Crystallization and Magnetic Properties of Fe$_{40}$Co$_{40}$Cu$_{0.5}$Al$_2$Zr$_9$Si$_4$B$_{4.5}$ and Fe$_{62}$Co$_{9.5}$Gd$_{3.5}$Si$_{10}$B$_{15}$ Amorphous Alloys

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Amorphous alloys with compositions Fe$_{62}$Co$_{9.5}$Cu$_{0.5}$Al$_2$Zr$_9$Si$_4$B$_{4.5}$ and Fe$_{62}$Co$_{9.5}$Gd$_{3.5}$Si$_{10}$B$_{15}$, were prepared by the melt spinning technique in the form of ribbons. Three stages of crystallization process were found in both the alloys and the crystallization kinetics was studied. Supper cooled region was found in Fe$_{40}$Co$_{40}$Cu$_{0.5}$Al$_2$Si$_4$B$_{4.5}$ alloy indicating the ability of formation of bulk amorphous alloy and 1 mm diameter rod was prepared by Cu-mould casting. Curie temperature and the saturation magnetisation of this alloy were found to be 596 K and 0.98 T respectively. Relatively, higher Curie temperature (736 K) and saturation magnetisation (1.18 T) were observed in the as-spun state of Fe$_{62}$Co$_{9.5}$Cu$_{0.5}$Al$_2$Zr$_9$Si$_4$B$_{4.5}$ alloy. Present study also indicated that partial crystallization of Fe$_{62}$Co$_{9.5}$Cu$_{0.5}$Al$_2$Zr$_9$Si$_4$B$_{4.5}$ alloy would further enhance the Curie temperature and saturation magnetisation.

(Received May 22, 2003; Accepted June 25, 2003)

Keywords: amorphous alloy, high temperature magnetic materials, crystallization, Curie temperature, coercivity

1. Introduction

Amorphous metallic alloys have unique mechanical and functional properties, which can be attributed to the atomic configuration of amorphous phase. Usually high cooling rates are required to produce amorphous alloys in the form of ribbons, wires and flakes resulting from the necessity of sample thickness less than 50 μm or diameter less than 130 μm. The dimension limitation restricts the use of these materials in many potential applications. Attempts were made to consolidate the amorphous materials in the bulk form of the alloys.

Recently, new multicomponent alloy systems, with much lower critical cooling rates (<10$^2$ K/s) have been developed and bulk amorphous alloys by the conventional melting casting process have been produced. Since the discovery of bulk amorphous materials, attempts have been made to understand the mechanism of amorphization so that system with better glass forming ability can be developed. So far three empirical rules have been defined for the formation of bulk amorphous alloys. These are (a) the constituent elements should be three or more, (b) significant differences in the atomic size ratios with about 12% among the three main constituent elements, and (c) negative heats of mixing of three main constituent elements. Based on the above empirical relations, a series of Fe-based bulk amorphous alloys were developed which exhibited excellent soft magnetic properties. However, most of these alloys have low Curie temperatures and can not used for high temperature applications. Recently, there is a trend to develop amorphous and nanocrystalline alloys for high temperature soft magnetic applications by partially replacing Fe by Co.

Extensive work was carried out by Willard et al. on (Fe$_{0.5}$Co$_{0.5}$)$_{38}$Zr$_2$B$_4$Cu$_1$ alloys, known as HITPERM, as potential materials for high temperature application. However, there is further scope for the improvement of soft magnetic properties of the above materials by addition of other alloying elements such as Si and Al. Such alloy addition may improve not only the soft magnetic properties but also the ability for the formation of bulk amorphous alloy. It has been found that addition of rare earth elements in FeCo system gives rise to large super cooled region, which indicates the ability of bulk amorphous alloy formation by Cu-mould casting.

The aim of the present work is to study the crystallization and magnetic properties of two melt-spun FeCo-based multicomponent alloys, Fe$_{40}$Co$_{40}$Cu$_{0.5}$Al$_2$Zr$_9$Si$_4$B$_{4.5}$ and Fe$_{62}$Co$_{9.5}$Gd$_{3.5}$Si$_{10}$B$_{15}$. Out of the two alloys, the later one shows supercooled region and hence has the ability for the formation of bulk amorphous alloy by conventional Cu mould casting while the former one can be made in the bulk form by consolidation of amorphous ribbon.

2. Materials

Two different materials with nominal composition Fe$_{40}$Co$_{40}$Cu$_{0.5}$Al$_2$Zr$_9$Si$_4$B$_{4.5}$ and Fe$_{62}$Co$_{9.5}$Gd$_{3.5}$Si$_{10}$B$_{15}$ were prepared in the form of ribbon by the melt spinning technique. The atomic size distribution of different constituent elements of the prepared materials is shown in the Fig. 1.

