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ARTICLE

Exploring a $Zr_{50}Ti_5Cu_{27}Ni_{10}Al_8$ Bulk Metallic Glass with Excellent Glass-forming Ability

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Abstract: The wide compositional space of multi-component Zr-based metallic glass gives rise to a huge challenge for the discovery of the Zr-based alloys with excellent glass-forming ability. Moreover, most of the bulk-sized Zr-based metallic glasses contain either the toxic element Be or precious metals. Thus, economical approaches to search multi-component bulk-sized Zr-based metallic glass free of poisonous and noble elements are extremely necessary. Here, a new $Zr_{50}Ti_5Cu_{27}Ni_{10}Al_8$ metallic glass, with a critical diameter of 10 mm, was explored after only a few experimental trials through the method of proportional mixing of the binary eutectics and slightly partial replacing of element. The thermal stability and the hardness of this metallic glass were also investigated by in-situ high-temperature X-ray diffraction and nanoindentation experiments, respectively.

Key words: bulk metallic glass; binary deep eutectic; glass-forming ability

Due to their extraordinary disordered atomic structures, bulk metallic glasses (BMGs) exhibit many excellent properties, such as high hardness, high strength, and good impact resistance, which are important qualities for engineering and structural materials[1-3]. Among these BMGs, Zr-based BMGs have been drawing extensive attention due to their good glass-forming ability (GFA)[4]. So far, many Zr-based BMGs with the critical diameter larger than 10 mm have been successfully explored in the systems such as Zr-Ti-Ni-Cu-Be[5], Zr-Cu-Ni-Al-Pd[6], Zr-(Ag,Cu)-Al[7]. It can be found that most of these bulk-sized Zr-based metallic glasses contain either the toxic element Be or precious metals, such as Ag and Pd, severely limiting their widespread practical applications. Therefore, there is an urgent need to explore new bulk-sized Zr-based BMGs free of poisonous and noble elements.

The wide compositional space of multi-component BMGs give rise to a huge challenge for the discovery of the alloys with excellent GFA, especially for the BMGs that are composed of five or more elements. Thus, economical approaches to search for potential compositions of multi-component bulk-sized BMGs are extremely necessary. A method called "proportionally mixing of binary eutectics" has been developed to directly predict bulk glass-forming compositions[8-10]. This straightforward method suggests that multi-component glass-forming compositions could be primarily determined by mixing binary eutectics of the constituent elements in the proper ratios. Usually, there are two features associated with these binary eutectics: relatively low eutectic temperatures and line compound products from eutectic reactions. The validity of this method has been verified in many alloy systems, such as Zr-[4], Ti-Cu- [11] and Ti-Zr-[8, 12] based alloys.

In the present paper, an amorphous alloy with the composition Zr-Ti-Cu-Ni-Al was explored through the method of proportional mixing of the binary eutectics and slightly partial replacing of element. A new $Zr_{50}Ti_5Cu_{27}Ni_{10}Al_8$ alloy, with a critical diameter of 10 mm, was obtained after only a few experimental trials. The thermal stability and the hardness of this metallic glass were also investigated by in-situ high-temperature X-ray diffraction (XRD) and nanoindentation experiments, respectively.

1 Experiment

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Ingots of quinary $Zr_{50}Ti_5Cu_{27}Ni_{10}Al_8$ alloys were prepared by arc melting the mixtures of component elements of 99.9 at% purity or higher in a Ti-gettered argon atmosphere. In order to ensure the homogeneity of the composition, each ingot was remelted at least four times, followed by casting the melted alloys into a copper mold to form rod-shaped samples with various diameters. A room-temperature XRD equipped with a Cu Kα X-ray source was used to examine the phase of deposited samples. The room-temperature XRD patterns were taken at 2θ angle from 20° to 100° at a scanning rate of 5° /min. To study the structure and phase nature of metallic glasses, samples were sliced by the dual beams focused ion beam (FIB) system (FEI HELIOS NanoLab 600i) and then subjected to transmission electron microscopy (TEM) observations. TEM were carried out on a Philips CM200 device at a voltage of 200 kV. The in-situ high-temperature XRD (HTXRD) data was collected on a Panalytical multifunction X-ray diffractometer, equipped with an Anton Paar high temperature accessory (APHTK-16N) and a 3D PIXcel detector. An argon atmosphere was provided. The heating process was divided into many continuous parts from room temperature to 600 °C. The heating rate was 10 °C/min. The diffraction patterns were recorded every 10 °C from 400 °C to 570 °C. The nanoindentation experiments were performed on the alloys at room temperature by an MTS Nanoindenter-XP, where the displacement and load resolution were lower than 0.1 nm and 50 nN, respectively. Prior to nanoindentation test, the specimens were mechanically polished to a mirror finishing using 1 μm diamond paste. The indentation procedure consisted of a loading segment at a rate of 1 mN/s, followed by a holding segment of 5 s at the maximum load of 20 mN, and then an unloading segment at a rate of 1 mN/s.

