

RAPID PUBLICATION

## Preparation of 16 mm Diameter Rod of Amorphous $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ Alloy

A. Inoue, T. Zhang, N. Nishiyama<sup>†</sup>,  
K. Ohba<sup>††</sup> and T. Masumoto

*Institute for Materials Research, Tohoku University, Sendai 980, Japan*

Bulky amorphous alloys in a cylindrical shape with diameters up to 16 mm were found to form by water quenching a  $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$  melt in a quartz tube. The amorphous phase of this alloy has the widest temperature interval of supercooled liquid region before crystallization. The glass transition temperature, crystallization temperature and Vickers hardness for the bulky amorphous alloy with a diameter of 16 mm are 625 K, 750 K and 465, respectively, being nearly the same as those for the corresponding melt-spun ribbon with a thickness of 30  $\mu\text{m}$ . The extremely large glass-forming ability is presumably due to a combination of significantly different atomic size ratios among the constituent elements and the necessity of redistribution of Al for the progress of crystallization. The finding of the extremely large glass-forming ability has a very important implication because it demonstrates the possibility of bulk amorphous alloy production by conventional casting processes.

(Received August 20, 1993)

**Keywords:** glass-forming ability, zirconium base alloy, bulky amorphous alloy, water quenching, low critical cooling rate

### I. Introduction

The search for new amorphous alloys with large glass-forming ability which enables the production of a bulky amorphous sample is quite important from materials science and engineering points of view. The glass-forming ability has a strong correlation with the stability of supercooled liquid against nucleation and growth reactions of a crystalline phase. There is a clear tendency for the glass-forming ability to increase with an increase in the temperature interval of the supercooled liquid region before crystallization for metallic amorphous alloys<sup>(1)</sup>. This tendency implies the importance of the search of an amorphous alloy with a wide supercooled liquid region before crystallization in the search of new amorphous alloys with larger glass-forming ability. Recently, we have reported that a supercooled liquid region above 90 K, which is wider than that for any other metallic amorphous alloys reported up to date, is obtained for amorphous alloys in the La-Al-Co-Ni-Cu<sup>(2)</sup> and Zr-Al-Ni-Cu<sup>(3)</sup> systems. The widest temperature interval of the supercooled liquid region defined by the difference between glass transition temperature ( $T_g$ ) and crystallization temperature ( $T_x$ ) has been reported to be 127 K for  $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ <sup>(3)</sup>. It is reasonable to expect for the La- and Zr-based amorphous alloys to have an extremely

large glass-forming ability which is superior to that of Pd- and Pt-based amorphous alloys which are previously known<sup>(4)</sup> to have a large glass-forming ability. More recently, we have performed a series of studies on the formation of bulky amorphous alloys by using various casting techniques such as water quenching of a melt in a quartz tube<sup>(5)</sup>, metallic mold casting<sup>(2)(6)(7)</sup> and high-pressure die casting<sup>(8)(9)</sup>. The application of the water quenching technique to the Zr-Al-Ni-Cu alloy with the widest supercooled liquid region was found to cause the formation of bulky amorphous alloys in a cylindrical shape with a diameter of 16 mm. This paper is intended to examine the critical cooling rate for formation of an amorphous phase as well as the structure, thermal stability and hardness for the cylindrical Zr-Al-Ni-Cu amorphous alloys with diameters of 10 and 16 mm and to investigate the possibility of producing a bulky amorphous alloy with a much larger cross-section.

### II. Experimental Procedure

A quaternary alloy with composition  $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$  was used in the present study because the amorphous alloy with this composition had the widest supercooled liquid region before crystallization. The ingot was prepared by arc-melting a mixture of pure metals in a purified argon atmosphere. The composition is nominally expressed in atomic percent. From the master alloy ingot, cylindrical samples with a length of 150 mm and different diameters ranging from 5 to 16 mm

<sup>†</sup> On leave from Teikoku Piston Ring Co., Ltd., Okaya 394, Japan.

