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Formation and properties of centimeter-size Zr–Ti–Cu–Al–Y bulk metallic glasses as potential biomaterials

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ABSTRACT

A series of Ni-free $(Zr_{0.5}Ti_{0.02}Cu_{0.38}Al_{0.1})_{100-x}Y_x$ (x = 0, 1, 2, 3 and 5 at.%) bulk metallic glasses (BMGs) with outstanding glass-forming ability (GFA) were synthesized by copper mold casting and the effects of yttrium addition on glass-formation, thermal stability, mechanical properties and *in vitro* biocompatibility of the BMGs were investigated. It was found that the addition of 1–3 at.% Y greatly enhanced the GFA and thermal stability of the $Zr_{50}Ti_2Cu_{38}Al_{10}$ alloy. The critical diameter (d_c) increased from 5 mm for the Y-free alloy to 20 mm by 2 at.% Y addition. The supercooled liquid region (ΔT_x) of the Zr-based alloys was also enlarged to 60–71 K by the 1–3 at.% Y doping from 59 K for the base alloy. The compressive strength and plastic strain decreased gradually with the increase in Y content, while the Zr-based BMGs containing 0–3 at.% Y still exhibited high yield strength of about 1750–1800 MPa and compressive plasticity. The Zr-based BMGs also exhibited Young's moduli of 82–89 GPa, which are lower than that of Ti–6Al–4V alloy. Cell proliferation and cytotoxicity of mouse MC3T3-E1 pre-osteoblast on the Zr-based BMGs demonstrated good biocompatibility comparable to Ti–6Al–4V alloy. The combination of outstanding GFA and good mechanical properties and *in vitro* biocompatibility makes these Ni-free Zr-based BMGs promising as biomedical materials.

1. Introduction

Zr-based bulk metallic glasses (BMGs) possess high strength and hardness, relatively low Young's moduli, and good corrosion and wear resistance, which enable them to be potential biomedical implant materials [1–4]. For extensive biomedical applications, it is required that the BMGs should also be free from highly toxic elements while possess high glass-forming ability (GFA). However, most of the Zr-based BMGs with high GFA contain high amounts of nickel [2], which may cause allergy and cancer [5]. Therefore, in the last decade, great efforts have been devoted to develop Ni-free Zr-based BMGs so as to further improve their biocompatibility, and a series of Ni-free Zr-based BMGs have been developed mainly based on the Zr–Al–Cu and Zr–Al–Co ternary systems by alloying of Ag [6–9], Fe [10,11], Ti [12], Nb and Pd [13–16], etc. Nevertheless, among them, the BMGs manifesting large GFA with a critical diameter (d_c) over 20 mm mostly contain high content of Ag and Pd, such as $Zr_{100-x-y}(Cu_{5/6}Ag_{1/6})_xAl_y$ [8], $Zr_{48}Cu_{36}Ag_8Al_8$ [9], and $Zr_{48}Cu_{34}Pd_2Al_8Ag_8$ [16]. The massive addition of noble elements in the BMGs is disadvantageous from the material cost point of view. It has been reported that Ni-free Zr–Ti–Cu–Al alloys with small amount of Ti can also possess high GFA revealed by the critical diameter of 10 mm and good biocompatibility comparable or even superior to Ti and Ti–6Al–4V [17,18]. For the wide applications as biomaterials, further improvement of GFA for the Zr–Ti–Cu–Al alloy system is still desired. On the other hand, the addition of rare-earth metal elements such as Y and Er has been demonstrated to benefit the formation of Fe- [19,20], Zr- [21–23], CuZr- [24], Ti- [25] and Mg-based bulk metallic glasses [26]. Besides, although relatively little is known about the cytocompatibility properties of Y for orthopedic applications, the addition of Y in biomedical materials has been reported and showed no cytotoxicity in *in vitro* and *in vivo* studies. For examples, some Mg alloys with Y addition were considered as good biodegradable implant materials [27,28] and Y doping hydroxyapatite (HA) coatings were found to promote osteoblast functions on titanium [29]. The addition of Y_2O_3 in biomedical materials also showed no cytotoxicity in animal studies [30]. Therefore, in this work, with the aim of developing Zr-based

