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RAPID PUBLICATION

Fabrication of Bulk Glassy $Zr_{55}Al_{10}Ni_5Cu_{30}$ Alloy of 30 mm in Diameter by a Suction Casting Method

Akihisa Inoue and Tao Zhang

Institute for Materials Research, Tohoku University, Sendai 980-77, Japan

A bulk glassy $Zr_{55}Al_{10}Ni_5Cu_{30}$ alloy in a cylindrical form with a diameter of 30 mm and a length of 50 mm was produced by sucking the molten alloy into a copper mold. The sucking force was generated from the rapid movement (5.0 m/s) of piston with a diameter of 30 mm which was set at the center of the copper hearth. The sucking velocity is evaluated to be as high as 22.1 kg/s. Neither cavity nor hole is seen in the transverse cross section of the bulk glassy alloy. The glass transition temperature (T_g), crystallization temperature (T_x) and supercooled liquid region defined by $\Delta T_x(=T_x-T_g)$ are nearly the same as those for the melt-spun glassy ribbon with a thickness of 30 μm, in spite of the significant difference in sample thickness by three orders. Furthermore, there is no appreciable difference in T_g, T_x and ΔT_x over the whole cast sample. The Vickers hardness number is 523, in agreement with that ($\fallingdotseq$510) for the corresponding melt-spun glassy ribbon and cast bulk glassy cylinders with diameters below 15 nm. Thus, the direct production of the bulk glassy alloy with a diameter of 30 mm by the suction casting method is important for the future development of bulk glassy alloys.

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Keywords: *bulk glassy alloy, zirconium base alloy system, suction casting, high speed casting, large glass-forming ability, glass transition, supercooled liquid region*

I. Introduction

Since the discoveries of a series of glassy alloys with large glass-forming ability in Ln–Al–TM[(1)(2)], Mg–Ln–TM[(3)(4)], Zr–Al–TM[(5)(6)], Ti–Zr–TM[(7)], Hf–Al–TM[(8)], Ti–Zr–Al–Be–TM[(9)] and Ti–Zr–Be–TM[(10)] (Ln = lanthanide metals, TM = transition metals) systems, bulk glassy alloys have attracted rapidly increasing interest because of the importance in both the scopes of materials science and engineering application. Among the above-described alloy systems, the Zr-based glassy alloys in Zr–Al–Ni–Cu system seem to be particularly important for applications because neither reactive elements such as Ln and Mg nor toxic element of Be are not dissolved. Consequently, it is important to examine the maximum sample thickness for glass formation and the castability in the Zr-based alloy system by various kinds of casting processes with slow cooling rates. We have already reported[(11)] that a glassy alloy is formed in a cylindrical bulk form with a diameter of 16 mm by water quenching the molten alloy in the quartz tube and the precipitation amount of crystalline phase is slight even for the water-quenched bulk alloy ingot with a diameter of 20 mm. Simultaneously, the previous paper[(11)] has pointed out the possibility that a further improvement of the solidification method causes the formation of a bulk glassy alloy with a larger diameter above 20 mm. More recently, we have reported[(12)] that the use of the suction casting method enables the production of a cylindrical Zr–Al–Ni–Cu glassy alloy with a diameter of 15 mm and no appreciable voids are seen over the whole cross section. Thus, the suction method developed by the present authors is very attractive as a new production technique of bulk glassy alloys without appreciable voids. We have subsequently made the modification of the suction casting equipment so as to enable the production of a cylindrical bulk ingot with a diameter up to 30 mm. By using the modified suction casting equipment, we tried to produce bulk glassy Zr-based alloys in a cylindrical form with a diameter of 30 mm. Little has been reported about the production technique and production evidence of a bulk glassy alloy with a large diameter of 30 mm. This paper is intended to present the preparation of a bulk glassy Zr–Al–Ni–Cu alloy ingot with a diameter of 30 mm by the suction casting method and the thermal stability of the cast bulk glassy alloy.

II. Experimental Procedure

A $Zr_{55}Al_{10}Ni_5Cu_{30}$ alloy was used in the present study because the alloy has a wide supercooled liquid region reaching 90 K. The prealloyed ingot was prepared by arc-melting a mixture of pure metals in a purified argon atmosphere. The composition is given in nominal atomic percentage. From the prealloyed ingot, a cylindrical sample with a diameter of 30 mm and a length of 50 mm was prepared by sucking the molten alloy into a copper mold through suction force resulting from the difference in gas pressure between melting chamber and casting chamber. In the suction casting equipment, the prealloyed ingot of

200 g was remelted on a copper hearth by arc heating system in an argon atmosphere of 5.3 kPa. Immediately before casting, the piston with a diameter of 30 mm which was set at the center of the copper hearth for arc melting was moved at a high speed of 5.0 m/s and the molten alloy was simultaneously sucked into a copper mold by utilizing the sucking force which was generated by the rapid movement of the piston. The diameter of the piston was 30 mm and the casting velocity was evaluated to be approximately as high as 22.1 kg/s.

