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Effect of Ni on glass-forming ability of Cu-Ti-based amorphous alloys

LIN Tao(林 涛)[1], JIANG Jiang(姜 江)[1], BIAN Xiu-fang(边秀房)[1], DONG Ying(董 瑛)[2]

1. Key Laboratory of Structure and Heredity of Materials, Ministry of Education, Shandong University, Ji'nan 250061, China;
2. Quality and Technology Supervision Bureau, Weifang 261031, China

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Abstract: Ribbons of amorphous Cu-Ti-Ni alloys were prepared by the melt spinning method. The amorphous structure of these ribbons was confirmed by X-ray diffractametry and transmission electron microscopy. The effect of Ni on the glass-forming ability of Cu-Ti-based alloys was studied by differential scanning calorimetry(DSC). It is found that the supercooled liquid region, ΔT_x value shows the maximum value of 61℃ at x=10 in the $Cu_{50}Ti_{50-x}Ni_x$ (x=0, 5, 10, 15 mole fraction, %) system. And the reduced glass transition temperature, T_{rg}, is smaller than 0.45. The glass forming ability(GFA) of Cu-Ti alloy is not effectively promoted by Ni addition.

Key words: Cu-Ti-based alloys; glass-forming ability; melt-spinning method; deep eutectics

1 Introduction

Recently, a number of bulk metallic glassy alloys have been reported, such as La-Al-Ni[1], Cu-Ti-Zr-Ni [2, 3], Cu-Ti-Zr-Ni-Be[4, 5], Cu-Ti-Zr-Ni-Si[6−8] and Cu-Ti-Zr-Ni-Sn[9]. Because of the exceptional good glass-forming ability, these multicomponent alloy systems attracted much attention. It is noted that all these alloy systems contain the element Ni, which plays an important role in obtaining these bulk amorphous alloys.

There have been many studies on binary amorphous Cu-Ti [10] and Ti-Ni [11] alloys, but the effect of Ni on GFA of Cu-Ti-based alloys is not studied further. In order to obtain some useful information in alloy design for achieving new bulk glassy alloys, we have prepared ternary $Cu_{50}Ti_{50-x}Ni_x$ glassy ribbons by the melt spinning method and investigated the effect of Ni on the glass-forming ability of the Cu-Ti-based alloys.

2 Experimental

The alloy ingots of nominal compositions $Cu_{50}Ti_{50-x}Ni_x$ were prepared by arc melting mixtures of Cu (99.9%), Ti (99.9%), Ni (99.9%) in a Ti-gettered argon high-purity atmosphere. The ribbons sample of approximately 40 μm in thickness and 2 mm in width were prepared by remelting the ingots in quartz tubes, and ejecting under pure argon through a nozzle onto a copper wheel rotating with a surface velocity of 44 m/s. The amorphous structure of the ribbons was confirmed by X-ray diffractometry(XRD, D/max-rB), using a monochromatic Cu K_α radiation of 10°−60° and by transmission electron microscopy(TEM, HITACHI-800). Thermal analysis of the ribbon samples was carried out to determine the glass transition temperature, T_g, the crystallization temperature, T_x, solidus temperature, T_m, and liquidus temperature, T_l , by differential scanning calorimetry (DSC, Netzsch404).

3 Results and discussion

Fig.1 shows the X-ray diffraction patterns of the melt-spun ribbons of the $Cu_{50}Ti_{50-x}Ni_x$ alloys. Each pattern shows a broad diffraction peak at the position of about 2θ=42° and no diffraction peaks from crystalline phases are detected. The $Cu_{50}Ti_{50}$ and $Cu_{50}Ti_{45}Ni_5$ alloys consist of a single glassy phase. But there are some nanocrystals in $Cu_{50}Ti_{40}Ni_{10}$ and $Cu_{50}Ti_{35}Ni_{15}$, which is reflected by the small peaks located at about 2θ=59° on the XRD patterns.

As show in Fig.2 the glassy structure of the melt-

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Corresponding author: BIAN Xiu-fang; Tel：+86-531-88395015; E-mail: xfbian@sdu.edu.cn

spun $Cu_{50}Ti_{50}$ ribbon was further confirmed by TEM analysis. The bright field TEM image shows no crystalline phase, and the selected area diffraction pattern (SADP) shows a diffuse halo ring, which is a characteristics of amorphous phase.

