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In situ atomic level observations of Al_2O_3 forming on surface of metallic glasses

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ABSTRACT

It is common wisdom that metallic glasses (MGs) exhibit excellent oxidative resistance due to their disordered structure and lack of defects and grain boundaries. A more interesting fact is that among normal MGs, aluminiferous MGs exhibit unsuspected and excessive strong antioxidant ability. However, the mechanism of antioxidation of aluminiferous MGs at very thin surface remains unknown. We report the direct atomic level observations on the dynamic process of Al_2O_3 forming at aluminiferous MGs surface by the high resolution transmission electron microscopy. The Al_2O_3 layer at surface serves as a compacted protective layer to slow down the further oxidation of MGs.

Metallic glasses (MGs) with excellent mechanical and chemical properties such as high strength, elasticity, castability, corrosion resistance and catalytic performance [1,2], have potential applications in precise instruments [3], aerospace industry [4], coating [5], and even biomedical filed [6]. Antioxidation ability is one of crucial issues for these practical applications. Oxidation rate of MGs is found to be closely related to the temperature, time, oxygen pressure, humidity, as well as surface morphology [7] and composition [8] of alloys. The general understanding of oxidation resistance attributes the high antioxidation of MGs to their structural characteristics, such as the disordered atomic structure, lack of defects and grain boundaries of crystals. Many studies of the oxidation have been done on MGs including the microstructure of the native oxide layer [9–11]. However, the dynamic microstructural mechanism of the oxidation on the very thin surface at room temperature remains unclear, which may control the rate and thickness of oxidation [12–18]. Therefore, the study on diffusion and structural evolution at the surface layer is essentially important. In addition, diffusion in crystal has been studied widely in crystalline solids [12–14], most of which are depended on vacancy and interstitial diffusion mechanisms. The diffusion coefficient is closely related to the temperature, crystalline structure, free volume, defects, chemical component and other external conditions such as irradiation and vacuum degree [15,16]. Owing to the excess free volume quenched in by rapid cooling from the liquid states, MGs display higher diffusion coefficient than that of their crystalline countparts [17]. It is reported that Cu atoms in ZrCu MG tend to diffuse into the surface below T_g [18]. It is possible that Al atoms in aluminiferous MGs diffuse from the bulk into the surface and form surface passivation layer with good oxidation or corrosion resistivity [19]. However, hitherto few microstructural studies have been done on the thin top layer at the surface of aluminiferous MGs.

In this work, we investigate the antioxidation mechanism at MG surface in atomic scale through observations of Al diffusion and oxidation process stimulated by the electron beam with the high resolution transmission electron microscopy (HRTEM). It reveals that under electron-beam irradiation, an Al_2O_3 layer is formed indeed on the surface of the aluminiferous MGs including typical $Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$, $La_{65}Ni_{20}Al_{15}$ and $Zr_{47.5}Cu_{47.5}Al_5$. The entire process from nucleation to crystal growth of Al_2O_3 at surface is observed and discussed. The direct atomic level observation on the oxidation process of aluminiferous MGs clarifies the role of Al in antioxidative performance of MGs, and an atomic level kinetic process is proposed to explain the mechanism of the improved antioxidative properties.

$Zr_{47.5}Cu_{47.5}Al_5$ and $Zr_{50}Cu_{50}$ ribbons were fabricated by melt spinning. $Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$, $La_{65}Ni_{20}Al_{15}$ and $Zr_{47.5}Cu_{47.5}Al_5$ bulk samples were fabricated by copper mold casting method [20]. TEM samples were prepared by the typical standard method including milling, dipping and thinning by Ar-ion beam at a vacuum of 5×10^{-4} Pa. The

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whole preparing process was operated below the temperature of 130 °C to ensure the amorphous state of the samples. The HRTEM experiments were performed on a Philips CM200 TEM with a field emission gun, with an electron dose of no more than 3×10^7 electrons s^{-1} nm^{-2}. The composition was examined by X-ray photoelectron spectroscopy (XPS) using an electron spectroscopy for chemical analysis (ESCA). The hardness test was performed using a Nano Indenter G200 XP.

Al element is found to be critical component in bulk MGs with excellent glass-forming ability [21]. Although Al is reported to act as a role which can enhance the oxygen tolerance [8], how it affects the rate and thickness in oxidation process is not discussed. Aluminiferous MGs are usually more antioxidative than MGs without aluminum. Fig. 1(a) shows pictures of the MGs with compositions of $Zr_{47.5}Cu_{47.5}Al_5$ and $Zr_{50}Cu_{50}$, which were exposed to the air for more than one year. The $Zr_{50}Cu_{50}$ sample was oxidized into black color and the surface became coarser, in contrast, the $Zr_{47.5}Cu_{47.5}Al_5$ remains the metallic glossy and smooth surface. In addition, XPS experiments on the surface of $Zr_{50}Cu_{50}$ and $Zr_{47.5}Cu_{47.5}Al_5$ that were exposed to the air for a week, were also performed as shown in Fig. 1(b) and (c). The peaks at 330 eV and 343 eV represent the Zr element without oxidization. The peaks at 334 eV and 347 eV correspond to the oxidized Zr element, implying the oxidation of Zr element enlarges its ionization energy of Zr 3p electrons [22,23]. We can see that Zr element was totally oxidized at the depth of 5 nm and 10 nm and partially oxidized at the depth of 30 nm in $Zr_{50}Cu_{50}$ (Fig. 1(b)). In contrast, $Zr_{47.5}Cu_{47.5}Al_5$ was also totally oxidized at the depth of 5 nm, partially oxidized at the depth of 10 nm, but was not oxidized at the depth of 30 nm (Fig. 1(c)), indicating that the oxidization process in aluminiferous MGs is much more sluggish than that in the non-aluminiferous MG.

