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Nanostructured bulk glassy $Cu_{60}Zr_{30}Ti_{10}$ alloy with high strength and good ductility in cast state①

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Abstract: The bulk glassy $Cu_{60}Zr_{30}Ti_{10}$ alloy with a diameter up to 4 mm and a length of 70 mm containing nanocrystalline phase was successfully developed by using copper mold casting method. The temperature interval of the supercooled liquid region before crystallization is above 37 K. The glass transition temperature (T_g) and the reduced glass transition temperature (T_g/T_l) of the cast bulk glassy $Cu_{60}Zr_{30}Ti_{10}$ alloy are 713 K and 0.62. The cast bulk glassy alloy, which has high glassy forming ability, shows expected mechanical properties. The elastic modulus, yield strength, fracture strength and elongation including elastic elongation are 114 GPa, 1 785 MPa, 2 150 MPa and 3.3% respectively in compressive deformation, and 112 GPa, 1 780 MPa, 2 000 MPa and 1.9% respectively in tensile deformation. High resolution transmission electron microscope (HRTEM) and nano-beam electron diffraction (NBED) studies indicate that the cast metallic bulk glassy $Cu_{60}Zr_{30}Ti_{10}$ alloy consists of nanocrystals with a size of ~4 nm embedded in glassy matrix. The nanoparticle is identified as CuZr and has point space group symmetry of $pm\bar{3}m$ and its lattice parameter is $a = 0.3\,262$ nm. The nanocrystalline phase grew up to 10 nm upon annealing at 430 ℃ for 10 min and caused the alloy brittle.

Key words: bulk glassy $Cu_{60}Zr_{30}Ti_{10}$ alloy; casting; microstructure; nanocrystalline phase; mechanical property

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1 INTRODUCTION

Since a series of metallic bulk glassy alloys with expected mechanical properties and high glass forming ability have been found[1-3], particular attempts have been done to improve the mechanical properties of the glassy alloys to meet engineering applications. By crystallizing the metallic glasses, nanostructured alloys containing nanocrystalline phases and glassy matrix were obtained and the mechanical properties of the alloys were enhanced by homogeneous dispersion of nanoscale metallic particles in the Al-[4,5], Fe-Ni-[6] and Mg-[7] based systems. However, the mechanical properties were sensitive to the volume fraction or average diameter of the nanocrystalline phases embedded in glassy matrix[8]. Xing et al[9] studied the influence of the volume fraction of quasicrystalline precipitates obtained by primary crystallization on mechanical properties in the Zr-based bulk alloys. They concluded that the strength of the alloy increases with increasing amount of quasicrystalline precipitates if the volume fraction of quasicrystalline precipitates is below 50%, but the ductility does not decrease significantly. More than 60% quasicrystalline precipitates led to reduction of ductility and strength. Similar results were reported by Fan[10, 11]. Chio et al[12] synthesized and characterized the composites with bulk metallic glassy matrixes by adding second crystalline materials such as WC, TiC, SiC, Td and W. The glassy forming ability of the matrix alloys remained unchanged. Unfortunately, no data associated with mechanical properties were given. Atom probe field ion microscopy and transmission electron microscopy study on the cast bulk metallic $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ glass, which was prepared by cooling the melt with a rate of about 10 K/s, revealed that the alloy exhibits phase separation in the undercooled liquid state[13]. Significant composition fluctuations were found in the Be and Zr concentration. An icosahedral quasicrystalline phase was obtained directly from the melt by copper casting of $Zr_{57}Ti_8Nb_{2.5}Cu_{13.9}Ni_{11.1}Al_{7.5}$ alloy[14]. However, little systematic research work on the relationship between the microstructure containing nanocrystalline phases and glassy matrix of the cast bulk metallic glasses has been reported up to now. In the present work, a cast metallic bulk glassy nanocrystalline $Cu_{60}Zr_{30}Ti_{10}$ alloy with high strength and good ductility was produced by means of copper mold casting method. The size effect of the nanoparticles embedded in the glassy matrix on the mechanical properties is considered.

