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A study of the nanoscale and atomic-scale wear resistance of metallic glasses

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ABSTRACT

Metallic glasses are found to be applicable in micromechanical systems. When the size of the mechanical components is reduced to the micrometer and sub-micrometer level, the native surface oxide layer starts playing an important role in contact mechanical applications of metallic glasses. The nanoscale and atomic-scale scratch wear resistance of metallic glasses is studied in the present work using an atomic force microscopy at different loads. The wear rate is correlated with the properties of the metallic glasses studied and their respective surface oxides.

1. Introduction

Metallic glasses [1,2] and particularly bulk metallic glass-forming alloys [3,4] initially obtained in the Pd-Ni-P system [5,6] exhibit high mechanical strength [7,8], good wear resistance [9,10], large elastic deformation [11], good corrosion resistance [12] and thermal stability [13]. Although noble-metals- [6] and lanthanide-metals- [14] based well known bulk metallic glasses (BMGs) are not particularly attractive for engineering applications due to their high cost and low oxidation resistance, respectively, Ti [15], Zr [16,17] and Mg-based [18] bulk metallic glasses discovered later on are quite promising engineering materials.

Successful applications of metallic glasses in micromechanical devices have been demonstrated recently [19,20]. This implies that the mechanical contact between the component surfaces leading to wear is a significant factor in limiting their durability. When the size of the mechanical components is reduced to the micrometer and sub-micrometer level, the native surface oxide layer begins to play an important role in the contact mechanical behavior of metallic glasses. The nanoscale tribological properties of the $Ni_{62}Nb_{38}$ and Pt-Cu-Ni-P metallic glasses have recently been studied [21–23]. The surface structure of the $Ni_{62}Nb_{38}$ metallic glass has also been characterized before and found to consist of atomic clusters [24,25]. In the present work we study the nanoscale scratch wear resistance of Ti-, Zr- and Mg-based bulk metallic glass-forming alloys (non-ferrous BMGs suitable for structural applications) in seizure wear regime using an atomic force microscope at ambient conditions.

2. Experimental procedure

The ingots of the $Ti_{43}Zr_{10}Cu_{36}Ni_9Sn_2$, $Zr_{62.5}Cu_{22.5}Fe_5Al_{10}$ and $Mg_{65}Cu_{25}Gd_{10}$ alloys were prepared by arc-melting the mixtures of pure metals (99.9 mass.% purity or above) under an argon atmosphere. Ribbon samples with thickness of $\sim$20 μm and width of $\sim$1 mm were prepared by melt spinning onto a single copper roller at a roller tangential velocity of about 40 m/s while 2 mm diameter bulk metallic glassy samples were prepared by Cu-mold casting. All the samples were found to be fully glassy by using conventional X-ray diffractometry (XRD) with monochromatic CuK_α radiation. The Vickers microhardness was also measured.

Tapping mode and contact mode of the atomic force microscopy (AFM) technique were used for obtaining the topography profiles and performing scratch tests, respectively. The diamond single crystal cantilevers (AFM Probe ART D300) used in this study

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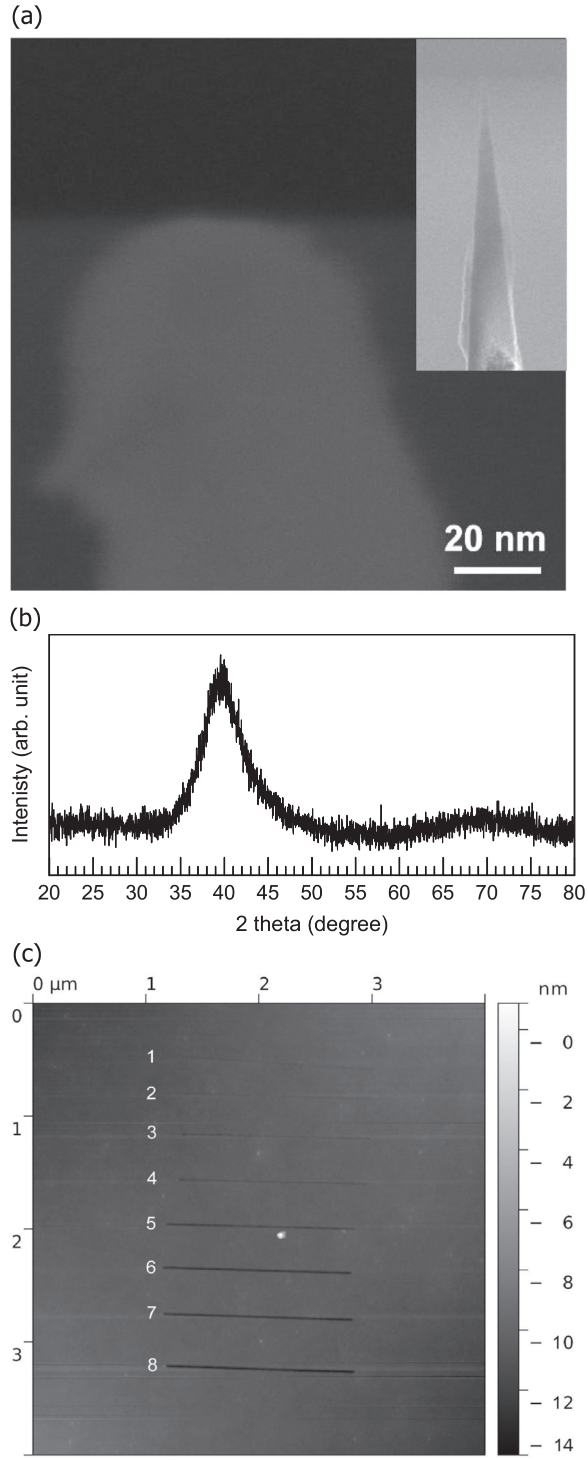

