Effect of over-doped yttrium on the microstructure, mechanical properties and thermal properties of a Zr-based metallic glass

Ming Yan [a,b], J. Zou [b,*], J. Shen [a,*]

[a] *School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China*
[b] *School of Engineering and Centre for Microscopy and Microanalysis, University of Queensland, St. Lucia, Qld 4072, Australia*

Abstract

The effects of over-doped yttrium on the microstructure, mechanical properties and thermal behaviour of an oxygen-contaminated $Zr_{51}Cu_{20.7}Ni_{12}Al_{16.3}$ bulk metallic glass are studied systematically. It has been found that, when yttrium doping is beyond the optimum doping, the glass-forming ability enhancement effect induced by yttrium addition decreases and the mechanical properties are adversely affected. In this study, a new phase with an orthorhombic structure ($a = 0.69$ nm, $b = 0.75$ nm and $c = 0.74$ nm) is identified in the yttrium over-doped alloys.
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1. Introduction

Due to their excellent glass-forming ability (GFA) and comprehensive mechanical properties and potential for engineering and structural materials [1,2], Zr-based bulk metallic glasses (BMGs) have attracted significant attention in the last decade. However, recent studies found that their structures and performances are very sensitive to impurities such as oxygen [3–5]. It has been reported that the existence of oxygen could have a significant adverse effect on BMG properties, such as thermal stability [5], the nucleation of crystalline phases in the solidification process [4] and the GFA [3,5].

One appropriate strategy to prevent the oxygen-contamination problem is to introduce impurity-gettering elements, so that the detrimental oxygen can be gettered away from the alloy system. Although a number of

oxygen-affinitive elements (such as carbon [6], boron [7], scandium [6], gadolinium [8] and yttrium [9–11]) have been used in this role and, consequently, to improve BMG performance, it still remains fundamentally unclear how the structures of BMGs and their corresponding properties respond when these additive elements are over-doped. In fact, it is critically important if this strategy is commercially employed to produce BMG materials.

In this study, we choose yttrium to be the oxygen-gettering element because of its significant affinity with oxygen [12] and aim to investigate systematically the structural and mechanical response of our newly developed BMG $Zr_{51}Cu_{20.7}Ni_{12}Al_{16.3}$ [13] to over-doping with yttrium. It is demonstrated that over-doped yttrium causes a reduction in the GFA enhancement effect and adversely affects the mechanical properties. A detailed investigation of crystallographic information also leads us to conclude that in situ crystallization results in the formation of metastable phases in the over-doped systems.

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* Corresponding authors.
  E-mail addresses: j.zou@uq.edu.au (J. Zou), junshen@hit.edu.cn (J. Shen).

2. Experimental

In our previous study [14] and shown later, we found that there is an optimum doping for a given fabrication condition and, for our current fabrication condition, 0.5 at.% yttrium would result in an optimum doping effect. Based on this, the present study is designed to carry out a detailed investigation of the over-doped systems. Alloys with nominal composition of $(Zr_{0.51}Cu_{0.207}Ni_{0.12}Al_{0.163})_{100-x}Y_x$, where $x = 0$, 0.5, 0.75, and 1 (referred as Zr51, Zr51Y0.5, Zr51Y0.75 and Zr51Y1 hereafter), were fabricated in 3 and 10 mm diameter samples. These samples were prepared by a non-consumed arc melting and copper mould casting technique. During the fabrication, raw materials were melted at least four times to ensure compositional homogeneity and high-purity argon atmosphere was used as the protective atmosphere.

These samples were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). XRD analysis was performed using a D/max IIIA diffractometer with a Cu Kα target operated at 40 kV and 60 mA. SEM and TEM investigations were carried out using a Philips XL30 operated at 20 keV and a Tecnai F20 operated at 200 keV, respectively. Energy dispersive spectroscopy (EDS) equipment attached to the SEM and TEM instruments was employed to obtain compositional information. TEM specimens were prepared by a tripod polisher technique, finished by low-angle (<6°) and low-energy (3.5 keV) precision ion-beam thinning to avoid the possibility of inducing crystallization. Oxygen concentration in these samples was determined using a Leco TC-436 oxygen/nitrogen determinator, which detected a 500 ppm content of oxygen in all yttrium-doped alloys. The nature of yttrium binding energies and hence their possible forms present were studied using a Kratos Axis ULTRA X-ray photoelectron spectroscopy (XPS) instrument for all 3 mm diameter yttrium-doped alloys, in which the incident radiation of monochromatic Al X-ray (1486.6 eV) was used and operated at 150 W. Before the experiments, a 4 keV argon ion beam was used to clean the sample surfaces. The analysis of the XPS spectra was carried out using Version 2 software. The mechanical properties of these samples were evaluated by quasi-static compression tests using 3 mm diameter ×6 mm samples with a strain rate of $\sim 2.5 \times 10^{-4}$ s^{-1} using an Instron 5500 instrument. Thermal analysis on 3 mm diameter samples was performed using a Perkin–Elmer DTA7 (differential thermal analyser) with a heating rate of 0.167 K/s.