2 Results and Discussion

As described above, good glass-forming composition is often at or near "deep" eutectics. We then firstly locate the composition with superior GFA based on the method of "proportional mixing of binary eutectics" in the Zr-Cu-Ni-Al system, which is designated as the starting composition to further optimize the alloy composition by minor element addition. Numerous previous results have revealed that the major crystalline phases of Zr-Cu-Ni-Al metallic glass systems are Zr-Cu, Zr-Ni and Zr-Al intermetallics[4, 13, 14]. Once the driving forces for the nucleation of these three competing crystalline phases are balanced, then the ability to hinder crystallization will be dramatically enhanced[9]. Following these results and according to binary alloy phase diagrams, the possible good glass-forming compositions in Zr-Ni-Cu-Al alloy system can be located by three binary eutectics $Zr_{44}Cu_{56}$, $Zr_{64}Ni_{36}$, and $Zr_{70}Al_{30}$[4, 15, 16]. Then, the composition C_{am} in the quaternary Zr-Ni-Cu-Al alloy system can be obtained as follows:

$$C_{am}=\alpha\ [Zr_{44}Cu_{56}] + \beta[Zr_{64}Ni_{36}] + \gamma[Zr_{70}Al_{30}] \quad (1)$$

$$\alpha + \beta + \gamma = 1 \quad (2)$$

where α, β, and γ are constants. The tendency to form crystalline phases from the individual binary clusters is dominated by their concentration and heat of mixing ΔH [10]. High concentration and large ΔH will facilitate the nucleation of crystalline phases. In order to minimize the tendency to form all the crystalline phases, the clusters with large ΔH should have relatively low concentration[8]. Therefore, α, β, and γ can be derived based on

$$\alpha\Delta H_{Zr\text{-}Cu}=\beta\Delta H_{Zr\text{-}Ni}=\gamma\Delta H_{Zr\text{-}Al} \quad (3)$$

where $\Delta H_{Zr\text{-}Cu}$=-23 kJ/mol, $\Delta H_{Zr\text{-}Ni}$=-49 kJ/mol, and $\Delta H_{Zr\text{-}Al}$=-44 kJ/mol are heat of mixing for the clusters Zr-Cu, Zr-Ni, and Zr-Al, respectively. Combining Eqs. (2) and (3) we can obtain that α=0.49, β=0.25, and γ=0.26, yielding composition of $Zr_{55.7}Cu_{27.5}Ni_9Al_{7.8}$ from Eq.(1). We then round the atomic percent and get $Zr_{55}Cu_{27}Ni_{10}Al_8$ as the initial composition to further modify it. To test the GFA of this alloy composition, we produce cylindrical rods in varied diameters from 2 mm to 10 mm by a copper mold casting method. We found that the largest diameter of $Zr_{55}Cu_{27}Ni_{10}Al_8$ alloy possessing the amorphous structure is 7 mm. The room-temperature XRD pattern of the $Zr_{55}Cu_{27}Ni_{10}Al_8$ alloy with diameter of ϕ=7 mm is presented in Fig.1, which consists of only broad diffraction maxima without any sharp Bragg peak.