Fig. 1. (a) A tip used for scanning and for wear tests, scanning electron microscopy image. The inset is the tip image recorded at lower magnification. (b) X-ray diffraction pattern of the $Ti_{43}Zr_{10}Cu_{36}Ni_9Sn_2$ alloy. (c) The $Ti_{43}Zr_{10}Cu_{36}Ni_9Sn_2$ glassy alloy surface after scratching at different loads (from 0.35 to 1.6μN). The scratches with increasing loads are marked as 1–8.

have a typical spring constant of 40N/m and a rounded tip (Fig. 1(a)). The spring constant of each cantilever was measured using a technique based on measuring the change in resonant frequency of the fundamental mode of vibration [26]. As the spring constant is rather large and the Young's modulus of the diamond tip is high its deformation is neglected. For each AFM session a new cantilever was taken. The wear rate (W_s) (the test was performed at 2μm/s) was calculated by dividing the wear volume (V) by the scratch length (L).

Thickness of the oxide layers was estimated by the analysis of the oxide film growth dynamics in an artificially created scratch of 20–30 nm depth on the surface of each sample. The atomic force microscope operating in contact mode was used for creating scratches and for measuring their profiles as well as the electrical conductivity (using a conducting Pt covered **AFM** probe: **ETALON HA_C/Pt**). The vertical electrical resistance was measured in the bottom of scratches in the contact mode at a load of 100 nN. The measurements of the profiles and a series of electrical resistance measurements were performed on the bottom of the scratches during 10 h. Profiles of the scratches and the electrical resistance ceased to change after about 8 h for the Ti- and Mg-based alloys and after ~ 4 h for the Zr-based one. The resistance immediately after scratching was less than 1 MOhm and became more than 10 GOhm at the end of the measurement cycle. The contact area of the tip-sample while measuring the electrical resistance was about 40×40 nm^2.

3. Results

Fig. 1(b) shows an X-ray diffraction pattern of the $Ti_{43}Zr_{10}Cu_{36}Ni_9Sn_2$ alloy. The other samples studied also had an amorphous structure. Each surface was scanned before and after the scratch test. The initial metallic glassy surfaces are found to be smooth. Root mean square roughness (R_q) was found to be 0.30 nm for Mg-based, 0.28 nm for Zr-based and 0.37 nm for Ti-based alloy. Fig. 1(c) shows the $Ti_{43}Zr_{10}Cu_{36}Ni_9Sn_2$ alloy surface recorded after scratching at different loads (P).

The scratch depth (h) and the wear volume (V) were measured by using a profile integrated through the scratch length (Fig. 2). This value is equal to the wear volume divided by the wear length (L) typically used for such calculations.

Fig. 3 shows the wear rate (W_s), the scratch depth (h) and the wear coefficient ($k_w = W_s/P$, where P is the load) as a function of load. The scratch depth of as small as an atomic layer is recorded in $Zr_{62.5}Cu_{22.5}Fe_5Al_{10}$ and $Ti_{43}Zr_{10}Cu_{36}Ni_9Sn_2$ alloys.

These properties, along with some others are shown in Table 1. The k_w of the $Zr_{62.5}Cu_{22.5}Fe_5Al_{10}$ and $Mg_{65}Cu_{25}Gd_{10}$ metallic glasses does not depend systematically upon the load while it does in the case of the $Ti_{43}Zr_{10}Cu_{36}Ni_9Sn_2$ one. The SEM image in Fig. 1(a) shows that the single crystal diamond tip of the probe is cylindrical rather than conical and the scratch widths correlate reasonably with the probe sizes. Thus, because the curvature of the diamond tip is significantly larger at a small scratch depth of below 3 nm than that of a larger depth (see Fig. 1(a)), the maximum width (W_m) of the scratch at the ground level and its full width at half maximum (FWHM) are almost independent of the load at such depth values.

As a result of a series of the scratch profiles as well as the electrical conductivity measurements thickness of the oxide layer after 10 h in case of the $Mg_{65}Cu_{25}Gd_{10}$, $Ti_{43}Zr_{10}Cu_{36}Ni_9Sn_2$ and $Zr_{62.5}Cu_{22.5}Fe_5Al_{10}$ alloys is estimated at 1.4 ± 0.1, 1.2 ± 0.3 and 1.2 ± 0.3 nm, respectively. This is significantly thinner than was observed for Cu-Zr-Al [27] and Ni-Nb [21,22] metallic glasses but close to that observed for the $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ one [28].

4. Discussion

It is known that the surface oxide can have a beneficial effect on reducing wear during the sliding of metals and alloys, particularly by preventing the metal to metal contact [29]. An oxide thickness of a few nanometers is typical for metallic glassy alloys. It was found that the $Ni_{62}Nb_{38}$ metallic glass forms an amorphous