Evolution of Mechanical Properties of Cast $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ Glassy Alloys by Structural Relaxation

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The volume of a quenched glassy alloy is a variable of cooling rates during the amorphization. Hence a change in the volume caused by the structural relaxation can be regarded as a degree of amorphousness. The density of $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ bulk glassy alloys (BGAs) increases linearly with the annealing temperature below the glass-transition temperature (T_g). With increasing the annealing temperature, the tensile strength and Vickers hardness show constant values, whereas the Young's moduli and Charpy impact values become larger and smaller, respectively. Especially, Charpy impact values of Zr–Cu–Al BGAs have a linear relationship with the relative value of excessive free volume, which correspond to the volume-change ratio caused by the full structural relaxation.

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1. Introduction

Glassy alloys have two distinct features: the glassy structure and metallic bonding. One of the interesting characteristics of glassy alloys is the mechanical property because a glassy alloy exhibits a ductile metallic bonding and non-periodic structure. Crystalline metals can exhibit a superior plasticity even at room temperature by the systematic dislocation movement. The deformation of crystalline metals can be roughly recognized by the Peierls stress, which is the minimum stress to move an operable dislocation. Therefore, elastic limits of crystalline metals can be allowed by a control of dislocation movements, whereas Young's moduli do not change. On the other hand, a glassy alloy can deform by overall atomic movements even at room temperature because no dislocation exists. The deformation mechanism of glassy alloys is, thus, achieved by a unique adiabatic shear-band operation.¹⁾ Microscopic fracture-surface images show a vein pattern, which is caused by a pseudo-melting state²⁾ in the shear band. Therefore, one-shear band movement leads to a final fracture with little uniform plastic deformation. However, the elastic limit of ductile glassy alloys is usually about 2% in strain.³⁾ This trend means that the initiation of the shear-band formation is probably determined by the macroscopic strain condition. Therefore, the lack of the uniform deformability of glassy alloys could limit toughness⁴⁾ since the final fracture might occur before the elastic strain reaches 2%. The structural relaxation probably causes the lack of the uniform deformability.

Recently, a certain kind of glassy alloys have been found to exhibit a very high glass-forming ability,⁵⁾ which enables the production of bulk-shaped samples by a conventional metallic mold casting process. Inoue et al. have succeeded for the first time in synthesizing bulk glassy alloys (BGAs) in Ln-,⁶⁾ Mg-⁷⁾ and Zr-⁸⁾ based alloy systems without metalloid elements by copper mold-casting methods. These groups of

alloys have been regarded as a new category of bulk metallic materials. Especially, Zr-based glassy alloys exhibit a good glass-forming ability, high strength and ductility. The Zr-based BGAs were fabricated in Zr–Al–Ni,⁸⁾ Zr–Ni–Al,⁸⁾ Zr–Al–Ni–Cu,⁹⁾ and Zr–(Ti,Nb)–Al–Ni–Cu¹⁰⁾ systems for the first several years, which were, then, followed by other Zr-based systems such as Zr–Ti–Be–Ni–Cu,¹¹⁾ Zr–(Pd,Ta)–Al–Ni–Cu¹²⁾ and Zr–Al–Be–Ni–Cu.¹³⁾ These Zr-based BGAs exhibit high tensile strengths of 1,500–1,900 MPa, and have been used as sporting goods materials and connection tubes for optical communication fibers.^{14–17)} Before the development of Zr-based glassy alloys, there exist no materials, which have high strengths¹⁸⁾ over 1,500 MPa and toughness¹⁹⁾ over 45 MPam^{0.5} in the as-cast state. The good mechanical properties make Zr-based glassy alloys particularly attractive, and the above-described applications were brought about by the use of unique casting techniques.^{20–22)} Especially, $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ BGA,²³⁾ whose composition is close to the ternary eutectic point, is known to exhibit a high glass-forming ability and superior mechanical properties. Therefore, we used this composition as a basic alloy in this study.

