1. Introduction

Bulk glassy alloys (BGAs) are a new material with good glass forming ability and excellent mechanical properties. Since the glassy alloys are characterized by an aperiodic random structure and flexible metallic bonding, we can expect the development of ductile, high-toughness and high-strength BGAs in various alloy systems. Furthermore, the deformation mechanism of BGAs is recognized to be an adiabatic shear band slip, which is accompanied by no work hardening and apparent work softening. It is critical to understand this deformation mechanism in order to control the mechanical properties of glassy alloys. Under uniform tensile or compressive stress, the shear band propagates immediately due to a huge elastic strain energy release. There is no barrier for shear band propagation under uniform stress distribution. However, a bending stress condition is characterized by gradient stress distribution, in which stress is maximized at the surface region. Since bending deformation is caused by maximized stress at the surface region, high-density shear band formation. 1) high-density shear band formation 2) highly dense shear band formation is also seen near the surface region. The Charpy impact test is a high-speed 3-point bending test. Moreover, stable fatigue crack propagation promotes numerous shear band networks in front of the fatigue crack tip to relax the localized strain. Therefore, shear band propagation is strongly influenced by stress conditions because of the lower work hardening feature of glassy alloys. The enhancement of both nucleation and shear band branching in front of the crack tip is extremely important to increase fracture toughness.

Recently, a certain kind of glassy alloy with high glass-forming ability has been developed, and those such enable the fabrication of bulk-shaped glassy alloys by conventional metallic mold casting methods. Inoue et al. have for the first time succeeded in synthesizing BGAs in Ln-, Mg- and Zr-based alloy systems without metalloid elements by copper mold casting methods. Zr-based BGAs exhibit a high tensile strength of 1500–1900 MPa, and have been used in sporting goods and connection tubes for optical communication fibers. Before the development of Zr-based glassy alloys, there were no cast materials with a high strength of over 1500 MPa and a high toughness of over 45 MPam^5/2. The good mechanical properties of Zr-based glassy alloys make them particularly attractive, and the applications described above were brought about by the use of unique casting techniques. Ternary eutectic Zr50Cu40Al10 BGA13 in particular exhibits excellent glass forming ability and superior mechanical properties, while the mechanical properties were significantly degraded by structural relaxation. However, it has been reported that hypoeutectic glassy alloys have significant advantages in improving embrittlement by structural relaxation.15–17

The aim of the present study was to improve embrittlement due to structural relaxation using hypoeutectic Zr-Cu-Al BGAs. The compositional dependence of the Charpy impact value on hypoeutectic Zr-Cu-Al BGAs after annealing was examined to determine the optimal composition with high resistibility to structural relaxation embrittlement. We also tried to clarify the origin of the high resistance to structural relaxation embrittlement in hypoeutectic BGAs.

2. Experimental Procedures

Ternary Zr-Cu-Al master alloys were prepared by arc-melting mixtures of pure Zr, Cu and Al metals in an argon atmosphere. To maintain a low-oxygen concentration, we used a special Zr crystal rod with a low-oxygen concentration of less than 0.05 atomic percent (at%). Zr-Cu-Al BGAs were cast into rod shapes (φ8 mm × 60 mm and 5 × 10 × 60 mm)
by tilt casting.\(^\text{18}\) This technique has the advantage of preventing a molten alloy flow from the formation of cold shuts, which act as crack initiation sites and also enhance crack propagation. The densities of as-cast and annealed Zr-Cu-Al BGAs were measured by the Archimedes method. The fluid for the Archimedes method was purified water. We examined the cast structure and Charpy impact fractured surface by optical microscopy (OM) and scanning electron microscopy (SEM) to confirm the quality of the glassy states. The phase characterization and crystalline ratio were examined by X-ray diffractometry and high-resolution transmission electron microscopy (HRTEM). Tensile tests were performed to estimate the tensile strength using an Instron 5582 type testing machine. Vickers hardness was measured using a micro Vickers testing machine (AKASHI-AVK). A Charpy impact test was also performed in dry air using half-notch samples with a size of \(55 \times 10 \times 5\) mm which were Unnotched to 2 mm in depth.

