Crystallization and Hardness Change of the Ti-Based Bulk Metallic Glass Manufactured by a Laser Powder Bed Fusion Process

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Abstract: Ti-2.5Zr-5.0Hf-37.5Cu-7.5Ni-1.0Si-5.0Sn (at. %) BMG has been successfully manufactured in amorphous powder with a size of about 25 µm (D50). Using this amorphous powder, a Ti-based BMG was manufactured by an additive manufacturing process based on a laser powder bed fusion (LPBF) technique. In 3D printing processes using amorphous powders, it is necessary and important to understand the crystallization behavior due to the difference in energy density applied to the powders. An LPBF process has been carried out with various energy density conditions to minimize the inner defects and identify the sound mechanical properties of 3D-printed BMG parts. At the lowest energy density condition (3.0 J/mm³), the most pores were generated. Even if the same energy density (3.0 J/mm³) was applied, the rapid laser movement caused many pores to form inside the material. The relatively sound 3D-printed Ti-based BMG was successfully fabricated with a size of about 5 mm × 5 mm × 3 mm. Peaks at 41° and 44° showing crystallization were observed in all conditions. The higher the laser power was, the greater each peak intensity and the more crystallization (CuTi, Ti₃Cu₄, etc) was present in the BMG, and the higher the scan speed, the more the internal defects were found.

Keywords: titanium amorphous powder; bulk metallic glass; additive manufacturing; laser powder bed fusion; crystallization

1. Introduction

Bulk metallic glasses (BMGs) are solidified without crystallization even in slow cooling after melting. They not only have high strength and hardness at the level of intermetallic compounds, but also have elastic strain limits similar to polymer materials because they fail to arrange regular crystal structures and represent disorderly arrangement compared with that of crystalline metals [1,2]. In particular, it has corrosion resistance and abrasion resistance comparable to that of ceramic materials, so it is a promising industrial material that goes beyond the traditional metal properties [3–6]. Although it has a variety of excellent properties, it does not produce proper plastic deformation based on the ambient temperature deformation load [7], which is applied by external conditions to manufacture parts and has a problem that can lead to unexpected fractures. Thus, in this study, 3D printing techniques that minimize machine processing and plastic deformation and produce products close to the near net shape are introduced in order to overcome the manufacturing difficulties of BMG parts that have low workability and formability [8].

The 3D printing technique applied here is laser powder bed fusion (LPBF) method, which uses laser as a heat source and is suitable for use in metal powders that require a high-power heat source to build material layer by layer for melting [9–15]. The LPBF method can produce very large BMGs because only small powder volumes are melted...
and subsequently solidified at very high cooling rates (up to $10^4$–$10^6$ K/s) [16–19]. This is difficult to produce by conventional preparation methods like casting. However, several possible problems should be considered when applying the 3D printing process to the manufacture of BMGs. First, defects such as pores inevitably occur inside the product as the melting and coagulation of powder progresses rapidly without external pressurization in the 3D printing process. Additionally, different defects may occur due to lack or excessive energy density, depending on the process conditions [20–26]. Internal defects in the process should be minimized because they adversely affect mechanical properties, such as the tensile and fatigue properties [27,28]. Second, since the 3D printing process is carried out using a BMG powder, crystallization can occur in the manufactured BMGs due to refusion and resolidification by the laser heat source applied in the process [29,30]. Therefore, efforts are required to inhibit crystallization in order not to lose the original BMG properties.

The Ti-based spherical BMG powder, which represents excellent specific strength and corrosion resistance, was successfully manufactured using the electrode induction melting gas atomization (EIGA) process in this study. In additive manufacturing using the Ti-based BMG powder, this study thus attempted to optimize the LPBF process through various changes in the process conditions, such as the laser power and scan speeds, to minimize inner defects and to confirm crystallization behaviors in Ti-based BMG LPBF parts. The sound Ti-based BMG 3D-printed specimens were manufactured with a size of $5 \text{ mm} \times 5 \text{ mm} \times 3 \text{ mm}$ to provide basic research data for the optimal process conditions for the LPBF AM of Ti-based BMG powders, and the correlation between crystallization and hardness property was evaluated according to the process conditions through microstructure observation, XRD analysis, and micro-hardness measurement for the specimens manufactured under different conditions.

