Thermal Behavior and Crystallization of Fe$_{81-x}$Co$_x$Zr$_7$Nb$_2$B$_{10}$ ($x = 2, 4, 6$) Alloys

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(Received March 21, 2011; revised version October 19, 2011; in final form November 9, 2011)

Thermal behavior and microstructure of Fe$_{81-x}$Co$_x$Zr$_7$Nb$_2$B$_{10}$ ($x = 2, 4, 6$) alloys were investigated by differential thermal analysis and X-ray diffraction. Both the supercooled liquid region $\Delta T_x$ and the first crystallization peak temperature $T_{p1}$ are the lowest and the span $\Delta T_p$ between $T_{p1}$ and $T_{p2}$ is the highest when 4 at.% Fe is substituted by Co. The crystallization activation energy $E_{p1}$ for Fe$_{77}$Co$_4$Zr$_7$Nb$_2$B$_{10}$ alloy is the minimum for the heating rates $\nu = 5$–20 K/min. $E_{p1}$ for Fe$_{77}$Co$_4$Zr$_7$Nb$_2$B$_{10}$ alloy is the minimum for the heating rates $\nu = 20$–50 K/min. The crystallization processes of Fe$_{81-x}$Co$_x$Zr$_7$Nb$_2$B$_{10}$ ($x = 2, 4, 6$) amorphous alloys are similar on the whole, which is as follows: amorphous $\rightarrow$ amorphous $+$ $\alpha$-Fe(Co) $\rightarrow$ $\alpha$-Fe(Co) $+$ Fe$_3$Zr $+$ Fe$_2$Nb$_{0.4}$Zr$_{0.6}$. PACS: 65.60.+a, 61.43.Dq

1. Introduction

Nanocrystalline soft magnetic alloys have attracted a great deal of attention from scientists over the past several decades. Among the soft magnetic nanocrystalline systems, considerable attention is devoted to the Fe-based alloys [1–10]. The microstructure, magnetic property and crystallization behavior of Fe-based alloys have been investigated in detail. The study of the crystallization behavior is very important in understanding the thermal stability of the amorphous phase [6]. The glass forming ability (GFA) of alloys can be evaluated by a temperature span of the supercooled liquid region $\Delta T_x$ (difference between the glass transition temperature $T_g$ and the onset crystallization temperature $T_x$). The wider is the $\Delta T_x$, the greater is the GFA [11]. The purpose of this study is to investigate the thermal behavior and crystallization of Fe$_{81-x}$Co$_x$Zr$_7$Nb$_2$B$_{10}$ ($x = 2, 4, 6$) amorphous alloys.

2. Experimental details

Fe$_{81-x}$Co$_x$Zr$_7$Nb$_2$B$_{10}$ ($x = 2, 4, 6$) amorphous alloys were prepared by melt-spinning and annealed at 803, 873, 943 and 1023 K for 40 min. The microstructure was examined by X-ray diffraction (XRD, D/Max 2500/PC, Cu $K_\alpha$, $\lambda = 1.5406$ Å). Thermal analysis was carried out in the Perkin Elmer TG/DTA-6300 instrument at different heating rates (5, 10, 20, 30 and 50 K/min). Detailed thermal analysis of samples reveals a spectrum of values for glass transition temperature $T_g$, onset crystallization temperature $T_x$, the first crystallization peak temperature $T_{p1}$ and the second crystallization peak temperature $T_{p2}$. The GFA of alloys can be evaluated by a temperature span of the supercooled liquid region $\Delta T_x$.

3. Results and discussion

Figure 1a–c shows the differential thermal analysis (DTA) traces of Fe$_{81-x}$Co$_x$Zr$_7$Nb$_2$B$_{10}$ ($x = 2, 4, 6$) amorphous alloys at different heating rates. The thermal parameters all increase with increasing heating rate. The first crystallization peaks $T_{p1}$ and the second crystallization peak $T_{p2}$ obtained at different heating rates are listed in Table I. Figure 2 shows the DTA traces of Fe$_{81-x}$Co$_x$Zr$_7$Nb$_2$B$_{10}$ ($x = 2, 4, 6$) amorphous alloys at a heating rate of 30 K/min. It can be seen that a low exothermic peak precedes the main crystallization peak.

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peak, which is supposed to be a pre-crystallization effect [12]. $T_g$, $T_x$, $\Delta T_x$, $T_{p1}$ and $\Delta T_p$ (difference between $T_{p1}$ and $T_{p2}$) of three amorphous alloys at a heating rate of 30 K/min as a function of Co content are shown in Fig. 3. Both $\Delta T_x$ and $T_{p1}$ are the lowest and the span $\Delta T_p$ is the highest when the partial substitution of Fe by Co is of the amount of 4 at.%. The heating rate has an important influence on the crystallization activation energy [13].

The first crystallization peak $T_{p1}$ and the second crystallization peak $T_{p2}$ of Fe$_{81-x}$Co$_x$Zr$_7$Nb$_2$B$_{10}$ ($x = 2$ (a), 4 (b), 6 (c)] amorphous alloys obtained at different heating rates.

<table>
<thead>
<tr>
<th>$V$ [K/min]</th>
<th>$T_{p1}$ [K]</th>
<th>$T_{p2}$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>a</td>
<td>872.0</td>
<td>877.9</td>
</tr>
<tr>
<td>b</td>
<td>866.9</td>
<td>873.0</td>
</tr>
<tr>
<td>c</td>
<td>868.1</td>
<td>877.0</td>
</tr>
</tbody>
</table>

Fig. 2. DTA traces of Fe$_{81-x}$Co$_x$Zr$_7$Nb$_2$B$_{10}$ ($x = 2$ (a), 4 (b), 6 (c)] amorphous alloys at a heating rate of 30 K/min.

