Microstructural Change by Friction Stir Processing in Zr-Al-Cu-Ni Bulk Metallic Glass

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Microstructural change by friction stir processing (FSP) is examined in Zr-Al-Cu-Ni bulk metallic glass. The microstructure in the friction zone (FZ) exhibits an amorphous “band-like” structure, and a small number of nanoscale crystalline particles are observed along the “band-like” structure. The change in hardness with the microstructural change is examined and it is revealed that the hardness in FZ greatly increases although the volume fraction of crystalline phase is very limited. The increasing hardness is possibly explained from the combined effect of low temperature annealing during FSP and nano-size of crystalline particles.

Keywords: bulk metallic glass, friction stir processing, microstructural change, shear band

1. Introduction

Bulk metallic glass (BMG) has many unique properties, such as superior strength, high hardness and excellent corrosion resistance. Although extensive research on the deformation of BMG at room temperature has been conducted, the relationships between shear bands and the mechanical properties of BMG have been paid a lot of attention in late years. In general, BMG hardly shows plasticity at room temperature, because the formation of shear bands and its propagation take place at almost the same time. The limited plastic deformation capacity of BMG was caused by localized deformation process. However, in recent years, it has been reported that monolithic BMG exhibits a large plastic strain in compression tests at room temperature. As the commonly observed feature in these cases, the formation and interactions of multiple shear bands play an important role in the controlling of a large plastic strain in deformation of BMG. Thus, if shear bands can be formed in the BMG with a processing on purpose, enhanced ductility of BMG can be expected.

Previous studies on improvements of the mechanical properties in amorphous alloys and BMG have focused on processing methods such as cold rolling and heat treatment. Yokoyama et al. have reported that the mechanical properties are improved by the formation of shear bands upon cold rolling in Zr-based BMG. Jiang et al. have reported the mechanical properties of an amorphous Al-based alloy in which nanoscale shear bands are introduced by cold rolling. It is an interesting experiments to improve mechanical properties by microstructural modification during processing, i.e., introducing shear bands on purpose. However, previous results have problems that only thin ribbon is obtained in amorphous alloy and BMG partially fractures after cold working. If we can prepare BMG with many introduced shear bands by processing without partial fracture due to cracking, we can investigate the effects of shear bands on the mechanical properties of BMG and may have the BMG having excellent mechanical properties.

One method to introduce shear bands into a material without partial fracture is friction stir processing (FSP). FSP, a development based on friction stir welding (FSW), is a new solid state processing for microstructural change. During this process, the material undergoes intense plastic deformation by a rotating tool with pin and shoulder. Previous studies reveal that the microstructural improvement occurs in aluminum and other alloys by FSP such as grain size refinement and randomization of the texture.

We postulated that the continual intense plastic deformation by FSP would be able to introduce shear bands into a BMG. Recently, we have successfully applied FSP to introduce shear band in Zr-base BMG. However, the change in the mechanical properties due to the formation of shear bands has not been clarified yet. In the present paper, nanoscale shear bands are introduced into Zr-base BMG by FSP, and as the first step, the change in hardness due to the formation of the shear bands is examined.

2. Experimental Procedure

The material used in this study was Zr55Al10Cu30Ni5 BMG having a thickness of about 2.5 mm. Zr55Al10Cu30Ni5 BMG was processed through only a single pass of FSP. Figure 1 shows a schematic illustration of the FSP geometry. The diameters of the shoulder and pin of the tool used in this study were 12 and 4 mm, and the pin was a right-handed screw-type pin. From the results of repeated experiments under various FSP conditions, FSP was carried out using a tool rotation rate of 900 rpm and a traverse speed of 100 mm/min. In this processing condition, there are few macroscale defects in the specimen obtained. Following FSP, a transverse cross section was observed by scanning electron microscopy (SEM) at 60-fold magnification. A thermal analysis of the friction zone (FZ) was carried out using a differential scanning calorimetry (DSC). The specimens for DSC were part of the FZ with 3 × 3 × 2 mm. The thermal cycle consisted of heating at...
40 K/min up to 823 K. The microstructure of the as-received sample and the FSP sample was determined by transmission electron microscopy (TEM). A thin disc for TEM was removed from part of the FZ parallel to the FS direction. TEM specimens were prepared using ion milling. The Vickers hardness profile of the FSP region was measured on the points 1.2 mm from the surface in cross section perpendicular to the FS direction at applied load of 0.5 kgf.

3. Results and Discussion

Figure 2 shows a transverse cross-sectional view of FSP specimen in Zr$_{55}$Al$_{10}$Cu$_{30}$Ni$_{5}$ alloy perpendicular to the processing direction. The dotted line exhibits the FZ. Remarkable microstructural changes and large defects could not be confirmed in the FSP region.