3. Results

It is known that the structural relaxation of BGAs brings about an increase in density. The hypoeutectic Zr\(_{59}\)Cu\(_{31}\)Al\(_{10}\) BGA also shows a density increase when annealed, although the range of density change is smaller than that of ternary eutectic Zr\(_{59}\)Cu\(_{50}\)Al\(_{10}\) BGA.\(^\text{19}\) Figure 1 shows the relationship between the density and the annealing time of annealed Zr\(_{59}\)Cu\(_{31}\)Al\(_{10}\) BGAs at 473, 573 and 648 K. Since the clear apparent saturation of density increase is seen at several annealing temperatures at times over \(5.4 \times 10^3\) s (90 min), we set the annealing time at 90 min. Furthermore, in order to make a standard of cast glassy alloys, we used a density of \(6.640 \pm 0.003\) g cm\(^{-3}\) for as-cast Zr\(_{59}\)Cu\(_{31}\)Al\(_{10}\) BGAs. Figure 2 shows the X-ray diffraction patterns of Zr\(_{59}\)Cu\(_{31}\)Al\(_{10}\) BGAs as cast and annealed at 648 K for 5.4 ks in a high-vacuum state. The top side of the cast rod, which was strongly heat-affected by the runner in the tilt cast method, was used for X-ray diffraction measurement. There were no distinct Bragg peaks in these X-ray diffraction patterns. Volume shrinkage due to structural relaxation was recognized by the shift of the hump pattern to a rather higher angle.

During structural relaxation, embrittlement phenomena are usually seen in BGAs.\(^\text{20}\) Accordingly, tensile strength, Vickers hardness and the Charpy impact value were examined in as-cast and annealed Zr\(_{59}\)Cu\(_{31}\)Al\(_{10}\) BGAs.

Figure 3 shows tensile strength changes as a function of annealing temperature. Tensile strength increases linearly with annealing temperature, and the slip from the linear relation was observed just under the glass transition temperature \(T_g\). Vickers hardness also shows the same tendency with annealing temperature, as shown in Fig. 4. The observed slight increases in the tensile strength and Vickers hardness just under the \(T_g\) probably originated due to the formation of short-range order changes and/or fine nanocrystallization. However, as shown in Fig. 5, the Charpy impact value of Zr\(_{59}\)Cu\(_{31}\)Al\(_{10}\) BGAs annealed at 648 K shows a significant increase up to 400 kJ/m\(^2\), a value comparable to that of engineering ductile steels. The enhanced Charpy impact value of Zr\(_{59}\)Cu\(_{31}\)Al\(_{10}\) BGAs annealed at 648 K also exhibits a large error range.

In order to determine the optimal composition with a significant increase in the Charpy impact value, the compositional dependence of the Charpy impact value of annealed hypoeutectic Zr-Cu-Al BGAs at 648 K was examined, as shown in Fig. 6. As a preliminary experiment, we also examined \(T_g\) change in these hypoeutectic Zr-Cu-Al BGAs: the maximum \(T_g\) was 674 K in a Zr\(_{57}\)Cu\(_{32}\)Al\(_{11}\) BGA and the minimum was 669 K in a Zr\(_{50}\)Cu\(_{50}\)Al\(_9\) BGA. Since the change in \(T_g\) was small enough, the annealing temperature of 648 K was deemed to be appropriate for use. Thus, annealed Zr\(_{59}\)Cu\(_{31}\)Al\(_{10}\) BGAs show the highest Charpy impact value of 285 \pm 118 kJ/m\(^2\), and there is a strong compositional dependence on Charpy impact value even in 1 at%. The Zr\(_{59}\)Cu\(_{31}\)Al\(_{10}\) BGA was considered to be the specified alloy with significant glass structural change in the formation of
Fig. 4 Relationship between Vickers hardness and annealing temperature of as-cast and annealed Zr$_{59}$Cu$_{31}$Al$_{10}$ BGAs.