<sup>††</sup> Graduate Student, Tohoku University.

were prepared by quenching the molten alloy in a quartz tube into flowing water. The amorphicity of the quenched cylindrical bulks was examined by X-ray diffraction and optical microscopy. Thermal stability associated with the sequential structural change in amorphous solid, glass transition, supercooled liquid and crystallization was measured at a heating rate of 0.67 K/s with a differential scanning calorimeter (DSC). The microstructure in the transverse cross section of the quenched cylindrical samples was also examined in an etched state by optical and scanning electron microscopy (OM, SEM). The etching was made for 30 s at 300 K in a hydrofluoric acid solution which was diluted with distilled water.

### III. Results and Discussion

It has been reported<sup>(10)</sup> that the critical cooling rate for formation of an amorphous phase,  $R_c$ , can be evaluated by measuring the change in the onset temperature of solidification,  $T_{xc}$  with cooling rate. Figure 1 shows the DTA curve of the Zr–Al–Ni–Cu amorphous alloy in a ribbon form of a thickness of 30  $\mu\text{m}$  produced by melt spinning. The offset temperature for fusion,  $T_L$ , upon heating at a constant rate of 0.33 K/s as well as  $T_{xc}$  upon cooling at different rates,  $R$ , can be accurately determined by differential thermal analysis. It is seen that  $T_{xc}$  decreases from 1135 to 1111 K with increasing cooling rate from 0.17 to 0.67 K/s. Based on the DTA data,  $R_c$  has been reported<sup>(10)</sup> to be evaluated from the following equation:

$$\ln R = \ln R_c - b / (T_L - T_{xc})^2.$$

Here,  $b$  is a constant.  $R_c$ , thus determined, is 1.5 K/s for

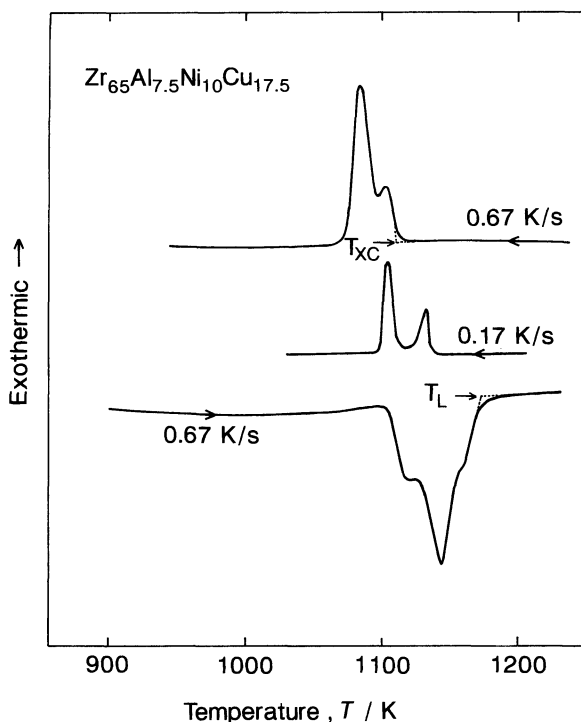


Fig. 1 Differential thermal analytical (DTA) curves of a  $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$  alloy.

the Zr–Al–Ni–Cu alloy. This  $R_c$  value is much lower than that (87 K/s)<sup>(1)</sup> for  $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$  with the wide supercooled liquid region of 69 K. The extremely low  $R_c$  value indicates the possibility of producing a bulky amorphous alloy with a thickness above 10 mm by casting, when the inhomogeneous nucleation of a crystalline phase is suppressed.

Figure 2 shows the external appearance of the cylindrical  $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$  alloy samples with diameters of 10 and 16 mm and a length of 150 mm which were prepared by water quenching. These bulk alloys have a good luster typical for metallic amorphous alloys and no distinct contrast revealing the precipitation of a crystalline phase is seen for any of the samples, indicating the formation of an amorphous structure even for the cylindrical sample with the large diameter of 16 mm. Figure 3 shows the X-ray diffraction patterns of the cylindrical alloys with diameters of 10 and 16 mm. The patterns consist only of broad peaks for both the samples and no diffraction peaks corresponding to crystalline

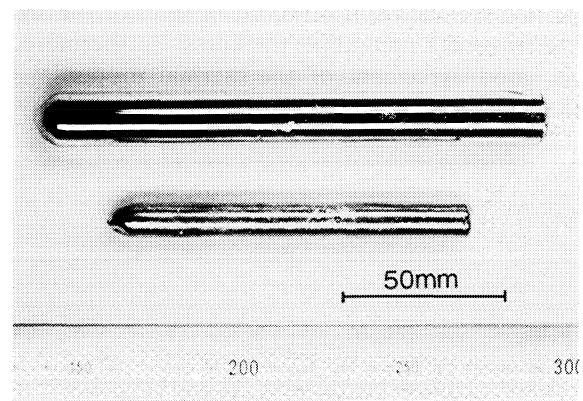


Fig. 2 External surface appearance of an amorphous  $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$  alloy in a cylindrical form with diameters of 10 and 16 mm and a length of 150 mm.

