Annealing Effects on Viscosity of Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_5$ Supercooled Liquids

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Viscous flow behavior in supercooled liquid region of as-cast and annealed Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_5$ bulk metallic glasses has been examined by using a penetration viscometer under various heating rates of 20, 200 and 400°C/min. Applied load for the cylindrical-shaped penetration indenter with a diameter of 1 mm was varied from 0.049 N to 0.294 N. Viscosity was quite independent of these applied loads under the various heating conditions. When the sample was slowly heated at the rate of 20°C/min, viscosity exhibited relatively high values that may be mainly due to the skin effects of oxides on the sample surface. At the heating rate of 200°C/min and above, viscosity ($\eta$) largely decreased and tended to saturate. By annealing the bulk metallic glasses at 400°C, the density of the glasses increased, while the crystallization temperature ($T_\text{c}$), the viscosity and the activation energy for viscous flow in their soopercooled liquid decreased gradually with increasing the annealing time. The specific behaviour of viscosity has been explained by the formation of particles during annealing for relaxation.

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1. Introduction

It is well known that a number of the multi-component alloys such as Zr-Cu-Al-Ni alloys exhibit a bulk glass forming ability.1) In the glass forming process from the liquid, the most important factor is the temperature dependence of the viscosity of the supercooled liquid, and the viscosity is sensitive to the liquid structure at molecular level.2–4) We have reported that the viscosity of the Zr-Cu-Al-Ni supercooled liquid alloys decreases largely with increasing the heating rate.5,6) This may partly reflect a decrease in the density of the glasses increased, while the crystallization temperature ($T_\text{c}$), the viscosity and the activation energy for viscous flow in their soopercooled liquid decreased gradually with increasing the annealing time. The specific behaviour of viscosity has been explained by the formation of particles during annealing for relaxation.2

2. Experimental Procedures

Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_5$ bulk metallic glasses (BMGs) with a length of 100 mm and a diameter of 8 mm were prepared by two-step arc melting and casting processes. The samples were cast into a cylindrical copper mold with an inner diameter of 8 mm and a length of 100 mm and a diameter of 8 mm were prepared by two-step arc melting and casting processes. The samples were cast into a cylindrical copper mold with an inner diameter of 8 mm in an argon atmosphere. In order to remove the residual crystalline inclusions in the arc-melted liquids, the flowing liquids during casting were reheated by using a second arc-touch. The glassy structures of as-cast and annealed samples were examined by using an X-ray diffractometer with a Cu-K$\alpha$ radiation (40 kV-20 mA). $T_g$ and $T_x$ temperatures have been measured by differential scanning calorimeter (Perkinelmer Diamond-DSC) at heating rates between 20 and 400°C/min. The densities of as cast and the annealed BMG samples were measured using a Ricimedes’-method. A penetration viscometer5,6) with a cylindrical W-indentation probe with a diameter of 1.0 mm was used to study the viscosity behaviour in a range between 10$^5$ and 10$^{10}$ Pa·s as a function of temperature under various heating rates between 20 and 400°C/min in a high purity He-gas atmosphere (purity: 99.9999%). Applied loads of 0.049, 0.098, 0.196 and 0.294 N were generated by using the probe to sample area ratio of about 0.02 and below. Thickness of the samples used for the viscosity measurements was about 2.5 mm. Sample temperatures during heating were detected by two thermo couples, i.e., one was a thin line-type thermo couple spot-welded to the side of the BMG samples, and another was a plate-type thermo couple set on the bottom of the specimen. Calibration temperature for each sample was the crystallization temperature that was detected by these two thermo couples and W-probe displacement behaviors during the viscosity measurements. These temperatures were well coincided with the crystallization temperature detected by the DSC measurement with an accuracy of less than ±1°C at the same heating condition as exemplified in Fig. 5 and Fig. 6 later.

