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Solid plasticity and supercooled-liquid thermoplasticity of Zr–Cu-enriched hypoeutectic Zr–Cu–Ni–Al cast glassy alloys

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ABSTRACT

The plasticity of Zr–Cu enriched hypoeutectic Zr–Cu–Ni–Al cast glassy alloys (CGAs) was investigated to determine their tensile elongation as a solid at room temperature, and their precise thermoplastic moldability in a supercooled liquid state. The viscosity of the supercooled liquids was measured by using a penetration viscometer at a high-speed heating rate of 400 K/min. The results obtained show that with an increase in the Zr content, the glass transition temperature (T_g) tends to decrease, whereas the crystallization temperature (T_x) tends to increase. We observed tensile elongation with plural sliding shear bands in the Zr–Cu enriched $Zr_{65}Cu_{20}Ni_5Al_{10}$ CGAs at room temperature. Furthermore, the hypoeutectic $Zr_{65}Cu_{18}Ni_7Al_{10}$ CGA exhibits the widest ΔT_x ($=T_x-T_g$) of about 170 K, with a low viscosity in the order of 10^5 Pa s being observed in the supercooled liquid under a heating rate of 400 K/min. The potential for printing micro-patterns on the surface of a glassy $Zr_{65}Cu_{18}Ni_7Al_{10}$ alloy is demonstrated by means of tough nanocrystalline Ni–W electro-plating molds.

1. Introduction

Cast glassy alloys (CGAs) possess excellent physical properties, such as an extremely high strength at room temperature and a thermoplastic moldability in a supercooled liquid state. These properties are particularly important for applications related to nano- and micro-fabrication technologies [1], in which a thermoplastic molding process is used. For example, Pd-based glassy alloys have already been applied to nano-meter scale molding in developing next-generation patterned media [2] owing to their low glass transition temperature (T_g) of around 540 K and the low viscosity of their supercooled liquids of less than 10^5 Pa s [3]. The Zr-based $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy also exhibits a high glass forming ability [4] and good mechanical properties [5], which are comparable to those of Pt- and Pd-based glassy alloys [6–8]. However, the supply cost of the raw materials for a Zr-based glassy alloy is around a hundredth of that for Pt- and Pd-based glassy alloys.

In thermoplastic molding, the T_g of $Zr_{55}Cu_{30}Ni_5Al_{10}$ glassy alloys (about 693 K [4]) is much higher than that of Pt- and Pd-based glassy alloys, with the viscosity of the supercooled liquid being an order of magnitude greater. The usage of Si-MEMS molds for the micro-precise molding of glassy alloys requires a supercooled liquid with a significantly low viscosity of about 10^5 Pa s in order to obtain a low forging force and high moldability [9]; this is due to the fact that the mold has a much lower strength. Both a high T_g and high viscosity necessitate a shift to a higher glass-forging temperature, which in turn shortens the lifetime of mold. In addition, chemical reaction between the mold and the supercooled liquid creates further problems in achieving both good moldability and a long mold life [9]; consequently, both a low T_g and low supercooled liquid viscosity are beneficial for high reproducibility of the molding process. Reduced thermal stability of the supercooled liquid promotes devitrification and crystallization [10]; therefore, a high-resistivity against crystallization is also a significant factor in glass-forming processing. The temperature range between T_g and T_x of the supercooled liquid region (ΔT_x) can be easily used to evaluate the resistivity against crystallization [11]. It has been previously reported that the ΔT_x of ternary Zr–Cu–Al CGAs [12] clearly varies with small compositional differences, and a similar tendency of compositional dependence of ΔT_x has also been recognized in quaternary Zr–Cu–Ni–Al CGAs [13]. This is particularly evident with a Zr-enriched

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hypoeutectic composition, in which a significant decrease in viscosity and increase in ΔT_x of the supercooled liquid under high-rate heating have been observed [14], thus revealing the superior thermal stability of the supercooled liquid state.

From the viewpoint of the mechanical properties of CGAs, the plasticity at room temperature has already been reported by means of a specific tensile test machine for precise strain rate control [15]. The apparent tensile plasticity and malleability at room temperature of a Zr-based CGA were previously reported by controlling the alloy composition to realize the highest possible Poisson's ratio, and lowest Young's modulus, in a Zr–Ni enriched hypoeutectic Zr–Cu–Ni–Al alloy system [16]. During tensile elongation, the viscosity in the sliding shear band was estimated at 3.8×10^3 Pa s, with the temperature rise in this sliding shear band being below the melting temperature [17]. The thermoplasticity of optimized Zr-based CGAs, which exhibit low viscosity and a low temperature dependence of viscosity in a supercooled liquid state, therefore has the potential to produce tensile elongation through a stable supercooled liquid state in the sliding shear band.

In this study, Zr–Cu enriched hypoeutectic Zr–Cu–Ni–Al CGAs are examined in order to determine the optimal alloy composition to produce a combination of low T_g, low viscosity and a wide ΔT_x of the supercooled liquid under high-rate heating, for glass processing. In addition, a precise thermoplastic molding process is demonstrated using optimized Zr–Cu–Ni–Al CGAs to produce good stampability, though with some technical issues which still need to be addressed. Finally, tensile testing of Zr–Cu enriched Zr–Cu–Ni–Al CGAs was also performed in order to reveal their tensile elongation and yielding phenomena.

