

Preparation and thermal stability of metallic glasses $\text{Cu}_{83.3-x}\text{Ni}_x\text{P}_{16.7}$

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The effect of nickel concentration in rapidly quenched $\text{Cu}_{83.3-x}\text{Ni}_x\text{P}_{16.7}$ ternary alloys on glass formation and stability was investigated by x-ray diffraction and differential scanning calorimetry. In the present work, the glass-forming range was found to be $x = 10\text{--}16$ at. % Ni. Estimates of the Gibbs free energy and activation energy of the crystallization process indicate that the driving force decreases and the potential barrier of crystallization increases with increasing nickel content, thereby increasing the stability of the amorphous state. This may be attributed to the formation of stronger Ni—P bonds and partial bonds formed by overlapping *s-p* hybrid orbitals and to the strengthening of the *s-p-d* orbitals of Cu and Ni with decreasing *d*-electron concentration.

I. INTRODUCTION

Glass-forming ability (GFA) and thermal stability, which are the most important characteristics of every metallic glass system, depend strongly on the composition.^{1–5} On the basis of the formation criterion of amorphous alloys proposed by one of the authors,^{6,7} Cu-P alloys are in the glass-forming region of amorphous alloys and are expected to form amorphous alloy. By adding another constituent to the alloy, the interaction between dissimilar atoms will be strengthened; it is therefore expected that the GFA of such alloys will increase. We have investigated the effect of the metalloid element phosphorus on the formation and stability of amorphous Cu-Ni-P alloys which are sometimes considered a brazing filler metal with Ni content of 10 at. %.⁸ But in this case, the stability of the alloy is not very satisfactory. It was reported that addition of refractory metals frequently increases the stability of amorphous alloys,^{9,10} and Donald and Davies¹ suggested that the glass transition temperature, T_g , of a metallic glass is related to the cohesive energy of the alloy. There is a substantial body of empirical evidence which illustrates a gradual trend of an increase in T_g (or T_c) with increasing heat of sublimation (as an estimate of cohesive energy for metallic glasses). Accordingly, addition of elements of higher sublimation heat to the base metal would be expected to increase the T_g , and hence the T_c , of the alloy.¹¹ The sublimation enthalpies ΔH_s for Cu and Ni are 342.5 and 430.4 kJ/mol, respectively.¹² Therefore, addition and the amount of nickel in Cu-P-based alloys may influence the characteristics of the GFA and the stability of these alloys. In the present work, we investigated, by varying the nickel concentration, the effect on the formation and stability of Cu-Ni-P ternary glassy alloys prepared by melt spinning.

II. EXPERIMENT

$\text{Cu}_{83.3-x}\text{Ni}_x\text{P}_{16.7}$ ($x=9.0, 10.0, 12.0, 14.7, 16.0,$ and 17.0 at. %) alloys were prepared by melting the appropriate starting elements in an induction furnace. Subsequently, the ingots were remelted twice in a quartz furnace to ensure homogeneity. Rapidly quenched ribbons were obtained by ejecting melts under argon pressure onto a single copper roller rotating with a surface velocity of about 20 m sec^{-1} . The ribbons obtained were about 8–10 mm wide, and 30–40 μm thick.

The structure of the as-received ribbons were examined in a Siemens D-500 diffractometer with Cu $K\alpha$ radiation. Thermal stability was studied using a Dupont 1090 differential scanning calorimeter (DSC) at heating rates of 5, 10, and 20 K min^{-1} in flowing argon. Estimates of the temperature of the liquid were obtained by differential thermal analysis (DTA) at a heating rate of 20 K min^{-1} on the same Dupont 1090 instrument.

III. RESULTS AND DISCUSSION

A. The glass-forming range and glass-forming ability of the alloys

Figure 1 shows the x-ray diffraction patterns of the as-received alloys. Only diffuse intensity maxima characteristics for amorphous alloys are observed for ribbons with 10–16 at. % nickel. But weak diffraction peaks corresponding to a crystalline phase were observed superimposed on the diffuse background of the amorphous phase for ribbons of 9 and 17 at. % Ni. Therefore, the Ni-content range of glass formation for the $\text{Cu}_{83.3-x}\text{Ni}_x\text{P}_{16.7}$ alloys is about 10–16 at. % in the present rapidly quenched experiment.

