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Crystallization of Al-based Amorphous Alloys in Good Conductivity Solution

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The corrosion-induced crystallization of $Al_{94-x}Ni_xGd_6$ (x = 6 and 10, in at.%) metallic glasses as well as phase separation, oxidation and cracking in good conductivity solution has been investigated by various techniques. The transmission electronic microscopy (TEM) result reveals that crystalline intermetallics and oxides present on the electrochemically thinned hole edge, and the phase separation occurs in the matrix of the as-spun ribbons with the circumferential speed R_c of 29.3 m/s. In addition, the bending and cracking of the samples occur after corrosion. The influence of Ni content on the phase separation, bending and cracking can be explained by the fact that the percolation of the backbone clusters in the amorphous alloy melts and glasses is enhanced by increasing the composition of Ni.

KEY WORDS: Crystallization; Oxidation; Percolation of backbone cluster; Al-based glassy alloy

1. Introduction

Lightweight Al−rare-earth−transition metal (Al−RE−TM) metallic glasses with Al concentrations above 80 at.% typically have good corrosion resistance, high yield strength and other key properties that make them interesting for potential structural applications[1−3]. Gao et al. found that when the temperature is approaching the glass transition temperature under annealing, the Al-based metallic glasses will crystallize to reduce the total free energy for the system with the presence of medium-range Al clusters in the as-spun samples[4]. The tensile strength can be further enhanced when the alloys are partially crystallized to precipitate nanometer-sized Al crystals[5]. Although people have reported that the stability of the Al-based amorphous phase as well as the pathway of crystallization is sensitive to the composition of these alloys[6], i.e. the addition of Ni[7,8] and Si[9] can improve the stability of the Al-based glassy alloys; the substitution for Ni by Co can worsen the glass forming ability (GFA)[9], there is still lacking of an understanding of the underlying processes. It is reported that if the annealing process leads to a phase separation into Al-rich and solute-rich amorphous regions, crystallization appears to be preceded for $Al_{88}Gd_6La_2Ni_4$[10]. It is known that the earlier investigations have focused on the phase separation and crystallization during the annealing process of the amorphous alloys[11−13]. There is little work devoted to uncovering the corrosion-induced crystallization of Al-based amorphous alloys.

The desirable properties of metallic glasses, such as superior specific strength, large ductility in bending, low coefficient of friction, high hardness and high resistance to corrosion, oxidation and wear are closely associated with the internal stress[14,15]. By dealloying the amorphous alloys, the selective dissolution of elements can introduce stress to the matrix and trigger the cracks[16,17]. Meantime, internal stress can lead to the elastic deformation of the samples, which will definitely decrease the service life of the products[18]. Cai et al. have reported that the stretched ribbons of $Cu_{50}Zr_{40}Ti_{10}$ metallic glass generate the corrosion cracks more easily than the as-quenched one[19]. Therefore, it is valuable to explore the effect of internal stress on the cracking or embrittlement of the metallic glasses.

In our earlier works, we have found that a shoulder peak in X-ray diffraction (XRD) pattern of as-spun Al−Ni−Gd glassy alloys is associated with the strong Al−Ni (Gd) bonds[8]. The predominant atomic pair plays a governing role in the frame of amorphous structure[20], i.e. the backbone clusters in Al−Ni−Gd

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glassy alloys[10]. The microstructure of a glassy alloy should determine its corrosion behavior[21], which is closely related to the forming of the passivation film[22] and the segregation of beneficial alloying elements due to partial crystallization[23]. Meantime, it is reported that the minor addition of Ni can increase the strength and corrosion resistance of the Fe-based metallic glass[24], which indicates that the corrosion of metallic alloys is strongly influenced by the alloying elements as well as by their microstructure. The nanoscale pit initiation events are sensitive to the heterogeneities of the Al-based metallic glasses[25]. Hence, it is valuable to study the relationship between the backbone clusters and the corrosion behavior of the Al-based glassy alloys.

Accordingly, this work intends to investigate the mechanism of corrosion-induced crystallization, phase separation, oxidation, cracking and structure character of Al−Ni−Gd glassy alloys in good conductivity solution by electropolishing, electrochemical test and immersion corrosion. We try to explain the involving results with the backbone clusters argument in the present glassy alloys.

2. Experimental

The ingots of $Al_{94-x}Ni_xGd_6$ ($x = 6$ and 10) glassy alloy used in this work were obtained by induction-melting the mixture of pure Al, Ni and Gd ingots (purity > 99.5 wt%) in the air. The $Al_{94-x}Ni_xGd_6$ ($x = 6$ and 10) ribbons were prepared by a single-roller melt-spinning technique in argon atmosphere. The diameter of the copper roller is 35 cm, and the circumferential speed R_c is 29.3 and 25.6 m/s. The ribbons are about 20−40 μm in thickness and 2−3 mm in width.

