The influence of casting temperatures on microstructures and mechanical properties of $Cu_{50}Zr_{45.5}Ti_{2.5}Y_2$ alloy prepared using copper mould casting

Z.W. Zhu[1, 2], H.F. Zhang[1, *], H. Wang[2], B.Z. Ding[1], Z.Q. Hu[1]

[1]Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China

[2]Faculty of Engineering and Surveying, The University of Southern Queensland, Toowoomba, Queensland, 4350, Australia

*Corresponding author. Fax: +86-2423971783 E-mail: hfzhang@imr.ac.cn.

Abstract

We investigated the influence of casting temperatures on microstructures and mechanical properties of rapidly solidified $Cu_{50}Zr_{45.5}Ti_{2.5}Y_2$ alloy. With casting temperatures increasing, the content of the crystalline phase decreases. At high casting temperature, i.e., 1723 K, glass forming ability (GFA) of the present alloy enhanced. It is implied that adjusting casting temperatures could be used for designing the microstructures of bulk metallic glass matrix composite (BMGC). Nano-indentation tests indicated that CuZr phases is a little softer and can accommodate more plastic deformation than the amorphous matrix. Compression tests confirmed that this kind of the second phase (CuZr) precipitated under lower casting temperatures helps to initiate multiple shear bands, resulting in great improvement of mechanical properties of the samples. Our work indicate that casting temperatures lead a great influence on GFA, microstructures and mechanical properties of rapidly solidified alloy and controlling casting temperatures is crucial to the application of BMGs.

Introduction

Properties of materials depend on their microstructures and microstructures are closely correlated to the process to manufacture the materials. Many processing methods, for example, quenching, annealing, cold rolling, etc., are developed to achieve the desired microstructures, further leading to obtaining the properties as expected.[1] Of which, melt treatment including ultrasonic vibration treatment[2] and superhigh temperature treatment[3-5] etc., is evidenced to be an effective way in changing the microstructures and improving the properties of Al-, Ni-, Fe-based alloys and have widely used in industrial production.

Metallic glass (MG) has been developed for almost 50 years.[6] Like steel industry, the database among process, microstructure and property for bulk metallic glasses (BMGs) should be built up in order to promote its commercial applications.[7] In the past few decades, the researchers in this field concentrate on how to discover alloy compositions with large glass forming ability in all common alloys based systems and building up the relationship of microstructures to properties.[8-10] Some great progress have been achieved, for example, BMG successfully developed in many alloy systems including Al, Fe, Ni, Cu, Zr, Mg, Re (rare earth metals) etc. -base alloys, the size of BMGs increasing from micron to inch[8-10] and the improvement of plasticity of BMGs by developing bulk metallic glass matrix composite reinforced with particle[11], fiber[12] etc.. However, only a few concerns on the relationship of properties of BMGs to their process techniques have been paid. Shen et al[13] studied the effect of cooling rate on plasticity of TiCu-based BMG. Popel et al[3-5] reported that the quenching temperature's effect on microstructure of Al and Fe-based ribbons. In fact, the knowledge on this aspect must be set up because it is crucial to boost BMGs' applications. As a result, we systematically studied the casting conditions on microstructures and properties of BMGs. In our two previous papers[14, 15], we argued that the relationship of casting temperatures to nano-crystal formation in the amorphous matrix and thermal stability of amorphous alloys. It is concluded that high casting temperature can effectively put out the degree of heterogeneity in alloy melts, leading to the enhancement of thermal stability and the decrease in plasticity of resultant amorphous alloys. As a consecutive work, in this paper, we further concentrate on the influence of casting temperatures on glass forming ability. Furthermore, we discuss the relationship of the microstructures obtained under different casting temperatures to their mechanical properties.

Experimental

Ingots with nominal composition of $Cu_{50}Zr_{45.5}Ti_{2.5}Y_2$ were obtained by arc-melting high purity elements under Ti-getter argon atmosphere. The amorphous ribbons with a thickness of about 60 μm were prepared by single roller melt-spinning method and the cylinder samples with different diameters were manufactured with copper mould injection casting method under a high purity argon atmosphere. The casting temperature (also called the quenching temperature in melt spinning process. The casting temperature is consistently used in the whole paper in order to avoid confusion.) was monitored by the infrared thermoscope, and three casting temperatures were chosen, 1323 K, 1523 K and 1723 K. The temperature fluctuation was estimated to be ± 10 K. The oxygen content of the samples fabricated under different temperature was measured to be below 500 ppm. The continuous differential scanning calorimeter (DSC) experiments of amorphous ribbons was performed on a Netzsch DSC 204 (Estes

Park, CO, Germany) at the heating rate of 20 K/min. The apparatus was calibrated for temperature and enthalpy using highly pure indium and zinc before the measurements. Microstructures were checked in use of X-ray diffraction [XRD (Cu K_α radiation); Philips PW1050, The Netherlands], Optical microscope and scanning electron microscope (SEM; S3400N and Supra 35, Hitachi, Tokyo, Japan). Compression tests (MTS 810, Eden Prairie, MN, US) and nanoindentation tests were performed to evaluate mechanical properties of the samples. The fractured samples were also observed with SEM.

