Crystallization Kinetics in an Amorphous Al–Ni–Mm–Fe Alloy

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Differential scanning calorimeter (DSC) has been used to study the crystallisation kinetics of Al$_{87.5}$Ni$_7$Mm$_2$Fe$_{0.5}$ alloy. Both isochronal and isothermal DSC plots showed that the Al$_{87.5}$Ni$_7$Mm$_2$Fe$_{0.5}$ alloy undergoes three stages crystallisation process. The first peak corresponds to the precipitation of fcc-Al from the amorphous matrix at around 160 °C. Isothermal DSC traces showed that there is a short incubation stage for the formation of nanoscale Al particles. The value of Avrami exponent suggests that the crystallization of Al crystals starts with a nucleation process for a short time and finally controlled by a growth mechanism. The second peak corresponds to the crystallization of Al$_{2}$Ni$_{4}$Ce$_{6}$ from the matrix at around 320 °C with a nucleation rate, which decreases with time, and a constant growth rate. The activation energy calculated for the crystallization of Al$_{2}$Ni$_{4}$Ce$_{6}$ phase is 288 ± 5.9kJ/mol, 324.6 ± 18kJ/mol, 292 ± 6kJ/mol by Kissinger, Johnson-Mehl-Avrami and Arrhenius type equations. The difference in the values of kinetic energy is mainly due to different annealing conditions. The third peak at around 340 °C corresponds to the precipitation of intermetallic compounds from the remaining matrix.

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1. Introduction

Since the first report on Al-based amorphous alloys with high strength and good bending ductility in Al–Ni–Si system, a number of Al-based amorphous alloys have been synthesised by rapid solidification techniques. Among these, Al-rich (>80 at%) Al-TM-RE (TM = transition metal, RE = rare earth) amorphous alloys with high specific strength and good ductility have attracted considerable attention because of their increasing social needs as lightweight materials and inherent scientific and technological importance. It has been reported that Al–Ni–Ln (Ln = Y, La or Ce) amorphous alloys exhibit tensile fracture strength above 1000 MPa with good bending ductility, even at Al-rich compositions of 84 to 86 at%. In this system, the highest strength reported is as high as 1250 MPa, which is about 2 to 2.5 times more than that of conventional high-strength aluminium alloys. By partially crystallizing the as-quenched Al-based amorphous alloys nano-sized fcc-Al precipitate homogeneously in the matrix. It is reported that the tensile strength reaches as high as 1560 MPa at room temperature in Al$_{88}$Ni$_{5}$Ce$_{5}$Fe$_{5}$ amorphous alloys containing around 25 percent volume fraction of fcc-Al particles with a particle size 3 to 5 nm. Such a high strength of the alloys results from the dispersion strengthening of defect free nanoscale fcc-Al particles in the amorphous matrix. In order to prepare these alloys in bulk one has to consolidate amorphous ribbons without losing their thermal stability and mechanical properties. To achieve this, it is necessary to understand the crystallization mechanism. Literature and report the formation of nano-scale Al-particles from Al–Ni based amorphous alloys. The crystallisation kinetics of fcc-Al in Al–Ni–Ce and Al–Ni–Y amorphous alloys have been intensively investigated. All these alloys contain expensive rare earth materials. Thus, substituting rare earth by cheaper rare earth mixtures such as misch metal (Mm) is potentially attractive. The crystallisation mechanism of Al-based amorphous alloys containing misch-metal is complex because of the presence of several glass-forming elements.

In this paper, the crystallization behaviour of an amorphous Al$_{87.5}$Ni$_{7}$Mm$_{2}$Fe$_{0.5}$ alloy has been investigated by differential scanning calorimetry (DSC). The amorphous nature and the microstructure of the alloy were studied by X-ray diffractometry (XRD). This study is necessary to determine the parameters for preparation of nanoscale Al containing Al–Ni–Mm alloys in bulk by rapid solidification-extrusion route.

2. Experimental Procedure

2.1 Preparation of alloy

An alloy ingot with a composition of Al$_{87.5}$Ni$_{7}$Mm$_{2}$Fe$_{0.5}$ (at%) was prepared by induction melting a mixture of pure Al (99.9 mass%), Ni (99.9 mass%) and Mm (Mm contains 55 mass% Ce, 25 mass% La, 10 mass% Nd, 7 mass% Pr and 3 mass% Fe) in a purified argon atmosphere. Rapidly solidified ribbons with a width of 12–15 mm, length of several meters and thickness of about 30 µm were prepared in an argon atmosphere by a single roller melt-spinning technique. The wheel speed was maintained at 12.3 m/s.