Fig. 5 Relationship between the U-notched Charpy impact (CUE) value and the annealing temperature of as-cast and annealed Zr$_{59}$Cu$_{31}$Al$_{10}$ BGAs.

Fig. 6 Compositional dependence of the CUE U value of Zr$_{59}$Cu$_{31}$Al$_{10}$ BGAs after annealing at 648 K for 5.4 ks.

Fig. 7 Relationship between the density and the annealing temperature of as-cast and annealed Zr$_{59}$Cu$_{31}$Al$_{10}$ BGAs after annealing for 5.4 ks.

In order to clarify the origin of extremely high U-notched Charpy impact (CUE) values after annealing at 648 K, density change with annealing temperature was also examined. Figure 7 shows the relationship between the density and the annealing temperature of Zr$_{59}$Cu$_{31}$Al$_{10}$ BGAs. There is a distinct linear relationship between them at T$_a$ < 620 K, and a significant increase in density can be seen above T$_g$ due to crystallization. The crystallization occurred in the supercooled liquid region by annealing for a long period of time (5.4 ks). A deviation from the linear relationship was clearly observed just under the T$_g$. The nonlinear density increase in annealed Zr$_{59}$Cu$_{31}$Al$_{10}$ BGAs indicates a specific glass structural change on the atomic scale because no structural difference can be seen by X-ray diffraction patterns, as shown in Fig. 2. A drastic increase in CUE values also occurred in the density range of nonlinear increase from 6.640 to 6.646 g cm$^{-3}$ with the hatched area shown in Fig. 7. Figure 8(a) shows the HRTEM image of an as-cast Zr$_{59}$Cu$_{31}$Al$_{10}$ BGA and (b) shows the HRTEM image of a Zr$_{59}$Cu$_{31}$Al$_{10}$ BGA annealed at 648 K for 5.4 ks. Fringe marks, which indicate the existence of a crystalline structure in glassy alloys, were not observed in either HRTEM image. However, the HRTEM image of the annealed Zr$_{59}$Cu$_{31}$Al$_{10}$ BGA shows a significant amount of onion-like contrast, which indicates the existence of an icosahedral-like cluster as a short- and medium-range order. Some of them are denoted with circle in Fig. 8(b). Therefore, the local glass structure was significantly changed by the annealing treatment in hypoeutectic Zr$_{59}$Cu$_{31}$Al$_{10}$ BGAs, and volume shrinkage also occurred due to structural relaxation as in the case of eutectic Zr$_{50}$Cu$_{40}$Al$_{10}$ BGAs. From the viewpoint of controlling alloy composition with low melting temperatures, the eutectic point should be a middle composition between both elements to enhance the mixing entropy factor. On the other hand, an off-eutectic composition as a solvent-rich composition is effective in enhancing the stability of glass structures through the formation of icosahedral-like clusters.

4. Discussion

In order to determine the origin of the differences in extremely high CUE values of annealed Zr$_{59}$Cu$_{31}$Al$_{10}$ BGAs, fractured surface observation was performed for samples 1 (annealed at 648 K) and 2 (annealed at 473 K), as shown in Fig. 9. Figure 10 shows the whole fracture surface (a) and the magnified SEM images (b) of the part of fracture surface of sample number 1. A wide shear step approximately 40 μm in
width which was formed by shear band movement before crack opening is seen at the bottom of the notch. On the other hand, the shear slip width of sample number 2 becomes narrower (approximately 5 μm) as shown in Fig. 11. Significant differences in the whole fractured surface were also observed. The smooth fractured surface of sample number 1 was covered with a well-grown vein pattern, while the rough fractured surface of sample number 2 showed a small vein pattern. Figure 12 shows schematic illustrations of shear slip formation during the U-notched Charpy impact test. Under homogeneous stress conditions such as uniaxial tensility, a shear band propagates immediately. However, under inhomogeneous stress distribution as in the case of a bend, deformation is concentrated at the tip of the shear band. An opening stress will work at a well-propagated shear band tip. Numerous branched fine shear bands, which spread from the main shear band tip, interrupt each shear band movement by crossover several times. Thus, the shear band exhibits high resistance to applied opening stress. If it becomes impossible for the shear

