Calculation of Activation Energy, Frequency Factor and Avrami Exponent of Amorphous Fe$_{76}$Pr$_4$B$_{20}$ and Fe$_{76}$Dy$_4$B$_{20}$ Alloys on the Basis of Crystallization Kinetics

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Research Article

INTRODUCTION

The Thermal stability of amorphous alloys is a subject of considerable interest, since the properties of these engineering materials may be significantly changed by the onset of crystallization. The crystallization is associated with nucleation and growth process. Activation energy ($E_a$) is one of the important parameters describing the transformation kinetics. $E_a$ values are found to be larger at higher temperatures in crystallization. These features probably originate from the crystallization micro-mechanism. Thus, crystallization kinetics of amorphous materials was investigated by explaining the crystallization mechanism and the crystallization activation energy in terms of isothermal and non-isothermal methods with different approaches. Different thermal analysis techniques used in crystallization kinetics were reported and a correlation between kinetic and structural investigations were made to determine the crystallization mechanism in these materials.[1,2] Therefore, the investigation of crystallization kinetics is important since it quantifies the effect of the nucleation and growth rate of the resulting crystallites [1]. In this paper, we present the Calculation of activation energy, frequency factor and Avrami exponent of amorphous Fe$_{76}$Pr$_4$B$_{20}$ and Fe$_{76}$Dy$_4$B$_{20}$ alloys on the basis of crystallization kinetics using Differential Scanning Calorimetry (DSC).

EXPERIMENTAL SECTION

Specimens of amorphous Fe$_{76}$Pr$_4$B$_{20}$ and Fe$_{76}$Dy$_4$B$_{20}$ ribbons prepared by single roller melt spinning technique under inert atmosphere were procured from our other researchers. The alloy ribbons were about 1 mm wide and about 30 µm thick. The amorphous nature of ribbons was confirmed by X-ray diffraction (XRD). The as-quenched samples of Fe$_{76}$Pr$_4$B$_{20}$ and Fe$_{76}$Dy$_4$B$_{20}$ alloys were heated in DSC (DSC-50, Shimadzu, Japan) at four linear heating rates (10, 20, 30 and 40 Kelvin/min) from room temperature to 1000 K. The DSC scans were recorded by a thermal analyzer interfaced to a computer.

RESULTS AND DISCUSSION

The DSC curves of as-quenched samples of amorphous Fe$_{76}$Pr$_4$B$_{20}$ and Fe$_{76}$Dy$_4$B$_{20}$ alloys at four heating rates of crystallization are shown in Figure 1.
The activation energy for crystallization of an amorphous alloy under a linear heating rate can be estimated using Kissinger’s peak shift method \[1\], which relates the peak temperature, \(T_p\), with heating rate (\(\beta\)) through the equation.

\[
\ln (\beta/T_p^2) = (E_a/R) + \ln(k_0R/E_a) \tag{1}
\]

Where \(E_a\) is the activation energy for crystallization, \(k_0\) the frequency factor which is defined as the number of attempts made by the nuclei per second to overcome the energy barrier and \(R\) is the universal gas constant. **Figure 2** shows the graph of \(\ln (\beta/T_p^2)\) vs \(1000/T_p\) of amorphous Fe\(_{76}\)Pr\(_{4}\)B\(_{20}\) and Fe\(_{76}\)Dy\(_{4}\)B\(_{20}\) alloys, which is a straight line with a slope \((-E_a/R)\) and an intercept of \(\ln (k_0R/E_a)\). The activation energy and the frequency factor \(k_0\) for crystallization peak calculated using Kissinger’s peak shift method for the given samples are given in **Table 1**.

**Figure 1.** The DSC curves of amorphous Fe\(_{76}\)Pr\(_{4}\)B\(_{20}\) and Fe\(_{76}\)Dy\(_{4}\)B\(_{20}\) alloys at four heating rates of crystallization in the temperature range 800 K–940 K (Blue - 10 K/min, Red - 20 K/min, Green - 30 K/min and Violet-40 K/min).

