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Time-scaling and crystallization kinetics of three Fe–B-based metallic glasses

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Time-scaling properties of the isothermal transformation kinetics have been tested for three Fe–B-based metallic glasses exhibiting two crystallization stages. The time scale was defined as the time at which crystallization has reached half completion and is derived from calorimetric (DSC) data. The temperature dependence of the time-scaling parameter shows a low-temperature freezing behaviour and can be described by empirical functions based on free-volume considerations.

1. Introduction

Crystallization on annealing (devitrification) of metallic glasses has been widely studied and is important from a technological standpoint (thermal stability) as well as being of scientific interest (nucleation and growth in highly undercooled melts, glass formation, etc.) and also in producing controlled mictrostructures.

The mechanisms involved in the irreversible transformation to the stable crystalline state and their kinetics are subject to variation due to composition, concentration of nucleation sites, diffusion parameters, thermal history of the sample, etc. yet, in spite of these differences, a similarity in the shape of the kinetic curves is observed.

The possibility of universal behaviour in systems far from equilibrium in which order develops as a function of time, has been explored in many recent studies [1-6]. 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.

The universality appears in time developments of various quantities, such as the fraction of transformed volume, and the most convenient method for determining the volume fraction transformed as a function of time is, perhaps, differential scanning calorimetry (DSC).

The purpose of the present study is to test the time-scaling properties of the transformation kinetics of three Fe–B-based metallic glasses previously reported [7-9]. All three alloys exhibit two crystallization stages, involving a precipitation of α-Fe phase in the amorphous matrix (first stage), and a polymorphic crystallization to give Fe_3B phase (second stage).

2. Theory

Crystallization of metallic glasses occurs by nucleation and growth processes and the overall rate of transformation will reflect the time and temperature dependence of both. The generally accepted model for the crystallization of metallic glasses is the Johnson–Mehl–Avrami (JMA) equation [10], based on phenomenological assumptions for nucleation and growth. This relation describes three-dimensional random nucleation and growth within an amorphous matrix and accounts for mutual impingement of growing regions through the concept of "extended volume". The transformed volume fraction, $x(t)$, is given by

$$x(t) = 1 - \exp(-x_{ex}) \qquad (1)$$

where x_{ex} is the extended volume fraction (ignoring impingement). For crystals with radii growing at a constant rate, u, on a fixed number, N_0 per unit volume, of nuclei, $x_{ex} = (4\pi/3) N_0 u^3 t^3$. When nucleation occurs at a constant rate, I per unit volume, $x_{ex} = (\pi/3) I u^3 t^4$. So the transformed fraction can be written as

$$x(t) = 1 - \exp(-kt^n) \qquad (2)$$

where n is an exponent which varies from $n = 4$ for a constant nucleation rate ($N_0 = 0$) to $n = 3$ for a zero nucleation rate ($I = 0$) and k is a temperature-dependent rate constant.

When the growth is controlled by long-range diffusion processes, as occurs in primary crystallization of metallic glasses, the growth rate decreases with time and the radii of crystals follows a parabolic relationship with the annealing time. For three-dimensional processes this leads to the above JMA equation with $n = 5/2$ for I constant and $n = 3/2$ for early site saturation of heterogeneous nuclei [11].

All the considered possibilities give sigmoidal curves for x against t and, as Avrami pointed out, all the curves with the same value of n would have the same shape and would differ only in the value of k, which is equivalent to a change of scale.

In this way, the JMA equation can be written in a universal form

$$x(\tau) = 1 - \exp(-1/3\pi\tau^n) \qquad (3)$$

where $\tau = t/t_0$ and t_0 is a characteristic time scale related to the nucleation and growth parameters (i.e.

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TABLE I Composition of the alloys and crystallization features

Alloy	Composition (at %)	T_{x_1} (K)	E_{a_1} (kJ mol^{-1})	T_{x_2} (K)	E_{a_2} (kJ mol^{-1})
I	$Fe_{79}B_{13}Si_8$	825	448	840	378
II	$Fe_{77}B_{16}Si_5Cr_2$	802	504	824	461
III	$Fe_{81}B_{13.5}Si_{3.5}C_2$	778	477	806	468

$t_0 = (Iu^3)^{-1/4}$ for a constant nucleation rate and linear growth process).