![Fig. 1 Plot of normalised atomic radius and the corresponding concentration of different constituents of the prepared alloys. Position of different elements are shown by their symbol.](image-url)
The nature of the distribution is similar to most of the Fe-based bulk amorphous alloy. Attempts have been made to prepare bulk alloy of composition Fe_{62}Co_{9.5}Gd_{3.5}Si_{10}B_{15} by using Cu-mould casting and 1 mm diameter rod has been obtained as shown in Fig. 2. However, all the measurement reported here has been conducted using melt-spun ribbon.

3. Experimental

The crystallization behavior was investigated using a Differential Scanning Calorimeter (Seiko Instruments Inc., DSC-6300) in Ar-atmosphere. The scanning rates were varied from 5 to 40 K/min within the temperature range of 300 to 1150 K. The melting point of the material was determined from the DTA study with a heating rate of 5 K/min. The magnetic hysteresis loop was evaluated using a B–H analyzer (Densi Jiki Industry Co. Ltd, Model-BH-5501) at a quasi dc magnetic field. The Curie temperature was evaluated from the derivative of temperature variation of magnetisation measurement using VSM (Riken Denshi, Model-VT 800) at a residual magnetic field of strength 2.8 kA/m. The saturation magnetisation was determined using VSM at an applied field of 200 kA/m.

4. Results and Discussion

4.1 Crystallization

Figure 3 represents the DSC results of the two measured samples when the scanning rate was 5 K/min. Three-stage crystallization behavior was observed within the measured temperature range. Glass transition temperature (T_g) was not clearly revealed for Fe_{40}Co_{40}Cu_{5}Al_{2}Zr_{5}Si_{4.5}B_{15} alloy whereas T_g was 898 K in case of Fe_{62}Co_{9.5}Gd_{3.5}Si_{10}B_{15}. The broad exothermic peak with an on-set 786 K marked the primary crystallization in Fe_{40}Co_{40}Cu_{5}Al_{2}Zr_{5}Si_{4.5}B_{15} alloy (Fig. 3(a)). The other two crystallization processes occurred at high temperatures. The primary crystallization in Fe_{62}Co_{9.5}Gd_{3.5}Si_{10}B_{15} occurred at the relatively higher temperature of 911 K with a sharper exothermic peak. A shallow exothermic peak just at the completion of the primary crystallization process marked the second stage of crystallization in this alloy whereas the third stage of crystallization occurred at 978 K with a very wide exothermic peak. The kinetics of the crystallization process were analysed using modified Kissinger expression relating to peak temperature (T_p) and the scan rate (S) as

\[ \ln\left(\frac{T_p^2}{S}\right) = \frac{E_{act}}{RT_p} + \ln\left(\frac{E_{act}}{Rk_0}\right). \]  

(1)

Where E_{act} is the effective activation energy for the process associated with the peak, R is the gas constant and k_0 is the pre-exponential factor in the Arrhenious equation for the rate constant k:

\[ k = k_0 \exp\left(-\frac{E_{act}}{RT}\right), \]  

(2)

or, the time constant,\n
\[ \tau = \frac{1}{k} = \frac{1}{k_0} \exp\left(\frac{E_{act}}{RT}\right), \]  

(3)

Combining eqs. (1), (2) and (3), the simple expression for the rate constant k_p (or time constant \( \tau_p \)) at temperature T_p can be obtained as

\[ k_p = \left(\frac{E_{act}}{R}\right) \times \left(\frac{S}{T_p}\right)^{3/2}, \]  

(4)

or,

\[ \tau_p = \left(\frac{R}{E_{act}}\right) \times \left(\frac{T_p}{S}\right)^{3/2}. \]  

(5)

The Kissinger plots of different crystallization processes of the measured Fe_{40}Co_{40}Cu_{5}Al_{2}Zr_{5}Si_{4.5} and Fe_{62}Co_{9.5}Gd_{3.5}Si_{10}B_{15} alloys are shown in Figs. 4 and 5 respectively. A good linear fit with the correlation factor (r) = 0.98 was observed for all the crystallization processes. The activation energies for the different crystallization process were calculated using eq. (1) and are presented in Table 1 together with other crystallization parameters. As the primary crystallization process is the major factor for the change in magnetic properties of the materials during high temperature application, the time constants for the transformation of those processes were also measured from Kissinger analysis. The results are shown in Fig. 6. Good linear fit (correlation factor, (r) = 0.99) with the following expression is observed:
The stability of the amorphous phase at any desired temperature could be obtained by using above equations.