Results

In order to check the influence of casting temperatures on glass formation in the $Cu_{50}Zr_{45.5}Ti_{2.5}Y_2$ alloy, we cast the alloy into 2 and 3-mm-diameter cylindrical samples under different casting temperatures of 1323 K, 1523 K and 1723 K. Figure 1 shows their XRD patterns. It can be seen that for the 2-mm-diameter samples, only the sample prepared under 1723 K possesses a broad peak in the XRD patterns, indicating that the sample could consist of the amorphous phase. The samples prepared under 1323 K and 1523 K exhibit some Bragg peaks on XRD patterns. For the samples with 3 mm diameter prepared under 1323 K, 1523 K and 1723 K, the Bragg peaks are clearly seen in the XRD patterns, showing that the 3-mm-diameter samples crystallized more or less. The crystalline phases formed during solidification were indexed as CuZr, maybe a mixture of austenite and martensite phase [Powder Diffraction Data, International Center for Diffraction Data, published by JCPDS, Pennsylvania, 2002]. Martensite transformation was furthermore proved in the DSC measurement (Figure 2). Some similar results were reported in some literatures.[16-20] For 3-mm-diameter cast samples, we found that the percentage of the crystalline phase reduces with increasing the casting temperature, which is inferred from the intensity of Bragg peaks.of the samples. It would be confirmed by DSC measurement and microstructure observation.

Figure 2 shows DSC curves of 2-mm-diameter samples prepared under different casting temperatures. We determined the glass transition temperature, onset crystallization temperature and crystallization enthalpy for these samples, which are tabulated in TABLE I. In comparison, the ribbon prepared under 1723 K was also measured. The results were also listed in Figure 2 and TABLE I. For the samples prepared under 1323 K and 1523 K, some small endothermic peaks are observed in the range from 420 K to 470 K, which are magnified in Figure 2 (b). Martensite transformation is thought to be responsible for these peaks. No peaks are found for the sample prepared under 1723 K. Some researchers reported that the $Cu_{50}Zr_{50}$-based alloys can exhibit a martensite transformation when cooled quickly to temperature below 440 K.[21] Thus, it is confirmed in this work and, meantime, it suggests that the sample prepared under 1723 K is amorphous from this viewpoint. It is supported by the calculation of crystallization enthalpy for these samples. The magnitude of crystallization enthalpy is thought to be a function of the content of the amorphous phase. From Figure 2 and TABLE I, we can see the value of the enthalpy of crystallization increases with the casting temperature increasing. The content of the crystalline phase in the amorphous matrix is calculated with the expression of "$1-\frac{E_{sample}}{E_{reference}}$", where E_{sample} and $E_{reference}$ are the enthalpy of the sample and the reference, respectively, supposed that the reference is fully amorphous. It can be applied in the present work because the compositions of the amorphous matrix prepared under different casting temperatures are similar. We used Energy Dispersive X-Ray Spectroscopy (EDS) to check the compositions of amorphous phase and crystalline phases, which are $Zr_{46.29}Cu_{49.31}Ti_{2.49}Y_{1.91}$ and $Zr_{46.55}Cu_{48.82}Ti_{2.58}Y_{2.05}$ (in atomic percentage), respectively. Herein, we take the sample prepared under 1723 K as the reference material. The content of the crystalline phase for the other samples is calculated and tabulated in TABLE I. It can be seen that the content of crystalline phases falls with increasing casting temperature and when the casting temperature reached 1723 K, none crystalline phases are formed. From these results, one may conclude that high casting temperature would enhance glass forming ability. It also implies that we can adjust the content and size of the crystalline phase in the BMG matrix composites (BMGCs) by controlling the casting temperature. It is very beneficial to the understanding of the relationship of microstructures to mechanical property for BMGCs, even for BMGs.

The morphologies of the crystalline phases in different samples are shown in Figure 3. Figures 3 (a)-(c) correspond to 2-mm-diameter samples prepared under 1323 K, 1523 K and 1723 K, respectively. When the casting temperatures are 1323 K and 1523 K, the crystals are observed in the form of spheres. Most of crystalline phases were aggregated together, which is due to the inhomogeneous distribution of cooling rate along the radial direction during casting. When the casting temperature elevates to 1723 K, no crystals are observed in Figure 3 (c). The content of the crystalline phases of samples with different casting temperatures is consistent with XRD and DSC measurements. These results also support the conclusion that increasing casting temperatures enhances glass forming ability of the alloy.

It is generally accepted that the introduction of second phase, such as fiber, dendrite, particle etc., into the amorphous matrix help improve the properties of BMGs[8-12], especially plasticity, which is one of principal restraints of BMGs' commercial applications. In the present work, we examined the effect of precipitated CuZr phases on mechanical properties of the samples using nanoindentation tests and compression tests.