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2 EXPERIMENTAL

Glassy alloy ingots with a nominal composition of $Cu_{60}Zr_{30}Ti_{10}$(mole fraction, %) were prepared by arc melting from a mixture of pure Cu, Zr and Ti(> 99.9% of purity in mass fraction) on a water-cooled copper crucible, under a Ti gettered argon atmosphere and remelting for several times to make the glassy alloy compositional uniform. The raw ingots were remelted in a quartz tube and then injected into copper mold resulting in bulk rods with different diameters. Thermal stability associated with the glass transition temperature (T_g) and crystallization temperature (T_x) was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. Mechanical properties under tensile and compressive deformation modes were measured at room temperature with an Instron-type testing machine. The elastic modulus was measured using a strain-gauge meter. The microstructure characterization of the bulk alloy was performed with X-ray diffraction (XRD) in a Rigaku X-ray diffractometer by using CuK_α and HRTEM in a JEOL JEM 3000F high-resolution transmission electron microscope equipped with NBED technique. To produce the TEM foil, disks with a thickness of 0.5 mm were cut from the center of the bulk rods and mechanically ground to about 50 μm, finally thinned by ion milling.

3 RESULTS

Fig. 1(a) shows the glassy $Cu_{60}Zr_{30}Ti_{10}$ alloy samples with diameters of 3 mm (Sample a) and 4 mm (Sample b). The rod samples exhibit good metallic luster and no appreciable concave. The DSC curve of the glassy bulk $Cu_{60}Zr_{30}Ti_{10}$ alloy with a diameter of 4 mm and a length of 70 mm is given in Fig. 1(b). The temperature interval of the supercooled liquid region before crystallization was 37 K. The glass transition temperature (T_g) and the reduced glass transition temperature (T_g/T_l) of the glassy bulk $Cu_{60}Zr_{30}Ti_{10}$ alloy are 713 K and 0.62, indicating that the alloy has high glass forming ability.

The mechanical properties of the glassy bulk $Cu_{60}Zr_{30}Ti_{10}$ alloy were tested under tensile and compressive deformation modes. Fig. 2 presents the compressive stress-elongation curve of the cast glassy bulk $Cu_{60}Zr_{30}Ti_{10}$ rod with a diameter of 2 mm and a length of 4 mm. It is found that the cast glassy bulk $Cu_{60}Zr_{30}Ti_{10}$ alloy exhibits elastic elongation up to 1.7%, followed by plastic elongation of about 1.6% and then fracture indicating the cast bulk alloy has good ductility. The elastic modulus (E), yield strength ($\sigma_{c,y}$) and fracture strength ($\sigma_{c,f}$) are 114 GPa, 1 785 MPa and 2 150 MPa, respectively. Fig. 3 shows the tensile stress-elongation curve of the cast bulk sheet $Cu_{60}Zr_{30}Ti_{10}$ alloy sheet with a gauge dimension of 1 mm thick, 2 mm wide and 10 mm long. The elastic modulus (E), tensile yield strength ($\sigma_{t,y}$), tensile fracture strength ($\sigma_{t,f}$) and tensile elongation including elastic elongation ($\varepsilon_{t,f}$) are 112 GPa, 1 780 MPa, 2 000 MPa and 1.9%, respectively. Fig. 4 shows the compressive stress-elongation curve of the bulk $Cu_{60}Zr_{30}Ti_{10}$ alloy annealed at 430 ℃ (10 ℃ lower than T_g of the alloy) for 10 min. The fracture strength of the alloy reaches 2 000 MPa but it has almost no ductility in the annealed state. The bulk glassy $Cu_{60}Zr_{30}Ti_{10}$ alloy becomes brittle upon annealing compared with that in cast state.