The structure of the as-cast cylindrical samples was examined by X-ray diffractometry and optical microscopy (OM) techniques. The OM observation was made on the transverse cross section which was etched for 30 s at room temperature in a 10% fluoric acid and 90% distilled water in volume. The thermal stability associated with glass transition and crystallization was measured at a heating rate of 0.67 K/s by differential scanning calorimetry (DSC). Vickers hardness was measured at room temperature with a Vickers microhardness tester with a load of 1 kg.

III. Results and Discussion

Figure 1 shows the outer surface and transverse cross section of the bulk $Zr_{55}Al_{10}Ni_5Cu_{30}$ alloy with a diameter of 30 mm and a length of about 50 mm prepared by the suction casting method. The cross sectional surface is in the etched state where a crystalline phase is observed, if it exists. Both the outer surface and the cross section have a highly white luster and no contrast corresponding to the precipitation of a crystalline phase is seen. The surface and cross sectional appearance indicates clearly that the surface and central regions consist only of a glassy phase without crystalline phase. Figure 2 shows the X-ray diffraction patterns taken from the central region in the transverse cross section. The diffraction patterns consist only of halo rings with the highest intensity at the wave vector ($K_p=2\pi \sin\theta/\lambda$) of 25.11 nm^{-1}, indicating that a glassy phase is formed for the bulk sample. In order to confirm the absence of a crystalline phase over the whole sample, an optical micrograph taken from the central region in the transverse cross section is shown in Fig. 3. The featureless contrast over the whole micrograph indicates the formation of the glassy phase without appreciable crystalline phase. Besides, one can notice the absence of distinct cavity and hole which are ordinarily observed for cast samples. The absence seems to be an advantage of the suction casting method. It is therefore said that the present suction casting method is appropriate for the elimination of cavity and holes because of the solidification under a sucking force and the rapid solidification resulting from the fast movement of the sucked melt. The success of the bulk Zr-based glassy alloys without any crystalline phase allows us to expect that a glassy phase in the Zr-based system is produced even in a bulk form with diameters much larger than 30 mm by the use of the same suction casting method.

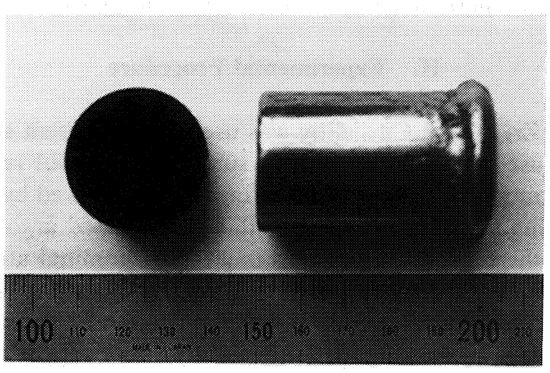

Fig. 1 Outer surface appearance and cross sectional surface of a bulk $Zr_{55}Al_{10}Ni_5Cu_{30}$ ingot with a diameter of 30 mm prepared by the suction casting method.

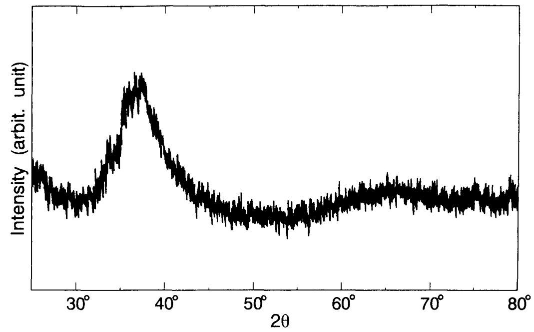

Fig. 2 X-ray diffraction pattern taken from the central region in the transverse cross section of the cast bulk $Zr_{55}Al_{10}Ni_5Cu_{30}$ ingot with a diameter of 30 mm.

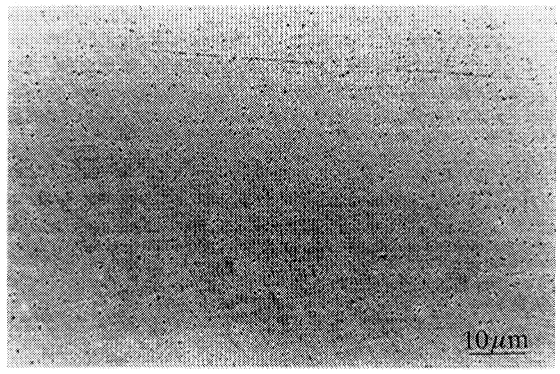

Fig. 3 Optical micrograph revealing the transverse cross sectional structure of the cast bulk $Zr_{55}Al_{10}Ni_5Cu_{30}$ ingot with a diameter of 30 mm.

