JOURNAL OF MATERIALS SCIENCE 21 (1986) 2553–2556

Crystallization kinetics of the amorphous alloy $Fe_{80}B_{20}$ studied using a thermomagnetic balance

STOJAN BUDUROV, TONI SPASSOV, TOMISLAV MARKOV
Department of Chemistry, University of Sofia, 1 Anton Ivanov str., 1126 Sofia, Bulgaria

The kinetics of isothermal crystallization of the amorphous metal alloy $Fe_{80}B_{20}$ have been studied using a Perkin–Elmer thermomagnetic balance. Well-defined and reproducible incubation periods were observed on the degree of crystallization against time curves, in agreement with the theory of non-steady state nuclear ions in glasses. Values from 1.4 to 2.4 were obtained for the exponent *n* in the Johnson–Mehl–Kolmogorov–Avrami equation. The activation energy of viscous flow in the glass was found from the incubation period against temperature dependences at temperature near the crystallization point. The activation energy of crystallization was determined from the temperature dependence of the 50% crystallization times. Metallographic observations show unambiguously that two crystallization reactions proceed simultaneously: the growth of ready athermal centres located on the more slowly quenched surface of the amorphous metal ribbon along two directions, and growth in the bulk of the ribbon.

1. Introduction

The crystallization kinetics of the amorphous alloy $Fe_{80}B_{20}$ have been extensively studied [1–10] both by direct and indirect methods. The direct methods (optical and electron microscopy) take into account correctly the changes in the structure, though for smaller areas this may be atypical for the entire amorphous ribbon. Moreover, in some cases the sample preparation procedure may change the initial conditions [8]. Resistometry, Mössbauer spectroscopy, differential scanning calometry (DSC), saturation magnetization, etc., have been used as indirect methods in most cases for studying the mechanism of isothermal crystallization kinetics. Our DSC measurements failed to confirm the two-stage crystallization of $Fe_{80}B_{20}$ described by Greer *et al.* [3], suggesting instead a process proceeding in a single thermal crystallization peak.

The eutectic amorphous alloy $Fe_{80}B_{20}$ was chosen as a model because of the following reasons: (i) the thermomagnetic method may be used to study the crystallization kinetics, and (ii) there are reliable literature data on these kinetics. Such data provide a possibility of comparing the results obtained and to comprise qualitatively new aspects of the crystallization process.

The literature data on the activation energy of the crystallization process of the alloys studied vary from 200 to 250 kJ mol^{-1}. This is evidently related to the different procedures of measurement, and to the method of preparation and thermal history of the amorphous metal ribbons.

Thermomagnetic methods have been used in studies on amorphous metal alloys at different constant scanning rates to track the temperature dependence of the relative magnetization, to determine the Curie point and the crystallization temperature. The isothermal crystallization kinetics of metal glasses have not been studied thus far by a thermomagnetic balance.

The kinetics of phase transformations including nucleation and growth is often described by the Johnson–Mehl–Kolmogorov–Avrami (JMKA) equation

$$x(t) = 1 - \exp(-k(t - \tau)^n) \qquad (1)$$

where $x(t)$ is the part having crystallized after time t, τ is the incubation period related to the so-called non-steady time, k is the rate constant (depending on the rate of nucleation and growth) and n is a constant related to the mechanism of nucleation and growth, usually taking values between 1.5 and 4. The activation energy E_a of the entire crystallization process may be obtained from the temperature dependence of the constant k where

$$k = k_0 \exp(-E_a/RT) \qquad (2)$$

Here E_a comprises both the activation energy of nucleation E_N and that of growth E_G. The determination of these activation energies separately is possible only when the nucleation kinetics and the growth kinetics are separately studied by direct microscopic methods.