Typical DSC curves for the $\text{Cu}_{83.3-x}\text{Ni}_x\text{P}_{16.7}$ glasses at

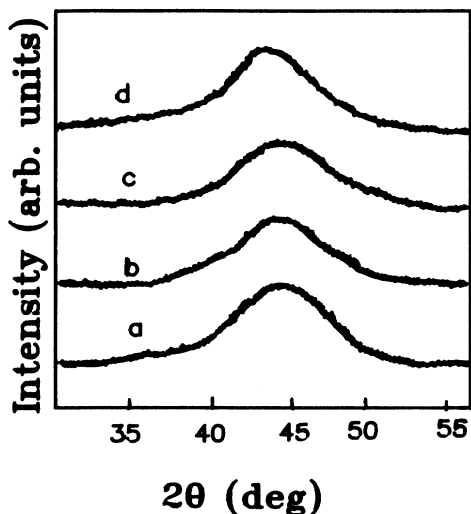


FIG. 1. X-ray diffraction patterns of rapidly quenched $\text{Cu}_{83.3-x}\text{Ni}_x\text{P}_{16.7}$ alloys (a) $x=10.0$, (b) $x=12.0$, (c) $x=14.7$, and (d) $x=16.0$.

a heating rate of 20 K min^{-1} are presented in Fig. 2. The DSC traces show that four exotherms are present for the glass with 10 at. % Ni (the first and the second peaks are overlapping partly), but only three exotherms appear for the glasses containing 12–16 at. % Ni. For the higher-nickel-content alloys, the first peak shifts to higher temperatures with increasing nickel concentration. It shows that the Ni component has influenced the crystallization process. Thus, the GFA and stability are improved.

The onset-crystallization temperature T_{cr} was taken as the temperature for which the extrapolation of the first exothermic peak reached the base line. The liquid temperature was determined based on the endothermic peak of the DTA traces. The reduced glass temperature T_g/T_m is an important parameter which influences the critical cooling rate for vitrification. The higher this ratio, the higher is the GFA.^{11,13} In our work a glass transition was not apparent in the DSC curves, and so T_{cr} was taken as an estimate of T_g and the reduced crystallization temperature, T_{cr}/T_l (where T_l is the liquid temperature of the alloys), served as an estimate of the GFA.¹⁴ The value of T_{cr}/T_l rises from 0.52 to 0.55 with increasing Ni content in the range of 10–15 at. %, and shows hardly any change afterwards. The improvement in the GFA may be attributed to the formation of a number of Ni—P bonds in the short-range order of the liquid alloy besides Cu—P bonds. Dissimilar atoms in the liquid are combined more tightly with the addition of Ni; thus the higher the nickel content, the greater the effect. It reduces the velocity of motion for the atomic group, and therefore reduces the nucleation rate and suppresses the crystallization under melt-spinning conditions.

B. The thermal stability of the alloys

The onset-crystallization temperature T_{cr} can serve as an important factor estimating the stability of amorphous

alloys. From our experiment, it can be seen that T_{cr} increases with increasing nickel content. The average increase in T_{cr} is about 5 K per at. % Ni in the 10–15-at. % Ni range (see Fig. 3). This experimental result shows that the stability of this metallic glass increases with increasing Ni content.

Glass is in a thermodynamically unstable state, and therefore its kinetic stability is a result of the complexity in the structure which creates a potential barrier against crystallization. To evaluate the stability of a glass, it is necessary to estimate the difference between the Gibbs free energy of the glass and that of the crystalline state, as well as this potential barrier against crystallization.

Since many amorphous alloys transform to undercooled liquids before crystallization, under the assumption of a constant difference of specific heat between the

