Enhanced Wear Resistance of Zr-Based Bulk Metallic Glass by Thermal Oxidation Treatment

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Enhancement of surface properties such as wear resistance of Zr-based bulk metallic glasses (BMGs) is important for many applications of the materials. In this paper, the effect of thermal oxidation on the tribological behavior of a Zr-Ti-Cu-Al-Y BMG was studied. It is found that oxidation treatment greatly improves the wear resistance of the BMG, which is ascribed to the formation of a layer of oxidized scale. This result is beneficial for the improvement of surface properties and further application of the Zr-based BMGs. [doi:10.2320/matertrans.M2016356]

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1. Introduction

Zr-based bulk metallic glasses (BMGs) possess excellent glass-forming ability (GFA), high strength and hardness, relatively low elastic modulus, good corrosion resistance, nanoscale imprintability, etc., which enable them to be utilized in many industrial applications such as sporting goods, micro-gear motor parts, pressure sensors and biomedical materials^{1,2}. Surface properties such as wear resistance should be taken into consideration in many engineering applications. The tribological behavior of Zr-based BMGs has been studied extensively^{3–14}, however, the results in different works are controversial. In some cases, Zr-based BMGs show high wear resistance, better than their crystallized counterparts and some conventional engineering alloy such as GCr15 steel^{5,7}, while in some other cases they exhibit no indication of superior tribological properties or even worse wear resistance than commonly used engineering materials like Al6061, 304 SS, 316 L SS and CoCrMo alloy^{3,4,9,12}. It has been reported that the tribological performance of Ti-6Al-4V could be improved by thermal oxidizing treatment^{15,16}, however, to the best of our knowledge, there has been no research about the effect of oxidation on the tribological behavior of BMGs. In this study, the tribological behavior of a Ni-free ($\text{Zr}_{0.5}\text{Ti}_{0.02}\text{Cu}_{0.38}\text{Al}_{0.1}\text{Y}_2$ (at.%) BMG before and after oxidation was studied and the results show that the wear resistance of the BMG can be significantly improved by oxidation treatment. The mechanism for the improvement of wear resistance was discussed.

2. Experimental

Alloy ingot with nominal composition of ($\text{Zr}_{0.5}\text{Ti}_{0.02}\text{Cu}_{0.38}\text{Al}_{0.1}\text{Y}_2$ (at.%) was prepared by arc melting the mixture of raw materials Zr, Ti, Cu, Al and Y under Ti-gettered highly purified argon atmosphere. From the master alloy, plates with dimension of 1.5 mm × 10 mm × 50 mm were fabricated by copper mold casting. Microstructures of the plates were examined by an X-Ray diffractometer (XRD; D/MAX-2500) with Cu-K α radiation.

The specimens were cut from these plates to a dimension of 1.5 mm × 8 mm × 16 mm and ground with SiC sandpaper down to 2000 grit, and then cleaned in acetone. The oxidation was carried out in a tubular furnace at 653 K (below T_g of the BMG¹⁷) and a holding time of 1.5 h in air atmosphere. After oxidation, the structures of the specimens were characterized by XRD. The morphology of the oxidized specimen was examined by SEM (CamScan 3400).

The tribological behaviors of the as-cast and oxidized ($\text{Zr}_{0.5}\text{Ti}_{0.02}\text{Cu}_{0.38}\text{Al}_{0.1}\text{Y}_2$) were tested by ball-on-disc linear reciprocating wear mode on a Universal Micro-Tribotester (UMT-2). Si_3N_4 spheres with a diameter of 4 mm were used as the counter material. The experiment parameters were set as normal load of 5 N, frequency of 1 Hz, sliding track length of 3 mm and duration of 0.5 h. After tribological test, the wear scar morphologies of the specimens were observed by SEM and chemical composition analysis was conducted by energy dispersive spectrometer (EDS) attached to SEM. The wear losses and surface roughness were measured by an optical interferometer (Phase Shift MicroXAm-3D). The microhardness (H) and reduced Young's modulus (E_r) of the specimens were measured by a nanoindenter (Nanoindenter XP).

