ARTICLE IN PRESS

Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Influence of oxygen on the glass formation of Mo–O binary alloys

F.H. Duan[a,b], Y. Lin[a,b], J. Pan[a,*], Y.X. Wang[a], J.H. Yao[a], Y. Li[a,*]

[a] *Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China*
[b] *University of Chinese Academy of Sciences, 19 Yuquan Road, Beijing, 100049, China*

ARTICLE INFO

Keywords:
Amorphous alloys
Oxygen-bearing
Glass forming ability
Electrodeposition
Refractory metal

ABSTRACT

Oxygen has usually been considered to be detrimental for the glass formation ability and rarely been taken as a main constituent of amorphous alloys. Here, the effect of oxygen on the glass formation of electrodeposited Mo–O binary alloys was systematically investigated by regulating the current density, and the existence of oxygen was found to promote and stabilize the glassy structure. Fully amorphous structure is obtained at the composition of 76 at.% Mo and 24 at.% O, which is close to the Mo–O binary eutectic point. With an increase in the current density from 0.4 to 2.5 A/cm^2, the oxygen content of the deposited films decreases from 24 to 14 at.%, leading to a transition in microstructure from fully amorphous to mixed amorphous/nanocrystalline. In addition, the crystallization behavior and mechanical properties of the as-deposited amorphous $Mo_{76}O_{24}$ films were studied. The present work not only shows a novel method for producing amorphous alloy with a high refractory metal and oxygen content, but also verifies that oxygen could act as a main constituent in the formation of amorphous alloys.

1. Introduction

Amorphous alloys, also known as metallic glasses (MGs), since their first time discovered by Duwez in 1960 [1], have gained considerable attention due to their extraordinary disordered atomic configuration and attractive properties [2, 3]. A large variety of amorphous alloys have been developed in the last 60 years. According to the constituent composition, amorphous alloys can be classified into two types, i.e. metal-metalloid (or nonmetal) type and metal-metal type [4]. For the metal-metalloid (or nonmetal) glass, typical metalloid (or nonmetal) atoms are B, C, P and Si, and their total amount is about 20 at.%. Some well-investigated systems in this category include $Ni_{80}P_{20}$ [5], $Fe_{80}B_{20}$ [6], $Pd_{81}Si_{19}$ [7] and $Fe_{80}P_{13}C_7$ [8]. The reason why these compositions can form amorphous alloys is that they all locate near their respective deep eutectic compositions [9]. Moreover, atomic size mismatch between metal and metalloid (or nonmetal) atoms also plays a significant role in the glass formation [10].

Recently, sulfur was also reported to facilitate the glass formation in many different systems, including Ti-, Zr-, Pd- and Cu- based alloys, making a whole new family of metallic glass-forming alloys accessible [11]. However, oxygen, the same main group element as sulfur, has rarely been reported as the main constituent in the amorphous alloys. Mostly, focuses were placed on understanding the effect of low level of oxygen content as impurity ($<$ 1 at.%) on glass formation ability (GFA) and plastic deformation in different metallic glass systems [12–20]. Usually, oxygen was considered to be detrimental for GFA because of the formation of an oxygen stabilized or oxide precipitate [12–14]. Nevertheless, improvement in the GFA was reported by a critical level of oxygen content (1000–4000 appm) in several systems, including Fe-based and Zr-based alloys [15–17]. For example, Wang et al. [16] found that a better glass former can be obtained in the Zr-Cu binary alloys with a relatively high oxygen content (~3700 appm), and they proposed that oxygen can be considered as an alloying element rather than impurity. However, the synthesis of amorphous alloys with oxygen as main constituent has not been accomplished yet and remains a challenge.

Among the variety of methods for synthesizing amorphous alloys, electrodeposition is a simple and effective technique. Amorphous alloys like Ni–P [21] and Ni–B [22] have been prepared by electrodeposition. The electrodeposition of amorphous Mo from saturated acetate ion solutions containing molybdate ions has been reported recently [23–27]. However, conclusions about whether oxygen exists in the amorphous films were rather contradictory. Some authors claimed that amorphous Mo without oxygen was deposited [23, 25], in contrast with the other work showing the existence of oxygen in the films [24]. Therefore, the role of oxygen to the formation of amorphous structure still needs to be clarified.

