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Dry and lubricated tribological behavior of a Ni- and Cu-free Zr-based bulk metallic glass

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ABSTRACT

In this study, tribological behavior of a $Zr_{53}Al_{16}Co_{23.25}Ag_{7.75}$ bulk metallic glass (BMG) in air and phosphate buffer saline (PBS) solution was investigated and compared with biomedical alloy Ti–6Al–4V. It is found that wear resistance of the Zr–Al–Co–Ag BMG sliding in air is superior to that of Ti–6Al–4V alloy. Under dry friction condition, wear deterioration of Zr-based BMG is controlled by oxidation and adhesive wear whereas Ti–6Al–4V alloy is jointly dominated by abrasive and adhesive wear. However, Zr-based BMG presents decreased wear resistance under lubricated friction condition in comparison with dry friction condition. In contrast, Ti–6Al–4V alloy shows improved wear resistance sliding in PBS. This is probably associated with the inferior pitting corrosion resistance of Zr–Al–Co–Ag BMG in the medium containing chloride ions, which may cause tribocorrosion controlled by synergistic effects of abrasive and corrosive wear. The possible mechanism for corrosion accelerating wear is discussed based on the tribological behavior of this Zr-based BMG.

1. Introduction

Increasing requirements for orthopedic implants, especially for load bearing applications, have heightened due to the increase of aging population and mechanical injuries. Despite the considerable clinical success in service, current implant alloys still face complexities, including stress shielding, particle disease, corrosion, etc. [1,2]. For instance, Co–Cr alloys possess good wear resistance but exhibit high Young's modulus (~210 GPa) which may cause stress shielding, the main cause of bone resorption. Ti alloys demonstrate low Young's modulus and excellent biocompatibility but suffer from poor wear resistance, which rising the risk of "particle disease", such as osteolysis and subsequent aseptic loosening [3,4]. To diminish these difficulties, the design of new biomedical alloys is directed toward optimized biomaterials which are both bio- and mechanocompatible.

Bulk metallic glasses (BMGs) are a class of revolutionary alloys which exhibit unique properties due to their amorphous structure. Since Zr is a highly biocompatible element, and Zr-based BMGs are among the most developed and investigated glass-forming systems, increasing attention has been drawn to the biomedical application of BMGs during the past two decades [5–7]. Their high strength and elasticity, exceeding those of currently used implant alloys, together with good wear and corrosion resistance are favorable for potential applications as implantable devices [8–13].

When an implant material attaches to the bone, during the cyclic loads, relative movements generate wear stresses due to the difference of Young's modulus between the bone and the implant material. Thus, wear resistance is crucial for implant materials [10,14]. Meanwhile, corrosion damage is also a very important issue for implant alloys serving in the harsh in vivo environment [11,12,15–17]. Under physiological conditions, material loss can be attributed to the combined wear and corrosion actions that simultaneously take place during the friction process. However, the assessment of tribological properties of metallic glasses as potentially applicable in situations where wear and corrosion act simultaneously is still very limited. On the other hand, tribological properties are not intrinsic properties of materials, but highly dependent on the service environment and counter pair. Therefore, tribological behavior of the BMGs has not been well understood so far, even in debate [18–25].

According to Archard's wear equation, wear resistance is proportional to hardness [18]. Gloriant et al. found that nanocrystallization increased both the hardness and the wear resistance of Al-based amorphous alloys, and that Al-based metallic glass obeyed Archard's wear equation [19]. Nevertheless, Tam et al. indicated that Cu-based BMG had a worse wear resistance than AISI 304 stainless steel, even though it had a higher hardness [20,21]. Meanwhile, Fu et al. showed that

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there was no indication of superior tribological properties for the Zr–Ti–Cu–Ni–Be BMG under dry friction condition [22]. However, Blau et al. reported that Zr-based BMG had better wear resistance than AISI 303 stainless steel and Ni-200 under atmosphere condition. Also, it was found that Zr–Ti–Cu–Ni–Be BMG had the highest friction coefficient and wear rate under diesel oil-lubricated condition [23]. Moreover, formation and subsequent peeling-off of oxygen rich tribolayers was defined as the predominant wear mechanism of Zr–Ti–Cu–Ni–Be BMGs during sliding tests by Jin et al. [24]. Fu et al. compared wear behavior of the same metallic glass under air and vacuum conditions and found that vacuum condition caused lower coefficient of friction and less wear loss [25]. Furthermore, Chen et al. showed that the wear resistance of Zr–Cu–Fe–Al–Ag BMG against ultra-high molecular weight polyethylene (UHMWPE) as counterpart was superior to that of conventional as-cast CoCrMo alloy under simulated physiological media, thus showing better suitability for orthopedic applications [26]. Espallargas et al. illustrated that in the simulated body fluid, Zr–Cu–Ni–Al BMG suffered from wear accelerated corrosion generating larger wear rates due to galvanic coupling effects [27]. Wang et al. investigated the wear resistance of a Zr–Ti–Cu–Al BMG in dry sliding and simulated physiological media using ball-on-flat tribological approach. Under dry friction condition, abrasive wear was a predominant wear mechanism for the BMG. In simulated physiological media, wear deterioration was a typical tribocorrosion dominated by synergistic effects of the abrasive and corrosive wear [28]. As the wear resistance is not an inherent property of materials and strongly depends on wear conditions and processing history of materials, the data in different works are contradictory. Thus, more insightful understandings on tribological behavior of bulk metallic glasses both under dry sliding and simulated physiological media lubrication conditions are still needed.