While bulk-shaped glassy alloys have yielded new application areas as specified structural materials,^{24,25)} much attention has been paid to cast defects^{26,27)} in BGAs. For example, crystalline inclusions, which act as crack-initiation sites and enhance crack propagation during the fatigue test, should be removed to improve intrinsic features of BGAs. In other words, mechanical properties of cast BGAs often depend on the quality of the cast structure, which can be controlled by a range of melting and casting methods. Furthermore, even for an as-cast sample having a single glass phase, its amorphous structure can be a sensitive function of composition and cooling rates. The difference in the glass structure is, thus, considered as the degree of amorphousness, which can be quantified and measured by parameters, such as

the fictive temperature, volume change, and so on. In this paper, the volume changes are normalized by a fictive solid Zr–Cu–Al solution with a close-packed structure. The volume change was calculated by the volume expansion ratio, which is regarded as a relative value of the free volume in this paper. In this regard, the free volume is an effective concept to express the degree of amorphousness caused by the expansion or shrinkage of a glass structure. A large sized BGA has a possibility of embrittlement because of much lower cooling rates. Some paper reported that the embrittlement phenomena in some amorphous alloys by the structural relaxation without any crystalline phase precipitation.^{28,29)} The embrittlement by the structural relaxation is originated from the intrinsic glass structural change, which is considered as the development of a reversible relaxed structure and annihilation of the disordered atomic configuration.³⁰⁾ The structural relaxation is also influenced by other physical properties.³¹⁾ Consequently, the determination the amorphousness quality of BGAs is an important study to improve mechanical and functional properties.

The aim of this paper is to elucidate the relationships among thermal, mechanical, and structural features of Zr–Cu–Al BGAs, and to reveal the origin of strength and toughness in the glass structure. We also examine the compositional dependence of volume changes of glass structures.

2. Experimental Procedure

Master-alloy ingots of ternary Zr–Cu–Al alloys were prepared by arc-melting mixtures of pure Zr, Cu and Al metals in an argon atmosphere. To maintain a low-oxygen concentration in the alloys, we used a special Zr crystal rod with the oxygen concentration less than 0.05 atomic percent (at%). Zr–Cu–Al BGAs were cast into rod-shaped specimens with 8 mm in diameter and 60 mm in length by the tilt-casting technique. This casting method has an advantage of preventing a molten alloy flow from forming cold shuts, which are likely to induce crack initiation and propagation. Densities at the same rod-shaped samples ($\phi 8 \times 20$ mm) were measured by an Archimedes method. The fluid used in the Archimedes method was purified water. Cold rolling was performed to introduce the shear bands and to observe the morphology change after annealing below T_g . The thermal stability of the cast glassy samples was measured using the differential scanning calorimetry (DSC) with a heating rate of 0.167 K/s. We examined the cast structure by the optical microscopy (OM) and scanning-microscopy (SEM) to confirm the quality of glassy states. The phase characterization and crystalline ratio were examined by the X-ray diffractometry. Tensile tests were conducted to estimate tensile strengths and Young's moduli using an Instron 5582 type testing machine. Vickers hardness was measured using a micro Vickers testing machine. Charpy impact tests were also done in air using a special sample size, 55 mm long, 10 mm wide, and 5 mm thick. The samples were U-notched to a 2 mm depth.

3. Results and Discussion

The high glass-forming ability of Zr–Cu–Al glassy alloys

Fig. 1 A schematic illustration of the relationship between the volume and temperature during amorphization and crystallization with different cooling rates.

enables the removal of the size restriction of previous amorphous alloys. However, large size glassy alloys sometimes exhibit significant drawbacks, such as the embrittlement, due to the structural relaxation caused by an insufficient cooling rate. Figure 1 schematically shows volume changes during a cooling process from the liquid to glassy or crystalline states. In the case of a high cooling rate (R_1), the solidification starts at a high glass-transition temperature (T_{g1}), and a large amount of free volumes are frozen in. In contrast, with a low cooling rate (R_2), the solidification starts at a lower glass-transition temperature (T_{g2}), and the resulting frozen BGAs exhibit a slightly smaller volume, typically about 0.5%. This reduction in the volume is regarded as the structural relaxation. Therefore, cast BGA specimens with the same composition have the possibility to display different densities and properties. The density of cast BGAs can also be changed with crystalline inclusions, *i.e.*, as-cast defects. Figure 2 presents a relationship between crystalline ratios and densities of cast $Zr_{50}Cu_{40}Al_{10}$ BGAs with different melting and casting conditions of. With a decrease in the glass formability, the crystalline ratio increases, which correlates with an increase of the density from 6.86 to 6.91 g/cm³. During this transition, τ_3 crystalline inclusions were formed, and, then, the Zr_2Cu crystalline phase was formed. It should also be pointed out, however, that even single glassy alloys have a wide density range from 6.825 to 6.86 g/cm³. The density value of 6.825 g/cm³ for the $\phi 8$ mm rod-shape cast $Zr_{50}Cu_{40}Al_{10}$ BGAs is an optimum value, which can be realized by the control of melting and casting conditions. Therefore, we employed the $Zr_{50}Cu_{40}Al_{10}$ BGAs with a density value of 6.825 g/cm³, a standard value in this study.

