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Bulk metallic glassy surface native oxide: Its atomic structure, growth rate and electrical properties

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ABSTRACT

Formation of a native oxide layer on the surface of bulk metallic glasses (BMGs) influences significantly the nanoscale tribological properties and mechanical behavior of the BMGs used in nanodevices. However, our knowledge of the native oxidation process on the BMG surface and structure of the corresponding oxides remains limited because the oxide layer is very thin. Here we conducted a combined state-of-the-art experimental technique study of the atomic structure, oxidations states and electrical conductivity of the native surface oxides on a Cu—Zr—Al BMG formed at ambient conditions by aberration-corrected scanning transmission electron microscopy (STEM), X-ray photoelectron spectroscopy (XPS) and conductive atomic force microscopy (AFM). This allowed shedding light on the atomic structure, metal oxidation state, growth behavior and nanoscale electrical properties of the surface oxide. The conductive AFM measurements reveal that the electrical conductivity of the native oxide layer transits from the initially metallic to a nonlinear one after some air exposure, and finally changes to insulative state. These findings represent a significant step forward in the knowledge of surface oxides and open up the possibility of fabricating nanoscale electrical devices based on BMGs with controllable conductivity.

1. Introduction

Bulk metallic glassy alloys, which are also known as bulk metallic glasses (BMGs) have become widely studied since the end of the past – beginning of the present Century [1] owing to their remarkable properties [2,3]. Such alloys exhibiting high mechanical strength [4,5], high hardness [6], good wear resistance [1], large elastic deformation [7], good corrosion resistance [8] and thermal stability [9] have been initially obtained in Pd-based [10,11] and later in many other alloy systems [12,13]. Zr—Cu- and Cu—Zr-based system ternary and quaternary BMGs are among the best bulk metallic glass formers exhibiting high glass-forming ability (GFA) [14] and high mechanical strength [15]. Their corrosion resistance is improved by alloying with Al [16] and BMG is more resistant to the onset of pitting corrosion under natural corrosion conditions than the crystalline counterpart.

Due to the high chemical activity of metals, any metal or alloy, crystalline or glassy, with the exception of certain noble metals, interacts with the environment through an oxide film on its surface, which is either native or artificially grown. As it is known, native oxide thin films play an important role in the protection of materials. For example, the oxides of reactive metals, such as Al and Ti, can provide high protection from further oxidation in dry environment. In the same way a Cr oxide film protects stainless steels from corrosion and further oxidation. Bulk metallic glasses, even those based on noble metals [17] also contain surface oxide films. As it was recently discovered, the Ni—Nb bulk metallic glassy alloy contains a thin layer of an amorphous niobium oxide [18] improving its nanoscale tribological behavior [19,20]. Thus, surface oxides are important because Ni- and Fe-based metallic glasses have found successful application in micro-motors [20] and other electro-mechanical devices [21], respectively. In addition, thin oxide films, for example, TiO_2 films exhibit the potential industrial

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application as dielectric materials, gas sensors, filters and photocatalysts [22,23]. Similarly, one can expect useful practical applications of the oxide films on the surface of BMGs, especially if they are homogeneously amorphous.

Typical native oxide films formed at ambient conditions on crystalline Ti and Al, are found to be quite thin (3–4 nm in thickness) and amorphous [24,25]. However, Cu and Zr form crystalline native oxides. A layer of crystalline Cu_2O and CuO oxides with a thickness of ~5 nm was found to be formed on the surface of Cu by room-temperature oxidation [26,27]. Oxidation of Zr at room temperature involves three stages: the initial solution of oxygen in α-Zr, the nucleation of ZrO_2 on the surface, and the further growth of the ZrO_2 layer [28]. The growth rate of crystalline oxides on a non-flat surface was found to be non-uniform [29,30] but its behavior in the glassy state is not so clear.

Thermal oxidation behavior of Zr—Cu and Cu—Zr glassy alloys on heating has been studied extensively, and relatively thick layers of various crystalline oxides were formed. Thermal oxidation of Zr—Cu-based BMGs was found to follow one of two mechanisms [31]: either nodules of tetragonal ZrO_2 with embedded nanocrystals of other late transition metals (CuO and ZrO_2 oxides on the surface of $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG [32] or Cu_2O, CuO and tetragonal ZrO_2 on Cu—Zr—Al BMG [33]); or formation of a lamellar structure of the tetragonal and monoclinic forms of ZrO_2 ($Cu_{50}Zr_{50}$ and $Cu_{46}Zr_{46}Al_8$ metallic glasses [34]). On the other hand layers of CuO/Cu_2O and a minor fraction of cubic-ZrO_2 were formed on Cu-rich $Cu_{60}Zr_{30}Ti_{10}$ metallic glassy surface [35]. Zr—Pd BMG forms two polymorphs of crystalline ZrO_2 at different temperature ranges [36]. Although Ti produces a ternary Ti_4Cu_2O oxide with Cu [37,38] it is not the case with Zr. Upon thermal oxidation at 573 K the amorphous niobium oxide film grew on the surface of $Ni_{62}Nb_{38}$ glassy alloy while crystalline Ni nanoparticles precipitated within the oxide layer after a substantial annealing (for 2 h) [39].

