RAPID PUBLICATION

Preparation of Bulky Zr-Based Amorphous Alloys
by a Zone Melting Method

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A bulk amorphous Zr_{60}Al_{15}Ni_{15}Cu_{5}Pd_{10} alloy was prepared by the zone melting method using an arc-type heat
source. The bulk amorphous alloy prepared on the copper hearth has a rectangular parallelepiped shape with a thickness
of 10 mm, a width of 12 mm and a length of 170 mm. A majority of the region except the bottom and side edge regions
contacted with copper hearth consists of an amorphous phase. The cooling rate achieved by the zone melting method
is high enough to cause an amorphous phase in the Zr-based alloy where heterogeneous nucleation is suppressed. The amor-
phous phase subjected to continuous heating exhibits a distinct glass transition, followed by a wide supercooled liquid
region and then an exothermic peak due to crystallization. The success of producing the bulk amorphous alloys by the
zone melting method implies the possibility of the continuous production of the bulk amorphous alloys and seems to
accelerate the subsequent progress of amorphous alloys.

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supercooled liquid

I. Introduction

For the last three decades, materials scientists have dreamed of the finding of alloys with large glass-forming ability which enables the preparation of metallic amorphous alloys in a bulk shape by various slowly cooled solidification methods. Recently, Inoue et al. have reported that a number of amorphous alloys in the Ln-Al-
TM\textsuperscript{(1)-(2)}, Mg-Ln-TM\textsuperscript{(3)-(5)}, Zr-Al-TM\textsuperscript{(6)-(8)}, Hf-Al-TM\textsuperscript{(9)}
and Ti-Zr-TM\textsuperscript{(9)-(10)} (Ln = lanthanide metal, TM = VI-VIII group transition metal) ternary systems have low
critical cooling rates for glass formation of the order 10\textsuperscript{2} K/s and can be produced in a bulk shape with thicknesses
up to about 9 mm by using a metallic mold casting or a high-pressure die casting method\textsuperscript{(11)-(12)}. It has subsequently been proposed\textsuperscript{(8)-(13)} that the large glass-forming ability of the ternary alloys is mainly due to the optimum
atomic size ratios of the constituent elements in which their atomic sizes differ by more than 10% from each other.
Based on the alloy design resulting from the importance of the significantly different atomic size ratios, we have noticed a significant effect of the multiplicity of the constituent elements with different atomic sizes and succeeded in finding amorphous alloys with much lower critical cooling rates in the range of 1 to 100 K/s in the Zr-Al-
Co-Ni-Cu and Zr-Ti-Hf-Al-Co-Ni-Cu systems\textsuperscript{(13)-(16)}. As a result, bulk amorphous alloys with diameters up
to 16 mm and a length of 150 mm have been produced in the Zr-Al-Ni-Cu system by quenching the melt in a quartz tube into water\textsuperscript{(15)}. It has furthermore been clari-
ted\textsuperscript{(17)} that the bulk amorphous alloys exhibit a high tensile strength of 1500 MPa which is nearly the same as the compressive strength and fracture accompanying a serrated plastic flow on the tensile stress-elongation curve. The high tensile strength and the serrated plastic flow phenomenon indicate that the bulk amorphous alloys have good ductility in spite of the large sample thickness
prepared by casting.

As described above, bulk amorphous alloys with thicknesses above 5 mm have been produced by various solidification methods. However, all these methods are a batch-type processing and cannot produce continuously long bulk amorphous alloys. The finding of an amorphous alloy with a further low critical cooling rate as well as the development of a new solidification technique leading to the continuous production of bulk amorphous alloys has strongly been desired because of the expectation of the conquest of the upper limit of sample shape for amorphous metallic materials. This paper aims to present the first evidence on the preparation of a bulk amorphous Zr_{60}Al_{15}Ni_{15}Cu_{5}Pd_{10} alloy with a maximum thickness of 10 mm, a width of 12 mm and a length of 170 mm by a zone melting method which enables the continuous preparation of a bulk amorphous alloy.