3. Results and discussion

3.1. Structure characterization

Fig. 1 shows the XRD patterns of the Zr51 alloy for sample diameters of 3 and 10 mm and of the Zr51Y0.5, Zr51Y0.75 and Zr51Y1 alloys with sample diameters of
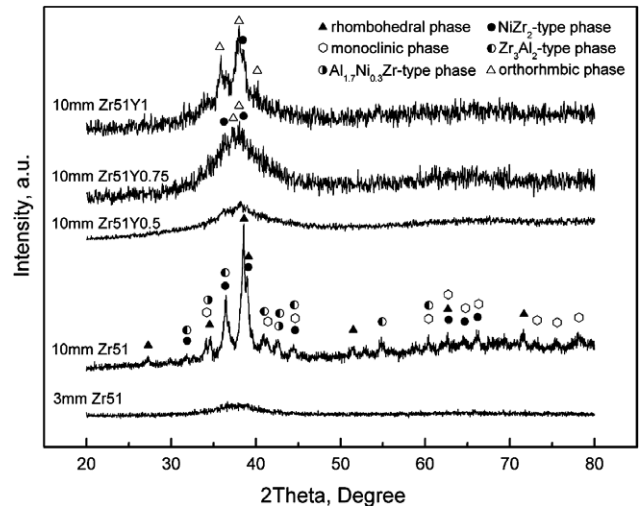

Fig. 1. XRD patterns for the 3 and 10 mm diameter alloy Zr51 and the 10 mm diameter alloys Zr51Y0.5, Zr51Y0.75 and Zr51Y1.

10 mm. The XRD pattern of the 3 mm diameter Zr51 alloy shows a unique broad diffuse halo, indicating the sample is essentially amorphous. The fact that the XRD pattern of the 10 mm diameter Zr51 alloy shows overwhelming diffraction peaks implies that the sample is fundamentally composed of crystalline phases. In strong contrast, the XRD pattern of the 10 mm diameter Zr51Y0.5 alloy exhibits a similar diffraction pattern to that of the 3 mm diameter Zr51 alloy, suggesting that the critical sample size for glass formation in the Zr51Y0.5 alloy is at least 10 mm in diameter. Interestingly, the XRD patterns of the 10 mm diameter Zr51Y0.75 and Zr51Y1 alloys show diffraction peaks superimposed with a diffuse halo. In fact, the 10 mm diameter Zr51Y1 alloy shows more distinct diffraction peaks than the 10 mm diameter Zr51Y0.75 alloy, indicating that crystalline phases have been formed in these two alloys with more crystalline phases in the 10 mm diameter Zr51Y1 alloy.

These XRD studies suggest that the GFA of the Zr51 alloy has been substantially enhanced with 0.5 at.% yttrium doping. However, the GFA enhancement effect decreases on increasing the amount of yttrium doping, evidenced by the presence of diffraction peaks in the XRD patterns for the Zr51Y0.75 and Zr51Y1 alloys. To further investigate the microstructure of these samples, SEM was used, since: (1) we suspect that the chemical composition of crystal phase(s) differs from the amorphous matrix; (2) SEM backscattered electron (BSE) signal is sensitive to the chemical composition, so that it can be employed to identify the number of crystalline phases; and (3) low-magnification BSE images can provide information on phase distribution.

Fig. 2 shows SEM BSE images and the typical as-cast microstructure of all 10 mm diameter alloys. Fig. 2(a) shows the SEM image of the 10 mm diameter Zr51 alloy, showing the well-crystallized microstructure that is in agreement with the corresponding XRD result. SEM