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Beneficial effects of oxygen addition on glass formation in a high-entropy bulk metallic glass

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ABSTRACT

Glass-forming ability (GFA) is one of critical scientific problems for the field of bulk metallic glass (BMGs), and how to facilitate glass formation is always a central yet important research theme for this field. Compared with conventional BMGs in the same alloy system, newly developed high-entropy BMGs (HE-BMG) usually show much enhanced thermal stability, but appreciably reduced GFA. In contrast to the conventional wisdom, we found that GFA of the $Zr_{20}Cu_{20}Hf_{20}Ti_{20}Ni_{20}$ HE-BMG could be enhanced by oxygen microalloying. The underlying mechanism was explored from both thermodynamic and kinetic point of view, and our analysis indicates that the high packing density resulted from addition of small oxygen atoms is responsible for the beneficial effect of oxygen. The current findings not only shed new insights into understanding of glass formation, but also broaden the view for exploring new kinds of HE-BMGs with enhanced properties and low manufacturing costs.

1. Introduction

Bulk metallic glasses (BMGs) have been regarded as a promising class of materials with numerous interesting properties including high elastic limit [1], high yield strength [2,3], exceptionally high hardness [4], superior corrosion resistance [5], and soft magnetic properties [6]. From an application-oriented perspective, BMGs with a favorable combination of high casting critical thickness (i.e., large glass-forming ability), low manufacturing cost [7,8] and high thermal stability are required. Inspired by the field of high entropy alloys (HEAs) [9,10] which contain multiple principal elements in equimolar or near equimolar ratios, the entropy stabilization concept was also led to discovery of equiatomic BMGs, termed as high-entropy BMGs (HE-BMGs) [11–14]. Preliminary studies confirmed that entropy-stabilized HE-BMGs possess much enhanced thermal stability [15], but unfortunately appreciably reduced glass-forming ability (GFA) [16], as compared with conventional BMGs consisting of the same constituents. Thus, it is of great importance to improve GFA of HE-BMGs so that these ultra-stable glassy alloys can be widely utilized as engineering materials.

Oxygen is one of the most abundant elements in the earth with strong interactions to most of the metallic elements. Although its beneficial effects on the GFA were reported in few marginal glass-forming systems, such as binary Zr-Cu [17] and Zr-Pt [18] MGs, oxygen is usually a contamination element to GFA in BMGs [19]. Particularly, the oxygen tolerance of most Zr-based BMGs is only several hundred-atomic ppm, above which [19–21], their GFA would be severely deteriorated. As a result, controlling the oxygen content during preparation, *e.g.*, use of high-purity raw materials and high vacuum conditions, inevitably raise the production costs of BMGs [7,8]. Therefore, it is vital to understand alloying effects of oxygen on glass formation of HE-BMGs as far as their production cost and GFA are considered. In contrast to the conventional wisdom, in this study, we found that minor additions of oxygen could significantly improve GFA of the ZrCuHfTiNi HE-BMG. The underlying mechanisms responsible for the enhanced GFA were systematically explored, and our findings not only are important for understanding the GFA, but also opens a new avenue for reducing production cost of BMGs.

2. Experimental

Alloy ingots with a nominal composition of $Zr_{20}Cu_{20}Hf_{20}Ti_{20}Ni_{20}$ [22] (refer to it as base alloy hereafter) were prepared by arc-melting a mixture of constituent elements with purity ≥99.9% under Ti-gettered argon atmosphere. To adjust oxygen concentration, different amounts of TiO_2 with a purity higher than 99.99 wt % were added with a nominal composition of $(Zr_{20}Cu_{20}Hf_{20}Ti_{20}Ni_{20})_{100-x}O_x$ (x = 0, 0.1, 0.2, 0.3 and 0.5). Samples were denoted as O0.1, O0.2, O0.3 and O0.5 based on the extra added oxygen content (at. %). Ingots were melted more than eight times to ensure TiO_2 was fully dissolved in the alloys. Before each melting process, the arc-melter chamber was pumped to below

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1×10^{-3} Pa. Cylindrical rods with different diameters from 1 to 3 mm were fabricated by water-cooled copper mold casting. Oxygen content in the as-cast rod samples was measured using a LECO instruments inert gas fusion (IGF) machine with IR detection.

