CRYSTALLIZATION PROCESS AND THERMAL STABILITIES OF THE MELT-SPUN AMORPHOUS Ni\(_{100-x}P_x\) (\(x=16.0-20.0\) at\%) ALLOYS

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(Received December 7, 1993)
(Revised March 15, 1994)

Introduction

Crystallization of amorphous transition metal-metalloid (TM-M) alloys has been intensively investigated not only because of its technical significance in estimating the thermal stability and service lifetime of amorphous materials, but also because it is of interest in studying the nucleation and growth process in the high undercooling liquids. Recently, the significance in studying crystallization of amorphous alloys has become multiplied because nanocrystalline materials with excellent properties can be formed by the appropriate crystallization [1-3].

As some of the earliest amorphous alloys formed by melt-spinning, the Ni-P alloys, especially those with eutectic composition, have been intensively investigated for reasons involving its preparation, structure, properties and crystallization process [4-6]. Thermal stability and crystallization processes of the electro-deposited Ni-P glasses with different compositions have been investigated previously by Bakonyi et al. [7]. In this work, we carry out an investigation on the crystallization processes of melt-spun Ni-P glasses. The influence of P content on the crystallization process and thermal stabilities will also be studied.

Experiments

The Ni-P alloys with hypoeutectic composition used in this work were made from a mixture of pure nickel blocks (99.99%) and Ni-P foundry alloy (with hypereutectic composition: P=31.2 at%). Ni\(_{100-x}P_x\) alloys with four kinds of compositions (\(x=16.0, 17.7, 18.2, 20.0\) at\%) were synthesized by multiple (repeated) melting of the mixture in a non-consumable electric-arc furnace. The samples about 2.2mm wide and 0.02mm thick with various compositions were prepared by the melt-spinning technique using single roller equipment. The amorphous state was examined by both X-ray diffraction (XRD) and transmission electron microscopy (TEM). A differential scanning calorimeter (DSC-II, Perkin-Elmer) was used to measure the crystallization kinetics of the alloys. The temperature and energy of the DSC were calibrated using standard In and Zn samples. The TEM used in this work is an EM420 transmission electron microscope with an accelerating voltage of 100kV. Thin foils used for TEM observation were prepared by the ion-thinning method. X-ray diffraction experiments were performed on a Rigaku X-ray diffractometer (D/max-RA, 12kw) using Cu K\(_{\alpha}\) radiation.

Experimental Results and Discussion

1. Crystallization processes

Figure 1 shows the DSC traces for as-quenched Ni\(_{100-x}P_x\) ribbons with four different P compositions at a heating rate of 20K/min. It can be seen that different crystallization types take place as the P content changes. In DSC curves of Ni-P
Fig. 1. The dynamic DSC traces for amorphous Ni$_{100-x}$P$_x$ with a heating rate of 20K/min
(a)x=16.0%, (b)x=17.7%, (c)x=18.2%, (d)x=20.0%

Fig. 2 The X-ray diffraction results of a Ni$_{82.3}$P$_{17.7}$ alloy (a) as-quenched (b) heated to $T_{p1}$ (c) heated to $T_{p2}$
alloys with x=16.0% and x=17.7%, two exothermal peaks were observed, which can be thought of as a primary crystallization taking place.

The crystallization products at various stages during crystallization of the samples were examined by use of X-ray diffraction and TEM observation. Figure 2 shows the XRD results of the Ni82.3P17.7 alloy. It illustrates the XRD results of (a) the as-quenched sample, (b) the product corresponding to peak 1 (refer to fig. 1b), and (c) the products corresponding to peak 2 (refer to fig. 1b). It can be easily found that the first exothermal DSC peak corresponds to the formation of a Ni solid solution with a fcc structure, and the second one is due to crystallization of two phases, Ni solution and Ni3P compound (bct structure), simultaneously. Figure 3 shows the TEM results for the same sample used for the XRD experiment. We can see that during the first stage of crystallization-peak 1-very small Ni fcc crystallites (about 20 nm) with random orientations were randomly formed in the amorphous matrix. The shape of this primary phase is irregular. During the second stage, peak 2, Ni and Ni3P phases were formed in the residual amorphous phase, forming large crystalline regions (see Fig. 3b), and it seems that there is a certain orientation relationship between the two phases. This crystallization process may be described as follows:

\[
\text{am- Ni-P --- cryst. - Ni + am- Ni-P (P-rich)} \quad (1) \\
\text{am- Ni-P (P-rich) --- cryst. - Ni + Ni3P} \quad (1')
\]

For the amorphous Ni-P samples with x=18.2% and x=20.0%, however, the DSC traces show only one exothermal peak, as in figure 1. Structural examination revealed that this exothermal peak corresponds to the formation of two crystalline phases, Ni solution and Ni3P compound, simultaneously, where eutectic crystallization occurs, but the crystallization temperatures for the two alloys are different. This crystallization may be presented as:

\[
\text{am- Ni-P --- cryst. - Ni + cryst. - Ni3P} \quad (2)
\]
The equilibrium phase diagram of the binary Ni-P system shows that the eutectic composition of Ni and Ni₃P is 19.0%. This means any compositional deviation of a melt from this specific composition will lead to a two-step crystallization during crystallization process. However, in the present case, the amorphous Ni-P alloys with P contents of 18.2% and 20.0% are crystallized in an eutectic manner. This result implies that there might be a composition range (not a point) for the eutectic crystallization of the amorphous Ni-P alloys.