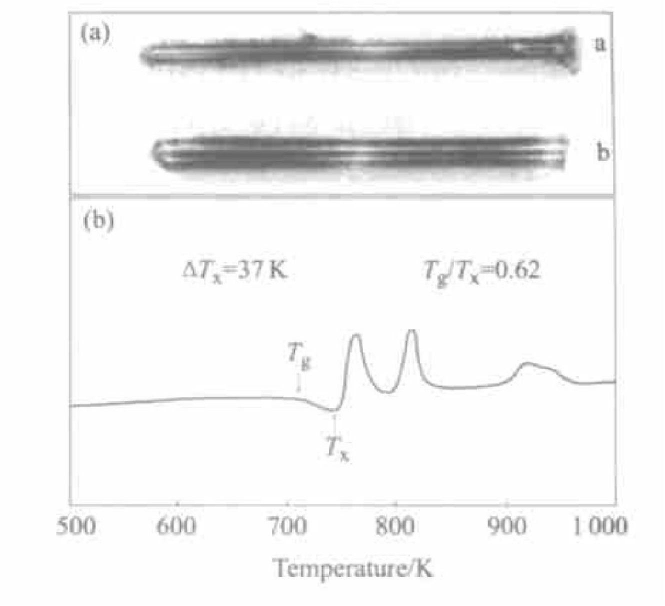

Fig. 1 Samples of glassy $Cu_{60}Zr_{30}Ti_{10}$ alloy (a) and DSC curve of sample b (b)

To identify the microstructure of the glassy $Cu_{60}Zr_{30}Ti_{10}$ rod, the XRD analysis and conventional TEM observation were firstly conducted and

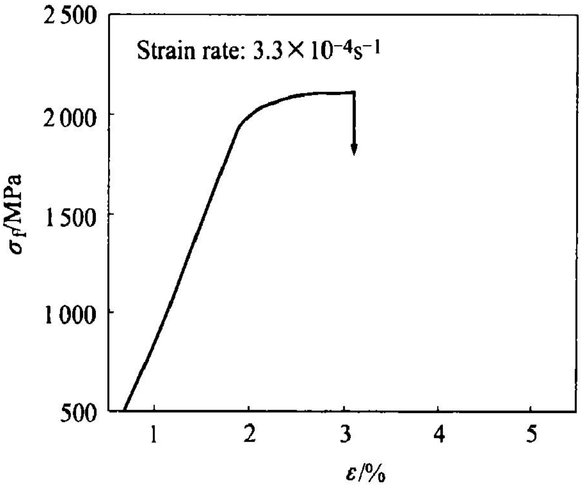

Fig. 2 Compressive stress-elongation curve of as-cast glassy $Cu_{60}Zr_{30}Ti_{10}$ alloy

an XRD pattern for the as-cast bulk glassy $Cu_{60}Zr_{30}Ti_{10}$ alloy with a diameter of 4 mm is shown in Fig. 5.

No distinct peak corresponding to crystalline phase is seen. The microstructure seems to be a single glassy phase without crystallization in the alloy during continuous cooling. Fig. 6 shows the bright field TEM image and the selected area electron diffraction (SAED) pattern of the bulk glassy alloy in cast state. The dark and bright contrast may imply that the alloy with a diameter of 4 mm in the as-cast state does not consist of the single amorphous microstructure. Unlike the microstructure of the Fe-[15] and Zr-[16] based metallic glasses, the microstructure of the cast bulk glassy $Cu_{60}Zr_{30}Ti_{10}$ rod with a diameter of 4 mm shows a slightly coarser structure although the SAED pattern is a broad one, characteristic of the metallic glassy phase. The darker and brighter regions may be related to phase separation associated with Cu-rich and Zr-rich areas.

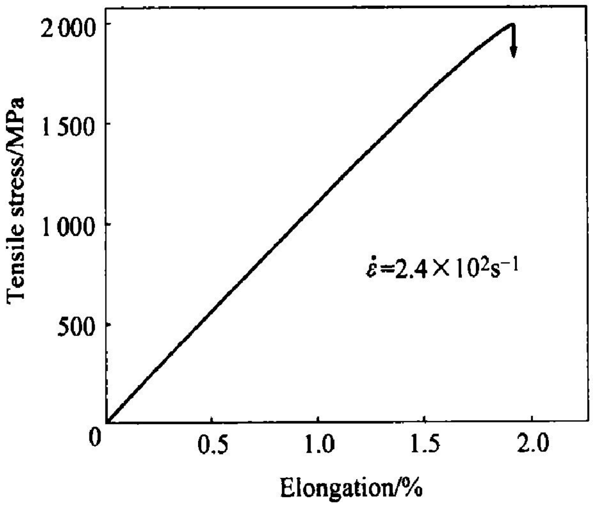

Fig. 3 Tensile stress-elongation curve of as-cast glassy $Cu_{60}Zr_{30}Ti_{10}$ alloy