By measuring the penetration depth (H) of the indentation probe versus time (t), the viscosity of the samples is given by the following equation,

\[
F = \eta \cdot 2\pi RH \cdot (dH/dt) + \eta \cdot \pi r^2 \cdot (dH/dt),
\]

where, F, $\eta$ and r are applied force for the probe, viscosity of the samples, radius of the cylindrical probe, respectively. The (2$\pi RH$) and ($\pi r^2$) indicate the side face area and the bottom face area of the cylindrical probe, respectively. Both sides of the eq. (1) are derived by $\eta$, and then integrated by time, t, as follows;

\[
\frac{Ft}{\eta} = A \cdot H^2 + B \cdot H = K \text{ (constant),}
\]

\[
\eta = \frac{Ft}{K}.
\]

Relationships between K and H at various temperatures were

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calibrated by use of standard samples of the NIST-SRL 710a bulk inorganic glass having main compositions of SiO\(_2\) (67.55 mass%), Al\(_2\)O\(_3\) (2.10 mass%), NaO\(_2\) (8.05 mass%), K\(_2\)O (9.30 mass%), CaO (8.50 mass%), ZnO (3.60 mass%).

3. Results

3.1 Viscosity measurements under high-speed heating conditions

Figure 1 shows the viscosity (\(\eta\)) of the Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_5\) supercooled liquids as a function of temperature at various heating rates of 20, 200 and 400°C/min. In each heating condition, viscosity was measured under various loads of 0.049, 0.098, 0.196 and 0.294 N on the cylindrical indentation probe with a diameter of 1.0 mm.

![Fig. 1 Viscosity (\(\eta\)) of the Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_5\) supercooled liquids as a function of temperature at various heating rates of 20, 200 and 400°C/min. In each heating condition, viscosity was measured under various loads of 0.049, 0.098, 0.196 and 0.294 N on the cylindrical indentation probe with a diameter of 1.0 mm.](image1)

In each heating condition, viscosity was measured under various applied loads of 0.049, 0.098, 0.196 and 0.294 N on the cylindrical indentation probe with a diameter of 1.0 mm. As shown in this figure, viscosity was quite independent of these applied loads under the various heating conditions. However, when the sample was slowly heated at the rate of 20°C/min, viscosity exhibited relatively high values that may be mainly due to the skin effects of oxides on the sample surface. With increasing the heating rate to 200°C/min, viscosity (\(\eta\)) largely decreased and the \(\ln \eta\) decreased linearly with increasing the temperature up to about 470°C and then increased with increasing the temperature for their crystallization. At the heating rate of 400°C/min, viscosity was also exhibited relatively high values at a low temperature region between 400 and 450°C. This may be due to the non-equilibrium liquid state under the high-speed heating condition. In the temperature region between 450 and 490°C, viscosity fitted precisely to the linear relationship measured under the heating rate of 200°C/min indicating the equilibrium viscosity may be measured in this temperature region. At the temperature of 490°C and above, viscosity increased with increasing temperature due to their crystallization.

3.2 Annealing effects on viscosity of supercooled liquids

Figure 2 shows the X-ray diffraction patterns of as-cast and annealed Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_5\) BMGs at 400°C for 30, 60 and 120 min. Density (g/cm\(^3\)), glass-transition temperature (\(T_g\)) and crystallization temperature (\(T_x\)) of as-cast and annealed samples are also shown.

![Fig. 2 X-ray diffraction patterns of as-cast and annealed Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_5\) BMGs at 400°C for 30, 60 and 120 min. Density (g/cm\(^3\)), glass-transition temperature (\(T_g\)) and crystallization temperature (\(T_x\)) of as-cast and annealed BMGs at 400°C for 30, 60 and 120 min. In this figure, density, glass-transition temperature (\(T_g\)) and crystallization temperature (\(T_x\)) of as-cast and annealed BMGs were also shown. The annealing temperature of 400°C is just below the glass transition temperature of 425°C obtained by the intersection point of the tangent lines of the DSC profile. In all cases, only a broad diffraction peak can be found for the diffraction angle, 2\(\theta\), between 30° and 45° that is the typical feature of the metallic glass phase. Density was increased largely with increasing the annealing time at 400°C and then tended to saturate. In addition, \(T_x\) were decreased with increasing the annealing time, and then, \(\Delta T_x = (T_x - T_g)\) decreased from 113 to 104°C.

