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# Tribological and corrosion behaviors of $Mg_{56.5}Cu_{27}Ag_5Dy_{11.5}$ bulk metallic glass in NaCl solution



Nengbin Hua <sup>a,b,c,\*</sup>, Yuxi Huang <sup>a,c</sup>, Zhiqiang Zheng <sup>a,c</sup>, Youting Huang <sup>a,c</sup>, Manyu Su <sup>a,c</sup>, Zhenlong Liao <sup>a,c</sup>, Wenzhe Chen <sup>a,b,c</sup>

<sup>a</sup> Department of Materials Science and Engineering, Fujian University of Technology, 350118 Fuzhou, China

<sup>b</sup> Department of Materials Science and Engineering, Fuzhou University, 350116 Fuzhou, China

<sup>c</sup> Fujian Provincial Key Laboratory of Advanced Materials Processing and Application, 350118 Fuzhou, China

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#### ABSTRACT

In this study, the tribological behaviors of  $M_{56.5}Cu_{27}Ag_5Dy_{11.5}$  bulk metallic glass (BMG) in air and NaCl solution were investigated using ball-on-disk reciprocating friction. The  $M_{56.5}Cu_{27}Ag_5Dy_{11.5}$  BMG exhibits higher strength and hardness than those of commercial AZ31B alloy and pure Mg. The wear rate of the  $Mg_{56.5}Cu_{27}Ag_5Dy_{11.5}$  in air is  $3.8 \times 10^{-7}$  mm<sup>3</sup>·mm<sup>-1</sup>·N<sup>-1</sup>, which is superior to those of AZ31B alloy ( $7.3 \times 10^{-7}$  mm<sup>3</sup>·mm<sup>-1</sup>·N<sup>-1</sup>) and pure Mg ( $6.5 \times 10^{-7}$  mm<sup>3</sup>·mm<sup>-1</sup>·N<sup>-1</sup>). The wear mechanism of  $Mg_{56.5}Cu_{27}Ag_5Dy_{11.5}$ , AZ31B, and pure Mg sliding in air is dominated by oxidation and abrasive wear. The wear rates of alloys in NaCl decrease in the following order:  $8.3 \times 10^{-7}$  mm<sup>3</sup>·mm<sup>-1</sup>·N<sup>-1</sup> for pure Mg,  $6.3 \times 10^{-7}$  mm<sup>3</sup>·mm<sup>-1</sup>·N<sup>-1</sup> for AZ31B, and  $5.4 \times 10^{-7}$  mm<sup>3</sup>·mm<sup>-1</sup>·N<sup>-1</sup> for Mg\_{56.5}Cu\_{27}Ag\_5Dy\_{11.5} and pure Mg demonstrate inferior corrosion resistance in NaCl to that of AZ31B. Thus, the  $Mg_{56.5}Cu_{27}Ag_5Dy_{11.5}$  and pure Mg subject to tribocorrosion controlled by synergistic effects of abrasive and corrosion exert which results in a large wear rate during sliding in NaCl. The possible mechanism of corrosion accelerating wear deterioration is discussed, which provides the guidance for the improvement in the tribocorrosion resistance of Mg-based BMGs for further load-bearing applications.

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#### 1. Introduction

Magnesium alloys exhibit low density, high strength to weight ratio, good machining ability, excellent shock resistance, and good electromagnetic shielding characteristics, which make them promising candidates for applications in the automotive, aerospace, and electronic fields [1,2]. However, the high electrochemical activity of Mg alloys results in an extremely poor corrosion resistance, particularly in saltspray conditions [3]. Moreover, high friction and poor wear resistance are critical issues seriously hindering the practical application of Mg alloys [4]. To date, improvements in the corrosion resistance and wear resistance have led to greater interest of Mg alloys for practical applications. Therefore, different strategies such as developing new alloys, composites, coatings, and microstructural modification have been widely adopted to address the issues of uncontrolled degradation and poor wear resistance for Mg alloys [5–7].

In comparison to crystalline materials, bulk metallic glasses (BMGs) with amorphous atomic structures lacking of microstructural defects

E-mail address: flower1982cn@126.com (N. Hua).

