Time-Scaling Properties and Crystallization Kinetics of Amorphous Alloys[†]

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We have investigated the time-scaling properties of the isothermal crystallization kinetics for amorphous $\text{Co}_{75}\text{B}_{25}$, $\text{Fe}_{80}\text{B}_{20}$, $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$, $\text{Fe}_{81}\text{B}_{17}\text{Si}_2$ and $\text{Fe}_{60}\text{Ni}_{20}\text{B}_{10}\text{Si}_{10}$ alloys by differential scanning calorimetry. All the alloys exhibit a single crystallization stage. The time scale was defined as the time when the crystallization has reached half completion. All the time-scaled crystallization curves of each alloy fall onto a single master curve of the Johnson-Mehl-Avrami form in each case. The Avrami exponent indicates that the crystallization process of the $\text{Fe}_{60}\text{Ni}_{20}\text{B}_{10}\text{Si}_{10}$ is governed by interface-controlled growth with a constant nucleation rate, whereas those of the other alloys are by interface-controlled growth of a fixed number of nuclei. The Williams-Landel-Ferry equation based on a free-volume consideration gives a universal function of time-scaling parameter as a function of temperature for all the alloys. This suggests that we have to take into account the relaxation occurring in the amorphous phase outside the crystallite in the crystallization process.

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I. Introduction

The study of the crystallization of amorphous alloys is of scientific interest as it represents a phase transformation occurring under extreme conditions far from equilibrium. The subject is also of technological interest because of the drastic deterioration of promising properties of amorphous alloys upon crystallization, as well as because of the possibility of using amorphous alloys as a starting material for producing desirable fine microstructures by controlled crystallization. The mechanisms involved in the transformation from the metastable amorphous state to the stable crystalline state and their kinetics depend on the composition, concentration of nucleation sites, diffusion parameters, thermal history of the sample, etc. However, we can observe a similarity in the shape of the kinetic curves in spite of difference of these factors.

The crystallization of amorphous alloys is a first-order phase transformation. A key concept in the modern understanding of nucleation and growth at first-order phase transformations is that with proper scaling, the pattern of phase transformation is reduced to a universal form. So far, the success of scaling concepts in describing the crystallization kinetics has been reported in amorphous Fe-Ni-P⁽¹⁾, Fe-B-Si⁽²⁾⁽³⁾, Fe-B-Si-(Cr or C)⁽⁴⁾ alloys. Only a few alloys focused on the Fe-B-Si system have been studied. The purpose of this study is therefore to perform a systematic investigation of the time-scaling

properties of the crystallization kinetics in five amorphous alloys that belong to four classes, monometal-monometalloid, multimetal-monometalloid, monometal-multimetalloid and multimetal-multimetalloid systems. All five alloys exhibit a single crystallization stage. Differential scanning calorimetry (DSC) is used to study the crystallization kinetics.

II. Experimental Procedure

Amorphous alloys of $\text{Co}_{75}\text{B}_{25}$, $\text{Fe}_{80}\text{B}_{20}$, $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$, $\text{Fe}_{81}\text{B}_{17}\text{Si}_2$ and $\text{Fe}_{60}\text{Ni}_{20}\text{B}_{10}\text{Si}_{10}$ were prepared by a single-roll melt-spinning method. The subscripts represent the chemically analyzed compositions (mol%). The ribbons prepared were about 1 mm wide and 30 to 40 μm thick. They were confirmed to be amorphous by X-ray diffraction using CuK_α radiation.

Calorimetric measurements were performed using a Rigaku DSC-8230B with computerized data acquisition system. The temperature and energy axes of the instrument were calibrated from the melting endotherms of pure lead, zinc and tin. Linear heating and isothermal annealing DSC curves were measured. In the isothermal experiments, all samples were heated at a rate of 0.33 K/s from room temperature to annealing temperatures and annealed. Annealing temperature were in the range of 91 to 96% of the crystallization temperature of each alloy. All measurements were carried out in a flow of oxygen-free argon gas. Powdery Al_2O_3 was used as a reference material. The crystallization temperatures, taken as the peak onset on linear heating at 0.33 K/s, were 720 K for $\text{Co}_{75}\text{B}_{25}$, 698 K for $\text{Fe}_{80}\text{B}_{20}$, 695 K for $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$, 753 K for $\text{Fe}_{81}\text{B}_{17}\text{Si}_2$ and 771 K for $\text{Fe}_{60}\text{Ni}_{20}\text{B}_{10}\text{Si}_{10}$.