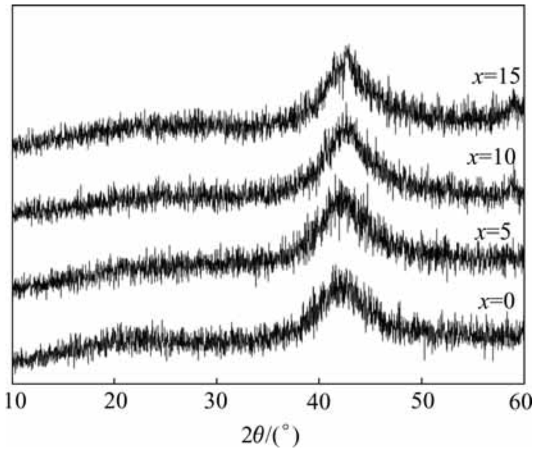

Fig.1 XRD patterns of melt-spun $Cu_{50}Ti_{50-x}Ni_x$ ribbons

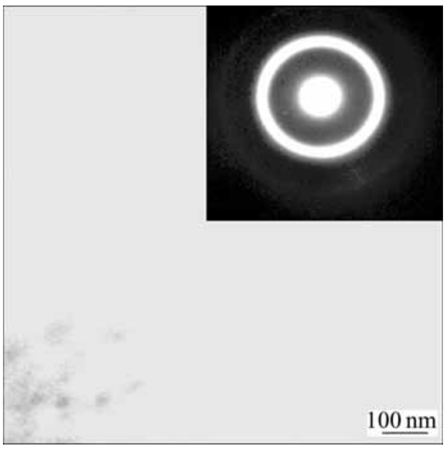

Fig.2 Bright field TEM image and selected area diffraction pattern of $Cu_{50}Ti_{50}$ ribbon

Fig.3 shows DSC traces obtained from melt-spun ribbons during continuous heating with a heating rate of 20 K/min. The amplified DSC trace of $Cu_{50}Ti_{45}Ni_5$ ribbon showing glass transition is also shown as an inset. With increasing x from 0 to 15, there is nearly no change in glass transition temperature, T_g. Crystallization temperature is assumed to be the onset temperature of the first exothermic peak. The crystallization temperature, T_x, increases from 409 ℃ to 445 ℃ with x value increasing from 0 to 10, and then decreases to 415 ℃ with x value further increasing to 15. Therefore the supercooled liquid region, $\Delta T_x = T_x - T_g$, exhibiting the same trend as T_x, increases from 24 ℃ to 61 ℃, and then decreases to 29 ℃.

In Fig.4 the DSC traces of melt-spun $Cu_{50}Ti_{50}$ and $Cu_{50}Ti_{45}Ni_5$ alloys are shown with a heating rate of 20 K/min from 700 to 1 100 ℃. The solidus temperature (T_m) and liquidus temperature(T_l) are marked with arrows. With increasing x from 0 to 5, T_m decreased from 898 to 896 ℃ and T_l decreased form 945 to 933 ℃. Both T_m and T_l increased with further increase of x.

Fig.5 shows the variations of T_g, T_x and T_m of the melt-spun $Cu_{50}Ti_{50-x}Ni_x$ (x=0, 5, 10, 15) alloys. It can be seen that the maximum value for ΔT_x is at x=10.

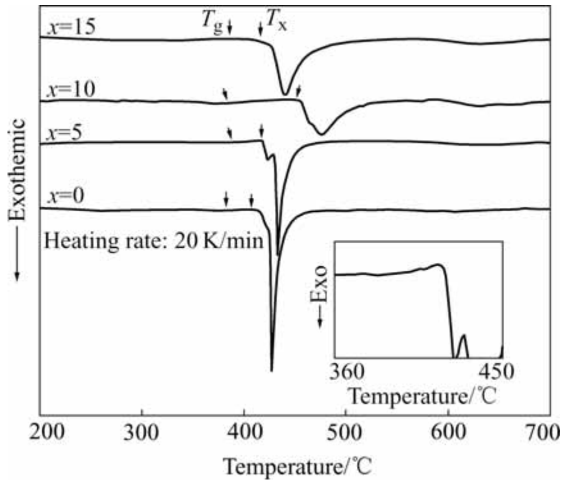

Fig.3 DSC traces of $Cu_{50}Ti_{50-x}Ni_x$ (x=0, 5, 10, 15) amorphous alloys and amplified DSC trace of $Cu_{50}Ti_{45}Ni_5$ ribbon (inset)

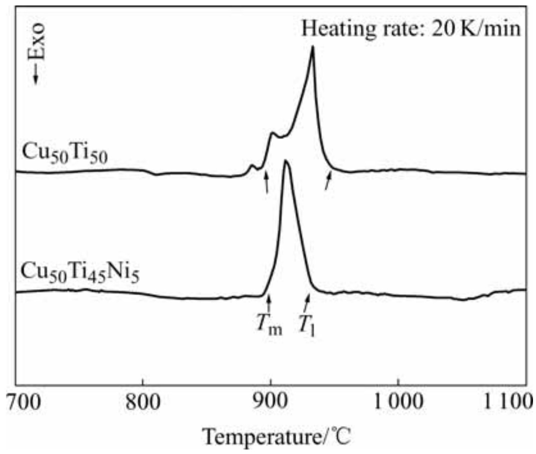

Fig.4 DSC traces of melt-spun $Cu_{50}Ti_{50}$ and $Cu_{50}Ti_{45}Ni_5$ amorphous alloys

