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Materials

Bulk metallic glass rings prepared by a modified water quenching method

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Abstract: Bulk metallic glass rings have the potential applications as annular gasket and active solder in special fields. The bulk metallic glass ring of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ with the outer diameter, the inner diameter, and the thickness of 38, 36, and 5 mm, respectively, was prepared by using a special shaped quartz tube water quenching method. The mechanical properties along the whole cross section were investigated by a nanoindentation method, and no evident variation of the Young's modulus and hardness was found, further indicating the single amorphous structure. Amorphous ring and tube-shape parts with different dimensions can be produced by this method.

Key words: bulk metallic glass; machine parts; water quenching; mechanical properties

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1. Introduction

Bulk metallic glasses (BMGs) have excellent mechanical properties such as high yield strength and high elastic limit (about 2% elastic strain limit in tension or compression), as well as good wear and corrosion resistance, which could be used in fine optical machinery parts, writing tools, sporting goods, and electrodes for generation of chloride gas [1-4]. Although it is now possible to fabricate BMGs with diameters of several millimeters, even several centimeters at certain chemical compositions, such as $Pd_{40}Cu_{30}Ni_{10}P_{20}$ [5] and $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ [6], the shapes of most metallic glasses fabricated by conventional copper-mold casting and water quenching method are rather simple, which limits their large-scale industrial applications. In order to overcome the limitation of the shape, the development and reformation of appropriate techniques are imperative.

Among various shapes, the ring form is especially well known. For example, some ferromagnetic glassy alloys with good soft magnetic properties are expected to be a new type of magnetic core with a metallic glass ring form. Several methods for the ring-shape fabrication of BMGs have been developed. For example, Zhang *et al*. have successfully produced a 1-mm wall-thick bulk $Zr_{55}Al_{10}Ni_5Cu_{30}$ metallic glass ring by centrifugal casting [7], and Wu *et al*. have prepared bulk $Fe_{75.5}Ga_3P_{10.5}C_4B_4Si_3$ metallic glass ring with the outer diameter of 10 mm, the inner diameter of 6 mm, and the thickness of 1 mm by copper mold casting [8]. Moreover, BMGs rings can also be made by mechanical machining from the cast plate [9]. In the present research, we have tried to prepare the bulk $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ metallic glass ring by a modified water quenching method using a special shaped quartz tube and investigated its mechanical properties.

2. Experimental procedure

A $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ (at%) alloy was used in the present study for its high glass forming ability [6]. The ingot was prepared by arc-melting a mixture of the pure elements Zr, Ti, Cu, Ni, and Be with a purity of at least 99.9% in titanium-gettered argon atmosphere. A schematic illustration of the set-up for preparation of metallic glass rings is shown in Fig. 1. There is a ring-shape groove at the bottom of the quartz tube, where D_1 is the entrance diameter of the quartz tube, and D_2 and D_3 are the inner and outer diameters of the ring-shape groove, respectively. The fabrication method of bulk metallic glass rings was

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somewhat similar to melt infiltration casting [10-11]. The pre-alloyed ingot was scrapped and then placed in the quartz tube. Prior to heating, the quartz tube was evacuated and then purged with argon gas. The assembly of the tube was heated to approximately 1123 K, which is higher than the liquidus temperature of the BMG, and then held for 10 min to allow the BMG to melt completely. After that the argon gas with a positive pressure of 0.2 MPa was applied to push the BMG melt to infiltrate through the ring-shape groove and the pressure was maintained for 5 min. Then, the assembly of the quartz tube was quickly removed from the resistive furnace and quenched in a supersaturated brine solution. A bulk metallic glass ring with the outer diameter of 38 mm, the inner diameter of 36 mm, and the thickness of 5 mm can be obtained accordingly.

