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Surface structure and properties of metallic glasses

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ABSTRACT

Surface state and its quality determine some important properties of metallic glasses. Control over of the nanoscale tribological behavior of metallic glasses is fundamental for their applications in micro- and nano-electromechanical devices. Owing to continuous miniaturization of these devices the mechanical contact area becomes of nanoscale, whereas the nanoscale wear resistance of metallic glasses can be improved taking into the account their surface oxides. Surface oxides also determine (bio)chemical properties of metallic glasses and alter their electrical properties. In the present paper we overview recent works on the subject and present the original research results related to the nanoscale tribological properties of metallic glasses.

1. Introduction

A bulk object interacts with the environment through its surface. Typical metallic alloys, except for noble metals and their mixtures are covered with native oxides which, in many cases, determine their properties. This work is devoted to the description of surface structure and properties of metallic glasses.

2. Experimental details

The paper contains some data from our previous works (where indicated) and the original research data obtained in the present research. The ingots of the studied alloys were prepared by arc-melting the mixtures of pure metals (99.9 mass% purity or above) under an argon atmosphere. 20 µm thick $Al_{85}Yb_8Ni_5Co_2$ ribbon samples were prepared by melt spinning onto a single copper roller while the $Zr_{62}Cu_{22}Fe_5Al_{10}Dy_1$ bulk metallic glassy samples were prepared by Cu-mould casting. The samples were studied by using conventional X-ray diffractometry (XRD) with monochromatic CuK_α radiation and found to be glassy. The atomic force microscopy (AFM) technique was used for obtaining the topography profiles and performing scratch tests.

3. General surface features

Single crystals have perfect structure and often atomically flat surface but are quite difficult to produce. Polycrystalline materials which are most commonly used by engineers contain lattice defects, grain size distribution and grain boundaries. Ordinary glasses, including metallic glasses [1,2], unless phase separated, are homogeneous and isotropic materials at the length scale of tens of nanometers and larger [3]. Viscous flow must be controlled for achieving high surface quality on mechanical polishing [4]. Metallic glasses are also used as surface coatings for crystalline alloys [5].

General surface effects observed in crystals near the surface are relaxation: change in the interatomic distances and reconstruction: rearrangement of the atomic positions compared to the bulk structure. Another interesting effect is surface melting in solids a few tens of degrees Kelvin bellow the bulk melting temperature (T_m) and surface crystallization in liquids slightly above the liquidus temperature (T_l). For pure substances and eutectic alloys $T_m=T_l$. A typical example is the surface melting of ice below 0 °C [6,7]. Moreover, the solid-liquid transition at the (110) surface of Pb starts about 40 K below T_m [8]. The thickness of the liquid surface film

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increases as the temperature approaches T_m. Also, an Au-based glass-forming alloy was found to contain a very thin layer of a crystalline phase up to 50 K above T_l [9].

An oxide-free polished surface of the $Ni_{62}Nb_{38}$ bulk metallic glass (BMG) (Fig. 1) was studied by the scanning tunneling microscopy (STM) and found to consist of the atomic clusters of 0.8–1 nm size [10,11] which could be partly responsible for nanoscale heterogeneity in BMGs [12]. One could admit excellent surface quality of the sample and low roughness. Unusual structure elements were observed on the surface of the $Ni_{40}Ta_{60}$ metallic glass [13].

Owing to good surface activity and large surface area Fe- [14], Mg- [15] and Al-based [16] metallic glassy powders, as well as metallic glass/TiO_2 mixtures [17] were successfully applied for water purification. Their efficiency was found to be significantly higher than that of the crystalline counterparts.

4. Native surface oxides

Typical metals and alloys at ambient conditions are always covered by a surface oxide (Fig. 2a). Even noble metal-based metallic glasses as they typically contain Si or P (Au- or Pd-based BMGs, respectively), also interact with the environment through an oxide film [18]. Formation of a native oxide layer on the surface of metallic glasses was studied by X-ray photoelectron spectroscopy (XPS) [18,19], high-resolution transmission electron microscopy [20] and atomic force microscopy [20]. The native oxide layer on the $Cu_{47}Zr_{45}Al_8$ BMG surface consists of the dominant Al_2O_3 and ZrO_2 amorphous oxides with Cu_2O crystalline nanoparticles embedded (Fig. 2b). Cu-enriched layer is formed at the metallic glass/oxide interface because Cu is the most noble metal among the components and diffuses towards the metallic matrix. Initially the oxide film grows nearly linearly with time, while later the growth rate of the film decreases quickly [20]. This process is difficult to describe by a singular mechanism.