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BMGs with higher GFA and good properties as biomaterials, the effects of Y on the glass formation, mechanical properties and *in vitro* biocompatibility of a Zr–Ti–Cu–Al BMG were studied. It is found that minor addition of Y can significantly improve the GFA of Zr–Ti–Cu–Al alloy and BMGs with critical diameters up to 20 mm can be prepared by copper mold casting. The present Ni-free Zr–Ti–Cu–Al–Y BMGs exhibited the combination of high strength, low Young's moduli and good biocompatibility, implying their promise to serve as biomedical materials. Mechanisms of the high glass-forming ability and properties for the Y-doped Zr-based BMGs are also discussed.

2. Experimental

Master alloys with nominal compositions of $(Zr_{0.5}Ti_{0.02}Cu_{0.38}Al_{0.1})_{100-x}Y_x$ (x = 0, 1, 2, 3 and 5 at.%) were prepared by arc melting the mixture of pure metals under Ti-gettered high-purity argon atmosphere. From the master alloys, rod samples with diameters no more than 5 mm were prepared by injection copper mold casting and larger samples were prepared by tilt-pouring copper mold casting under an argon atmosphere. Microstructure of the cast rods was characterized by a X-ray diffractometer (XRD; Bruker AXS D8) with Cu-Kα radiation. Thermal behaviors were investigated by a differential scanning calorimeter (DSC; Netzsch 404C) at a heating rate of 0.33 K/s.

Vickers hardness of the glassy alloys was measured on a microhardness tester (HXZ 1000) under a load of 100 gf and a dwell time of 15 s. Compressive mechanical properties were investigated on a universal testing machine (SANS CMT5504) using glassy rod samples of 2 mm in diameter and 4 mm in length at a strain rate of 2.1×10^{-4} s^{-1} at room temperature. The lateral and fracture surfaces of deformed samples were observed with scanning electron microscopy (SEM; CamScan 3400). Elastic properties of the bulk glassy alloys were measured by ultrasound velocity measurement (Olympus Panametrics-NDT 5703PR). The density of the BMGs was determined by the Archimedean method.

In vitro biocompatibility of the glassy alloys was preliminarily evaluated by adopting mouse MC3T3-E1 pre-osteoblast cell line. Ti–6Al–4V alloy and 316L stainless steel were employed as counterparts, due to their wide clinical use as orthopedic implants. The samples with a size of ϕ 6 mm $\times$ 1 mm were polished to mirror-like finish and ultrasonically cleaned in acetone, enthanol and distilled water for 10 min sequentially. Each side of the alloy substrates was sterilized for 1 h by exposure to UV light, respectively, and then 1 ml cell suspension was seeded onto the surface of the alloys at a density of 5×10^3 cells per well in a 24-well plate. Cell culture was performed on three samples of each alloy simultaneously. The cells were incubated in Dulbecco's modified Eagle's medium–high glucose (DMEM), supplemented with 10% fetal bovine serum (FBS) and 1% Penicillin in a 5% CO_2 balanced air incubator at 310 K for three days. The cell morphology was observed by SEM (JEOL JSM-6010LA). For evaluating the cell viability, semi-quantitative analysis of the attached cell numbers on the surface of each alloy was also analyzed using image J software by randomly choosing five areas on the surface of each sample.

Potential cytotoxicity of the BMGs was evaluated by MTT assay on three samples of each alloy. After 3 days of incubation, the specimens were fetched out and put into a new 24-well plate, and then MTT solution (5 mg/ml in sterile PBS diluted 1:4 with growth medium) was added to each well for further 4 h incubation at 310 K. After that, MTT solution was discarded and the formazan crystals were resolved with dimethylsulphoxide (DMSO). The spectrophotometrical absorbance of the supernatants was then measured at 492 nm using a microplate reader.

