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ARTICLE

Preparation of High Entropy Alloy $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ with High Glass Forming Ability

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Abstract: High entropy alloy (HEA) $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ consisting of two solid solution phases and bulk metallic glass (HE-BMG) with the same composition were prepared separately by casting in a copper mold. The results indicate that the alloy has high glass forming ability. The compressive strength of as cast HEA $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ is 1127 MPa. HEA $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ shows good tempering resistance. The hardness (HV) of $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ remains 8260 MPa after it is treated at 750 ℃ for 2 h.

Key words: high entropy alloy; bulk metallic glass; glass forming ability; compressive strength

High entropy alloys (HEAs) were firstly defined by Yeh et al [1], consisting of at least five principal metallic elements in equimolar or near equimolar ratio whose concentration lies between 0.05 and 0.35 (mole fraction). The HEAs possess the ability to form simple solid solution phases from the melt in preference to intermetallics [2,3]. This can be attributed to the multiple principal elements which can be considered as solute atoms. Elements with small atomic size differences are easily interchangeable and able to sit on lattices sites forming solid solutions. Furthermore, the high enthalpy of mixing of HEAs acts to lower the free energy of the solution phases and does not favor the formation of compounds [4]. HEAs exhibit excellent properties such as high strength even at elevated temperature, high corrosion resistance, and good soft magnetic properties. This new alloy design strategy also extends the research field of phase diagram and alloy strength theory [5].

According to Inoue et al [6], multiple components with a large negative enthalpy of mixing between atom pairs promote dense random packing of atoms, accelerating the glass phase formation. And Ref. [7] reported that the high mixing entropy also favors bulk metallic glass formation. So, glassy high entropy alloys can be expected. The successful preparation of high entropy bulk metallic glasses (HE-BMG) [3,7-9] turned this hypothesis out to be correct. Up to now, a series of HE-BMGs have been reported, such as $Ti_{20}Zr_{20}Hf_{20}Cu_{20}Ni_{20}$, $Zn_{20}Ca_{20}Sr_{20}Yb_{20}(Li_{0.55}Mg_{0.45})_{20}$, $Er_{20}Tb_{20}Dy_{20}Ni_{20}Al_{20}$, $Sr_{20}Ca_{20}Yb_{20}Mg_{20}Zn_{20}$, $Sr_{20}Ca_{20}Yb_{20}Mg_{20}Zn_{10}Cu_{10}$, $Sr_{20}Ca_{20}Yb_{20}Mg_{20}(Zn_{0.5}Cu_{0.5})_{20}$, $Pd_{20}Pt_{20}Cu_{20}Ni_{20}P_{20}$ and $Ti_{20}Zr_{20}Cu_{20}Ni_{20}Be_{20}$. The unique composition of HE-BMGs may result in improved performances contrary to ordinary BMGs. Yet HE-BMGs are not well studied due to the limited examples. Our previous works[10] found out a rough qualitative method of estimating the microstructure of HEAs. Considering that the atomic size difference plays a very important role in the formation of solid solution phases or bulk metallic glasses[9-12] and high mixing entropy and large negative enthalpy of mixing favor the formation of BMGs, a new HEA $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ with high glass forming ability (GFA) was fabricated and investigated in the present paper.

1 Experiment

The master alloy ingot with a nominal chemical composition of $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ (in atomic percentage) was prepared by arc-melting the mixture of pure bulk metals (purity higher than 99.9wt%) under a Ti-gettered high purity argon atmosphere. The ingot was then reversed and re-melted 4 times to assure chemical homogeneity. The arc-melted ingot was then re-melted and cast into a rod-shaped cavity in a

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copper mold with a diameter of Φ1~3 mm. The samples were cut into small rods with a low speed diamond saw (SYJ 160, China).