Phase identification of the as-cast samples was conducted by X-ray diffraction (XRD) with Cu K_α radiation (Rigaku D_{max}-RB). Cross-section surfaces of the as-cast samples were examined by scanning electron microscopy (SEM) in a ZEISS SUPRA 55 instrument equipped with an energy dispersive X-ray spectrometer (EDS). Transmission electronic microscopy (TEM) experiment was carried out with a Tecnai-F30 S-TWIN microscopy. High energy synchrotron X-ray diffraction measurements were carried out using a high-energy monochromatic beam on the beamline 11-ID-C at Advanced Photon Source, Argonne National Laboratory. The synchrotron radiation wavelength was set to $\lambda = 0.11798$ Å (photon energy 10^5 keV). The sample was illuminated with well collimated incident beam having a cross-section of 0.5 mm × 0.5 mm. The diffracted photons were collected up to a maximum wave vector momentum transfer $q = 30\,nm^{-1}$ ($q = 4\pi\sin\theta/\lambda$) using Perkin Elmer 2D detector (Perkin Elmer amorphous silicon detector, 2048 × 2048 pixels, each pixel having an effective dimension of 200 μm × 200 μm) carefully aligned orthogonal to the X-ray beam. The two-dimensional diffraction patterns were integrated with Fit2D software package. The data were further analyzed in the program package PDFgetX3 to retrieve structure factors *S(q)*. The radial distribution function (PDF) *G(r)* and pair correlation function *g(r)* were thus obtained by the Fourier transform of the *S(Q)* [23]

$$G(r) = \frac{2}{\pi}\int_0^\infty q[S(q)]\sin(qr)dq = 4\pi r[\rho(r) - \rho_0] \quad (1)$$

$$g(r) = \frac{\rho(r)}{\rho_0} = 1 + \frac{G(r)}{4\pi r\rho_0} \quad (2)$$

where ρ_0 is the sample number density and $\rho(r)$ is the microscopic number density. Based on the Archimedean principle, density measurements of the BMGs were performed with a microbalance having a sensitivity of 0.1 mg.

Thermal properties associated with glass transition, crystallization and melting behavior were investigated by differential scanning calorimeter (DSC) and differential thermal analysis (DTA) with a Netzsch STA404F. Samples for the DSC measurements were cut from the as-cast, 1.5 mm rods to eliminate influences of cooling rates and those for the DTA measurements were prepared from the master alloys. Viscosity in the supercooled liquid region was determined in thin film tension experiments using a TA Q800 dynamic mechanical analysis (DMA) with a heating rate of 3 K/min under a stress of 5 MPa. The viscosity of the deflecting glassy ribbons can be determined as

$$\eta = \frac{\sigma}{3\frac{d\varepsilon}{dt}} \quad (3)$$

where σ is the applied stress and ε is strain.

3. Results

3.1. Glass formation with oxygen addition

IGF analysis of oxygen contents in the as-cast, 3 mm rods doped with different amounts of TiO_2 was conducted. Base alloy (the specimens without addition of oxygen) has an oxygen concentration of 490 appm, which mainly came from the raw materials and the melting process. The average oxygen concentration for the alloys doped 0.1, 0.2, 0.3 and 0.5% O (denote as O0.1, O0.2, O0.3 and O0.5, respectively) was determined to be 1680, 2790, 3920 and 5710 appm (see Table 1), respectively. Although these concentrations are higher than the targeted values, the trend is reasonable, indicating that the addition of TiO_2 as a resource of oxygen is successful in this study.

Table 1
Measured oxygen concentration, thermal properties and GFA indicators of the alloys with different amounts of oxygen addition.