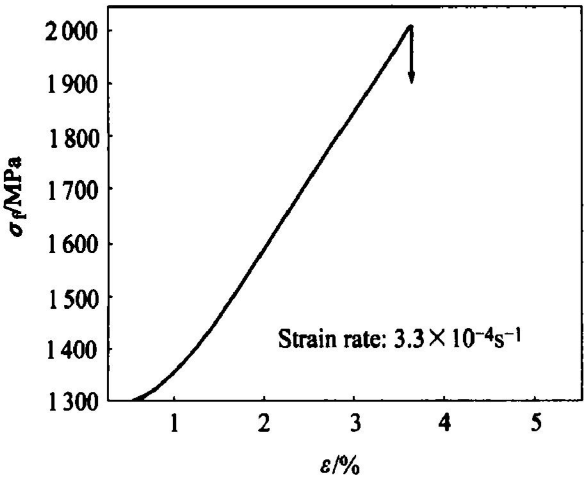

Fig. 4 Compressive stress-elongation curve of glassy $Cu_{60}Zr_{30}Ti_{10}$ alloy annealed at 430 ℃ for 10 min

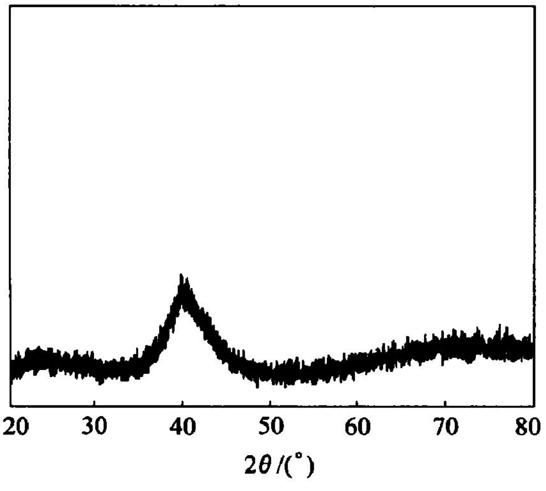

Fig. 5 XRD pattern of as-cast glassy $Cu_{60}Zr_{30}Ti_{10}$ alloy with diameter of 4 mm

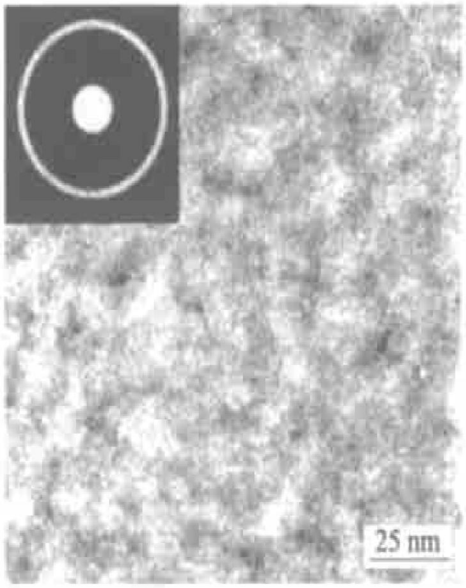

Fig. 6 TEM image of as-cast glassy $Cu_{60}Zr_{30}Ti_{10}$ rode with diameter of 4 mm

Since the particle size or the volume percentage of the particles is too small to be discerned by XRD and electron diffraction convincingly, HRTEM is used to clarify the microstructure in detail. Fig. 7 shows the HRTEM image of the bulk glassy $Cu_{60}Zr_{30}Ti_{10}$ alloy in the cast state, clearly indicating that the cast bulk glassy $Cu_{60}Zr_{30}Ti_{10}$ rod with a diameter of 4 mm and a length of 70 mm consists of glassy matrix and nanocrystalline phase with a size of about 4 nm . NBED with a diameter of 2. 4 nm was used to identify the nanocrystalline phase. Fig. 8 shows the NBED patterns of the nanocystalline phase in Fig. 7. Referring to the composition of the alloy, the nanocrystalline phase is identified to be CuZr, its lattice parameter is $a=0.3\,262$ nm and has point space group symmetry pm3m. Since the crystalline particle size is too small, the diffraction halo from the glassy matrix is also recognized in the NBED pattern.

