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Production of Bulk Glassy Alloy Parts by a Levitation Melting-Forging Method

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A levitation melting-forging (LMF) method was developed to prepare glassy $Zr_{55}Cu_{30}Ni_5Al_{10}$, $Ni_{53}Nb_{20}Ti_{10}Zr_8Co_6Cu_3$, $Ti_{45}Cu_{25}Ni_{15}Zr_5Sn_5Al_5$ and $Cu_{55}Zr_{25}Ti_{15}Ni_5$ alloy parts with various shapes of coin, ring and dumbbell of 1 mm in thickness. The glassy alloy samples of 1 mm in thickness for tensile test were also produced by the LMF method. These samples were shaped directly from liquid without any intermediate process. The glassy structure in the samples examined by XRD and DSC is independent of sites. The results show the absence of partial crystallization in the glassy alloy coin prepared by LMF, however, a small quantity of crystallization is found in the glassy alloy coin prepared by copper mold casting. This may be due to the suppression of heterogeneous nucleation resulting from non-contact with container. The density of defects in the glassy alloys prepared by the LMF was decreased significantly because of the absence of spurt.
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1. Introduction

Since the success of forming bulk glassy alloys in Ln- and Mg-based systems in late 1980's,[1,2] metallic glassy alloys in a bulk form requiring low critical cooling rates to vitrify without crystallization have attracted widespread interest ranging from technological aspects of preparation and potential applications to scientific curiosity about the structure and the resulting properties. A number of multi-component alloy systems, such as Zr-, Ti-, Fe-, Pd-, Co-, Ni- and Cu-based alloys, had been developed up to date.[3–5] In contrast to amorphous alloys in binary and ternary systems produced in a thin ribbon form, these multi-component alloys are characterized by high glass-forming ability together with a large supercooled liquid region $\Delta T_x = T_x - T_g$ (where T_x and T_g are the crystallization and glass transition temperature, respectively), thus giving rise to high thermal stability against crystallization.

Bulk glassy alloys have been prepared by various methods, such as water quenching, copper mold casting, mold-clamp casting, die casting, rotating disk casting and suction casting.[6–10] Levitation melting has also been used to investigate the undercooled liquid metal.[11–13] As a kind of container-less technique, in the absence of the introduction of impurities from wall, the levitation melting method is of particularly interest for metallic alloys with high melting points, high reactivity and high purity. Since the container-less state, the heterogeneous nucleation resulting from the contact with container wall is completely eliminated.[14] This character is favor for the formation of homogeneous glassy structure.

Zr-based metallic glasses have attracted much interest because of their high glass-forming ability (GFA) and large supercooled liquid region since the discovery by Inoue group in 1990.[15–20] The bulk glassy alloys exhibit high mechanical strength and good corrosion resistance which enable to use as structural materials. In this paper, several kinds of bulk glassy alloys including Zr-based alloy system were used to prepare the parts with different outer shapes, *e.g.*, coin, ring and dumbbell, by electromagnetic levitation melting and forging (LMF) processes and fundamental properties of the resulting LMF alloys were investigated.

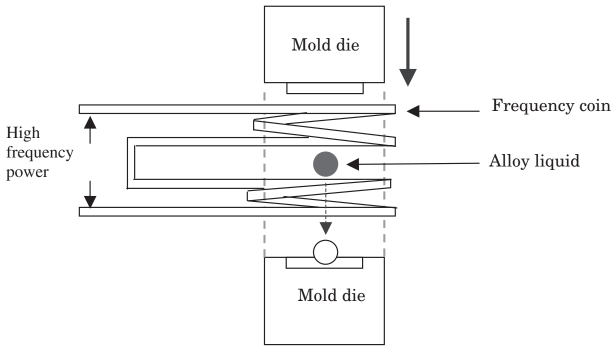

Fig. 1 Schematic illustration of electromagnetic levitation melting equipment used in present study.