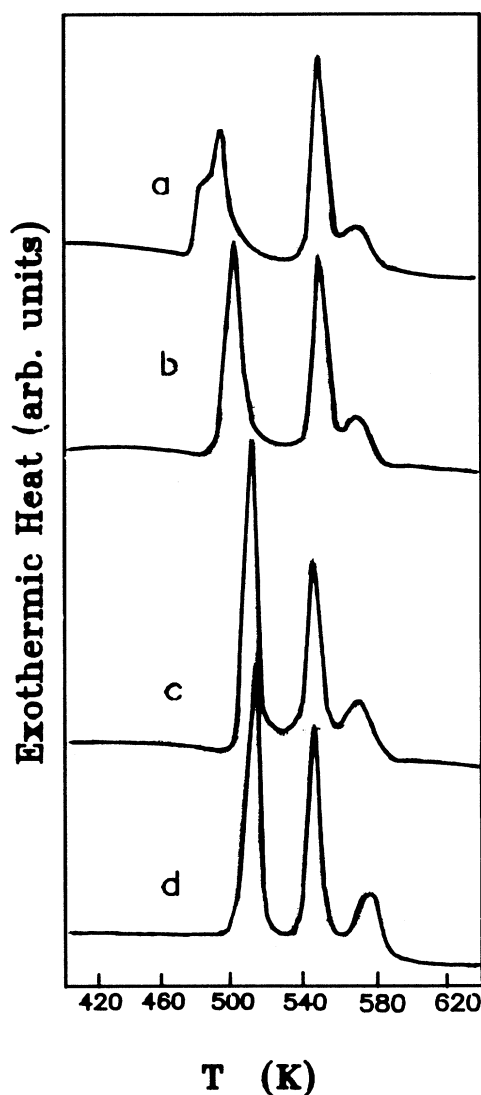


FIG. 2. DSC traces of the amorphous $\text{Cu}_{83.3-x}\text{Ni}_x\text{P}_{16.7}$ alloys (a) $x=10.0$, (b) $x=12.0$, (c) $x=14.7$, and (d) $x=16.0$ obtained at a scanning rate of 20 K min^{-1} .

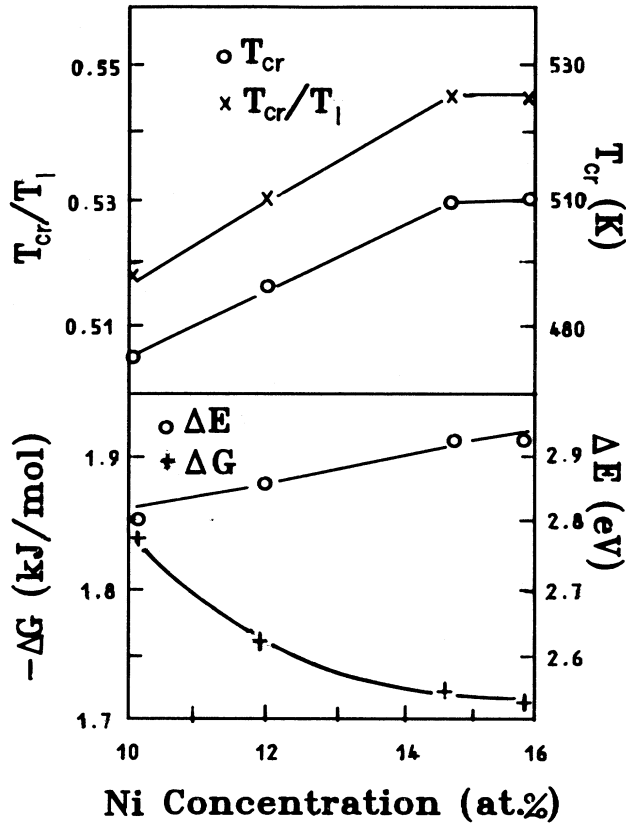


FIG. 3. The onset temperature T_{cr} for crystallization, reduced crystallization temperature T_{cr}/T_l , Gibbs free energy ΔG , and activation energy ΔE of crystallization vs nickel atomic percentage for amorphous $\text{Cu}_{83.3-x}\text{Ni}_x\text{P}_{16.7}$ alloys.

undercooled liquid and equilibrium crystalline phase, the formula for calculating the Gibbs-free-energy difference between the undercooled liquid and the equilibrium crystalline phase is¹⁵

$$\Delta G = \Delta H_m / T_m \{ (T_m - T) - [(1 - \Delta H_{exo} / \Delta H_m)(1 - T_c / T_m)] \times [(T_m - T) - T \ln(T_m / T)] \}, \quad (1)$$

where T_m , T_c , and ΔH_{exo} are the melting point, crystallization temperature, and crystallization enthalpy, respectively. They can be obtained by DSC and DTA measurements. The solidification enthalpy ΔH_m can be calculated from the formula¹⁶

$$\Delta H_m = T_m \Delta S_m = T_m \sum_i X_i \Delta S_{mi}, \quad (2)$$

where ΔS_m , ΔS_{mi} , and X_i are, respectively, the alloy-system melting entropy, component melting entropy, and component atom fraction.

