Relationship between Deformation and Crystallization in Zr$_{60}$Al$_{15}$Ni$_{25}$ and Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$ Metallic Glass

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Deformation behavior of a supercooled liquid region in melt-spun Zr$_{60}$Al$_{15}$Ni$_{25}$ and Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$ metallic glass was investigated. The viscous flow behavior is very sensitive to the strain rate and the size of crystalline precipitates, which can be classified into 4 types based on shape of the stress–strain curve: stress overshoot mode, stable viscous flow mode with constant flow stress, strain hardening mode and strain softening mode. The strain hardening and strain softening are due to the crystalline phase distribution in supercooled liquid. The strain hardening mode was observed in Zr$_{60}$Al$_{15}$Ni$_{25}$, while Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$ deformed with strain softening mode rather than strain hardening mode. Tensile deformation enhanced thermal crystallization in a supercooled liquid region was observed in Zr$_{60}$Al$_{15}$Ni$_{25}$.

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1. Introduction

Metallic glasses are known to show extremely high thermal stability against crystallization and have a wide supercooled liquid region below the crystallization temperature. They show inhomogeneous or homogeneous deformation behavior depending on the deformation temperature. At high temperatures, particularly in a supercooled liquid region, homogeneous deformation occurs and a unique viscous plasticity appears.$^{1,2}$ Poor workability, which is one disadvantage of amorphous alloys for industrial applications, can be overcome using the viscous plasticity. In fact, the viscous plasticity in the supercooled liquid region has been applied for production of complex and unique shaped components for micro-electro-mechanical systems.$^{3,4}$

Metallic glass often transforms to some crystalline phases in supercooled liquid phase during high-temperature deformation. When thermal crystallization occurs, the viscous plastic behavior is influenced by formation of a crystalline phase.

In the present study, plastic deformation behavior in the supercooled liquid region of Zr$_{60}$Al$_{15}$Ni$_{25}$ and Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$ metallic glass was examined focusing on the relationship between the thermal crystallization behavior and shape of the stress–strain curve in tensile deformation. Effect of plastic deformation on crystallization in Zr$_{60}$Al$_{15}$Ni$_{25}$ was also examined. To examine the effect of tensile deformation on crystallization in Zr$_{60}$Al$_{15}$Ni$_{25}$, TEM microstructures of specimens deformed at 743 K and undeformed specimens with the same thermal profiles were observed.

2. Experimental Procedure

Master ingots of Zr$_{60}$Al$_{15}$Ni$_{25}$ and Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$ (at %) alloys were prepared by arc melting in a purified Ar atmosphere. Rapidly quenched ribbon with a cross section of 2.0 mm × 0.02 mm was produced from the ingots by a single roller melt-spinning method in an Ar atmosphere. The thermal properties were examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 Ks$^{-1}$ in an Ar atmosphere. Tensile specimens with the gauge length of 10 mm were prepared from the melt-spun ribbon and were rapidly heated to the test temperature and held for 200 s before the tensile test in air. These temperatures were chosen to be in the range of 723 to 743 K for Zr$_{60}$Al$_{15}$Ni$_{25}$ alloy and 693 to 723 K for Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$ alloy, respectively. The tensile testing temperatures were higher than the glass transition temperature ($T_g$) in both alloys. The tensile tests were performed using an Instron-type testing machine at a constant crosshead velocity in the range of 8.3 × 10$^{-6}$ to 1.7 × 10$^{-2}$ s$^{-1}$ for Zr$_{60}$Al$_{15}$Ni$_{25}$ and 1.7 × 10$^{-5}$ to 8.3 × 10$^{-3}$ s$^{-1}$ for Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$, respectively. Structures of melt-spun and deformed specimens were examined by X-ray diffractometry using Cu-Kα radiation, transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HREM) and TEM-EDX analysis.

3. Results

3.1 Tensile deformation behavior of melt-spin Zr$_{60}$Al$_{15}$Ni$_{25}$ and Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$ metallic glass

An amorphous phase without any crystallinity was confirmed in melt-spin Zr$_{60}$Al$_{15}$Ni$_{25}$ and Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$ ribbon$^{5}$ by X-ray diffractometry, TEM and HREM. Transition temperature ($T_g$) from an amorphous phase to a supercooled liquid state, supercooled liquid temperature range (Δ$T_s$) and crystallization temperature (T$_c$) were determined to be 701, 83 and 784 K for Zr$_{60}$Al$_{15}$Ni$_{25}$ and 645, 89 and 734 K for Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$ by DSC analysis, respectively. The large Δ$T_s$ values indicate that the supercooled liquid state can be maintained in both Zr-based metallic glasses for a prolonged interval and the viscous plastic deformation can be performed.

