Relationship Between Crystallization Temperature and Pre-existing Nuclei in Amorphous Ni–P Alloys*

K. LU and J. T. WANG
Institute of Metal Research, Academia Sinica, Shenyang (China)

Abstract

A pre-anneal treatment was performed on a Ni$_{80}$P$_{20}$ glass to form pre-existing crystal nuclei which were detected by scanning electron microscopy. The density of the nuclei increases linearly with pre-anneal time after a time lag. Following classical phase transformation theory, a relationship was derived between crystallization temperature $T_p$ and the number of pre-existing nuclei in the crystallization process dominated by growth of nuclei. Using a DSC-II, the as-quenched samples and samples pre-annealed for various times were crystallized on linear heating and the new equation was found to agree with the experimental results. The growth rate of crystals can be estimated from this relationship.

1. Introduction

One of the most important parameters in interpreting the stability of an amorphous alloy is the crystallization temperature. This is normally defined as the peak temperature $T_p$ in the exothermal curve of crystallization at a heating rate of 5–40 K min$^{-1}$. $T_p$ is closely related to the microstructure of the amorphous alloy, and hence to the composition, the forming process and some external factors, such as irradiation and surfaces. The significance of quenching rate in the forming process $T_p$ has been found by several authors [1–5]. Greer and Drehman [2, 3] reported that a high quenching rate causes $T_p$ to increase in the Fe–B and Pd–Ni–P amorphous alloys. But Kiminami and Sahm [4] obtained the opposite results in the Pd–Cu–Si glasses, and Baricco et al. [5] pointed out that quenching rate had almost no influence on the crystallization temperature $T_p$.

Because of the high values of the quenching rate required to form amorphous alloys, accurate quantitative measurement seems difficult. So the study of the relationship between quenching rate and $T_p$ has been limited. As discussed in ref. 2, different quenching rates create different populations of pre-existing nuclei which lead to different behaviours of crystallization kinetics of amorphous alloys [6]. The pre-existing nuclei can also be formed during the later treatment to the as-quenched glass. Therefore, the study of the relationship between crystallization temperature and pre-existing nuclei becomes meaningful in experiment.

In this work, a pre-anneal treatment was performed on a melt-spun Ni–P amorphous alloy to create different populations of pre-existing nuclei. By crystallizing the as-quenched and pre-annealed samples in a differential scanning calorimeter (DSC), a relationship between $T_p$ and pre-anneal time was obtained, and was found to agree with the equation derived from classical phase transformation theory.

2. Experimental procedures

The Ni–P amorphous ribbon was made using a single roller melt-spinning apparatus in an argon atmosphere. The ribbon was about 2.2 mm wide and 0.02 mm thick; its composition was Ni$_{80}$P$_{20}$ (at.%). All experimental samples were taken from the same ribbon to ensure experimental accuracy.

The procedure of the pre-anneal treatment was as follows: the as-quenched Ni–P glass was heated at a rate of 320 K min$^{-1}$ to a temperature $T_a$, and held for a certain time $t_a$ before cooling quickly to room temperature. Pre-annealing temperatures about 50 K below the crystallization temperature were chosen ($T_p = 626$ K at heating rate of 10 K min$^{-1}$): 565 K for group A, 570 K for group B and 580 K for group C respectively. The treatments were performed in a Perkin-Elmer DSC-II and gold sample pans were used in the experiments.

Measurement of crystallization of as-quenched and pre-annealed Ni–P samples was performed in the DSC-II connected to a Perkin-Elmer 3600 data station. Five heating rates were used to crystallize the 3–5 mg samples: 10 K min$^{-1}$, 20 K min$^{-1}$,
40 K min\(^{-1}\), 80 K min\(^{-1}\) and 160 K min\(^{-1}\) respectively. The experimental data were automatically collected and treated by use of a Perkin-Elmer TADS standard program.

To obtain the densities of pre-existing nuclei in the samples, a scanning electron microscope (SEM, Amary model 1000-B) was used to examine polished, etched samples of Ni–P glass.

