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Nanocrystallization of Cu-Based Bulk Glassy Alloys upon Annealing

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The Cu-based bulk glassy alloys in Cu-Zr-Ti-Ni systems were prepared by means of copper mold casting. The Cu-based bulk glassy alloys samples were tested by X-ray diffractomer (XRD), differential scanning calorimeter, scanning electron microscopy (SEM), Instron testing machine and Vickers hardness instruments. The result indicated that the prepared Cu-Zr-Ti-Ni alloys were bulk glassy alloys. The temperature interval of supercooled liquid region (ΔT_x) was about 45.48 to 70.98 K for the Cu-Zr-Ti-Ni alloy. The Vickers hardness was up to 565 HV for the $Cu_{50}Zr_{25}Ti_{15}Ni_{10}$ bulk glassy alloy. The $Cu_{50}Zr_{25}Ti_{15}Ni_{10}$ bulk glassy alloys were annealed in order to obtain nanocrystals. The results showed that the Vickers hardness was raise up to 630 HV from 565 HV. As shown in XRD results, the amorphous alloys changed to nanocrystals, which were Cu_8Zr_3, Cu_3Ti_2 and CuZr, improved the hardness. The SEM analysis showed that the compression fractured morphology of amorphous alloys was brittle fracture, and the fracture morphology after annealing was ductile fracture. This proved that annealing of amorphous to nanocrystals can improve the plasticity and toughness of amorphous alloys.

Key Words: Cu-Zr-Ti-Ni alloys, Cu-based bulk glassy alloys, Nanocrystallization, Annealing of amorphous, Mechanical properties

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INTRODUCTION

Cu-based bulk glassy alloy is a new amorphous system developed recently, which has large glass forming ability and relatively low cost (Dai et al., 2006; Fu et al., 2008; Kim et al., 2006; Malekana et al., 2010; Zhang & Zhang, 2008). The tensile fracture strength is much higher than crystals, reaching up to 2,000 to 2,400 MPa, with certain ductility. And compared to Zr-based and Pd-based bulk glassy alloys, the strength of Cu-based bulk glassy alloy is also on the top, which can be used as ultra-high strength structural materials in the future. Until now, many researchers in the world have done a lot of deep studies on Cu-based bulk glassy alloy. But as structural materials, the plastic property of prepared Cu-based bulk glassy alloy which has lowers plastic property than steel materials also need to be improved. Therefore, it's an urgent problem to improve the plasticity and toughness of amorphous alloys.

Based on the research of bulk glassy alloy, in recent years, the research on the composite material of bulk glassy and nanocrystalline alloy has been carried out (Barekara et al., 2010; Liu et al., 2009; Xie et al., 2008; Yang et al., 2009; Zhang et al., 2013). Because when the nanocrystalline evenly distributed in the bulk glassy alloy matrix, the properties of bulk glassy alloy can be further optimized, while maintaining high strength and improving the lower plastic. So the application field of high strength structural material can be expanded. In this paper, Cu-based bulk glassy alloy was prepared through copper mold casting method. The nanocrystallization of bulk glassy alloy was obtained by annealing. The annealing process, microstructure and properties of the nanocrystallization were investigated. The preparation of Cu-based bulk glassy-nanocrystalline alloy composite materials on the basis of the theory and technology

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were discussed. Cu-based bulk glassy-nanocrystalline alloy composite lays the theory foundation for the future preparations. And it has important practical significance for the promotion as a future ultra-high strength structural material of Cu-based bulk glassy alloy composite material.