2.2 Characterisation of the alloy

The amorphous nature of the ribbons and the microstructure of the metastable and stable crystalline phases were assessed by X-ray diffraction (Philips, 35 kV, 25 mA, Cu K$_{α}$, scan rate 2 degree min$^{-1}$). The crystallization behaviour of the ribbon was characterised by differential scanning calorimetry (Perkin-Elmer DSC-7) under a high purity argon atmosphere. The DSC was calibrated by using pure In and Zn standards, giving an accuracy of ±0.3°C for temperature and ±0.02 mW for the energy measurements. The DSC study was conducted by heating the sample from room temperature to 450°C at different heating rates ranging from 5 to 40°C/min. For the isothermal DSC analysis, as-quenched amorphous ribbons were heated at a rate of 200°C/min to the desired temperatures and held for maximum 30 minutes of time before rapidly cooling to room temperature.

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3. Results and Discussion

X-ray diffractogram of the as-quenched sample (Fig. 1a) showed only a broad halo centred on sin θ/λ = 0.207, which is characteristic of a glassy phase. Figure 2 shows the continuous heating DSC plots of the alloy at heating rates of 5, 10, 20, 30 and 40 °C min⁻¹. DSC scans in Fig. 2 reveal three peaks indicating that the crystallization occurs through three stages contrary to earlier findings where only two crystallization peaks have been reported. The crystallization peak temperatures (T_p) of the three peaks can be determined from the DSC curves.

The most extensive used equation for the determination of the apparent activation energy E_a is proposed by Kissinger and can be expressed as:

$$\frac{\beta}{T^2} = \frac{k e^{-E_a/RT}}$$

where β is the heating rate, T is the peak temperature in Kelvin, R is the gas constant and k is the pre-exponential factor. The activation energy is calculated from the slope of the linear plot of ln(β/T²) as a function of the peak temperature (Fig. 3). The activation energy for the crystallization evaluated from the slope of the linearity is 128.8 ± 6 kJ/mol, 288 ± 5.9 kJ/mol and 256 ± 4.4 kJ/mol for the first, second and third peak respectively.

XRD results proved that the first exothermic peak around 160 °C corresponds to the crystallization of fcc-Al from the amorphous matrix (Fig. 1b) and the second peak around 320 °C corresponds to the precipitation of Al₁₁(La,Ce)₃ along with fcc-Al from the amorphous matrix (Fig. 1c). The third peak around 340 °C corresponds to the precipitation of intermetallic compounds Al₃Ni, Al₁₁(La,Ce)₃ and Al₃Ce from the matrix (Fig. 1d). With the increase of heating rate the crystallisation peak shifts towards higher temperatures.

Figure 4(a) shows the isothermal DSC traces of the amorphous Al₈₇.₅Ni₇Mm₇Fe₀.₅ alloy at the temperature range of 145 to 160 °C for the first exothermic peak. Table 1 shows the kinetic parameters determined from the isothermal analysis for the crystallization of fcc-Al from the amorphous matrix. The exothermic reaction begins to appear after a short incubation period, followed by a maximum exothermic peak and then a rapid decrease in the reaction. This feature is in good agreement with that for the ordinary precipitation behaviour that takes place through the nucleation and growth reaction. The smaller activation energy derived from the Kissinger equation also suggests that crystallization takes place through the short nucleation stages followed by a growth mechanism. By integrating the exothermic peaks in Fig. 4(a) the volume fraction of the crystallised phase as a function of time was obtained as shown in Fig. 4(b). The figure displays the familiar sigmoidal relationship. The isothermal phase transformation is generally described by the well known Johnson-Mehl-Avrami (JMA) transformation kinetics equation.