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III. Results and Discussion

Figure 1 shows the isothermal DSC curves. All alloys show only a single exothermic peak. Also, single exothermic peak was observed on linear heating DSC runs for all alloys. This indicates that the crystallization of these alloys occurs in a single stage. The crystallization kinetics was characterized from the isothermal annealing DSC curves. For kinetic studies the time origin was taken as the start of the crystallization exotherm. This is the point where the DSC curve starts to deviate from the baseline. The fraction crystallized $x(t)$ at any time t was determined as the ratio $A(t)/A(\infty)$, where $A(t)$ is the area under the exothermic peak up to time t and $A(\infty)$ is the total area. The areas were derived by measuring the ordinates at closely spaced values of t and using a Simpson-type integration. The extrapolation of the baseline under the peak was estimated using the assumption that the con-

tributions of the amorphous and crystalline phases to the specific heat of the partially crystallized sample were in direct proportion to their volume fractions⁽⁵⁾. The fraction crystallized versus time relationships for each annealing temperature in $\text{Co}_{75}\text{B}_{25}$ alloy are illustrated in Fig. 2 and are of the familiar sigmoidal type. The other alloys also showed same feature. The crystallization process is accelerated with increasing temperature. The qualitative similarity in the shape of these isotherms strongly suggests that the data can be replotted on a scaled time axis.

The crystallization of amorphous alloys is well described by the Johnson-Mehl-Avrami equation,

$$x(\tau) = 1 - \exp\left(-\frac{1}{3} \pi \tau^n\right) \quad (1)$$

where $\tau = t/t_0$ and n is the Avrami exponent that depends on the process of crystallization. A characteristic time scale t_0 is related to the nucleation and growth parameters as follows:

Fig. 1 Isothermal DSC curves at various temperatures for all the amorphous alloys.

Fig. 2 Fraction crystallized, X , of the amorphous $\text{Co}_{75}\text{B}_{25}$ alloy as a function of time for various annealing temperatures.

$$\begin{aligned} t_0 &= (4Nu^3)^{-1/3} & \text{for } n=3 \\ t_0 &= (Iu^3)^{-1/4} & \text{for } n=4 \end{aligned}$$

where N is the number of nuclei per unit volume, u is the growth rate and I is the nucleation rate per unit volume.

We may characterize the time scale of the crystallization by defining the time $t_{1/2}$ at which the crystallization is 50% complete. From $x(t_{1/2}/t_0)=1/2$ one can obtain the relations $t_{1/2}=t_0/1.15$ for $n=3$ and $t_{1/2}=t_0/1.11$ for $n=4$. Therefore, the value of $t_{1/2}$ can be interpreted as a measure of nucleation and growth parameters of the crystallization process. For each isotherm, we experimentally found the time $t_{1/2}$ and redefined the time scale of each isotherm to be $t/t_{1/2}$. Figure 3 shows the results of the rescaling procedure for all alloys. All the time-scaled isotherms of each alloy lie on a single master curve in each case. These results demonstrate that the crystallization kinetics obeys a time-scaling law. It is noteworthy that the annealing temperatures used here are in the range of 91 to 96% of the crystallization temperature for each alloy. Scaling characteristics of some iron-based amorphous alloys have been reported⁽¹⁾⁻⁽⁴⁾ but, to our knowledge, this is the first systematic test of time-scaling properties of crystallization kinetics on amorphous alloys with single crystallization stage.