MATERIALS AND METHODS

The alloy ingots with multiple alloys of Cu-Zr-Ti-Ni and Cu-Zr-Ti-Ni-Co were prepared by arc melting from a mixture of pure Cu, Zr, Ti, Ni, Co under argon atmosphere protection for four times in copper crucible to ensure chemical homogeneity. The purities of all elements are above 99.9% with nominal composition of atomic percentage. A bulk glassy alloy bar was prepared with the diameter of 2 to 5 mm using copper mold casting method in high vacuum. The structure of specimens was examined by X-ray diffractomer (XRD) with CuK_{α}. Meanwhile, the glass transition temperature (T_g), crystallization start temperature (T_x) and ΔT_x ($\Delta T_x = T_x - T_g$) of the bulk glassy alloy were examined by differential scanning calorimeter with the heating rate of 0.67 K/s.
The prepared Cu-based bulk glassy alloys were annealed, and the compression test was performed by using universal material testing machine with the sample size of 2 mm in diameter, 4 mm in length and the strain rate is 5×10^{-4}/s. The fracture surface morphology were observed using scanning electron microscopy (SEM), and the hardness were obtained through Vickers hardness. Meanwhile, the phase structure of Cu-based bulk glassy-nanocrystalline alloy was analyzed using XRD.

Table 1. Thermal stability of the Cu-based Cu-Zr-Ti-Ni system bulk glassy alloys

Alloy	T_g (K)	T_x (K)	ΔT_x (K)
$Cu_{55}Zr_{25}Ti_{15}Ni_5$	716.58	762.06	45.48
$Cu_{54}Zr_{22}Ti_{18}Ni_6$	714.44	767.66	53.22
$Cu_{50}Zr_{25}Ti_{15}Ni_{10}$	703.66	774.64	70.98
$Cu_{45}Zr_{25}Ti_{15}Ni_{15}$	718.01	767.69	49.68

Table 2. Thermal stability of the Cu-based Cu-Zr-Ti-Co system bulk glassy alloys

Alloy	T_g (K)	T_x (K)	ΔT_x (K)
$Cu_{60}Zr_{20}Ti_{20}$	707.65	743.39	35.74
$Cu_{54}Zr_{22}Ti_{18}Co_6$	711.05	756.87	45.82
$Cu_{50}Zr_{25}Ti_{15}Co_{10}$	715.99	773.19	57.20
$Cu_{50}Zr_{22}Ti_{18}Ni_6Co_4$	702.52	777.02	74.50

RESULTS AND DISCUSSION

Thermophysical Properties of Bulk Glassy Alloys

The thermophysical properties such as T_g, T_x and ΔT_x of the Cu-based Cu-Zr-Ti-Ni and Cu-Zr-Ti- Co system bulk glassy alloys were listed in Tables 1 and 2. All the alloys showed a large supercooled liquid temperature interval ΔT_x.
As shown in Tables 1 and 2, alloys showed high glassy forming ability, and it matched well with amorphous alloy composition design principle of chaos, namely with the increase of elements number and the difference between atomic radius, the amorphous formation ability of alloys enhanced. From the thermodynamic condition of amorphous formation, the difference of Gibbs free energy (ΔG) for liquid transformation is smaller, the more favorable for the formation of amorphous phase. According to $\Delta G = \Delta H - T\Delta S$, ΔG decreased with the decrease of ΔH and increase of ΔS. So the increase of component number may decrease the crystallization driving force ΔG, which may increase the glass forming ability. In this paper, the alloy system had four components, and the difference between atomic radii is over 12%, so these alloys had larger ΔT_x and higher glass forming ability.

X-ray Diffractomer Results

Fig. 1 shows the XRD patterns of the cast Cu-based alloy rods with the diameter of 2.0 to 5.0 mm. Only single peak can be seen in all the XRD patterns, which means only single glassy phase appears without crystalline phase.