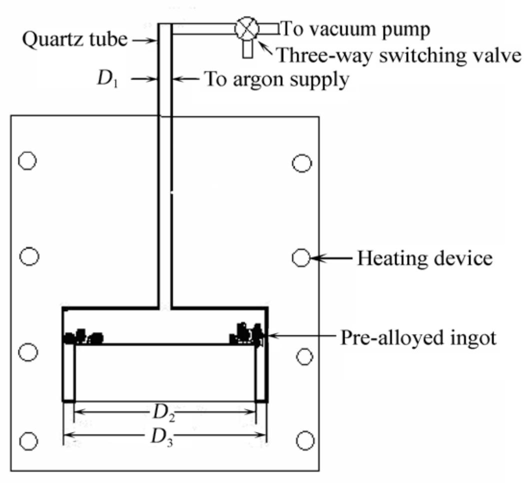

Fig. 1. Schematic illustration of the set-up for preparation of metallic glass ring.

The amorphous structures of the inner and outer surfaces and the cross section were identified by an MXP21 VAHF X-ray diffractometer with Cu K_α radiation. The cross section of the sample was mechanically polished for mechanical properties tests. Nanoindentation tests were conducted using an MTS Nano Indenter XP with a Berkovich diamond tip at 100 μm spacing from the outer surface to the inner surface. The specimens were indented to the depth of 500 nm at a constant displacement rate of 10 nm/s. The hardness and elastic modulus were measured using the continuous stiffness option, which yields the elastic modulus and hardness as a function of indentation depth.

3. Results and discussion

The outer morphology of the as-cast $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ ring with the outer diameter of 38 mm, the inner diameter of 36 mm, and the thickness of 5 mm is shown in Fig. 2, which exhibits a good luster. Fig. 3 shows the X-ray diffraction (XRD) patterns taken from the outer surface, the cross section, and the inner surface of the bulky $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ ring. The patterns from outer and inner surfaces and the cross section consist only of a broad diffraction maximum characteristic of amorphous structure and no distinct crystalline peak is seen for the cast ring (within the limits of XRD detection). These results indicate that this ring is composed of a single amorphous phase.

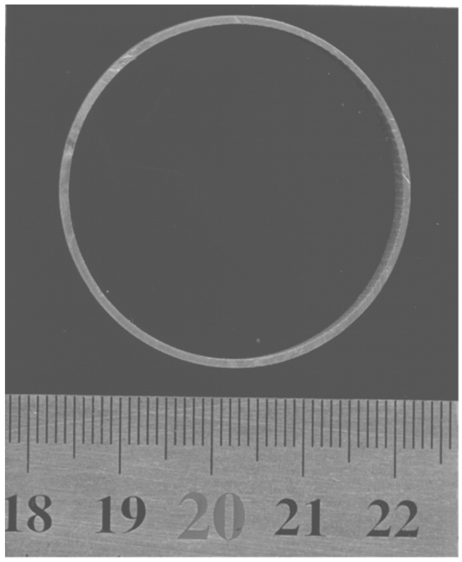

Fig. 2. Outer morphology of the as-cast $Zr_{41.2}Ti_{13.8}Cu_{12.5}$-$Ni_{10.0}Be_{22.5}$ metallic glass ring.

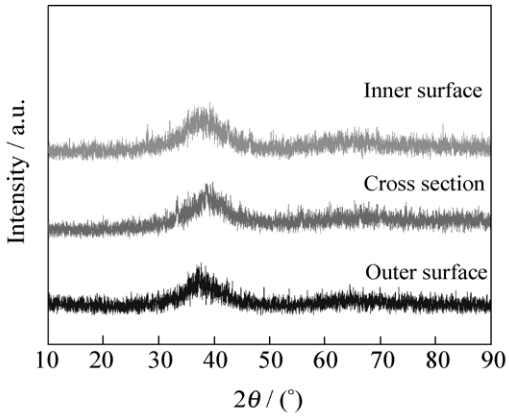

Fig. 3. XRD patterns taken from the outer surface, the cross section, and the inner surface of the cast $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ alloy ring.