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II. Experimental Procedure

A Zr_{60}Al_{10}Ni_{10}Cu_{18}Pd_{8} alloy was chosen because the multicomponent alloy has large glass-forming ability combined with high resistance against the generation of heterogeneous nucleation of a crystalline phase\(^{19}\). Several ingots with a weight of about 100 g were prepared by arc melting a mixture of pure metals in a purified argon atmosphere. The prealloyed ingots have a rectangular parallelepiped shape. The nominal composition will be given in atomic percent. Subsequently, a bulk alloy ingot of 500 g in weight in a rectangular parallelepiped shape with a height of 10 mm, a width of 12 mm and a length of 170 mm was prepared from the five prealloyed ingots by zone melting in a purified argon atmosphere using an arc electrode as a heat source. Figure 1 shows a schematic illustration of the zone-melting equipment. The arc furnace consists of a tungsten cathode electrode and a copper hearth cooled with water. The current and voltage during arc melting are 250 A and 20 V respectively, and the moving velocity of the cathode electrode was controlled to be 5.7 mm/s. The distance between the anode electrode and the prealloyed ingot was adjusted to be about 3 mm. The structure of the zone-melted ingot was examined by X-ray diffractometry, optical microscopy (OM) and scanning electron microscopy linked with energy dispersive X-ray (EDX) spectroscopy. The etching treatment for the OM samples was made for 1.8 ks at 303 K in a 30% fluoric acid solution. Thermal stability associated with the structural relaxation, glass transition temperature (T\(_g\)), crystallization temperature (T\(_c\)) and heat of crystallization (\(\Delta H_c\)) was measured by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. Hardness was measured by a Vickers microhardness tester with a 0.98 N load.

III. Results and Discussion

Figure 2 shows the outer surface appearance of the bulky Zr–Al–Ni–Cu–Pd alloy ingot prepared by the zone melting method. The ingot has an approximately rectangular parallelepiped shape with a maximum thickness of 10 mm, a maximum width of 12 mm and a length of 170 mm. The freely solidified surface has a good white luster, even though the trace of the movement of the melted zone with a width of about 13 mm is clearly seen. The width of the trace roughly agrees with that (about 10 mm) of the melted zone in the arc melting.

Figure 3 shows the X-ray diffraction pattern taken from the central region in the transverse and longitudinal cross sections of the bulky Zr–Al–Ni–Cu–Pd ingot. The pattern consists only of halo peaks and no distinct crystalline peak is seen, indicating that the ingot is composed of

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Fig. 1 Schematic illustration of the zone melting equipment using an arc electrode as a heat source which was used for the preparation of a bulk amorphous alloy ingot. (a) front view, (b) lateral view.

Fig. 2 Photograph revealing the outer surface appearance of a bulky Zr_{60}Al_{10}Ni_{10}Cu_{18}Pd_{8} alloy ingot prepared by the zone melting method.

Fig. 3 X-ray diffraction pattern taken from the central region of a bulky Zr_{60}Al_{10}Ni_{10}Cu_{18}Pd_{8} alloy ingot in a rectangular parallelepiped shape with a thickness of 10 mm, a width of 12 mm and a length of 170 mm.
a mostly single amorphous phase. In order to confirm the formation of the mostly single amorphous phase in the central region, we examined the transverse cross sectional structure by optical microscopy. As exemplified in Fig. 4, small regions with a size of about 80 \( \mu \text{m} \) corresponding to a crystalline phase are seen, but almost all the area of the photograph is occupied by the featureless contrast revealing the formation of an amorphous phase, being consistent with the result obtained by X-ray diffractometry. The dispersion of the small crystalline particles is surmised to occur through the convection-induced circulation of crystalline particles which have heterogeneously nucleated in the region contacted with the copper hearth during solidification of the alloy melt after the passage of the arc cathode.