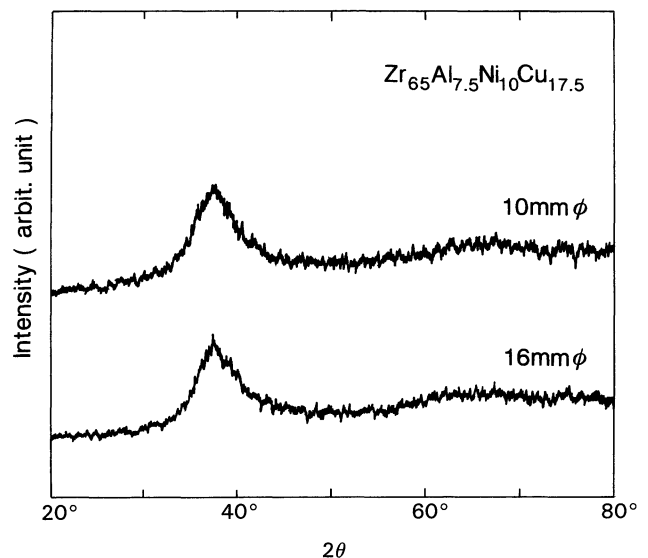


Fig. 3 X-ray diffraction patterns of the cylindrical  $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$  amorphous alloys with diameters of 10 and 16 mm.

phases are seen.

In order to confirm whether or not the bulky amorphous alloys consist only of an amorphous single phase, etched transverse cross sections were examined by OM. As shown in Fig. 4, most part of the cross-sectional areas are occupied by featureless contrast, indicating that the bulk alloys consist of an almost completely amorphous phase. This is consistent with the results obtained by X-ray diffractometry. However, a number of dark spots with a size below  $10\ \mu\text{m}$  and several bright regions with a size of about 20 to  $50\ \mu\text{m}$  are seen in the cross section, indicating that a small amount of crystalline phases may have precipitated rather homogeneously.

Figure 5 shows the DSC curves of the cylindrical  $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$  amorphous samples with diameters of 10 and 16 mm, along with the data of the melt-spun amorphous ribbon.  $T_g$  and  $T_x$  are 627 and 751 K, respectively, for the 10 mm cylinder and 625 and 750 K, respectively, for the 16 mm cylinder, being nearly the same as those (622 and 749 K) for the melt-spun ribbon. These results indicate that there is no distinct difference in the amorphous structure between the cylindrical amorphous alloys and the melt-spun ribbon, in spite of the significant difference in the sample thickness. Furthermore, the rather good agreement of the thermal properties also implies that the small precipitates do not have any ap-

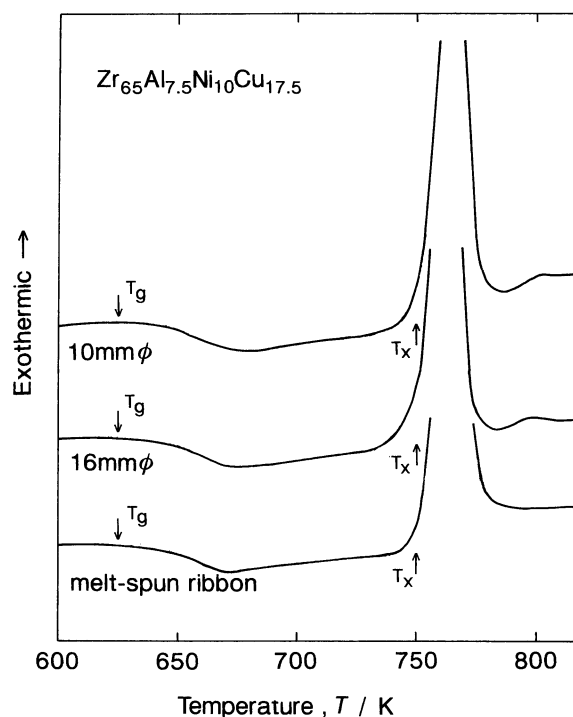


Fig. 5 DSC curves of the cylindrical  $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$  amorphous alloys with diameters of 10 and 16 mm. The data of the melt-spun ribbon are also shown for comparison.  $T_g$  values determined from the thermograms shown in Fig. 6 are marked with arrows.