The $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ alloy exhibited excellent glass forming ability, and a cylindrical specimen of at least 14 mm in diameter could be prepared by water quenching method [6]. The quartz tube had large enough surface area to contact the brine solution during water quenching (as shown in Fig. 1), so a bulk metallic glass ring with large dimension in wall-thickness could be obtained by this method owing to high cooling rate. However, the outer and inner diameters and the thickness in ring form were almost not limited by cooling rate, so amorphous tube-shape parts with larger dimensions in thickness could also be produced by this method.

In this article, nanoindentation tests were used to study the material mechanical properties along the whole cross section of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ ring. Young's modulus and hardness profiles as a function of the distance from the outer surface to the inner surface for the as-cast ring are presented in Fig. 4. No evident variation of the Young's modulus and hardness are found, further indicating the single amorphous structure along the whole cross section. However, the Young's modulus and hardness values near the inner surface are slightly higher than that near the outer surface, which is likely due to the difference in cooling rate. It is more difficult to conduct heat for the inner surface resulting from the special shaped quartz tube (as shown in Fig. 1), resulting in a lower quenching rate, so the structure near inner surface can be expected denser, with a higher Young's modulus and hardness, which is corresponding to Golovin's results [12]. At the same time, the Young's modulus and hardness at the inner surface are lower than that near the inner surface, which is also due to a quicker cooling rate at the inner surface. The averaged Young's modulus value across the sample is about 115 GPa, which is larger than the value of 101 GPa obtained in a precision ultrasonic investigation of bulk glassy samples with the same normal composition [1]. The reason may be attributed to the effect of pile-up around the indents or plastic flow during nanoindentation [13-15].

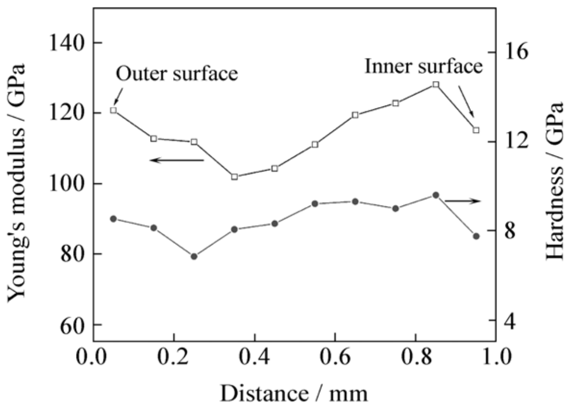

Fig. 4. Young's modulus and hardness profiles as a function of the distance from the outer surface to the inner surface for the as-cast ring.

Metallic glass rings with the thickness of 0.5 mm can be fabricated by wire electro-discharge machining of the as-cast ring, as shown in Fig. 5. The homogeneous amorphous structure and a lack of cast defects such as shrinkage porosity make the wire electro-discharge machining process successfully. The thinner rings have the potential applications as annular gasket and active solder in special fields.

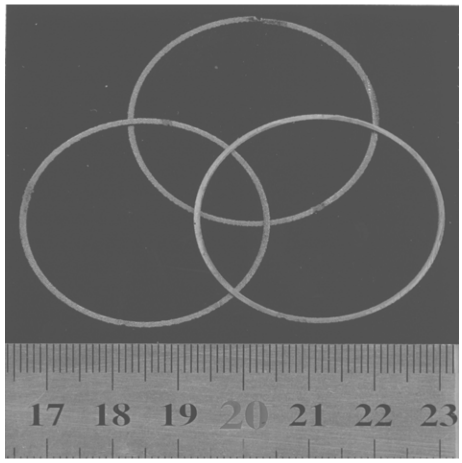

Fig. 5. Photograph of metallic glass rings with the thickness of 0.5 mm fabricated by wire electro-discharge machining of the as-cast ring.

