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Effects of lutetium addition on formation, oxidation and tribological properties of a Zr-based bulk metallic glass

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ABSTRACT

Enhancement of glass-forming ability (GFA) and surface properties are important for the application of Zr-based bulk metallic glasses (BMGs), and surface oxidation is an effective strategy for surface strengthening. In this paper, the effects of rare earth element Lu addition on GFA and oxidation properties of a $Zr_{50}Ti_2Cu_{38}Al_{10}$ bulk metallic glass were studied. The tribological properties of Lu-free and Lu-doping BMGs before and after oxidation were also investigated. It is found that 2 at.% Lu addition in this alloy significantly enhance the critical diameter (d_c) from 5 mm to 20 mm. The oxidation rate of 2 at.% Lu-doping alloy is higher than Lu-free alloy, indicating that the addition of Lu facilitates the formation of oxidized scale on the surface of $Zr_{50}Ti_2Cu_{38}Al_{10}$ alloy. Moreover, surface oxidation treatment remarkably improves the wear resistance of $Zr_{50}Ti_2Cu_{38}Al_{10}$ and $(Zr_{0.5}Ti_{0.02}Cu_{0.38}Al_{0.1})_{98}Lu_2$. This study is beneficial for the improvement of surface properties and further application of Zr-based BMGs.

1. Introduction

Owing to their amorphous microstructure, Zr-based bulk metallic glasses (BMGs) possess many superior properties over traditional crystalline alloys, such as high strength and hardness, relatively low Young's modulus, good corrosion resistance, net-shape castability, nanoscale imprintability, etc., which enable them to be used or tested for applications such as sporting goods, watch part, electromagnetic device casing, micro-geared motor parts, pressure sensors etc. [1]. Glass forming ability is crucial for many applications of BMGs and also important for industrial production of BMGs. $Zr_{50}Cu_{40}Al_{10}$ has a high glass-forming ability due to close to the ternary eutectic point of the alloy system [2]. However, it can only be cast into amorphous rod with a diameter less than 5 mm by copper mold casting under the vacuum of 3×10^{-2} Pa. In our previous studies, Ti was further incorporated into the alloy to improve the GFA and a fully amorphous rod with diameter of 5 mm can be fabricated by copper mold casting [3], but its GFA need to be further enhanced. Surface properties such as wear resistance are also important for various applications of Zr-based BMGs. In the last two decades, the tribological behaviors of some Zr-based BMGs have been studied [4–12], but the results on wear resistance of these BMGs are somewhat contradictory, probably due to wear resistance is not an inherent property of materials but strongly depends on the testing methods and experimental parameters. For instance, Ma et al. [6] found that the bearing rollers made from the Vit1 BMG show a better wear resistance than the commercial GCr15 ones. Blau [4] found that when sliding against 52100 steel, the ZrCuNiTiAl BMG performed comparably or slightly better than 303 stainless steel and commercially-pure Ni under dry conditions, but under lubricated conditions, it had the highest wear rate. Fu et al. [5] investigated the wear behavior of a ZrTiCuNiBe BMG using sliders made from the same material or 52100 steel, and the results showed that there was no indication of exceptional tribological properties for the Zr-based BMG. Parlar et al. [7] studied the wear and friction characteristics of Zr-based BMG under dry sliding conditions and found that the BMG exhibit worse wear resistance than Al6061 and SS304. Thus, enhancing GFA and surface properties are of great importance for further application of Zr-based BMGs. As it has been reported that the wear resistance of some materials could be improved by thermal oxidizing treatment [13–17], it is worth expecting that Zr-based BMGs could have better tribological performance after oxidation. Besides, due to the high affinity between O and rare earth (RE) element, the RE-containing BMGs may be prone to be oxidized comparing with the RE-free BMGs under the same condition. Moreover, it is noticed that the addition of RE elements such as Y, Er, Gd, etc. is beneficial for the formation and properties of various glassy alloys [3,18–22]. Therefore, the RE-containing BMGs may possess larger

