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Effects of non-steady state nucleation in the kinetics of crystallization of the amorphous alloy $Fe_{80}B_{20}$

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The existence of non-steady state nucleation in the isothermal crystallization of the amorphous alloy $Fe_{80}B_{20}$ is shown. The incubation time τ_0 of isothermal volume crystallization of the alloy is investigated in a wide range as a function of temperature. From these data an equation for the temperature dependence of the viscosity $\eta = \eta(T)$ is derived: $\eta = 6.62 \exp(2526.97/T) \times \exp[836.52/(T - 530)]$.

1. Introduction

In 1943 Zeldovich [1] drew attention to the fact that the processes of nucleation have a non-steady state character. Moreover time is needed for the formation of a chain of clusters with steady-state concentration, required by theory. This time is a function of the rate of transport to the nucleus, determined by viscous flow. Zeldovich [1] and Frenkel [2] have derived a differential equation describing the non-steady state kinetics of nucleation. A number of approximate solutions have been proposed in the literature, e.g. the approximation of Zeldovich

$$I = I_0 \exp(-\tau/t) \qquad (1)$$

Here I is the rate of nucleation after time t, I_0 is the steady-state rate of nucleation and τ the so-called non-stationary time. τ is given by

$$\tau = 4/\pi^3\Gamma^2 D_k \qquad (2)$$

where

$$\Gamma = (A_k/3\pi k T n_k^2)^{1/2}$$

is the so-called Zeldovich factor, A_k the free energy for the formation of a nucleus and n_k the number of atoms in the critical nucleus at temperature T. D_k is the rate of supply of atoms to the nucleus:

$$D_k = z_k\omega \propto z_k/\eta \qquad (3)$$

depending for nucleation from the melt on the viscosity η and on the fraction of active sites at the cluster surface z_k; ω is the impingement rate of building units. For a eutectic melt with negative deviations from ideality, it is possible to assume an Arrhenius-like dependence $z_k \propto e^{-Q/RT}$, which leads to Equation 10 used below.

A more accurate solution of the Frenkel–Zeldovich equation was obtained in 1969 by Kashciev [3] in the form of the series

$$I(t) = I_0[1 + 2\Sigma(-1)^n \exp(-n^2 t/\tau)] \qquad (4)$$

Kelton *et al.* [4], as well as Volterra and Cooper [5] have shown numerically that the solution by means of a series (Equation 4) [3] is indeed a very good approximation.

Using simplifying assumptions, Gutzow and Toschew [6] and Gutzow and Kashchiev [7] obtained for the number of nuclei $N(t)$ formed after an annealing time t

$$\begin{aligned} N(t) &= 0 && \text{for } 0 \leqslant t \leqslant b \\ &= I_0(t - b\tau) && \text{for } b\tau < t \\ b &= \pi^2/6 \end{aligned} \qquad (5)$$

It was shown [7] that as a result of transient nucleation the Johnson–Mehl–Avrami (JMA) kinetics are delayed by the so-called incubation time τ_0, proportional to the non-steady state time. The authors originally obtained $\tau_0/\tau = 1.6$; later they showed that τ_0/τ may vary from 0.02 to 0.1. Gutzow and Toschew [8] have demonstrated the following connection between the incubation time τ_0, the viscosity η and the supercooling of the melt:

$$\tau_0 \sim \eta(/\Delta T)^2$$

where $\Delta T = T_E - T$.

The existence of the incubation times in the isothermal crystallization kinetics of glassy alloys predicted from the theory of transient nucleation has already been described repeatedly in the literature. For the temperature dependence of τ_0 equations of the following type:

$$\tau_0 \propto \eta \propto e^{U/RT} \qquad (7)$$

have been used or of the type

$$\tau_0(\Delta T)^2 \propto \eta \propto e^{U/RT} \qquad (8)$$

An attempt at an indirect approximate determination of the viscosity on calorimetric data has been made by Chen [9]. He has demonstrated that for palladium-based amorphous alloys the temperature dependence of the viscosity, determined by the creep velocity, as well as evaluated by the time needed for attaining the glass transition, the beginning of crystallization and the maximum rate of crystallization, can

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be fitted in one curve. This curve gives the temperature dependence of the viscosity if the calorimetric data are stretched along the ordinate by means of suitable multiplying constants.