2. Experimental procedures

2.1. Sample fabrication and measurements

Using a eutectic $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy [4] as a basis, the effect of Zr and Cu on the glass-forming, thermal properties and viscosity was investigated with hypoeutectic alloys of $Zr_{55+X}Cu_{30-X}Ni_5Al_{10}$ (where $X=0$–11 at%). Subsequently, a $Zr_{65}Cu_{14+Y+Z}Ni_{9-Y}Al_{12-Z}$ alloy, (where Y and $Z=0$–4 at%) was examined to further optimize the alloy composition for thermoplastic processing. The master alloys were fabricated by melting pure elements in an arc-melting furnace, under an Ar atmosphere. Cast glassy rods 8 mm in diameter were obtained by an arc-tilt casting technique [18]. Phase characterization of the as-cast and heated glassy rods was performed by X-ray diffractometry (RIGAKU RINT-2200V). As a preliminary experiment, the amorphization of the cast rods was also identified by X-ray diffraction patterns taken from the cross sectional area of the topside of cast rod, which exhibited the lowest cooling rate for vitrification. Thermal analysis was also performed using differential scanning calorimetry (DSC) under an Ar atmosphere, at a heating rate from 40 to 400 K/min. Tensile tests were conducted at a constant stroke rate by using a Shimadzu servo-hydraulic fatigue machine with a 4830-type control device. Tensile load was measured using a strain-gauge-type load cell (Shimadzu SFL-5-350 50 kN), with the uniaxial elongation in the direction of the load being measured using a high-speed camera (Photron FASTCAM-APX RS). An embossing process was performed using a micropatterned Ni–W electroplated mold [19] and a penetration viscometer, with the final embossed glassy alloy being produced by a multi-target sputter machine. To prevent oxidization of the sputtered glassy alloy film, a thin Au layer of about 10 nm was also applied by sputtering. The microstructure of the embossed glassy alloy specimen was examined by transmission electron microscope (TEM) (JEOL JEM-400EX), with the sample being prepared by focused ion beam (Hitachi FB-2100) from the precise-molded glassy alloy film on a Si substrate.

2.2. Viscometer

The viscosities of the supercooled liquid state of Zr–Cu enriched hypoeutectic Zr–Cu–Ni–Al CGAs were measured by a penetration viscometer (ULVAC), which comprises a penetration viscometer, image furnace, and a vacuum system to control the heating/cooling rate and atmosphere during measurement. The penetration rate was measured under a constant load of 0.020 N, with a penetration diameter of 0.5 mm. In order to minimize the effect of oxidization on viscosity, the penetration measurements were performed using a high heating rate of about 400 K/min and a He gas atmosphere after evacuation. The samples were subsequently polished to a mirror-like finish down to a thickness of about 1.5 mm, taking care to ensure that the sample surfaces remained parallel. The viscosity relates to the penetration rate as per the following Eq. (1), if the supercooled liquid is assumed to obey Newtonian flow.

$$F=\eta 2\pi rD\left(\frac{dD}{dt}\right)+\eta\pi r^2\left(\frac{dD}{dt}\right) \tag{1}$$

where D, t, F, and r are the penetration depth, penetration time, penetration load, and penetration radius, respectively, whereas $2\pi rD$ and πr^2 are the lateral area and cross sectional area of the penetrated mark, respectively. The viscosity is calculated from Eq. (2), which is an integration of Eq. (1) around a penetration time of t.

$$\frac{Ft}{\eta}=AD^2+BD=K \tag{2}$$

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

where K is a constant, and was determined using a material standard (NIST-SRL 710a) of SiO_2 (67.55 wt%), NaO_2 (8.05 wt%), K_2O (9.30 wt%), CaO (8.50 wt%), ZnO (3.60 wt%), and Al_2O_3 (2.10 wt%). The viscosity of a $Zr_{55}Cu_{30}Ni_5Al_{10}$ supercooled liquid has previously been reported using this equipment [20], with it being concluded that it could be regarded as a Newtonian liquid based on two experimental observations: (1) there is no loading dependence on viscosity in the range of 0.01–0.08 N; and (2) there is no heating rate dependence on viscosity in the range of 200–400 K/min, when the absolute value of viscosity is below 10^8 Pa s.

3. Results and discussion

3.1. Zr–Cu enriched hypoeutectic Zr–Cu–Ni–Al CGAs and tensile tests

Fig. 1 shows the DSC data for $Zr_{55+X}Cu_{30-X}Ni_5Al_{10}$ ($X=0$–11 at%) CGAs, at a heating rate of 40 K/min. The distinct endothermic heat flow indicates the observed glass transition phenomena, with the temperature onset of this glass transition (T_g) exhibiting a decreasing linear relationship as the Zr content is increased from 55 ($X=0$, $T_g=683$ K) to 66 at% ($X=11$, $T_g=644$ K). An increase in Zr content causes an increase in the number of metallic Zr–Zr atomic bonds; thus, T_g decreases with an increase in the Zr concentration of Zr–Cu enriched hypoeutectic alloys. The crystallization temperature (T_x) also decreases with an increasing Zr content in the X range of 0–6. Subsequently, the shape of the exothermic heat flow on the DSC curves indicates a change in the crystallization phenomena at $X=7$, with a gap about 12 K created in the value of T_x from that of $X=6$. The maximum value of T_x of about 771 K is obtained at $X=9$, with the widest temperature range of ΔT_x CGAs being observed at $X=10$ ($Zr_{65}Cu_{20}Ni_5Al_{10}$, $\Delta T_x=119$ K). Fig. 2 shows the X-ray diffraction patterns of specimens ($X=6$ and $X=7$) heat treated up to the peak