4. Conclusions

A fully amorphous ring of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}$-$Be_{22.5}$ with the outer diameter, the inner diameter, and the thickness of 38, 36, and 5 mm, respectively, has been successfully prepared by a modified water quenching method using a special shaped quartz tube. The mechanical properties along the whole cross section were investigated by a nanoindentation method, and no evident variation of the Young's modulus and hardness were found. Metallic glass rings with the thickness of 0.5 mm can be fabricated by wire electro-discharge machining of the as-cast ring, which have the potential applications as annular gasket and active solder in special fields. Amorphous ring and tube-shape parts with different dimensions can be produced by this method.

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References

[1] W.L. Johnson, Bulk glass-forming metallic alloys: science and technology, *Mater. Res. Bull*., 24(1999), No.10, p.42.

[2] A. Inoue, *Bulk Amorphous Alloys*, Trans. Tech. Publ. Ltd., Switzerland, 1998, p.2.

[3] M.F. Ashby and A.L. Greer, Metallic glass as structural materials, *Scripta. Mater.*, 54(2006), No.3, p.321.

[4] Y. Zhang, D.Q. Zhao, R.J. Wang, and W.H. Wang, Formation and properties of $Zr_{48}Nb_8Cu_{14}Ni_{12}Be_{18}$ bulk metallic glass, *Acta Mater.*, 51(2003), No.7, p.1971.

[5] A. Inoue, N. Nishiyama, and H. Kimura, Preparation and

thermal stability of bulk amorphous $Pd_{40}Cu_{30}Ni_{10}P_{20}$ alloy cylinder of 72 mm in diameter, *Mater. Trans. JIM*, 38(1997), No.2, p.179.

[6] A. Peker and W.L. Johnson, A highly processable metallic glass: $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$, *Appl. Phys. Lett.*, 63(1993), No.17, p.2342.

[7] Q.S. Zhang, D.Y. Guo, A.M. Wang, H.F. Zhang, B.Z. Ding, and Z.Q. Hu, Preparation of bulk $Zr_{55}Al_{10}Ni_5Cu_{30}$ metallic glass ring by centrifugal casting method, *Intermetallics*, 10(2002), No.11-12, p.1197.

[8] S.S. Wu, B.L. Shen, and A. Inoue, Preparation and properties study of bulk $Fe_{75.5}Ga_3P_{10.5}C_4B_4Si_3$ metallic glass ring by copper mold casting, *Intermetallics*, 12(2004), No.10-11, p.1261.

[9] A. Urata, N. Nishiyama, K. Amiyaa, and A. Inoue, Continuous casting of thick Fe-base glassy plates by twin-roller melt-spinning, *Mater. Sci. Eng. A*, 449-451(2007), p.269.

[10] R.B. Dandliker, R.D. Conner, and W.L. Johnson, Melt infiltration casting of bulk metallic glass matrix composites, *J. Mater. Res*., 13(1998), No.10, p.2896.

[11] M.L. Wang, G.L. Chen, X. Hui, Y Zhang, and Z.Y. Bai, Optimized interface and mechanical properties of W fiber Zr-based bulk metallic glass composites by minor Nb addition, *Intermetallics*, 15(2007), No.10, p.1309.

[12] Y.I. Golovin, V.I. Ivolgin, V.A. Khonik, K. Kitagawa, and A.I. Tyurin, Serrated plastic flow during nanoindentation of a bulk metallic glass, *Scripta. Mater*., 45(2001), No.7, p.947.

[13] A. Schuh and T.G. Nieh, A survey of instrumented indentation studies on metallic glasses, *J. Mater. Res.*, 19(2004), No.1, p.46.

[14] B.C. Wei, T.H. Zhang, W.H. Li, Y.F. Sun, Y. Yu, and Y.R. Wang, Serrated plastic flow during nanoindentation in Nd-based bulk metallic glasses, *Intermetallics*, 12(2004), No.10-11, p.1239.

[15] L. Liu and K.C. Chan, Plastic deformation of Zr-based bulk metallic glasses under nanoindentation, *Mater. Lett*., 59(2005), No.24-25, p.3090.