We may characterize the time scale of the transformation by defining the time at which the crystallization has reached half completion; i.e. $x(t_{1/2}) = 1/2$. From $x(t_{1/2}/t_0) = 1/2$ one can obtain the relations $t_0 = 1.15\ t_{1/2}$ for $n = 3$ and $t_0 = 1.11\ t_{1/2}$ for $n = 4$. For diffusion-controlled growth processes, a more complicated relation, involving a concentration gradient, should exist. The value of $t_{1/2}$ obtained from experimental curves can therefore be interpreted as a measure of nucleation and growth parameters of the crystallization process. In general, we can write the scaled JMA equation as

$$x(t/t_{1/2}) = 1 - \exp\left[-b(t/t_{1/2})^n\right] \qquad (4)$$

where b should be characteristic of the Avrami index, n.

3. Results

Isothermal crystallization of three amorphous Fe–B-based alloys supplied by Allied Chemical Corp. (USA) was studied by differential scanning calorimetry (DSC). Two crystallization stages were resolved for all three alloys and the characteristic peak temperatures (at a heating rate of 20 K min^{-1}) along with composition are shown in Table I. The kinetics of the two exotherms were characterized from isothermal annealing experiments and the crystallized fraction as a function of time was derived from the integrated area under the DSC exotherm, as detailed elsewhere [8].

Fig. 1 shows the sigmoidal patterns, typical of the JMA transformations, for the two crystallization events in the three alloys. Logarithmic plots of $-\ln(1 - x)$ against t can be roughly fitted to a straight line and values of the Avrami index, for the three alloys, are $n = 2.5 \pm 0.1$ for the first crystallization stage and