Figure 1 shows a typical example of the flow stress–nominal strain curves at various strain rates for Zr$_{60}$Al$_{15}$Ni$_{25}$
at 733 K (a) and Zr_{65}Al_{15}Ni_{25} at 713 K (b). Super-plastic deformation with more than 200% elongation was achieved in the specimen deformed at $3.3 \times 10^{-3}$ s$^{-1}$ for Zr$_{65}$Al$_{15}$Ni$_{25}$. One can see that the morphology of deformation curves is very sensitive to strain rate in both metallic glasses. At the strain rate equal to or higher than $8.3 \times 10^{-4}$ s$^{-1}$ for Zr$_{60}$Al$_{15}$Ni$_{25}$ and $3.3 \times 10^{-3}$ s$^{-1}$ for Zr$_{65}$Al$_{15}$Cu$_{27.5}$, respectively, the stress yields at a maximum after an initial rapid increase and then decreases. The abrupt decrease in flow stress at the yield point corresponds to a stress overshoot phenomenon due to the visco-elastic property of the alloy. The yield drop is thought to occur as a result of rapid increase in free volume in supercooled liquid during high strain rate deformation. The stress overshoot mode region is marked by A in Fig. 1. At a strain rate lower than $8.3 \times 10^{-4}$ s$^{-1}$ for Zr$_{60}$Al$_{15}$Ni$_{25}$, the yield drop phenomenon at the initial stage of deformation disappears. In the Zr$_{60}$Al$_{15}$Ni$_{25}$ specimen deformed at $3.3 \times 10^{-4}$ s$^{-1}$, a relatively stable viscous flow stress continues until fracture after an initial hardening as shown by B. At a strain rate lower than $3.3 \times 10^{-4}$ s$^{-1}$, the stress increases again after remaining stable. Remarkable strain hardening is observed even in the supercooled liquid of Zr$_{60}$Al$_{15}$Ni$_{25}$ as shown by C. In contrast strain hardening cannot be observed in Zr$_{65}$Al$_{15}$Cu$_{27.5}$ at 693 K as shown in Fig. 1(b). At a low strain rate of $8.3 \times 10^{-5}$ s$^{-1}$, the flow stress in Zr$_{65}$Al$_{15}$Cu$_{27.5}$ gradually decreased with increasing nominal strain after showing a maximum stress. The unique stress–strain behavior in Zr$_{65}$Al$_{15}$Cu$_{27.5}$ at $8.3 \times 10^{-5}$ s$^{-1}$ is referred to as a strain softening mode in the present study which is indicated by D.

Figure 2 shows a classification map of the various deformation behavior as functions of deformation temper-
ature and strain rate for Zr60Al15Ni25 and Zr65Al7.5Cu27.5. In Zr60Al15Ni25 the stress overshoot mode, stable viscous flow mode with constant flow stress and strain hardening mode can be seen in the A, B and C region, respectively. However, the strain softening mode which was observed in Zr65Al7.5Cu27.5 does not appear in Zr60Al15Ni25. The stress overshoot behavior appears at a strain rate equal to or higher than 8.3 × 10^{-4} s^{-1}. As the strain rate decreases, the deformation mode changes from the stress overshoot mode to the strain hardening mode through the stable viscous mode with a constant flow stress. The C region spreads to the higher strain rate area with increasing temperature but the A region shows no significant temperature dependence; therefore, the B region becomes narrow with rising temperature. In Zr65-Al7.5Cu27.5, four types of deformation mode can be seen. The stress overshoot mode occurs at a strain rate equal to or higher than 3.3 × 10^{-4} s^{-1} showing no temperature dependence. As the strain rate decreases, the stress overshoot mode changes to strain softening mode. Although strain hardening mode is observed at low strain rate and high temperature, stable viscous flow mode appears in a limited area at around 693 K.

The supercooled liquid is not in a stable phase and its devitrification through thermal crystallization cannot be avoided during annealing, resulting in change in viscous deformation behavior. To examine the relationship between thermal crystallization and viscous flow behavior, the flow stress in Fig. 1 was replotted as a function of testing time in Fig. 3. In Zr60Al15Ni25 deformed at 733 K (a), the flow stress after the onset of crystallization changes depending on the strain rate; at 3.3 × 10^{-4} s^{-1} a constant flow stress is maintained until fracture but at a strain rate slower than 3.3 × 10^{-4} s^{-1}, strain hardening occurred at a later stage of deformation after showing a constant flow stress. In Zr65Al7.5Cu27.5 deformed at 713 K (b), strain softening occurs at 8.3 × 10^{-5} s^{-1} after 500 s. The onset time for strain hardening or strain softening is much longer than that for thermal crystallization. These results imply that strain hardening or strain softening behavior occurs through large structural change of supercooled liquid under tensile deformation. Structures of the deformed specimens are given in section 3.2.