Fig. 2(a) presents a schematic of the electron irradiation experiment. There are three major functions of the electron irradiation: one is to image the sample and record the process; the second is to speed up the atomic diffusion, as demonstrated in the simulation method applied in the geology [24]; the last is to provide energy to activate nucleation and growth [15]. Fig. 2(b) shows the initial amorphous state of the surface of the MG sample. Fig. 2(c) shows the Al_2O_3 film is formed outside the surface after the electron irradiation. The interplanar distance of 0.24 nm proves the film to be Al_2O_3 as shown in the HRTEM image in Fig. 2(d). To confirm the elements at surface of the film, energy-filtered TEM (EFTEM) images of Al and O elements were collected as shown in Fig. 2(e). The results indicate that Al and O elements assemble themselves on the surface with scale of a few nanometers, further confirming that the crystal at the surface is Al_2O_3.

The detail evolution process was also recorded and shown in Fig. 3 and Video 1 in Supplementary material. The $Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$ was irradiated under the electron beam with an electron dose of 2.49 $\times 10^6$ electrons s^{-1} nm^{-2}, and the process can be divided into four stages as shown in Fig. 3(a)–(d). When the electron beam began to

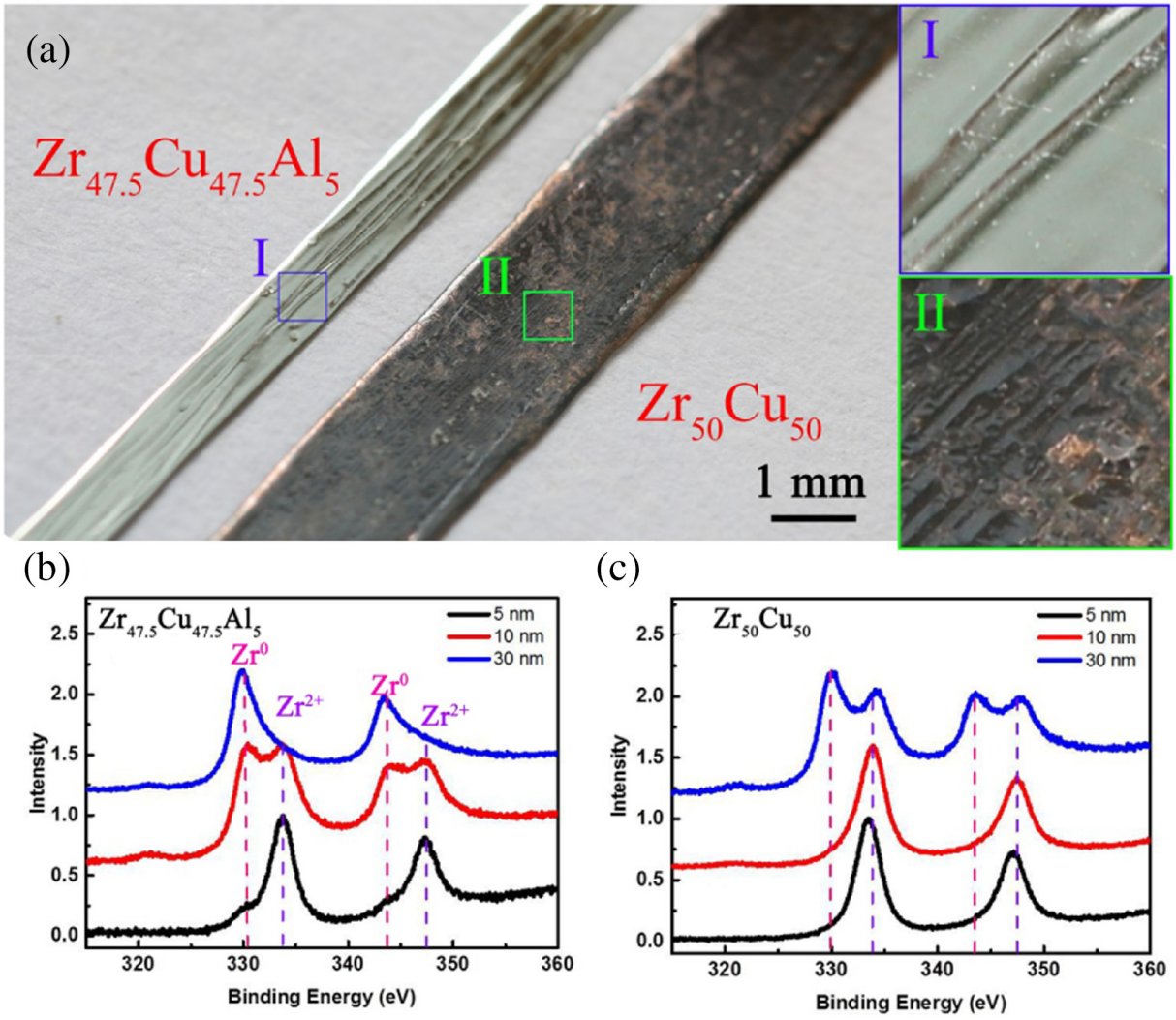

Fig. 1. (a) The images of $Zr_{47.5}Cu_{47.5}Al_5$ and $Zr_{50}Cu_{50}$ MG ribbons after expose in the air for more than one year, and the enlarged pictures show the difference of the surface of the two MGs; (b) and (c) XPS of $Zr_{47.5}Cu_{47.5}Al_5$ and $Zr_{50}Cu_{50}$ at the depth of 5 nm, 10 nm and 30 nm from the surface, respectively. Both samples were exposed in the air for a week before the XPS measurements.