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Crystallization kinetics of Ni–P glass – activation energies for nucleation and growth of nuclei

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A pre-anneal treatment was introduced to a melt-spun Ni–P alloy. By crystallizing the as-quenched and pre-annealed samples in a differential scanning calorimeter at different heating rates and isothermal process, the apparent activation energies for the total crystallization of the Ni–P samples were obtained by using the Kissinger technique and the Arrhenius relation. It was found that the apparent activation energy, E_c, decreased and tended to a certain value of 180 kJ mol^{-1}, with increase of pre-anneal time. According to the classical phase transformation theory, the activation energies for nucleation and growth of nuclei in the Ni–P glasses were deduced to be 324 and 180 kJ mol^{-1}, respectively, which are very close to the values previously reported by our laboratory. The weight parameters of nucleation, *a*, and growth, *b*, decrease monotonically and increase and tend to certain values with an increase of pre-anneal time, respectively.

1. Introduction

One of the most important parameters which mark the stabilities of amorphous alloys in scientific research and technology is the activation energy for crystallization, which is defined as the energy that must be reached by the atoms to transfer them from the amorphous state to the crystalline state. As the crystallization processes are generally considered as two-exponent processes (nucleation and growth of nuclei), the apparent activation energy for total crystallization, E_c, can be reasonably divided into two components: activation energy for nucleation, E_n, and activation energy for growth of nuclei E_g, in the relation below [1, 2].

$$E_c = a E_n + b E_g \qquad (1)$$

where *a*, *b* are the weight parameters of the activation energies for nucleation and growth of nuclei respectively, and $a + b = 1$. It is clear that *a* and *b* may reflect the mechanisms of crystallization processes in the amorphous alloys.

Determination of the values of *a* and *b*, in fact, focuses on the determination of E_n and E_g. However, accurate experimental measurements of E_n and E_g seem difficult. Determination of E_n and E_g in experiment can always be performed by quantitative transmission electron microscopy (TEM) (counting nuclei and measuring crystal sizes) [3–5]. Wu *et al.* [6] developed a technique to determine E_n and E_g in the crystallization with polymorphic and eutectic growth using isothermal crystallization in the differential scanning calorimeter. But the experimental accuracy of both TEM measurements and the isothermal DSC technique is limited, and no satisfactory results can be obtained.

Accurate measurement of E_c can usually be carried out by integration methods such as differential scanning calorimetry (DSC, DTA), dilatometry, etc., using the Kissinger analysis [7], or Ozawa's method [8], or the Arrhenius relation. So if the activation energies for nucleation and growth can be obtained directly using these methods, the results must be more accurate and the experimental procedure simplified.

In our previous work [9], the activation energy for growth of nuclei was obtained by use of early nucleation saturation in an Ni–P sample, which was detected by TEM. According to the Arrhenius equation, the apparent activation energies in the small transformation ranges were calculated, obtaining E_n and E_g by extrapolation.

In this work, an Ni–P glass was subjected to a pre-anneal treatment in order to create different populations of pre-existing nuclei in the samples. By crystallizing the as-quenched and pre-annealed samples in a DSC, the apparent activation energies for total crystallization processes of the samples were calculated using the Kissinger analysis. From the relationship between the apparent activation energies and the pre-anneal time obtained from experiment, the activation energies for both nucleation and growth of crystal nuclei were obtained.

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, and of composition Ni80P20 (at %). All experimental samples were taken from the same ribbon to ensure experimental accuracy.

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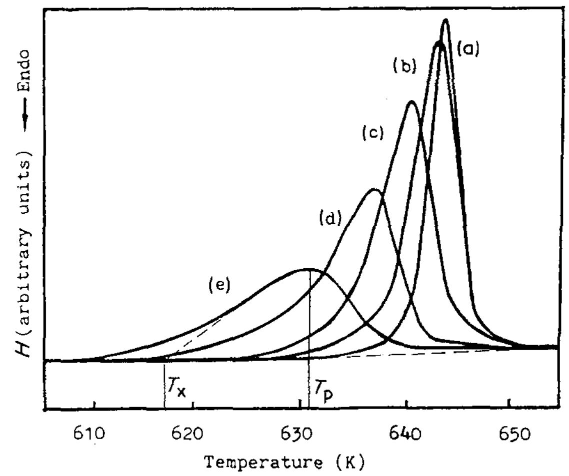

Figure 1 Typical DSC curves of crystallizations of (a) as-quenched Ni–P glass and (b, c, d, e) Ni–P glasses pre-annealed at 570 K for 20, 40, 60, and 80 min, respectively; heating rate 20 K min^{-1}.