Thompson *et al.* [10] have obtained for the activation energy of viscous flow for the amorphous metallic alloy $(Au_{85}Cu_{15})_{77}Si_9Ge_{14}$ from crystallization data the value $46\,kcal\,mol^{-1}$ ($193\,kJ\,mol^{-1}$). From the Arrhenius dependence of $\ln \tau_0 \Delta T^2$ on $1/T$ for the glass $Fe_{80}P_{13}C_7$, Scott and Ramachandrarao [11] obtained an activation energy $U = 170\,kcal\,mol^{-1}$ ($712\,kJ\,mol^{-1}$). The effects of non-steady state nucleation have been observed metallographically by Köster [12] and by Blanke and Köster [13, 14]. By fitting to the Vogel–Fulcher–Tammann equation they derived an activation energy of $67\,kcal\,mol^{-1}$ ($281\,kJ\,mol^{-1}$) and a T_0 temperature of 631 K.

From the temperature dependence of the incubation times during isothermal crystallization of amorphous metallic alloys it could be possible to obtain information about the temperature dependence of η and to determine T_0 in the Vogel–Fulcher–Tammann equation

$$\eta = \eta_0 \exp\,[A/(T - T_0)] \tag{9}$$

Macedo and Litowitz [15] and Spaepen [16] proposed for this dependence the equation

$$\eta = \eta_0 \exp\,[A/(T - T_0)]\,\exp\,(B/T) \tag{10}$$

The simple Arrhenius dependence

$$\ln \eta = A + B/T \tag{11}$$

is sometimes used for a small temperature range of the temperature dependence of η.

The aim of the present paper is to investigate in a wide temperature range the temperature dependence of the incubation time of the JMA crystallization kinetics of the amorphous metallic alloy $Fe_{80}B_{20}$. This alloy was selected owing to the existence of reliable literature data on its crystallization kinetics [17–20].

2. Experimental procedure

Experiments were carried out on a planar flow cast amorphous metal alloy $Fe_{80}B_{20}$, kindly provided by Dr H. Liebermann from Allied Corporation, Parsipanny, New Jersey (USA). The main part of the studies was carried out by means of microcalorimetry and thermogravimetry, to which metallography and dilatometry were added.

2.1. Calorimetric investigations

These were carried out using a Perkin-Elmer differential scanning microcalorimeter DSC-2C. The experiments were made on samples weighing 5 to 10 mg in an argon stream under isothermal conditions. The samples were heated in the calorimeter with a scanning rate $320\,K\,min^{-1}$, and after the final temperature was reached, the kinetics of crystallization were determined by the rate of heat release. The direct recording of the temperature of the sample holder demonstrated a delay by 1 to 2 sec of the real temperature compared with the programme-determined temperature when the isothermal regime was reached. For this reason only incubation times exceeding 30 sec were processed. Thermograms were processed using a computer program for obtaining the kinetics of isothermal crystallization. Fig. 1 shows an experimental calorimetric curve in coordinates dH/dt, time t, as well as the kinetic curve degree of transformation (crystallization $X(t)$, time t). The time when the signal from the calorimeter indicated the beginning of the deviation from the basic line was designated as τ_0.

2.2. Thermomagnetic investigations

An investigation of the kinetics of isothermal crystallization of the alloy studied has already been described elsewhere [21]. The experiments were carried out using a Perkin-Elmer thermobalance TGS-2 with the aid of Faraday's method. For this purpose, the sample which was weighed continuously was placed in a magnetic field with intensity between the poles H and with vertical gradient dh/dz. At temperatures higher than the Curie temperature (651 K) the initial amorphous alloy is paramagnetic, whereas two ferromagnetic phases (α-Fe and Fe_3B, proved by our X-ray diffraction as well) are formed during its crystallization. The additional loading of the thermobalance is proportional to the magnetization.

