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Viscosity measurements of $Zr_{55}Cu_{30}Al_{10}Ni_5$ and $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ ($x = 0$, 3 and 7 at.%) supercooled liquid alloys by using a penetration viscometer

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Abstract

Viscosity of $Zr_{55}Cu_{30}Al_{10}Ni_5$ and $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ ($x = 0$, 3 and 7 at.%) supercooled liquid alloys having bulk metallic glass forming ability has been measured by using a penetration viscometer with a cylindrical probe under high speed heating conditions at heating rates between 20 and 400 K/min in the temperature range from the glass transition temperatures (T_g) up to above the crystallization temperatures. Effect of Pd addition on the viscosity of Zr-base supercooled liquid alloys has been also examined. The viscosity of these alloys decreased with increasing the heating rate and tended to saturate at the heating rate of 200 K/min and above. These viscosities can be well represented by the Arrhenius relation. The activation energy for viscous flow for $Zr_{55}Cu_{30}Al_{10}Ni_5$ supercooled liquid alloys was about 350 kJ/mol. In the $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ ($x = 0$, 3 and 7 at.%) alloys, the viscosities increased with increasing the Pd-content, while the activation energy for viscous flow decreased from 337 to 276 kJ/mol.

Keywords: Viscosity; $Zr_{55}Cu_{30}Al_{10}Ni_5$; Supercooled liquid; Penetration viscometer; Oxygen contamination

1. Introduction

It is well known that a number of the multi-component alloys such as $Zr_{55}Cu_{30}Al_{10}Ni_5$ (number indicate at.%) alloys exhibit a bulk glass forming ability [1]. 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. In the case of the Zr-based alloys, however, it has been reported that the viscosity of the alloys increased significantly with increasing the solute-oxygen content [2]. In addition, the skin effects of oxide might be prominent on the viscosity measurements [3–5]. In the present study, the temperature dependence of the viscosity of the $Zr_{55}Cu_{30}Al_{10}Ni_5$ and $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ ($x = 0$, 3 and 7 at.%) supercooled liquid alloys has been measured in the short time periods by using a penetration viscometer under high speed heating conditions at the heating rate between 20 and 400 K/min for reducing the influencein of oxygen contamination from the measuring atmosphere.

2. Experimental procedures

$Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk metallic glass sheets with a thickness of 2.5 mm, a width of 50 mm and the length of 50 mm were prepared by squeeze copper mold casting method in an argon atmosphere. $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ ($x = 0$, 3 and 7 at.%) bulk metallic glasses with a length of 100 mm and a diameter of 8 mm were also prepared by high-pressure die-casting of the melt into cylindrical copper molds with an inner diameter of 8 mm. The glassy structures of as-casted samples were examined by using an X-ray diffractometer using the Cu Kα radiation (40 kV to 20 mA). A penetration viscometer [6,7] with a cylindrical W-indentation probe with a diameter of 1.0 mm was used to study the viscosity measurements in the viscosity range between 10^7

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and 10^{13} mPa s (cP) as a function of temperature under the high speed heating rate conditions at the heating rate of between 20 and 400 K/min in a high purity He-gas atmosphere (purity: 99.999%). Applied stresses of 6.4 kPa were generated by the probe giving the probe to sample area ratio of about 0.015. The samples used for the viscosity measurements are a plate shape with a size of 5 mm × 5 mm and a thickness of 2.5 mm for $Zr_{55}Cu_{30}Al_{10}Ni_5$ and a cylindrical shape with 8 mm diameter and a thickness of 2.5 mm for $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ ($x = 0$, 3 and 7 at.%). By measuring the penetration depth (H) of the indentation probe versus time (t), the viscosity of the samples is given by the following equation:

$$F = \eta 2\pi r H \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right) + \eta \pi r^2 \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right), \tag{1}$$

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

$$\frac{Ft}{\eta} = AH^2 + BH = K\,(\text{constant}), \tag{2}$$

$$\eta = \frac{Ft}{K}. \tag{3}$$

Relationships between K and H at various temperatures were calibrated by use of standard samples of the NIST-SRL 710a bulk inorganic glass having main compositions of SiO_2 (67.55 wt.%), Al_2O_3 (2.10 wt.%), NaO_2 (8.05 wt.%), K_2O (9.30 wt.%), CaO (8.50 wt.%), ZnO (3.60 wt.%).