Fig. 8 HRTEM images of an as-cast Zr<sub>59</sub>Cu<sub>31</sub>Al<sub>10</sub> BGA (a) and a Zr<sub>59</sub>Cu<sub>31</sub>Al<sub>10</sub> BGA annealed at 648 K for 5.4 ks (b).

Fig. 9 Relationship between the CUE values and the density of as-cast and Zr<sub>59</sub>Cu<sub>31</sub>Al<sub>10</sub> BGAs annealed for 5.4 ks.
band to endure the opening stress, it will open and become a crack. Shear band slip can be used to evaluate the shear band deformation process until shear band opening. Thus, the ability of branching to form a network of fine and dense shear bands is an important factor to consider in evaluating fracture behavior.

Figure 13 shows the relationship between the CUE values and the shear slip width of as-cast and annealed Zr$_{59}$Cu$_{31}$Al$_{10}$ BGAs. One clear linear relationship was seen in the relationship between the CUE value and the shear slip width of as-cast and annealed Zr$_{59}$Cu$_{31}$Al$_{10}$ BGAs with a high value of the square correlation function (over 0.9). However, although wide dispersion was observed in the CUE values of the Zr$_{59}$Cu$_{31}$Al$_{10}$ BGAs annealed at 648 K, the difference was not observed in the HRTEM images. Since the linear relationship was not sufficient to definitively identify the origin of the drastic increase in the CUE values of structurally relaxed Zr$_{59}$Cu$_{31}$Al$_{10}$ BGAs, we can conclude that the drastic increase was caused by the enhancement of the forming and branching abilities of the shear bands. Furthermore, the enhancement of shear band branching was probably caused by the change in the microscopic glass structure of the formation of icosahedral-like clusters, as shown in Fig. 8. Icosahedral-like cluster formation, which probably causes the volume shrinkage of glassy alloys, brings about a non-linear density increase in annealed hypoeutectic Zr-Cu-Al BGAs just below $T_g$, as shown in Fig. 7. The non-linear density increase in annealed Zr-Cu-Al BGAs just below $T_g$ could not be observed around the ternary eutectic composition. Since the toughness of bulk glassy alloys originates in the mobility of atoms for applied stress relaxation, both open volume and flexible metallic bonds are important parameters to control in order to enhance fracture toughness. The nature of the flexible metallic bond, which can not be degraded by structural relaxation, is probably enhanced in hypoeutectic BGAs.

5. Summary

In order to improve embrittlement due to structural relaxation, we examined hypoeutectic as-cast and annealed Zr-Cu-Al BGAs. The results obtained are summarized as follows:
Density increases significantly during annealing times from $10^3$ to $10^4$ s and apparent saturated values differ according to annealing temperature.

By structural relaxation, hardness and tensile strength do not change remarkably with annealing temperature; the Charpy impact value in particular increases significantly under annealing at 648 K just under the glass transition temperature of 671 K. The tendency of the Charpy impact value to increase distinctly is maximized in bulk Zr$_{59}$Cu$_{31}$Al$_{10}$ glassy cast rods (5 x 10 x 55 mm).

A significant increase in the Charpy impact value is accompanied by an increase in nonlinear density with annealing temperature. Furthermore, the mechanical features of fully structurally relaxed Zr$_{59}$Cu$_{31}$Al$_{10}$ BGAs are characterized by their superior shear band formation and branching ability, which can be estimated by the shear slip width before crack opening.

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