

CRYSTALLIZATION KINETICS OF Fe-Si-B-Cu-Nb AMORPHOUS RIBBONS

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Abstract-The crystallization kinetics of Fe_{73.5}Si_{13.5}B₉Cu₁Nb₃ amorphous alloy has been investigated using differential scanning calorimetry (DSC). The crystallization process had two stages, i.e. precipitation of the α -Fe(Si) solid solution and the tetragonal borides. The isothermal transformation data of the amorphous alloy has been fitted successfully to the generalized Johnson-Mehl-Avrami equation. The mean time exponent, n , obtained is close to 2.5. The value of $n = 2.5$ may be interpreted as being due to a diffusion-controlled transformation process with a constant nucleation rate, one likely transformation mode for the crystallization of metallic amorphous alloys. The activation energy of the overall crystallization process deduced from the time to 50% crystallization are about 81 kcal/mole. The value is of the same order as those estimated from viscous flow.

I. INTRODUCTION

The nanocrystalline Fe-Si-B-Cu-Nb alloy developed by Yoshizawa et al.¹ in 1988 shows excellent soft magnetic properties. The alloy is produced by quenching into amorphous ribbons, followed by a heat treatment around its crystallization temperature to produce a homogeneous and ultrafine microstructure with grain size of 10-50 nm. It is suggested that the excellent magnetic properties are closely associated with the nanoscale microstructure.^{2,3} According to Yoshizawa et al.,¹ the additions of Cu and Nb play a profound role in inhibiting the formation of borides and in limiting grain growth of the α -Fe(Si) phase. In order to understand the effect of the additives on the crystallization behaviour of the amorphous alloy, it is essential to study its crystallization kinetics.

Since the crystallization of a metallic glass is a highly exothermic process, differential scanning calorimetry (DSC) is a powerful technique for studying crystallization kinetics of the amorphous alloys. In this study the isothermal crystallization behaviour of Fe-Si-B-Cu-Nb amorphous alloy was investigated using DSC to see if the observed transformation enthalpy is described by the generalized Johnson-Mehl-Avrami equation.

II. EXPERIMENTAL PROCEDURE

Alloy with nominal composition of Fe_{73.5}Si_{13.5}B₉Cu₁Nb₃ was prepared by induction melting in a graphite crucible under an argon atmosphere. The ribbon casting was done in a laboratory melt-spinner, on a copper wheel at speed corresponding to a surface velocity of 40 m/s.

A DSC was used for thermal analysis. Calorimetric specimens weighing 3-6 mg were isothermally annealed under N₂ atmosphere at a heating rate of 70 °C/min to the required isothermal temperatures. The transformation kinetics were determined by the enthalpy evolved as a function of time, because the integrated enthalpy to a certain time divided by the total heat evolved is directly proportional to the volume fraction transformed as a function of time. These data were then fit to the generalized Johnson-Mehl-Avrami equation^{4,5}

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

In its logarithmic form the above equation becomes

$$\log[-\log(1-x)] = \log\left(\frac{k}{2.303}\right) + n \log t \quad (2)$$

where x is the fraction transformed, k is the rate constant and n is the time exponent.

Activation energy for the overall crystallization process was obtained from the temperature dependence of the time to 50% crystallization:

$$t_{0.5} = t_0 \exp\left(\frac{E}{RT}\right) \quad (3)$$

where E is the activation energy, t_0 is a constant and R is the gas constant.

III. RESULTS AND DISCUSSION

X-ray diffraction shows that all as-quenched ribbons are amorphous. The crystallization temperature of the amorphous alloy was examined by DSC at a heating rate of 10 °C/min. Fig. 1 shows the DSC curve of the alloy. Two exothermic peaks observed on the DSC curve reveal that the crystallization process included two stages to obtain the final stable rearrangement. According to x-ray analysis and electron diffraction patterns, the first exothermic peak was due to the precipitation of the α -Fe(Si) solid solution, and the second peak was attributed to tetragonal borides. The initial crystallization temperature of the alloy determined from the DSC data is 536 °C, and was used as guideline for the isothermal annealing experiments. Fig. 2 shows a typical DSC curve of the $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Cu}_1\text{Nb}_3$ alloy for an isothermal annealing at 515 °C. It reveals that there exists an