The microstructure of $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ with diameter of Φ3 mm was identified by X-ray diffraction (XRD, D/Max2500V, Ultima IV, Japan) using Cu Kα radiation on the cross section of rod sample. The rod sample with Φ1 mm was carefully polished to its central plane and put together closely to make a 2 mm×2 mm surface. The glassy nature of $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ with diameter of Φ1 mm was then identified by XRD. The microstructure of $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ as cast was observed by scanning electron microscopy (SEM, JEOL JSM-6360LV). The samples cut from the Φ3 mm rod were heated to 450~850 ℃ in an electric resistance furnace for 2 h and then cooled in a furnace to investigate the thermal stability. Hardness of these samples were tested on hardness testing machines (FM-700). The diameter of rods used for room temperature compressive testing is 3 mm, and the height to diameter ratio is 2:1. Room temperature compressive properties of samples were analyzed on a materials testing machine (Instron MTS569) at a strain rate of 3×10^{-4} s^{-1}. And the fracture morphologies were examined by SEM.

2 Results and Discussion

2.1 Microstructure of the as-cast alloy

Fig.1 shows the XRD patterns of the as cast $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$. As it can be seen, only one hexagonal and one fcc phase can be found in Fig.1b, meaning microstructure of typical high entropy alloy is obtained in rod shape $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ with Φ3 mm. The diffraction peaks of hexagonal phase are similar to the peak positions of $Zr_{0.89}Ti_{1.2}Ni_{0.9}$ (CSD: 96323, No: 01-072-6478). And the diffraction peaks of fcc phase are similar to the peak positions of CuZr (CSD: 103163, No: 01-071-7931). Meanwhile, only a broad diffraction peak without any detectable sharp diffraction peak corresponding to crystalline phase is observed from Fig.1a,

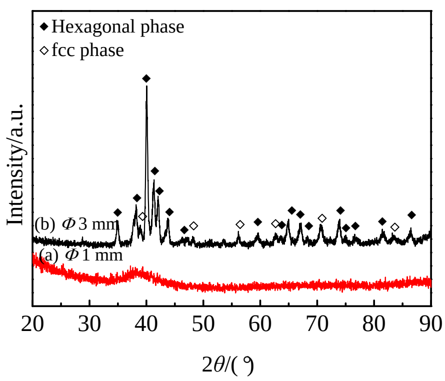

Fig.1 XRD patterns of the as cast $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ with diameter of Φ1 mm (a) and Φ3 mm (b)

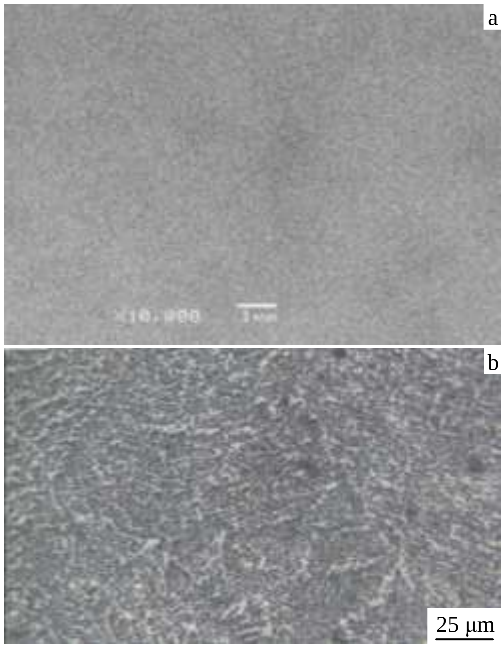

Fig.2 Microstructure characteristic of the as cast $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ with diameter of Φ1 mm (a) and Φ3 mm (b)

meaning the rod shape $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ with Φ1 mm is fully amorphous. Fig.2 shows the microstructure characteristic of the as cast $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$, which is consistent with the results of Fig.1.