2. Experimental

Multi-component alloys with compositions of $Zr_{55}Cu_{30}Ni_5Al_{10}$, $Ni_{53}Nb_{20}Ti_{10}Zr_8Co_6Cu_3$, $Ti_{45}Cu_{25}Ni_{15}Zr_5Sn_5Al_5$ and $Cu_{55}Zr_{25}Ti_{15}Ni_5$ were examined. The alloy ingots were prepared by arc melting of pure metals under an argon atmosphere. A schematic illustration of electromagnetic levitation melting is shown in Fig. 1. Different molds were used to fabricate alloy parts with different outer shapes. A glassy state of the samples was examined by X-ray diffraction (XRD, Rigaku) with Cu Kα radiation. Thermal behavior of the alloy was studied using a differential scanning calorimeter (EXSTAR 6000/DSC 6300) with a heating rate of 40 K/min in a heating temperature range up to 1000 K. Mechanical properties under tensile deformation mode were measured at room temperature with an Instron-type testing machine. The glassy alloy samples for tensile test were directly fabricated by the LMF method. Vickers hardness was also measured with a Vickers hardness indenter under a load of 2 N during 10 s.

3. Results and Discussion

Rapid forging of the levitation melting liquid can produce the net shape parts directly. Some glassy alloy parts with

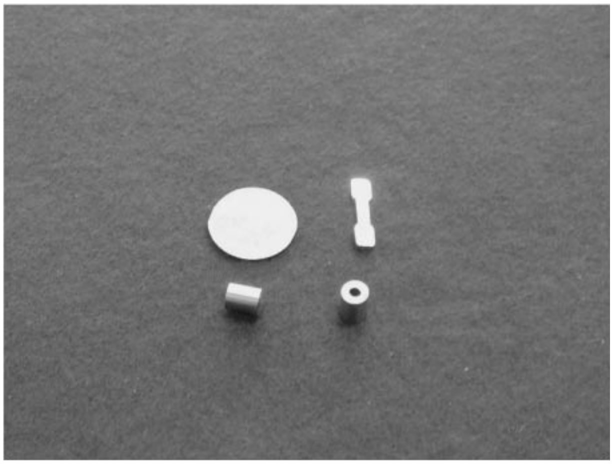

Fig. 2 Outer surface of some glassy alloy parts prepared by LMF.

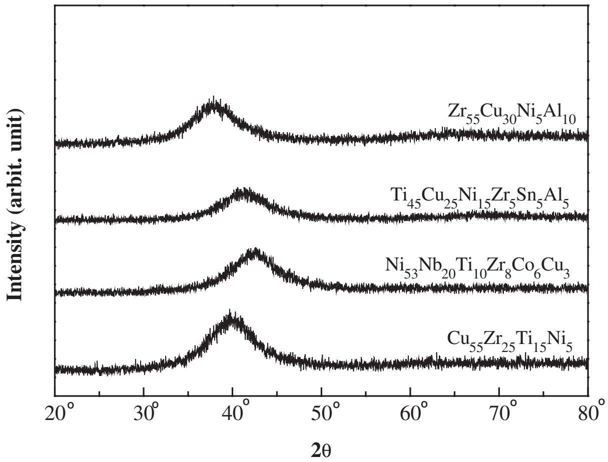

Fig. 3 X-ray diffraction patterns of $Zr_{55}Cu_{30}Ni_5Al_{10}$, $Ti_{45}Cu_{25}Ni_{15}Zr_5Sn_5Al_5$, $Ni_{53}Nb_{20}Ti_{10}Zr_8Co_6Cu_3$ and $Cu_{55}Zr_{25}Ti_{15}Ni_5$ alloy in a disc shape of 20 mm in diameter and 2 mm in height prepared by LMF.