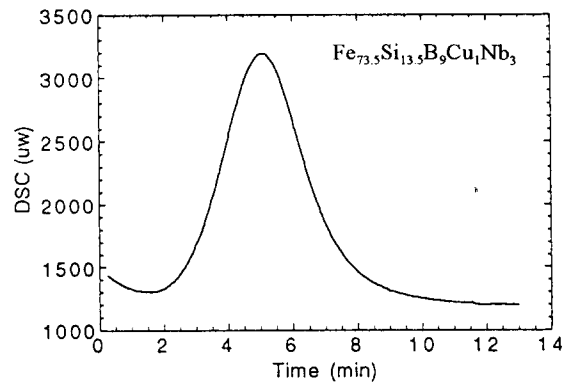


Fig. 2 Typical DSC curve of $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Cu}_1\text{Nb}_3$ alloy for an isothermal annealing at 515 °C.

incubation period before the onset of the transformation. This incubation time depends on the isothermal annealing temperature. The significance of the incubation time was discussed by Scott et al.⁶ For kinetic studies the time $t = 0$ was taken as the end of this incubation period. The fraction transformed $x(t)$ up to any time t was obtained by the integrated enthalpy up to this time divided by the total heat evolved. The $x(t)$ of the amorphous alloy as a function of time, t , for each annealing temperature are shown in Fig. 3. The $x-t$ curves have a sigmoidal shape with a central region where the rate is highest. The transformation data for the alloy were then fitted to Eq. (2) by plotting $\log[-\log(1-x)]$ versus $\log t$, for $0.1 \leq x \leq 0.85$, as shown in Fig. 4. As can be seen, there is no systematic variation of slope with annealing temperature for

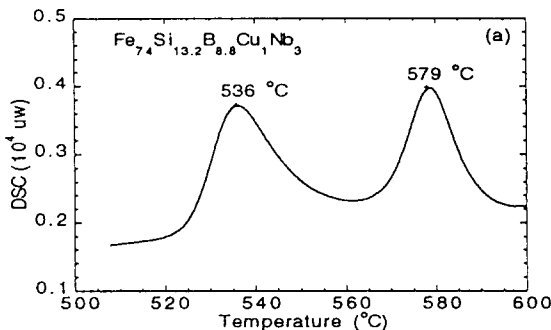


Fig. 1 DSC curve at a heating rate of 10 °C/min, showing two exothermic peaks at 536 and 579 °C.

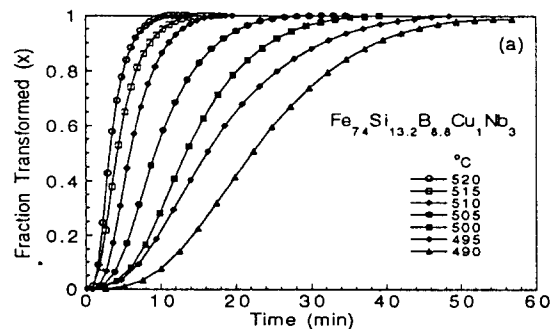


Fig. 3 Volume of fraction transformed at various annealing temperatures as a function of time.

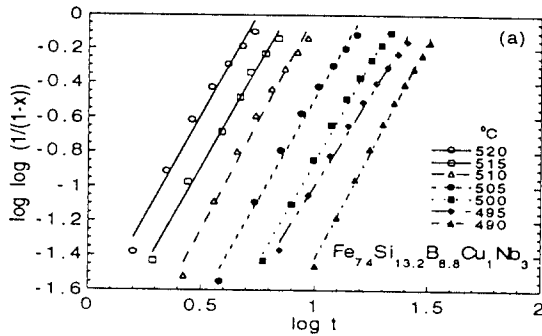


Fig. 4 $\log[-\log(1-x)]$ versus $\log t$ plots within $0.1 \leq \text{fraction transformed}, x, \leq 0.85$.

the alloy. The average value of n determined by the slope of the graphs is close to 2.5 as listed in Table I. It is well known that two major types of transformations may be treated by the application of the Johnson-Mehl-Avrami equation, i.e. diffusion controlled transformation and diffusionless or cellular transformations. All the evidence up to date is that the crystallization of metallic glasses is diffusion controlled. To explain the experimental data we may theoretically consider a special case in which circumstance the fraction transformed is given by⁴:

$$x(t) = 1 - \exp\left[-\left(\frac{c_\beta - c_\alpha}{c_m - c_\beta - c_\alpha}\right) \int_0^t v I dt\right] \quad (4)$$

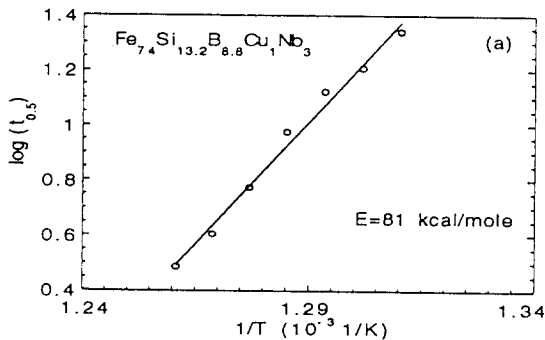


Fig. 5 Determination of activation energy from the time taken for 50% transformation.