Nanoindentation test was employed to investigate the properties of CuZr phases and the amorphous matrix. The results are shown in Figure 4. The specimen is 2-mm-diameter as-cast rod prepared under 1523 K. As mentioned in the proceeding part, the composition of the crystalline phase is nearly the same as that of the amorphous matrix. Accordingly, the results shown in Figure 5 would work for specimens with different casting temperatures. Figure 4(a) shows the load-depth curves under different maximum loads. The area enveloped by the load-depth curves and the horizon axis is bigger for CuZr phases than for the amorphous matrix under different maximum loads, indicating that CuZr phases can accommodate more plastic deformation in the localized zone than the matrix. In addition, the CuZr phases are a little bit softer than the amorphous matrix. It is indicated by the hardness, which is 6.1 GPa for the CuZr phases and 6.3 GPa for the amorphous matrix shown in Figure 5 (c). Figure 5 (b) shows that the CuZr phases have a little higher Young's modulus than the amorphous matrix.

Mechanical properties of samples prepared under different casting temperatures were studied using compression test. Figure 5 shows typical true strain-stress curves. The samples prepared 1723 K yielded at about 1600 MPa and immediately fractured at 1770 MPa with a little plastic deformation of about 0.5%. For samples prepared under 1323 K and 1523 K, the yield strength falls to about 1100 MPa and 1220 MPa, respectively. After yielding, the samples exhibit obvious work hardenability. The stress increases to 1770 MPa and 1820 MPa, respectively, when the samples were subject to plastic deformation of about 5% and 7% till fracture. Very interestingly, similar phenomena were reported in other CuZr-[16-20, 22-24] and TiCu-[23] based amorphous alloys. Profuse shear bands were believed to soften BMG materials.[25] Figure 5 also shows the compressive stress-strain curve of the 3-mm-diameter as-cast sample, which consists of CuZr phases as shown in Figure 1. It exhibits an extraordinary work hardenability, which yields at about 460 MPa and rapidly increases to about 1750 MPa with about 6% plastic deformation. As a result, we considered that CuZr phases formed under the casting temperatures of 1323 K and 1523 K largely improves mechanical properties of BMGs and were responsible for their work hardenability.

Discussion

As shown in Figure 1, the casting temperature has a large influence on the glass forming ability of the alloy. Generally, one always correlates glass formation to nucleation and growth of crystals on considering glass forming ability.[8-10, 26] To obtain high glass forming ability, how to avoid the crystallization in the melt is widely concerned all the time. From Figure 1, we identified the primary competing crystalline phase against glass formation as CuZr phases in the present alloy. To better understand the crystallization process of CuZr phases, we observed the morphology of CuZr phases at higher magnification with compared to Figures 3 (a) and (b), as shown in Figure 3 (d). In Figure 3, crystals are heterogeneously distributed in the amorphous matrix whether on a macroscopic (Figures 3 (a) and (b)) or microscopic (Figure 3 (d)) scale. It sheds light on the mechanism of formation of CuZr phases. Heterogeneous distribution of CuZr phases may be attributed to the following two reasons. The first one is the inhomogeneous distribution of cooling rate along the radial direction, as mentioned above, which leads to the macroscopic inhomogeneity. The second one is the occurrence of heterogeneity in the melt,[4, 27-29] which induces preferential nucleation and growth in some sites. These nuclei grow by the form of spheres, different from the growth mechanism of dendrites. With crystallization proceeding, the aggregation occurs, as marked in Figure 3 (d). It would accelerate the crystallization, easily leading to the morphology of crystals shown in Figure 3 (a) and (b).

The pre-existing nuclei in the melt have two possibilities. One is the local ordering cluster, which is suggested to exist in the melt by many literatures. [4, 27-29] The other one is the surviving crystals, which can melt at ultrahigh temperature. They are thought to be metastable and gradually dissipate with the temperature up. [4, 27-29] For the local ordering cluster, the rate of its transformation into the melt is closely correlated to the temperature. At the temperature far below the critical temperature, the heterogeneities were reported to be kept for more than one day. When the temperature is over the critical temperature, the heterogeneities simultaneously dissipate. The critical temperature of this transformation was proposed to be about $1.4T_m$ (melting temperature of the alloy).[3, 4, 27-29] For the surviving crystal, it might be Cu_5Zr phase. In $Cu_{50}Zr_{50}$ alloy, metastable eutectic involving Cu_5Zr and Zr is suggested to be responsible for its high glass forming ability by Wang and co-workers.[30] Cu_5Zr is primarily precipitated when annealing the amorphous $Cu_{50}Zr_{50}$ alloy. The similar result was reported in $Cu_{46}Zr_{54}$ alloy by Wang et al.[31] Some other papers reported the discovery of nanoscale Cu_5Zr in the rapidly solidified $Cu_{50}Zr_{50}$[32] and Zr-Cu-Ni-Al alloys.[33] In the present work, the investigated alloy is $Cu_{50}Zr_{50}$-based. A few of tiny Cu_5Zr is possible to form in the rapidly cooled master ingot obtained by arc melting. These tiny particles survive to the temperature with $0.2T_{m,\,Cu5Zr}$ ($T_{m,\,Cu5Zr}$ is the melting temperature of Cu_5Zr.) over its melting temperature (1388 K) due to the effect of free electrons according to Tournier's theory[34] when master ingot is remelted to prepare the samples using copper mould casting. The survival of these tiny crystals would affect microstructures of the as-cast samples. As a result, the occurrence of heterogeneity in the melt depends on the casting temperature. When the casting temperature is very high (1723 K in the present work), heterogeneity disappear in the melt and glass forming ability will be enhanced. It is consistent with the enhancement of thermal stability of amorphous alloys prepared under high casting temperature. Contrarily, some crystals will precipitate under low casting temperatures (1323 K and 1523 K in the present work).