3.2 Microstructure analysis of deformed specimen in melt-spun Zr60Al15Ni25 and Zr65Al7.5Cu27.5 metallic glass

To investigate the structural instability of supercooled liquid during tensile viscous deformation, two specimens showing strain softening or strain hardening mode, indicated by X and Y were prepared (Fig. 3). The structures were examined by X-ray diffraction (XRD) pattern, DSC curve, TEM observation and TEM-EDX analysis. Figure 4 shows TEM microstructures and SAD patterns of deformed specimens X and Y. In specimen X, ellipsoidal crystalline precipitates with an average grain size of 100 nm order formed in an amorphous matrix. The precipitates were identified as hexagonal-Zr2AlNi (hex-Zr2AlNi) phase from the SAD pattern analysis. The previous report revealed that the origin of strain hardening in Zr60Al15Ni25 metallic glass is due to the thermal crystallization of this phase.\textsuperscript{9)} In specimen Y deformed with strain softening mode (b), bright and dark granular contrast can be seen accompanied by Debye rings together with a broad halo ring. Figure 4(c) shows a dark field image (DFI) of specimen Y obtained using a reflection indicated by the arrow in the SADP (b). A large quantity of spherical nano-precipitates with an average grain size of about 10 nm is uniformly distributed in an amorphous matrix. The size and morphology of the precipitates in specimen Y were greatly different from those in specimen X.

Although b.c.t.-Zr2Cu phase with circular morphology was reported to precipitate from supercooled liquid in Zr65Al7.5Cu27.5 during thermal annealing in a vacuum,\textsuperscript{10)} spherical nanocrystalline precipitates were observed during high temperature deformation. Figure 5 shows the XRD pattern of specimen Y deformed with strain softening mode in Zr65Al7.5Cu27.5. Sharp diffraction peaks corresponding to
crystalline phases are observed together with broad halo ring corresponding to an amorphous matrix. The crystalline phases were identified as b.c.t.-Zr$_2$Cu, tetragonal-ZrO$_2$ (tetra.-ZrO$_2$) and $\alpha$-Al$_2$O$_3$. The formation of oxide precipitates was confirmed by a TEM-EDX analysis. The size of b.c.t.-Zr$_2$Cu crystalline phase was much smaller than that obtained by thermal annealing in a vacuum. The role of nano precipitates on the strain softening behavior is discussed in section 4.1.

3.3 Deformation enhanced crystallization in Zr$_{60}$Al$_{15}$Ni$_{25}$ metallic glass

The stress overshoot can be explained by rapid increase in free volume during high strain rate deformation. The introduction of free volume in supercooled liquid may enhance atomic diffusion and crystallization. Effect of deformation on crystallization was examined using deformed and undeformed Zr$_{60}$Al$_{15}$Ni$_{25}$ specimens with the same thermal history. Figure 6 shows TEM microstructures and SAD patterns of deformed and undeformed specimens at 743 K, where the heating profile of undeformed specimens was the same as that of deformed specimens. Ellipsoidal precipitates are observed in an amorphous matrix in Figs. 6(a), (b) and (c). The precipitates were identified as hex.-Zr$_6$Al$_2$Ni by XRD and SAD analysis. It should be noticed that the quantity of hex.-Zr$_6$Al$_2$Ni phase in deformed specimens is larger than that in undeformed specimens [see Figs. 6(a), (b), (c) and (d)].

Figure 7 shows DSC measurements of undeformed and deformed specimens at 743 K at the strain rate of $8.3 \times 10^{-3}$ s$^{-1}$. The undeformed specimen had the same thermal history to the deformed one. Both DSC curves show the exothermic peak corresponding to thermal crystallization of the supercooled liquid. Although the intensity of the exothermic peak in a deformed specimen is 24% smaller than that in an undeformed specimen, there is no significant difference in $T_x$ between undeformed and deformed specimens. Thus, tensile deformation enhances thermal crystallization but does not change the composition of supercooled liquid phase.