manifest intriguing superior properties, such as high yield strength, high elastic limit, good wear and corrosion resistance [8-10]. By now many glass-forming alloy systems have been developed, such as Zr-, Ti-, Cu-, Fe-, and Mg-based BMGs [9-11]. During last decade, Mgbased BMGs have attracted much attention due to their relatively low cost, superior mechanical properties, together with excellent process ability [11-20]. Basically, Mg-based BMGs could be summarized into three groups: (i) Mg-Cu-based BMGs [11-16], (ii) Mg-Ni-based BMGs [17,18], and (iii) Mg-Zn-based BMGs [19,20]. In the last decade, various Mg-based BMGs have been explored, where the majority of these are based on the Mg-Cu-based BMGs which exhibit a large supercooled liquid region and high glass forming ability (GFA) as well as much higher mechanical strength compared to crystalline Mg alloys [11-16]. Typically, the Mg<sub>61</sub>Cu<sub>28</sub>Gd<sub>11</sub> alloy with a critical diameter of 12 mm fully glassy rod was fabricated. This alloy exhibited a compressive strength of 1100 MPa and a plasticity of 0.4% [11]. Then on the basis of the Mg-Cu-Gd alloy, many quaternary and quinary Mg-based BMGs have been developed and studied by modifying composition and alloying elements [12–16]. For example, the critical diameter of Mg-Cu-Y-Nd reached 14 mm, the compressive strength reached 1200 MPa, and the plasticity was 1.2% [12]. The alloying of Mg-Cu-Y system by Ag had a positive effect on the GFA. The compressive strength of Mg-Cu-Y-Ag reached

<sup>\*</sup> Corresponding author at: Department of Materials Science and Engineering, Fujian University of Technology, 350118 Fuzhou, China.

1330 MPa [13]. Those centimeter scale Mg-based BMGs have superior mechanical properties in comparison to crystalline Mg alloys, which makes them promising for a wide variety of applications.

In most cases, material failures occur due to wear, corrosion and fatigue. These failures are very sensitive to its microstructure and properties. Inevitably, wear stresses are generated by the relative movements during cyclic loads when Mg alloys are in service [21]. Therefore, wear resistance is crucial for Mg alloys in load-bearing applications. Under corrosive conditions, especially in chloride-ion-containing solutions, wear loss of material can be attributed to the combined wear and corrosion actions that simultaneously occur during the friction process [22, 23]. Nevertheless, the investigations on the wear behavior of Mgbased BMGs as potentially applicable in situations where wear and corrosion simultaneously act are still very limited. Moreover, the wear mechanism of Mg-based BMGs in corrosive solutions has not been well understood so far. It is therefore important to investigate the corrosive wear mechanism of Mg-based BMGs in order to forecast and minimize their degradation and failure in service.

In our previous research, a group of pseudo-ternary Mg-(Cu-Ag)-Dy BMGs was developed by copper mold casting [24]. The critical diameter for glass formation increases from 10 mm for ternary Mg<sub>56.5</sub>Cu<sub>32</sub>Dy<sub>11.5</sub> alloy to 18 mm for pseudo-ternary Mg<sub>56.5</sub>Cu<sub>27</sub>Ag<sub>5</sub>Dy<sub>11.5</sub> alloy. To promote potential applications of this BMG as structural material, the aim of this work was therefore to investigate the tribological behavior of Mg<sub>56.5</sub>Cu<sub>27</sub>Ag<sub>5</sub>Dy<sub>11.5</sub> under dry sliding condition and under lubricated sliding condition in 3.5 wt.% NaCl solution. Commercial AZ31B alloy and pure Mg were employed as reference materials. Individual wear mechanisms under the different frictional conditions were also clarified from the series of investigations. All of the results provide the foundational information of the Mg-based BMG for further load-bearing applications.

#### 2. Experimental

Master alloys with nominal compositions of Mg<sub>56.5</sub>Cu<sub>27</sub>Ag<sub>5</sub>Dy<sub>11.5</sub> (in atomic percentage) were prepared by arc melting the mixtures of pure Mg, Cu, Ag, and Dy metals under Ti-gettered high purified argon atmosphere. From the master ingots, alloy plates with a dimension of  $50 \times 10 \times 1.5$  mm<sup>3</sup> were cast in copper molds. Rectangular BMG plates for wear tests were mechanically machined to the size of  $10 \times 10 \times 1.3$  mm<sup>3</sup>. Commercial alloy of AZ31B and pure Mg were processed with the same dimension as that of Mg<sub>56.5</sub>Cu<sub>27</sub>Ag<sub>5</sub>Dy<sub>11.5</sub> 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 K\alpha radiation.