Microhardness Test

The microhardness were taken for $Cu_{50}Zr_{25}Ti_{15}Ni_{10}$ bulk glassy

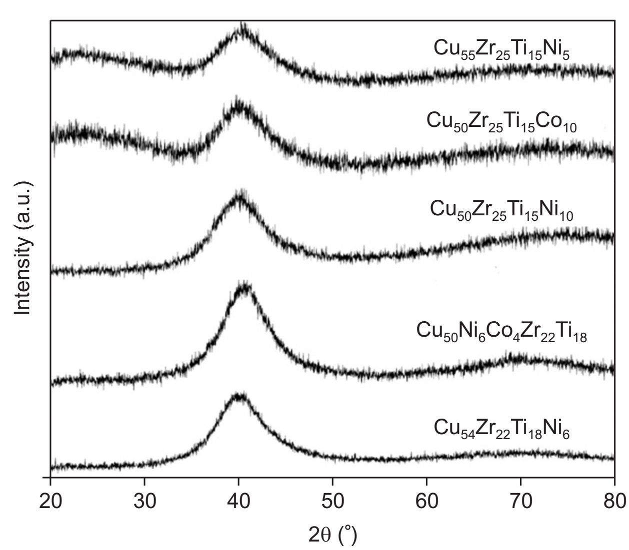

Fig. 1. X-ray diffraction patterns of the cast Cu-based alloy rods with diameter from 2.0 to 5.0 mm.

alloys (marked as 1, 2, 3, 4, 5 and 6), two points for each sample. The results were shown in Table 3.

As shown in Table 3, the average microhardness of $Cu_{50}Zr_{25}Ti_{15}Ni_{10}$ bulk glassy alloys is very high, about 565.9 HV. The arrangement of atoms in bulk glassy alloys is disordered, the atoms packed one by one just like in a liquid with the same compression level. The difference is that the atoms in liquid are easy to slide with small viscosity coefficient. When the liquid becomes viscous, the sliding of atoms becomes more difficult. At last, atoms cannot slide in the bulk glassy alloys with a definite shape and large stiffness, leading to high hardness.

Table 3. Microhardness of $Cu_{50}Zr_{25}Ti_{15}Ni_{10}$ bulk glassy alloys

Sample No.	HV_1	HV_2	$\overline{HV}$	HV
1	583.7	539.3	561.5	
2	572.1	544.5	558.3	
3	555.3	572.4	563.9	565.9
4	566.4	601.3	583.9	
5	589.6	608.0	598.8	
6	539.3	518.7	529.0	

Table 4. Microhardness of $Cu_{50}Zr_{25}Ti_{15}Ni_{10}$ bulk glassy alloys after annealing

Sample No.	HV_1	HV_2	$\overline{HV}$	HV
1	714.2	706.2	710.2	
2	595.7	647.5	621.6	
3	589.6	560.8	575.2	630.7
4	654.4	620.8	637.6	
5	614.3	633.9	624.1	
6	620.8	610.8	615.5	

Annealing Process

Annealing was performed for bulk glassy alloys in order to investigate the effect of annealing process on the microstructure. The $Cu_{50}Zr_{25}Ti_{15}Ni_{10}$ bulk glassy alloy was chosen to perform annealing treatment. The annealing temperature was set slightly higher than 703.66 K (T_g of $Cu_{50}Zr_{25}Ti_{15}Ni_{10}$). The annealing temperature was not much higher to avoid rapid crystallization and coarsen crystal which may perform degradation. The $Cu_{50}Zr_{25}Ti_{15}Ni_{10}$ bulk glassy alloy with number of 1 to 6 were heated to 708 K, 718 K, 728 K, 738 K, 748 K, and 758 K, respectively for 5 minutes and then air cooling. The microhardness was performed for each sample and the results were shown in Table 4.

The microhardness results of these samples showed that after annealing, the hardness increased from 565.9 HV to 630.75 HV. It also showed that, the annealing temperature is slightly higher than the glass transition temperature T_g.

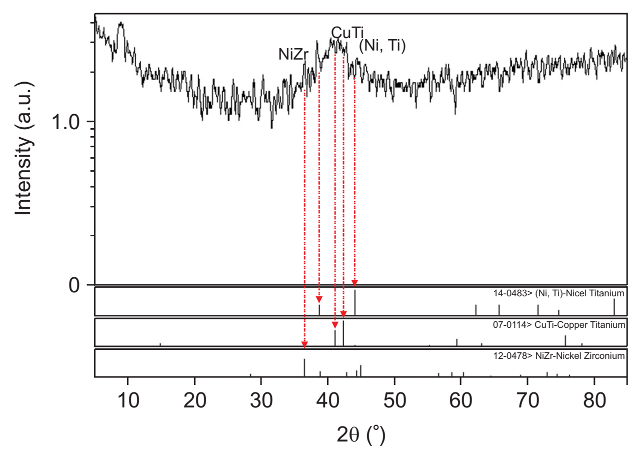

Fig. 2. X-ray diffraction patterns of $Cu_{50}Zr_{25}Ti_{15}Ni_{10}$ after annealing.