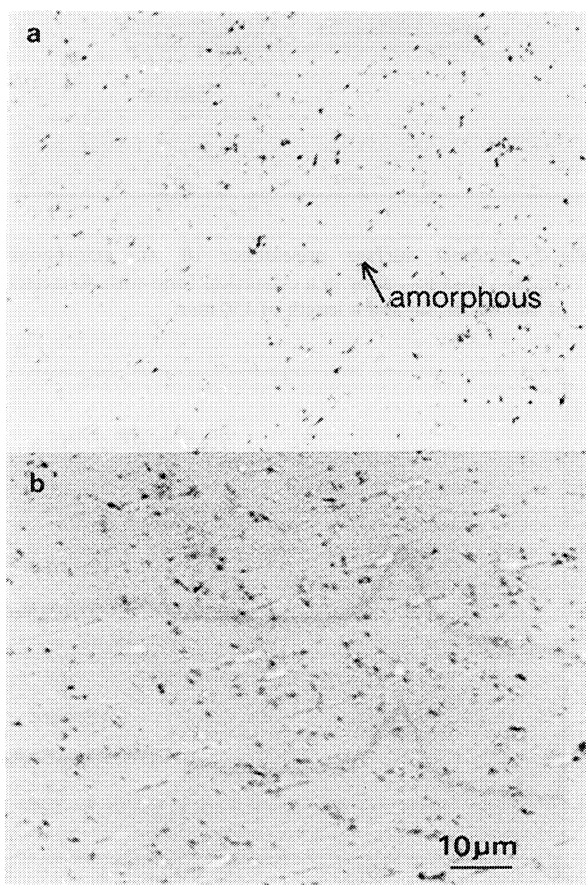


Fig. 4 Optical micrographs revealing the etched cross-sectional structure of the cylindrical  $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$  amorphous alloys with diameters of 10 mm (a) and 16 mm (b).

preciable harmful influence on the acceleration of the nucleation and growth reactions of a crystalline phase from the supercooled liquid state.

Although no distinct difference in  $T_g$  and  $T_x$  is seen between the bulky amorphous alloys and the melt-spun amorphous ribbon, it is expected that the heat of structural relaxation ( $\Delta H_r$ ) which is more sensitive to cooling rate changes significantly for both the samples. Figure 6 shows the thermograms of the cylindrical Zr–Al–Ni–Cu amorphous alloys with diameter of 10 and 16 mm, along with the data on the melt-spun ribbon.  $\Delta H_r$  defined by  $\int \Delta C_p (=C_{p,s} - C_{p,a}) dT$  where  $C_{p,s}$  and  $C_{p,a}$  are the heat capacities of the relaxed and as-quenched amorphous phases, respectively, is measured to be 89 J/mol for the 10 mm cylinder, 56 J/mol for the 16 mm cylinder and 1340 J/mol for the ribbon and decreases in the order of ribbon  $\gg$  10 mm cylinder  $>$  16 mm cylinder. It can therefore be said that the cooling rate in the temperature range below  $T_g$  is much lower for the cylindrical samples. The Vickers hardness ( $H_v$ ) is 465 for the 16 mm cylinder and 435 for the melt-spun ribbon. The slightly higher  $H_v$  value for the cylinder is mainly due to the formation of a more relaxed amorphous structure resulting from the lower cooling rate.

