The effect of cooling rate on the wear resistances of a ZrCuAlAg bulk metallic glass

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Abstract

In the present work, the local atomic ordering and the wear resistance of ZrCuAlAg bulk metallic glass (BMG) samples with different diameters have been studied using transmission electron microscopy plus autocorrelation function analysis, and pin-on-disc dry sliding wear experiments. DSC and TEM studies show that smaller diameter BMG samples have shorter structural relaxation time and therefore high free volume content and less local atomic ordering. While the wear experiments demonstrated that, with the same chemical composition, the smaller BMG sample exhibits higher coefficient of friction, higher wear rate, and tougher worn surface than the larger ones. Compared with larger BMG sample, the fast cooling rate of the smaller diameter samples result in looser atomic configuration with more free volume, which facilitates the formation of the shear bands, and thus leads to larger plasticity and lower wear resistance. The results provide better understanding on the relationship among the cooling rate, local atomic ordering and the wear resistance of BMGs.

Keywords: Metallic glasses; Cooling rate; Free volume; Wear resistance; Electron microscopy

1. Introduction

Bulk metallic glasses (BMGs) usually have many unique chemical, physical and mechanical properties compared with their crystalline counterparts. They have great potentials to be developed as functional and/or structural materials in sports, structural, engineering and medical industry [1-8]. For example, the high hardness coupled with high strength and corrosion resistance make BMGs promising materials of choices in tribological applications such as audio/video recording heads, foil bearings, electrical razors and razor blades [9-13]. Some of the previous studies have shown that parts made by metallic glasses often have higher wear resistance than those made by the crystalline alloys [14,15]. For example, the micro-sized Ni-based metallic glass gear was >300 times durable than the conventional carbon tool steel microgears [14], and the bearing rollers made by Zr-based BMGs have better wear resistance than the commercial GCr15 steel rollers [15]. Extensive attempts have been also devoted on studying the wear behaviors of different BMGs based on Cu- [16,17], Zr-[18,19], Ni-[14], and Ti [20]. Tam and Shek [17] compared wear behaviors of a $Cu_{60}Zr_{30}Ti_{10}$ BMG in different annealing states. Jin et al. [19] investigated the role of structural relaxation on wear resistance of a Zr-based BMG.

Fundamentally, the intrinsic functional or mechanical properties of a BMG alloy are strongly dependent on its internal atomic configuration [23], and the atomic structure of BMGs can be regarded as solids of frozen liquid atomic structure, composing of tightly bonded atomic clusters and loosely bonded free-volume zones [21,22]. For a given BMG chemical composition, the cooling rate applied during the materials preparation plays a vital role on determining the atomic structure and hence the their deformation behaviors [24]. Hu et al. [25] studied the effect of cooling rates on the bending plasticity of a Zr-based BMG and suggested that both free volume and structural heterogeneity control its plasticity. Liu et al. [26] reported cooling-rate induced softening from the surface to the interior in a binary CuZr BMG. Normally, a faster cooling rate can lead to lower yield strength but higher plastic deformation capacity [27,28]. Huang et al. demonstrated that the as-cast metallic glass sample with a smaller size often has larger plasticity upon compression [29,30], and also found that the glassy ribbon experiencing faster cooling rate has lower hardness, and greater pile-up height than the bulky sample during nanoindentation [31]. However, a systematic study that quantifies the relationship between the cooling rate, the local atomic ordering, and the resulting wear resistance of BMGs has not yet been reported in the open literatures so far.

In this paper, the correlation between the cooling rates and the local atomic ordering of a ZrCuAlAg BMG and the resulting sliding wear resistance were investigated with aims to understand more quantitatively the relationship between the materials manufacturing conditions, the atomic configuration, and the wear resistance.

2. Experimental details

A Zr-based bulk metallic glassy alloy, $Zr_{46}(Cu_{4.5/5.5}Ag_{1/5.5})_{46}Al_8$ (at. %), was selected as the experimental alloy because of its high glass forming ability [32]. The alloy ingots were prepared by arc melting the mixture of Zr (99.9 wt.%), Cu (99.9 wt.%), Ag (99.99 wt.%) and Al (99.99 wt.%) elements in Ti-gettered high-purity argon atmosphere. The master alloys were melted at least 4 times to achieve homogenous composition, and then cast into a copper mold to form different diameter (2, 3, 4, and 5 mm) samples of the similar length (~60 mm). Thermal properties of the as-cast alloy samples were examined using a Perkin-Elmer differential scanning calorimetry (DSC) operated at a continuous heating rate of 0.33 K/s under a flow of purified argon atmosphere. The microstructure of the as-cast samples was characterized using X-ray diffraction (XRD) with Cu Kα radiation, and a high resolution transmission electronic microscope (HRTEM, Philips Tecnai TF30ST) operated at 200 keV. The thin foils for the HRTEM analysis were prepared by mechanically polishing to a thickness of ~80 μm first, and then twin-jet electropolishing with 30 % nitric acid + 70 % methanol solution (vol. %) to electron transparent. Liquid nitrogen was used to prevent overheating of the thin foils during electropolishing. For the acquired HRTEM images, an autocorrelation function (ACF) analysis was applied to measure the amount and extent of local atomic structure ordering, and the results were used to compare quantitatively the degree of local ordering among the different diameter samples. The ACF analysis is actually as a statistical interpretation of the HRTEM images [33], and is often applied to assess the degree of local ordering in non-periodic objects [34,35], showing the reliability of the data obtained.