Fig.3 shows the DSC curve of as cast $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ with 1 mm in diameter. From Fig.3, distinct endothermic and subsequent exothermic reactions can be observed, suggesting the glass transition and crystallization occur during heating. It also exhibits a glass transition temperature (T_g) of 432 ℃, an onset temperature for crystallization (T_x) of 465 ℃, an onset melting temperature (T_m) of 894 ℃ and a liquidus temperature (T_l) of 959 ℃. Accordingly, the supercooled liquid range ($\Delta T_x=T_x-T_g$) of the $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ HE-BMG is 32 K, and the reduced glass transition temperature ($T_{rg}=T_g/T_l$) is as high as 0.57. And one thing should be noted during calculation i. e. the T_{rg} should be calculated by absolute temperature value. As we know, ΔT_x and T_{rg} are the widely accepted parameters indicating the glass forming ability (GFA). According to Ref.[13], most conventional metallic glasses show T_{rg} no more than 0.4, and most BMGs with high GFA exhibit T_{rg} from 0.5 to 0.7. Meanwhile, very few HEAs with full amorphous microstructure were reported when cast by a copper mold. So we can accordingly conclude that the alloy $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ is of high GFA. In other words, the microstructure of millimeter scale $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ can be controlled to consist of typical solid solution phases or full amorphous.

As it mentioned above, atomic size difference (δ), the mixing enthalpy (ΔH^{mix}) and the mixing entropy (ΔS^{mix}) play a collective role in the formation of solid solution phases or

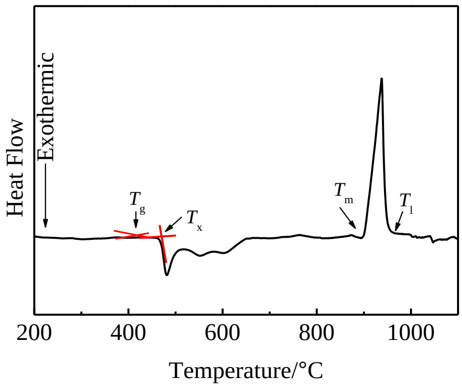

Fig.3 DSC curve of as cast $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ with 1 mm diameter at a heating rate of 20 K/min

BMGs. The values of δ, ΔH^{mix} and ΔS^{mix} can be calculated by following equations [10,12].

$$\Delta H^{mix} = \sum_{i=1, i \neq j}^{n} \Omega_{ij} c_i c_j = 4 \sum_{i=1, i \neq j}^{n} \Delta H_{i-j}^{mix} c_i c_j \quad (1)$$

Where, ΔH_{i-j}^{mix} is the mixing enthalpy of atomic pairs between the ith and jth element. Ω_{ij} is the interaction parameter between the ith and jth elements in regular solution. c_i and c_j are the atomic fraction of the ith and jth component, respectively. The values of ΔH_{i-j}^{mix} can be obtained from Ref. [14].

$$\Delta S^{mix} = -R\sum_{i=1}^{n} c_i \ln c_i \quad (2)$$

$$\delta = \sqrt{\sum_{i=1}^{n} c_i (1 - r_i / r_a)^2} \quad (3)$$

$$r_a = \sum_{i=1}^{n} c_i r_i \quad (4)$$

Where, R is the ideal gas constant, R=8.314 J/(mol·K), and c_i is the atomic fraction of the ith component. r_i is the radius for the ith atom. r_a is the average atomic radius. The atomic radii of Cu, Zr, Ti, Al, and Ni are 0.127, 0.160, 0.145, 0.143, and 0.124 nm, respectively [15]. Accordingly, the values of δ, ΔH^{mix} and ΔS^{mix} for $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ are 0.32, –30 K J mol^{-1} and 12.25 J (mol·K)$^{-1}$, respectively. The high mixing entropy means the highly randomly arrangement of multiple elements and great difficulty for atoms diffusing, which favors either simple solid solution phases or BMG formation. The large negative mixing enthalpy also exhibits the precipitation of complex compounds and favors the formation of BMGs[16,17]. According to Ref. [7,11], small atomic size difference favors the formation of simple solid solution phases, while large atomic size difference favors the formation of amorphous phase. So, moderate value of atomic size difference combining multi principal component makes the atoms act as either a solute atom or a solvent atom. Accordingly, the alloy is capable to form either simple solid solution phases or amorphous phase. In a word, the unique multi principal composition provides strong interattractions among the components and difficult cooperative migration of the various elements. As a result, simple solid solution phases prefer to form inter-metallic compounds. When the melt HEA is cooled more quickly, the diffusion and rearrangement of various atoms are so hard that disordered amorphous phase forms. So, HE-BMG $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ is formed.