The glassy structure of the specimens was investigated by high energy powder X-ray diffraction (PXRD) at room temperature using a PANalytical X'Pert PRO diffractometer equipped with a graphite monochromator in a reflection mode (2θ: 10°−80°, step: 0.017° and scan speed: 5 s/step) utilizing Cu$K\alpha$ radiation (40 kV, 40 mA).

Transmission electron microscopy (TEM, JEM-2100) was used to study the structure of the $Al_{94-x}Ni_xGd_6$ ($x = 6$ and 10) glassy alloy. Samples were investigated for TEM by electrochemical thinning only. A 26 vol.% nitric acid and 74 vol.% methanol electrolyte were used at approximately −25 °C until a hole was formed. All the samples were checked at least three times to ensure the accuracy. Composition of the phases was obtained by energy dispersive X-ray spectrometry (EDS), which is available in conjunction with TEM.

Electrochemical measurements were carried out by using a typical three-electrode system: working electrode, platinum counter electrode and $Hg|Hg_2Cl_2$ (SCE) reference electrode. As we all know, the solution chosen for the electropolishing is commonly regarded as the good conductivity solution and has a heavier corrosion behavior for the sample, so the electrolytes for the electrochemical test were chosen as 7 wt% HNO_3 methanol solution. LK 2005A advanced electrochemical workstation was used for measuring the potentiodynamic polarization curves with a scanning rate of 5 mV/s at room temperature. Corroded ribbons were cleaned with ethanol and deionized water. All the electrochemical measurements were repeated at least three times, which showed a good reproducibility. For immersion experiments, the as-spun ribbons were immersed in 27 wt% methanol solution open to air at room temperature (about 298 K) for 120 h. The surface morphologies of the ribbons after polarization experiments and immersion experiments were examined by scanning electron microscopy (SEM, Hitachi S-570). The compositions of the corresponding regions were analyzed by energy dispersive spectroscopy (EDS).

3. Results

3.1. XRD patterns and TEM images of as-spun $Al_{94-x}Ni_xGd_6$ (x = 6 and 10) glassy alloys

Prior to the corrosion studies, the microstructure of the ribbon pieces prepared from the specimens by single-roller melt-spinning has been checked in detail. Fig. 1 shows the XRD patterns of the as-spun $Al_{94-x}Ni_xGd_6$ ($x = 6$ and 10, in at.%) samples with R_c of 29.3 and 25.6 m/s. For the ribbons spun with R_c of 29.3 m/s, a typical broad diffraction peak can be observed in the XRD patterns, which suggests that fully amorphous structure is formed under this circumferential speed. In the XRD patterns of samples with R_c of 25.6 m/s, several crystalline peaks can be found in the ribbon with the composition of Ni, c_{Ni} equal to 6 at.%, which are identified as α-Al phase, but are absent in the ribbon with c_{Ni} of 10 at.%. Apparently, those results confirm the argument that increasing c_{Ni} is helpful to improve the GFA of Al-based alloys[9] and the high cooling rate is beneficial to the increase in the amount of amorphous matrix. In addition, a shoulder diffraction peak is observed at about $2\theta = 44°$, which is often ascribed to the combined effects of strong interaction of Al−Ni bond[1,8] and pre-existed α-Al nuclei[26] in the glassy matrix.

The TEM images and the corresponding selected area electron diffraction (SAED) patterns of the as-spun amorphous samples with R_c of 29.3 m/s are shown in Fig. 2. For the sample with c_{Ni} of 6 and 10 at.% just after electrochemical thinning, a layer of black precipitates is formed on the hole edge, and the image of the sample with c_{Ni} of 10 at% can be found in our earlier

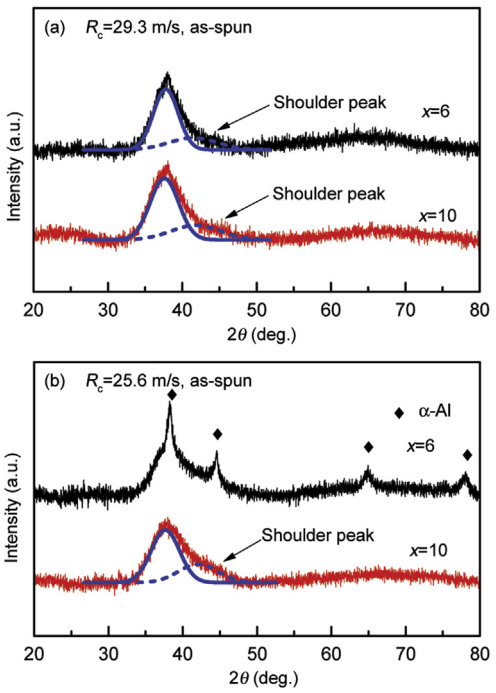

Fig. 1 XRD patterns of the as-spun $Al_{94-x}Ni_xGd_6$ ($x = 6$ and 10) samples with R_c of: (a) 29.3 m/s, (b) 25.6 m/s.