In isothermal experiments, Equation 1 is often transformed into

$$\ln\left[\ln\left(\frac{1}{1-x}\right)\right] = \ln k + n \ln(t - \tau) \qquad (3)$$

2. Experimental procedure

The crystallization kinetics of the amorphous metal alloy $Fe_{80}B_{20}$ were studied by tracking the changes in the relative magnetization $\sigma = \chi H$ as a function of the annealing time at different temperatures. The

0022–2461/86 \$03.00 + .12 © *1986 Chapman and Hall Ltd.*

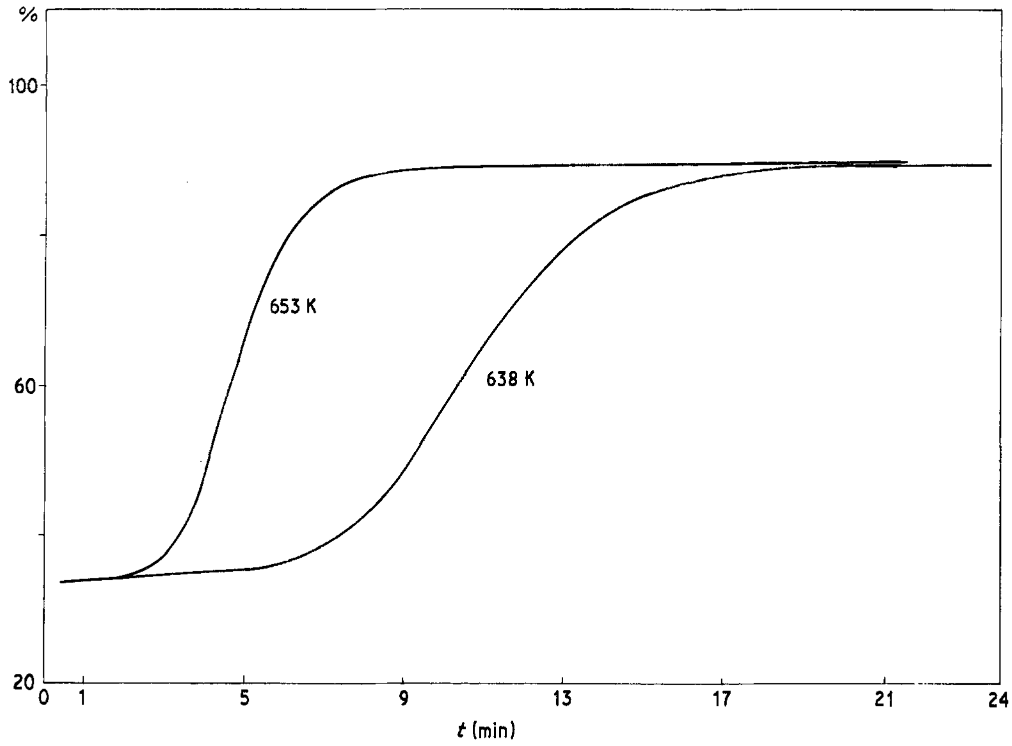

Figure 1 TGS-2 output for isothermal crystallization of $Fe_{80}B_{20}$ (ZFW) at 638 and 653 K.

sensitivity of the procedure is based on the formation and growth of ferromagnetic crystals in the metal glass, which is paramagnetic at this temperature. The quantity of these crystals is recorded by the appearance of a force of attraction along the vertical, f_z:

$$f_z = m\chi H \frac{\partial H}{\partial z} = m\sigma \frac{\partial H}{\partial z}$$

for

$$\frac{\partial H}{\partial x} = \frac{\partial H}{\partial y} = 0, \quad \frac{\partial H}{\partial z} = \text{constant} \quad (4)$$

where m is the weight in mg, σ is the relative magnetization and H is the external magnetic field intensity ($A\,m^{-2}$).

The samples were measured by a Perkin–Elmer computer-controlled thermomagnetic balance TGS-2 with a constant external magnet, positioned at a distance below the sample. Parallel metallographic studies were carried out with the purpose of compiling additional direct information on the mechanism of metal glass crystallization, and obtaining estimates for the rate of nucleation and growth by the Herold–Köster [1] method.