The solid lines in Fig. 3 are fits to the scaled Johnson-Mehl-Avrami equation,

$$x\left(\frac{t}{t_{1/2}}\right) = 1 - \exp\left[-b\left(\frac{t}{t_{1/2}}\right)^n\right] \quad (2)$$

where b is a constant. The agreement between the curve and experimental data is satisfactory. The values of b and n used in the calculation are given in Table 1 together with the values of activation energy E for crystallization. The Kissinger method was used to determine the activation energy. We obtain $n=3.0 \pm 0.1$ for the four alloys ex-

cept $\text{Fe}_{60}\text{Ni}_{20}\text{B}_{10}\text{Si}_{10}$. This suggests that the crystallization process is governed by interface-controlled growth of a fixed number of nuclei. For the $\text{Fe}_{60}\text{Ni}_{20}\text{B}_{10}\text{Si}_{10}$ alloy the value of the exponent is $n=4.1$. This means interface-controlled growth with a constant nucleation rate. Several authors have reported the values of n and E for these alloys as follows: $n=2.8$ and $E=239$ kJ/mol for $\text{Fe}_{80}\text{B}_{20}$ ⁽⁶⁾, $n=3.0$ and $E=299$ kJ/mol for $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ ⁽⁷⁾, $n=2.8$ and $E=328$ kJ/mol for $\text{Fe}_{82}\text{B}_{17}\text{Si}_1$ ⁽⁸⁾ and $E=220$ kJ/mol for $\text{Co}_{75}\text{B}_{25}$ ⁽⁹⁾. Furthermore, the studies⁽⁸⁾⁽⁹⁾ of the morphology of the crystallization in these amorphous alloys by optical and transmission electron microscopy have revealed that the crystallization of $\text{Fe}_{80}\text{B}_{20}$, $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ and $\text{Fe}_{82}\text{B}_{17}\text{Si}_1$ alloys is eutectic and the crystallization of $\text{Co}_{75}\text{B}_{25}$ alloy is polymorphic. Our results agree with these reports.

Figure 4 illustrates the time-scaled plots of fraction of crystallized volume for the four alloys except $\text{Fe}_{60}\text{Ni}_{20}\text{B}_{10}\text{Si}_{10}$. As can be seen, all data points fall into a universal curve. This demonstrates the universality of the time-scaled Johnson-Mehl-Avrami equation for the constant value of the exponent n in the alloys.

Next, we discuss the temperature dependence of the time-scaling parameter $t_{1/2}$. The rapid increase in the time-scaling parameter with decreasing temperature was observed for all the alloys used in this study. Roig *et al.*⁽⁴⁾ have also reported similar behavior in Fe-Ni-P alloy. They suggest that it is inappropriate to regard the very large temperature variation of the characteristic time as a simple activated process. The activation assumption is based on a gradual freezing and does not allow for a divergence of the scaling parameter. Recent computer simulations performed on quenched Ising models have demonstrated that the time scale that characterizes recrystallization tends to diverge at low temperatures (low-temperature freezing) in the conserved order-parameter case⁽¹⁰⁾.

The abrupt increase of the time-scaling parameter with decreasing temperature means slowing down of the crystallization process. This is characteristic of relaxation phenomena in the amorphous state. So far, several empirical expressions have been proposed to describe the temperature dependence of relaxation processes in amorphous state. Among them we used the Williams-Landel-Ferry (WLF) equation⁽¹¹⁾ to describe the temperature dependence of the scaling parameter. This is because the WLF equation involves only two parameters as shown in the equation,

Table 1 Fitted parameters b and n of the scaled Johnson-Mehl-Avrami equation and activation energies for crystallization.

Alloy	b	n	$E/\text{kJ} \cdot \text{mol}^{-1}$
$\text{Co}_{75}\text{B}_{25}$	0.70	3.0	228
$\text{Fe}_{80}\text{B}_{20}$	0.69	2.9	218
$\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$	0.72	3.0	324
$\text{Fe}_{81}\text{B}_{17}\text{Si}_2$	0.71	3.1	350
$\text{Fe}_{60}\text{Ni}_{20}\text{B}_{10}\text{Si}_{10}$	0.73	4.1	337

Fig. 3 Time-scaled curves of fraction of crystallization. Solid lines are fits of the scaled Johnson-Mehl-Avrami equation with the parameters given in Table 1.