### 3. Results and discussion

The typical DSC curves of crystallization of as-quenched and pre-annealed Ni–P samples are shown in Fig. 1. This shows that the exothermic peaks of crystallization become flatter and appear earlier with increasing pre-anneal time, i.e. the peak temperatures \(T_p\) and the onset temperatures \(T_x\) decrease, and the difference between them, \(\Delta T_{px} = T_p - T_x\), increases. Table 1 lists the values of \(T_p\), \(T_x\) and \(\Delta T_{px}\) of the crystallizations of as-quenched and pre-annealed samples (at 570 K), with three heating rates. The decrease of \(T_p\) and \(T_x\), and increase of \(\Delta T_{px}\), can be understood by the increases of number and sizes of the pre-existing nuclei in the samples with pre-anneal time.

Figure 2 shows the scanning electron micrographs of the etched pits in the pre-annealed Ni–P samples. The etched pits are expected to be the positions of the pre-existing crystal nuclei where microelectric cells would be formed during the etching processes. From Fig. 2, the number of pre-existing nuclei is increasing with increasing pre-anneal time. By counting the number of pits in the samples, the densities of the pre-existing nuclei in the Ni–P samples were obtained. For the samples pre-annealed at 570 K for 10, 50, 70, 90 and 120 min, the densities of the nuclei were 3.20 \(\times\) 10\(^{14}\), 1.13 \(\times\) 10\(^{15}\), 4.83 \(\times\) 10\(^{15}\), 8.18 \(\times\) 10\(^{15}\) and 1.20 \(\times\) 10\(^6\) respectively. As shown in Fig. 3, the density of the pre-existing crystal nuclei increases with the pre-anneal time in an approximately linear relation after a time lag \(\tau\). The slope of the straight line is the steady-state nucleation rate \(I_n\), and is 2.60 \(\times\) 10\(^{12}\) (nuclei s\(^{-1}\) m\(^{-3}\)) at 570 K; \(\tau\) is about 40 min.

The Johnson–Mehl–Avrami equation is as yet the most useful model for describing the crystallization kinetics of amorphous alloys. If the crystallization process is dominated by radial growth of pre-existing nuclei (in three dimensions), the equation can be expressed as follows [7]:

\[
x = 1 - \exp\left(-\frac{4\pi}{3} U^3 N_0 \tau^3\right)
\]

where \(x\) is the volume fraction transformed, \(N_0\) is the

### Table 1

<table>
<thead>
<tr>
<th>(B) (K min(^{-1}))</th>
<th>80</th>
<th>40</th>
<th>20</th>
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<tr>
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<td>652.2</td>
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<td>120</td>
<td>635.4</td>
<td>613.7</td>
<td>621.4</td>
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number of pre-existing nuclei and $t$ is the transformation time. The radial growth velocity $U$ may be expressed as

$$U = U_o \exp \left( - \frac{E_g}{RT} \right)$$

where $U_o$ is a constant, $E_g$ is the activation energy for growth of nuclei, $T$ is the absolute temperature and $R$ is the gas constant. Taking the first derivative of $x$ with respect to $t$

$$\frac{dx}{dt} = 3K^{1/3}(1-x)\{-\ln(1-x)^{2/3}\}$$

where

$$K = \left(\frac{4\pi}{3}\right)N_0U_o^3\exp\left(-\frac{3E_g}{RT}\right)$$

Taking the second derivative of $x$ with respect to $t$

$$\frac{d^2x}{dt^2} = B \frac{dx}{dt} \left[ \frac{d\ln(K^{1/3})}{dT} + 3K^{1/3} \frac{dx}{dt} \right] \times \frac{d[(1-x)\{-\ln(1-x)^{2/3}\}]}{dx}$$

where $B = dT/dt$ is the heating rate in the linear heating crystallization. As

$$\frac{d\ln(K^{1/3})}{dT} = \frac{1-E_g/RT}{RT} = \frac{E_g}{RT^2}$$

and when $T = T_p$, $\frac{dx}{dt} \frac{d^2x}{dt^2} = 0$, and $x$ can normally be equal to a constant $[8]$, $x_p \approx 0.63$, then

$$\frac{(BE_g)}{(RT_p^2K_p^{1/3})} = -3 \left[ \{-\ln(1-x_p)^{2/3}\}^2 + \frac{2}{3} \{-\ln(1-x_p)\}^{-1/3} \right] \approx 0.985$$