The structural relaxation is also achieved by a past annealing process below the glass-transition temperature (T_g). Figure 3 exhibits the DSC curve of the cast $Zr_{50}Cu_{40}Al_{10}$ BGA. The broken DSC curve shows the structurally-relaxed $Zr_{50}Cu_{40}Al_{10}$ BGA prepared by annealing just above T_g of 706 K. The irreversible exothermic heat

Fig. 2 The relationship between the crystallization ratio and density of cast $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ alloys with several casting conditions.

Fig. 3 DSC curves of $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ BGAs with virgin (solid line) and after relaxed (dotted line) samples.

Fig. 4 The relationships between the density and annealing time at several annealing temperatures at 473 K (▲), 573 K (■), and 673 K (◆).

flow between the solid and broken curves below T_g suggests that structural relaxation has taken place. Concurrently, it also means that the structural relaxation is closely related to the enthalpy decrease by the volume shrinkage. In order to control the degree of the structural relaxation, annealing temperatures were selected as 473, 573, and 673 K. Figure 4 demonstrates changes in densities of $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ BGAs as a function of the annealing time at 473, 573, and 673 K. Each of these curves shows a saturated density value. The lower annealing temperature is responsible for the low density and the higher annealing temperature is responsible for the high density. Consequently, a BGA with the same composition but

Fig. 5 X-ray diffraction patterns of as-cast and annealed samples at 473, 573, and 673 K. Where, V_r means the volume-change ratio from the as-cast state by the annealing treatment.

Fig. 6 The relationship between the annealing temperature and density of $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ BGAs.

with a different degree of structural relaxation as manifested by the irreversible volume shrinkage, which is usually accompanied with an exothermic heat, is originated from the structural transition of many intermediate states from as-cast to fully-relaxed states.

The volume shrinkage with the structural relaxation is also examined by the X-ray diffractometry. Figure 5 shows the X-ray diffraction spectra of as-cast and annealed $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ BGAs. The 2θ values of halo peaks and volume changes estimated from them are shown in this figure. Thus, the volume shrinkage can also be qualitatively recognized by the X-ray diffraction data, even though the values probably contain some accidental errors. In order to determine the volume shrinkage in detail, the density of as-cast and annealed samples of $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ BGAs were measured by the Archimedes method, as presented in Fig. 6. The annealing time is fixed at 3.6 ks, which is sufficient to obtain saturated density values at several annealing temperatures, as exhibited in Fig. 4. This figure demonstrates that the density and annealing temperature possess a good linear relationship. Therefore, we can estimate the density of the fully-relaxed state by extrapolating the density to T_g .

The structural relaxation, which is considered as a glass structure change with the volume shrinkage, can be related to certain physical properties of the glassy alloys. Figure 7 shows tensile strengths and Vickers hardnesses against the annealing temperature. Both of them do not change with the

Fig. 7 Tensile strength and Vickers hardness changes with the annealing temperature of $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ BGAs.

Fig. 8 The relationship between Young's modulus and annealing temperature of $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ BGAs.

annealing temperature. However, the tensile strength of the 673 K annealed samples demonstrates a slight decrease within a margin of error. Some 673 K annealed samples show a vertical fracture surface with respect to the tensile direction, whereas the annealed samples below 673 K usually show a shear-slip fracture surface after tensile testing. This observation suggests that the decrease of the tensile strength of the 673 K annealed sample is caused by a change in fracture mechanisms due to the embrittlement by the structural relaxation. Thus, in general, static mechanical properties, such as the tensile strength and Vickers hardness, which are recognized as structure-sensitive properties in ordinary crystalline materials, are unalterable against the annealing below T_g . However, Young's modulus significantly increases with increasing the annealing temperature. Figure 8 suggests that Young's modulus increases about 5.6% with increasing the annealing temperature from 473 to 673 K. The Young's modulus, which is recognized as non-structural sensitive properties in ordinary crystalline materials, changed by the structural relaxation for about a maximum value of 10%. In general, Young's modulus change of irons/steels is about a few percents during phase transitions from the bcc ferrite to fcc austenite. Accordingly, Young's modulus is probably a structure-sensitive property in glassy alloys. Since the tensile strength exhibits almost a constant value, the increase of Young's modulus by the structural relaxation causes the decrease of the fracture strain. Therefore, in some cases, the structural relaxation brings