Even though the heterogeneity surviving in the melt under low casting temperature deteriorate glass forming ability of the alloy, the crystals grown up from those heterogeneity improve mechanical properties of BMGs,[14] as shown in Figure 5. The samples with homogeneous amorphous structure obtained by high-casting-temperature casting exhibit brittleness, like most of BMGs. CuZr phases formed in the samples prepared under low casting temperatures is softer and more ductile than the amorphous matrix. Under loading, it would prefer to plastic deformation at relatively low stress level while the amorphous matrix keeps elastic. This kind of inconsistency of deformation behaviors between the amorphous matrix and CuZr phases leads to the stress concentration on the interface. It is generally accepted that the in-situ formed CuZr crystals are well bonded with the glassy matrix, which avoids the initiation of the crack on the interface. To keep the consistency of deformation behaviors between the amorphous matrix and CuZr phases, shear bands initiate in the amorphous matrix under further loading. This leads to the loss of yield strength of the materials. However, profuse shear bands initiating in the amorphous matrix can accommodate much plastic deformation, contributing to the improvement of plasticity of the materials (Figure 4).

In a word, glass forming ability and property of BMGs are closely related to their solidification conditions.[3, 14, 15] Controlling solidification conditions, for example, casting temperatures in the present work, not only enhance glass forming ability of the alloy, but also improve mechanical properties of BMGs by introducing structural heterogeneity on a macro- or nano-[14] scale. To investigate the relationship of solidification conditions to properties of BMGs would be significant and benefit to promote BMGs' commercial applications.

Conclusion

The influence of casting temperatures on microstructures and mechanical properties of $Cu_{50}Zr_{45.5}Ti_{2.5}Y_2$ alloy prepared using copper mold casting were investigated in the present work. It leads us to draw the following conclusions:

1. With increasing the casting temperature, glass forming ability of the alloy enhances. Under the casting temperature of 1723 K, the 2 mm diameter amorphous sample was successfully made in the $Cu_{50}Zr_{45.5}Ti_{2.5}Y_2$ alloy. Under the lower casting temperatures, CuZr phases was primarily precipitated in the alloy. It is thought to be attributed to the crystals or clusters surviving in the melt.
2. A CuZr-phase reinforced BMG matrix composite with good mechanical properties was prepared in the $Cu_{50}Zr_{45.5}Ti_{2.5}Y_2$ alloy. The content of CuZr phases is related to the casting temperature. Mechanical tests indicate that CuZr phases are softer and more ductile than the amorphous matrix. Under loading, CuZr phases induce the initiation of multiple shear bands, leading to largely improving the plasticity of the materials.
3. Through comparing the deformation behaviors between CuZr phases, amorphous and composite, work-hardenability the composite exhibited in the compression tests is thought to be attribute to the bearing CuZr phases instead of the amorphous matrix.

Acknowledgment

YQ Wu and H Huang from the University of Queensland are appreciated for the assistance of nanoindentation tests. The authors also gratefully acknowledge the financial supports from the Ministry of Science and Technology of China (Grant No. 2006CB605201) and the National Natural Science Foundation of China (Grant No. 50731005).