It is worthy of noting that elements with high toxicity to cellular metabolism, such as Ni or Cu, are found in Zr-based BMGs discussed above, which is disadvantageous to their practical applications as biomaterials. To overcome this drawback, in our previous works, Ni- and Cu-free Zr–Al–Co–Ag BMGs have been explored to reduce the hazardous elements and their biocompatibility and mechanocompatibility have been extensively studied [29,30]. The Zr–Al–Co–Ag BMG exhibits high glass-forming abilities with critical diameters larger than 2 cm as well as good mechanical biocompatibility of higher hardness and lower Young's modulus in comparison with Ti–6Al–4V, 316 L stainless steel, and Co–Cr–Mo alloys. Moreover, as assessed by in vitro cellular responses [30], the Zr–Al–Co–Ag BMG manifests good biocompatibility comparable to pure Zr and Ti–6Al–4V alloy. Thus, this Ni- and Cu-free Zr-based BMG is considered to be a more promising biomaterial. To promote potential biomedical applications of Zr-based BMGs as implant materials, the aim of this work was therefore to investigate the tribological behavior of Zr–Al–Co–Ag BMG under dry sliding condition and in simulated physiological fluid. Commercial Ti–6Al–4V, which was widely used for clinical biomedical implants, was employed as reference material. All of the results provide the foundational information of the Ni- and Cu-free Zr-based BMGs for further biomedical applications.

2. Experimental

Master alloys with nominal compositions of $Zr_{53}Al_{16}Co_{23.25}Ag_{7.75}$ (in atomic percentage) were prepared by arc melting the mixtures of pure Zr, Al, Co, and Ag metals under Ti-gettered high purified argon atmosphere. From the master ingots, alloy plates with a dimension of $70 \times 10 \times 2$ mm^3 were cast in copper molds. Rectangular BMG plates for wear tests were mechanically machined to the size of $10 \times 10 \times 1.8$ mm^3. Commercial alloy of Ti–6Al–4V was processed with the same dimension as that of Zr–Al–Co–Ag BMG. The surfaces of alloy samples were polished to 2000 grit, and then polished with 1.0–2.5 μm diamond paste. The structure of the alloy specimens was verified by X-ray diffraction (XRD, Bruker AXS D8) with Cu Kα radiation and scanning electron microscopy (SEM, CS-3400) with energy dispersive X-ray spectrometry (EDS).

Ball-on-disk reciprocating wear experiments were conducted on the surfaces of Zr–Al–Co–Ag BMG and Ti–6Al–4V alloy using Si_3N_4 ball as the counterpart. A normal load of 3 N, sliding track length of 4 mm, experiment duration of 20 min, and frequency of 8 Hz were selected as the operating parameters. The tribological tests were carried out under dry friction condition in air and lubricated friction condition in phosphate buffer saline (PBS) solution. Under each given condition, at least three specimens were tested to ensure reproducibility. Topography of worn surfaces of samples and counterpart balls were observed by SEM attached with EDS. An optical interferometer was used to calculate the wear losses of samples.

The corrosion resistance of Zr–Al–Co–Ag BMG and Ti–6Al–4V alloy in PBS solution was examined by electrochemical measurements. Electrochemical measurements were conducted using a three-electrode cell composed of a working electrode, a platinum counter electrode, and a saturated calomel reference electrode (SCE). Potentiodynamic polarization curves were measured at a potential sweep rate of 50 mV min^{-1} after open circuit immersion for about 20 min when the open circuit potential (OCP) became almost steady. After polarization testing, samples were washed with acetone, distilled water, air-dried, then observed by SEM and analyzed by EDS.

3. Results and discussion

3.1. Materials characterization

Fig. 1 shows the XRD patterns of Zr–Al–Co–Ag BMG and Ti–6Al–4V alloy. The glassy structure of Zr-based alloy is confirmed by a broad halo peak around 38° and the absence of detectable crystalline diffraction peaks. The analysis of Ti–6Al–4V sample exhibits peaks corresponding to α and β crystalline phases.

3.2. Tribological behavior

3.2.1. Wear performance

The wear rate values of Zr–Al–Co–Ag BMG and Ti–6Al–4V alloy under different conditions are illustrated in Fig. 2. Under dry friction condition, the wear rate of Ti–6Al–4V alloy is 5 times higher than that of Zr–Al–Co–Ag BMG. However, under lubricated friction condition in PBS solution, the wear rate of Ti–6Al–4V alloy decreases from 28.01×10^{-6} mm^3/mm to 9.29×10^{-6} mm^3/mm, whereas that of Zr–Al–Co–Ag BMG increases from 5.76×10^{-6} mm^3/mm to 8.18×10^{-6} mm^3/mm. This denotes that Zr–Al–Co–Ag BMG suffers from corrosion wear synergistic interaction sliding in PBS, which accelerates the wear damage of Zr–based BMG.

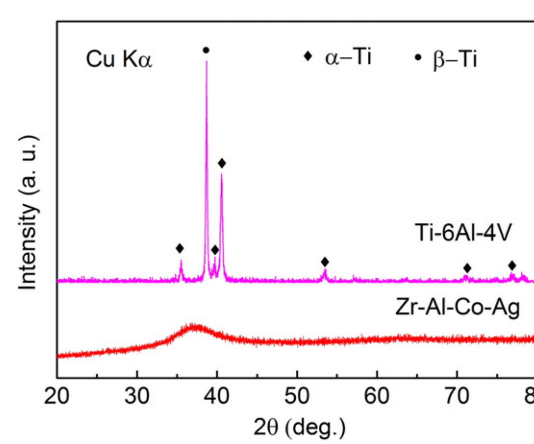

Fig. 1. The XRD patterns of Zr–Al–Co–Ag BMG and Ti–6Al–4V alloy.