Although, as it is shown above, thermal oxidation process of metallic glasses on heating in air was studied substantially little is known about the detailed structure and growth rate of native oxides. Also, thin amorphous oxide films can be used in the field of microelectronics, because of their uniform thickness and related properties such as low leakage current and high dielectric constant [40,41]. And, of course, needless to mention that surface oxide often determines corrosion resistance of the sample. Earlier XPS studies estimated thickness of the native surface oxide thin film on Cu—Zr-based BMGs at about 3 nm [42]. However, detailed structural information is not available so far.

Also, as ZrO_2 and Al_2O_3 (in addition to their high hardness) are good insulators but become conductive if the layer is extremely thin, a study of the structure and properties of the native oxide surface film on a Cu—Zr-based metallic glass deserves significant interest from both fundamental and applied science viewpoints. The $Cu_{47}Zr_{45}Al_8$ alloy (composition is given in nominal atomic percentages), a typical representative of Cu—Zr BMGs with high strength and exceptionally high GFA among ternary Cu—Zr—Al and Zr—Cu—Al alloys (its critical sample diameter obtained by copper mold casting is 15 mm) [43], was chosen for study.

2. Experimental procedure

An ingot of the $Cu_{47}Zr_{45}Al_8$ alloy was prepared by arc-melting the mixtures of Cu (99.99 mass.% purity), Zr (99.9 mass.% purity) and Al (99.9 mass.% purity) under an argon atmosphere. Bulk cylindrical glassy samples of 2 mm in diameter were prepared by Cu mold casting of the as-prepared ingot. Ribbon samples with thickness of ~20 μm and width of ~1 cm were prepared by melt spinning onto a single copper roller at a roller tangential velocity of about 40 m/s. All the samples were confirmed to be fully glassy by the conventional X-ray diffractometry (XRD) with monochromatic CuK_α radiation and exhibited glass transition, supercooled liquid region and crystallization on heating in a differential scanning calorimeter. Transmission electron microscopy (TEM) observations of the cross-sectional bulk samples were carried out using a JEM-2010F microscope (JEOL Co. Ltd.) with an aberration coefficient of objective lens of 1.0 mm operated at 200 kV. The scanning transmission electron microscopy (STEM) images and energy dispersive X-ray Spectroscopy (EDS) mapping were taken with a 200 kV STEM (JEM-ARM200FC, JEOL Co. Ltd.) equipped with a probe corrector (CEOS, Gmbh) and the NORAN System 7 X-ray Microanalysis System. A probe size of 1.3 Å and a probe convergence angle of ~25 mrad were used for the STEM imaging and EDS mapping. The high-resolution high-angle annular-dark-field (HAADF) images were taken by an annular-dark field detector with a collection semiangle of 68–280 mrad. The annular-bright field (ABF) images were taken by an annular-bright field detector with a collection semiangle of 12–24 mrad. EDS mapping was acquired by integration of 500 frames with the frame exposure time of 15 s per frame. Thin-foil specimens for TEM observations were prepared by cutting, mechanical grinding and dimpling slices of the as-prepared BMG alloy down to 20 μm. In the final Ar ion-beam thinning process, we applied an accelerating gun voltage of as low as 2 kV, incident beam angles of 4–5°, and cooled the sample by liquid nitrogen to avoid radiation damage and thermal effect.

X-ray photoelectron spectroscopy (XPS) was carried out using an apparatus equipped with Scienta MX650 X-ray source of 0.2 kW power with the Al K α (1486.7 eV) radiation. Each XPS analysis session was preceded by the recording of the Au $4f_{7/2}$ peak (Binding energy (BE) = 84.00 eV) for the energy calibration. Each sample was placed perpendicular to the electron energy analyzer axis. The spectra were analyzed using «NIST X-ray photoelectron spectroscopy» database as a source of the binding energy values [44]. Subtraction of the background was done by the Shirley–Pro ctor–Sherwood method [45,46].

Tapping mode and contact mode of atomic force microscopy (AFM) technique were used for obtaining the topography profiles and a series of local current–voltage characteristics (CVCs), respectively. Pt coated conductive cantilevers (Microscience, model N14/Pt) used in this study have the spring constant of 6–10 N/m and the cantilever tip radius of ~40 nm. The spring constant was measured for each cantilever using a technique based on measuring the change in resonant frequency of the fundamental mode of vibration [47]. For each AFM session a new cantilever was taken. The CVC curves were recorded in contact mode with a voltage sweeping rate 15 mV/s and within ±3 Volts range. The AFM cantilever load was kept constant during CVC measurements.

Topography of a surface area was recorded continuously for 4 days after the polishing. A typical place containing scratches induced by polishing was chosen and the topography profiles were recorded. Thickness of the oxide was calculated each time as a half of the difference between the current scratch width compared to the width of the scratch immediately after polishing.

3. Results and discussion

High-resolution TEM observations were conducted to investigate the formation of a native oxide layer on the surface of $Cu_{47}Zr_{45}Al_8$ BMG alloy by using a cross-sectional sample. As shown in Fig. 1(a), a layer of native oxide with a thickness of ~10 nm is formed on the surface of the $Cu_{47}Zr_{45}Al_8$ BMG alloy. It consists of the dominant amorphous oxides with homogenously embedded crystalline Cu_2O nanoparticles of 5–10 nm in size with an average distance of 20 nm between them. For example, the 2.13 Å-spaced lattice fringes in the crystalline nanoparticle correspond to {2 0 0}