Reference

1. D.R. Askeland, P.P. Phule: The Science and Engineering of Materials, 4th ed. (Tsinghua Univ. Press, Beijing, China, 2004), pp. 5, 27.
2. G. I. Eskin: Ultrasonic treatment of light alloy melts (Gordon and Breach Science Publishers, 1998).
3. V. Manov, P. Popel, E. Brook-Levinson, V. Molokanov, M. Calvo-Dahlborg, U. Dahlborg, V. Sidorov, L. Son and Y. Tarakanov: Influence of the treatment of melt on the properties of amorphous materials: ribbons, bulks and glass coated microwires. Mater. Sci. Eng. A 304-306, 54 (2001).
4. P. S. Popel, O. A. Chikova and V. M. Matveev: Metastable colloidal states of liquid metallic solutions. High Temp. Mater. Processes 14, 219 (1995).
5. P. S. Popel, M. Calvo-Dahlborg and U. Dahlborg: Metastable microheterogeneity of melts in eutectic and monotectic systems and its influence on the properties of the solidified alloy. J. Non-Cryst. Solids 353, 3243 (2007).
6. W. Klement, R. H. Willens and P. Duwez: Non-crystalline Structure in Solidified Gold-Silicon Alloys. Nature 187, 869 (1960).
7. C. J. Byrne and M. Eldrup: MATERIALS SCIENCE: Bulk Metallic Glasses. Science 321, 502 (2008).
8. W. L. Johnson: Bulk glass-forming metallic alloys: Science and technology. MRS Bull. 24, 42 (1999).
9. W. H. Wang, C. Dong and C. H. Shek: Bulk metallic glasses. Mater. Sci. Eng.:R 44, 45 (2004).
10. Y. Li, S. J. Poon, G. J. Shiflet, J. Xu, D. H. Kim and J. F. Löffler: Formation of Bulk Metallic Glasses and Their Composites. MRS Bull. 32, 624 (2008).
11. H. Choi-Yim and W. L. Johnson: Bulk metallic glass matrix composites. Appl. Phys. Lett. 71, 3808 (1997).
12. R. D. Conner, R. B. Dandliker and W. L. Johnson: Mechanical properties of tungsten and steel fiber reinforced $Zr_{41.25}Ti_{13.75}Cu_{12.5}Ni_{10}Be_{22.5}$ metallic glass matrix composites. Acta Mater. 46, 6089 (1998).
13. J. Shen, Y. J. Huang and J. F. Sun: Plasticity of a TiCu-based bulk metallic glass: Effect of cooling rate. J. Mater. Res. 22, 3067 (2007).
14. Z. W. Zhu, S. J. Zheng, H. F. Zhang, B. Z. Ding, Z. Q. Hu, P. K. Liaw, Y. D. Wang and Y. Ren: Plasticity of bulk metallic glasses improved by controlling the solidification condition. J. Mater. Res. 23, 941 (2008).
15. Z. W. Zhu, H. F. Zhang, H. Wang, B. Z. Ding and Z. Q. Hu: The influence of casting temperature on the thermal stability of Cu- and Zr-based MGs: theoretic analysis and experiments. J. Mater. Res. In press, (2008).
16. Y. F. Sun, B. C. Wei, Y. R. Wang, W. H. Li, T. L. Cheung and C. H. Shek: Plasticity-improved Zr--Cu--Al bulk metallic glass matrix composites containing martensite phase. Appl. Phys. Lett. 87, 051905 (2005).
17. Q. Zhang, H. Zhang, Z. Zhu and Z. Hu: Formation of high strength in-situ bulk metallic glass composite with enhanced plasticity in Cu50Zr50Ti2.5 alloy. Mater. Trans. 46, 730 (2005).
18. F. Jiang, Z. B. Zhang, L. He, J. Sun, H. Zhang and Z. F. Zhang: The effect of primary crystallizing phases on mechanical properties of Cu46Zr47Al7 bulk metallic glass composites. J. Mater. Res. 21, 8 (2006).
19. S. Pauly, J. Das, C. Duhamel and J. Eckert: Martensite formation in a ductile $Cu_{47.5}Zr_{47.5}Al_5$ bulk

metallic glass composite. Adv. Eng. Mater. 9, 487 (2007).
20. J. Das, K. B. Kim, W. Xu, B. C. Wei, Z. F. Zhang, W. H. Wang, S. Yi and J. Eckert: Ductile Metallic Glasses in Supercooled Martensitic Alloys. Mater. Trans. 47, 2606 (2006).
21. E. M. Carvalho and I. R. Harris: Constitutional and structural studies of the intermetallic phase, ZrCu. J. Mater. Sci. 15, 1224 (1980).
22. Z. W. Zhu, H. F. Zhang, W. S. Sun, B. Z. Ding and Z. Q. Hu: Processing of bulk metallic glasses with high strength and large compressive plasticity in Cu50Zr50. Scripta Mater. 54, 1145 (2006).
23. K. B. Kim, J. Das, S. Venkataraman, S. Yi and J. Eckert: Work hardening ability of ductile $Ti_{45}Cu_{40}Ni_{7.5}Zr_5Sn_{2.5}$ and $Cu_{47.5}Zr_{47.5}Al_5$ bulk metallic glasses. Appl. Phys. Lett. 89, 071908 (2006).
24. J. Das, M. B. Tang, K. B. Kim, R. Theissmann, F. Baier, W. H. Wang and J. Eckert: ``Work-Hardenable'' Ductile Bulk Metallic Glass. Phys. Rev. Lett. 94, 205501 (2005).
25. H. Bei, S. Xie and E. P. George: Softening Caused by Profuse Shear Banding in a Bulk Metallic Glass. Phys. Rev. Lett. 96, 105503 (2006).
26. K. F. Kelton: Crystal Nucleation in Liquids and Glasses. Solid State Phys. 45, 75 (1991).
27. W. Hoyer and R. Jodicke: Short-range and medium-range order in liquid Au---Ge alloys. J. Non-Cryst. Solids 192-193, 102 (1995).
28. K. F. Kelton, G. W. Lee, A. K. Gangopadhyay, R. W. Hyers, T. J. Rathz, J. R. Rogers, M. B. Robinson and D. S. Robinson: First X-Ray Scattering Studies on Electrostatically Levitated Metallic Liquids: Demonstrated Influence of Local Icosahedral Order on the Nucleation Barrier. Phys. Rev. Lett. 90, 195504 (2003).
29. H. Jónsson and H. C. Andersen: Icosahedral Ordering in the Lennard-Jones Liquid and Glass. Phys. Rev. Lett. 60, 2295 (1988).
30. W. H. Wang, J. J. Lewandowski and A. L. Greer: Understanding the glass-forming ability of $Cu_{50}Zr_{50}$ alloys in terms of a metastable eutectic. J. Mater. Res. 20, 2307 (2005).
31. H. R. Wang, Y. F. Ye, Z. Q. Shi, X. Y. Teng and G. H. Min: Crystallization processes in amorphous Zr54Cu46 alloy. J. Non-Cryst. Solids 311, 36 (2002).
32. A. Inoue, W. Zhang, T. Tsurui, A. R. Yavari and A. L. Greer: Unusual room-temperature compressive plasticity in nanocrystal-toughened bulk copper-zirconium glass. Phil. Mag.Lett.85, 221 (2005).
33. T. A. M. Aboki, F. Brisset, J. P. Souron, A. Dezellus and P. Plaindoux: Microstructure studies of Zr65Cu17.5Al7.5Ni10 and Zr65Cu15Al10Ni10 glass forming alloys: Phase morphologies and undercooled melt solidification. Intermetallics 16, 615 (2008).
34. R. F. Tournier: Presence of intrinsic growth nuclei in overheated and undercooled liquid elements. Physica B: Conden.Matter 392, 79 (2007).

