Crystallization of the metallic glass $Cu_{73.9}Ni_{9.2}Sn_{3.5}P_{13.4}$

LETTER TO THE EDITOR

Crystallization of the metallic glass $Cu_{73.9}Ni_{9.2}Sn_{3.5}P_{13.4}$

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Abstract. The crystallization behaviour of the metallic glass $Cu_{73.9}Ni_{9.2}Sn_{3.5}P_{13.4}$ has been investigated by differential scanning calorimetry (DSC) and x-ray diffraction (XRD). Three exothermic peaks occur at 216, 295 and 365 °C. Based on the exothermic peaks and observations from XRD at various stages of crystallization, the crystallization sequence and the structure of the crystallization phase of the glass can be described as follows:

amorphous → Cu_3P (hexagonal) + α–Cu (FCC)
amorphous → Ni_2P (hexagonal) + NiSn (or orthorhombic) + Cu_xSn_y
amorphous + NiSn + Cu_xSn_y → $(Cu_xNi_{1-x})_3Sn$ (tetragonal) + $Ni_{2.55}P$ (hexagonal) + SnP(cubic)
amorphous + Ni_2P + $Ni_{2.55}P$ → Ni_3P (hexagonal).

Only a typical Cu–Cu_3P microcrystalline structure can be obtained when rapid solidification is used with a Cu–P binary alloy [1]. Our recent work indicates that the transition element nickel can improve the glass-forming ability in the system [2–3]. Furthermore, the glass-forming ability can be enhanced further when the element tin is added [4]. This also influences the stability and properties of the alloy [5].

It is known that the thermal stability of an amorphous alloy depends not only on its thermodynamic behaviour but also on the crystallization sequence and characteristics of the crystallization phases [6]. The main crystallization products for Cu–Ni–P ternary metallic glass consist of a–Cu, Cu_3P and Ni_xP_y [7–9]. However, the crystallization process and products for Cu–Ni–Sn–P quaternary glass will be more complicated because of the addition of tin. Little work on this quaternary has been published until recently [10, 11]. In this letter, we report the crystallization behaviour of the metallic glass $Cu_{73.9}Ni_{9.2}Sn_{3.5}P_{13.4}$ during heating.

Amorphous $Cu_{73.9}Ni_{9.2}Sn_{3.5}P_{13.4}$ (at.%) alloy was prepared by melt-spinning using a copper wheel rotating at a surface speed of about 20 m s⁻¹. The ribbons are about 8–10 mm wide and 30–40 μm thick. The thermal stability of the glass was measured by means of a differential scanning calorimeter (DSC) (Dupont 1990) at a scanning rate of 10 K min⁻¹ in flowing argon. According to the DSC trace, several distinct temperatures corresponding to the exothermic peaks were selected as the annealing temperatures. The specimens for XRD analysis were heated to selected temperatures at a heating rate of 10 K min⁻¹ and isothermally annealed for 0.5 hours under a vacuum of 5×10^{-4} Torr. In order to identify the final stable phase, a specimen was annealed at 480 °C for 4 hours and at 510 °C for 15 hours. The structures of the crystallization phase were determined
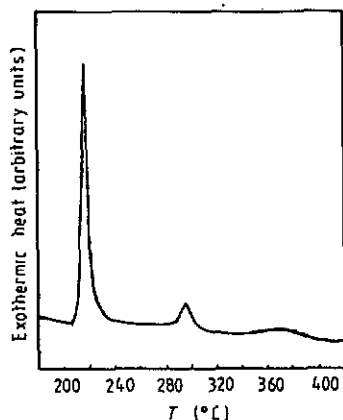
Figure 1. DSC trace of the amorphous $Cu_{73.9}Ni_{9.2}Sn_{3.5}P_{13.4}$.

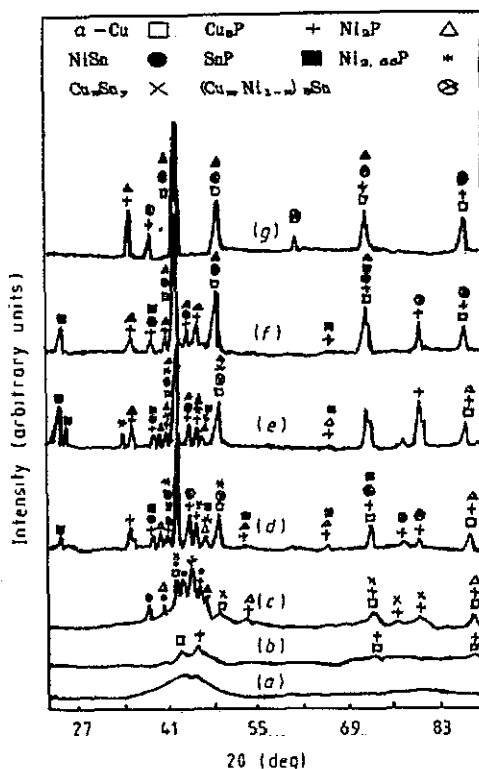**Figure 2.** XRD patterns of the amorphous $Cu_{73.9}Ni_{9.2}Sn_{3.5}P_{13.4}$ alloy (*a*) as-quenched, and after annealing at: (*b*) 220 °C, (*c*) 260 °C, (*d*) 305 °C, (*e*) 400 °C for 0.5 hours, (*f*) 480 °C for 4 hours, and (*g*) 510 °C for 15 hours.

by x-ray diffraction (XRD) measurements in a Siemens D-500 diffractometer with Cu Kα radiation.