**Figure 2.** \(\ln (\beta/T_p^2)\) vs. \(1000/T_p\) of amorphous Fe\(_{76}\)Pr\(_{4}\)B\(_{20}\) and Fe\(_{76}\)Dy\(_{4}\)B\(_{20}\) alloys.
The activation energy for crystallization of an amorphous alloy under a linear heating rate can also be estimated using Matusita-Sakka’s peak shift method [4], which relates the peak temperature, $T_p$, with heating rate ($\beta$) through the equation.

$$\ln (\beta) = -\frac{E_a}{RT_p} + \text{constant} \quad (2)$$

where $E_a$ is the activation energy for crystallization and $R$ is the universal gas constant. Figure 3 shows the graph of $\ln (\beta)$ vs $1000/T_p$ of amorphous Fe$_{76}$Pr$_4$B$_{20}$ and Fe$_{76}$Dy$_4$B$_{20}$ alloys, which is a straight line with a slope ($-E_a/R$). The activation energy calculated using Matusita-Sakka’s peak shift method for the given samples, is given in Table 1.

Figure 3: $\ln (\beta)$ vs. $(1000/T_p)$ of amorphous Fe$_{76}$Pr$_4$B$_{20}$ and Fe$_{76}$Dy$_4$B$_{20}$ alloys.

The activation energy for crystallization of an amorphous alloy under a linear heating rate can be estimated using Augis & Bennett method [5], which relates the peak temperature, $T_p$, with heating rate ($\beta$) through the equation.

$$\ln (\beta/T_p) = -\frac{E_a}{RT_p} + \ln k_0 \quad (3)$$

Where $E_a$ is the activation energy for crystallization, $R$ is universal gas constant and $k_0$ the frequency factor. Figure 4 shows the graph of $\ln (\beta/T_p)$ vs. $1000/T_p$ of amorphous Fe$_{76}$Pr$_4$B$_{20}$ and Fe$_{76}$Dy$_4$B$_{20}$ alloys, which is a straight line with a slope ($-E_a/R$) and an intercept of $\ln k_0$. The activation energy $E_a$ and the frequency factor $k_0$ for crystallization peak using Augis & Bennett method for the given samples are also given in Table 1.

Figure 4: $\ln (\beta)$ vs. $(1000/T_p)$ of amorphous Fe$_{76}$Pr$_4$B$_{20}$ and Fe$_{76}$Dy$_4$B$_{20}$ alloys.
Table 1: Composition, Activation Energy, $E_a$ (kJouls/mole) and Frequency factor, $k_0$ (sec)$^{-1}$ of amorphous Fe$_{76}$Pr$_4$B$_{20}$ and Fe$_{76}$Dy$_4$B$_{20}$ alloys.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Activation Energy, $E_a$ (kJouls/mole)</th>
<th>Frequency factor, $k_0$ (sec)$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_{76}$Pr$<em>4$B$</em>{20}$</td>
<td>372.625</td>
<td>409.315</td>
</tr>
<tr>
<td>Fe$_{76}$Dy$<em>4$B$</em>{20}$</td>
<td>571.3</td>
<td>578.488</td>
</tr>
</tbody>
</table>

Table 1 also gives the average value of activation energy of the samples. Thus, the average activation energy for primary crystallization of amorphous Fe$_{76}$Pr$_4$B$_{20}$ and Fe$_{76}$Dy$_4$B$_{20}$ alloys using a Kissinger’s Method, Augis-Bennet’s Method and Matusita-Sakka’s Method is determined as 389.67 kJouls/mole and 578.59 kJouls/mole, respectively. The activation energy increases as the atomic number increases. It is observed that the activation energies of amorphous alloys calculated by means of the different theoretical models differ slightly from each other which may be attributed to the different approximations used in the models. The frequency factor $k_0$ of amorphous Fe$_{76}$Pr$_4$B$_{20}$ and Fe$_{76}$Dy$_4$B$_{20}$ alloys using Kissinger method is found to be 4.542 $\times$ 10$^{19}$ (sec)$^{-1}$ and 8.5 $\times$ 10$^{31}$ (sec)$^{-1}$, respectively. Also, the frequency factor $k_0$ of amorphous Fe$_{76}$Pr$_4$B$_{20}$ and Fe$_{76}$Dy$_4$B$_{20}$ alloys using Augis-Bennet’s method is found to be 2.37 $\times$ 10$^{21}$ (sec)$^{-1}$ and 2.92 $\times$ 10$^{33}$ (sec)$^{-1}$, respectively.