Captions of figures and table

TABLE I Thermal parameters of the samples prepared under different casting temperatures obtained by DSC measurement at a heating rate of 20 K/min. T_1, T_2 and $\Delta E_{m,t}$ are onset temperature, finishing temperature and heat of martensite transformation. T_g, T_x and $\Delta E_{cryst.}$ are glass transition temperature, onset crystallization temperature and the enthalpy of crystallization.

FIG. 1. XRD patterns of as-cast rods with different diameter and different casting temperatures in $Cu_{50}Zr_{45.5}Ti_{2.5}Y_2$ alloy.

FIG. 2. (a) DSC scanning of as-cast rods with 2 mm diameter of $Cu_{50}Zr_{45.5}Ti_{2.5}Y_2$ alloy prepared under different casting temperatures. For comparison, DSC curve of ribbon quenched at 1723 K is listed together. The inset figure (b) is high magnification of the rectangle in (a).

FIG. 3. Optical images of as-cast rods with different diameters in $Cu_{50}Zr_{45.5}Ti_{2.5}Y_2$ alloy prepared under different casting temperatures: (a) 2 mm, 1323 K, (b) 2mm, 1523 K, (c) 2 mm, 1723 K and (d) 1.5 mm, 1323 K.

FIG. 4. (a) Load-depth curves, (b) Young's modulus and (c) hardness of as-cast rod with 2 mm diameter prepared under 1523 K in $Cu_{50}Zr_{45.5}Ti_{2.5}Y_2$ alloy, obtained by nanoindentation tests under different maximum loads.

FIG. 5. Typical true stress-strain curves of as-cast rods with different diameters and different casting temperatures in $Cu_{50}Zr_{45.5}Ti_{2.5}Y_2$ alloy, obtained by uniaxial compression tests at the strain rate of $2\times10^{-4}s^{-1}$. The ratio of length to diameter of all the specimens is 2:1.

Table

TABLE I Thermal parameters of the samples prepared under different casting temperatures obtained by DSC measurement at a heating rate of 20 K/min. T_1, T_2 and $\Delta E_{m,t}$ are onset temperature, finishing temperature and heat of martensite transformation. T_g, T_x and $\Delta E_{cryst.}$ are glass transition temperature, onset crystallization temperature and the enthalpy of crystallization.

	T_1 (K)	T_2 (K)	$\Delta E_{m.t.}$ (J/g)	T_g (K)	T_x (K)	$\Delta E_{cryst.}$ (J/g)
1323 K Φ=2 mm	437	466	2.6	660	709	-33.9
1523 K Φ=2 mm	435	461	2.0	663	709	-37.0
1723 K Φ=2 mm	--	--	--	663	710	-49.6
1723 K Ribbon	--	--	--	666	712	-50.8

Figures

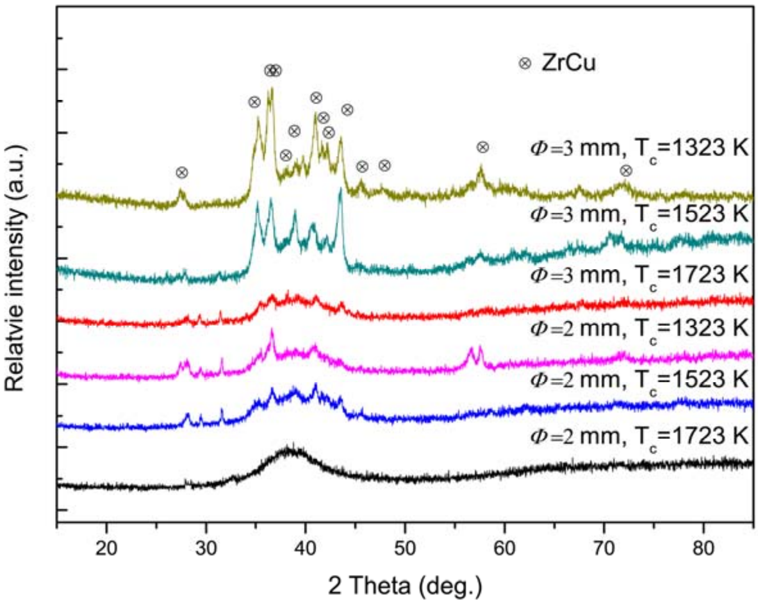

FIG. 1. XRD patterns of as-cast rods with different diameter and different casting temperatures in $Cu_{50}Zr_{45.5}Ti_{2.5}Y_2$ alloy.

