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Enhanced thermal stability of $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ metallic glass at temperature range near glass transition by oxygen impurity

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Abstract

The 'panoramic effects' of oxygen impurity on the thermal stability of $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ metallic glass have been investigated by constructing time–temperature-transformation diagram and analyzing the precipitation kinetics of primary phase. It is found that oxygen has contrary effects on the alloy's thermal stability exhibiting in high- and low-temperature ranges because of primary phase selection. The primary phase for $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ glassy alloy depends on its oxygen content as well as the temperature range in which crystallization takes place. For the alloy containing higher oxygen and crystallized at higher temperature, oxygen-induced metastable f.c.c.-Zr_2Ni precipitates as primary phase. However, for the alloy with lower oxygen content, or with higher oxygen content but crystallized at lower temperature, stable b.c.t.-Zr_2Cu forms as initial precipitation phase. Oxygen retards the precipitation of b.c.t.-Zr_2Cu phase and stabilizes glassy matrix, enhanced thermal stability in the temperature range near glass transition is possessed by the alloy with higher oxygen.

Keywords: Metallic glasses; Phase transitions; Thermodynamic properties; Thermal analysis

1. Introduction

Since the 1980s, many of the investigations about bulk metallic glasses (BMGs) have aimed at Zr-based system with high glass-forming ability (GFA) and thermal stability. Zr-based BMGs containing no noble or toxic element are considered the most promising candidate for next generation of structural materials because of their excellent strength, high corrosion and wear resistance [1,2]. However, there are still some problems which limit the lager-scale engineering applications of Zr-based BMGs. For example, although it is now possible to fabricate Zr-based BMGs with diameters of several centimeters by copper-mold casting method, their maximum dimensions are still controlled by critical cooling rate and their shapes are also rather simple. Recently, powder consolidation by hot-pressing (HP) sintering process was reminded again [3]. Based on the higher thermal stability, metastable supercooled liquid states for Zr-based BMGs can be kept for longer time at the temperature above glass transition temperature (T_g), which can make the HP sintering process much more easier. Using this method, the dimensions of Zr-based BMGs will no longer be restricted by their critical casting thicknesses, BMGs with unlimited dimensions and complicated shapes could be possible if sintering parameters based on time–temperature-transformation (TTT) diagrams are properly controlled. In addition, powder consolidation by HP process can also provide a way to fabricate BMG composites reinforced with a large variety of second phases, even oxides or plastic metals with low-melting-temperature [4], and a way to fabricate porous BMGs [3].

It has been well known that the GFA of Zr-based BMGs strongly depends on their oxygen impurity content [5–7]. Schroers et al. [8] found that boron oxide fluxing method can significantly improve the GFA of a Pd-based BMG containing impurities. However, it is very difficult to find such a fluxing agent which can remove or deactivate the oxygen impurity in Zr-based BMGs because of the very strong chemical activity of element Zr. Thus, expensive starting materials with low oxygen impurity such as Zr in crystal bar quality need to be used for the alloying of Zr-based BMGs, which makes their fabrication costly and hinders them from commercial consideration. For the HP sintering process, only glassy alloy powders with particle sizes usually less than 100 μm need to be prepared

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by appropriate atomization method [9], high GFA of Zr-based BMGs will not be necessary in this situation and relatively cheap starting materials with higher oxygen such as sponge Zr may be used, which will improve the commercial attractiveness of Zr-based BMGs for industrial applications. As a precondition, the information about how oxygen impurity affects Zr-based BMGs' thermal stability needs to be obtained. Usually, the thermal stability of BMGs is characterized by the parameter ΔT_X ($=T_X - T_g$, T_X is the onset temperature for crystallization above T_g at a certain heating rate). However, ΔT_X is not the intrinsic characteristic of BMGs because it depends on the heating rate used, we cannot get the panorama about BMGs' thermal stability just from ΔT_X. Although it was found that oxygen decreases Zr-based BMGs' ΔT_X just like that for their GFA [10,11], the 'panoramic effects' of oxygen on Zr-based BMGs needs to be checked based on their TTT-diagrams. The aim of this paper is to examine the effect of oxygen impurity on Zr-based BMGs' TTT diagrams and provide reference information to the powder consolidation by HP process for the Zr-based BMGs with higher oxygen impurity.

2. Experimental methods

Quaternary $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ alloy was used as the base alloy in the current study, which has the largest ΔT_X among Zr-based BMGs found up to date ($\Delta T_X = 127$ K at a heating rate of 0.67 K/s) [12]. In order to protrude the effect of oxygen on thermal stability, a very high purity crystal Zr containing about 500 atom ppm [O] (atom ppm is abbreviated as appm hereinafter) and a sponge Zr with about 5000 appm [O] were used respectively for alloy preparation. Other starting materials Cu, Ni and Al used have purities of 99.9 mass%. ZrO_2 with high purity was employed to further increase the oxygen content in the alloy made of sponge Zr. Master alloys were completely melted more than four times under a Ti-gettered argon atmosphere, and melts were electromagnetically stirred during the melting process to make oxygen in the melts homogeneously distributed especially for the alloy with higher oxygen content. Oxygen concentration was measured by hot extraction using a LECO RO-416D2 analyzer. Analysis indicated that the master alloy made of high purity crystal Zr contains only 600 appm [O], the master alloy made of sponge Zr and stoichiometric ZrO_2 addition contains 5200 appm [O]. From the master alloy ingots, ribbons with a cross-section about 2.5 mm × 0.05 mm were prepared by a single-roller melt-spinning method at a rotation speed of 26.2 m/s in an Ar atmosphere.