In the present work, dense MoO_x (14–24 at.%) films were

---

[*] Corresponding authors.
E-mail addresses: jiepan@imr.ac.cn (J. Pan), liyi@imr.ac.cn (Y. Li).

https://doi.org/10.1016/j.jnoncrysol.2018.07.064
Received 10 May 2018; Received in revised form 4 July 2018; Accepted 31 July 2018
0022-3093/ © 2018 Elsevier B.V. All rights reserved.

Please cite this article as: Duan, F.H., Journal of Non-Crystalline Solids (2018), https://doi.org/10.1016/j.jnoncrysol.2018.07.064

electrodeposited at a series of current densities ranging from 0.4 to 2.5 A/cm^2. The oxygen content, which can be controlled by regulating the current density, was found to have a prominent influence on the glass formation of Mo–O alloys. The as-deposited film having a fully amorphous structure exhibits the composition of ~76 at.% Mo and ~24 at.% (i.e., 5 wt%) O, which is close to that of Mo–O binary eutectic alloy. The crystallization behavior and mechanical properties of the as-deposited amorphous films were also studied.

2. Experimental

A saturated aqueous salt bath having a high concentration of acetate [23] was employed to prepare the Mo–O alloys, containing 3.6 mol/L potassium acetate, 3.7 mol/L ammonium acetate, 3.3 mol/L acetic acid, and 1 mmol/L ammonium heptamolybdate. All the chemicals used in the bath were analytical reagent-grade. Electropolished copper sheets with dimensions of 10 mm × 15 mm × 1 mm were used as the substrate, and a high purity platinum foil was used as the anode. Meanwhile, the bath was maintained at a pH value of 6.7 ± 0.1and a stirring rate of 600 rpm throughout the deposition. Comparing with the experimental conditions employed by Morley et al. [23], temperature was adjusted to 323 ± 2 K and the current density was regulated from 0.4 to 2.5 A/cm^2 in this work.

The microstructure of the films was characterized by X-ray diffraction (XRD, Bruker D2) and transmission electron microscopy (TEM, JEOL 2010 HR & FEI Tecnai F20). The elemental analysis of the films was investigated using an energy dispersive X-ray spectrometer (EDS) attached to a field emission scanning electron microscopy (SEM, Zeiss Supra 55). The observation of the cross-sectional morphologies was performed on the confocal laser scanning microscope (CLSM, LEXT OLS4000). To determine the compositions and the chemical states of the films, X-ray photoelectron spectroscopy (XPS, ESCALAB250, Thermo VG) analysis was conducted. The C 1s peak at 284.6 eV was uniformly taken as an internal standard. To rule out the possible effect of oxide layer on the surface, the as-deposited films were etched for 180 s to the steady state prior to the analysis.

In order to investigate the crystallization behavior, the as-deposited amorphous films were sealed in quart tubes with an argon atmosphere, and then annealed at various temperatures (from 673 to 1273 K) for 2 h. Subsequently, the structure of annealed samples was examined by XRD. Specimens for nanoindentation measurements were mechanically polished to a mirror finish and then tested using Agilent Nano indenter G200 with a maximum indentation load of 15 mN and a loading rate of 0.05 mN/s. At least ten indenters were conducted to verify the accuracy and scatter of the testing data. Microcompression testing was performed in Agilent nanoindenter XP with a diamond plat punch tip at a strain rate of 10^{-3} s^{-1}, where the micropillars with a diameter of ~1 μm were machined using the FEI Scios Dual-Beam focused ion beam (FIB) from the cross-section of the films. The length-to-diameter ratio of the pillars was about 3:1, and the taper angle from the top to the bottom was < 2°.

3. Results and discussion

3.1. Structure characterization

Fig. 1a shows the XRD patterns of the as-deposited films prepared at various current densities, ranging from 0.4 to 2.5 A/cm^2. The film prepared at a current density of 0.4 A/cm^2 exhibits a broad diffraction hump and an absence of Bragg peaks, which are typical characteristics of amorphous structure. When the current density is above 0.8 A/cm^2, the broad hump (at ~40.3°) becomes sharp along with the appearance of body-centered cubic (BCC) (200) and (220) peaks, showing a formation of BCC crystalline phase. With further increase in current density, the diffraction peaks (i.e., (110), (200) and (220)) shift to a higher angle and get closer to those of pure Mo. When the current density is above 1.0 A/cm^2, these diffraction peaks are almost identical to those of pure Mo, suggesting the appearance of BCC Mo. Moreover, the intensities of the peaks increase with the increase in current density, indicating the increase in the volume fraction of crystalline phase (V_f). Calculating V_f using the method of peak fitting and evaluating it as a function of current density confirms this trend (see Fig. 1b). The result shows that V_f is linear correlated to current density, and it reaches about 56% when the current density is 2.5 A/cm^2. The average grain sizes of these crystalline phases are below 6 nm, which are estimated from the full-width half-maximum of (110) peaks based on Debye–Scherrer equation.