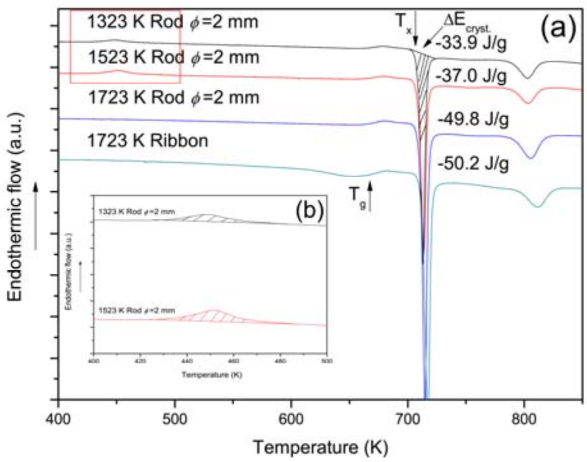

FIG. 2. (a) DSC scanning of as-cast rods with 2 mm diameter of $Cu_{50}Zr_{45.5}Ti_{2.5}Y_2$ alloy prepared under different casting temperatures. For comparison, DSC curve of ribbon quenched at 1723 K is listed together. The inset figure (b) is high magnification of the rectangle in (a).

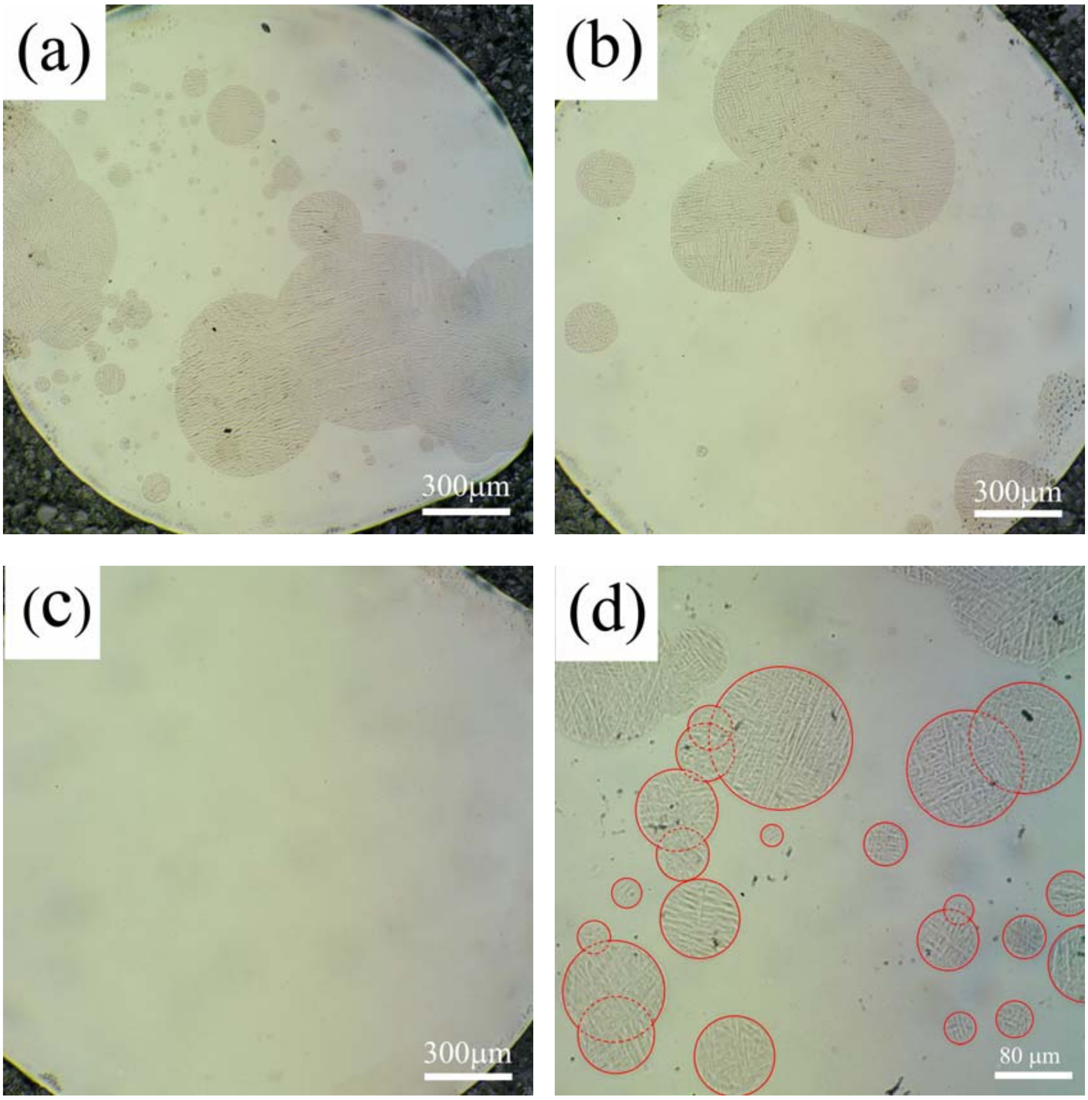

FIG. 3. Optical images of as-cast rods with different diameters in $Cu_{50}Zr_{45.5}Ti_{2.5}Y_2$ alloy prepared under different casting temperatures: (a) 2 mm, 1323 K, (b) 2mm, 1523 K, (c) 2 mm, 1723 K and (d) 1.5 mm, 1323 K.