Partially replacing Zr with Ti is very effective and has been widely applied to improve the GFA of Zr-based metallic glasses. For example, Ma et al. found that a significant increase in the GFA of more than 100% in terms of the critical diameter formed from the $Zr_{56.2}Cu_{31.3}Ni_{4.0}Al_{8.5}$ alloy with the addition of 4.9% Ti[17]. Along this way, we partially replace Zr with Ti to further improve the GFA of $Zr_{55}Cu_{27}Ni_{10}Al_8$ metallic glass. To examine the dependence of GFA on the Ti addition, we cast the $Zr_{55\text{-}x}Ti_xCu_{27}Ni_{10}Al_8$ (x=1, 3, 5, 7) alloys into a group of cylindrical rods with diameters ranging from 5 mm to 12 mm and test their room-temperature XRD patterns.

The typical examples of the room-temperature XRD patterns of the $Zr_{55\text{-}x}Ti_xCu_{27}Ni_{10}Al_8$ (x=1, 3, 5, 7) alloys with the diameter of ϕ=10 mm and ϕ=12 mm are shown in Fig. 1. We found that for all the samples, the 10 mm-diameter alloy

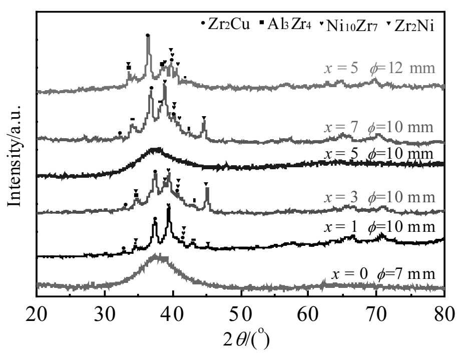

Fig.1 XRD patterns of $Zr_{55\text{-}x}Ti_xCu_{27}Ni_{10}Al_8$ (x=0, 1, 3, 5, 7) at room-temperature

containing 5% Ti is the largest diameter sample that exhibits a perfect halo peak in the room-temperature XRD pattern, indicating that the critical diameter of $Zr_{50}Ti_5Cu_{27}Ni_{10}Al_8$ (Zr50) metallic glass is 10 mm. The macroscopic feature of the Zr50 metallic glass with the diameter of 10 mm is shown in Fig.2. To further confirm the amorphous structure of the Zr50 metallic glass in the diameter of 10 mm, TEM experiment was performed. Fig.3 shows a typical bright-field TEM micrograph of the Zr50 metallic glass. The corresponding selected area electron diffraction (SAED) pattern is presented in the inset of Fig.3. The SAD pattern reveals a full ring, which is the inherence of an amorphous phase, confirming that the Zr50 metallic glass with a diameter of 10 mm indeed has a fully glassy structure.

To investigate the thermal stability and the structural features of the Zr50 metallic glass, the in-situ HTXRD experiments were performed for the amorphous sample. The XRD patterns heated at different temperatures are shown in Fig.4. Clearly, every XRD pattern measured below 460 °C exhibits a broad peak, without any detectable sharp peaks, which is the characteristic of the amorphous structure. While two crystalline Bragg peaks, indicated by arrows in Fig.4, start to appear on the XRD curve at 460 °C, demonstrating that the Zr50 metallic glass has a good thermal stability and can maintain the amorphous nature up to 460 °C.

The mechanical property of the Zr50 metallic glass was evaluated via nanoindentation tests. To obtain reliable indentation data, 40 indents, along a line, were reduplicated. The interval between two neighboring indents was set at 20 μm. The hardness was calculated by the method of Oliver and Pharr[18]. From the load-displacement curve, hardness can be obtained at the peak load P_{max} as $H=P_{max}/A$, where A is the projected contact area. The hardness measured from the nanoindentation tests is plotted in Fig. 5. As can be seen, the mean hardness of the Zr50 metallic glass is about 8.5 GPa.

