ground with 180, 360, 600, 800, 1000, 1500 and 2000 grit SiC sandpapers perpendicular to the Z-axis, followed by mechanical polishing and finally processed by ultrasonic cleaning with alcohol for ten minutes. The polished samples were etched with a mixed reagent of 10 vol% HF + 40 vol% HNO₃ + 50 vol% H₂O for 15-20 s. Finally, an optical microscope (Leica DM 15000M) machine was utilized to observe the microstructure of the corroded samples. A multi-position automatic sampling X-ray diffractometer (PANalytical X’pert Powder) with a rotating Cu anode and crossbeam optics selection Cu-Kα (λα1=1.54059 Å, λα2=1.54441 Å) was used for the phase analysis of the polished samples. Its scanning step was 0.02°, and the angular 2θ range was 20°<θ<90°.
Differential Scanning Calorimetry (DSC Netzsch 214 Polymer) was used to analyze the phase transformation temperatures at a heating/cooling rate of 10 °C/min in a nitrogen atmosphere based on ASTM F2004-05. The SLM NiTi SMA samples were cut along the x-y cross-section into cylindrical compression samples of Φ3×6mm by using wire cutting equipment. Room temperature compression test on the samples was carried out via the electronic universal testing machine (SUNS UTM5105), the strain rate was 5×10⁻⁴ s⁻¹, and each sample was tested three times.

3. Results & Discussion

![XRD patterns of the alloys fabricated by laser power of 150, 210 and 270 W, respectively (ν = 1200 mm·s⁻¹ and h = 80 μm)](image)

Fig. 2 XRD patterns of the alloys fabricated by laser power of 150, 210 and 270 W, respectively (ν = 1200 mm·s⁻¹ and h = 80 μm)

Fig. 2 presents XRD patterns of the alloys manufactured by different laser powers. Fig. 2 displays that the alloys consist of B2 austenite and B19' martensite phase. With the increase of laser power, the diffraction intensity of the peak (100) and (200) in B2 phase gradually decrease. When P = 270 W, the (100) peak of the B2 phase even almost disappears. The volume fraction of the B2 phase shows a clear downward trend. Meanwhile, the diffraction intensity of the (002) peak of the B19' phase gradually increases, indicating that the volume fraction of the B19' phase gradually increases and becomes more stable at room temperature. The results can be mutually confirmed with the DSC results, that is, as laser power increases, the phase transformation temperature of the sample will increase, which will eventually lead to an increase in the volume fraction of the B19' phase at room temperature.

Fig. 3 demonstrates the microstructure evolution of SLMed NiTi SMA fabricated by different laser powers (150 W, 210 W and 270W). The microstructure of the as-fabricated alloy with laser power of 150 W presents a fine and uniform honeycomb morphology. With the increase of laser power, the grain size of the alloys gradually increases, and the grain shape changes from polygon to quadrilateral. This is mainly due to the fact that, the increase of laser power will gradually increase the input energy density during alloy forming, thereby forming an overheated molten pool inside the alloy. Too high temperature on the surface of the overheated molten pool will make the cooling rate too slow. In addition, the overheated molten pool will also remelt more areas in the alloy, so the liquid metal in the remelted area will take longer to solidify, so that coarser grains will be formed inside the alloy.
Fig. 3 Optical micrographs for the as-built NiTi alloys fabricated by SLM with laser power of 150W, 210W and 270W, respectively ($v = 1200 \text{ mm} \cdot \text{s}^{-1}$ and $h = 80 \mu\text{m}$).

Fig. 4 DSC curves of the as-built NiTi alloys fabricated by SLM with laser power of 150, 210 and 270 W, respectively ($v = 1200 \text{ mm} \cdot \text{s}^{-1}$ and $h = 80$).

Tab. 1 Characteristic temperatures of phase transformations in the DSC curves above

| Sample | $M_f$ (℃) | $M_s$ (℃) | $A_s$ (℃) | $A_f$ (℃) |
|--------|-----------|-----------|-----------|-----------|
| 150W   | -33.9     | 5.2       | 0.0       | 37.3      |
| 210W   | -14.3     | 15.6      | 16.1      | 49.6      |
| 270W   | -9.3      | 20.9      | 22.0      | 57.5      |

Fig. 4 shows the DSC curve of bulk NiTi alloy prepared by SLM. It can be found from the figure that all alloys exhibit a one-step phase transformation behavior during the temperature increase and decrease process, and the shape of the phase transformation curve is basically the same. Combined with the phase diagram of NiTi alloy, it can be known that the only phase transformation peak is the
mutual transformation between martensite and austenite. In addition, it is also found from the Tab. 1 that as the laser power increases, the phase transformation peak of the bulk alloy shifts to the right as a whole, indicating that the phase transformation temperature of the alloy increases. Taking the martensitic transformation start temperature Ms as an example, when the laser power for preparing the bulk alloy increases from 150 W to 210 W, Ms increases from 5.2 ℃ to 15.6 ℃. When the laser power was further increased from 210 W to 270 W, Ms increased from 15.6 ℃ to 20.9 ℃. In fact, the other three phase transformation temperatures also have similar trends.