The original microstructure of two melt-spun alloys were checked by transmission electron microscopy (TEM) observation with JEOL JEM-200CX microscopy. The thermal properties and crystallization behavior were examined by differential scanning calorimetry (DSC) using a SETARAM Labsys^{TM} TG DSC calorimeter in an argon atmosphere. For conventional continuously heating mode, the heating rates of 0.033, 0.083, 0.17, 0.33 and 0.67 K/s were chosen. For isothermal mode, samples were rapidly heated to the designed temperature at a constant heating rate of 0.67 K/s. All the sample masses used for DSC measurements were 30 ± 1 mg. Melt-spun alloys were sealed in quarts tubes under vacuum (base pressure 10^{-4} Pa) and put into a pre-heated tube furnace for isothermal annealing treatments, the temperature fluctuation during annealing treatments was less than 0.5 K. Changes in the structures of melt-spun alloys after isothermal annealing were examined by X-ray diffraction (XRD) using a D/MAX 2400 diffractometer with Cu Kα radiation.

3. Experimental results

The formation of an amorphous single phase with no crystallinity was confirmed in two ribbons with different oxygen contents by X-ray diffraction and TEM observation as shown in Fig. 1.

Fig. 2 shows the continuously heating DSC curves of two melt-spun alloys at heating rates of 0.67 and 0.033 K/s. It can be seen that oxygen obviously reduces the onset temperature for crystallization, T_{X1}, and raises the glass transition temperature, T_g, at higher heating rate of 0.67 K/s, this makes ΔT_X value ($=T_{X1} - T_g$) of $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ alloy decreased from 119.2 K for 600 appm [O] to 80.9 K for 5200 appm [O], which is consistent with the result reported by Eckert et al. [11]. However, T_{X1} values for two alloys are very close at 0.033 K/s heating rate. From the relationship between T_{X1} and heating rate shown in Fig. 3, it is clear that the difference of T_{X1} for $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ alloy induced by oxygen becomes smaller as heating rate decreased.

In order to get the 'panoramic effects' of oxygen on the thermal stability of $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ alloy, TTT-diagrams of two alloys with different oxygen contents were constructed by isothermal DSC measurements. From the isothermal DSC curves, the onset time for crystallization corresponding to each isothermal annealing temperature was determined according to the method used

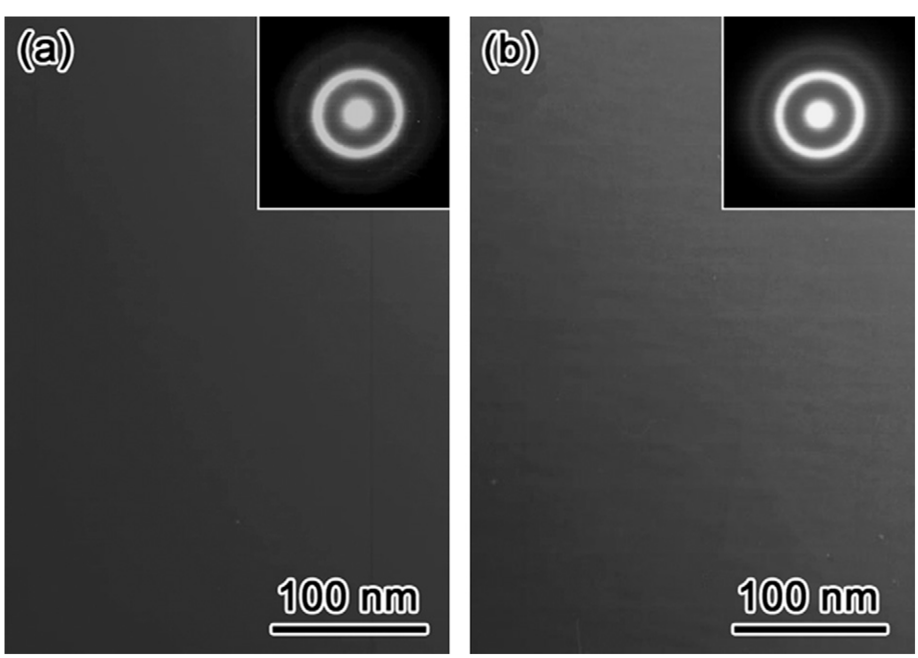

Fig. 1. Bright-field TEM images and corresponding SAD patterns of melt-spun alloys with 600 appm [O] (a) and 5200 appm [O] (b).