4.2 Magnetic property

The room temperature magnetic properties of the melt-spun ribbon were measured and shown in Table 2. Both the alloys exhibited excellent soft magnetic properties in their as-spun state with the coercivity 5.19 A/m and 2.75 A/m for the alloys Fe\(_{40}\)Co\(_{40}\)Cu\(_{0.5}\)Al\(_2\)Zr\(_9\)Si\(_4\)B\(_{4.5}\) and Fe\(_{62}\)Co\(_{9.5}\)Gd\(_{3.5}\)Si\(_{10}\)B\(_{15}\) respectively. As the major emphasis of using FeCo-based materials is for high temperature applications, the temperature variations of saturation magnetisation were measured for the two alloys and are shown in Figs. 7 and 8 respectively. The inset of the figures shows the Curie temperature of these alloys evaluated from the derivative of temperature variation of magnetisation measured at a low magnetising field (2.8 kA/m). Although Fe\(_{62}\)Co\(_{9.5}\)Gd\(_{3.5}\)Si\(_{10}\)B\(_{15}\) alloy has excellent soft magnetic properties, its Curie temperature (596 K) and room temperature saturation magnetisation (0.98 T) were low compared to the other measured alloy. An increase in magnetisation of this alloy is observed at 900 K due to the formation of iron boride phase during primary crystallization process. Curie temperature of Fe\(_{40}\)Co\(_{40}\)Cu\(_{0.5}\)Al\(_2\)Zr\(_9\)Si\(_4\)B\(_{4.5}\) alloy becomes 736 K with room temperature saturation magnetisation as 1.18 T. Magnetisation starts increasing with temperature from 765 K indicating the formation of magnetic phase due to primary crystallization. Saturation magnetisation of the system increases rapidly and becomes maximum with 0.92 T at 900 K. Such high value of saturation magnetisation at high temperature suggests the formation of FeCo phase after primary crystallization and is confirmed by XRD study. Magnetisation decreases when the temperature is
above 900 K. Saturation magnetisation again increases at 950 K due to the formation of iron boride phase during secondary crystallisation process. High saturation magnetisation and Curie temperature of FeCo phase produced after primary crystallization suggests that FeCo₄₀Cu₀₉₅Al₂Zr₁₅Si₁₁B₁₅ alloy after partial crystallization will lead to potential material for high temperature application. Annealing behaviour of the two studied materials are in the progress and will be reported soon.

5. Conclusions

Crystallization kinetics of two melt-spun ribbons having composition Fe₄₀Co₄₀Cu₀₉₅Al₂Zr₁₅Si₁₁B₁₅ and Fe₆₂Co₅₅Gd₉₅Si₁₀B₁₅ were studied. Three stages of crystallization process were observed in both the alloys. Super cooled region was observed in Fe₆₂Co₅₅Gd₉₅Si₁₀B₁₅ indicating the ability of formation of bulk alloy by Cu-mould casting and 1 mm diameter rod was prepared. Measurement of time constant for the formation of primary crystallization indicated that the temperature stability of the amorphous phase in Fe₆₂Co₅₅Gd₉₅Si₁₀B₁₅ was better compared to the other measured alloy, which was primarily due to the higher crystallization temperature. Both the alloys exhibited excellent soft magnetic properties. However, formation of strong ferromagnetic FeCo-based phase after primary crystallization in Fe₄₀Co₄₀Cu₀₉₅Al₂Zr₁₅Si₁₁B₁₅ alloy suggested that both Curie temperature and saturation magnetisation could be enhanced by partial crystallization of this amorphous material and could be a promising candidate for high temperature application.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coercivity, (H_c) (A/m)</th>
<th>Remanence, (M_r) (T)</th>
<th>Saturation magnetisation, (M_s) (T)</th>
<th>Curie temperature, (T_c) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₄₀Co₄₀Cu₀₉₅Al₂Zr₁₅Si₁₁B₁₅</td>
<td>5.19</td>
<td>0.40</td>
<td>1.18</td>
<td>736</td>
</tr>
<tr>
<td>Fe₆₂Co₅₅Gd₉₅Si₁₀B₁₅</td>
<td>2.75</td>
<td>0.27</td>
<td>0.98</td>
<td>596</td>
</tr>
</tbody>
</table>

Fig. 7 Temperature variations of saturation magnetisation for Fe₄₀Co₄₀Cu₀₉₅Al₂Zr₁₅Si₁₁B₁₅. Inset shows the Curie temperature of the alloy.

Fig. 8 Temperature variations of saturation magnetisation for Fe₆₂Co₅₅Gd₉₅Si₁₀B₁₅. Inset shows the Curie temperature of the alloy.

Acknowledgement

Financial support to one of the authors (AM) from JSPS is gratefully acknowledged.

REFERENCES