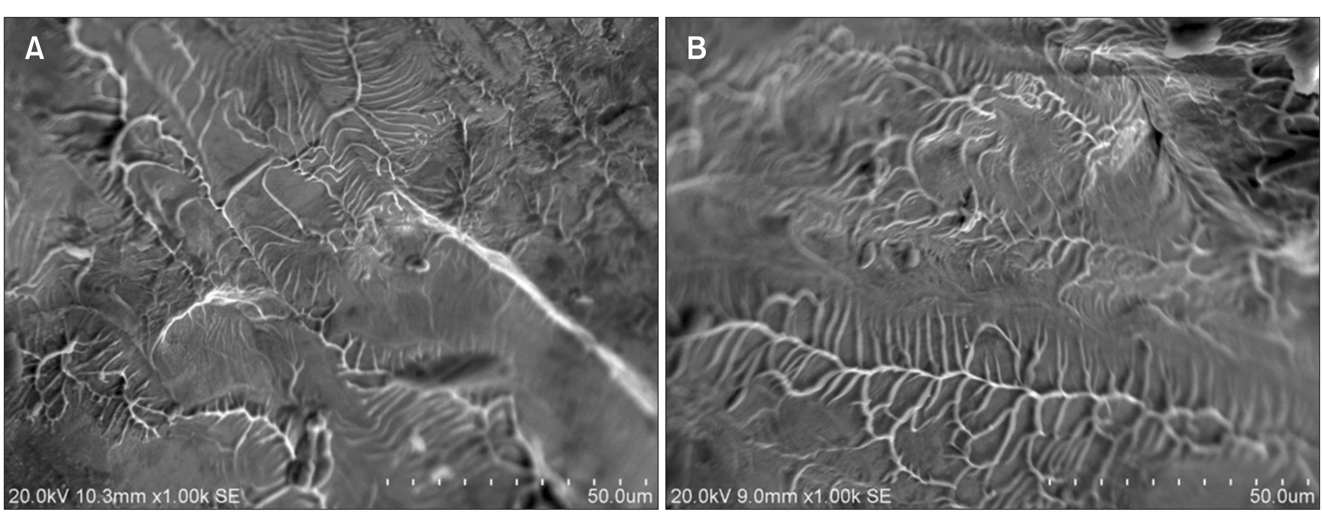

Fig. 3. Scanning electron microscopic images of $Cu_{50}Zr_{25}Ti_{15}Ni_{10}$ fractured surface morphology.