3. Results

3.1. Glass-forming ability and thermal stability

Fig. 1 shows XRD patterns of the as-cast $(Zr_{0.5}Ti_{0.02}Cu_{0.38}Al_{0.1})_{100-x}Y_x$ (x = 0, 1, 2, 3 and 5 at.%) rods with their critical diameters for glass formation. The XRD patterns exhibit a main halo without Bragg peaks corresponding to any crystalline phase, indicating their amorphous structure. It can be found that the Y addition of 1–3 at.% can greatly improve the GFA of the Zr-based alloy, revealed by the critical diameters of 5 mm at x = 0, 18 mm at x = 1, 20 mm at x = 2, 16 mm at x = 3 and 6 mm at x = 5. Especially it is notable that the $(Zr_{0.5}Ti_{0.02}Cu_{0.38}Al_{0.1})_{98}Y_2$ alloy can be cast into a glassy rod with a diameter four times larger than the Y-free $Zr_{50}Ti_2Cu_{38}Al_{10}$ alloy under the present experimental condition.

The glassy structure of the as-cast $(Zr_{0.5}Ti_{0.02}Cu_{0.38}Al_{0.1})_{98}Y_2$ rod with critical diameter can be further confirmed by comparing the DSC curves of the 20 mm rod with that of the 2 mm rod. The sample for DSC examination was taken from the center of the rod for the 20 mm sample. The DSC curves are nearly identical and indicate the amorphous structure of $(Zr_{0.5}Ti_{0.02}Cu_{0.38}Al_{0.1})_{98}Y_2$ rod with critical diameter. The glassy nature of other compositions was also confirmed by the same method.

Fig. 2 presents DSC curves of the $(Zr_{0.5}Ti_{0.02}Cu_{0.38}Al_{0.1})_{100-x}Y_x$ glassy rods with their critical diameters. The DSC traces exhibit a distinct glass transition, followed by a wide supercooled liquid region prior to crystallization. The glass transition temperature (T_g), onset temperature of crystallization (T_x), solidus temperature (T_m), liquidus temperature (T_l) determined from the DSC curves and supercooled liquid region ΔT_x ($=T_x - T_g$), reduced glass transition temperature T_{rg} ($=T_g/T_m$) and the GFA criteria γ defined by $T_x/(T_g + T_l)$ of the Zr-based BMGs are summarized in Table 1. It is seen that the T_g and T_x decrease with the increase in Y content up to 5 at.%, while the ΔT_x increases gradually from 59 K at x = 0 to the maximum value of 71 K at 3 at.% Y, then decreases abruptly to 57 K when the Y content is as high as 5 at.%. It is also seen from Table 1 that the change in critical diameter of the Zr–Ti–Cu–Al–Y BMGs with Y content is not exactly consistent with those in ΔT_x, T_{rg} and γ criteria of GFA. The superior glass-forming ability of the present Zr-based BMGs with critical diameters up to 20 mm is favorable to the practical applications as biomedical materials.

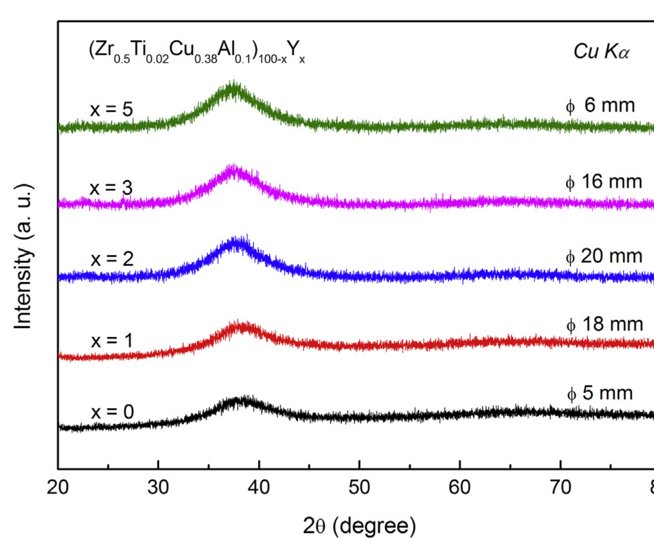

Fig. 1. XRD patterns of $(Zr_{0.5}Ti_{0.02}Cu_{0.38}Al_{0.1})_{100-x}Y_x$ (x = 0, 1, 2, 3 and 5 at.%) glassy rods with their critical diameters.