Activation energies for crystal nucleation and growth in amorphous alloys

K. Lu and J. T. Wang
National Lab for RSA, Institute of Metal Research, Academia Sinica, Shenyang 110015 (China)

Abstract

A new method to determine the activation energies for crystal nucleation and growth ($E_n$ and $E_g$) during crystallization of amorphous alloys is developed. The activation energy for crystallization at a certain stage, i.e. the local activation energy $E_c(x)$, is obtained by use of the Arrhenius relation. According to the nucleation and growth processes at different stages revealed by measurement of the local Avrami exponent, the activation energies for nucleation and growth are obtained. Values of $E_n$ and $E_g$ are obtained using this method in a Ni-P glass. The variation of $E_n$ and $E_g$ in the pre-annealed Ni-P glasses by means of a new crystallization mechanism is also demonstrated and discussed.

1. Introduction

Crystallization of amorphous alloys is normally regarded as a process of nucleation and growth of crystalline phase(s) in the amorphous matrix. The apparent activation energy for the total crystallization process ($E_c$) can then be divided into two components: the activation energy for nucleation ($E_n$) and for growth ($E_g$). Accurate measurement of these energies is necessary for understanding the crystallization process and mechanism of nucleation and growth in amorphous alloys.

At present, there are several experimental methods to determine the values of $E_n$ and $E_g$ by means of quantitative TEM [1] and kinetic measurements [2]; but none of them is satisfactory either with regard to experimental accuracy or in its theoretical basis. In this work, a new method is developed based on the kinetic parameters of the local Avrami exponent and local activation energy during the crystallization process. Determination of $E_n$ and $E_g$ of the as-quenched and pre-annealed Ni-P glasses is demonstrated and discussed.

2. Experimental procedures

A Ni$_{50}$P$_{20}$ (at.%) amorphous alloy was prepared by using a single-roller melt-spinning equipment. The amorphous ribbon is about 0.02 mm thick and 2.1 mm wide. A differential scanning calorimeter (DSC-II, Perkin-Elmer) was used to measure the isothermal crystallization kinetic processes of which the experimental procedure is as follows: the amorphous sample is heated at a rate of 320 K min$^{-1}$ to a fixed temperature, the TADS program (Perkin-Elmer) is started to record the process after a few seconds when the indicated temperature is reached because there is a time lag between the actual temperature and the indicated one.

3. Experimental results and discussion

The isothermal crystallization process of the Ni-P amorphous alloy at different temperatures exhibits a single exothermal peak in the DSC curve. The crystallized volume fraction during the crystallization procedure can be accurately determined by measuring the partial area of the exothermal peak. The measurement results are shown in Fig. 1(a) as sigmoid curves of plots of crystallized volume fraction ($x$) vs. annealing time at different temperatures.

3.1. Local activation energy $E_c(x)$

The apparent activation energy for crystallization normally presents the average value over the total process. Actually, during crystallization, the behavior of nucleation and growth is changing from time to time. Different crystallization stages exhibit different values of activation energy. So
we define a local activation energy, $E_c(x)$, which presents the activation energy at a stage when the crystallized volume fraction is $x$. Apparently, $E_c(x)$ is closely related to the crystallized volume fraction.

During an isothermal crystallization process, the transformation time when the crystallized volume fraction is $x$, $t(x)$, is related to the anneal temperature ($T$) by an Arrhenius relationship [3]:

$$t(x) = t_0 \exp\left[ -\frac{E_c(x)}{RT} \right]$$

where $t_0$ is a time constant, $E_c(x)$ is the activation energy for crystallization at the time when transformed volume fraction is $x$, i.e., the local activation energy, and $R$ is the gas constant.

By using the experimental data of $x(t) - t$ at different temperatures (632–596 K), we plot $\ln[t(x)]$ vs. $1/T$ with a certain value of $x$ and an approximately straight line is obtained, as in Fig. 2(a). As the slope of the straight line gives the value of $E_c(x)$, we obtain $E_c(2\%) = 319.5 \pm 8.5$ kJ mol$^{-1}$ and $E_c(99\%) = 279.4 \pm 4.5$ kJ mol$^{-1}$. Using the same method, the values of the local activation energy at different $x$ can be obtained. Figure 2(b) shows a plot of $E_c(x)$ vs. $x$ for the as-quenched Ni–P glass, from which variation of $E_c(x)$ with $x$ is evident. At the beginning of crystallization, the value of $E_c(x)$ is large; it decreases with proceeding crystallization and decreases sharply at the last stage of crystallization. This variation can be attributed to the variation of the nucleation and growth processes during crystallization.