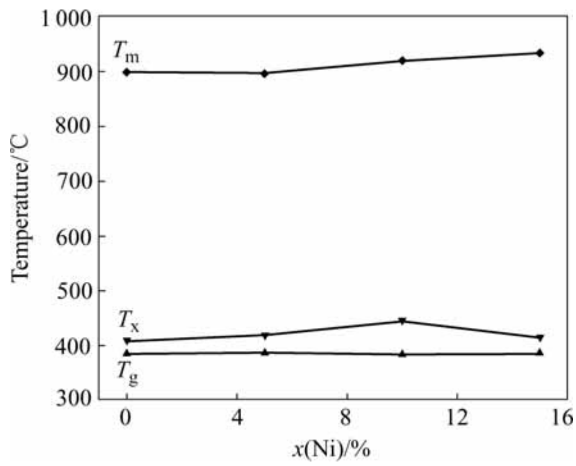

Fig.5 Thermal analysis of melt-spun $Cu_{50}Ti_{50-x}Ni_x$ (x=0, 5, 10,

15) alloys showing variations of T_g, T_x and T_m as function of x

Table 1 lists the supercooled liquid region and the reduced glass transition temperature of the four Cu-Ti-Ni melt-spun amorphous alloys. It can be seen that the reduced glass transition temperature, $T_{rg}=T_g/T_m$, changes a little and is not larger than 0.45 with increasing value x.

Table 1 Thermal parameter of $Cu_{50}Ti_{50-x}Ni_x$ (x=0, 5, 10, 15) amorphous alloys with heating rate of 20 K/min

x	ΔT_x/℃	T_{rg}
0	24	0.429
5	31	0.432
10	61	0.417
15	29	0.414

ΔT_x is supercooled liquid region and T_{rg} is reduced glass transition temperature.

Bulk glassy alloys may be obtained for the alloys with T_{rg} above 0.60 by copper mold casting method[12]. The addition of Ni to Cu-Ti alloy can not promote its glass forming ability essentially.

There are three empirical rules suggested to get a high glass-forming ability for metallic alloys[13] as follows. 1) Multicomponent systems with more than three components; 2) A significant difference in atomic size ratios above 12% among the three main constituent elements; 3) Large negative heats of mixing in the liquid. The atomic radius is 0.128 nm and 0.125 nm for Cu and Ni respectively, leading a difference of only 2.3% in atomic size ratio between Cu and Ni atoms. On the other hand, the enthalpy of mixing between Cu and Ni is 4 kJ/mol[14]. These two factors are not favourable to forming an amorphous structure in Cu-Ti-Ni alloys. In order to obtain a glass transition during solidification, the nucleation and growth of a crystalline phase should be prevented. If the crystal nucleus has a different composition from that of the undercooled liquid, the srystallization can occur only when the composition of a local liquid region and the size of a critical crystalline nucleus satisfy the composition requirements of the crystalline phase[2]. The small atomic size ratio of Cu and Ni determines that the addition of Ni to Cu-Ti alloy does not play an important role in preventing rearrangement of different species of atoms and nucleation.

A number of previous observations demonstrate that high GFA often occurs around deep eutectics. A deep eutectic means that the liquid state is energetically favored over ordered solid state in a large temperature range above the eutectic temperature. Compared with the case of noneutectic, the energy difference between these two states (i.e. the driving force for crystal nucleation and growth) is relatively small below the eutectic temperature. So it is easier to quench the liquid to an amorphous state before a detectable fraction of ordered crystals can be formed[15]. With x value increasing from 0 to 5, T_l is only lowered by 12 ℃, and the liquidus temperature of $Cu_{50}Ti_{40}Ni_{10}$ and $Cu_{50}Ti_{35}Ni_{15}$ is higher than that of $Cu_{50}Ti_{50}$. The deviation from deep eutectics leading by increasing of Ni content is another reason that results in the poor GFA of Cu-Ti-Ni alloys.

4 Conclusions

With increasing Ni content(x) from 0 to 15, the supercooled liquid region ΔT_x reaches the maximum value of 61 ℃ at x=10, and the reduce glass transition temperature, T_{rg} reaches the maximum value of 0.432 at x=5. The small value of T_{rg} determined that the GFA of Cu-Ti-Ni alloys was not effectively promoted by Ni addition.

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