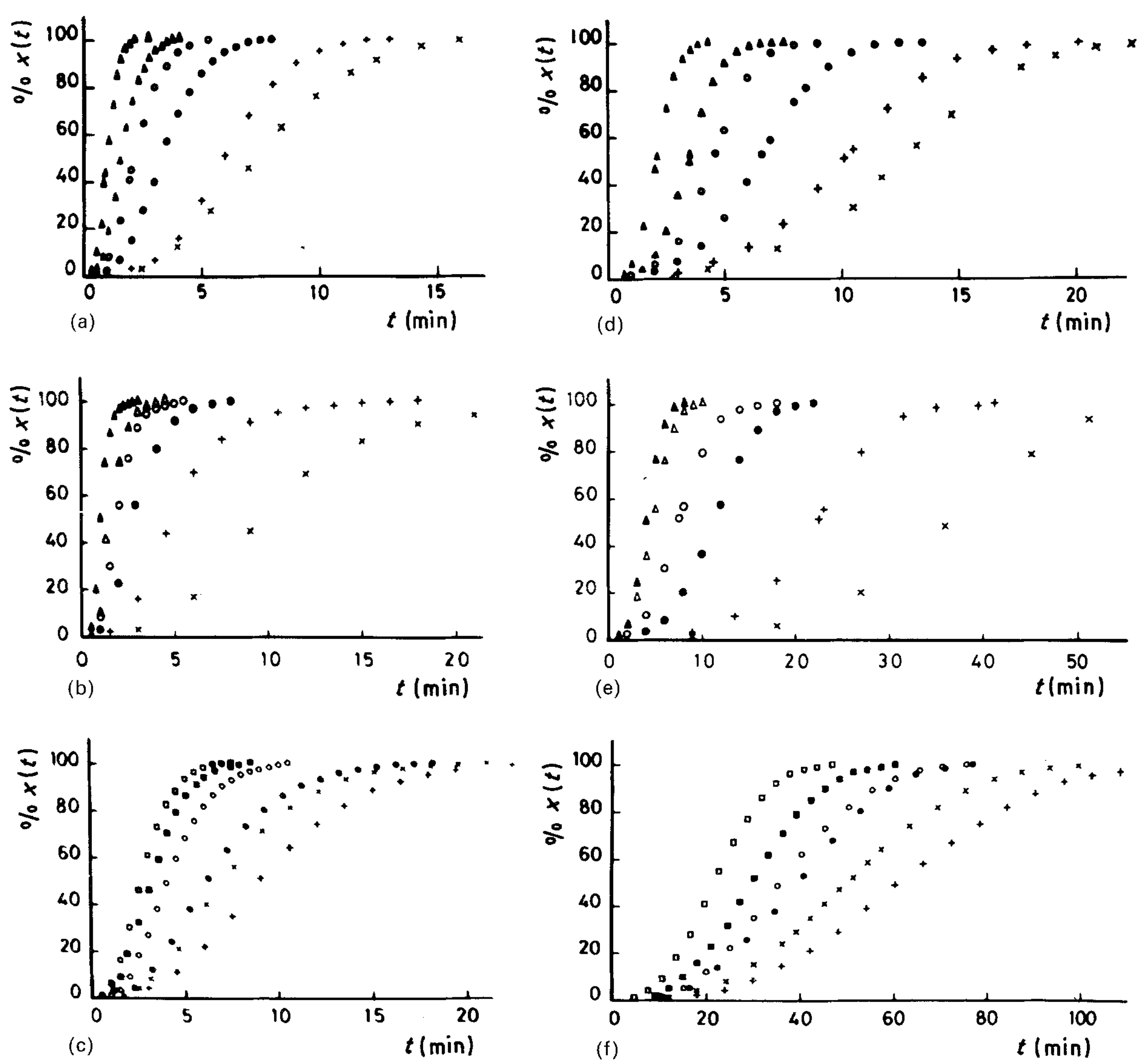

Figure 1 Crystallized fraction plotted against time: (a), (b) and (c) first stage of alloys I, II and III, and (d), (e), and (f) second stage of I, II and III, respectively. (a), (d) (▲) 810 K, (△) 805 K, (○) 800 K, (●) 795 K, (+) 790 K, (x) 785 K. (b), (e) (▲) 790 K, (△) 785 K, (○) 780 K, (●) 775 K, (+) 770 K, (x) 765 K. (c), (f) (□) 752 K, (■) 749 K, (○) 747 K, (●) 745 K, (x) 742 K, (+) 740 K.