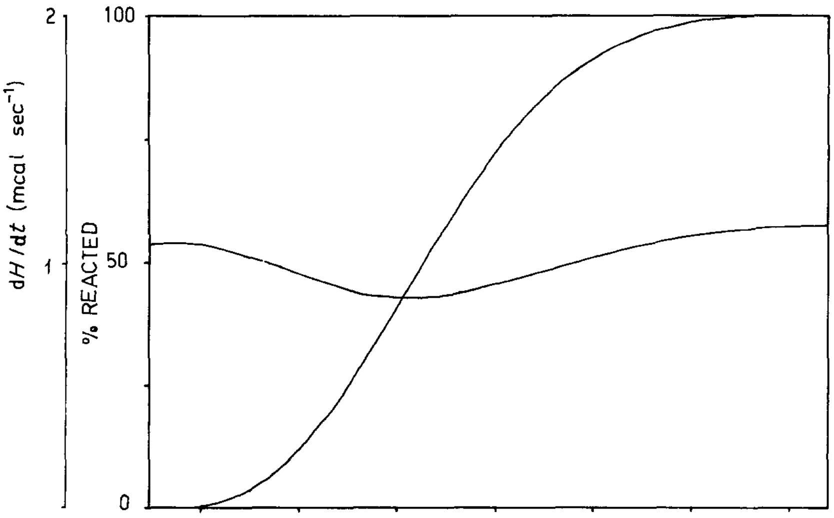

Figure 1 DSC isothermal curve in coordinates dH/dt against t and a kinetic curve for the degree of transformation $x(t)$ against t at 675 K. 1 mcal = 4.1868 mJ.

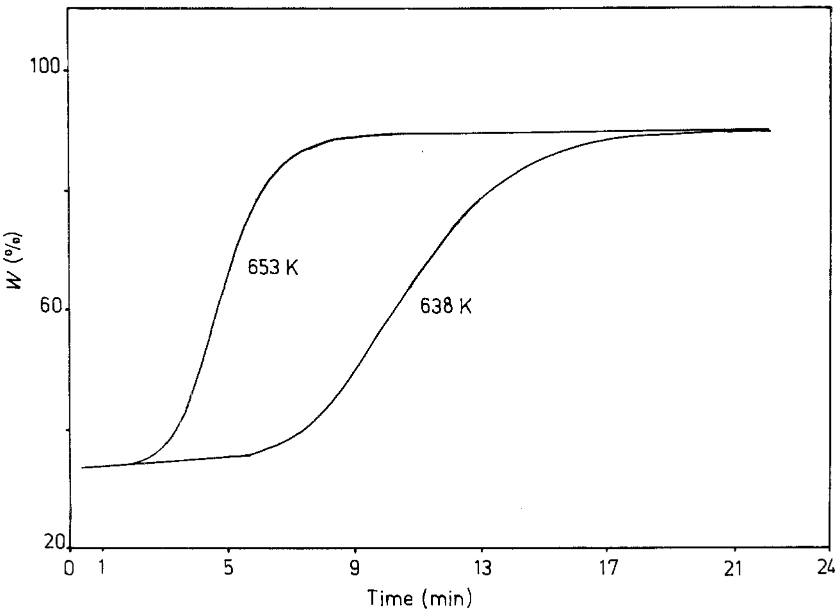

Figure 2 Two TGS experimental curves.

$$f = \lambda m H (\mathrm{d}H/\mathrm{d}z) \qquad (12)$$

where m is the mass of the sample and λ its magnetic susceptibility. The kinetic curves can be obtained directly from the dependence of f on t. Two such experimental curves are shown in Fig. 2. The test to see how fast the oven reaches its real isothermal hold temperature demonstrated a delay of 2 to 4 sec. Consequently, only incubation times exceeding 90 sec were processed. As in the case of calorimetry, τ_0 was assumed to be that time for which the signal of the thermobalance deviated from zero as a result of the onset of crystallization.