The DSC result for the as-quenched alloy is shown in figure 1. Three exothermic peaks were observed at 216, 295 and 365 °C, with no evidence of a glass transition. The XRD patterns for the as-quenched and annealed specimens are shown in figure 2. The transformations corresponding to the three exothermic peaks can be identified by observing the XRD patterns at different stages of annealing. According to figure 2, the quenched alloy has a typical amorphous structure. When heated to the first exothermic peak, several very weak crystalline peaks occurred on the amorphous diffuse peak. As the temperature rose to 260 °C, sharp crystalline peaks on the more diffuse background were observed. At an annealing temperature above the second exothermic peak, the XRD patterns were almost totally crystalline.

From the XRD patterns and ASTM data, several types of crystallization phases can be identified as follows: α–Cu (FCC, $a = 0.3615$ nm), Cu_3P (hexagonal, $a = 0.6959$ nm, $c = 0.7143$ nm), Ni_2P (hexagonal, $a = 0.5846$ nm, $c = 0.3372$ nm), NiSn (orthorhombic, $a = b = 0.146$ nm, $c = 0.148$ nm), $Ni_{2.55}P$ (hexagonal, $a = 0.6608$ nm, $c = 2.4634$ nm), SnP (cubic, $a = 0.180$ nm), Ni_3Sn (tetragonal, $a = 0.5110$ nm, $c = 0.4881$ nm), Ni_3P (tetragonal, $a = 0.8934$ nm. $c = 0.4398$ nm) and copper-rich copper–tin Cu_xSn_y.

Based on the three exothermic peaks of the DSC curve, it may be inferred that the crystallization of the glass can be divided into three stages. When the glass was heated to 220 °C, two very weak crystalline peaks appeared corresponding to α–Cu and Cu_3P overlapping the amorphous diffuse peak, which is similar to $Cu_{64}Ni_{18}P_{18}$ glass [8]. As the annealing temperature increased to 260 °C (at which the first exotherm ended), Ni_2P, NiSn and a Cu-rich copper–tin phase Cu_xSn_y were also detected (the overlapping of several of the strongest lines for a number of copper–tin intermetallic phases makes it difficult to identify them by the XRD analysis above, so that we use x and y to represent the atomic ratios of Cu and Sn at this stage). Obviously, over the temperature range of the first exotherm, initially Cu_3P and α–Cu precipitated from the glass matrix and then, soon afterwards, NiSn, Ni_2P and Cu_xSn_y generally formed. The appearance of such a large number of crystalline phases led to the evolution of a large amount of crystallization enthalpy which corresponds to the most exothermic peak.

When the temperature rose to 305 °C, the diffuse background of glass phase nearly disappeared, and the crystalline diffraction peaks became sharper in intensity and greater in number. Contrast this pattern (d) with pattern (c) (figure 2)—several diffraction lines relating to SnP, Ni_3Sn and $Ni_{2.55}P$ appeared, but those of NiSn disappeared. From this, we are certain that NiSn is an intermediate metastable phase, and may be displaced by the more stable Ni_3Sn phase with increasing temperature. Considering the greater micro-segregation of tin for the Cu–Ni–Sn system, even in the case of melt-spinning and such precipitates as the γ phase $(Cu_xNi_{1-x})_3Sn$ [12–14], we can infer that a metallic glass containing the elements Cu, Ni and Sn will have a greater tendency to form in the γ phase directly during crystallization. Connecting the diffraction peaks of both the Cu_xSn_y phase formed during the first exothermic peak and the Ni_3Sn phase which appeared during the second exothermic reaction, it is reasonable for us to attribute them to the $(Cu_xNi_{1-x})_3Sn$ phase. In fact, $(Cu_xNi_{1-x})_3Sn$ can also be seen as a partial replacement of Ni by Cu atoms for the Ni_3Sn phase. Hence the second exothermic reaction consists of the formation of SnP, $Ni_{2.55}P$ and $(Cu_xNi_{1-x})_3Sn$ and the disappearance of NiSn. Because the amount in the crystallization phase is limited at this stage, the change in free energy of the system is not as large as for the first exothermic reaction, and the crystallization enthalpy is much less.
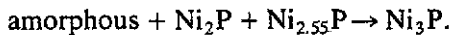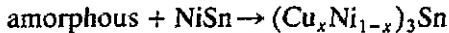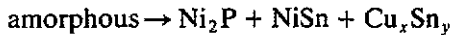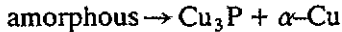
The XRD pattern for the sample annealed at 400 °C shows that the intensity and number of diffraction peaks related to SnP increased but those related to Ni_2P decreased. On the other hand, Ni_3P occurred in this temperature range, and its formation may be attributed to the transformation of phosphorus-rich, metastable phosphorus–nickel [7, 8]. Since the main crystallization reaction was nearly completed before the third exothermic reaction, the size of the exotherm for the latter is small.

