Effect of Microstructural Change on High-Temperature Deformation in Pre-Annealed $\text{Zr}_{65}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}$ Bulk Metallic Glass

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The effect of the microstructural change on the high-temperature tensile deformation behavior in the supercooled liquid region is investigated in the pre-annealed $\text{Zr}_{65}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}$ bulk metallic glass. The microstructure before the tensile test on the specimen annealed at 673 K for 1.8 ks shows that a small amount of icosahedral phase precipitates and a large amount of amorphous phase still remains. On the contrary, the specimen annealed at 673 K for 2.7 ks shows that a large amount of icosahedral phase precipitates and the presence of amorphous phase is hardly noticeable. From the fact that flow stress of the specimen annealed at 673 K for 2.7 ks increases in comparison with that of as-received specimen as well as the specimen annealed at 673 K for 1.8 ks in the tensile test, it seems that the deformation behavior in the tension tests is greatly influenced by the difference in the degree of the precipitation of icosahedral phase. Since the m value is about 0.5 and many grain boundaries of icosahedral phase are formed in the specimen annealed at 673 K for 2.7 ks, the interaction between the icosahedral phase particles must be the cause of increase in initial stress. Accordingly, the microstructure of the gage section after tensile test in the specimen annealed at 673 K for 1.8 ks shows that the large amount of icosahedral phase precipitates in the amorphous matrix. The strain hardening must be caused by the interaction between the icosahedral phase particles whose precipitation and growth are enhanced by deformation.

(Received June 21, 2005; Accepted October 11, 2005; Published December 15, 2005)

Keywords: bulk metallic glass, zirconium–aluminum–nickel–copper alloy, high-temperature plastic flow, supercooled liquid region, icosahedral phase, microstructural change

1. Introduction

Bulk metallic glasses have been found to have excellent mechanical properties such as high strength, hardness, high corrosion resistance and so on.¹⁾ Among the bulk metallic glasses, the Zr–Al–Ni–Cu glassy alloys attract attention in the bulk metallic glasses because they have high glass forming ability and a wide supercooled liquid region.^{2,3)}

As one of the important characteristics of bulk metallic glasses, deformation behavior of metallic glasses is classified as Newtonian or non-Newtonian viscous flow. Superplastic behavior due to the Newtonian viscous flow has also been reported.^{4–7)} The superplastic behavior in the supercooled liquid region is useful for shape forming and fabricating.⁸⁾ Therefore, the Zr–Al–Ni–Cu metallic glasses can be expected in processing at the high temperature.

Recently, the study of such high-temperature plastic flow of bulk metallic glasses in supercooled liquid have been conducted, and an interesting result that the strain hardening occurs due to the crystallization during deformation has been reported.^{9–13)} Takigawa *et al.* have been reported that pre-annealed $\text{Zr}_{65}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}$ bulk metallic glass exhibits large homogeneous elongation in a supercooled liquid region.¹³⁾ The reported results are shown in Figs. 1 and 2.¹³⁾ As-received specimen exhibits significant necking, but uniform deformation occurs and large elongation is obtained in the specimen annealed at 673 K for 1.8 ks before tensile test as shown in Fig. 1. As shown in Fig. 2, apparent strain hardening occurs in the specimen annealed at 673 K for 1.8 ks, but, on the contrary, initial stress increase compared with in as-received in the specimen annealed at 673 K for 2.7 ks. They concluded that the strain hardening due to precipitation and growth of icosahedral phase, which is enhanced by deformation in a supercooled liquid region

make a positive contribution to neck stability, and result in the large elongation from the XRD and DSC analysis. However, the microstructural observation has not been get in the previous work. Therefore, it is necessary to confirm the precipitation and growth of icosahedral phase directly.

In the present study, we newly focus on the microstructural change during deformation in pre-annealed $\text{Zr}_{65}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}$ bulk metallic glass, to clarify the effect of the change in microstructure on high-temperature plastic flow.

2. Experimental Procedure

The material used in this study is $\text{Zr}_{65}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}$ bulk metallic glass having a thickness of about 1.5 mm supplied by YKK corporation. High temperature tensile tests are conducted at 673 K and in a constant true strain $1 \times 10^{-2} \text{ s}^{-1}$. Tensile test specimens having a gauge length of 5.0 mm, a width of 5.0 mm and thickness of 1.47 mm were fabricated from the as-received metallic glass by mean of electrical discharge machining. (Fig. 1) Some specimens are annealed for 1.8 or 2.7 ks at 673 K before the tensile tests. The heating rate is rapid in order to minimize the change in microstructure because of structural instability during the testing of the specimens at high temperature. Strain rate sensitivity exponent (m) is evaluated by strain rate change tests in the strain rate range from 2.4×10^{-5} to $1.5 \times 10^{-2} \text{ s}^{-1}$ at 673 K. The microstructure and structural change was analyzed by transmission electron microscopy (TEM), X-ray diffraction (XRD) and differential scanning calorimetry (DSC).