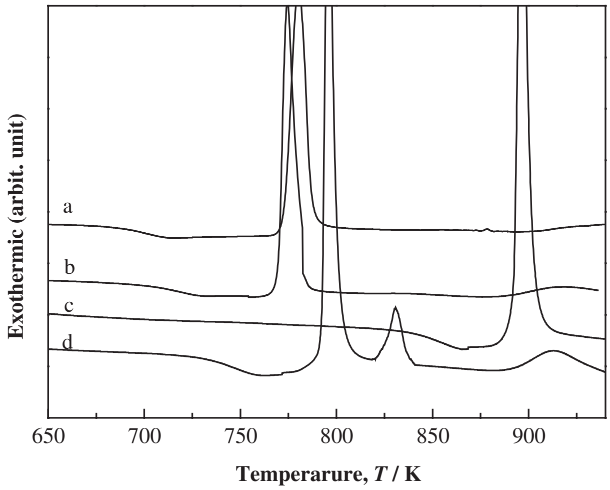

Fig. 4 DSC curves of $Zr_{55}Cu_{30}Ni_5Al_{10}$ (a), $Ti_{45}Cu_{25}Ni_{15}Zr_5Sn_5Al_5$ (b), $Ni_{53}Nb_{20}Ti_{10}Zr_8Co_6Cu_3$ (c) and $Cu_{55}Zr_{25}Ti_{15}Ni_5$ (d) glassy alloy discs prepared by LMF.

Table 1 T_g, T_x, ΔT_x and mechanical properties of glassy alloy prepared by LMF.

Alloy (at%)	T_g /K	T_x /K	ΔT_x /K	Vickers Hardness	Tensile Strength (MPa)
$Zr_{55}Cu_{30}Ni_5Al_{10}$	683	775	92	480	1860
$Ti_{45}Cu_{25}Ni_{15}Zr_5Sn_5Al_5$	719	772	54	630	2210
$Ni_{53}Nb_{20}Ti_{10}Zr_8Co_6Cu_3$	844	897	52	821	2750
$Cu_{55}Zr_{25}Ti_{15}Ni_5$	742	792	49	680	2080

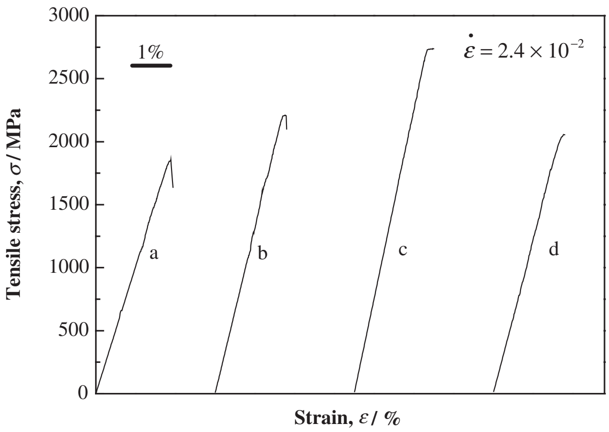

Fig. 5 Tensile stress-strain curves of $Zr_{55}Cu_{30}Ni_5Al_{10}$ (a), $Ti_{45}Cu_{25}Ni_{15}Zr_5Sn_5Al_5$ (b), $Ni_{53}Nb_{20}Ti_{10}Zr_8Co_6Cu_3$ (c) and $Cu_{55}Zr_{25}Ti_{15}Ni_5$ (d) glassy alloy in a tensile testing specimen shape with a dimension of 20 mm in the length, 5 mm in width and 1 mm in thickness prepared by LMF.

different outer shapes produced by the LMF method have neat and glossy surface, as shown in Fig. 2.

Figure 3 shows X-ray diffraction patterns of the Zr-, Ni-Ti-, and Cu-based alloys produced by the LMF method. No diffraction peaks corresponding to a crystalline phase are seen. Figure 4 shows DSC curves of these glassy alloys. All the samples exhibit a sequent phase transition of an endothermic reaction due to glass transition, followed by a large supercooled liquid region and then an exothermic reaction due to crystallization. The glass transition temperature (T_g) and onset temperature of crystallization (T_x) are summarized in Table 1. Figure 5 shows the tensile stress-strain curves of the $Zr_{55}Cu_{30}Ni_5Al_{10}$, $Ti_{45}Cu_{25}Ni_{15}Zr_5Sn_5Al_5$, $Ni_{53}Nb_{20}Ti_{10}Zr_8Co_6Cu_3$ and $Cu_{55}Zr_{25}Ti_{15}Ni_5$ glassy alloys. Their mechanical properties are also shown in Table 1.