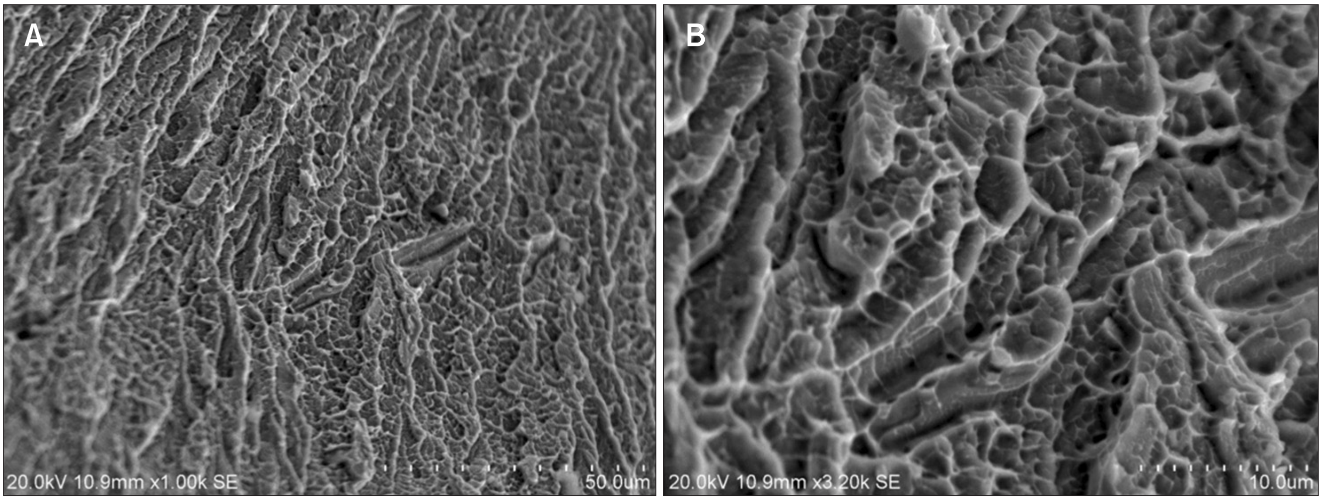

Fig. 4. Scanning electron microscopic images of $Cu_{50}Zr_{25}Ti_{15}Ni_{10}$ fractured surface morphology after annealing.

The influence of annealing temperature is not obvious on the microstructure in the range of T_g and T_x. But when the annealing temperature is slightly higher than T_g, the hardness increased most significantly. The hardness increasing after annealing in Cu-based bulk glassy alloy is due to the precipitation of nanocrystalline, which may increase the grain boundary, having dispersion strengthening effect (Li et al., 2007), to increase the plastic deformation resistance.

XRD result showed that not only one single peak, but also several small peaks (between 40° to 45°) can be found after annealing, which means that the main phase appeared to be glassy phase with a small amount of second phase (Fig. 2). Compared to the Joint Committee on Powder Diffraction Standards (JCPDS) card, these small peaks can be determined to Cu_8Zr_3, Cu_3Ti_2, and CuZr nanocrystals. The result matched well with the reason for high hardness after annealing.

SEM analysis of compression fracture surface showed brittle fracture with rivers shaped pattern and cleavage fracture before annealing (Fig. 3). Meanwhile, nest shaped and fibrous were found in the sample after annealing which indicated ductile fracture (Fig. 4), suggesting that nanocrystallization of bulk glassy alloy can improve the plasticity toughness of amorphous. Because the nanocrystalline can delay the crack extension, and local plastic deformation occurs to lessen the stress concentration.

According to the above research, Cu-based bulk glassy alloy can be prepared using copper mold casting method, and the nanocrystallization of bulk glassy alloy was obtained through annealing process, which can improve the hardness, plasticity and toughness of bulk glassy alloy, and also the problem of poor plasticity. It can be used as high strength structural materials for popularization and application.

SUMMARY

(1) Cu-based bulk glassy alloy can be prepared using copper mold casting method, and the nanocrystallization of bulk glassy alloy was obtained through annealing process.

(2) The annealing temperature is slightly higher than the glass transition temperature T_g. The influence of annealing temperature is not obvious on the microstructure in the range of T_g and T_x. But when the annealing temperature is slightly higher than T_g, the hardness increased most significantly.

(3) After annealing, Cu_8Zr_3, Cu_3Ti_2, and CuZr nanocrystals precipitated, which improves the microhardness of bulk glassy alloy from 565 to 630 HV.

(4) The compression fracture morphology of the bulk glassy alloy is brittle fracture. After annealing, the nanocrystal shows ductile fracture which improves the bulk glassy alloy plasticity and toughness.

(5) Cu-based bulk glassy alloy and nanocrystalline alloy shows excellent mechanical properties, it can be used as high strength structural materials for wide application.

CONFLICT OF INTEREST

No potential conflict of interest relevant to this article was reported.

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