The above trend is mainly due to the fact that when the laser power for preparing NiTi alloy increases, higher temperatures will be generated around the molten pool, which will cause more nickel to evaporate. It has been reported that every time the nickel content in NiTi alloy decreases by 0.1at%, the phase transformation temperature will increase by 8.3℃. This is mainly due to the fact that the boiling point of nickel (2913°C) is lower than that of titanium (3287°C), so Ni will be preferentially evaporated at high temperatures, resulting in a decrease in the content of Ni in the alloy and an increase in the alloy phase transformation temperature. In addition, with the further increase of laser power, the evaporation of Ni element will gradually stabilize, therefore, the change range of the phase transformation temperature will also decrease. At the same time, the high residual stress introduced by the non-equilibrium rapid solidification of the molten pool will also affect the phase transformation temperature. The above results indicate that the phase transformation temperature of NiTi SMA manufactured by SLM is highly dependent on the process parameters, which is especially reflected in the laser power in this study. This provides theoretical guidance for the subsequent additive manufacturing of NiTi SMA to control the phase transformation temperature.

Fig. 5 shows the engineering compressive stress-strain curve of the alloy fabricated with different laser powers. The characteristic values of the mechanical properties are listed in the inserted table. It can be seen that as the laser power increases from 150 W to 270 W, the compressive strength of the alloy shows a decreasing trend, which is 3302.7 MPa, 3184.6 MPa and 3145.1 MPa, respectively. The fracture strain of the alloy also has a similar trend, which is 34.46%, 34.13% and 33.27% in order. According to Fig. 3, it is found that the alloy prepared by 150 W laser power has the smallest internal grain size, so the strength change trend of the alloy conforms to the Hall-Petch theory. However, due to the equiaxed crystal grains in the alloy prepared with laser power of 210W, the fracture strain reduction trend of the alloy is not obvious. However, when the laser power was further increased to 270 W, the crystal grain shape changed from equiaxed to quadrilateral, resulting in a drastically dropped in fracture strain from 34.13% to 33.27%.
4. Conclusions
In this study, Ni\textsubscript{50.7}Ti\textsubscript{49.3} powders were used to additive manufacture NiTi SMA, and the effect of SLM laser power (150 W, 210 W and 270 W) on the microstructure, phase transformation temperature and mechanical properties of SLMed NiTi SMA was revealed in detail. The main conclusions can be summarized as follows:

(1) In the SLM process, the increase of laser power will cause the surface temperature of the molten pool to be too high, thereby reducing the cooling rate of the molten pool, and the internal grains of the alloy grow and coarsen.

(2) With the increase of laser power, the phase transformation temperature of NiTi SMA gradually increased, which is mainly related to the evaporation of Ni element during SLM and high residual stress during nonequilibrium rapid solidification of molten pool.

(3) NiTi SMA with best compression mechanical properties was successfully fabricated with low laser power (150 W). Specifically, the ultimate compressive strength (\(\sigma_{\text{max}}\)) and fracture strain (\(\varepsilon\)) of the alloy are 3302.7 MPa and 34.5\%, respectively. Those are mainly related to its fine and equiaxed crystal grains.

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References
[1] Jani J M, Leary M, Subic A, et al. A review of shape memory alloy research, applications and opportunities[J]. Materials & Design, 2014, 56: 1078-1113.
[2] Hassan M R, Mehrpouya M, Dawood S. Review of the Machining Difficulties of Nickel-Titanium Based Shape Memory Alloys[J]. Applied Mechanics & Materials, 2014, 564: 533-537.
[3] Saedi S, Moghaddam N S, Amerinatanzi A, et al. On the effects of selective laser melting process parameters on microstructure and thermomechanical response of Ni-rich NiTi[J]. Acta Mater, 2018, 114: 552-560.
[4] Ma J, Franco B, Tapia G, et al. Spatial control of functional response in 4D-printed active metallic structures[J]. Scientific Reports, 2017, 7: 46707.
[5] Dadbakhsh S, Speirs M, Kruth J, et al. Effect of SLM Parameters on Transformation Temperatures of Shape Memory Nickel Titanium Parts[J]. Advanced Engineering Materials, 2014, 16: 1140-1146.
[6] Andani M T, Saedi S, Turabi A S, et al. Mechanical and shape memory properties of porous Ni\textsubscript{50.1}Ti\textsubscript{49.9} alloys manufactured by selective laser melting[J]. Journal of the Mechanical Behavior of Biomedical Materials, 2017, 68: 224-231.