Since Cu-Zr-Ti bulk glassy alloys were found in 2001, the new Cu-based bulk glassy alloys have attracted interest as a new type of bulk glassy alloy which can be used for structural materials because of their high GFA, high fracture strength above 2000 MPa and distinct plastic elongation.[21)] The addition of small amounts of Ni, Co and Fe increased further the stability of supercooled liquid and improved the GFA and mechanical properties of bulk glassy alloys.[22)] Here, we successfully prepared a $Cu_{55}Zr_{25}Ti_{15}Ni_5$ glassy alloy with good mechanical properties by the LFM method. The glassy alloy had a supercooled liquid region of 49 K. The supercooled liquid region of the alloys containing larger amounts of Ti is smaller than those for $(Cu_{0.6}Zr_{0.3}Ti_{0.1})_{100-x}Ni_x$ glassy alloys.[22)] We previously synthesized for the first time a $Ni_{53}Nb_{20}Ti_{10}Zr_8Co_6Cu_3$ glassy alloy with high strength by the copper mold-clamp casting method.[23)] The glass tran-

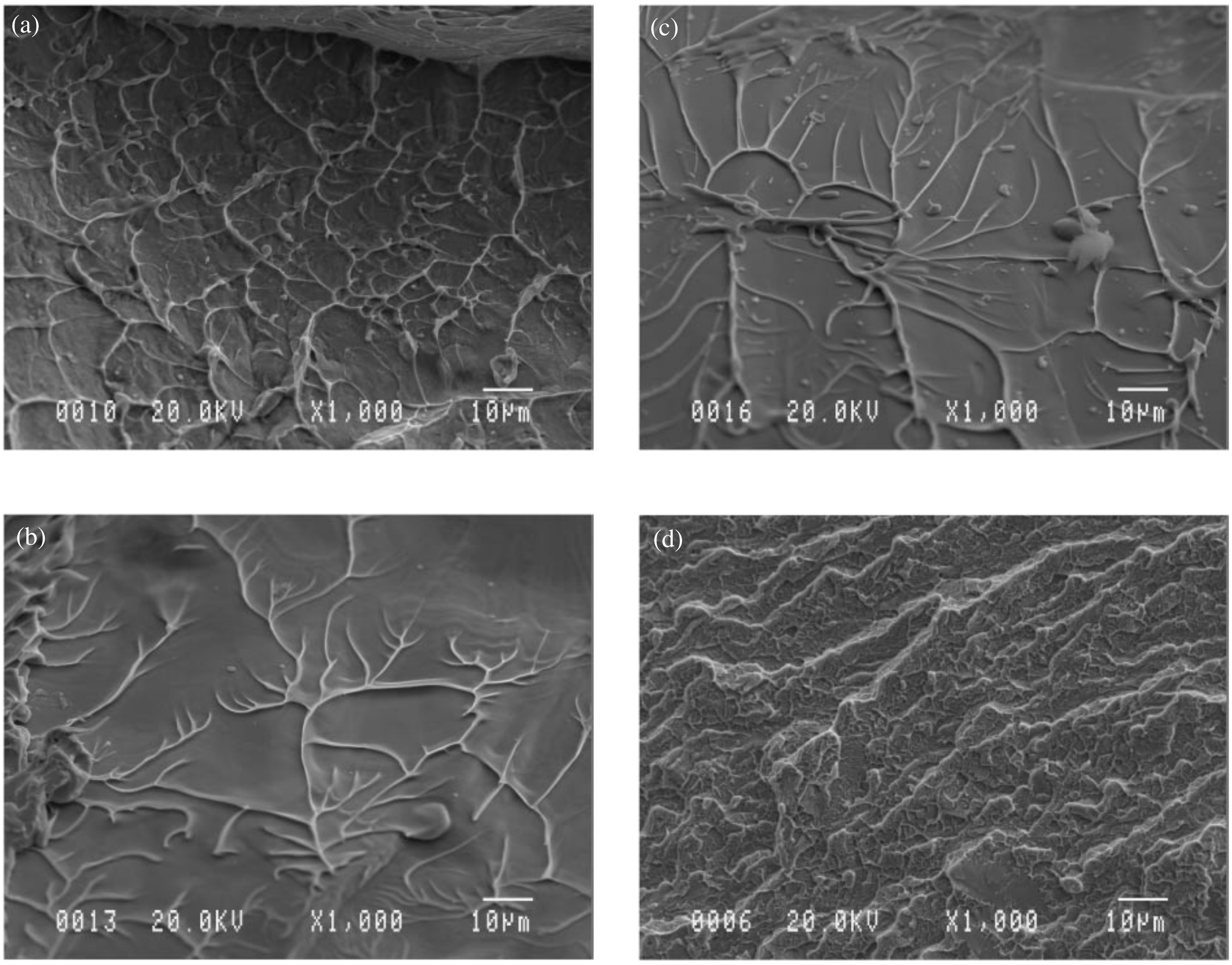

Fig. 6 Tensile fracture surface of the $Zr_{55}Cu_{30}Ni_5Al_{10}$ (a), $Ti_{45}Cu_{25}Ni_{15}Zr_5Sn_5Al_5$ (b), $Ni_{53}Nb_{20}Ti_{10}Zr_8Co_6Cu_3$ (c) and $Cu_{55}Zr_{25}Ti_{15}Ni_5$ (d) glassy alloys prepared by LMF.

sition temperature (T_g) and the supercooled liquid region (ΔT_x) of the bulk glassy alloy were 846 and 51 K, respectively. The bulk glassy alloy exhibited Young's modulus of 140 GPa, and tensile fracture strength of 2700 MPa.[23)] In the present study, we also produced the $Ni_{53}Nb_{20}Ti_{10}Zr_8Co_6Cu_3$ glassy alloy by the LMF method, and the similar results were obtained. The ΔT_x value is measured as 52 K and the relatively large ΔT_x value indicates that the supercooled liquid of the new metal-metal type Ni-based alloy has a rather high stability against crystallization. The tensile fracture surface appearance is shown in Fig. 6. All of the fracture surfaces consist of vein and smooth patterns.