Figure 3 shows the viscosity (\(\eta\)) of the supercooled liquids of as-cast and 400°C-annealed Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_5\) BMGs as a function of temperature under the high-speed heating rate of 400°C/min. At a low temperature region of 450°C and below, viscosity (\(\eta\)) of as-cast and annealed specimens was exhibited relatively high values that may be due to the non-equilibrium liquid state under the high-speed heating condition. With increasing the temperature of 450°C and above, \(\ln \eta\) decreased linearly and then increased for their crystallization. Especially, the large decrease of the viscosity of the 400°C-annealed specimens in the linear relationship region between 450 and 490°C was observed as compared with that of the as-cast specimen. Onset temperature of the \(\ln \eta\)-increase for their crystallization was largely decreased with increasing the annealing time at 400°C due to the decrease of their crystallization temperatures. Figure 4 shows the relationships between \(\ln \eta\) and the inverse absolute temperature of the Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_5\) BMGs in the temperature range from 450°C up to about 490°C. The viscosity of these alloys can be well represented by Arrhenius relationships in this temperature region. As shown in this figure, the viscosity and the activation energy for viscous flow decreased with increasing the annealing time at 400°C.

4. Discussion

Haruyama et al. have investigated the isothermal structural relaxation process of Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\) BMGs by
DSC, electrical resistivity and density measurements. On annealing just below the glass transition temperature, the Pd$_{42}$Cu$_{30}$Ni$_{7}$P$_{20}$ BMGs can reach a fully relaxed state without the onset of crystallization. Annihilation of free volume of this glassy alloy increased with increasing the annealing time, while the contribution of chemical ordering to electrical resistivity was small. Slipen'nyuk and Eckert have also investigated the structural relaxation of the Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ BMGs by DSC. When the samples were annealed at about 402°C, low-temperature exothermic peak in the temperature range of about 187–422°C completely disappeared. It is expected that this exothermic peak may be mainly due to the annihilation of excess free volume.

In the present study, however, when the Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ BMG samples were annealed at 400°C, low-temperature endothermic peak in the temperature range of about 320–420°C completely disappeared due to the samples-softening was observed by the viscosity measurements and DSC. Figure 5 shows the temperature dependence of the W-probe displacement of the as-cast Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ BMG specimen and the corresponding DSC profile measured under the high-speed heating rate of 400°C/min.

The activation energy for viscous flow of the as-cast Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ supercooled liquid phase exhibited the very
high values of about 335 kJ/mol shown in Fig. 6. This value is well coincided with the activation energy of 363 kJ/mol for the diffusion-penetration of $^{63}\text{Ni}$ atoms in Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ supercooled liquid phase at the temperature of above $T_g$. With increasing the annealing time at 400°C, the activation energy of the Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ supercooled liquid decreased largely to about 202 kJ/mol. Gilman$^{10}$ has speculated that the formation of small particles having strong chemical interactions between the constituent atoms tends to decrease the liquid viscosity because their particles interact relatively weakly. According to the theory proposed by Frenkel,$^{11}$ the activation energy for the viscous flow is equivalent to the energy necessary to form holes in the liquid. Therefore, the formation of the particles that interact relatively weakly might decrease the activation energy.

5. Conclusions

On isothermal annealing of the Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ BMGs at 400°C, density was increased, while onset temperature of crystallization, viscosity and activation energy for viscous flow of the supercooled liquid decreased with increasing the annealing time. Especially, starting temperature of the softening, i.e., the temperature for initiation of the drop displacement of the W-indentation probe was largely decreased. This may be due to the progress of the compositional inhomogeneity such as formation of particles or phase separation in the annealed glassy phase.

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