For the electro-deposited Ni-P glasses, the eutectic crystallization takes place at a composition of about 20.0%, but not a composition range [7].

2. Thermal stabilities

It can be seen from figure 1 that not only the crystallization type but also the crystallization temperature changes with the composition. The peak temperature of the first exothermal peak (TP₁) and the second one (TP₂) is listed in table 1. The first peak corresponds to primary crystallization of α-Ni phase and the second one to eutectic crystallization of the amorphous phase. For the DSC curves (c and d), there is only an eutectic exothermal peak. It is obvious in table 1 that, at the same heating rate, the peak temperatures are different for different P contents. Figure 4 shows the variation of the peak temperature changes with P content: both TP₁ and TP₂ increase with the increase of P content and TP₂ has the

<table>
<thead>
<tr>
<th>P content (at%)</th>
<th>16.0</th>
<th>17.7</th>
<th>18.2</th>
<th>20.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tp₁ (K)</td>
<td>585.1</td>
<td>609.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tp₂ (K)</td>
<td>612.8</td>
<td>626.7</td>
<td>636.1</td>
<td>634.4</td>
</tr>
</tbody>
</table>
maximum value (636.1 K at a heating rate of 20 K/min) when P content reaches 18.2%. With reference to a previous work on melt-quenched amorphous Ni-P alloys [8], maximum value of crystallization temperature (about 650 K) was obtained near P = 19%, the eutectic point in the equilibrium phase diagram of Ni-P system alloys. After the maximum value, the crystallization temperature (T_p2) decreases with an increment of P content.

Activation energy for crystallization is one of the significant parameters characterizing the thermal stability of amorphous alloys. By using the results of crystallization temperatures heated at different heating rates, one can evaluate the crystallization activation energy by using the Kissinger equation [9]:

$$\ln(\Phi/T^2) = -E_c/RT + \text{const.}$$  \hspace{1cm} (3)

where $R$ is the universal gas constant, $\Phi$ the heating rate, $T$ the peak temperature, and $E_c$ the activation energy. The crystallization activation energies corresponding to both of the two exothermic peaks for different alloys are listed in Table 2, and the data obtained were also marked in figure 4.

It can be found that the activation energy calculated from the Kissinger plot for the eutectic crystallization also changes due to different P compositions. The value of $E_c$ increases with the P content increasing below the eutectic composition. At the eutectic P composition, $E_c$ reaches a maximum value. Further addition of P leads to a reduction of the activation energy of the eutectic crystallization. Both variation tendencies of crystallization temperature and crystallization activation energy are evidence that the thermal stability of the amorphous Ni-P alloys is strongly dependent on the P content. A maximum thermal stability exists at the eutectic composition with which the amorphous alloy has the highest crystallization temperature and crystallization activation energy among the samples used.

It should be noted that the tendency of the variation of crystallization temperature with P-content in the present study is close to that found for the electro-deposited amorphous Ni-P alloys [7], in which no data on variation of the crystallization activation energy was presented.

The crystallization process and the thermal stability of the amorphous Ni-P alloys might be better understood according to the microstructures of the amorphous states. It has been verified that there are quantities of ordered clusters existing in alloy melts [10, 11], and these clusters will be preserved in an amorphous matrix when melts are quenched rapidly; the size and distribution strongly depend on the quenching rate and chemical composition [12]. Two kinds of clusters of Ni-Ni type and Ni-P type would exist in an amorphous Ni-P phase, which would form the basic units of the Ni solid solution and Ni$_3$P compound, respectively [13]. Based on the crystallization micromechanism for amorphous alloys developed recently by Lu et al. [14], the present results may be understood according to the quantity and distribution of the ordered clusters [15].

Conclusions:

(1) The crystallization types of the melt-spun Ni$_{100-x}$P$_x$ are strongly dependent on the P content: for the composition with $x < 18.2\%$, a primary phase of Ni is first formed, followed by eutectic crystallization of two phases of Ni and Ni$_3$P; for the composition with $x = 18.2$-20.0\%, only eutectic crystallization occurs.

(2) The crystallization temperature and the activation energy for the overall crystallization, or the thermal stability of the amorphous Ni-P alloys, increases when the P content approaches the eutectic composition.

(3) The influence of P content on the crystallization processes could be well understood based on the new crystallization micromechanism of the ordered clusters deposition.
Acknowledgements

This work is supported by National Science Foundation of China under grant No. 59001447.

References