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• *Rapid Communication*

TiZr-base Bulk Metallic Glass with over 50 mm in Diameter

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Low-cost TiZr-base bulk metallic glasses (BMGs) $(Ti_{36.1}Zr_{33.2}Ni_{5.8}Be_{24.9})_{100-x}Cu_x$ (x=5, 7 and 9) with a maximum size of over 50 mm in diameter were developed by optimizing the alloy composition. The idea is initiated by selecting a particular microstructure comprising primary β-Ti dendrite and amorphous phase. Afterwards, based on this composition of amorphous phase, a class of TiZr-base bulk metallic glasses was designed step by step to reach the optimum composition range. The glass transition temperature (T_g), initial crystallization temperature (T_x) and width of supercooled region (ΔT) of $(Ti_{36.1}Zr_{33.2}Ni_{5.8}Be_{24.9})_{91}Cu_9$ BMG are 611, 655 and 44 K, respectively. The $(Ti_{36.1}Zr_{33.2}Ni_{5.8}Be_{24.9})_{91}Cu_9$ BMG exhibits low density of 5.541 g·cm^{-3} and high compressive fracture strength of 1800 MPa, which promises the potential application as structural materials.

KEY WORDS: TiZr-base alloy; Bulk metallic glass (BMG); Fracture strength

1. Introduction

Ti-base bulk metallic glass (BMG) as one of light alloys received much attention in the past decades. A series of Ti-base metallic glasses with promising properties and different glass forming ability (GFA) were developed[1–4], for example, Ti-base amorphous ribbons were prepared in binary and ternary alloys, and Ti-base BMGs were obtained in quaternary or quintuple alloys. It is well known that highly processable Zr-Ti-Cu-Ni-Be BMGs (Vitreloy series) have been designed and characterized by Johnson′s group[5,6], which exhibit excellent GFA and properties. Whereafter, a series of Ti-base BMGs and their BMG composites with excellent properties were developed by different groups[7–9] in the same alloy system as Vitreloy amorphous alloys, and the maximum glass-forming size reached 14 mm[10]. One novel semi-solid processing technique[11] used for producing highly toughened metallic glass matrix composites was designed successfully. These to large extent promote the application of Ti-base BMG and its composites. However, comparing with the Pd-base and Zr-base BMG with larger glass-forming size[5,12], the GFA of Ti-base BMGs is expected to have more improvements since the low GFA to some extent limits their application. The development of Ti-base BMG with high GFA is of technical and scientific importance to promote its application as candidate for engineering materials. In this work, the present authors prepared successfully a very large piece of TiZr-base BMG with 50 mm in diameter using a metallographic method. A particular structure consisting of primary β-Ti phase and amorphous matrix was selected. Then based on this composition of amorphous phase, a class of TiZr-base bulk metallic glasses was designed step by step to reach the optimum composition range. The thermal and mechanical properties of the TiZr-base BMG were tested carefully. It exhibits high compressive strength of about 1800 MPa. On the other hand, low-purity industrial sponges Ti and Zr were used as raw materials, which leads to a low-cost and promotes the application of Ti-base BMG as structural materials easily.

2. Experimental

The pancakes were prepared by arc melting Ti, Zr, Ni, Cu, Fe and Be elements in a water-cooled copper hearth under a Ti-gettered high-purity argon

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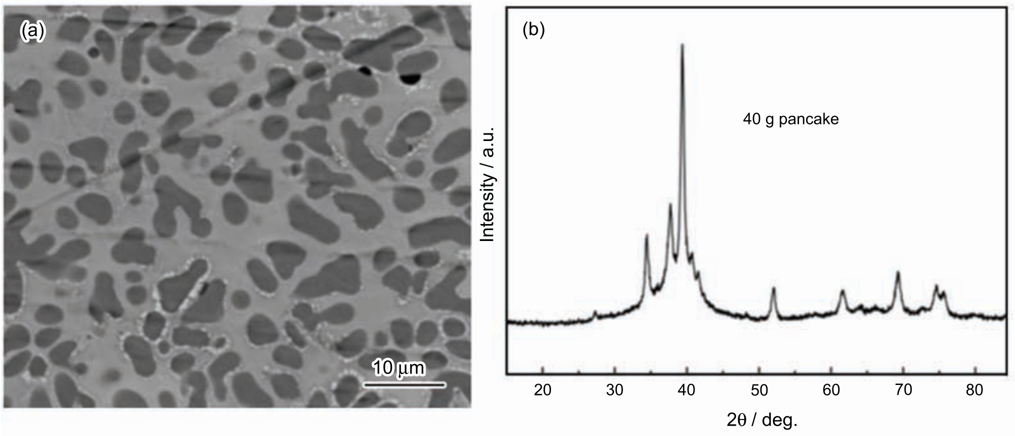