So

$$T_p^2 \exp\left(-\frac{E_g}{RT_p}\right) = \frac{L}{N_0^{1/3}}$$

where

$$L = \frac{BE_g}{0.985RU_o \left(\frac{4\pi}{3}\right)^{1/3}}$$

is a constant for a given heating rate.

The number of pre-existing crystal nuclei in the pre-annealed Ni-P samples can be related to $t_a$ as follows, according to Fig. 3

$$N_0 = N_0(t_a - \tau)$$

where $\tau$ is a time lag.
TABLE 2 Calculation of the growth rate frequency $U_0$ by plotting $f(T_p)$ against $f(t_a)$ for the Ni–P glasses pre-annealed at 570 K, crystallized at four heating rates

<table>
<thead>
<tr>
<th>$B$ (K min$^{-1}$)</th>
<th>160</th>
<th>80</th>
<th>40</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d[f(T_p)]/d[f(t_a)]$</td>
<td>$1.06 \times 10^{-5}$</td>
<td>$5.18 \times 10^{-6}$</td>
<td>$2.46 \times 10^{-6}$</td>
<td>$1.38 \times 10^{-6}$</td>
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<tr>
<td>$U_0$ (m min$^{-1}$)</td>
<td>$1.45 \times 10^7$</td>
<td>$1.49 \times 10^7$</td>
<td>$1.56 \times 10^7$</td>
<td>$1.40 \times 10^7$</td>
</tr>
<tr>
<td>$U_0$ (m min$^{-1}$)</td>
<td>$1.48 \times 10^7$</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Fig. 4. Plots of $f(T_p)$ against $f(t_a)$ using experimental results of the samples pre-annealed at: (a) 570 K and (b) 580 K; for various heating rates: O, 160 K min$^{-1}$; ■, 80 K min$^{-1}$; ●, 40 K min$^{-1}$; □, 20 K min$^{-1}$.

According to eqns. (8) and (9), we let

$$f(T_p) = T_p^2 \exp\left(-\frac{E_s}{RT_p}\right)$$

and

$$f(t_a) = (t_a - \tau)^{-1/3}$$

Plotting $f(T_p)$ against $f(t_a)$, we obtain an approximate straight line with a gradient of $L \cdot t_a^{-1/3}$.

Using the experimental results of $T_p$ of the pre-annealed (at 570 K) Ni–P samples on four heating rates of 160, 80, 40 and 20 K min$^{-1}$, we plotted $f(T_p)$ against $f(t_a)$, as shown in Fig. 4(a). The graphs give straight lines when $t_a \geq 70$ min. This may be explained by the pre-existing nuclei which were sufficient to dominate crystallization in the samples with $t_a$ of 70 min, as eqn. (8) was restricted to the growth dominating crystallization process. (It has been demonstrated by X-ray diffraction that crystals appeared in these samples with $t_a \geq 80$ min [10].)

From the slopes of the straight lines, the values of $U_0$ can be estimated, as listed in Table 2. The values of $U_0$ obtained from four different heating rates are very similar, with an average value of about $1.48 \times 10^7$ m min$^{-1}$.

Figure 4(b) shows the plots of the samples pre-annealed at 580 K. The value of $\tau$ was obtained using the Arrhenius relation with an activation energy of 180 kJ mol$^{-1}$ for Ni$_{50}$P$_{20}$ glass [10]. These figures confirm that the experiment agrees with the theory.

References