Production of Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$ Glassy Alloy Rod of 30 mm in Diameter by a Cap-Cast Technique

Yoshihiko Yokoyama$^1$, Enrico Mund$^2$, Akihisa Inoue$^1$ and Ludwig Schultz$^2$

$^1$Institute for Materials Research, Tohoku University, Katahira, Aobaku, Sendai 980-8577, Japan
$^2$ IFW Dresden, Institute for Metallic Materials, P.O. Box 270116, D-01171 Dresden, Germany

In order to produce bulk glassy alloys with diameters above 1 cm, various cast techniques have been developed. The maximum diameter of Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$ alloy achieved was 16 mm by the copper metallic mold cast technique and 20 mm by the tilt cast technique. In order to produce a much larger sized bulk glassy alloy, a cap-cast technique, leading to the achievement of a higher cooling rate even in an upper region, was developed through the modification of the tilt casting technique. This paper presents the production of a glassy Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$ alloy rod with a diameter of 30 mm. [doi:10.2320/matertrans.MRP2007164]

(Received July 12, 2007; Accepted October 9, 2007; Published November 25, 2007)

Keywords: bulk glassy alloy, large scale rod, cap casting, high purity alloy

1. Introduction

Since the first synthesis of Zr-based bulk glassy alloy (BGA)$^{11}$ in 1990, a variety of Zr-based BGAs have been reported$^{1-6}$ by modification of alloy composition. Especially, Zr-TM-Al (TM: Ni, Cu, Pd, Nb, Ti) bulk glassy alloys have an outstanding advantage to realize high strength of over 2 GPa, high fracture toughness of over 100 MPa$\cdot$m$^{1/2}$ and high fatigue limit over 1 GPa.$^{7-9}$ Thus, the Zr-based bulk glassy alloys have been characterized to be new typical as cast state alloys with high performance for industrial application. Furthermore, since neither grain boundary nor crystalline anisotropy is recognized in the glassy alloy, the alloys have very smooth surface on nano-meter scale.$^{10}$ In addition, the Newtonian flow of super cooled liquid has enabled to high level of nano-meter scale imprimatibility.$^{11}$ The most appropriate application field of bulk glassy alloys seems to be small size of parts in high-performance machines.$^{12}$

Inoue et al. have succeeded in the industrial applications of Zr-based BGAs for micro geared motor$^{10}$ and pressure sensor.$^{13}$ It is confirmed that the performances of these industrial parts are much higher in comparison with those of crystalline alloys. The Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$ BGA,$^{14}$ which has been named as Inoue alloy in the world, exhibits high glass-forming ability, high toughness, high strength, high resilience and high reliability. It is known that industrial applications of the Zr-based BGA have been extended to golf clubs,$^{15}$ optical parts,$^{16}$ pressure sensors$^{13}$ and so on. Based on high glass-forming ability of this alloy, the critical diameter size is estimated to be 16 mm by the conventional metallic mold cast technique. This study aims to investigate an improved cast process for the production of large scale Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$ BGA.

2. Experimental Procedure

A quaternary Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$ alloy ingot was prepared by arc melting the mixture of pure Zr, Cu, Ni and Al elements in an argon atmosphere. To minimize the oxygen effect, pure Zr metal with low oxygen content (less than 45 mass ppm) was used for the preparation of the master alloy. The purity of these metals; Zr(+Hf), Cu, Ni and Al were 99.99 mass%, 99.999 mass%, 99.99 mass% and 99.999 mass%, respectively. The alloy ingots were completely remelted, and cast into cylindrical rod samples with diameters from φ16 mm to φ30 mm by a modified cap-casting method, as shown in Fig. 1. The cap-cast technique was designed to obtain high cooling rate even at the upper part of cast specimen. The cast structure was examined by scanning electron microscopy (SEM), and the compositions of the quenched samples were determined with an electron probe microanalyzer (EPMA). The phase identification of the cast samples was performed by X-ray diffractometry. Oxygen concentration of the bulk glassy alloys was measured by a helium carrier fusion-infrared absorption. Microscopic cast structures were examined by transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) using a JEOL 4000 FX. TEM samples were prepared by an electrolytic polishing machine using nitric methanol (30 vol% HNO$_3$) at about 250 K.

Fig. 1 Schematic illustration of a newly designed cap-cast technique.
3. Results and Discussion

As the first step for fabrication of large-sized $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_{5}\text{Al}_{10}$ BGAs, the purity and homogeneity of the master alloys were investigated. We observed the surface morphology of the as-solidified master alloys because the master alloy is frequently observed vitrification and then metallic luster of the surface is associated with the degree of vitrification of master alloy. If the quality of master alloy is not sufficient a well shining vitrified surface cannot be recognized.\textsuperscript{17)} In this study, raw materials were carefully purified to achieve a large-sized $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_{5}\text{Al}_{10}$ BGA.