The microstructure of the films electrodeposited at current densities of 0.4 and 2.5 A/cm^2 was further verified by TEM, and the results are exhibited in Fig. 2. Referring to the film deposited at 0.4 A/cm^2, the bright-field TEM image (Fig. 2a) shows a homogeneous structure with no sign of different phases or crystals, and the corresponding selected area electron diffraction (SAED) pattern consists only diffused and continuous rings (the inset in Fig. 2a). The high-resolution TEM (HRTEM) image (Fig. 2b) exhibits a maze-like pattern with no traces of crystalline phases. These observations confirm the amorphous structure of the film deposited at 0.4 A/cm^2. For the film deposited at 2.5 A/cm^2, tiny grains having an average grain size of ~6 nm are homogeneously distributed in the matrix (Fig. 2c), and the corresponding SAED pattern (the inset in Fig. 2c) reveals that these tiny grains have a BCC structure and are randomly oriented. The HRTEM image (Fig. 2d) shows that tiny grains are embedded in the amorphous matrix, and the volume fraction of these grains is about 60%. The volume fraction and grain size are consistent with those calculated by XRD curves.

As revealed by the cross-sectional image in Fig. 3, the amorphous film deposited at 0.4 A/cm^2 for 24 h possesses a uniform thickness of ~10 μm, as well as a good adhesion to the substrate. The corresponding EDS spectrums only give the signals of Mo and O and their contents are 80 ± 5 at. % and 20 ± 5 at. %, respectively. The EDS mapping results show that the oxygen element is homogeneously distributed without any element segregation in the film.

3.2. The oxygen content in the films

The oxygen signal in Mo-based deposits has been reported to originate from the absorbed oxygen on the surface [25]. To accurately detect the chemical states and oxygen content, XPS spectra of the films deposited at current density ranging from 0.4 to 2.5 A/cm^2 were measured, together with a pure Mo foil (99.9 wt%) for comparison. Here, only spectra of films deposited at 0.4 and 2.5 A/cm^2 as well as pure Mo are shown in Fig. 4a–c. The peak separation for the Mo 3d spectra reveals the presence of two types of molybdenum species in all these samples. The peaks at ~228.0 and ~231.2 eV are assigned to Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ of metallic Mo (Mo^0), and the peaks at ~229.3 and ~232.4 eV are assigned to Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ of MoO$_2$ (Mo^{4+}), respectively [28]. Moreover, the peak separation gives the atomic ratio of Mo^0/Mo^{4+}, from which oxygen content of the films with different current densities can be calculated. The results, shown in Fig. 5, indicate that the oxygen content decreases with the increase in current density. The oxygen content of film deposited at 0.4 A/cm^2 is ~24 at.%, while the oxygen content of film deposited at 2.5 A/cm^2 is ~14 at.%. For the film deposited at 2.5 A/cm^2, the volume fraction of nanocrystalline Mo (V_f) is 56%, thus we calculate that the oxygen content of the amorphous matrix is 28 at.% (labelled as calculation in Fig. 5), which matches well with that of the amorphous film.

Furthermore, the direct comparison between the O 1s spectra (Fig. 4d) of the deposited films and pure Mo also gives the same results. The O 1s spectra of pure Mo is flat with no peaks, while the O 1s spectra of the deposited films all peak at a binding energy of 530.7 eV, corresponding to Mo oxides [29]. The intensities of peaks decrease with an increase in the current density, which also suggests a decrease in the oxygen content.

All the results from XPS, EDS and calculation as shown in Fig. 5,

Download English Version:

https://daneshyari.com/en/article/10155545

Download Persian Version:

https://daneshyari.com/article/10155545

Daneshyari.com