Sliding wear experiments were conducted on all samples using a CJS111B pin-on-disc wear testing machine in air at room temperature according to the procedure specified in ASTM: G99. The pins were made from the BMG sample while the counterbody disc was composed of hardened steel with a hardness of HRC63. The load applied was 10 N and the rotation speed of the disc was 0.4 m/s. The wear loss of the material was measured by weighing the sample before and after each wear step (5 minutes) using a high precision digital scale with ±0.0001 g resolution. The surface morphologies of the worn samples were examined by a FEI Quanta 200F scanning electron microscopy (SEM). Microhardness measurements of the as-cast samples were performed using a MICRO-586 micro-hardness tester on the polished samples with a load of 50 g and a load-dwelling time of 10 s. Ten measurements were made on each specimen to ensure the standard deviations < 5 %.

3. Results and discussion

Figure 1 shows the XRD patterns for all different diameter samples. It can be seen that except for one broad diffraction peak between the diffraction angles 30° and 50°, no detectable sharp Bragg diffraction peak corresponding to crystalline structure was found. These are typical XRD patterns commonly found in amorphous structures, indicating the glassy nature of all samples. Interestingly, the larger diameter sample exhibits higher XRD intensity compared to the smaller one, indicating its higher degree of atomic order within the XRD resolution. Meanwhile, the full width at half maximum (FWHM) was measured at 5.8^0, 5.5^0, 5.2^0, and 4.8^0 for the 2, 3, 4, and 5 mm samples, respectively, further confirming that larger diameter sample has higher degree of ordered structure.

HRTEM observations were performed to reveal the atomic structure. Figure 2 shows the HRTEM images and the corresponding selected area electron diffraction (SAED) patterns (inset) for all samples. All images [see Figs. 2a, 2c, 2e, and 2g] exhibit a homogeneous contrast without any noticeable long-range atomic orders. The corresponding SAED patterns for each image show one strong inner diffraction ring with a rather faint and diffuse halo, further confirming the amorphous nature of the samples, and agreed well with the outcomes of the XRD analysis above.

The ACF analysis was carried out to determine statistically the local ordering in the acquired images for all samples. Firstly, an area of 17.8×17.8 nm^2 was randomly selected from the images showed in Figs. 2a, 2c, 2e, and 2g and divided into 49 sub-images of 2.54×2.54 nm^2, a size approximate to the medium-range order (MRO) atomic cluster, and then fast Fourier transformed into images as shown in Figs. 2b, 2d, 2f, and 2h, respectively. In each group of the 49 sub-images, one sub-image, which has crystal-like diffraction spots (the one marks by red square), was chosen as the reference pattern to compare and quantify the local ordering level of other sub-images. Thus the sub-images with clearer atomic fringe features than the reference pattern contain more ordered atomic configuration. Statistical analysis of all sub-images in Figs. 2b, 2d, 2f, and 2h revealed that the local ordering levels on the MRO scale are 8.2±1 %, 14.3±1 %, 16.3±1 %, and 24.5±1 %, for the 2, 3, 4, and 5 mm diameter samples, respectively, as also listed in Table I, indicating that the local ordering level of the studied glassy sample increases with the increasing of the sample diameters.

Figure 3 displays the DSC curves for all samples. As seen, the DSC curves of all samples are very similar, except some differences around the glass transition temperature (T_g), as more clearly seen in the inset of Fig. 3. The exothermic heat due to the structural relaxation below T_g for all samples can be calculated by integrating the heat flow in the nearby range below T_g (the area delineated by the tangent lines and the concave curves below in Fig.3 inset) and they are 8.59 , 6.41, 2.84, and 1.86 J/g for the 2, 3, 4, and 5 mm diameter glassy alloy samples, respectively, as also summarized in Table I. It is well known that below T_g, the exothermic heat release is directly related to the structural relaxation, i.e., the change of free volume in BMGs [36, 37], and can be calculated by:

$$(\Delta H)_{fv} = \beta \Delta v_f \tag{1}$$

where $(\Delta H)_{fv}$ is the change in enthalpy, Δv_f is the change of free volume per atomic volume, and β is a constant. Figure 3 inset displays the magnified views of the DSC curves below the glass transition temperatures. The calculation of the enthalpy release reveals that the smaller the diameter of the sample, the more the enthalpy release, and thus the more the free volume content of the sample. Apparently, the 2 mm diameter sample possesses the highest free volume content. The free volume content in a BMG actually represents the atomic packing density and is one of the important fundamental parameters governing the mechanical properties of BMGs. Here we focus on studying its effect on the wear resistance of the different diameter samples.