![Fig. 1 X-ray diffraction pattern of Al₈₇.₅Ni₇Mm₇Fe₀.₅ alloy](image1.png)

![Fig. 2 Continuous heating DSC curves of amorphous Al₈₇.₅Ni₇Mm₇Fe₀.₅ alloy at different heating rates.](image2.png)
Fig. 3 The Kissinger plots of the peak temperatures of the first, second and third exothermic reactions for amorphous Al$_{87.5}$Ni$_7$Mm$_5$Fe$_{0.5}$ ribbon. The activation energies for their exothermic reactions evaluated from the slope of the linear relation are also presented.

\[ E = 250 \pm 4.4 \text{ kJ/mol} \]

\[ E' = 208 \pm 3.5 \text{ kJ/mol} \]

Fig. 4 (a) Isothermal DSC curves and (b) crystallised volume fraction as a function of annealing time for amorphous Al$_{87.5}$Ni$_7$Mm$_5$Fe$_{0.5}$ ribbon annealed at the temperature range from 145 to 160°C.

\[ x = 1 - \exp[-(K(t - t_0))^n] \]  

where \( x \) is the transformed volume fraction at any time \( t \), which is measured as \( A(t)/A(\text{tot.}) \), where \( A(t) \) is the area under the peak up to time \( t \), and \( A(\text{tot.}) \) is the total area; \( n \) is the Avrami exponent, which depends on the nucleation and growth mechanism; \( t_0 \) is the time lag and \( K \) is the reaction rate constant. The values of \( K \) and \( n \) can be calculated using the relationship

\[ \ln[\ln(1/(1-x))] = n \ln(K) + n \ln(t - t_0) \]  

Plots of \( \ln[\ln(1/(1-x))] \) against \( \ln(t - t_0) \) for each annealing temperature are shown in Fig. 5(a). For the range of data between \( x = 0.06 \) to \( 0.50 \) the graphs could be fitted by straight lines with a correlation better than 0.997. The Avrami exponent \( n \) calculated from the slope of equation in Fig. 5(a) and the reaction rate constant \( K \) calculated from the eq. (3) for the first peak are listed in Table 1. The reaction rate constant \( K \) related to the activation energy for the process, \( E_a \), is given by the equation

\[ K = K_a \exp\left(-\frac{E_a}{RT}\right) \]

where \( K_a \) is a constant. Fig. 5(b) shows the variation of \( n \) with the crystallised volume fraction \( x \). Initially, the value of Avrami exponent is in the range of 1.2 to 1.8 then it slightly decreases during the precipitation of fcc-Al. This indicates that the nucleation rate is maximum at the initial stage and then the nucleation rate decreases rapidly followed by growth of Al particles.

The isothermal DSC traces of the amorphous Al$_{87.5}$Ni$_7$Mm$_5$Fe$_{0.5}$ alloy at temperature range of 320 to 340°C (second peak) are shown in Fig. 6(a), in which the exothermic peak represents the precipitation of Al$_{11}(\text{La,Ce})_3$ intermetallic compounds. Figure 6(b) shows the crystallised volume fraction as a function of annealing time. Figure 7(a) shows the JMA plots for the second peak in the continuous heating DSC plots (Fig. 2(a)). The range of data for \( x = 0.1 \) to 0.7 are almost in straight line. The value of \( n \) and \( K \), calculated from the Fig. 7(a) and eq. (3), are also listed in Table 1. Figure 7(b) shows the plot of ln\( K \) against \( 1/T \) (eq. 4) from which the activation energy of the second peak is obtained. The activation energy is found to be 324 ± 18 kJ/mol. Figure 8 shows the variation of the Avrami exponents

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( t_0 ) (min)</th>
<th>( t_1 ) (min)</th>
<th>( \Delta H (J/g) )</th>
<th>Avrami exponent, ( n )</th>
<th>Reaction rate constant, ( K ) (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>145</td>
<td>0.86</td>
<td>1.52</td>
<td>18.26</td>
<td>1.5 ± 0.008</td>
<td>0.98 ± 0.006</td>
</tr>
<tr>
<td>150</td>
<td>0.74</td>
<td>1.16</td>
<td>36.30</td>
<td>1.29 ± 0.005</td>
<td>0.65 ± 0.005</td>
</tr>
<tr>
<td>155</td>
<td>0.42</td>
<td>0.82</td>
<td>32.89</td>
<td>1.26 ± 0.002</td>
<td>0.64 ± 0.002</td>
</tr>
<tr>
<td>160</td>
<td>0.37</td>
<td>0.72</td>
<td>31.05</td>
<td>1.48 ± 0.007</td>
<td>0.55 ± 0.003</td>
</tr>
<tr>
<td>320</td>
<td>19.08</td>
<td>25.14</td>
<td>42.12</td>
<td>3.93 ± 0.012</td>
<td>0.16 ± 0.02</td>
</tr>
<tr>
<td>325</td>
<td>10.94</td>
<td>14.66</td>
<td>59.94</td>
<td>4.07 ± 0.013</td>
<td>0.26 ± 0.01</td>
</tr>
<tr>
<td>330</td>
<td>6.88</td>
<td>9.12</td>
<td>53.2</td>
<td>3.65 ± 0.015</td>
<td>0.43 ± 0.005</td>
</tr>
<tr>
<td>335</td>
<td>1.54</td>
<td>2.04</td>
<td>54.4</td>
<td>3.26 ± 0.05</td>
<td>0.80 ± 0.05</td>
</tr>
</tbody>
</table>