3 DISCUSSION

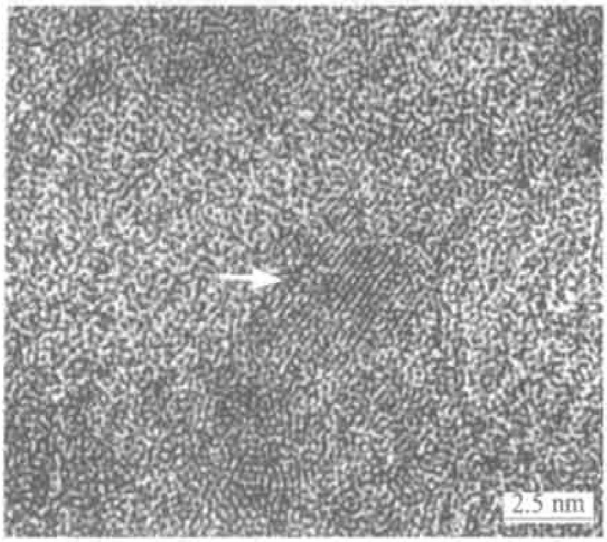

Fig. 7 HRTEM image of as-cast glassy $Cu_{60}Zr_{30}Ti_{10}$ alloy with diameter of 4 mm

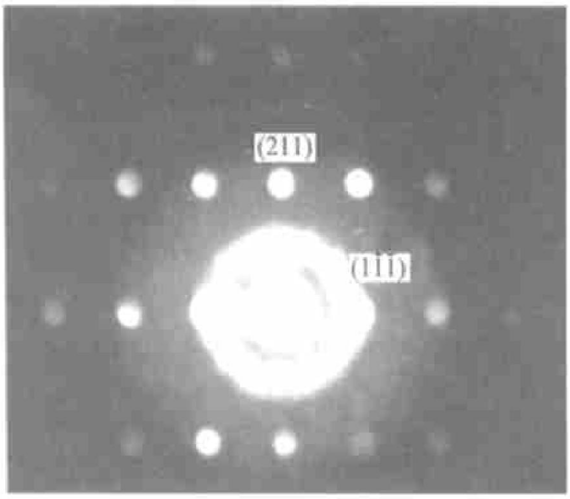

Fig. 8 NEBD diffraction pattern of one nanocrystalline phase in Fig. 7

The recent HRTEM and NBED investigations apparently demonstrate the existence of nanocrystalline phase indexed as CuZr in the as-cast bulk glassy $Cu_{60}Zr_{30}Ti_{10}$ alloy with good mechanical properties, especially better ductility than Zr- based cast glassy alloy[15]. Such bulk glassy alloy may be classed to be nanocrystalline/glassy matrix composite. It is reasonable to deduce that the dispersion of such nanocrystals embedded in the glassy matrix exhibits a contribution to good mechanical properties of the alloy in the cast state. However, the bulk glassy $Cu_{60}Zr_{30}Ti_{10}$ alloy exhibited brittle tendence upon annealing (Fig. 4). Similar phenomena were found in Chen's work on Fe-based metallic glasses and binary Fe-B and Fe-Cu systems[17], which were ductile in the as-quenched state became brittle upon annealing-induced crystallization. He proposed that the embrittlement arose from the resulting in the stress concentration around the clusters.

There is no doubt that the nanocrystalline phases scattered in glassy matrix are obtained either by annealing or by slow cooling. The melt during cast process has a remarkable effect on mechanical properties. In general, the nanoparticles embedded in amorphous matrix homogeneous with a size of less than 10 nm can improve the properties of the alloy. However, a detrimental effect of bigger particles on mechanical properties of the bulk glassy $Cu_{60}Zr_{30}Ti_{10}$ alloy was observed. Fig. 9 shows HRTEM micrograph of the bulk glassy $Cu_{60}Zr_{30}Ti_{10}$ rod with a diameter of 4 mm annealed for 10 min at 430 ℃. The nanocrystals grow up to about 10 nm upon annealing from about 4 nm in the cast state and lead to loss of ductility (Fig. 4).

