Cap Casting and Enveloped Casting Techniques for Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$ Glassy Alloy Rod with 32 mm in Diameter

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Abstract. In order to produce centimetre-sized bulk glassy alloys (BMGs), various cast techniques have been developed. We succeed in the development of cap casting and enveloped casting technique to accomplish the fabrication of centimetre sized BMGs. The former has an advantage to increase cooling rate and the later has an advantage to joint another materials instead of welding. This paper presents the production of a glassy Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$ alloy rod with a diameter of 32 mm and joined glassy Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$ alloy parts with another materials for industrial applications.

1. Introduction

Since the first synthesis of Zr-based bulk glassy alloy (BMG) [1] in 1990, a variety of Zr-based BMGs 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 [7], high fracture toughness of over 100 MPa m$^{0.5}$ [8] and high fatigue limit of over 1 GPa [9]. Thus, the Zr-based bulk glassy alloys have been characterized to be a new type alloys with high performance for industrial applications. Furthermore, since neither grain boundary nor crystalline anisotropy is recognized in the glassy phase, the alloys have very smooth surface on a nano-meter scale [10]. In addition, the Newtonian flow of supercooled liquid has enabled high level of nano-meter scale imprintability [11]. One of the appropriate application fields of bulk glassy alloys seems to be small size parts in high-performance machines [12].

Inoue et al. have succeeded in the industrial applications of Zr-based BMGs for micro geared motor [10] and pressure sensor [13]. It is confirmed that the performance/characteristics of these industrial parts are much better in comparison with those for crystalline alloys. The Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$ BMG [14], which has been named as Inoue alloy in the world, exhibits superior performance with combination of high glass-forming ability, high toughness, high strength, high resiliency and high reliability. It is known that industrial applications of the Zr-based BMG have been extended to golf clubs [15], optical parts [16], pressure sensors [13] and so on. In particular, the Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$ BMG enables the preparation of centimetre-sized cast samples of diameter 30 mm using the suction casting [17] and cap casting [18] techniques.

This study aims to investigate the usefulness of an improved cast process for the production of large scale Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$ BMG and its joint with another materials.

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2. Experimental Procedure

Quaternary Zr_{55}Cu_{30}Ni_{5}Al_{10} master alloys were 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 40 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 master alloys were completely remelted, and cast into cylindrical rod shape with diameters up to $\phi 32$ mm. The cap-cast technique was designed to obtain high cooling rate even at the upper region of cast rod. The cast structure was examined by optical microscope (OM) and scanning electron microscopy (SEM). The compositions of the quenched samples were determined by an electron probe microanalyzer (EPMA). The phase identification of the cast samples was performed by X-ray diffractometry (18kw, rotating Cu target). Oxygen concentration of the bulk glassy alloys was measured by a fusion in helium gas-infrared absorption method.

3. Results and Discussion

As the first step for the fabrication of large-sized Zr_{55}Cu_{30}Ni_{5}Al_{10} BMGs, the purity and homogeneity of master alloys were investigated. We observed the surface morphology of the as-solidified ingots to examine the degree of mirror image meaning the vitrification. If the quality of master alloy is not sufficient a good shining lustre surface cannot be recognized [19]. In this study, raw materials were carefully purified to achieve a large-sized Zr_{55}Cu_{30}Ni_{5}Al_{10} BMG. Figure 1 (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) after etching by nitric-hydrofluoric acid (30 vol. % HNO3 + 5 vol. % HF aqua) at room temperature 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 lustre in the case of the increased oxygen concentration of about 1500 mass ppm, as shown in Fig. 1 (d). Figure 1 (e) and (f) show OM and SEM images for the 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 [20]. Although the cross sectional OM image shows the distinct interface between the columnar and the glassy phase regions, the glassy phase region includes a lot of $\tau_3$-crystals. The precipitation of crystalline $\tau_3$-phase [21] is strongly dependent on oxygen content in master alloy. Consequently, we conclude that the high-purity and surface-vitrified master alloy is necessity factor for the fabrication of centimeter sized BMG to reduce the probability of heterogeneous nucleation during glassy solidification.

![Figure 1](image-url)
By making full use of the quality control for master alloy, we succeeded in the production of a larger sized glassy alloy rod of 32 mm in diameter by the cap cast technique, as shown in Fig. 2(a). Figure 2 (a) shows outer view of cap cast BMG and copper cap die just after casting. We cut cap cast sample with length about 25 mm, shown in Figs. 2(b) and (c). In order to confirm the glassy structure of cap cast BMG, we measure X-ray diffraction patterns shown in Fig. 3. X-ray diffraction patterns were taken from the near surface and core regions in middle height cross sectional zone. We can see broad halo patterns without trace of Bragg peaks corresponding to any nanocrystallization.

Furthermore, we tried to apply the enveloped casting technique for BMG. Since the enveloped casting method can use the BMG only for a partial place needed, it enables reduction of cost for...
industrial application. Figure 4(a) shows the model of artificial hip joint, left is the inner core parts made by biomedical stainless steel, and the ball head is enveloped by Zr_{55}Cu_{30}Ni_{5}Al_{10} BMG (right part). The advantage of BMG using for biomedical joint part is surface flatness in atom scale to reduce the formation of debris by wear-abrasion. Accordingly, we tried to use the BMG only for the surface of ball parts by enveloped casting process. Figure 4(b) shows joined parts between the brass and Zr_{55}Cu_{30}Ni_{5}Al_{10} BMG produced by quick cast-in insertion process. Since there is no alloying reaction between the brass and Zr_{55}Cu_{30}Ni_{5}Al_{10} BMG, the interface of joint is not embrittled. It is one of the suitable ways to joint BMG to another materials instead of welding. At last, by using a water-cooled copper core parts, we can produce the ring shaped BMG with outer diameter of 45 mm, inner diameter of 17 mm and thickness of 10 mm. Consequently, we will be able to fabricate much more enlarged BMG and further complicate joint BMG parts by combination of these advanced cast techniques.

4. Summary
In order to produce centimeter sized Zr_{55}Cu_{35}Ni_{5}Al_{10} BMGs and those joined parts, we designed cap casting and enveloped casting techniques. The results obtained are summarized as follows.
(1) We succeeded in the fabrication of a Zr_{55}Cu_{35}Ni_{5}Al_{10} BMG rod of 32 mm in diameter by the cap casting technique.
(2) We can produce some joint parts between the Zr_{55}Cu_{35}Ni_{5}Al_{10} BMG and other metallic materials by the enveloped casting technique.

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