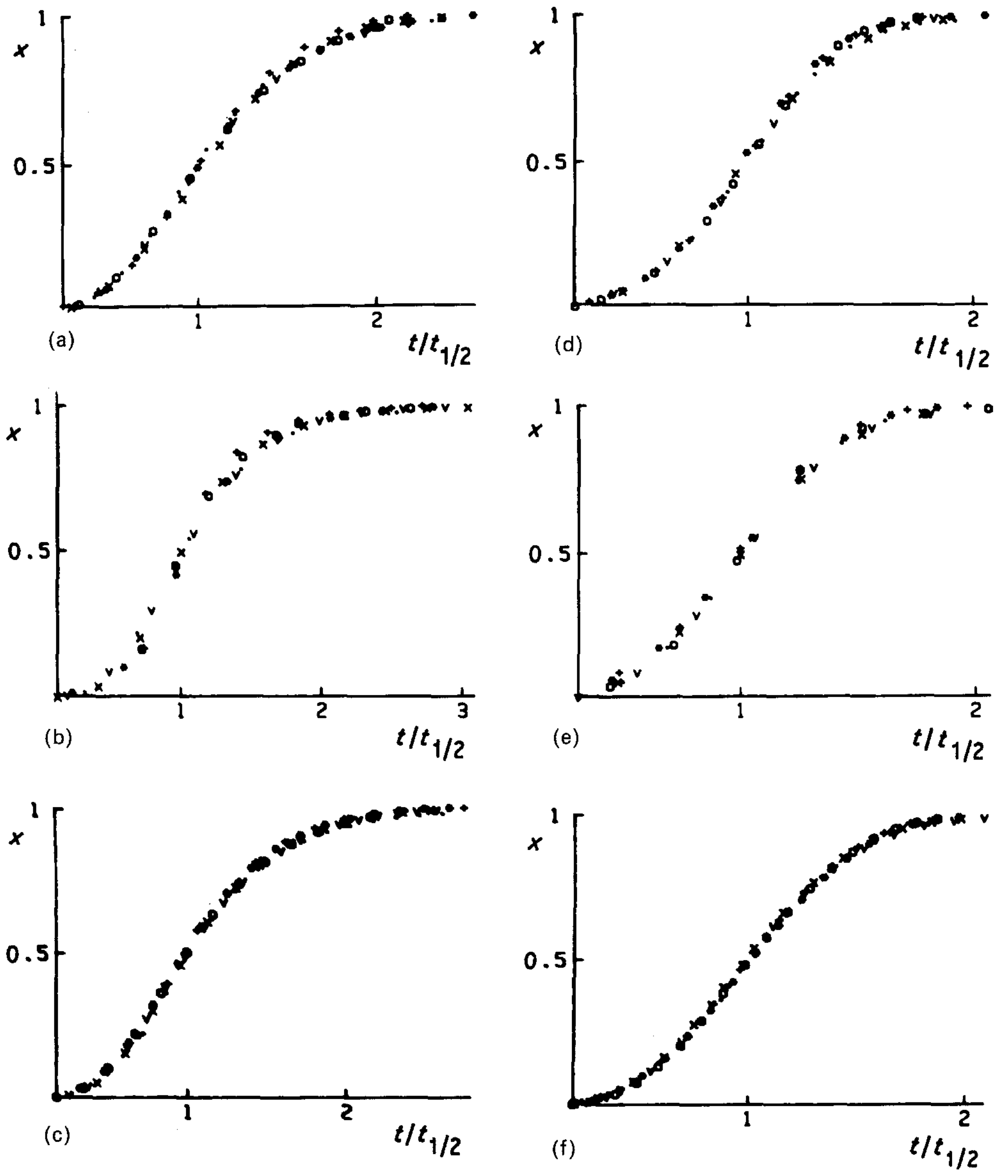

Figure 2 Time-scaled curves of crystallized fraction. Isotherms of (a), (b), (c), (d), (e) and (f) from Fig. 1 collapse on (a), (b), (c), (d), (e) and (f) curves, respectively.

$n = 3.0 \pm 0.1$ for the second one, respectively. In fact, because during the first stage of devitrification in each alloy, the amorphous phase must be progressively enriched in boron, the enthalpy of crystallization per mole of amorphous phase must be a function of the fraction transformed, and this should call into question the value obtained for the Avrami exponent for the first stage. In spite of this, the values obtained for the Avrami exponent suggest that three-dimensional diffusion-controlled growth with a constant nucleation rate, as expected for primary crystallization, is the mechanism involved in the first crystallization stage. For the second stage, interface-controlled growth is the suggested mechanism.

As expected, the crystallization process accelerates with increasing temperature. For each isotherm we can experimentally find the time $t_{1/2}$ for which $x = 0.5$, and redefine the time scale of each isotherm to be $t/t_{1/2}$. In this way, all the time-scaled isotherms relative to each transformation stage of each material lie on a single curve in each case, as shown in Fig. 2, demonstrating that the transformation kinetics obey a time-scaling law.

Scaling properties of some iron-based metallic glasses with a single crystallization stage, studied by thermomagnetic methods, have been recently reported [5, 6] but, as far as we know, this is the first test on alloys with two crystallization stages. A second stage could result in overlapping of first- and second-stage mechanisms at the high-temperature end of the first stage and at the low-temperature limit of the second stage.

Fitting parameters for the scaled JMA equation in the form $\ln[-\ln(1 - x)]$ against $\ln(t/t)_{1/2}$, obtained from a least-squares line for each material and transformation stage, are indicated in Table II. As observed, a good fit is obtained in all cases in spite of the possible error arising from the above-mentioned partial overlapping of the two stages. The lowest value of the correlation coefficient ($r = 0.989$) is found for the first stage of the alloy II, in which two crystalline phases are formed: α-Fe and σ-(Fe, Cr).

Time-scaled isotherms for both stages of crystallization for the three alloys studied collapse in a single curve as shown in Fig. 3, demonstrating the universality of the reduced form (time-scaled) of the

TABLE II Fitting parameters of the scaled JMA equation

	Alloy	b	n	r*
Primary crystallization	I	−0.45	2.49	0.997
	II	−0.59	2.50	0.989
	III	−0.50	2.45	0.995
	I + II + III	−0.51	2.47	0.993
Polymorphic crystallization	I	−0.27	2.98	0.996
	II	−0.33	3.02	0.996
	III	−0.37	2.97	0.998
	I + II + III	−0.33	2.99	0.997

*Correlation coefficient.

transformation kinetics for a constant value of the n exponent.