Avrami [6] expresses that $x$ is the volume fraction transformed after time $t$ as:

$$x = 1 - \exp(-kt^n)$$

(4)

Where $n$ is called “the Avrami ‘$n$’ or a dimensionless quantity called the kinetics exponent”.

The kinetics exponent $n$ is described by the equation

$$n = \frac{\langle dx/dt \rangle_p RT^2}{0.37\beta E_a^{-1}}$$

(5)

Values of Avrami exponent, $n$ and the reaction rate constants $k$ can be determined by least square fits of the experimental data. The Avrami kinetics exponent $n$ was calculated from the above equation developed by Gao and Wang [7]. The crystallization rates, $(dx/dt)$ versus temperature ($T$) of amorphous Fe$_{76}$Pr$_4$B$_{20}$ and Fe$_{76}$Dy$_4$B$_{20}$ alloys are presented in Figure 5. The maximum crystallization $(dx/dt)$ for each heating rate gives $n$, according to the equation $n = \langle dx/dt \rangle_p RT^2 (0.37\beta E_a^{-1})$. Thus, mean values of the kinetics exponent, $\langle n \rangle$ of amorphous Fe$_{76}$Pr$_4$B$_{20}$ and Fe$_{76}$Dy$_4$B$_{20}$ alloys is found to be 1.67 and 0.831, respectively. The Avrami exponent decreases as the atomic number increases.

**Figure 5.** Crystallization rate, $(dx/dt)$, vs. temperature, $T$ at different heating rates for Fe$_{76}$Pr$_4$B$_{20}$ and Fe$_{76}$Dy$_4$B$_{20}$ alloys.

Table 2. Avrami (or) mean values of the kinetics exponent, $\langle n \rangle$ values calculated from $(dx/dt)$ vs Temp(K) curves.

<table>
<thead>
<tr>
<th>Composition</th>
<th>10 K/min</th>
<th>20 K/min</th>
<th>30 K/min</th>
<th>40 K/min</th>
<th>$\langle n \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_{76}$Pr$<em>4$B$</em>{20}$</td>
<td>2.59</td>
<td>1.52</td>
<td>1.16</td>
<td>1.42</td>
<td>1.67±2</td>
</tr>
<tr>
<td>Fe$_{76}$Dy$<em>4$B$</em>{20}$</td>
<td>0.6314</td>
<td>0.6644</td>
<td>0.92</td>
<td>1.11</td>
<td>0.831±1</td>
</tr>
</tbody>
</table>

**CONCLUSIONS**

The average activation energy ($E_a$) for primary crystallization of amorphous Fe$_{76}$Pr$_4$B$_{20}$ and Fe$_{76}$Dy$_4$B$_{20}$ alloys using the a Kissinger’s Method, Augis-Bennet’s Method and Matusita-Sakka’s Method is found to be 389.67 kJouls/mole and 578.59 kJouls/mole, respectively. The activation energy increases as the atomic number increases. The frequency factor ($k_0$) of amorphous
Fe\textsubscript{76}Pr\textsubscript{4}B\textsubscript{20} and Fe\textsubscript{76}Dy\textsubscript{4}B\textsubscript{20} alloys using Kissinger method is found to be $4.542 \times 10^{19}$ (sec)$^{-1}$ and $8.5 \times 10^{31}$ (sec)$^{-1}$, respectively. Also, the frequency factor ($k_o$) of amorphous Fe\textsubscript{76}Pr\textsubscript{4}B\textsubscript{20} and Fe\textsubscript{76}Dy\textsubscript{4}B\textsubscript{20} alloys using Augis-Bennet’s method is found to be $2.37 \times 10^{21}$ (sec)$^{-1}$ and $2.92 \times 10^{33}$ (sec)$^{-1}$, respectively. The Avrami exponent of the kinetics exponent, <n> of amorphous Fe\textsubscript{76}Pr\textsubscript{4}B\textsubscript{20} and Fe\textsubscript{76}Dy\textsubscript{4}B\textsubscript{20} alloys is found to be 1.67 and 0.831, respectively. The Avrami exponent decreases as the atomic number increases.

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