Figure 2(a) shows an outer appearance of the Zr$_{55}$Cu$_{30}$Ni$_5$Al$_{10}$ ingots. (a, d) arc-melted ingots, (b, e) cross sectional images, (c, f) magnified SEM images of glassy region of Zr$_{55}$Cu$_{30}$Ni$_5$Al$_{10}$ ingots. (a, b, c): high purity type ingot including about 150 mass ppm oxygen, (d-g): low purity type ingot including about 1500 mass ppm oxygen.\textsuperscript{17)}

In this study, raw materials were carefully purified to achieve a large-sized Zr$_{55}$Cu$_{30}$Ni$_5$Al$_{10}$ BGA. Figure 2(a) shows an outer view of the Zr$_{55}$Cu$_{30}$Ni$_5$Al$_{10}$ master alloy with mirror like surface, and (b) and (c) shows the cross sectional optical micrograph (OM) and SEM images, respectively, indicating the formation of a single glassy phase in the half topside of master alloy. Here, it is important to point the difficulty of producing the master alloy with good luster in the case of the increased oxygen concentration of about 1500 mass ppm, as shown in Fig. 2(d). Figure 2(e) and (f) show OM and SEM images for a master alloy with more than 1500 mass ppm oxygen concentration. Vitrification of the master alloy was started during unidirectional solidification of columnar structure with B2 structure, which was transformed to martensitic B19' and other phases after solidification.\textsuperscript{17)} Although the cross sectional OM image shows the distinct interface between the columnar and the glassy phase regions, the glassy phase region includes fine $\gamma_1$-crystalline phase, which cannot be observed in the high-purity master alloy. The precipitation of crystalline $\gamma_1$-phase\textsuperscript{18)} is strongly dependent on oxygen content in master alloy. Therefore, we used only the high-purity type master alloy in the subsequent study.

Figure 3 shows an outer appearance of the cast Zr$_{55}$Cu$_{30}$Ni$_5$Al$_{10}$ bulk glassy alloy of 20 mm in diameter. Besides, Fig. 3(b) shows an OM image of the cross section, which is located at 10 mm from the bottom side of the cast rod. Neither, crystalline inclusion nor void is seen in the cross section. The X-ray diffraction pattern shown in Fig. 3(c) consists only of distinct halo peaks indicating the formation of a high quality of glassy phase in the cast alloy. We further examined the possibility of producing the larger sized glassy alloy. As shown in Fig. 4(a), we succeeded in producing a larger sized glassy alloy rod of 30 mm in diameter by the cap-cast technique. Figure 4(b) shows the absence of crystalline inclusion over the cross sectional area at the site of 10 mm from the bottom side. The X-ray diffraction pattern of the cross section shown in Fig. 4(c) is also composed of no Bragg peaks implying the formation of the single glassy phase. Figure 5 shows a HRTEM image of the Zr$_{55}$Cu$_{30}$Ni$_5$Al$_{10}$ BGA of 30 mm in diameter. The HRTEM was cut from the center area at the site of 10 mm from the bottom side corresponding to the site of Fig. 4(b). The HRTEM image shows typical mazelike contrast of a glassy single structure and no appreciable fringe marks is seen even on nanometer scale. The X-ray diffraction pattern as well as the HRTEM image reveals that the cast Zr$_{55}$Cu$_{30}$Ni$_5$Al$_{10}$ BGA of 30 mm in diameter consists only a single glassy phase. However, there is a possibility of the structural deviation in such a large sized cast glassy alloy. We are trying to clarify the nanoscale structural deviation over the whole cast sample even at present.
4. Summary

In order to produce a large sized cast Zr-based glassy alloy, we designed a cap cast technique. The results obtained are summarized as follows.

1) The purity of alloy component was an important factor to produce the large sized cast alloy and the decline in the purity caused the precipitation of $\text{Cr}_2\text{Si}_3$ intermetallic compound.

2) We produced a $\text{Zr}_{55}\text{Cu}_{35}\text{Ni}_5\text{Al}_{10}$ glassy alloy rod of 30 mm in diameter by the cap-cast technique, though the critical size of $\text{Zr}_{55}\text{Cu}_{35}\text{Ni}_5\text{Al}_{10}$ glassy alloy rod was 20 mm by the conventional cast technique.

Acknowledgement

This research was funded in part by Grant-in-Aid for Scientific Research on Priority Area (Materials Science of Bulk Metallic Glasses) and Grant-in-Aid for Exploratory Research from the ministry of Education, Culture, Sports, Science and Technology, and NEDO (the New Energy and Industrial Technology Development Organization).

REFERENCES