Fig.2 Macroscopic feature of the Zr50 metallic glass with the diameter of 10 mm

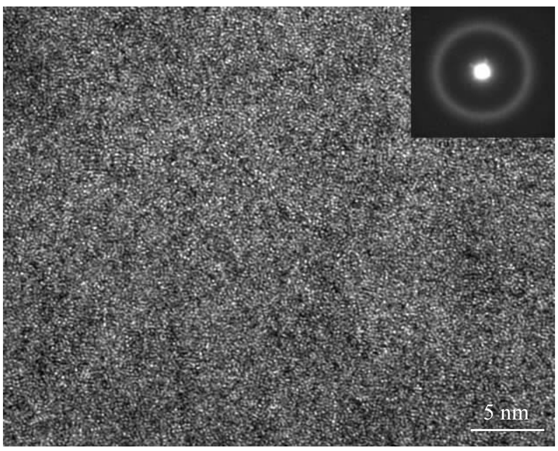

Fig.3 Bright-field TEM image of the Zr50 metallic glass with the diameter of 10 mm, and the corresponding SAED pattern presented in the inset

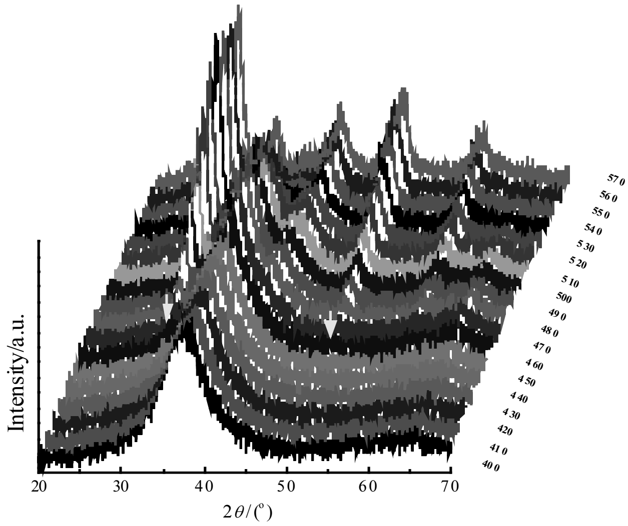

Fig.4 In-situ HTXRD patterns of the Zr50 metallic glass heated at different temperatures

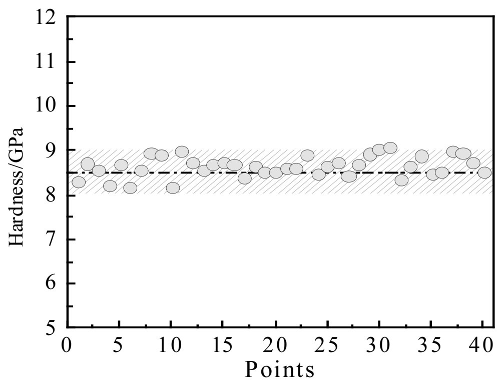

Fig.5 Hardness of the Zr50 metallic glass measured from the nanoindentation tests

3 Conclusions

1) A new Zr50 metallic glass, with a critical diameter of 10 mm, is explored after only a few experimental trials

through the method of proportional mixing of the binary eutectics and slightly partial replacing of element.

2) The Zr50 metallic glass has a good thermal stability and can maintain the amorphous nature up to 460 °C. The mean hardness of the Zr50 metallic glass, measured from the nanoindentation tests, is about 8.5 GPa.

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一种具有优异玻璃形成能力的 $Zr_{50}Ti_5Cu_{27}Ni_{10}Al_8$ 大块非晶合金的开发

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摘 要：多组元的 Zr 基非晶合金成分的复杂性对开发具有优异玻璃形成能力的 Zr 基非晶合金提出巨大的挑战。另外，大部分 Zr 基非晶合金含有有毒元素 Be 或者贵金属。因此，采用一种简单有效的方法开发无毒无贵金属元素的多组元 Zr 基非晶合金十分必要。本研究中采用二元共晶比例法和部分元素替代法快速的开发出了一种新的临界尺寸大于 10 mm 的 $Zr_{50}Ti_5Cu_{27}Ni_{10}Al_8$ 非晶合金。这个非晶合金的热稳定性和硬度也通过原位高温 X 射线衍射和纳米压痕方法测量得出。

关键词：大块非晶合金；二元共晶比例法；玻璃形成能力

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