2.3. Metallographic investigations

Preliminary experiments were carried out for determining the rate of nucleation through direct counting of the nuclei formed after time t. With this method, proposed by Tammann [22], nucleation proceeded with different annealing times at a sufficiently high temperature (669 K). The subsequent growth of the nuclei to dimensions which are visible metallographically took place at a lower temperature (573 K) at which no new nuclei were formed, but only the existing crystallization centres grew. The above method was developed to perfection by Herold and Köster [19] for investigating the crystallization of amorphous metallic alloys. Transverse sections of $Fe_{80}B_{20}$ glasses subjected to different types of thermal treatment were ground and polished metallographically. Their microstructure was developed with 5% HNO_3 in C_2H_5OH. It was shown clearly that frozen-in athermal nuclei were able to grow at 573 K (Fig. 3), whereas practically no new nuclei are formed at this temperature. Fig. 4 demonstrates the nuclei formed after 7 min at 669 K and developed at 573 K for 30 min. From the curve obtained an incubation time of about 2 min was determined.

2.4. Dilatometric investigations

Dilatograms for the amorphous alloy at constant scanning rates, plotted using a computer-aided Perkin-Elmer dilatometer TMS-2, clearly demonstrate the transition of glass into a supercooled melt, as well as its softening and crystallization.

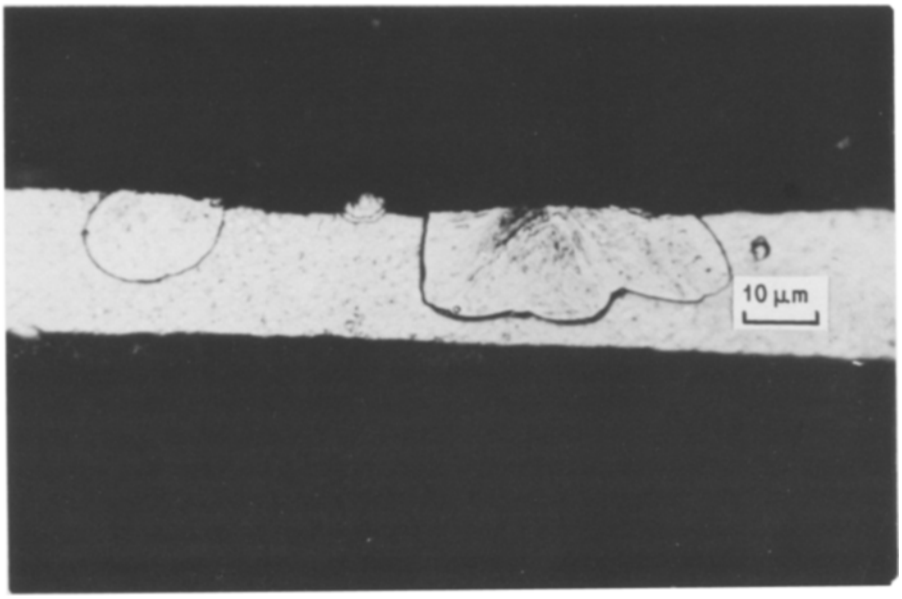

Figure 3 Growth of frozen-in nuclei at 573 K (metallographic cross-section, 950 ×).