Microhardness tests were carried out using a load of 300 g applied during 10 s. Rectangular samples  $(2 \times 2 \times 4 \text{ mm}^3)$  for compressive test were prepared and tested in a CMT5305 electronic universal testing machine at a strain rate of  $2 \times 10^{-4}$  s<sup>-1</sup> at room temperature. The lateral surface of the deformed samples was observed by SEM. Ball-ondisc reciprocating wear experiments were conducted on the surfaces of Mg<sub>56.5</sub>Cu<sub>27</sub>Ag<sub>5</sub>Dy<sub>11.5</sub> BMG, pure Mg, and AZ31B Mg-alloy using Si<sub>3</sub>N<sub>4</sub> ball of 6 mm in diameter as a counterpart. The tribological tests were conducted on the universal tribotester and the schematic of the measuring system was shown in Fig. 1. The reciprocating motion was based on a crank-slider mechanism. The BMG plate specimen was fixed onto the precision linear stage, which was connected to a rod driven by a motor. The frictional force was measured by the load sensor of the tribotester. A normal load of 20 N, sliding track length of 5 mm, experiment duration of 10 min, and reciprocating speed of 2 m/min were selected as the operating parameters. In evaluating effect of media, two sets of testing were conducted in air and 3.5 wt.% NaCl solution. At least three specimens were tested for each given condition to ensure reproducibility. The weight change of specimen before and after each test (namely, wear loss) was determined using a balance with an accuracy



Fig. 1. Schematic of the tribological measuring system.

of  $\pm$  0.0001 g. The topography and chemical composition of the worn surfaces and wear debris of samples was examined by scanning electron microscopy (SEM, CS-3400) equipped with energy dispersive X-ray spectrometry (EDS).

The corrosion resistance of  $Mg_{56.5}Cu_{27}Ag_5Dy_{11.5}$  BMG, pure Mg, and AZ31B Mg-alloy in 3.5 wt.% NaCl solution was examined by electrochemical measurements 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<sup>-1</sup> 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 examined by SEM and EDS. The uncertainties of the data are their standard deviations.

#### 3. Results and discussion

#### 3.1. Mechanical properties

Fig. 2(a) displays the room temperature uniaxial compressive stressstrain curve of as-cast Mg<sub>56.5</sub>Cu<sub>27</sub>Ag<sub>5</sub>Dy<sub>11.5</sub> rod with 2 mm in diameter. Mechanical properties of the Mg<sub>56.5</sub>Cu<sub>27</sub>Ag<sub>5</sub>Dy<sub>11.5</sub> BMG including the 0.2% offset compressive yield strength ( $\sigma_v$ ), plastic strain ( $\varepsilon_p$ ), and fracture strength ( $\sigma_{\rm f}$ ) are summarized in Table 1. The mechanical properties of pure Mg and AZ31B alloy in literatures are also listed for comparison [25,26]. The Mg<sub>56.5</sub>Cu<sub>27</sub>Ag<sub>5</sub>Dy<sub>11.5</sub> has a  $\sigma_v$  of 1030 MPa,  $\sigma_f$  of 1050 MPa, and  $\varepsilon_{\rm p}$  of 0.2%. The morphology after compression was examined by SEM, as described in the inset of Fig. 2(a). According to the fractographic appearance, like featureless mirror area and parallel shear bands (see inset of Fig. 2(a)), it is suggested that the dominant fracture behavior of the as-cast BMG sample, namely Mg<sub>565</sub>Cu<sub>27</sub>Ag<sub>5</sub>Dy<sub>115</sub> alloy is a typical brittle fracture mode, which means there is no plastic deformation occurs during the fracture process [27]. This finding is just associated with its compressive stress-strain curve. Fig. 2(b) presents the Vickers hardness (Hv) of Mg<sub>56.5</sub>Cu<sub>27</sub>Ag<sub>5</sub>Dy<sub>11.5</sub> BMG, AZ31B alloy, and pure Mg. It can be seen that their Vickers hardness are 296 HV, 66 HV, and 47 HV, respectively. The highly dense random packed structure of fully amorphous Mg<sub>56.5</sub>Cu<sub>27</sub>Ag<sub>5</sub>Dy<sub>11.5</sub> shows higher Vickers hardness and yield strength, which is an indicative of good wear resistance [22, 23].

#### 3.2. Tribological behaviors

Fig. 3(a) illustrates the wear rate and coefficient of friction for the  $Mg_{56.5}Cu_{27}Ag_5Dy_{11.5}$  BMG, AZ31B alloy, and pure Mg tested under dry friction condition with a sliding load of 20 N and a sliding speed of 2 m/min. The wear rates of the  $Mg_{56.5}Cu_{27}Ag_5Dy_{11.5}$  BMG, AZ31B alloy, and pure Mg are  $3.8 \times 10^{-7}$  mm<sup>3</sup>·mm<sup>-1</sup>·N<sup>-1</sup>,  $7.3 \times 10^{-7}$  mm<sup>3</sup>·mm<sup>-1</sup>·N<sup>-1</sup>, and  $6.5 \times 10^{-7}$  mm<sup>3</sup>·mm<sup>-1</sup>·N<sup>-1</sup>, respectively. It is noted that the wear resistance of  $Mg_{56.5}Cu_{27}Ag_5Dy_{11.5}$ 

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