The coefficient of friction is used as an important parameter to evaluate the wear resistance of the material [38]. Figure 4a shows the friction coefficients as a function of time during the sliding wear experiments for all samples. The coefficient of friction was found to reach a steady-state stage after an initial rapid period, similar to those reported in [38,39]. The coefficients of friction in the steady-state stage were measured at 0.29, 0.26, 0.22, and 0.21 for the 2, 3, 4, and 5 mm samples, respectively. Smaller coefficient of friction means higher wear resistance because it requires more energy to remove the same volume of the materials. The wear rate was calculated using the following equation:

$$Q = \frac{V_W}{N.S} \tag{2}$$

where Q is the wear rate in mm^3/N.m, V_W is the wear volume (mm^3), and N and S are the applied load (N) and the total sliding distance (m), respectively. Figure 4b shows the wear rates of all different diameter samples as a function of sliding time during the wear experiments. As seen, compared with smaller Zr-based glassy alloy sample, larger sample with the same chemical composition has lower wear rate, and therefore higher wear resistance. In general, wear resistance is directly related to the hardness of the material. Archard’s empirical wear equation [40] shows that the sliding wear resistance is approximately proportional to the material’s hardness. Greer and coworkers also reported that the wear resistance of both BMG alloys and conventional hardened crystalline alloys increases with the increasing of their hardness [9].

For the present work, the microhardness of all samples were measured at 520.74, 534.34, 546.07, and 553.93 HV for the 2, 3, 4, and 5 mm samples, respectively, clearly suggesting that the faster the cooling rate for sample during solidification, the lower the microhardness; and the hardness and wear rate relationship follows the Archard’s empirical rule.

To better understand the difference in wear performance between the Zr-based BMG samples with different diameters, the worn surfaces were further examined by SEM observations. Figure 5 shows the corresponding SEM images of the worn surfaces of all samples after 40 minutes contact sliding. Clearly, 2 mm BMG sample has deeper and wider worn grooves with more materials ploughed out on the worn surface, as shown in Fig. 5a, suggesting that a severe plastic deformation occurs along the sliding direction. As sample diameters increase to 3, 4, and 5 mm, the ploughed grooves became shallower (Figs. 5b, 5c, and 5d), and much less ploughed debris can be found on the worn surfaces of 4 and 5 mm samples (Figs. 5c, and 5d). The above SEM observations further confirm that the smaller sample exhibits severe wear and more ductility, compared with the larger one with the same chemical composition.

It is generally accepted that the wear resistance of materials is a structural sensitive property [9]. For the present work, the difference in wear performance of the as-cast Zr-based BMG samples should be ascribed to the difference in the microstructure resulted from different cooling rates during sample preparation. Lin and Johnson [41] proposed a simple relationship between the sample diameter (D) and the cooling rate (dT/dt) as follows:

$$dT/dt = 10/D^2 \text{ (cm)} \tag{3}$$

Based on this. the cooling rates are calculated as 1000, 444, 250, and 160 °K/s, for the 2, 3, 4, and 5 mm samples, respectively.

During the sliding wear experiment, the wear pins that are made from the studied samples are subject to a continuous shear force, and the sliding-contact surfaces of the pin plastically deform via a mechanism of shear transformation zones (STZs) [42-44], a cluster of atoms that experienced inelastic shear straining under the applied stress. The activation of STZs takes place preferentially in the areas where the atomic packing density is relatively smaller (*i.e.*, higher free volume content). Hence, the materials with more free volume is expect to have a higher probability of forming STZs and is able to nucleate more shear bands [26,30,44], leading to larger plastic deformation capacity [45,46]. It is obvious that, during solidification process, the larger sample experiences slower cooling rate than the smaller one, and has longer structural relaxation time to allow atoms to diffuse a comparatively longer distance to form a denser atomic configuration with less free volume, as shown in Table I and Figs. 2 and 3. For larger sample, the increase of the stable local ordering with lower energy also leads to higher energy barriers for the activation of local stress events and a lower capability for the BMG to deform plastically. Therefore, structural relaxation leads to degradation in ductility and enhancement in hardness [Table I] as a consequence of the increased resistance to the activation of STZs, resulting in the lower wear rate [Fig. 4b], and lower coefficient of friction [Fig. 4a], and smoother worn surface [Fig. 5].

4. Conclusions

The effect of cooling rate on the local atomic ordering and the resulting wear resistance of a ZrCuAlAg bulk metallic glass has been studied. As the sample diameters increase, the samples experience slower cooling rate, leading to more structural relaxation time, less free volume content, and therefore more local atomic ordering. This more ordered atomic configuration result in lower coefficient of friction, lower wear rate and smoother worn surface for the larger diameter samples when compared to the smaller ones. These results indicate that cooling rate is one of the important processing parameters to control the local atomic ordering of BMGs, and can be used to tailor the wear resistance of BMGs for different applications.

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