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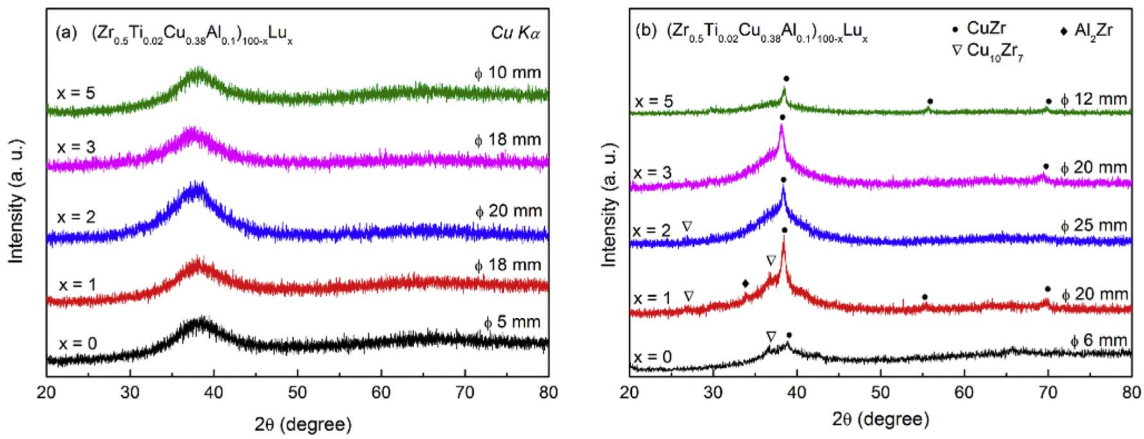

Fig. 1. XRD patterns of $(Zr_{0.5}Ti_{0.02}Cu_{0.38}Al_{0.1})_{100\text{-}x}Lu_x$ (x = 0, 1, 2, 3 and 5 at.%) rods with (a) their critical diameters (d_c) for glass formation and (b) diameters larger than d_c.

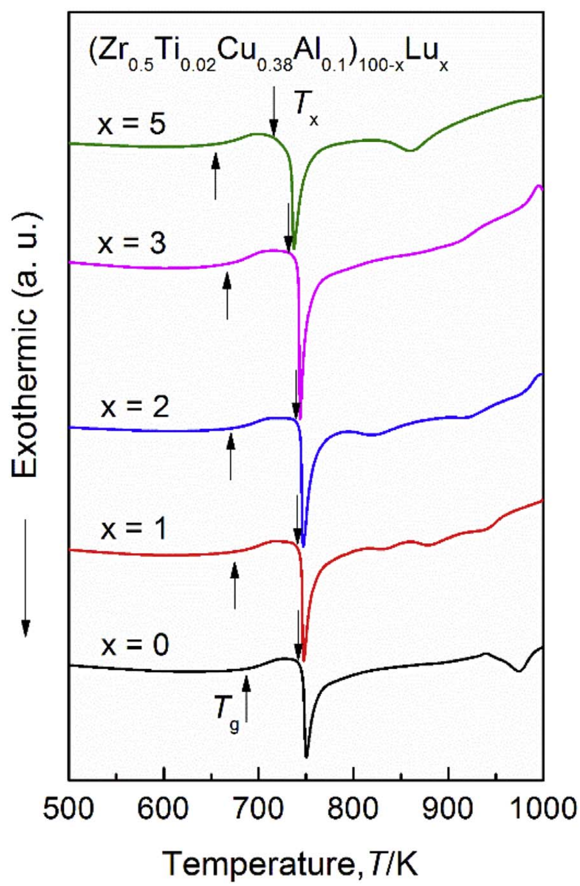

Fig. 2. DSC curves of $(Zr_{0.5}Ti_{0.02}Cu_{0.38}Al_{0.1})_{100\text{-}x}Lu_x$ (x = 0 and 2 at.%) glassy rods with their critical diameters at a heating rate of 0.33 K/s.

Table 1
Critical diameters and thermal properties of bulk glassy $(Zr_{0.5}Ti_{0.02}Cu_{0.38}Al_{0.1})_{100\text{-}x}Lu_x$ alloys.