2. Experimental

2.1. Ti-BMG Powder and Additive Manufacturing

In this study, the Ti-based BMG powder (Ti-2.5Zr-5.0Hf-37.5Cu-7.5Ni-1.0Si-5.0Sn, at.%) was successfully manufactured using the EIGA method, which produced spherical powder through heating electrodes with a high frequency and spraying gas. The manufactured Ti-based BMG powders represented spherical powder with a particle size distribution of $D_{50} = 25 \mu m$ and $D_{90} = 40 \mu m$. Figure 1 shows the powder morphology observed using a scanning electron microscope (SEM) (JSM-7001F, JEOL ltd., Tokyo, Japan), and the composition of the powder is presented in Table 1.

![Figure 1](attachment:image.png)

**Figure 1.** Particle morphology of the Ti-based BMG powder manufactured by electrode induction melting gas atomization. (a) $500 \times$ magnification and (b) $2000 \times$ magnification.
Table 1. Chemical compositions of the Ti-based BMG powder.

| Elements | Ti  | Zr  | Hf  | Cu  | Ni  | Si  | Sn  |
|----------|-----|-----|-----|-----|-----|-----|-----|
| at.%     | 41.5| 2.5 | 5.0 | 37.5| 7.5 | 1.0 | 5.0 |
| wt.%     | 30.3| 3.5 | 13.7| 36.4| 6.7 | 0.4 | 9.0 |

In order to manufacture Ti-based BMGs using the Ti-based BMG powder, among 3D printing methods, the LPBF method selectively irradiates high-power lasers to the metal powder, which has a certain thickness, for melting and solidifying materials. In addition, the laser power and scan speed were adjusted in the process conditions, and a Ti-based BMG of 5 mm (width) × 5 mm (length) × 3 mm (depth) was manufactured by six different process conditions based on the additive manufacturing process.

2.2. Observation of Microstructures and XRD and Hardness Measurement

The observation of the microstructures and XRD analysis were performed to determine whether the Ti-based BMGs were crystallized according to the process conditions. For observing the microstructures, an optical microscope (BX53MRF-S, Olympus, Tokyo, Japan) was used after abrading the specimens precisely as a mirror-like processing method, using abrasive papers of #220~#2000, abrasives of 6 and 1 µm, and colloidal silica. X-ray diffraction (XRD) (Brucker D8, Billerica, MA, USA) analysis was performed under the following conditions: 2θ = 25–90°, step size = 0.05°, and time/step = 2 s. In addition, a micro Vickers hardness tester (HM-200, Mitutoyo, Takatsu, Japan) was used to evaluate the hardness and to verify the crystallized region according to the process conditions. The hardness properties were evaluated by pressing at the following conditions: load = 200 gf, keeping time = 10 s, and 11 points from the center to the side of the fabricated specimens, which were tested three times. The mean value was calculated while excluding the maximum and minimum values.

3. Results and Discussion

3.1. Microstructural Properties

The LPBF process was applied to the spherical Ti-based BMG powder manufactured by the EIGA process, and the Ti-BMG 3D printing specimens were successfully manufactured through the additive process. The process conditions for each specimen were as follows. Among the names of the specimens, the “L” condition and the “H” condition stand for a low laser power and scan speed and a high laser power and scan speed, respectively, and the laser power of the “L” condition specimen was 80 W, while the laser power of the “H” condition specimen was 160 W. The scan speeds of the #1L, #2L, and #3L specimens were 1200 mm/s, 1029 mm/s, and 900 mm/s, respectively, and the scan speeds of the #1H, #2H, and #3H specimens were 2400 mm/s, 2057 mm/s, and 1800 mm/s, respectively. The calculated energy densities (E) of the #1, #2, and #3 specimens were 3.0 J/mm³, 3.5 J/mm³, and 4.0 J/mm³, respectively. The calculated energy densities of the specimens with the same numbers were the same, but the laser power and scan speeds of the “H” condition specimens were twice as high as those of the “L” condition specimens for implementing the additive manufacturing process.