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

The measurements of as-quenched and pre-annealed Ni–P samples were performed in the DSC-II connected to a 3600 Data Station (Perkin–Elmer). Five heating rates were used to crystallize the samples of 3 to 5 mg: 10, 20, 40, 80 and 160 K min^{-1}.

The isothermal crystallization procedure for the samples was as follows: the as-quenched samples were heated at 160 K min^{-1} to a specific temperature; the automatic TADS program began a few seconds later, after the indicated temperature had been reached, because of the temperature lag between the sample pans and the indicator.

X-ray diffraction of the pre-annealed samples was performed using a Rigaku diffractometer (*D*/max-γA, 12 kW) with Cuk_α radiation.

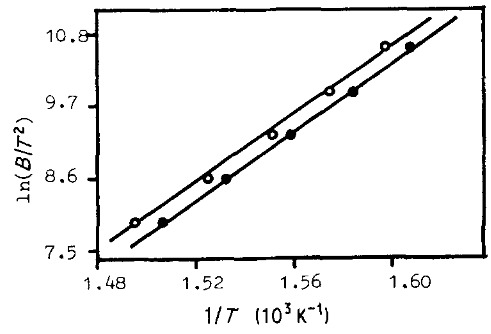

Figure 2 Kissinger plots of as-quenched Ni–P glass using (○) T_p and (●) T_x.

3. Results and discussion

Typical DSC curves of the crystallization of as-quenched and pre-annealed Ni–P samples are shown in Fig. 1. The exothermic peaks of crystallization become flatter and appear earlier with increasing pre-anneal time, i.e. the peak temperature, T_p, and the onset temperature, T_x, decrease and the difference between them, $\Delta T_{px} = T_p - T_x$, increases.

Using the Kissinger analysis, i.e.

$$\ln(B/T^2) = -E_c/RT + \text{constant} \qquad (2)$$

where B is the heating rate, E_c is the apparent activation energy for the total process, R is the gas constant, and T is a specific temperature which can be T_p or T_x, and using values of T_p and T_x for the pre-annealed samples at 570 K and plotting $\ln(B/T^2)$ against $1/T$, we obtained approximately straight lines, as shown in Fig. 2. The slopes of the two straight lines of T_p and T_x are very close. The apparent activation energy for crystallization of the as-quenched Ni–P sample is 216.6 ± 4.5 kJ mol^{-1}.

From the Kissinger plots of T_p and T_x of the pre-annealed Ni–P samples (570 K, group B), it was found that the apparent activation energy of total crystallization decreases and tends to a certain value, about 180 kJ mol^{-1}, with increasing pre-anneal time, t_a (see Fig. 3). This decreasing tendency of activation energy was confirmed by the same plots of T_p and T_x of pre-annealed samples of groups A and C, at 565 and 580 K, respectively, as shown in Fig. 4.