3.2. Local Avrami exponent $n(x)$

The crystallization kinetics of amorphous alloys is normally modelled by the JMA equation [4]:

$$x = 1 - \exp\left[ -K_r(t - \tau)^n \right]$$

where $\tau$ corresponds to a time lag, $n$ to the Avrami exponent which reflects the characteristics of nucleation and growth during transformation, $K_r$ is a kinetic parameter which is a function of temperature ($T$):

$$K_r = K_0 \exp\left( -\frac{E_c}{RT} \right)$$

where $K_0$ is a constant, $E_c$ is the apparent activation energy for the process. The concept of local Avrami exponent was developed recently defined as [5]:

$$n(x) = \frac{\partial \ln[-\ln(1-x)]}{\partial \ln(t - \tau)}$$
The value of local Avrami exponent \( n(x) \) gives information about the nucleation and growth behavior when the crystallized volume fraction is \( x \).

Figure 1(b) shows plots of \( \ln[-\ln(1-x)] \) vs. \( \ln(t-r) \) within the region of \( 0.5\% < x < 99.5\% \) at different annealing temperatures. The values of the local Avrami exponent \( n(x) \) are presented in Fig. 2(b) as a plot of \( n(x) \) vs. \( x \).

The characteristics of crystallization at different stages and their corresponding JMA equations are analyzed according to the classical theory of phase transformations and listed in Table 1.

3.3. Activation energies \( E_n \) and \( E_g \)

The activation energies for nucleation and growth are related to the nucleation rate \( (I) \) and growth velocity \( (U) \) by the following formulas:

\[
I = I_0 \exp\left(-\frac{E_n}{RT}\right) \tag{5a}
\]
\[
U = U_0 \exp\left(-\frac{E_g}{RT}\right) \tag{5b}
\]

From the results of the local Avrami exponent \( n(x) \), the apparent activation energies for crystallization at three different stages can be expressed by \( E_n \) and \( E_g \). Relationships between \( E_c, E_n \) and \( E_g \) at the three stages are also listed in Table 1. Using the values of \( E_c(2\%) \) and \( E_c(99\%) \) in the early and last stage respectively, we get \( E_n = 359.6 \text{ kJ mol}^{-1} \), \( E_g = 279.4 \text{ kJ mol}^{-1} \). From the \( n(x)-x \) relationship (average value in the temperature range), \( x = 25\% \) when \( n(x) = 4.0 \). Using \( E_c(2\%) \) and \( E_c(25\%) \), we obtain \( E_n = 363.3 \text{ kJ mol}^{-1} \), \( E_g = 275.7 \text{ kJ mol}^{-1} \). It can be seen that the values of two sets of \( E_n \) and \( E_g \) are very close.

3.4. Effect of pre-anneal treatment on \( E_n \) and \( E_g \)

A pre-anneal treatment was introduced to the as-quenched Ni-P glass to change its microstructure. After the treatment, the crystallization kinetic parameters vary significantly. The measured results of the \( E_c(x)-x \) relationships of different pre-annealed Ni-P amorphous samples are shown in Fig. 3. It can be seen that with increasing pre-annealing time, the values of \( E_c(x) \)

<table>
<thead>
<tr>
<th>TABLE 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Three specific stages during crystallization of the Ni-P glass</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Early stage</th>
<th>Middle stage</th>
<th>Final stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D surface N &amp; G</td>
<td>3D bulk N &amp; G</td>
<td>3D bulk G</td>
</tr>
<tr>
<td>( n = 2.0 )</td>
<td>( n = 4.0 )</td>
<td>( n = 3.0 )</td>
</tr>
<tr>
<td>( x = 1 - \exp[-IU(t-r)^2] )</td>
<td>( x = 1 - \exp[-\frac{1}{2}IU(t-r)^2] )</td>
<td>( x = 1 - \exp[-\frac{1}{2}N_0U(t-r)^3] )</td>
</tr>
<tr>
<td>( E_x = \frac{(E_n+E_g)}{2} )</td>
<td>( E_c = \frac{(E_n+3E_g)}{4} )</td>
<td>( E_c = E_g )</td>
</tr>
</tbody>
</table>

\( N_0 \) is the number of growing crystalline nuclei.