Fig. 9 The relationship between the U-notched Charpy impact value and annealing temperature of $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ BGAs.

about the embrittlement. Figure 9 presents a relationship between the U-notched Charpy impact value and annealing temperature. The U-notched Charpy impact values dramatically decrease about 40% with increasing the annealing temperature from 473 to 673 K. As a result, the structural relaxation brings about the fatal embrittlement of $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ BGAs. In other word, the toughness of cast $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ BGAs can be estimated by Young's modulus and density in a way similar to a nondestructive test.

The aforementioned density changes of the annealed samples arise from the structural relaxation, which can be regarded as the volume shrinkage during the annealing. We can roughly estimate the glass-structure change of BGAs by the volume change. Apart from the structural relaxation, the glass structure can also be changed by the compositional change. A fictional Zr, Cu, and Al solution alloy with a close-packed structure, which was used as a standard of a crystalline phase to determine the free volumes of as-cast and relaxed glass structures. In this study, we define the free volume to be a volume-expansion ratio of the glassy phase minus the fictive crystalline phase to the fictive crystalline phase. Since the free volume is a degree of the expansion from the standard fictive solution, it probably takes a range from 0% (like a highly dense crystal) to 5% (like a liquid). Furthermore, by using the fictive ideal solutions, glass-structure changes with alloy composition is emphasized, whereas the value of the free volume is not an absolute value but an apparent relative value. Accordingly, the free volume for the amorphization is, thus, estimated by the volume expansion ratio of the fully-relaxed glassy alloy. Since the preparation of fully-relaxed BGAs is quite difficult, we estimate the density of the fully relaxed state by extrapolating the density to T_g in Fig. 6. The total free volume is also estimated by the volume expansion ratio of the as-cast glassy alloy. Therefore, the excessive free volume can be estimated by the difference between the total free volume and free volume for amorphization. Figure 10 shows the compositional dependence of the (a) total free volume, (b) free volume for amorphization, and (c) excessive free volume of the rod-shaped cast ($\phi 8 \times 60$ mm) Zr–Cu–Al BGAs. We can see that all the free volumes have a maximum point at the composition of the ternary eutectic point of $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$.

Fig. 10 Compositional dependence of total free volume (a), free volume for amorphization (b), excessive free volume (c), and Charpy impact value (d) in the Zr–Cu–Al alloy system.

This trend suggests that ternary eutectic glassy alloys might have a unique glass structure to increase the free volume. However, the compositional dependence of free volumes around the ternary eutectic composition is quite different. Namely, in the case of the total and amorphization free volumes, they decrease with the Al concentration around the binary eutectic line ($\text{Al} = 10\text{at}\%$). In the case of the excessive free volume, however, it increases with the Al concentration around the binary eutectic line ($\text{Al} = 10\text{at}\%$). This behavior is quite similar to that of Charpy impact values, as shown in Fig. 10(d). The relationship between Charpy impact values and excessive free volumes is shown in Fig. 11. The correlation function is about 0.9 with a linear relationship. Since Charpy impact testing requires an immediate release of an applied impact stress, this ability is a sensitive function of the degree of the stress accommodation. Since the excessive free volume is probably composed of thermally unstable voids and/or vacancies, atoms surrounding the void are probably easy to move. This flexibility of atom movements around excessive free volumes means the superior stress accommodation. Consequently, the excessive free volume is one of the significant structural parameters to influence the toughness of glassy alloys.