Alloy (at.%)	d_c (mm)	T_g (K)	T_x (K)	ΔT_x (K)
$Zr_{50}Ti_2Cu_{38}Al_{10}$	5	687	746	59
$(Zr_{0.5}Ti_{0.02}Cu_{0.38}Al_{0.1})_{99}Lu_1$	18	674	745	71
$(Zr_{0.5}Ti_{0.02}Cu_{0.38}Al_{0.1})_{98}Lu_2$	20	671	745	74
$(Zr_{0.5}Ti_{0.02}Cu_{0.38}Al_{0.1})_{97}Lu_3$	18	666	739	73
$(Zr_{0.5}Ti_{0.02}Cu_{0.38}Al_{0.1})_{95}Lu_5$	10	655	715	60

critical diameter (d_c), higher oxidation rates and better wear resistance after oxidation thus the comprehensive properties of this material could be enhanced. In this study, the effects of Lu (with a low degree of toxicity [23]) on GFA and oxidation behaviors of the $Zr_{50}Ti_2Cu_{38}Al_{10}$ BMG were investigated, and the tribological behaviors of the as-cast and oxidized BMGs were also studied. The mechanisms for these properties were further discussed.

2. Experimental

Master alloys with nominal compositions of $(Zr_{0.5}Ti_{0.02}Cu_{0.38}Al_{0.1})_{100\text{-}x}Lu_x$ (x = 0, 1, 2, 3 and 5 at.%) were prepared by arc melting the mixtures of pure Zr, Ti, Cu, Al and Lu metals under Ti-gettered high-purity argon atmosphere. From the master alloys, cylindrical rods with different diameters from 5 mm to 25 mm were cast in copper molds under highly purified argon atmosphere. The structure of the rods was verified by X-Ray diffraction (XRD; Bruker AXS D8) with Cu-Kα radiation for transverse cross-section (all the cross sections of the rods were chosen at least 25 mm from the bottom). Thermal stability of the specimens was measured by a differential scanning calorimeter (DSC; Netzsch 404C) at a heating rate of 0.33 K/s under a flowing purified argon atmosphere.

To investigate the effects of Lu element on the oxidation behavior of the Zr-based BMGs, $(Zr_{0.5}Ti_{0.02}Cu_{0.38}Al_{0.1})_{98}Lu_2$ were chosen to compare with $Zr_{50}Ti_2Cu_{38}Al_{10}$. Rods with the diameter of 4.5 mm were prepared. The specimens were cut from these rods to a thickness of 1 mm and ground with SiC sandpaper down to 2000 grit, and then cleaned in acetone. The oxidation rates of the specimens were measured by a synchronous thermal analyzer (TG-DSC; Netzsch STA449 F3) in nitrogen/oxygen mixed air (with the ratio of 4:1). The net flow rate of air was kept constant at 40 mL/min throughout the test. The testing temperatures were selected as 603 K, 628 K, and 653 K, which were below T_g of both glassy alloys. The holding time at each temperature was 1.5 h. After oxidation, the structure of the specimens was characterized by XRD (D/MAX-2500). The morphologies of the topmost surface and cross sections were examined by scanning electron microscope (SEM; CamScan 3400 and JSM7500), and chemical composition analysis was conducted using energy dispersive spectrometer (EDS) attached to SEM. X-ray photoelectron spectroscopy (XPS) analysis was also conducted on $Zr_{50}Ti_2Cu_{38}Al_{10}$ and $(Zr_{0.5}Ti_{0.02}Cu_{0.38}Al_{0.1})_{98}Lu_2$ specimens oxidized at 603 K using photoelectron spectrometer (ESCALAB 250Xi) with Al Kα radiation ($h\nu$ = 1486.6 eV).

Ball-on-disc linear reciprocating wear experiments were conducted on the $Zr_{50}Ti_2Cu_{38}Al_{10}$ and $(Zr_{0.5}Ti_{0.02}Cu_{0.38}Al_{0.1})_{98}Lu_2$ specimens both before and after oxidation at 653 K on a Universal Micro-Tribotester (UMT-3) with a Si_3N_4 upper ball of 4 mm in diameter. All specimens were polished to 2000 grit and cleaned in acetone before testing. The experiment parameters were set as normal load of 10 N, frequency of