	Oxygen content (appm)	T_g (°C)	T_x (°C)	T_m (°C)	T_l (°C)	T_{rg}	γ
base alloy	490	388	426	871	1017	0.512	0.358
O0.1	1680	392	429	869	1015	0.517	0.360
O0.2	2790	395	431	873	1014	0.519	0.360
O0.3	3920	396	432	873	1018	0.518	0.360
O0.5	5710	–	–	875	1050	–	–

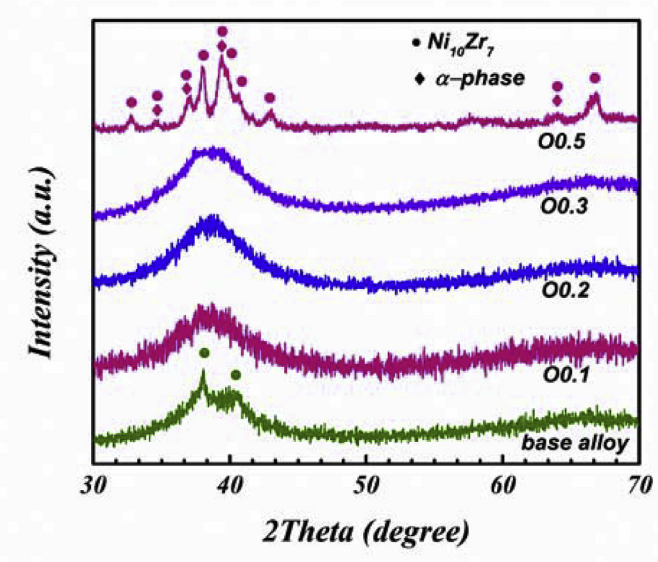

Fig. 1. XRD curves for the as-cast, 3 mm rods of $Zr_{20}Cu_{20}Hf_{20}Ti_{20}Ni_{20}$ HE-BMGs with different amounts of oxygen.

Typical XRD spectra of the as-cast, 3 mm rods with different oxygen concentrations are shown in Fig. 1. For base alloy without oxygen addition, sharp crystalline peaks identified as $Ni_{10}Zr_7$, superimposed on the amorphous halo are observed, indicating that this sample is partially amorphous. In contrast, with 0.1–0.3% oxygen addition, only a typical amorphous hump is present with no appreciable crystalline peaks. When the oxygen addition increases up to 0.5 at. %, however, the amorphous halo almost disappears and strong reflection peaks corresponding to $Ni_{10}Zr_7$ and α-phase are seen. Therefore, micro-alloying with 0.1–0.3 at. % oxygen promoted glass formation of the $Zr_{20}Cu_{20}Hf_{20}Ti_{20}Ni_{20}$ alloy, while excessive oxygen addition (above 0.5 at. %) deteriorated its GFA.

Microstructures of these specimens were analyzed by SEM and the corresponding results are shown in Fig. 2a–c. For the as-cast, 3 mm rod of base alloy, the primary phase $Ni_{10}Zr_7$ embedded in the amorphous matrix with a typical size of 100 μm is shown (Fig. 2a), which is consistent with the XRD trace shown in Fig. 1. The crystalline phase is absent in O0.1, O0.2 and O0.3 specimens and no sharp contrast is visible across the entire section (SEM image of O0.1 is shown in Fig. 2b as an example), indicating addition of a proper amount of oxygen could effectively suppress precipitation of the $Ni_{10}Zr_7$ phase. For O0.5, distinguishable dendrites of the α-phase enriched in Zr and Ti with small grain sizes of several micrometers embedded in the crystalline matrix are seen, confirming that addition of 0.5 at. % oxygen deteriorated the GFA and no amorphous phase formed, as illustrated in Fig. 2c. In general, oxygen atoms can exist in BMGs as dissolved oxygen, oxides or other oxygen-containing crystalline phases [13]. From the SEM observation, no oxides were formed in all the studied alloys containing up to 0.5 at.%. EDS line scanning analysis verified that the oxygen actually dissolved homogeneously in base alloy and O0.2, regardless of the