With the aim of examining the homogeneity of the Zr-based bulk glassy alloy prepared by LMF, XRD was made at different sites of the glassy alloy coin, in comparison with the glassy alloy coin prepared by conventional copper-mold casting method. Figure 7 shows XRD patterns taken from different sites in the $Zr_{55}Cu_{30}Ni_5Al_{10}$ glassy alloy coin. The XRD patterns consist only of halo peaks and no distinct crystalline peak is seen for the glassy alloy coin prepared by LMF. But one can see some weak crystalline peaks of Zr_2Cu in the XRD pattern of the glassy alloy coin prepared by conventional copper-mold casting. The glassy alloy obtained by either LMF or conventional copper-mold casting had the similar feature of DSC curve, *i.e.*, the same T_g (about 683 K) and T_x (about 775 K), while, their crystallization exothermic are different. For the coin prepared by copper-mold casting, sites 1 and 4 have smaller crystallization exothermic than the others because of partial crystallization (shown in Fig. 8).

Although Zr-based glassy alloys have high GFA, their fabrication is strongly dominated by the purities of alloy liquid, giving the significant influence on the properties of glassy alloy products. Due to avoiding the introduction of impurity from container wall in the liquid state, the heterogeneous nucleation resulting from the contact with container wall may be greatly reduced. For conventional copper-mold casting, the density of casting-induced defects such as inner hole, crystal impurity and crude surface would increase. The defects of the LMF alloys decreased presumably because of the absence of spurt. Some small holes were observed in the inner part of the glassy alloy coin prepared by conventional copper-mold casting, while no holes were found in the inner part of the coin prepared by LMF.