After annealing at 480 °C for 4 hours, Ni_2P and $Ni_{2.55}P$ totally disappeared—it is apparent that they were all intermediate metastable phases and were replaced by Ni_3P. In addition, some diffraction lines related to SnP disappeared, and the others decreased in intensity. After further annealing at 510 °C for 15 hours, the characteristic diffraction peak ($d = 0.3570$ nm, corresponding to the SnP phase) wholly vanished. It means that SnP is also a metastable phase. In addition, from the XRD pattern (figure 2(a)) we can find that the relative diffraction intensities of $(Cu_xNi_{1-x})_3Sn$ and some special peaks corresponding to Cu_3P and Ni_3P evidently increase. This shows that the amounts of intermetallic compounds Cu_3P, Ni_3P and intermetallic phase $(Cu_xNi_{1-x})_3Sn$ increase due to the system tending to approach the equilibrium state after annealing for a long time.

A distinct phenomenon in XRD patterns is noticeable: several main diffraction peaks overlap and shift to lower angles with the increase in temperature, especially for α–Cu.

It is known that α–Cu can contain nickel and phosphorus atoms and exist in the form of α–Cu(Ni, P) [7, 8] in the Cu–Ni–P system. In fact, tin is also a solid-solution element in the copper matrix [15]. Furthermore, the atomic radius of tin, 0.1405 nm, is much larger than that for Cu. The solid solution of Sn in Cu thus results in an expansion of the crystal lattice constant so that the diffraction peaks shift to lower angles and some of them also overlap with those of $(Cu_xNi_{1-x})_3Sn$. This typical solid solution can also exist in other phases. Increasing the temperature can enhance the solubility of other elements and leads to greater distortion of the crystal lattice. Hence, several main crystalline lines shift to lower angles. Based on the above analysis, after annealing for a long time, α–Cu will be replaced by either α–Cu (Ni, P) [7, 8] or α–Cu (Ni, Sn, P, Ni) and Cu_3P will be replaced by $(Ni, Cu)_3P$ [8]. Some of these suggestions have already been proven for the Cu–Ni–P system, but need further research in the Cu–Ni–Sn–P system.

Synthesizing the DSC and XRD experimental results and above analyses, the crystallization sequence of the amorphous $Cu_{73.9}Ni_{9.2}Sn_{3.5}P_{13.4}$ alloy is described by the following sequence:

$$\text{amorphous} \rightarrow Cu_3P + \alpha\text{–Cu}$$

$$\text{amorphous} \rightarrow Ni_2P + NiSn + Cu_xSn_y$$

$$\text{amorphous} + NiSn \rightarrow (Cu_xNi_{1-x})_3Sn$$

$$\text{amorphous} + Ni_2P + Ni_{2.55}P \rightarrow Ni_3P.$$

The final stable phases present in the alloy are α–Cu, Cu_3P and Ni_3P. In addition, Ni_2P, $Ni_{2.55}P$ and NiSn are observed as intermediate phases and SnP is also a metastable phase. Evidently, the crystallization process and products for the Cu–Ni–Sn–P metallic glass are very complicated. It is necessary to combine DSC and XRD with TEM, EDAX and other methods in order to obtain more details related to the structure of the crystallization phase. This work is currently under way.

References

[1] Selke H and Ryder P L 1988 *Acta Metall.* **36** 2387
[2] Zhang H, Tan Z, Zhang B *et al* 1990 *J. Mater. Sci. Lett.* **9** 45
[3] Zhang H, Zhang B, Tan Z *et al* 1991 *Phys. Rev.* B **43** 6430
[4] Shu X, Tan Z, Zhang H, Zhang B *et al* 1991 unpublished
[5] Data A, Rabinkin A and Bose D 1984 *Weld. J.* **10** 14
[6] Jiu J and Zumio S 1987 *J. Non-Cryst. Solids* **88** 493
[7] Kovenriatii Y K, Musin V K, Kebrikova L K and Vovilova V V 1989 *Izv. Akad. Nauk* **25** 1067
[8] Adlwarth R, Selke H and Kyeler P L 1988 *Mater. Sci. Eng.* **97** 351
[9] Zhang H, Zhang B and Tan Z 1991 *J. Non-Cryst. Solids* at press
[10] Liu W, Li S *et al* 1990 *J. Mater. Sci. Lett.* **9** 904
[11] Dejong L, Tremblay R and Angers R 1990 *Mater. Sci. Eng.* A **124** 223
[12] Miki M and Ogino 1984 *Japan. Inst. Met.* **25** 593
[13] Lefevre B G, D'Annessa A T and Kalish D 1978 *Metall. Trans.* A **9** 557
[14] Plewes J T 1975 *Metall. Trans.* A **6** 537
[15] Smithells C J (ed) 1976 *Metals Reference Book* (London: Butterworth) p 593