3. Results

Three types of amorphous metal alloy with a nominal composition $Fe_{80}B_{20}$ were examined. The first was supplied by Allied Chemical Corporation, Morriston, New Jersey, and the other two samples were prepared by planar flow casting in the Central Research Institute Academy of Science (zFW), GDR and in the

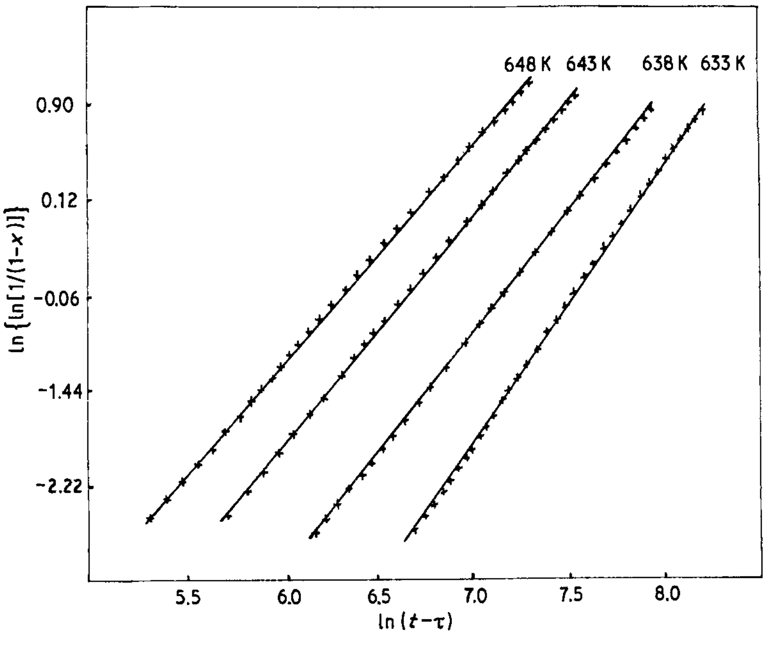

Figure 2 Johnson–Mehl–Avrami plots for $Fe_{80}B_{20}$ ribbons at various temperatures in logarithmic coordinates. (t and τ in sec.)

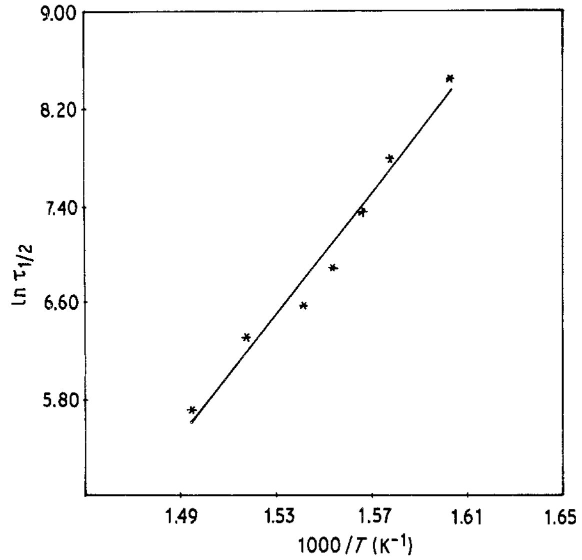

Figure 3 Plot of $\ln(\tau_{1/2})$ against $1/T$ for $Fe_{80}B_{20}$ (ZFW). (τ in sec.)

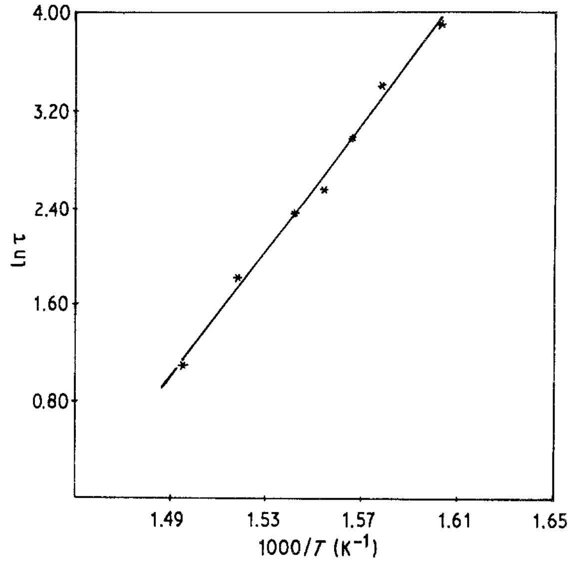

Figure 4 Arrhenius plot of effective time lag τ (min) as a function of temperature T for isothermal crystallization of $Fe_{80}B_{20}$.