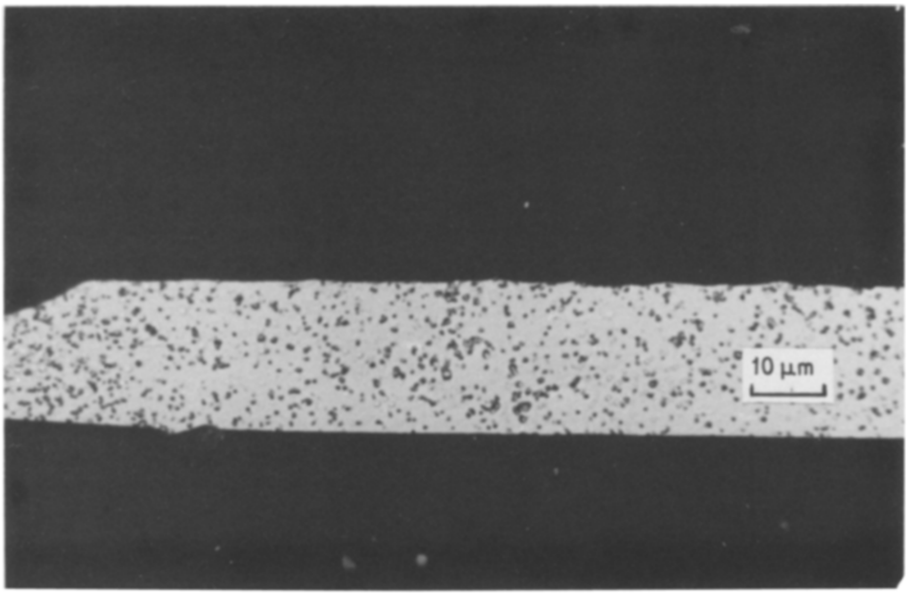

Figure 4 Nucleation 7 min at 669 K, growth 30 min at 573 K (metallographic, 950 ×).

The temperatures recorded by DSC-2, TGS-2 and TMS-2 were corrected using two types of standard: the Curie transformation of pure nickel, and the crystallization of $Fe_{80}B_{20}$.

3. Results and discussion

Table I presents the incubation times obtained at different temperatures: from 620 to 660 K by means of the TGS-2, and from 665 to 695 K by means of the DSC-2. The incubation time of 120 sec at 669 K, determined from the $N(t)$ curves, was not taken into account during the processing of the data.

The dependence of $\ln \tau_0$ on $1000/T$ is shown in Fig. 5. As seen, the data are unsatisfactorily described by the simple Arrhenius equation with a correlation coefficient of the straight line 0.9856 (Fig. 5) and an activation energy of the viscous flow $49.7 \pm 2.4\,\mathrm{kcal\,mol^{-1}}$ ($208\,\mathrm{kJ\,mol^{-1}}$). For the activation energy of the linear velocity of growth for the same alloy we obtained $U = 42.2\,\mathrm{kcal\,mol^{-1}}$ ($177\,\mathrm{kJ\,mol^{-1}}$) while Herlod and Köster [19] obtained $U = 47\,\mathrm{kcal\,mol^{-1}}$ ($197\,\mathrm{kJ\,mol^{-1}}$). From the Arrhenius dependence of $\ln \tau_0$ on $1000/T$ Thompson *et al.* [10] have obtained $U = 46.1\,\mathrm{kcal\,mol^{-1}}$ ($193\,\mathrm{kJ\,mol^{-1}}$) for the activation energy in the alloy $(Au_{85}Cu_{15})_{77}Si_9Ge_{14}$. Drehman and Greer [23] have obtained the same value for the activation energy of the incubation period for alloy $Pd_{40}Ni_{40}P_{20}$, as for the activation energy of crystallization.

The systematic deviation of our $\ln \tau_0$, $1000/T$ data (Fig.5) clearly suggests that it is necessary to use a dependence of the type of the Vogel–Fulcher–Tammann equation

$$\ln \tau_0 = a + \frac{b}{T - T_0} \qquad (13)$$

The constants a, b and T_0 were varied by means of a computer to fit the data in coordinates $\ln \tau_0$, $1000/(T - T_0)$ with the highest correlation coefficient. The most probable straight line in these coordinates (Fig. 6) was obtained at values of the constants: $b = 885.3 \pm 25\,\mathrm{K}$, $a = 1.9295 \pm 0.2039$, $T_0 = 530 \pm 1\,\mathrm{K}$ with a correlation coefficient of the straight line 0.9948.