3. Results

Fig. 1 shows the displacement behaviors of the indentation probe on the $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk metallic glasses during heating at 20 and 100 K/min. After heating, the samples were rapidly quenched at the cooling rate of 7 K/s by spraying a He-gas from four-exhaust nozzles around the samples. As shown in this figure, the first drop displacement of the probe was observed at their glass transition temperatures of about 420 °C, and then the displacement was stopped at their crystallization temperatures. At the temperature of their melting temperature of above 800 °C, drastic displacement of the indentation probe was also observed. At the heating rate of 100 K/min, however, drastic displacement of the indentation probe was observed at the melting temperature of about 800 °C. The displacement of the probe at this condition was attained to the maximum measuring scale-length of this viscometer, so the skin effects of oxides can be reduced by increasing the heating rate.

Fig. 2 shows the viscosity (η) of the $Zr_{55}Cu_{30}Al_{10}Ni_5$ supercooled liquid alloys as a function of temperature at the various heating rate between 20 and 400 K/min. Viscosity exhibited relatively high values when the samples were slowly heated at the rate of 20 K/min. With increasing the heating rate, the

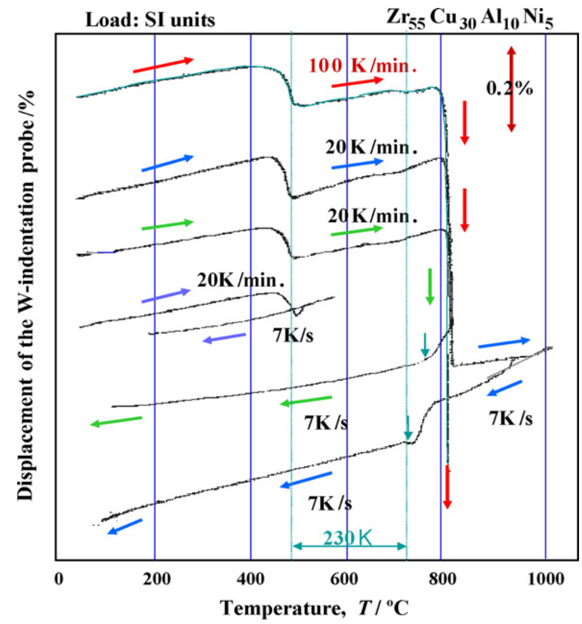

Fig. 1. The displacement behavior of the indentation probe on the $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk metallic glasses during heating 20 and 100 K/min, and then rapidly quenching at the rate of 7 K/s.

viscosity largely decreased and tended to saturate at the heating rate of 200 K/min and above. So, the acceptable values of the viscosity of these alloys can be measured under the high-speed heating conditions at the heating rate of 200 K/min and above. Fig. 3 shows the relationships between $\ln \eta$ and the inverse absolute temperature of the $Zr_{55}Cu_{30}Al_{10}Ni_5$ supercooled liquid alloys. The viscosity of these alloys can be well represented by the Arrhenius relation. The activation energies for viscous flow for the $Zr_{55}Cu_{30}Al_{10}Ni_5$ supercooled liquid alloys was about 350 kJ/mol. Fig. 4 shows the viscosity (η) of the $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ ($x = 0$, 3 and 7 at.%) supercooled liquids as a function of temperature at the heating rate of 300 K/min. For comparison, viscosity of the $Zr_{55}Cu_{30}Al_{10}Ni_5$ alloys at the heating rate of 300 K/min are also shown. In these alloys, viscosity increased with increasing the Pd-content. Fig. 5 shows the relationships between $\ln \eta$ and the inverse absolute temperature of the $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ ($x = 0$, 3 and 7 at.%) supercooled liq-

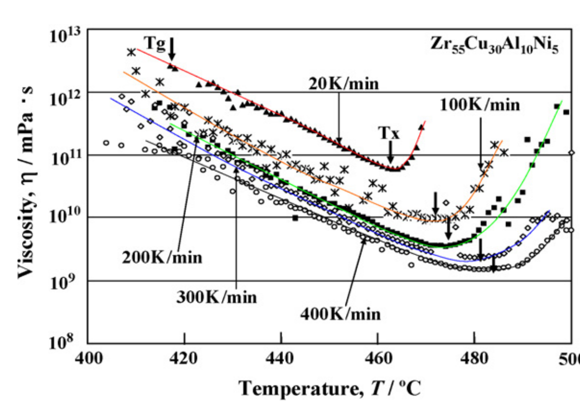

Fig. 2. Viscosity (η: mPa s) of the $Zr_{55}Cu_{30}Al_{10}Ni_5$ supercooled liquid alloys as a function of temperature at the various heating rate between 20 and 400 K/min.