The maximum diameter (16 mm) for formation of the amorphous cylinder is about three times as large as the maximum thickness (5.3 mm)<sup>(11)</sup> for  $\text{Pd}_{60}\text{Ni}_{20}\text{P}_{20}$  which has previously been reported to be the largest value for metallic amorphous alloys. The extremely large glass-forming ability which enables the formation of an amor-

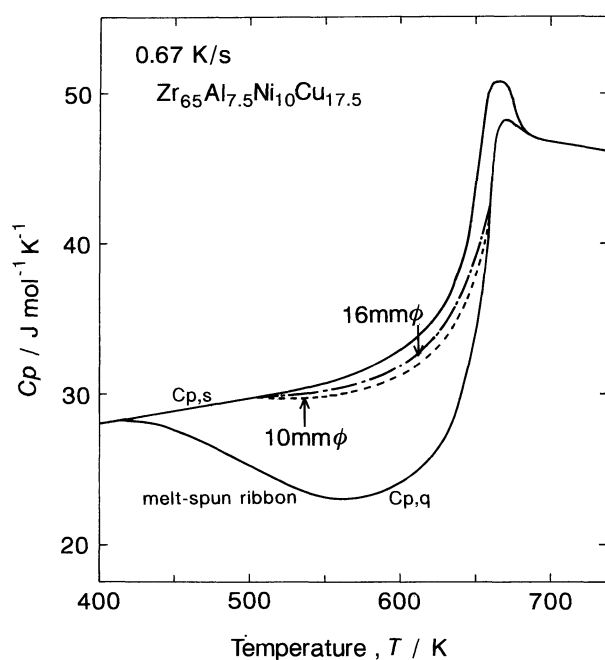


Fig. 6 The thermograms of the cylindrical  $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$  amorphous alloys with diameters of 10 and 16 mm. The data of the melt-spun ribbon are also shown for comparison.

phous phase even at very low cooling rates for the Zr–Al–Ni–Cu alloy has been interpreted<sup>(1)</sup> to be due to the combination of the three factors of significantly different atomic size ratios among the constituent elements, large negative heat of mixing and the necessity of distinct redistribution of Al for the progress of crystallization.

#### IV. Summary

The  $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$  alloy had the extremely low

critical cooling rate ( $R_c$ ) of 1.5 K/s and bulky amorphous Zr base alloys in a cylindrical shape with diameters up to 16 mm and a length of 150 mm were formed by water quenching. It is therefore concluded that the Zr–Al–Ni–Cu amorphous alloy with the widest supercooled liquid region reported previously by the present authors has an extremely large glass-forming ability. Finally, it is important to report that a cylindrical Zr–Al–Ni–Cu sample with a diameter of 30 mm and a length of 150 mm also contains an amorphous phase in the as-quenched state, in addition to a crystalline phase. Accordingly, the suppression of inhomogeneous nucleation of the crystalline phase is expected to cause the formation of a mostly single amorphous phase even for the bulk sample with a much larger thickness than 16 mm.

#### REFERENCES

- (1) A. Inoue, T. Zhang and T. Masumoto: *J. Non-Cryst. Solids*, **156–158** (1993), 473.
- (2) A. Inoue, T. Nakamura, T. Sugita, T. Zhang and T. Masumoto: *Mater. Trans., JIM*, **34** (1993), 531.
- (3) T. Zhang, A. Inoue and T. Masumoto: *Mater. Trans., JIM*, **32** (1991), 1005.
- (4) H. S. Chen: *Rep. Prog. Phys.*, **3** (1980), 353.
- (5) A. Inoue, K. Kita, T. Zhang and T. Masumoto: *Mater. Trans., JIM*, **30** (1989), 722.
- (6) A. Inoue, A. Kato, T. Zhang, S. G. Kim and T. Masumoto: *Mater. Trans., JIM*, **32** (1991), 609.
- (7) A. Inoue, T. Saito, H. Yamamoto and T. Masumoto: *J. Mater. Sci. Lett.*, **12** (1993), 946.
- (8) A. Inoue, T. Nakamura, N. Nishiyama and T. Masumoto: *Mater. Trans., JIM*, **33** (1992), 937.
- (9) A. Inoue, T. Nakamura, T. Sugita, N. Nishiyama and T. Masumoto: *Amorphous Metallic Materials III*, ed. by P. Duhaï, Trans Tech Publications, Switzerland, (1993), p. 147.
- (10) G. Fonteneau, A. Bouaggad and J. Lucas: *Proc. 4th Int. Symposium Halide Glasses*, Monterey, CA, (1987), p. 72.
- (11) A. J. Drehman, A. L. Greer and D. Turnbull: *Appl. Phys. Lett.*, **41** (1982), 716.