The fitting of the experimental data in the coordinates in the equation of Gutzow and Kaschiev [7] was used as the subsequent approximation, resulting in the

TABLE I Temperature dependence of incubation times τ_0

Method	T (K)	τ_0 (sec)
TGS-2	620	2532
	625	1775.8
	635	672
	640	552
	645	255
	650	198
	655	174
	660	116
DSC-2C	665	117
	670	107
	675	73.2
	680	49.7
	685	39.2
	690	34.8
	695	30.7
$N(t)$ curves	669	120

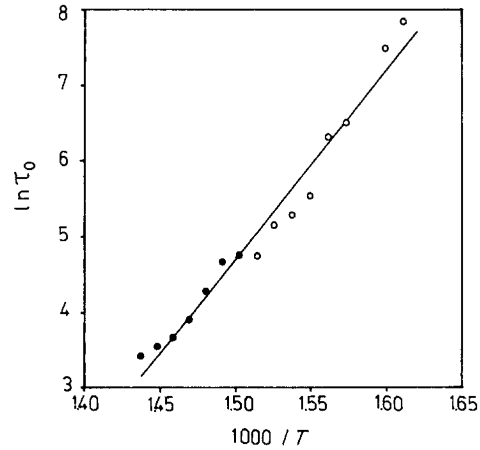

Figure 5 Dependence of $\ln\tau_0$ on $1/T$.

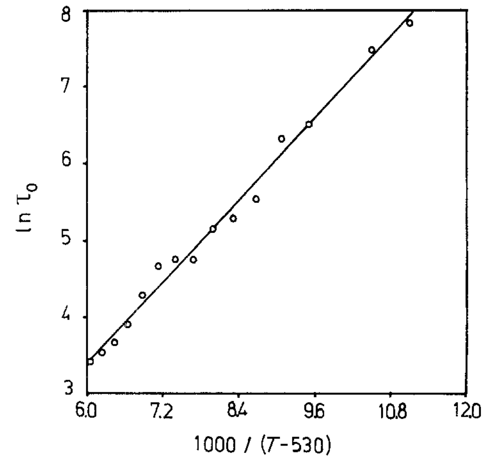

Figure 6 Fit of the data in Vogel–Fulcher–Tammann coordinates, ln τ_0 against $1/(T - 530)$.

expression

$$\ln(\tau_0 \cdot \Delta T^2) = 11.0321 \pm 0.20627 + \frac{924.3 \pm 25.4\,\mathrm{K}}{T - (530 \pm 1)\,\mathrm{K}} \qquad (14)$$

with correlation 0.9951.

Finally, using $\eta = k\tau_0(\Delta T)^2$ and Equation 10, the proportionality coefficient, i.e. the constant η_0, was determined so that the viscosity of the melt at the eutectic temperature of 1422 K could have a conditionally accepted reasonable value of 1 P (0.1 Pa sec). Moreover, the expression

$$\eta = 6.62148845 \exp(2526.973/T) \times \exp[836.516/(T - 530)] \qquad (15)$$

was obtained for the temperature dependence of the viscosity of $Fe_{80}B_{20}$, which – compared with earlier data – manifested the least mean quadratic deviation. The value 559.7 K was obtained for the glass transition temperature T_g at which $\eta = 10^{13}$ P (10^{12} Pa sec). The calculated viscosities of the glass varied from 4×10^2 to 4×10^4 P (40 to 4000 Pa sec) within the temperature range studied, and these values are obviously very low. The authors have difficulties in choosing between even simple models for the temperature dependence of the viscosity from kinetic data in a narrow temperature range. We hope to check directly this dependence in a future paper. At temperatures for which no new nuclei are formed (around 570 K), but existing athermal crystallization centres are able to grow, the estimated viscosities are of the order of 10^9 P (10^8 Pa sec) (Fig. 7). We are not familiar with data about the viscosity and of its temperature dependence for the investigated alloy $Fe_{80}B_{20}$, neither about its glass transition temperature. It is not clear to us to what extent these calculated low values of the viscosity may have been influenced by systematic errors due to extrapolation within a very wide temperature range. This may also be connected with some specific chemical features of iron–boron melts. Another unclear question remains why no changes in the heat capacity are observed at the glass transition temperatures in DSC, estimated or determined from the dilatograms.