By introducing T_m , ΔH_m , ΔH_{exo} , T_c , and X_i of the $\text{Cu}_{83.3-x}\text{Ni}_x\text{P}_{16.7}$ alloys into Eq. (1), a relationship between $\Delta G(T)$ and the nickel concentration can be given (Fig. 3): $\Delta G(T)$ decreases with increasing Ni-atom fraction; this means that the crystallization for the alloys will be more difficult with increasing Ni content because $\Delta G(T)$ is a measure of the driving force for crystallization. On the other hand, the activation energy for crystallization ΔE for the first exothermic peak, which was determined by Kissinger's method,¹⁷ shown also in Fig. 3, is proportional to the Ni content. ΔE is a measure of the potential-energy barrier against crystallization; and the higher the potential-energy barrier, the more difficult the cooperative atomic transitions will be. According to available information on the variation of both the Gibbs free energy and activation energy for crystallization with Ni concentration, it is clear that ΔG decreases, while ΔE increases, with increasing Ni-atom fraction. This will make crystallization more difficult; the amorphous state is thus more stable.

It is well known that one of the primary factors determining the properties of metals is the relative valence of the alloy elements. Chen¹⁸ suggested that chemical bonding plays a major role in determining certain properties of amorphous alloys. The measured values of the crystallization temperature are plotted against the average outer-electron concentration of the metallic atoms in the amorphous $\text{Cu}_{83.3-x}\text{Ni}_x\text{P}_{16.7}$ alloys (see Fig. 4), it is customary to take as a measure of the valence of the transition elements in the alloys the numbers of outer electrons, which are 10 and 11 for Cu and Ni, respectively. The average concentrations are given by the weighted means according to the atomic percentage of the transition-metal elements. It can be seen that the average valence of the outer electrons has a significant effect on the T_{cr} . The lower the outer-electron concentration, the higher is the crystallization temperature. This observation may result

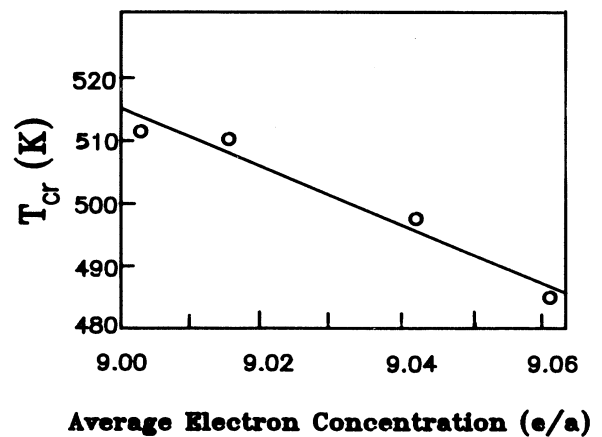


FIG. 4. The onset temperature T_{cr} for crystallization plotted against the average outer-electron concentration of the metallic atoms (e/a) for amorphous $\text{Cu}_{83.3-x}\text{Ni}_x\text{P}_{16.7}$ alloys.

from the strengthening of partial bonds by overlapping *s-p* hybrid orbitals of phosphorus atoms with the *s-p-d* orbitals of the transition elements, when the *d*-electron concentration decreases with increasing Ni content. This strengthening leads a more stable structure with increasing T_{cr} .¹⁹ On the other hand, as suggested by Chen,¹⁸ an indication of the strength of bonding between the transition elements and phosphorus can be obtained from the eutectic temperature of *M-P* binary alloys in the metal-rich region. The eutectic temperatures of Cu—P and Ni—P are 714 °C and 880 °C, respectively. This suggested that the interaction of P with Ni is larger than that of P with Cu. With the increase of Ni in Cu-Ni-P alloys, the fraction of Ni—P bonds should increase, leading to an improvement in both the glass-forming ability and the stability of the metallic glasses.

IV. CONCLUSIONS

According to the above analyses, we have the following.

(1) In the present work, the glass-forming range for liquid-quenched $\text{Cu}_{83.3-x}\text{Ni}_x\text{P}_{16.7}$ alloys is about 10.0–16.0 at. % nickel.

(2) The addition of nickel to Cu-Ni-P alloys can improve both the glass-forming ability and the thermal stability of the alloy. This improvement is enhanced with increasing nickel concentration.

(3) The effect of Ni on both the GFA and stability of Cu-Ni-P alloys may be attributed to the formation of strong Ni—P bonds and partial bonds by overlapping *s-p* hybrid orbitals of phosphorus atoms and *s-p-d* orbitals of the Cu and Ni atoms. This kind of bond is strengthened as the *d*-electron concentration decreases.

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