The distribution of excessive free volume is also an important factor for affecting mechanical properties. For example, the initiation and propagation of a shear band influence the mechanical properties of glassy alloys at room temperature. If glassy alloys are homogeneous elastic-plastic materials, there would be no reason to explain wiggly

Fig. 11 The relationship between the U-notched Charpy impact value and excessive free volume in the Zr–Cu–Al alloy system. Alloy compositions; 1: $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$, 2: $\text{Zr}_{52.5}\text{Cu}_{37}\text{Al}_{10}$, 3: $\text{Zr}_{50}\text{Cu}_{37.5}\text{Al}_{12.5}$, 4: $\text{Zr}_{50}\text{Cu}_{42.5}\text{Al}_{7.5}$, 5: $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$, 6: $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, and 7: $\text{Zr}_{47.5}\text{Cu}_{42.5}\text{Al}_{10}$. r : correlation number.

morphology of shear bands. In reality, however, the morphology of shear bands is not linear but slightly wavy with a long period. This observation indicates that a BGA does not possess a completely homogeneous structure. We can further suggest that the inhomogeneity of glass structures is originated from the inhomogeneity of the free-volume distribution. Since the wavy curved shear bands can restrict the shear-slip displacement, some BGAs exhibit a large plastic deformation under the compression load. In the case of tensile testing, we can obtain the plastic tensile elongation³²⁾ by controlling the cross shear-band structure in cold rolled BGAs to interrupt each shear-bands operation. In order to fabricate ductile BGAs, controlling shear-bands slip is an important factor to prevent the final fracture of a large shear slip. Cold rolling of annealed $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ BGAs was performed to observe morphological changes with annealing temperature. Figure 12 shows side-view SEM images of 10% cold-rolled $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ BGAs after the annealing treatment. The cold-rolled structure of BGAs is characterized by the fine multi-layered structure of shear bands, which were introduced along the shear direction, about 45 degree from the rolling direction (R.D). Since the cold-rolled BGAs samples were rolled up to 10%, the angle between shear bands and R.D. is not 45 degree. It should also be pointed out that the 723 K annealed BGA could not be cold rolled. The annealing treatment over T_g caused the $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ BGA to have a significant embrittlement. Figure 13 presents the effect of annealing on the density and curvature of shear bands of cold-rolled samples. The density of shear bands is slightly increased with increasing the annealing temperature, and saturated above $T_a = 573\text{ K}$. The increase of the shear-bands density is probably caused by the severe surface roughness (with embrittlement and/or surface oxidization) rewrite this phrase. The most important point in this figure is the significant decrease of the curvature of shear bands by annealing. In other words, wavy curved shear bands might be originated from the inhomogeneous distribution of excessive free volumes in BGAs. Accordingly, the decrease of the excessive free volume with increasing the annealing temperature transforms the wavy curved shear band to linear one. The excessive free volume, which is considered as the origin of the toughness of glassy alloys, might be distributed

Cold Rolled Structure Change by Annealing

Fig. 12 Side-view SEM images of 10% cold-rolled $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ BGAs with different annealing temperatures for 3.6 ks.

Fig. 13 The changes of the density and curvature of shear bands of 10% cold-rolled $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ BGAs versus the annealing temperature.

inhomogeneously with a large scale (on a mm-scale). Measurements of the structural fluctuation with a large scale in BGAs will be necessary for a sound evaluation of glass structures, which affect mechanical properties.

4. Summary

In order to clarify the relationship between the glass structure and mechanical properties, we examined the density of $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ glassy alloys, studied tensile, Charpy impact, Vickers hardness and cold-rolling behaviors. The change in the glass structure is evaluated by free volumes. The results obtained are summarized below.

- (1) The density of $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ BGA increases linearly with increasing the annealing temperature.

- (2) Young's modulus of $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ BGAs increases by about 5.6% with increasing the annealing temperature from 473 to 673 K.
- (3) The Charpy impact value of $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ BGAs decreases by about 40% with increasing the annealing temperature from 473 to 673 K.
- (4) Toughness of BGAs is suggested to arise from the relative value of excessive free volume, which corresponds to the volume changes by the full structural relaxation.
- (5) Wavy curved shear bands, which are often seen in plastically-deformed ductile BGAs, becomes straight with increasing the annealing temperature.