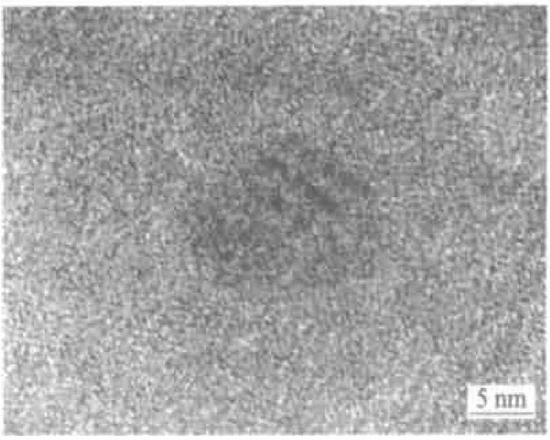

Fig. 9 HRTEM image of bulk glassy $Cu_{60}Zr_{30}Ti_{10}$ rode annealed at 430 ℃ for 10 min

Next, we try to discuss the brittle tendency of the bulk glassy $Cu_{60}Zr_{30}Ti_{10}$ alloy due to nanocrystals coarsening upon annealing. A schematic diagram presenting the interface structure of crystalline-amorphous matrix is shown in Fig. 10. It is well known that the crystalline phase is formed by nucleation and growth mechanism in devitrification process or continuous cooling from a melt. At the initial stage or in the cast state when a crystalline phase is formed, the elastic bonding force among the atoms at the crystalline-amorphous matrix interface remains strong as shown in Fig. 10(a) and (b). A crack may change its propagation direction under the extra stress when it meets a nanocrystalline phase. This requires more energy to initiate the crack propagation and run across the nanocrystals. As a result, more extra force is necessary and the mechanical properties are improved.

On the other hand, to a certain extent of crystallization, nanocrystals grow upon annealing and the elastic bonding force among the atoms at the interfaces becomes weak, as shown in Fig. 10(c). A crack may be easily formed at crystalline-amorphous matrix interface and the stress concentrates at the cracks when an extra force is loaded as shown in Fig. 10(d). This causes the alloy brittle.

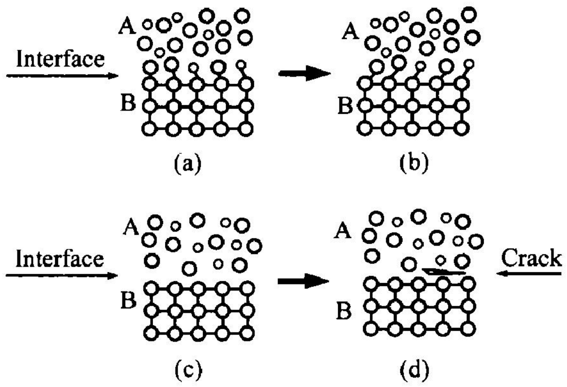

Fig. 10 Schematic illustration of nanocrystalline-amorphous matrix interface structure

4 CONCLUSIONS

1) The bulk glassy $Cu_{60}Zr_{30}Ti_{10}$ alloy containing nanocrystals with a size of about 4 nm and glassy matrix with a diameter up to 4 mm and a length of 70 mm was produced by copper mold casting method. The alloy has a good glass forming ability with $T_g/T_l = 0.62$.

2) The alloy has good mechanical properties with compressive fracture strength and elongation, tensile fracture strength and elongation of 2 150 MPa, 3.3%, 2 000 MPa and 1.9%, respectively, and exhibits brittle tendency when annealed at 430 ℃ for 10 min due to nanocrystals coarsening.

3) The nanocrystalline phase identified as CuZr with a size of about 4 nm, which is primitive cubic structure and its lattice parameter is $a = 0.3262$ nm, is found in the cast bulk glassy Cu_{60}-$Zr_{30}Ti_{10}$ rod with a diameter of 4 mm and a length of 70 mm. Such nanocrystals, which is difficult to be detected by traditional XRD and SAD techniques due to their small particle size and/or less amount of volume fraction, can advantage the improvement of mechanical properties of the alloy.

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