Fig. 4 Time-scaled plots of the crystallization for the four amorphous alloys, which give the same universal curve with the value of Avrami exponent $n=3$.

$$t_{1/2} = t_1 \exp \left\{ \frac{-20.4(T - T_0)}{101.6 + T - T_0} \right\} \quad (3)$$

where T_0 is the reference temperature and t_1 is the value of $t_{1/2}$ at T_0 . This equation is based on free-volume considerations and very useful in describing the temperature dependence of relaxation processes in amorphous polymers. As mentioned in the original paper⁽¹¹⁾, the universality of the equation suggests that the free volume at the glass transition temperature T_g and the rate of increase of the free volume with temperature are the same for all polymers. Quite satisfactory fits were obtained for all the alloys and the values of the fitting parameters are given in Table 2. The value of T_0 is in the range of 567 to 669 K. It has been found for a wide variety of polymers that T_0 is typically 50 K above T_g . Since the glass transition is not thermally manifest in all the alloys used here, we take the

Table 2 Fitted parameters t_1 and T_0 of the Williams-Landel-Ferry equation and the values of $T_x - T_0$, where T_x is the crystallization temperature.

Alloy	t_1/s	T_0/K	$T_x - T_0/K$
Co ₇₅ B ₂₅	7.0×10^7	586	157
Fe ₈₀ B ₂₀	2.9×10^7	567	149
Fe ₄₀ Ni ₄₀ B ₂₀	2.3×10^7	581	133
Fe ₈₁ B ₁₇ Si ₂	1.0×10^7	649	112
Fe ₆₀ Ni ₂₀ B ₁₀ Si ₁₀	2.0×10^7	669	139

crystallization temperature T_x measured dynamically as an acceptably close estimate of T_g . So, the values of T_0 are approximately 110 to 160 K below T_x as indicated in Table 2. This shows a low-temperature freezing behavior. It should be noted here that our experimental data refer to temperatures in the range of 30 to 65 K below T_x (T_g), whereas data of polymers correspond to temperatures above T_g .

Figure 5 illustrates a plot of the ratio of $t_{1/2}$ to t_1 against $T - T_0$ for all the alloys. Although values of two coefficients (-20.4 and 101.6) in eq. (3) are determined from the composite curves calculated for polymers, all the data points fall on a universal curve in the range covered. This demonstrates that the temperature dependence of the time-scaling parameter for the crystallization of these amorphous alloys can be described by the WLF equation. For amorphous polymers, the WLF equation gives a universal function for the temperature dependence of relaxation processes which depend on free volume⁽¹¹⁾. Basically, the WLF equation is an expression

Fig. 5 Time-scaling parameter vs temperature curve for all the amorphous alloys showing the universality of the Williams-Landel-Ferry equation.

which represents the temperature dependence of free volume. Therefore, the result of Fig. 5 strongly suggests that we have to take into account relaxation behavior accompanied with free volume changes occurring in the amorphous phase outside the crystallites in the crystallization process. As pointed out by Roig *et al.*⁽¹⁾, this means that outward motion of the growing crystallization front can not be simply understood in terms of the usual surface-tension and volume-energy arguments.

IV. Conclusion

The time-scaling properties of the isothermal crystallization kinetics were studied for amorphous Co₇₅B₂₅, Fe₈₀B₂₀, Fe₄₀Ni₄₀B₂₀, Fe₈₁B₁₇Si₂ and Fe₆₀Ni₂₀B₁₀Si₁₀ alloys. The results obtained are summarized as follows:

(1) All the crystallization curves for various temperatures of each alloy collapse into a single master curve of the Johnson-Mehl-Avrami form in each case when the time axis is rescaled by the time $t_{1/2}$. This demonstrates that the crystallization kinetics of all the alloys obeys a time-scaling law under the present annealing condition.

(2) The Johnson-Mehl-Avrami analysis suggests that the crystallization kinetics of the Fe₆₀Ni₂₀B₁₀Si₁₀ alloy is governed by interface-controlled growth with a constant nucleation rate and that of the other alloys is by interface-controlled growth of a fixed number of nuclei.

(3) The temperature dependence of the time-scaling parameter ($t_{1/2}$) shows a low-temperature freezing behavior and can be described by the Williams-Landel-Ferry equation based on a free-volume consideration. This strongly suggests that we have to take into account the relaxation behavior occurring in the amorphous phase outside the crystallites in the crystallization process.

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