<table>
<thead>
<tr>
<th>TABLE 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Values of ( E_n ) and ( E_g (\pm 10 \text{ kJ mol}^{-1}) ) for pre-annealed Ni-P glasses</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pre-annealing time (min)</th>
<th>Temperature range (K)</th>
<th>( E_c(2%) )</th>
<th>( E_c(99%) )</th>
<th>( E_n )</th>
<th>( E_g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>596–628</td>
<td>319.5</td>
<td>279.4</td>
<td>359.6</td>
<td>279.4</td>
</tr>
<tr>
<td>5</td>
<td>600–628</td>
<td>313.0</td>
<td>273.3</td>
<td>352.7</td>
<td>273.7</td>
</tr>
<tr>
<td>10</td>
<td>600–628</td>
<td>296.1</td>
<td>267.5</td>
<td>324.7</td>
<td>267.5</td>
</tr>
<tr>
<td>20</td>
<td>600–624</td>
<td>281.5</td>
<td>255.8</td>
<td>307.2</td>
<td>255.8</td>
</tr>
<tr>
<td>30</td>
<td>600–624</td>
<td>271.7</td>
<td>250.4</td>
<td>293.0</td>
<td>250.4</td>
</tr>
<tr>
<td>50</td>
<td>596–620</td>
<td>260.1</td>
<td>238.9</td>
<td>281.3</td>
<td>238.9</td>
</tr>
<tr>
<td>70</td>
<td>596–616</td>
<td>244.4</td>
<td>236.8</td>
<td>252.0</td>
<td>236.8</td>
</tr>
</tbody>
</table>

Fig. 3. Relationship between \( E_c(x) \) and \( x \) for different pre-annealed Ni-P glasses with pre-annealing time of a: 0 min, b: 5 min, c: 10 min, d: 20 min, e: 30 min, f: 50 min, and g: 70 min.
and \([E_N(2\%) - E_N(99\%)]\) decrease. Using the same method mentioned above, \(E_n\) and \(E_g\) of the pre-annealed samples are obtained, as listed in Table 2. It is found that the values of \(E_n\) and \(E_g\) decrease with increasing pre-annealing time, and for the sample with annealing time of 70 min \(E_n\) and \(E_g\) are approximately equal.

The variation of the activation energies for the crystal nucleation and growth processes cannot be interpreted by using the classical crystallization mechanism. Recently a new crystallization micromechanism was advanced in which crystal nucleation and growth are composed of two fundamental processes: diffusion of single atoms (AJ) and shearing deposition or combination of ordered clusters (CD or CC) \([7, 8]\). So \(E_n\) and \(E_g\) should be composed of the activation energies for the AJ and CD (or CC) processes. The CD process has a relatively smaller activation energy than AJ. A pre-anneal treatment to the as-quenched glass will enhance its ordering, \textit{i.e.} increase the ordered clusters in the amorphous sample, and thereby increase the CD or CC process during crystallization. So the values of \(E_n\) and \(E_g\) are reduced with increasing pre-annealing time. If the nucleation and growth processes are dominated by the CD or CC process with no AJ at all, the activation energies \(E_n\) and \(E_g\) will tend to the same value, as CD and CC are equally clusters transformation processes with approximately the same activation energy.

4. Conclusion

According to the crystallization kinetics of amorphous alloys, a new method to determine the activation energies for crystal nucleation and growth is developed by means of the local activation energy and local Avrami exponent. The values of \(E_n\) and \(E_g\) in a Ni–P amorphous alloy are obtained using this method. The variation of \(E_n\) and \(E_g\) with the pre-anneal treatment to the glass is demonstrated and discussed by the use of the newly developed crystallization micromechanism.

References