Institute of Metal Science and Technology of the Bulgarian Academy of Sciences. The samples crystallized under isothermal conditions in the thermobalance under additional charging created by a constant external magnet. The magnetic field intensity between the magnet poles was 0.01 T and its vertical gradient was 0.003 to $0.004\,T\,cm^{-1}$. The crystallization temperatures were considerably higher than the Curie temperature of the glass.

Fig. 1 shows the curves of two isothermal crystallization experiments carried out at 365 and 380° C, respectively. As seen, after a certain incubation period τ, the initial signal from the thermal balance starts to rise and attains some constant value. Part of the data at several temperatures, plotted in coordinates $\ln \{\ln [1/(1 - x)]\}$, $\ln (t - \tau)$, are shown in Fig. 2. Data-fitting to the JMKA equation shows that this equation describes relatively well the process of isothermal crystallization. The n values determined from Fig. 2 are in the range 1.4 to 2.0 with a mean value of 1.7. The deviation from the linear dependence in coordinates $\ln \{\ln [1/(1 - x)]\}$, $\ln (t - \tau)$ for large crystallization times probably indicates a change in mechanism at the end of the crystallization process. The time for 50% crystallization was also calculated ($\tau_{1/2} = (\ln 2/k)^{1/n}$).

Fig. 3 shows the dependence of $\ln \tau_{1/2}$ on $1000/T$, from which $E = 211 \pm 15\,kJ\,mol^{-1}$ is found for the activation energy of total crystallization.

It is clearly seen from the experimental curves for isothermal crystallization, which are similar to those presented in Fig. 1, that there exist incubation periods of the Avrami kinetics during which no crystallization occurs. From the temperature dependence of τ, shown in Arrhenius coordinates in Fig. 4, $E = 217 \pm 8\,kJ\,mol^{-1}$ was obtained for the activation energy of the non-steady state time, a value close to that of total crystallization.

Similar studies were carried out with the metal glass $Fe_{80}B_{20}$ supplied by Allied Chemical Corporation*. The results shown in Table I display a larger scattering of the n values about a higher mean value ($n = 2$) as compared with the values obtained for the self-made metal glasses $Fe_{80}B_{20}$. This is probably due to the different methods of preparation and to the different width and thermal history of the three amorphous metal alloys studied here.

To obtain a more accurate quantitative description of the kinetics of the total isothermal crystallization of the studied amorphous alloys we fitted the experimental data by a non-linear regression procedure to the JMKA equation. Moreover, we minimized the expression

$$F(k, n, \tau) = \sum_{i=1}^{m} (x_i - 1 + e^{-k(t_i - \tau)^n})^2$$

and found the k, n and τ parameters that fit the

TABLE I Results of the isothermal crystallization kinetics for the $Fe_{80}B_{20}$ amorphous alloy (Allied Chemical Co.)

T (K)	Parameters determined by linear regression			Parameters determined by non-linear regression		
	n	$\ln k$	Correlation coefficient	n	$k/3600^n$	τ (min)
613	1.57	−11.134	0.999	1.68	7.36	42.2
618	1.50	−9.99	0.998	1.75	12.61	29.6
623	2.00	−13.39	0.999	1.75	20.38	18.1
628	2.22	−14.16	0.999	2.21	88.42	11.2
633	1.72	−10.24	0.999	1.77	51.35	9.2
638	1.72	−9.72	0.999	–	–	–
643	2.29	−13.21	0.999	2.38	481.36	3.3
648	2.12	−11.67	0.999	2.23	387.68	2.9
653	2.57	−13.62	0.998	2.18	732.83	1.8

---

*The authors are grateful to Dr H. H. Liebermann for the samples, kindly supplied by him.

experimental results with a minimum square deviation. This minimization in primitive coordinates (not in the logarithmic coordinates) was performed with a computer using two different numerical methods (the Newton–Raphson method and the Nelder–Mitt method). The differences in the parameter values were not significant. The k, n and τ values are listed in Table I.