3. Results and Discussion

Figure 3 shows the results of XRD analysis obtained (a) as-received, (b) annealed at 673 K for 1.8 ks and (c) annealed at 673 K for 2.7 ks. In both as-received specimen and the specimen annealed at 673 K for 1.8 ks, diffraction patterns

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Fig. 1 The view of two deformed specimens exhibited large elongation at 673 K and in a constant true strain rate of $1 \times 10^{-2} \text{ s}^{-1}$; (a) as-received (without annealing) and (b) annealed at 673 K for 1.8 ks before the tensile test.¹³⁾

Fig. 2 The stress-strain curves obtained at 673 K and in a constant true strain rate of $1 \times 10^{-2} \text{ s}^{-1}$ in the specimens (a) as-received, (b) annealed at 673 K for 1.8 ks, and (c) annealed at 673 K for 2.7 ks.¹³⁾

consist of broad peaks without any diffraction peaks corresponding to crystalline phases. In the specimen annealed at 673 K for 2.7 ks, icosahedral phase precipitated in the glassy matrix.

Figure 4 shows DSC curve obtained from as-received specimen and the specimen at 673 K for 1.2 ks at the heating rate of 0.4 K/s. The both results exhibit two exothermic peaks. The first exothermic peak is due to the precipitation of the icosahedral phase in view of the result of XRD analysis. The second exothermic peak is due to the equilibrium crystalline phases.¹³⁾ The appearance of the exothermic peak due to the precipitation of icosahedral phase indicates that the Zr-Al-Ni-Cu bulk metallic glass used in this study contains some oxygen.^{13,14)}

Fig. 3 The results of XRD analysis obtained from the specimen (a) as-received, (b) the specimen annealed at 673 K for 1.8 ks, (c) the specimen annealed at 673 K for 2.7 ks.

Comparing the result of two specimens, the first exothermic peak due to precipitation of icosahedral phase in the specimen annealed at 673 K for 1.2 ks is lower than that in as-received specimen. This result indicates that icosahedral phase has already precipitated in the specimen annealed at 673 K for 1.2 ks. Therefore, in the specimen annealed at 673 K for 1.8 ks, icosahedral phase less than 50 nm that is not detected in the XRD analysis must have precipitates in the glassy phase.

To obtain detailed information about the specimens before the tensile tests, TEM observation is conducted. Figure 5 shows a bright-field TEM image (a) and nanobeam electron diffraction patterns (b) to (d) of the specimen at 673 K for

Fig. 4 DSC curve obtained from as-received specimen and the specimen annealed at 673 K for 1.2 ks at the heating rate of 0.4 K/s.

1.8 ks. Spherical particles with a size of about 50 nm or smaller are dispersed in the glassy phase. Nanobeam electron diffraction patterns of the five-, three- and two-fold symmetries are obtained. Therefore, these results suggest that the precipitated phase is the icosahedral phase. Figure 6 shows the a bright-field TEM image (a) and corresponding SAED pattern (b) of the specimens annealed 673 K for 1.8 ks, and a bright-field TEM image (c) and corresponding SAED pattern (d) of the specimen annealed 673 K for 2.7 ks. The spherical grains observed in Figs. 6(a) and (c) are icosahedral phase. In the specimen annealed at 673 K for 1.8 ks, a small amount of icosahedral phase precipitates and a large amount of glassy phase still remain. On the contrary, in the specimen annealed at 673 K for 2.7 ks, a large amount of icosahedral phase precipitates and glassy phase hardly remains. From the result of the tensile test as shown in Fig. 2, apparent strain hardening occurs in the specimen annealed at 673 K for

Fig. 5 Bright-field TEM image (a) and corresponding nanobeam electron diffraction patterns (b) to (d) obtained from the specimen annealed at 673 K for 1.8 ks.

Fig. 6 Bright-field TEM image (a) and corresponding SAED pattern (b) obtained from the specimen annealed at 673 K for 1.8 ks; and Bright-field TEM image (c) and corresponding SAED pattern (d) obtained from the specimen annealed at 673 K for 2.7 ks.

1.8 ks. On the contrary, strain hardening doesn't occur, but initial stress increase in comparison with that in as-received specimen and the specimen annealed at 673 K for 2.7 ks. In this result, it seems that the deformation behavior in the tensile tests is highly affected by the difference in the degree of the precipitation of icosahedral phase.