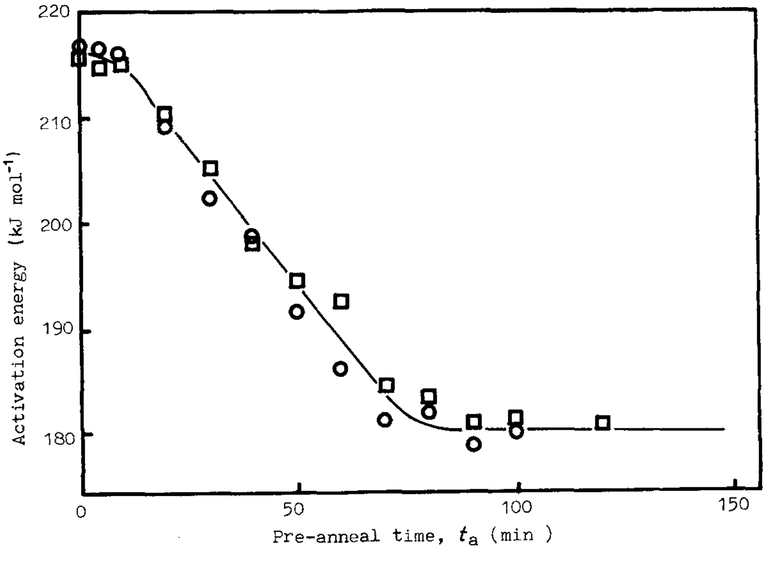

Figure 3 Decreasing apparent activation energy of the pre-annealed Ni–P samples obtained from Kissinger plots using (□) T_p and (○) T_x, with the pre-anneal time, t_a.

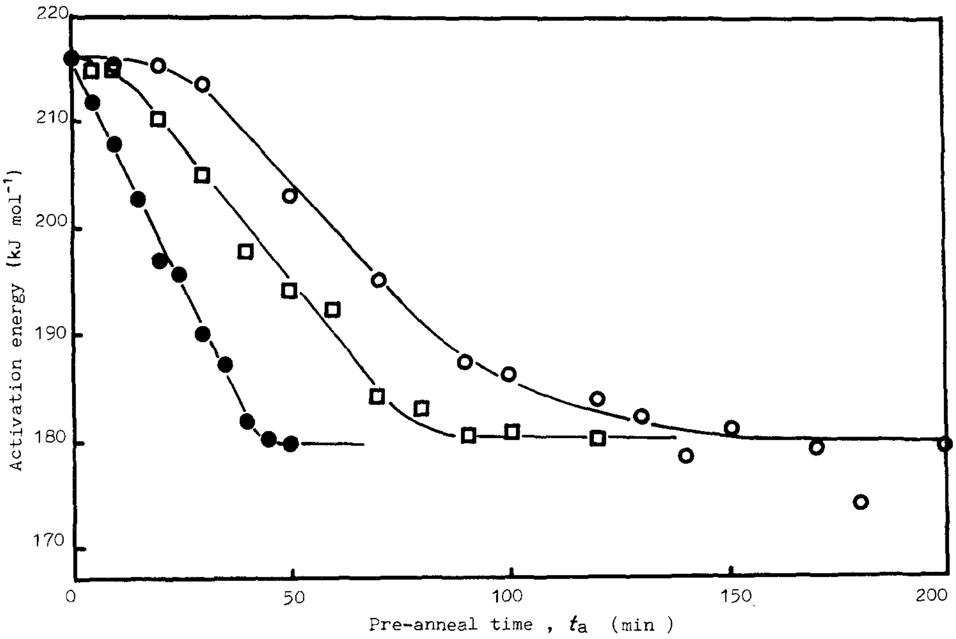

Figure 4 The relationship between apparent activation energy and the pre-anneal time with three pre-anneal temperatures: (○) 565 K, (□) 570 K, (●) 580 K.

In the isothermal crystallization of the Ni–P samples, the transformation time, t, and the temperature, T, obey the Arrhenius behaviour

$$t = t_0 \exp(-E_c/RT) \tag{3}$$

where t_0 is a constant and t is a specific time which was chosen to be the time when the crystallization rate is maximum, t_p. Plotting ln (t_p) against $1/T$, an approximate straight line with a slope of $(-E_c/R)$ was obtained. Fig. 5 is the Arrhenius plot of the isothermal crystallization of as-quenched Ni–P glass, the apparent activation energy of the glass is about $263 \pm 5.0\,\text{kJ}\,\text{mol}^{-1}$. Although the values of activation energies obtained from the Arrhenius plots are larger than that from Kissinger plots, the decreasing tendency of apparent activation energy remains unchanged (see Fig. 6). The exothermal peaks of the samples with $t_a > 80$ min were to small to measure the activation energy accurately.