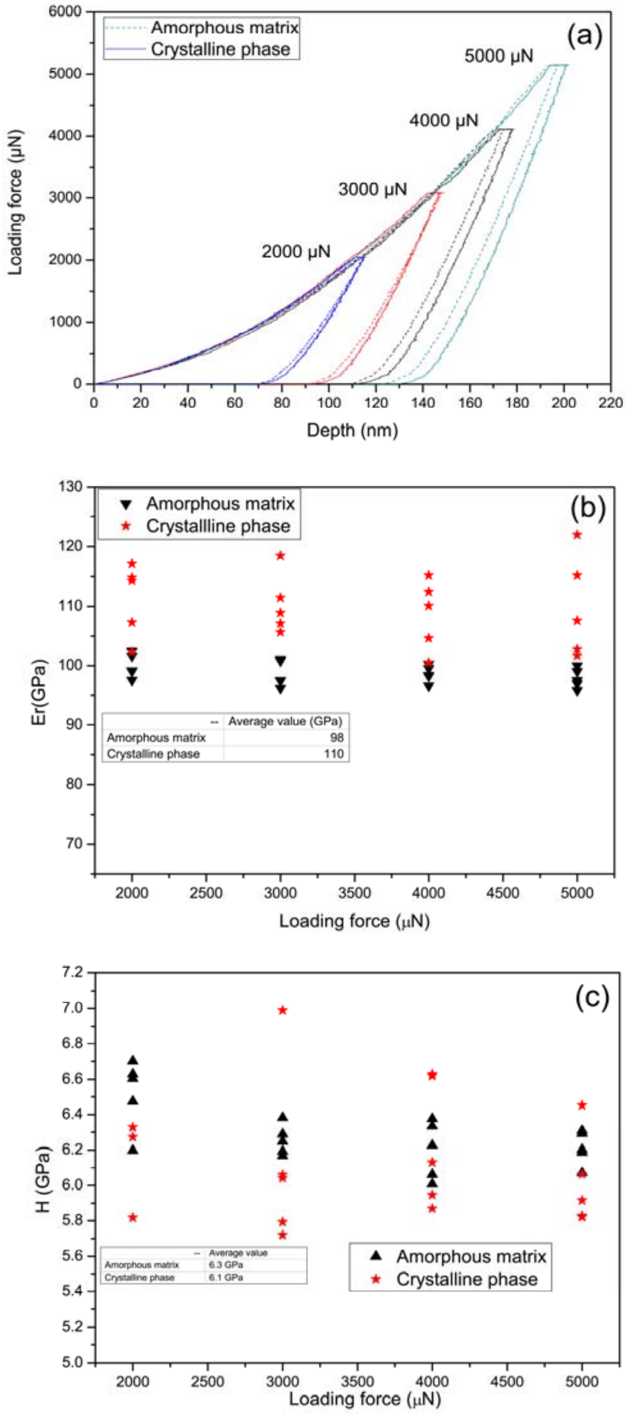

FIG. 4. (a) Load-depth curves, (b) Young's modulus and (c) hardness of as-cast rod with 2 mm diameter prepared under 1523 K in $Cu_{50}Zr_{45.5}Ti_{2.5}Y_2$ alloy, obtained by nanoindentation tests under different maximum loads.

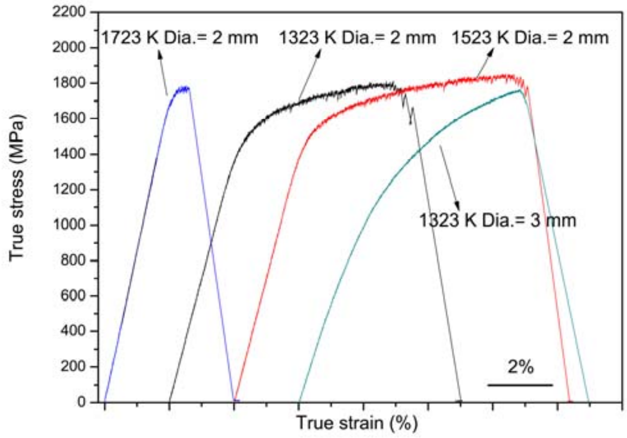

FIG. 5. Typical true stress-strain curves of as-cast rods with different diameters and different casting temperatures in $Cu_{50}Zr_{45.5}Ti_{2.5}Y_2$ alloy, obtained by uniaxial compression tests at the strain rate of $2\times10^{-4}s^{-1}$. The ratio of length to diameter of all the specimens is 2:1.