2.2 Compressive properties of the as-cast alloy

Fig.4 shows the compressive stress-strain curves of the as cast rod shape $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$, and the corresponding fracture morphologies are shown in Fig.5.

From Fig.4, HEA $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ shows high compressive strength (1127 MPa) while poor ductility. Several long cracks and multiple fracture platforms can be found in Fig.5, which indicate the fast propagation of cracks within $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ during compressing. The severe brittleness may be attributed to the fact that the as cast $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ mainly consists of brittle hexagonal phase with minor ductile fcc phase.

2.3 Thermal stability of $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$

Fig.6 shows the microstructures of $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ after heat treatment at different temperatures for 2 h. The corresponding variation in hardness of the alloy after heat treatment is indicated in Fig.7.

From Fig.6 and Fig.7, HEA $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ shows good thermal stability and tempering resistance, and the microstructures exhibit no dramatic evolutions under 750 °C. After treatment at 750 °C, the hardness (HV) decreases from 9410 MPa (as-cast) to 8260 MPa. And the total hardness loss of the alloy is about 12.2% after treatment at 750 °C. After heating at 850 °C for 2 h, the HV drops to 7190 MPa, which may result from the grain coarsening.

The excellent thermal stability may be attributed to the existence of multi-principal elements which restrict the diffusion of atoms.

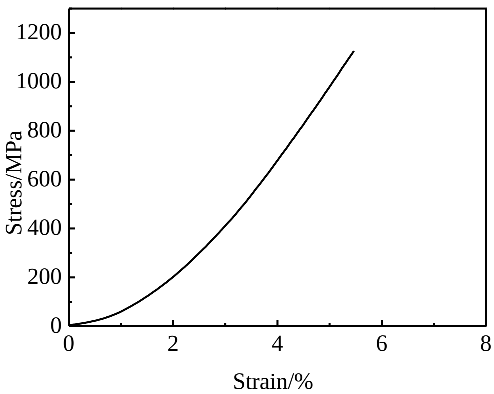

Fig.4 Room temperature compressive stress-strain curve of as cast $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$

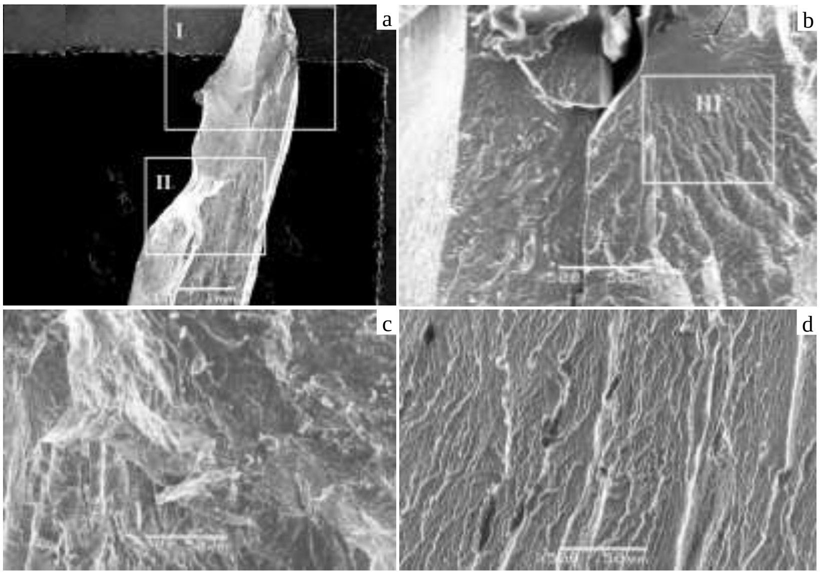

Fig.5 Fracture morphologies of HEA $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ (a), the magnification of zone I (b), zone II (c), and zone III (d)