4. Conclusions

Some bulk glassy alloy parts with various outer shapes

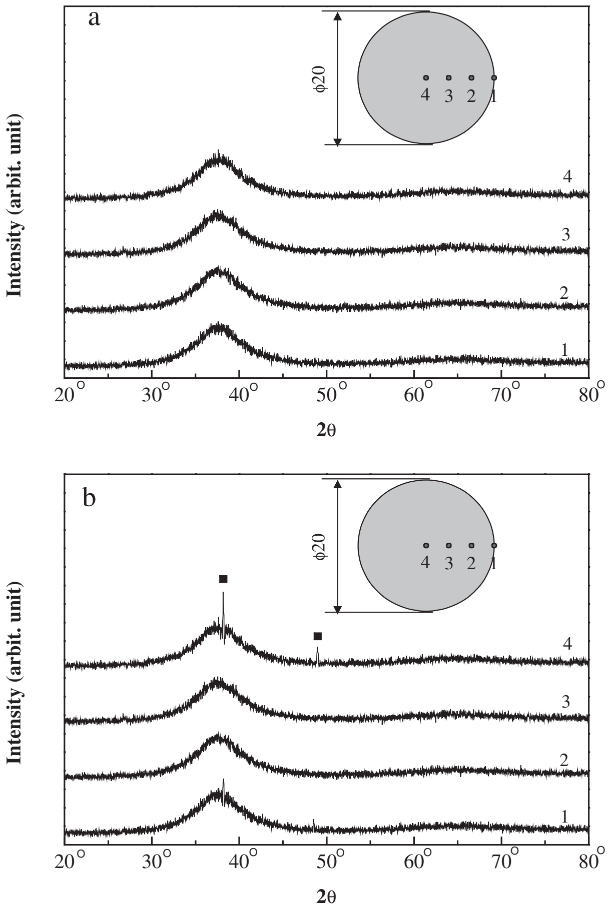

Fig. 7 XRD patterns taken from different sites in the $Zr_{55}Cu_{30}Ni_5Al_{10}$ glassy alloy coins prepared by a) LMF and b) conventional copper casting.

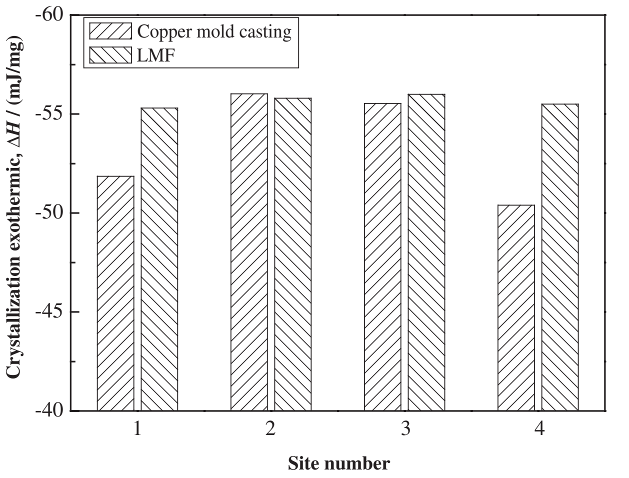

Fig. 8 Crystallization exothermic of different sites in the $Zr_{55}Cu_{30}Ni_5Al_{10}$ glassy alloy coins prepared by LMF and conventional copper casting.

were produced directly for $Zr_{55}Cu_{30}Ni_5Al_{10}$, $Ni_{53}Nb_{20}Ti_{10}$-$Zr_8Co_6Cu_3$, $Ti_{45}Cu_{25}Ni_{15}Zr_5Sn_5Al_5$ and $Cu_{55}Zr_{25}Ti_{15}Ni_5$ by the levitation-melting-forging (LMF) method. In comparison those of the glassy alloys produced by conventional copper mold casting method, the glassy alloys prepared by LMF have a more homogeneous structure due to the absence of partial crystallization. This is presumably because of the absence of heterogeneous nucleation resulting from contacting with container. The defects in the glassy alloys prepared by LMF were significantly decreased because no spurt occurred.

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