Figure 2 represents the cross-section images of the microstructures of the specimens for each process condition measured using OM. Figure 2a,b shows the microstructures of the #1 specimens, Figure 2c,d shows the #2 specimens, and Figure 2e,f shows the #3 specimens, and the effects of laser power and scan speeds could be verified under the same energy density conditions. Wave patterns were commonly observed in the microstructures of all specimens, and a dark region (D) and a light region (B) were observed that could be identified with the naked eye (“D” and “B” in Figure 2). The #1, #2, and #3 specimens each had a wider dark region (D) under the “H” conditions, where the laser power and scan speeds were twice as high as under the “L” conditions, and more defects such as pores occurred [31,32]. Among them, the most pores were generated in the
#1 specimen (3.0 J/mm$^3$), which had the lowest energy density, and the energy density was considered insufficient in the additive manufacturing process compared with other conditions (configured in the #2 and #3 specimens) [33,34]. Additionally, as shown in Figure 2a,b, although the same energy density (3.0 J/mm$^3$) was applied, it can be seen that the rapid laser movement during its solidification process after melting it caused defects, including many pores inside the material.

![Figure 2](image_url)

XRD analysis was performed to determine the crystallization of each specimen for each 3D printing process condition and to determine the type of crystal phase, and the results are shown in Figure 3. Figure 3a shows the intensity values in the range of 2$\theta$ = 25–90$^\circ$ for each specimen, showing a typical curve of an amorphous alloy. Although this shows a typical curve of an amorphous material, a peak that is commonly considered to have been crystallized within the specimen at 41$^\circ$ and 44$^\circ$ was observed in all specimens. According to the existing literature, the 41$^\circ$ and 44$^\circ$ peaks observed in the XRD graph are identified as CuTi [35] and Ti$_3$Cu$_4$ [36], respectively. Figure 3b,c shows the peak intensity of each specimen in the 41$^\circ$ and 44$^\circ$ peaks as bar graphs. At the 41$^\circ$ peak, the intensity ratios of condition “H”, compared with condition “L”, for #1, #2, and #3 specimens, commonly, the higher the laser power and scan speed (condition L→H), the greater each peak intensity. At the 41$^\circ$ peak, the intensity ratios of condition “H”, compared with condition “L”, for #1, #2, and #3 increased by 11.5%, 4.4%, and 12.7%, respectively. At the 44$^\circ$ peak, the intensity ratios of #1, #2, and #3 increased by 5.1%, 0.6%, and 10.1%, respectively. In addition, by calculating the ratio of the crystallization peak area to the total area, the overall degree of crystallinity of condition “H”, compared with condition “L”, increased by approximately 2% according to the increase in the laser power and scan speed. Comparing this to the OM images (Figure 2), the relatively dark region (D) in the OM images was considered to be the crystallized region in the specimen, and the higher the laser power, the greater (condition H) the effect of the heat energy on the surroundings, which led to more crystallization in the BMG.
Figure 3. (a) X-ray diffraction patterns obtained from the Ti-based BMGs. (b) The 41° peak intensity (CuTi) and (c) 44° peak intensity (Ti$_3$Cu$_4$).

3.2. Hardness Change

Based on the OM images, the hardness of each specimen was measured by separating the bright region (B) and dark region (D) in order to determine whether the bright region (B) and the dark region (D) of the cross-section of the specimens were crystallized, and the results are presented in Figure 4. One common trait among all the specimens was that the hardness of the dark region tended to decrease (a minimum of 30 Hv to a maximum of 90 Hv) compared with the bright region. Considering the experimental error (even the micro Vickers tester) in which some bright regions were measured together during the hardness measurements in the dark regions, it is believed that the hardness values in the dark region decreased due to the crystallization of the BMG powder because of the refusion and resolidification from the laser output of the LPBF process. Based on these results, it was verified that the dark region was consistent with the microstructural analysis from the hardness measurement results, which predicted that the dark region would be a crystallized region in the BMG.
4. Conclusions

- Using the Ti-based BMG powder manufactured by the EIGA method, the Ti-2.5Zr-5.0Hf-37.5Cu-7.5Ni-1.0Si-5.0Sn bulk metallic glass was successfully fabricated by the laser powder bed fusion additive manufacturing process.
- In the results of the analysis of the microstructural properties according to the process conditions, it was confirmed that the Ti-based BMG powder, inevitably, was partially crystallized in all specimens due to refusion and resolidification. Under the same energy density conditions, the higher the laser power, the more crystallization was carried out, and the higher the scan speed, the greater the internal defects were found.
- In the results of the hardness measurement in the Ti-based BMG manufactured by the LPBF process, the relatively dark region returned lower hardness values compared with the light region, and the XRD analysis showed that crystallization of CuTi, Ti₃Cu₄, etc in the dark region was partially carried out.

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