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REFERENCES

- 1) H. S. Chen and T. T. Wang: J. Appl. Phys. **41** (1970) 5338–5339.
- 2) H. J. Leamy, H. S. Chen and T. T. Wang: Met. Trans. **3** (1972) 699–708.
- 3) C. C. Hays, C. P. Kim and W. L. Johnson: Phys. Rev. Lett. **84** (2000) 2901–2904.
- 4) M. F. Ashby: *Metals Selection in Mechanical Design*, (Butterworth-Heinemann, Oxford, UK, 1999) p. 188.
- 5) For example, A. Inoue: *Bulk Amorphous Alloys*, (Trans. Tech. Publication, Zurich, 1998).
- 6) A. Inoue, T. Zhang and T. Masumoto: Mater. Trans., JIM **30** (1989) 965–972.
- 7) A. Inoue, K. Ohtera, K. Kita and T. Masumoto: Jpn. J. Appl. Phys. **27** (1989) L2258–L2261.
- 8) A. Inoue, T. Zhang and T. Masumoto: Mater. Trans., JIM **31** (1990) 177–183.
- 9) A. Inoue, T. Zhang and T. Masumoto: Mater. Trans., JIM **32** (1991) 1005–1010.
- 10) A. Inoue, T. Shibata and T. Zhang: Mater. Trans., JIM **36** (1995) 1420–1426.
- 11) A. Pecker and W. L. Johnson: Appl. Phys. Lett. **63** (1993) 2342–2344.
- 12) A. Inoue, Y. Yokoyama, Y. Shinohara and T. Masumoto: Mater. Trans., JIM **35** (1994) 1234–1237.
- 13) A. Inoue, T. Zhang, N. Nishiyama, K. Ohba and T. Masumoto: Mater. Trans., JIM **34** (1994) 923–926.
- 14) Y. Yokoyama, H. Inoue, K. Fukaura and A. Inoue: Mater. Trans., JIM **43** (2002) 575–579.
- 15) A. Inoue: Mater. Trans., JIM **36** (1995) 866–875.
- 16) A. Inoue: Acta Mater. **48** (2000) 279–306.
- 17) A. Inoue: Mater. Sci. Eng. A **304–306** (2001) 1–10.
- 18) *Supercooled Liquid, Bulk Glassy, and Nanocrystalline State of Alloys*, ed. By A. Inoue, A. R. Yavari, W. L. Johnson and R. H. Dauskardt (MRS, Warrendale, 2001) pp. L12.13.1–L12.13.6.
- 19) H. Kato, Y. Kawamura and Akihisa Inoue: Mater. Trans., JIM **37** (1996) 70–77.
- 20) C. J. Gilbert, R. O. Ritchie and W. L. Johnson: Appl. Phys. Lett. **71** (1997) 476–478.
- 21) A. Inoue, T. Zhang and T. Masumoto: Mater. Trans., JIM **37** (1996) 185–187.
- 22) H. Kakiuchi, A. Inoue, M. Onuki, Y. Takano and T. Yamaguchi: Mater. Trans., JIM **42** (2001) 678–681.
- 23) M. Ishida, T. Uehara, T. Arai, H. Takeda, T. Yamaguchi, T. Tniguchi, T. Katsumi, M. Kobayashi and H. Ofune: Intermetallics **10** (2002) 1259–1263.
- 24) H. Kakiuchi, A. Inoue, M. Onuki, Y. Takano and T. Yamaguchi: Mater. Trans., JIM **42** (2001) 678–681.
- 25) W. L. Johnson: JOM **3** (2002) 40–43.
- 26) Y. Yokoyama, T. Shinohara, K. Fukaura and A. Inoue: Mater. Trans., JIM **45** (2004) 1891–1823.
- 27) Y. Yokoyama, A. Kobayashi, K. Fukaura and A. Inoue: Mater. Trans., JIM **43** (2002) 571–574.
- 28) H. S. Chen: Rep. Prog. Phys. **43** (1980) 353–432.
- 29) A. L. Greer: J. Non-Cryst. Solids **61&62** (1984) 737–748.
- 30) A. Inoue, T. Zhang, E. Matsubara, Y. Waseda and T. Masumoto: Mater. Trans., JIM **32** (1991) 201–206.
- 31) O. Haruyama, H. M. Kimura, N. Nishiyama, A. Inoue and J. Arai: Mater. Trans., JIM **43** (2002) 1931–1936.
- 32) Y. Yokoyama, K. Inoue and K. Fukaura: Mater. Trans., JIM **43** (2002) 3199–3205.