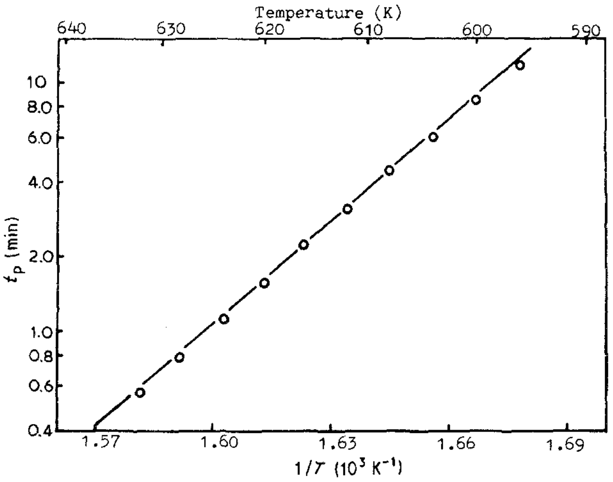

Figure 5 The Arrhenius plot of as-quenched Ni–P glass using the peak time, t_p, in the isothermal crystallization.

As the crystallization kinetics of amorphous alloys (both linear heating and isothermal) can be modelled by the classical phase transformation theory, i.e. the Johnson–Mehl–Avrami equation, the volume fraction transformed could be written as [1, 10–12]

$$x = 1 - \exp[-K(t - \tau)^n] \tag{4}$$

where K is a kinetic parameter and τ is the time lag or "incubation time". n is the Avrami exponent which reflects nucleation behaviour and growth of nuclei during crystallization. In the crystallization of eutectic growth radially in three dimensions, when nucleation occurs randomly in the sample, $n = 4$ is for constant nucleation with time, and $n = 3$ for the growth of a constant number of pre-existing nuclei. When these two processes occur simultaneously, the value of n is in the range of $3 < n < 4$, and with increasing pre-existing nuclei, n will decrease from 4 to 3 [13, 14].

For a process with $n = 3$, the crystallization kinetics should be dominated by growth of pre-existing nuclei, then the activation energy for the total process should be equal to the activation energy for growth of nuclei, E_g. When $n = 4$, the process will be dominated by constant nucleation and subsequent growth, then the activation energy for the total process is equal to

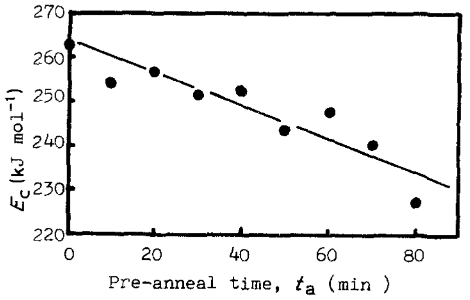

Figure 6 Apparent activation energy obtained from Arrhenius plots, decreasing with pre-anneal time (at 570 K).

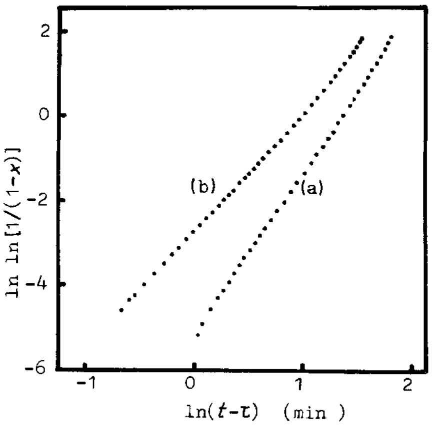

Figure 7 Plots of ln ln $[1/(1-x)]$ against ln $(t-\tau)$ of (a) the as-quenched and (b) pre-annealed (at 570 K for 80 min) glasses, at 600 K.

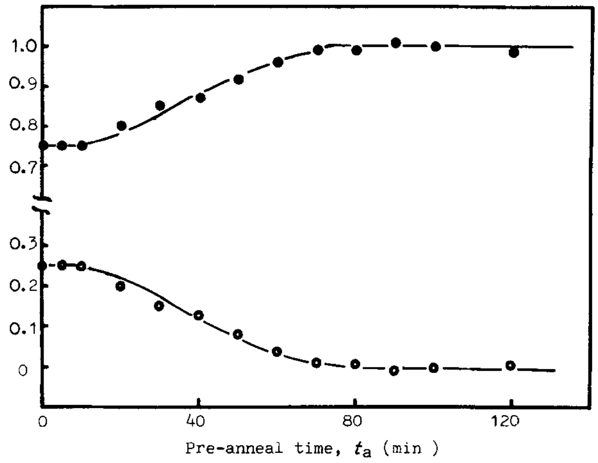

Figure 9 Relationship between (○) a and (●) b, and the pre-anneal time, t_a.