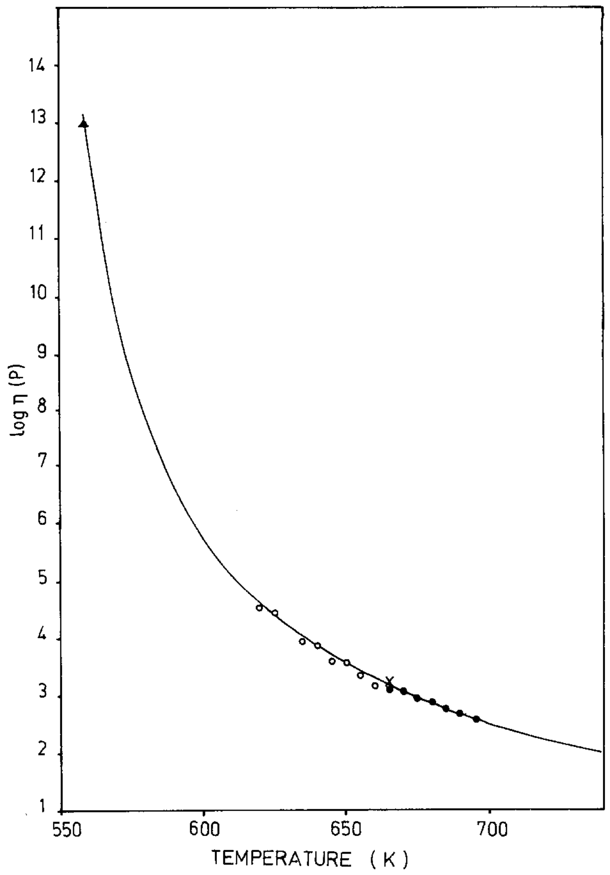

Figure 7 Plot of the temperature dependence of the viscosity in $Fe_{80}B_{20}$ alloy. 1 P = 10^{-1} Pa sec.

In order to determine to what extent the rheological constants obtained are reasonable, we shall adduce the equations for the temperature dependence of η, obtained from direct measurements for some metal glass-forming melts. For the alloy $Pd_{48}Ni_{32}P_{20}$ Chen [9] has obtained the expression

$$\eta = 1.7 \times 10^{-3} \exp \frac{5920}{T - 392} \qquad (16)$$

For the alloy $Pd_{40}Ni_{40}P_{20}$ Drehman and Greer [23] have obtained

$$\eta = 1.815 \times 10^{-6} \exp \frac{2247}{T - 529} \qquad (17)$$

Naka *et al.* [24] have obtained for $Pd_{84}Si_{16}$

$$\log \eta = -0.418 + \frac{858}{T - 551} \qquad (18)$$

and for $Pd_{78}Cu_6Si_{16}$

$$\log \eta = -0.234 + \frac{1330}{T - 520} \qquad (19)$$

Blanke and Köster [13, 14] have obtained for the alloy $Fe_{65}Ni_{10}B_{25}$

$$\eta = \eta_0 \exp \frac{4700}{T - 631} \qquad (20)$$

The ratio T_0/T_e or T_g/T_e, may also be used for assessing whether the values obtained by us for T_0 and T_g are reasonable, where $T_e = 1422$ K is the eutectic temperature of the iron–boron eutecticum. The values $T_0/T_e = 0.37$ and $T_g/T_e = 0.40$ were obtained.

From the data presented above it is clearly evident that there exist non-steady state effects in the crystallization of the metallic glass $Fe_{80}B_{20}$.

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