Metal oxidation process includes: O_2 gas surface absorption, oxygen dissolution, a thin oxide film formation, the oxide layer growth, formation of a thick oxide layer which later starts to crack [21]. Native oxides on the surface of metallic glasses are usually amorphous and thin while crystalline oxides growing at high-temperature upon thermal oxidation become thick, polycrystalline and fragile [22].

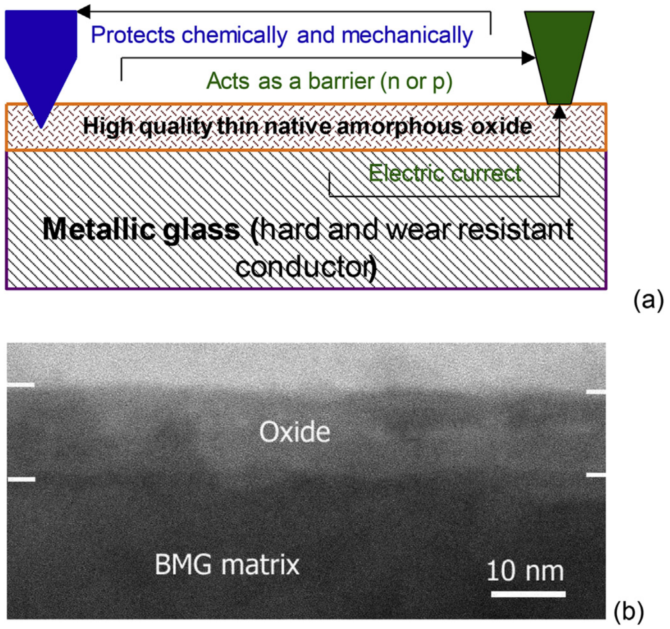

Fig. 2. (a) Schematic representation of the role of the surface oxides on metallic glasses. (b) High-resolution transmission electron microscopy image of a native oxide layer on the $Cu_{47}Zr_{45}Al_8$ BMG surface.

5. Role of surface oxides in corrosion resistance

A high quality protective surface oxide is preferred for chemical and mechanical stability. The $Ti_{45}Zr_{10}Pd_{10}Cu_{31}Sn_4$ BMG possesses high corrosion resistance after immersion in 3 mass% NaCl, 1 N H_2SO_4 and 1 N H_2SO_4 + 0.01 N NaCl solutions [23]. The high corrosion resistance of the alloy is attributed to its chemically homogeneous glassy phase, absence of grain boundaries and formation of the Ti^{4+}- and Zr^{4+}-enriched highly protective thin surface oxide film in the corrosive solutions. Zr-based [24] and Cu-based BMGs [25] also exhibited good corrosion resistance. Good biocompatibility was observed in case of Ti-based BMGs [26,27] and nanostructured Ti-based metallic glasses [28]. Biodegradable BMGs containing elements existing in a human body interact with the body fluid and dissolve after a certain period of time [29].

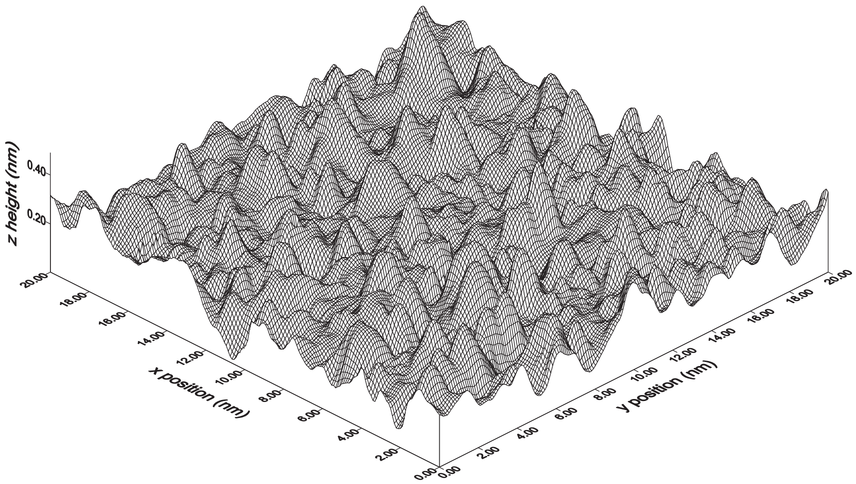

Fig. 1. An isometric projection of the $Ni_{62}Nb_{38}$ bulk metallic glass surface studied by STM. Courtesy of A. Oreshkin.