TEM observation and DSC measurement reveal that the kinetics of thermal crystallization of the supercooled liquid is promoted by tensile deformation for Zr$_{60}$Al$_{15}$Ni$_{25}$. However, there are no changes in the phase selection or the preferential orientation of crystalline precipitates by deformation.
4. Discussion

4.1 Strain hardening in Zr$_{60}$Al$_{15}$Ni$_{25}$ and strain softening in Zr$_{65}$Al$_{7}$Cu$_{27.5}$ metallic glass

Strain hardening in Zr$_{60}$Al$_{15}$Ni$_{25}$ and strain softening in Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$ occurred after crystallization started. In X and Y specimens, crystalline precipitates were observed in an amorphous matrix. These results indicate that the origin of strain hardening and strain softening is the structural change in supercooled liquid based on thermal crystallization. It should be noticed that there is a great difference in the size and morphology of crystalline precipitates between X and Y specimens. Strain hardening of supercooled liquid in Zr$_{60}$Al$_{15}$Ni$_{25}$ is caused by the precipitation of hex.-Zr$_6$Al$_2$Ni crystalline phase during deformation. The hex.-Zr$_6$Al$_2$Ni phase with the average grain size of about 100 nm precipitated from the supercooled liquid by thermal crystallization. The flow stress increased with increase in the crystallization ratio, when the fraction of hex.-Zr$_6$Al$_2$Ni crystalline phases exceeded about 10%. The coarse crystalline precipitates may interact with each other during deformation and suppress the viscous flow in supercooled liquid matrix resulting in strain hardening. Since $T_x$ does not vary for undeformed and deformed specimen, the stress–strain behavior after crystallization does not directly relate to the change in chemical composition of supercooled liquid during deformation.

In contrast, not strain hardening but strain softening behavior was observed in Zr$_{65}$Al$_{7}$Cu$_{27.5}$ containing nanocrystalline precipitates. It was reported that nanocrystalline precipitates in metallic glasses cannot lead to an increase in flow stress. The flow stress of supercooled liquid phase containing randomly distributed nano-crystalline precipitates reaches a peak just after yielding and then decreases with increasing strain. Nano crystalline precipitates of tetra.-ZrO$_2$, α-Al$_2$O$_3$ and b.c.t.-Zr$_2$Cu in Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$ cannot suppress the viscous flow of supercooled liquid matrix. The viscous flow behavior in Zr-based metallic glasses is very sensitive not only to crystallization ratio but also to the size and morphology of crystalline precipitates.

4.2 Formation of oxides in Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$ metallic glass

There is a great difference in oxide precipitation behavior between Zr$_{60}$Al$_{15}$Ni$_{25}$ and Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$. The oxide precipitates were not observed in Zr$_{60}$Al$_{15}$Ni$_{25}$, while such precipitates formed during tensile deformation in Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$. Little is known about the oxidation behavior in metallic glasses because of the difficulty of avoiding structural change during oxidation test. Triwikantoro and U. Koster et al. reported the difference in oxidation behavior...
The increase in free volume increases the crystallization ratio of deformation induced free volume is thought to increase. As the strain rate rises in viscous plasticity, the quantity of deformation induces free volume in supercooled liquid-phase deformation. The deformation induces free volume in supercooled liquid rather than by the crystallization ratio.

5. Conclusions

The deformation behavior of supercooled liquid in Zr$_{60}$Al$_{15}$Ni$_{25}$ and Zr$_{65}$Al$_{15}$Cu$_{27.5}$ metallic glass in the wide strain rate region was investigated focusing on strain hardening and softening behavior. Tensile deformation promoted the thermal crystallization in Zr$_{60}$Al$_{15}$Ni$_{25}$. The results were summarized and the following conclusions were reached:

1. The stress–strain behavior of supercooled liquid in Zr$_{60}$Al$_{15}$Ni$_{25}$ and Zr$_{65}$Al$_{15}$Cu$_{27.5}$ can be classified into four types: stress overshoot mode, stable viscous flow mode with constant flow stress, strain hardening mode, strain softening mode.
2. Strain softening mode was not observed in Zr$_{60}$Al$_{15}$Ni$_{25}$, while Zr$_{65}$Al$_{15}$Cu$_{27.5}$ deformed with strain softening mode rather than strain hardening mode.
3. Nanocrystalline oxides appeared in supercooled liquid of Zr$_{65}$Al$_{15}$Cu$_{27.5}$ during high temperature deformation. The nanocrystalline oxide is effective in suppressing the crystal growth of b.c.t.-Zr$_2$Cu phase.
4. Nanocrystalline precipitates in supercooled liquid do not lead to strain hardening in Zr-based metallic glass, resulting in the occurrence of strain softening.
5. The kinetics of crystallization of supercooled liquid is promoted by high strain rate tensile deformation with stress overshoot in Zr$_{60}$Al$_{15}$Ni$_{25}$.

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