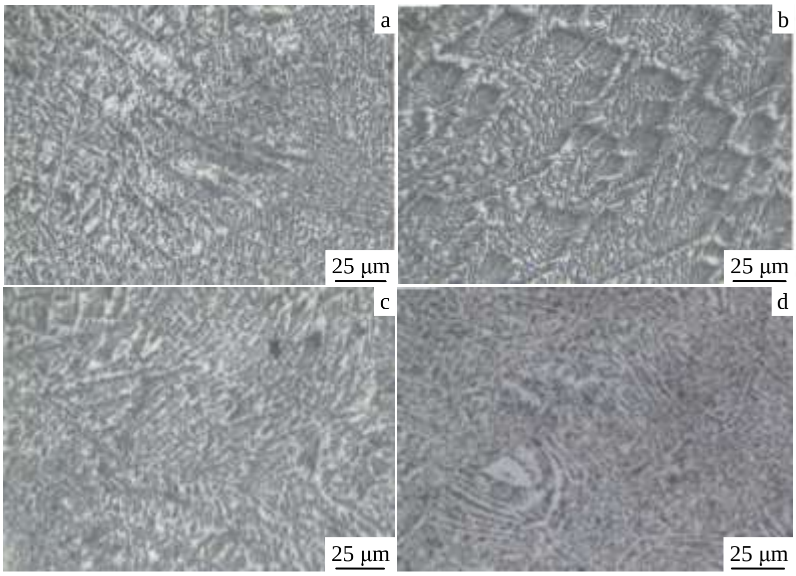

Fig.6 Microstructures of $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ after heated at different temperatures for 2 h: (a) 450 ℃, (b) 650 ℃, (c) 750 ℃, and (d) 850 ℃

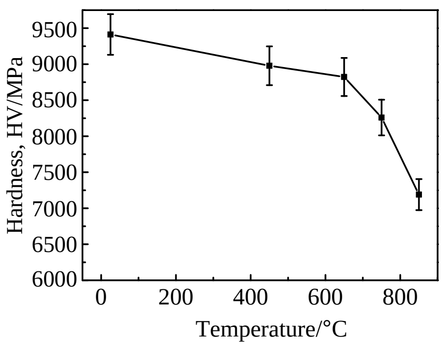

Fig.7 Hardness of $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ for as-cast and after heat treated for 2 h

3 Conclusions

1) Thanks to the unique multi principal component composition, $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ can be prepared to both BMG with full amorphous and HEA consisting of two solid solution phases by casting in a copper mold. It indicates this alloy shows high glass forming ability.

2) The compressive strength of as cast HEA $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ is 1127 MPa. The brittleness of HEA $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ may be attributed to the hexagonal phase which results in the fast propagation of cracks.

3) HEA $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ shows good tempering resistance. The hardness of $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ remains 8260

MPa after it is treated at 750 ℃ for 2 h.

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具有高非晶形成能力的高熵合金 $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$

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摘　要：用铜模吸铸法成功地合成了由 2 个固溶体相构成的高熵合金(HEA) $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ 和相同成分的非晶态合金(HE-BMG)。实验结果表明该成分的高熵合金具有高的非晶形成能力。铸态高熵合金 $Cu_{29}Zr_{32}Ti_{15}Al_5Ni_{19}$ 的抗压强度为 1127 MPa。该合金表现出良好的抗回火性能，经 750 ℃ 处理 2 h 后，该合金硬度保持在 8260 MPa。

关键词：高熵合金；块体非晶合金；非晶形成能力；抗压强度

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