A further point of interest concerns the temperature dependence of the scaling parameter $t_{1/2}$. Whereas a conventional Arrhenius law fits the scaling-parameter data quite satisfactorily in some cases [5], in others [6] this fit yields very high and clearly unphysical values for the prefactor. On the other hand, Roig *et al.* [6] suggest that it is inappropriate to regard the very rapid variation of the characteristic time with temperature as reflecting a simple activated process. The activation assumption is based on a gradual freezing and does not allow for a divergence of the time-scaling parameter. Recent Monte Carlo simultations performed on quenched Ising models have evinced a low-temperature divergence of the time scale in the case of conserved order parameter transformations [3] and the recrystallization processes, having this conservation law, should exhibit a low-temperature freezing behaviour.

The slowing down of the crystallization process as temperature is decreased is characteristic of relaxation phenomena in the glassy state and several empirical functions have been proposed to fit experimental data for the temperature dependence of relaxation processes in the amorphous state. Along with the conventional Arrhenius law

$$t_{1/2} = t_0 \exp (E/kT) \qquad (5)$$

We have also tried a Vogel–Fulcher law [12]

$$t_{1/2} = t_0 \exp [E/k(T - T_0)] \qquad (6)$$

and the Williams–Landel–Ferry function [13]

$$t_{1/2} = t_0 \exp [-20.4(T - T_0)/(101.6 + (T - T_0)] \qquad (7)$$

The two last expressions are based on free-volume considerations.

Values of the fitting parameters for the different proposed laws are given in Table III. The Arrhenius law fits the experimental data well but the values obtained for the activation energy and for the prefactor, as shown in Table III, are not satisfactory, leading to clearly unphysical values of the growth velocity prefactor. As pointed out by Köster [14], the observed pre-exponential factor for the crystal growth velocity are orders of magnitude larger than predicted by the theory, especially in ternary or more complicated glasses, but no satisfactory explanation of the parameters has been provided.

For the two other expressions to which the present data are fitted, it can be observed that the parameters obtained are within physically reasonable ranges. Because the experimental data correspond to a narrow temperature range we cannot obtain conclusive differences based on the fitting of either form. As observed, the Vogel–Fulcher law predicts freezing above 400 K in all cases and, therefore, finite crystallization should not occur at room temperature.

The Williams–Landel–Ferry (WLF) function is very useful in describing the temperature dependence of relaxation processes in amorphous polymers. If a separate reference temperature, T_c, is suitably chosen for each system, the law turns out to be identical, when expressed as a function of T–T_0, for polymers and a variety of organic and inorganic glass-forming liquids over a wide temperature range above the vitrification point [13], in spite of the great difference in chemical composition and actual location on the absolute temperature scale.

In our case, the WLF function fits the experimental data for the three alloys studied quite satisfactorily, leading to T_0-values in the range 670 to 730 K. As the glass transition is not thermally manifest, the crystallization temperature, measured dynamically at high $\dot{T}$, can be taken as an acceptably close estimate of T_g [11]. So, the values of T_0 should be approximately 100 K below T_g, whereas for the polymers, an average value $T_0 - T_g$ of 50 ± 5 K has been found [13]. However, it should be noted that, in our case, the experimental data refer to temperatures in the range 10 to 60 K below T_g, whereas polymer data correspond to temperatures above T_g.

Fig. 4 shows a plot of the ratio of $t_{1/2}$ at temperature,

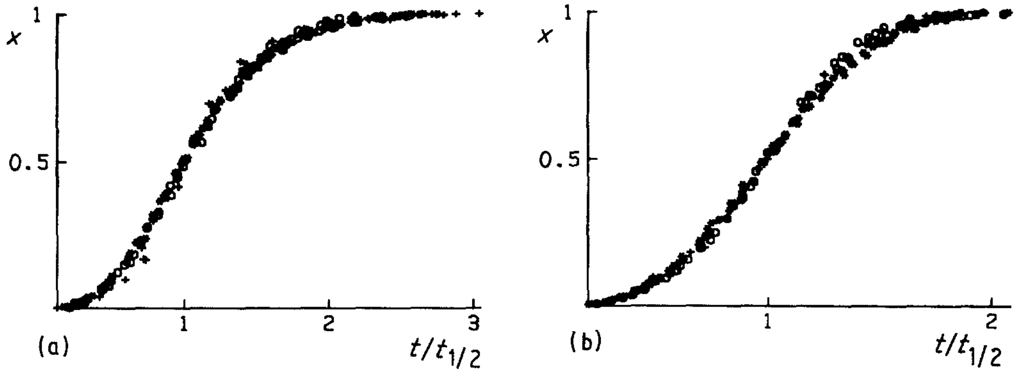

Figure 3 Time-scaled composite curves for the three alloys: (a) first stage, (b) second stage.