Figure 4 shows the DSC curve of the $Zr_{55}Al_{10}Ni_5Cu_{30}$ sample taken from the central region of the cast ingot. The sample shows a distinct endothermic reaction due to the glass transition, followed by a supercooled liquid region and then an exothermic reaction due to crystallization. The glass transition temperature (T_g) and crystallization temperature (T_x) are measured to be 683 and 767 K, respectively, in agreement with those for the corresponding melt-spun glassy ribbon with a thickness of 30 μm. The data on the thermal stability suggest that the bulk glassy alloy does not have any appreciable difference in both alloy composition and atomic configuration, in comparison with the melt-spun glassy ribbon.

Figure 5 plots the T_g, $\Delta T_x(=T_x-T_g)$, heat of crystalli-

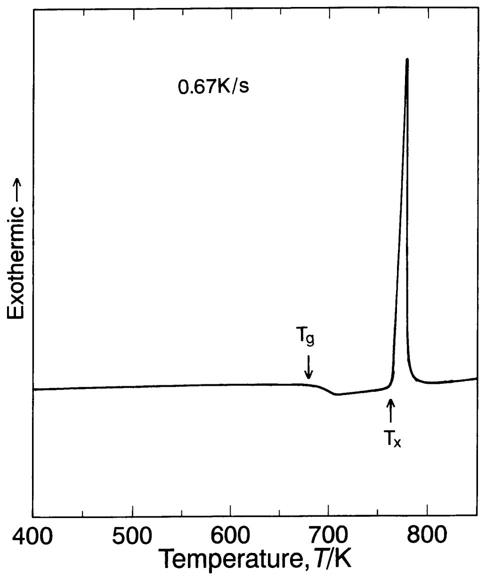

Fig. 4 Differential scanning calorimetric (DSC) curves taken from the central region of the cast glassy $Zr_{55}Al_{10}Ni_5Cu_{30}$ ingot with a diameter of 30 mm.

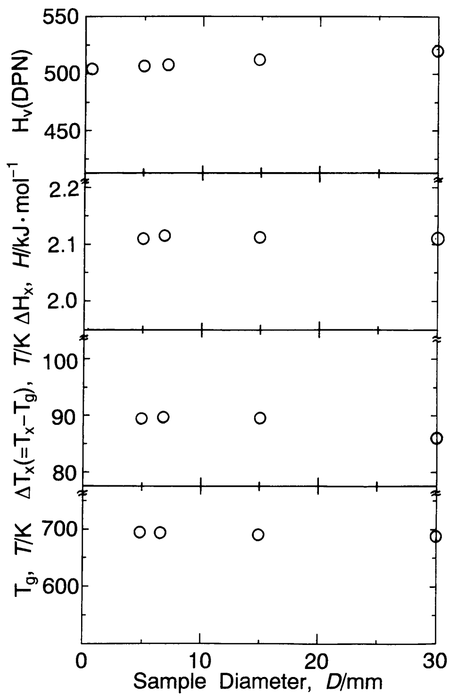

Fig. 5 The glass transition temperature (T_g), temperature interval of supercooled liquid region, $\Delta T_x(=T_x-T_g)$, heat of crystallization (ΔH_x) and Vickers hardness (H_v) as a function of sample diameter for the cast glassy $Zr_{55}Al_{10}Ni_5Cu_{30}$ specimens. The H_v values for the samples with diameters above 5 mm were measured in the central region.

zation (ΔH_x) and Vickers hardness number (H_v) as a function of sample diameter for the cast bulk $Zr_{55}Al_{10}Ni_5Cu_{30}$ samples. The samples with diameters of 5 and 7 mm were prepared by the copper mold casting method and the sample with a diameter of 15 mm was made by the same suction casting method as that for the sample with a diameter of 30 mm. The T_g, ΔT_x, ΔH_x and H_v keep nearly constant values of about 690 K, 90 K, 2.11 kJ/mol and 515, respectively, even in the extremely wide thickness range of 0.03 to 30 mm and no distinct changes in the thermal stability and hardness with sample thickness are recognized. The nearly constant values in the thermal stability and mechanical strength suggest that the glassy structure is analogous among the samples with the widely different thicknesses.

IV. Summary

A suction casting method in which the instantaneous casting was made by utilizing the sucking force was found to enable the production of a bulk glassy alloy with a diameter of 30 mm and a length of about 50 mm for a $Zr_{55}Al_{10}Ni_5Cu_{30}$ alloy with large glass-forming ability. The sucking force was generated by rapid movement of the piston which was set at the center of the copper hearth. The diameter of the piston was 30 mm and the moving speed was fixed to be 5.0 m/s. The resulting casting velocity is evaluated to be as high as 22.1 kg/s. No appreciable crystalline phase is observed on the outer surface and in the inner region. Furthermore, neither cavity nor hole is detected for the cast sample. Thus, the suction casting method is very useful for the suppression of a heterogeneous nucleation of a crystalline phase and casting defects such as cavity and hole. The thermal stability and Vickers hardness are nearly the same as those for the corresponding melt-spun glassy ribbon and cast bulk glassy alloys with diameters below 15 mm. The success of producing the bulk glassy alloy without difference in the thermal stability and mechanical strength in a bulk form with a diameter of 30 mm by the use of the suction casting method is very encouraging for the future development of bulk glassy alloys.

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