The Kissinger plots for $T_{p1}$ are shown in Fig. 4. The crystallization activation energies $E$ for the crystallization peaks $T_p$ are calculated using the Kissinger equation [14] by plotting $\ln(\nu/T^2)$ versus $1/T$ (a straight line with the slope of $E/R$ can be obtained), where $R$ is the gas constant, $\nu$ is the heating rate (K/min) and $T$ is a specific absolute temperature such as crystallization peak $T_p$. A critical heating rate, $\nu_{crit} = 20$ K/min, is evident. The Kissinger plot is divided into two intervals according to the different slope. Yuan et al. [13] studied the non-isothermal crystallization of Co$_{43}$Fe$_{20}$Ta$_5$B$_{31.5}$ amorphous alloy and reported similar phenomenon. At low heating rates, the crystallization activation energy is composed of the activation energy of nucleation and the activation energy of growth. At high heating rates, the crystallization activation energy is mainly composed of the activation energy of growth. The crystallization activation energies $E_{p1}$ are listed in Table II. $E_{p1}$ for Fe$_{75}$Co$_{6}$Zr$_7$Nb$_2$B$_{10}$ alloy is the minimum for the heating rates $\nu = 5$–20 K/min. $E_{p1}$ for Fe$_{77}$Co$_{4}$Zr$_7$Nb$_2$B$_{10}$ alloy is the minimum for the heating rates $\nu = 20$–50 K/min.

XRD patterns of Fe$_{81-x}$Co$_x$Zr$_7$Nb$_2$B$_{10}$ ($x = 2$, 4, 6) alloys corresponding to different annealing temperatures are shown in Fig. 5a–c. The crystallization processes of the three alloys are similar on the whole. No crystalline peaks are observed for three alloys as-quenched, which in-
The crystallization activation energies $E_{p1}$ of Fe$_{81-x}$Co$_x$Zr$_7$Nb$_2$B$_{10}$ ($x = 2, 4, 6$) amorphous alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$E_{p1}$ [kJ/mol]</th>
<th>$\nu = 5$–20 K/min</th>
<th>$\nu = 20$–50 K/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_{79}$Co$_2$Zr$_7$Nb$<em>2$B$</em>{10}$</td>
<td>863.3 ± 46.5</td>
<td>319.5 ± 2.6</td>
<td></td>
</tr>
<tr>
<td>Fe$_{77}$Co$_4$Zr$_7$Nb$<em>2$B$</em>{10}$</td>
<td>766.1 ± 43.0</td>
<td>273.6 ± 28.2</td>
<td></td>
</tr>
<tr>
<td>Fe$_{75}$Co$_6$Zr$_7$Nb$<em>2$B$</em>{10}$</td>
<td>531.8 ± 36.1</td>
<td>355.6 ± 30.9</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5. XRD patterns of Fe$_{81-x}$Co$_x$Zr$_7$Nb$_2$B$_{10}$ [$x = 2$ (a), $4$ (b), $6$ (c)] alloys corresponding to different annealing temperatures.

The intensity of $\alpha$ phases and Fe$_{3}$Zr and Fe$_{2}$Nb$_{0.4}$Zr$_{0.6}$ phases are observed in the final crystallization stage. There are two exothermal peaks after pre-crystallization effect in the DTA curves. The first exothermal peak in the DTA curve corresponds to the precipitation of $\alpha$-Fe(Co). The second exothermal peak corresponds to the precipitations of Fe$_3$Zr and Fe$_{2}$Nb$_{0.4}$Zr$_{0.6}$ phases. The crystallization processes of the three alloys are as follows: amorphous $\rightarrow$ amorphous + $\alpha$-Fe(Co) $\rightarrow$ $\alpha$-Fe(Co) + Fe$_3$Zr + Fe$_{2}$Nb$_{0.4}$Zr$_{0.6}$.

### 4. Conclusions

Thermal behavior and crystallization of Fe$_{81-x}$Co$_x$Zr$_7$Nb$_2$B$_{10}$ ($x = 2, 4, 6$) alloys were investigated in this work. Both the supercooled liquid region $\Delta T_p$ and the first crystallization peak temperature $T_{p1}$ are the lowest and the span $\Delta T_p$ between $T_{p1}$ and $T_{p2}$ is the highest when 4 at.% Fe is substituted by Co. $E_{p1}$ for Fe$_{75}$Co$_{4}$Zr$_{7}$Nb$_{2}$B$_{10}$ alloy is the minimum for the heating rates $\nu = 5$–20 K/min. $E_{p1}$ for Fe$_{77}$Co$_{4}$Zr$_{7}$Nb$_{2}$B$_{10}$ alloy is the minimum for the heating rates $\nu = 20$–50 K/min. There are two exothermal peaks after pre-crystallization effect in the DTA curves. The first exothermal peak in the DTA curve corresponds to the precipitation of $\alpha$-Fe(Co). The second exothermal peak corresponds to the precipitations of Fe$_3$Zr and Fe$_{2}$Nb$_{0.4}$Zr$_{0.6}$ phases. The crystallization processes of Fe$_{81-x}$Co$_x$Zr$_7$Nb$_2$B$_{10}$ ($x = 2, 4, 6$) amorphous alloys are similar on the whole, which is as follows: amorphous $\rightarrow$ amorphous + $\alpha$-Fe(Co) $\rightarrow$ $\alpha$-Fe(Co) + Fe$_3$Zr + Fe$_{2}$Nb$_{0.4}$Zr$_{0.6}$.

### Acknowledgments

This work was funded by Science and Technology Development Project of Jilin Province (No. 201105083), Science and Technology Studying Project of “12th five-year” Office of Education of Jilin Province (No. 2011-158) and Graduate Innovative Research Programs of Jilin Normal University (No. 201103).

### References