TABLE III Parameters of fits to the $t_{1/2}(T)$ data for the different proposed functions

	Function	Alloy I		Alloy II		Alloy III	
		1st*	2nd*	1st*	2nd*	1st*	2nd*
Arrhenius	t_0 (sec)	1.1×10^{-28}	3.7×10^{-24}	1.1×10^{-34}	1.2×10^{-26}	1.1×10^{-28}	3.7×10^{-24}
	E (eV)	4.7	4.1	5.5	4.3	4.7	4.0
Vogel–Fulcher	t_0 (sec)	2.3×10^{-13}	3.3×10^{-8}	5.6×10^{-11}	1.9×10^{-7}	1.1×10^{-10}	1.8×10^{-8}
	E (eV)	1.1	0.6	0.7	0.5	0.7	0.7
	T_0 (K)	405	490	510	520	480	435
Williams–Landel–Ferry	t_0 (sec)	8.9×10^5	1.1×10^6	5.4×10^5	9.8×10^5	2.1×10^6	4.7×10^6
	T_0 (K)	724	730	715	720	670	685

*1st and 2nd refer to primary and polymorphic crystallization, respectively.

T, to its value at a reference temperature, T_0, against $T - T_0$ for all the isothermal transformations (first and second stages) for the three alloys. As can be seen, in the range covered, the coincidence is remarkable, even more so if we bear in mind that the coefficients in the WLF expression have been taken from the composite curves [13] calculated for polymers.

The fact that the temperature dependence of the time-scaling parameter can be described by the WLF function should suggest, as stated by Roig *et al.* [6], that the rate-limiting steps in crystallization involve relaxation processes in the glassy phase. The universal function for temperature dependence of relaxation phenomena in glass-forming liquids should arise from the fact that the rates of all such processes depend on the temperature primarily through their dependence on free volume. As pointed out in the original paper [13], the universality of the expression implies that the free-volume at the glass transition temperature and the rate of increase of the free-volume with temperature are the same for all the glasses.

A major implication of the above interpretation of the WLF analysis is that structural relaxation should still be freely occurring during the second stage of crystallization in which, according to the Avrami analysis, interface-controlled growth prevails. The latter can hardly be consistent with the statement that the rate-limiting steps in crystallization involve relaxation processes in the glassy phase.

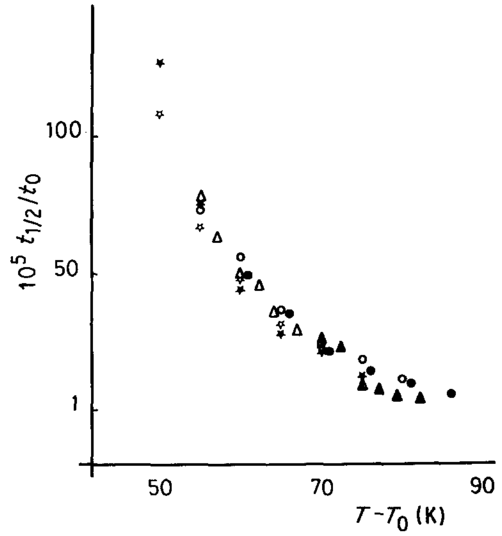

Figure 4 Temperature dependence of time-scaling parameter for the three alloys showing the universality of the WLF description. (●) Alloy I, 1; (○) alloy I, 2; (★) alloy II, 1; (☆) alloy II, 2; (▲) alloy III, 1; (△) alloy III, 2.

In conclusion, the crystallization kinetics of the three Fe–B-based alloys obey a time-scaling law and the JMA equation can be reduced to an universal form for a constant Avrami exponent, if the time axis is rescaled by a characteristic time, dependent on the nucleation and growth parameters. The temperature dependence of the time-scaling parameter shows a low-temperature freezing behaviour and can be described by Vogel–Fulcher and Williams–Landel–Ferry functions, both based on free-volume considerations. The WLF expression gives a universal function for the temperature dependence of time-scaling parameters for the two crystallization stages of the three alloys.

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