3. Results and Discussion

Figure 1 (a) shows the XRD patterns of the as-cast and oxidized ($\text{Zr}_{0.5}\text{Ti}_{0.02}\text{Cu}_{0.38}\text{Al}_{0.1}\text{Y}_2$) specimens. For the as-cast specimen, only a broad diffusion peak for typical amorphous structure without any appreciable Bragg peaks can be seen. After oxidized at 653 K, t-ZrO₂, Al₂O₃ and Cu₂O can be identified on the alloy surface while the substrate remains amorphous. Figure 1 (b) shows the backscattered electron image (BEI) of the cross-section of the oxidized specimen, revealing a uniform, well-adherent scale with a thickness of about 4.2 μm .

The microhardness (H), reduced Young's modulus (E_r) and the ratio of hardness to reduced Young's modulus (H/E_r) of the as-cast and oxidized BMGs are listed in Table 1. For the oxidized BMG, H and E_r of the substrate slightly increase, while the H/E_r ratio exhibits no significant difference compared with that of the as-cast one. However, the scale on the oxidized BMG exhibits much higher H and H/E_r ratio than

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the substrate and as-cast BMG.

The three-dimensional and two-dimensional profiles of the wear scars after sliding tests are shown in Fig. 2. A deep furrow can be observed on the as-cast specimen in Fig. 2 (a). In contrast, the wear scar is much shallower on the oxidized specimen as can be seen in Fig. 2 (b). The widths and depths of the scars are shown in Fig. 2 (c) and also listed in Table 1. It can be seen that the scar depth is much reduced after the

Fig. 1 (a) XRD patterns of the as-cast and oxidized $(\text{Zr}_{0.5}\text{Ti}_{0.02}\text{Cu}_{0.38}\text{Al}_{0.1})_{98}\text{Y}_2$, (b) the backscattered electron image (BEI) of the cross-section of the oxidized specimen.

oxidation treatment. This result indicates that the wear resistance of the BMG can be significantly enhanced by surface oxidation. Besides, the scar depth of the oxidized specimen ($0.217\ \mu\text{m}$) is much smaller than the thickness of the oxidized scale ($4.2\ \mu\text{m}$), which means that the wear could not penetrate the scale under this condition and the enhancement of wear resistance of the BMG is mainly attributed to the formation of oxidized scale.

Figure 3 (a) and (b) show the SEM images and EDS results of the wear scars on the as-cast and oxidized specimens respectively. As seen in Fig. 3 (a), a number of ploughed grooves are present in the worn surface, which is a typical topography feature of abrasive wear controlled mechanism. The wear scar exhibits two distinct regions (marked by A and B in Fig. 3 (a)). The EDS results indicate that higher O and Si elements exist in region A, in which Si is transferred from the Si_3N_4 sphere, and O originated from the oxidation during the wear test. The composition of region B is almost identical with the nominal composition of the Zr-based BMG. This result indicate that surface oxidation happened during the sliding, however, the oxidized scale formed during the sliding process is inhomogeneous. Surface oxidation also took place in some other studies for Zr-based BMGs under dry-sliding tests^{4,8,14}, which may be caused by the high flash temperature generated on the friction surface^{11,14}. In Fig. 3 (b), the oxidized BMG shows a much smoother worn surface than the as-cast one, only some tiny scratches and a few shallow pits can be observed on the scar. The EDS results indicate that the composition of most of the surface area (marked by C in Fig. 3 (b)) is close to the original composition of the oxidized surface. The small pits (represented by D in Fig. 3 (b)) show slightly higher O and Si contents. These pits are probably the original defects on the specimen or caused by the microfragmentation of a small fraction of the scale. Figure 4 shows the SEM images of the surfaces of the Si_3N_4 counter spheres sliding against the as-cast BMG and oxidized BMG respectively. In Fig. 4 (a), wear debris (marked by white arrow) can be seen on the surface of the Si_3N_4 sphere after sliding against the as-cast BMG. Corresponding EDS analysis indicates that the wear debris adhered to Si_3N_4 sphere has similar composi-