Although the amorphous phase is formed in the central region of the zone-melted ingot, the precipitation of a crystalline phase with a rather large size of about 200 \( \mu \text{m} \) is observed in the bottom and the both side edge regions which are contacted with the copper hearth because of the ease of heterogeneous nucleation. Figure 5 shows an optical micrograph of the transverse cross section at about 2 mm from the bottom. The structure consists of coexistent amorphous and crystalline phases. This result indicates that the crystalline phase nucleates heterogeneously in the outer region contacted with the copper hearth and grows into the inner region along the direction of heat flux, although the cooling rate in the bottom region contacted with copper hearth is expected to be much higher than that in the inner region. The result is due to the ease of heterogeneous nucleation of a crystalline phase at the region contacted with the copper hearth, where the temperature of the molten alloy is surmised to be just near the melting temperature. It is therefore thought that the complete suppression of heterogeneous nucleation of the crystalline phase is rather difficult for the present zone-melting process using the water-cooled copper hearth. The crystalline phase shown in Fig. 5 consists mainly of a bct structure which agrees with that for \( \text{Zr}_2\text{Cu}^{19} \) and seems to be a metastable phase represented by \( \text{Zr}_2(\text{Cu, Al, Ni, Pd}) \). Furthermore, Fig. 5 shows that the interface between the amorphous and the \( \text{Zr}_2\text{M} \) phases has a rather smooth morphology, presumably because of the difficulty of the redistribution of the constituent elements resulting from the solidification of the highly supercooled liquid.

Figure 6 shows the DSC curve of the bulky Zr–Al–Ni–Cu–Pd amorphous ingot prepared by the zone melting method. The bulk sample exhibits a distinct glass transition, followed by the appearance of a wide supercooled
liquid region and then a large exothermic peak due to crystallization. The glass transition temperature \(T_g\), onset temperature of crystallization \(T_x\) and heat of crystallization \(\Delta H_c\) are measured to be 412 K, 494 K and 3.46 kJ/mol, respectively. The appearance of the wide supercooled liquid region spanning 82 K clearly indicates that a bulky amorphous specimen can easily be prepared for the present alloy. The Vickers hardness \(H_v\) in the central region of the bulk amorphous ingot is measured to be 530 which is nearly the same as that (550) for the ribbon sample.

It is difficult to measure directly the cooling rate of the present molten alloy because of the use of arc electrode as a heat source. Consequently, we tried to estimate the cooling rate through the measurement of secondarily dendrite arm spacing for an Al-33 mass\%Cu alloy where a definite relation between the arm spacing and cooling rate has previously been reported\(^{[20]}\). The Al-Cu alloy ingot with the same parallelepiped shape was prepared in the same zone-melting condition as that for the present Zr-based alloy. The secondarily dendrite arm spacing in the central region is measured to be about 1.6 \(\mu\)m and hence the cooling rate is estimated to be about 1.9 \(\times\) 10\(^2\) K/s from the previous relation. This result indicates that the critical cooling rate for glass formation for the present Zr-Al-Ni-Cu-Pd alloy is below 1.9 \(\times\) 10\(^2\) K/s when heterogeneous nucleation of a crystalline phase does not come in. When the present critical cooling rate is compared in the relations between the critical cooling rate \(R_c\) and the reduced glass transition temperature \(T_g/\Delta T_c\) or the temperature interval of the supercooled liquid \(\Delta T_c\) which have been obtained for a number of amorphous alloys, it is confirmed that the present amorphous alloy belongs to the alloy group with large glass-forming ability.

In conclusion, the success of producing the bulk amorphous alloy by the zone melting method implies the elimination of the upper limitation of the sample shape for the metallic amorphous alloys. A further improvement of the preparation technique and the glass-forming ability is expected to cause a significant influence on the subsequent development in the science and engineering of amorphous metallic materials.

REFERENCES

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