$(E_n/4 + 3E_g/4)$ [5], where E_n is the activation energy for nucleation. So the apparent activation energy for the total crystallization process can be expressed as

$$E_c = \begin{cases} E_g & n = 3 \\ a\,E_n + b\,E_g & 3 < n < 4 \\ (E_n + 3\,E_g)/4 & n = 4 \end{cases}$$

$$(0 < a < 0.25,\ 0.75 < b < 1) \qquad (5)$$

In the isothermal crystallization of amorphous alloys, plotting ln ln $[1/(1-x)]$ against ln $(t-\tau)$ shows an approximate straight line with a gradient of n. The plots of the as-quenched and pre-annealed (at 570 K for 80 min) samples are shown in Fig. 7. The values of τ and corresponding values of n of the samples at 600 K are given in Table I.

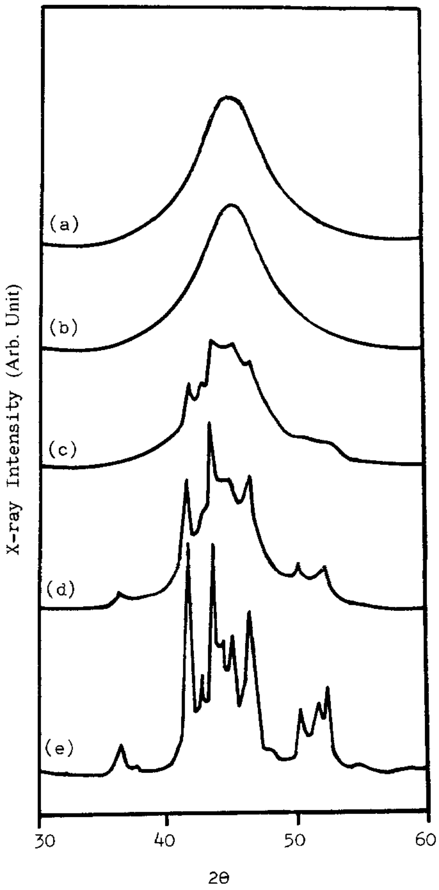

Figure 8 X-ray diffraction spectra from Cu$K\alpha$ radiation for (a) the as-quenched glass, and (b, c, d, e) glasses pre-annealed for 70, 80, 100 and 120 min, respectively, at pre-anneal temperature of 570 K.

It is clear from Table I that the crystallization of as-quenched Ni–P glass is dominated by constant nucleation (after a time lag), and by growth of pre-existing nuclei in the sample pre-annealed at 570 K for 80 min, which can also be seen from the X-ray diffraction patterns in Fig. 8. The reason for this is that the pre-anneal treatment of the as-quenched Ni–P glass created more and larger ordered clusters by atomic rearrangement, which will be discussed in detail elsewhere [14, 15].

From Equation 5, the activation energies for nucleation and growth of nuclei during the crystallization process are found to be $E_n = 324 \pm 4.5\,\mathrm{kJ\,mol^{-1}}$, $E_g = 180 \pm 4.5\,\mathrm{kJ\,mol^{-1}}$. These values are very close to that reported by Wang *et al.* [9], in which $E_g = 184.7\,\mathrm{kJ\,mol^{-1}}$ obtained by early nucleation saturation and $E_n = 317.8\,\mathrm{kJ\,mol^{-1}}$ from extrapolation.

The values of a and b of different Ni–P samples can be obtained from Equation 5 and the relationship between them and the pre-anneal time is shown in Fig. 9. The decrease in a indicates a decrease in the nucleation during crystallization because of the high density of pre-existing nuclei in the pre-annealed Ni–P samples [15], which can also be seen from Table I.

TABLE I Incubation time, τ, and the Avrami exponent, n, of the Ni–P glasses pre-annealed at 570 K for different periods, at 600 K.

t_a (min)	τ (min)	n
0	6.15	4.02
10	5.90	4.00
20	4.61	4.01
30	3.63	3.96
40	3.01	3.62
50	1.95	3.53
60	1.57	3.20
70	1.15	3.01
80	0.49	3.00

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