As the result of investigating the strain rate sensitivity exponent (m) obtained by strain rate change testes at 673 K, the m value is about 0.8 in as-received specimen and the specimen annealed at 673 K for 1.8 ks. On the contrary, the m value is about 0.5 in the specimen annealed at 673 K for 2.7 ks. This result indicates that the plastic flow is Newtonian in as-received specimen and the specimen annealed at 673 K for 1.8 ks, but the plastic flow is Non-Newtonian in the specimen annealed at 673 K for 2.7 ks in which a large amount of icosahedral phase precipitate in the glassy matrix. It is necessary to discuss the reason that the m value decreases

in the specimen annealed at 673 K for 2.7 ks. As the deformation mechanism that the m value is 0.5, the grain boundary sliding accommodated by dislocation slip is possible. As shown in Fig. 6(c), the microstructure of the specimen annealed at 673 K for 2.7 ks shows that the large amount of the icosahedral phase precipitates, and many grain boundaries are formed. Therefore, it seems that the interaction between the icosahedral phase particles takes place and the grain boundary sliding of icosahedral phase controls the deformation. The interaction between the icosahedral phase particles must be the origin of the increasing initial stress in the specimen annealed at 673 K for 2.7 ks. The observed behavior that the m value is about 0.5 is super-plastic-like deformation, but the stress increases and the tensile ductility is limited in the specimen. This must be explained from the difficulty of accommodation of stress concentration accompanying with grain boundary sliding as

Fig. 7 Bright-field TEM image (a) and corresponding SAED pattern (b) obtained from the gage section of the specimen annealed at 673 K for 1.8 ks deformed at 673 K at a strain rate of $1 \times 10^{-2} \text{ s}^{-1}$.

has been pointed out by Nieh *et al.*¹¹⁾

It has been reported that the precipitation and growth of crystal phase is promoted by deformation from the microstructure observation of gage section after the tensile test,^{10–12)} and comparable result is obtained the alloy used in this study.¹³⁾

Figure 7 shows a bright-field TEM image (a) and corresponding SAED pattern (b) of the gage section of the specimen annealed at 673 K for 1.8 ks deformed at 673 K at a constant true strain rate of $1 \times 10^{-2} \text{ s}^{-1}$. Many icosahedral particles precipitate homogeneously in the glassy matrix, and the grain size of the gage section in the specimen annealed at 673 K for 1.8 ks after the tensile test glows greatly compared with that in the specimen before tensile test as shown in Fig. 6(a). Moreover, it grows more than that in the specimen annealed at 673 K for 2.7 ks as shown in Fig. 6(c).

From these results, strain hardening in the tensile test of the specimen annealed at 673 K for 1.8 ks is discussed here. In the specimen annealed at 673 K for 2.7 ks, the microstructure before the tensile test has a small amount of icosahedral phase and a large amount of amorphous phase. However, with increasing the strain, the degree of the icosahedral phase increases and crystallization in deformation section progresses due to the precipitation and growth of icosahedral phase, which is enhanced by deformation. As the result, the interaction between the icosahedral phase particles takes place and the stress rises, *i.e.*, strain hardening occurs. These experimental results support the conclusion of the previous work.¹³⁾

4. Summary

We investigated the microstructural change on the high-temperature tensile deformation behavior in the supercooled liquid region of pre-annealed $\text{Zr}_{65}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}$ bulk metallic glass, in order to clarify the effect of the change in

microstructure on high-temperature plastic flow. The results obtained are summarized as follows.

- (1) Microstructure in the specimens of annealed 673 K for 1.8 ks shows that a small amount of icosahedral phase precipitates and a large amount of amorphous phase still remain. On the contrary, microstructure in the specimens of annealed 673 K for 2.7 ks shows that a large amount of icosahedral phase precipitates and amorphous phase hardly remains
- (2) In the specimen annealed at 673 K for 2.7 ks, the m value is about 0.5 and the microstructure shows that many grain boundaries with precipitation of icosahedral phase are formed. It seems that the interaction between the icosahedral phase particles takes place and the grain boundary sliding of icosahedral phase controls the deformation. The interaction between the icosahedral phase particles must be the origin of the increasing initial stress in the specimen annealed at 673 K for 2.7 ks.
- (3) TEM micrograph of the gage section in the specimen annealed at 673 K for 1.8 ks after the tensile test shows that many icosahedral particles precipitate homogeneously in the amorphous matrix, and the grains size glow greatly. Therefore, strain hardening is caused by the interaction with the particles between the icosahedral phase particles that the precipitation and growth are enhanced by deformation.

Acknowledgements

This work was supported by a Grant-in-Aid of the Ministry of Education, Culture, Sports, Science and Technology, Priority Area on “Materials Science of Bulk Metallic Glasses” (grant #15074217). We would like to thank Dr. M. Nakamoto and Dr. M. Yamamoto of Osaka Municipal Technical Research Institute for the DSC work.

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