Fig. 1 Back-scattering image (a) and XRD pattern (b) of Ti50 pancake with a mass of 40 g

atmosphere. Industrial sponges Zr and Ti with purities of about 99.4% were used as raw materials. Each pancake was remelted at least four times to obtain homogeneity. As-cast rods with 2 and 5 mm in diameter were obtained using suction casting. The as-cast rods with 50 and 60 mm in diameter and 65 and 62 mm in height, respectively, were prepared by using water-quenching technique. The microstructures were characterized by X-ray diffraction (XRD, Philips PW1050, Netherlands, Cu$K\alpha$) and scanning electron microscopy (SEM, Hitachi S3400N, Japan). The XRD samples were cut from the centre of pancakes and as-cast rods. Thermal behavior was examined by differential scanning calorimetry (DSC) (Netzsch 404C, Germany, alumina crucible, with a constant heating rate of 0.33 K/s). Mechanical properties were measured on material testing system (Instron 5582, USA) at a constant strain rate of 1×10^{-4}s^{-1}. Densities were measured by the Archimedes method using Mettler Toledo XS105 analytical balance (Switzerland).

3. Results and Discussion

Figure 1 shows that the back-scattering image and XRD pattern of $Ti_{50}Zr_{23}Ni_3Cu_6Be_{18}$ (denoted as Ti50) pancake with a mass of 40 g. It can be seen that the structures mainly consist of amorphous phase and primary β-Ti phase. Some white crystalline phase particles are precipitated around the β-Ti phase. XRD pattern shows that the β-Ti phase peaks superimpose on halo diffraction peaks corresponding to amorphous structure. One unknown crystalline phase forms besides amorphous and β-Ti phases. This is in well agreement with SEM results.

The formation of amorphous alloy is a competing process between amorphous and possible crystalline phases[13]. It is assumed that the composition of amorphous phase in Ti50 structure shows strong glass-forming ability. Therefore, the composition of the amorphous phase is examined by energy

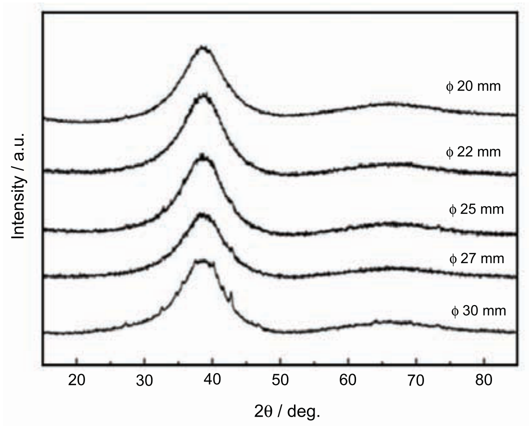

Fig. 2 XRD patterns of as-cast Ti33 alloy with different sizes

disperse X-ray spectrum (EDS) technique, which is $Ti_{33.4}Zr_{24.4}Ni_{4.4}Cu_{8.4}Be_{29.4}$, denoted as Ti33. Figure 2 is XRD patterns of as-cast Ti33 alloy with different diameters. It is clear that XRD patterns present one main broad peak characteristic of amorphous structure when diameters are 20 and 22 mm. Some sharp Bragg peaks appear on the halo peaks when diameter is over 22 mm. Their intensity increases as the diameter increases from 25 to 30 mm. It is concluded that the maximum glass-forming size of Ti33 is 22 mm in diameter.

Based on the Ti33 alloy, the ratios of Ti/Zr and Ni/Cu fixed at 33.4/24.4 and 4.4/8.4, respectively. A pseudo ternary phase diagram is set up to trace down the best BMG-forming compositions by systematical examining the compositional region around the Ti33 alloy, which lies at the TiZr-rich corner in order to obtain the high-GFA Ti-base BMG, as shown in Fig. 3. The compositional zone is refined by examining the structures of about 50 mother ingots with a mass of 100 g at compositional step of 2 at. pct. It is worth noting that one alloy $Ti_{45.7}Zr_{33}Ni_3Cu_{5.8}Be_{12.5}$ (denoted as ZT-M) with a particular microstructure was