Table 1 Microhardness; reduced Young's modulus; H/E_r ; roughness; scar depth and width for the as-cast and oxidized $(\text{Zr}_{0.5}\text{Ti}_{0.02}\text{Cu}_{0.38}\text{Al}_{0.1})_{98}\text{Y}_2$ BMG.

Specimen	H (GPa)	E_r (GPa)	H/E_r	R_a (nm)	Scar depth (μm)	Scar width (μm)
as-cast BMG	6.540	118.328	0.055	153	12.2	458
oxidized BMG (scale)	11.341	181.825	0.062	150	0.217	282
oxidized BMG (substrate)	6.625	120.934	0.055	-	-	-

Fig. 2 The three-dimensional profiles of the wear scars on (a) the as-cast and (b) oxidized $(\text{Zr}_{0.5}\text{Ti}_{0.02}\text{Cu}_{0.38}\text{Al}_{0.1})_{98}\text{Y}_2$ and (c) two-dimensional profiles of the wear scars.

Fig. 3 The morphologies and EDS results of the wear scars on (a) the as-cast and (b) oxidized specimens.

Fig. 4 The morphologies of the Si₃N₄ counterparts sliding against (a) the as-cast and (b) oxidized specimens.

tion with the Zr-based BMG. In Fig. 4 (b), after sliding against the oxidized BMG, only a few tiny wear scars and almost no wear debris can be found on the surface of Si₃N₄ sphere. The EDS result shows that the composition of the sphere remains Si and N elements. The Vickers hardness value of Si₃N₄ is about 15 GPa¹²⁾, much higher than the hardness of the as-cast (Zr_{0.5}Ti_{0.02}Cu_{0.38}Al_{0.1})₉₈Y₂ BMG (about 6.5 GPa), thus during sliding under this condition, wear mostly took place on the BMG. The hardness of Si₃N₄ is also higher than that of the oxidized scale (about 11.3 GPa) on the BMG, however, their hardness values are much closer than that between Si₃N₄ and the BMG, besides, both the Si₃N₄ and the scale are ceramics and they possess high hardness thus the wear are inconspicuous on them.

Based on the above results, the mechanism for the enhancement of wear resistance of the BMG by oxidation treatment can be explained as follows. After oxidation treatment, the surface of the BMG is covered by a layer of oxidized scale, therefore the friction pair is altered from metal-ceramic to ceramic-ceramic. The wear mechanism is thus different for the as-cast BMG and the oxidized BMG, for the as-cast one, the wear mechanism is a combination of abrasive wear and

oxidative wear, while for the oxidized BMG, the predominant wear mechanism is abrasive wear. It is well known that ceramics possess good wear resistance^{18,19)} due to their high hardness, thus the change of friction pair and wear mechanism may lead to the enhancement of wear resistance of the BMG. Besides, a higher H/E_r ratio usually indicates better wear resistance²⁰⁾, the scale on the oxidized BMG has a higher H/E_r ratio than the as-cast BMG, as a result the wear resistance is improved.

4. Conclusions

The tribological behavior of the as-cast and surface oxidized (Zr_{0.5}Ti_{0.02}Cu_{0.38}Al_{0.1})₉₈Y₂ BMG was studied by ball-on-disc sliding tests. The results show that the wear resistance of the BMG could be remarkably improved by oxidation treatment. The improvement is mainly attributed to the formation of a layer of oxidized scale. The oxidation treatment could be an effective way to improve the surface properties of Zr-based BMGs and beneficial for many applications of Zr-based BMGs.

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