Table 1 Kinetic parameters analysed from the isothermal analysis of the first and second peak crystallization of the Al$_{87.5}$Ni$_7$Mm$_5$Fe$_{0.5}$ alloy.
during the crystallisation of Al$_{11}$(La,Ce)$_3$ phases. The mechanism of crystallisation during the second peak is different from that of first peak. The initial value of $n$ is around 2, then the value of $n$ increases suddenly followed by slow increase with crystallised volume fraction. The values of $n > 4$ are not considered in theories of phase change kinetics. The value $n = 4$ means that the phase transformation occurs in a three-dimensional mode with a constant nucleation rate and a constant growth rate. Transformation for which $3 < n < 4$ are taken to imply that process is diffusion controlled with a nucleation rate which decreases with time. An increasing nucleation rate with time may result in the value of $n > 4$. A possible cause of an increasing nucleation rate may be due to exothermic reaction during transformation.

The activation energy for the crystallisation can also be determined from the Arrhenius type equation which relates the time required $t(x)$ for a given crystallised fraction ($x$) and the annealing temperature. $^{23}$

$$ t(x) = t_0 \exp \left( - \frac{E(x)}{RT} \right) + t, \quad (5) $$

where $t_0$ is a constant and $E(x)$ is the activation energy at any time $t(x)$. When $t(x)$ is replaced by the time for the 50% transformation ($t_{0.5}$), $E(x)$ should be equal to the apparent activation energy $E_a$. Figure 9 shows the apparent activation $E_a$ of the second peak from the time to 50% transformation. The apparent activation energy calculated from eq. (5) at $t_{0.5}$ is 292 ± 6 kJ/mol. The activation energy calculated from the JMA (eq. 3) and Arrhenius type (eq. 5) equations are different from that calculated from the Kissinger equation (eq. 1). The same phenomenon was observed by other Al-based amorphous alloys. $^{14}$ The difference of values of activation energy may be due to different annealing conditions. The crystallisation process of Al$_{11}$(La,Ce)$_3$ precipitates is progressed with a decreasing nucleation rate and is mainly governed by the diffusion controlled growth mechanism. In the isochronal annealing, new nuclei are formed continuously with increasing temperature. Thus, the activation energy for the crystallisation of amorphous alloys should include the sum of the activation energy of nucleation and growth process.

4. Summary

In order to investigate the crystallisation kinetics of amorphous Al$_{87.5}$Ni$_7$Mm$_5$Fe$_{0.5}$ alloy, melt-spun ribbon was heated isochronally and isothermally in DSC. The results obtained are summarised as follows:

(1) The crystallisation takes place in three stages in an Al$_{87.5}$Ni$_7$Mm$_5$Fe$_{0.5}$ alloy. The first peak corresponds to
the crystallization of fcc-Al from the amorphous matrix. The second peak corresponds to the precipitation of $\text{Al}_{11}(\text{La},\text{Ce})_3$ and the third peak corresponds to the precipitation of other intermetallic compounds from the matrix.

(2) The activation energy for the crystallization evaluated from the Kissinger equation is $128 \pm 8$ kJ/mol, $288 \pm 5.9$ kJ/mol and $256 \pm 4.4$ kJ/mol for the first, second and third peak respectively.

(3) From the variation of Avrami exponent, one can see that primary crystal of Al nucleated for the short time at the start of isothermal annealing and finally the crystallisation process is mainly controlled by growth of Al crystals.

(4) The crystallisation of second peak, $\text{Al}_{11}(\text{La},\text{Ce})_3$, takes place with a nucleation rate, which decreases with time and with a constant growth rate with an activation energy $324 \pm 18$ kJ/mol according to JMA equation.

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REFERENCES