Figure 3 show the DSC curves obtained from the as-received specimen and the FSP specimen. From the results of the DSC analysis for the as-received specimen, the glass transition temperature and the crystallization temperature of the base alloy are 699 K and 770 K, respectively. Both of these results indicate an exothermic peak due to crystallization. However, the exothermic peak of the FSP specimen is a little lower than that of the as-received specimen. This result indicates that slight crystallization has taken place during FSP. From this result, the FSP specimen consists largely of a glassy phase with a small amount of crystalline phase.

Figure 4 shows a bright-field TEM image and the related selected-area electron diffraction (SAD) pattern of the as-received Zr$_{55}$Al$_{10}$Cu$_{30}$Ni$_{5}$ alloy (a) and those of the FZ in the FSP specimen (b). The TEM sample is obtained from the point 1 mm from the surface in the center of the FZ. The arrow in Fig. 4(b) shows the FSP direction. Since the SAD pattern indicates only a halo ring in Fig. 4(a), the as-received specimen is a single glassy phase. From the bright-field TEM images shown in Fig. 4(b), a “band-like” nanoscale structure composed of the dark and bright regions is observed. In addition, nanoscale spherical particles of 5–20 nm in size are present along the “band-like” nanoscale structure. Both of the dark and bright regions are identified as the glassy phase because the SAD pattern obtained from the region without spherical particles shows only a halo ring. The nanoscale spherical particles are crystalline particles because diffraction spots are seen in the SAD pattern in Fig. 4(b).

As has been reported in the previous paper, we consider the “band-like” nanoscale microstructure as the shear bands. The shear bands are introduced by continual intense plastic deformation with the moving the spinning tool of the FSP, and the precipitation of nanoscale crystalline particles would then be induced by the deformation. As a consequence, the “band-like” nanoscale structure with nanoscale crystalline particles is formed in the FZ.

Next, the effect of the microstructural change on the hardness is examined. Figure 5 shows the hardness profile across the FSP region. The base material of Zr$_{55}$Al$_{10}$Cu$_{30}$Ni$_{5}$ glassy alloy has an average hardness value of 495 Hv, while the FZ has a higher hardness value compared with that of the base material. In the previous research on the BMGs, it has been reported that the hardness increases due to the nanoscale spherical particles dispersed in the glassy matrix. This trend can be explained from the inverse Hall-Petch relationship reported in the amorphous/nanocrystalline duplex composite. In the figure, the maximum peak is located at the position shifted to the advancing side, which is in good agreement with the previous report in crystalline material, and which may be originated from the difference of the material flow between the advancing side and the retreating side.

Figure 6 shows the normalized hardness as a function of the volume fraction ($V_f$) of the crystalline phase for the FSP specimen in this study and those of other BMGs. The data in this study is a normalized average hardness in FZ estimated from the data in Fig. 5. The $V_f$ of the crystalline phase is determined from the change in the heat of the
exothermic reaction in the DSC curve. To relate the difference in hardness in each material as a function of the volume fraction of the crystalline phase, the hardness data of each BMG were normalized to the hardness of the crystalline phase-free glassy matrix alloy by

$$H_v,\text{norm} = \frac{H_v}{H_v,\text{glass}}$$

Where $H_v$ is the hardness of BMG with the crystalline phase in each volume fraction and $H_v,\text{glass}$ is the hardness of the glassy matrix alloy. The hardness value rises as the volume fraction of the crystalline phase increases in all materials. However, in this study, the hardness in FZ increases greatly with a small volume fraction of the crystalline phase.

As the reason of increasing hardness in FZ, three explanations are considered. One is the effect of low temperature annealing with deformation. Jiang et al. have reported that the hardness of the cold rolled and annealed specimen increases in an amorphous Al-Ni-Y alloy.\(^{21}\) This result has been explained from the reduction of excess free volume. In the present study, intense plastic deformation and friction heat generation occur simultaneously during the FSP, which would be the similar situation with cold rolling and annealing. Another one is the effect of the band-like structure. However, it is difficult to explain how the band-like structure affects the increment of the hardness at the present stage. The other possibility is the effect of the size of the crystalline phase. Although the effect of the particle size on the hardness in the amorphous/nanocrystalline composite has not been clarified yet, it is expected that hardness greatly increases in the composite with smaller particles in the same volume fraction, because the number of interaction sites with shear bands increases with decreasing particle size. The small particle size with 5–20 nm may be a reason that the hardness in FZ increases greatly with a small volume fraction of the crystalline phase in this study. To clarify the each contribution, the effect of the size and volume of crystalline phase on hardness will be examined in the future works.

4. Conclusion

We investigated the microstructural change by friction stir...
processing (FSP) in Zr-Al-Cu-Ni BMG, and the change in hardness with the microstructural change. The results obtained in this study are as follows:

1. FSP is successfully applied to Zr-based BMG. The microstructure in the FZ exhibited a nanoscale amorphous “band-like” structure with nanoscale crystalline particles.

2. The hardness in FZ increases greatly with a small volume fraction of the crystalline phase. The increasing hardness is possibly explained from the combined effect of low temperature annealing during FSP and nano-size of crystalline particles.

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