Table I. Parameters determined from experiment and the equations of $x = 1 - \exp(-kt^n)$ and $t_{0.5} = t_0 \exp(E/RT)$; n , the time exponent; $t_{0.5}$, the time to 50% transformation; and E , the activation energy.

Temperature	n	$t_{0.5}$	$E(\text{kcal/mole})$
520	2.4	3.1	
515	2.4	4.0	
510	2.5	5.9	
505	2.4	9.4	81
500	2.4	13.2	
495	2.2	16.1	
490	2.5	21.8	

where c_β and c_α are the concentrations of solute in the crystal and the amorphous matrix, respectively. Here c_m is the initial solute concentration in the amorphous matrix, I the nucleation rate, and v the volume of the transformed region nucleated at $t = 0$. In the absence of interfacial instabilities, the growth follows parabolic law with time. Therefore, at time t the radius of a crystal nucleated at time $t = 0$ is given by⁴

$$r = \left(2D \frac{c_m - c_\alpha}{c_\beta - c_\alpha}\right)^{\frac{1}{2}} t^{\frac{1}{2}} \quad (5)$$

If the crystal is assumed to be spherical, the rate of the volume growth of the crystal is

$$\frac{dv}{dt} = \frac{4\pi}{3} \frac{dr^3}{dt} = 4\sqrt{2}\pi D^{\frac{3}{2}} \left(\frac{c_m - c_\alpha}{c_\beta - c_\alpha}\right)^{\frac{3}{2}} t^{\frac{1}{2}} \quad (6)$$

The volume at time t is then given by

$$v = \int_0^t dv = \frac{8\sqrt{2}\pi}{3} D^{\frac{3}{2}} \left(\frac{c_m - c_\alpha}{c_\beta - c_\alpha}\right)^{\frac{3}{2}} t^{\frac{3}{2}} \quad (7)$$

Substituting Eq. (7) into Eq. (4) gives

$$x(t) = 1 - \exp\left[-\frac{16\sqrt{2}\pi}{15} D^{\frac{3}{2}} I \left(\frac{c_m - c_\alpha}{c_\beta - c_\alpha}\right)^{\frac{1}{2}} t^{\frac{5}{2}}\right] = 1 - \exp(-kt^{\frac{5}{2}}) \quad (8)$$

where

$$k = \frac{16\sqrt{2}\pi}{15} D^{\frac{3}{2}} I \left(\frac{c_m - c_\alpha}{c_\beta - c_\alpha}\right)^{\frac{1}{2}}$$

Eq. (8) is a form of the Johnson-Mehl-Avrami equation with time exponent of $n = 2.5$. It is apparent that the calculation gives a same time-exponent n , as the experimental value of the amorphous alloy $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Cu}_1\text{Nb}_3$. Therefore, we may conclude that the crystallization of the $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Cu}_1\text{Nb}_3$ amorphous alloy is diffusion controlled with a constant nucleation rate. However, any precise interpretation of the value of n requires detailed microstructural investigations which is now being performed in our laboratory.

Fig. 5 shows plots of $\log t_{0.5}$ versus $1/T$ for the alloy. Activation energy obtained from the slope by fitting the experimental data to a straight line are 81 kcal/mole for the $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Cu}_1\text{Nb}_3$ alloy. The value is comparable with those reported by Scott⁷ for Fe-Ni-P-B and Fe-Ni-P-B-Si metallic amorphous alloys. Based on a structure relaxation model, Chen⁸ has calculated the apparent activation energy for viscous flow, which ranges from 10-20 kcal/mole for unstable amorphous alloys to 100-150 kcal/mole for stable metallic amorphous alloys. The activation energy obtained in the present work lies between the two extreme cases, indicating that the amorphous alloy is less stable near their glass temperatures, T_g .

IV. SUMMARY AND CONCLUSIONS

The $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Cu}_1\text{Nb}_3$ amorphous alloy shows

two exothermic peaks in the DSC curve, indicating that the crystallization takes place through two stages. The two transition peaks have been identified, by x-ray analysis, to be due to the precipitation of the α -Fe(Si) phase and the tetragonal borides respectively.

The isothermal crystallization of the amorphous alloy was well described by the generalized Johnson-Mehl-Avrami equation with the mean time-exponents $n = 2.5$. This result has been interpreted as being due to a diffusion controlled transformation process with a constant nucleation rate.

Activation energy deduced from the time to 50% transformation is 81 kcal/mole for the alloy. The value is of the same order as those predicted for viscous flow.

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