4. Discussion of the results

The results obtained show that the thermomagnetic method is convenient and sensitive for studies on the kinetics of isothermal crystallization of amorphous metal alloys in which ferromagnetic or paramagnetic crystalline phases are formed. Well-expressed non-steady state times were observed in the kinetics of total crystallization of the metal glass $Fe_{80}B_{20}$, in agreement with the non-steady state nucleation theory developed by Zeldovich [11], Kashchiev and Gutszov [12] and with the experimental results of Gutszov *et al.* [13]. According to the theory [13] the incubation periods in the Avrami kinetics are related to the non-steady state times τ_0 through the expression $\tau \approx \tau_0 + \tau_\beta$ in which τ_β is the time required to attain an experimentally observable degree of crystallization β. According to Zeldovich [11], the temperature dependence of the non-steady state times $\tau_0 \sim \eta$ should be the same as that of the melt's viscosity near the crystallization point.

As is known, the formalism of the JMKA kinetics procedure gives the following values for the exponent n in the equation

$$x = 1 - \exp[-k(t - \tau)^n]:$$

(a) $n = 1$: growth of ready (athermal) centres of crystallization along one direction;

(b) $n = 2$: growth of ready crystallization centres along two directions, or nucleation at a constant rate and growth along one direction;

(c) $n = 3$: growth of ready nuclei along three directions, or nucleation at a constant rate and subsequent growth along two directions at a constant rate.

The experimental data yield n values between 1.4 and 2.4. Direct metallographic observations by Herold and Köster [1] provide evidence for the simultaneous proceeding of two reactions: the growth of ready athermal centres over the more slowly quenched side of the amorphous metal ribbon along two directions, and creation and growth in the bulk of the ribbon.

It is difficult to decide on the basis of the results obtained which mechanism leads to n values comprised within 1.4 and 2.4. Our results are in good agreement with Greer's results [3]; Greer has also obtained higher exponents for the isothermal crystallization of industrial amorphous alloys $Fe_{80}B_{20}$ as compared with alloys prepared by fast quenching of the melt in a laboratory melt-spinning device.

Greer's rate constant values $k = 3.4 \times 10^{-4}\,\mathrm{min}^{-2.8}$ at 400° C is three orders of magnitudes higher than our k value at a similar temperature ($T = 395°$ C, $k = 2.0 \times 10^{-7}\,\mathrm{min}^{-1.6}$). The difference between the exponents is also considerable. Using Köster's linear growth rates at different temperatures [2] we have estimated the density of the frozen-in subnuclei at $T = 395°$ C. The density thus obtained is considerably lower than those of Greer and of Köster.

Evidently, the kinetics and the mechanism of nucleation and of linear crystallization can be elucidated on the one hand by directly tracking the course of these processes, and on the other hand by precise mathematical modelling of the total crystallization kinetics.

References

1. U. HEROLD and U. KÖSTER, in "Rapidly Quenched Metals III", Vol. 1, edited by B. Cantor (Metals Society, London, 1978) p. 281.
2. U. KÖSTER, *Metallkde* **75** (1984) H.9, 691.
3. A. L. GREER, *Acta Metall.* **30** (1982) 171.
4. A. L. GREER and J. A. LEAKE, in "Rapidly Quenched Metals III", Vol. 1, edited by B. Cantor (Metals Society, London, 1978) p. 299.
5. T. KEMENY, I. VINCZE, B. FOGARASSY and J. BALOGH, "Physics and Applications", Vol. 5 (Central Research Institute for Physics, Has, Budapest, 1980) p. 183.
6. T. KEMENY, I. VINCZE, B. FOGARASSY and S. ARAJS, in "Rapidly Quenched Metals III", Vol. 1, edited by B. Cantor (Metals Society, London, 1978) p. 291.
7. A. S. SCHAAFSMA, H. SNIJDERS, F. VAN DER WONLDE, J. W. DRIJVER and S. RADELOAR, *Phys. Rev.* **B20** (1979) 4423.
8. K. V. RAO, R. MALMHÄLL, S. M. BÄCKSTRÖM and H. S. CHEN, *IEE Trans. Magn.* **MAG-16** (5) (1980) 896.
9. A. S. SCHAAFSMA, H. SHIJDERS and F. VAN DER WONLDE, in Proceedings of 3rd International Conference on Rapidly Quenched Metals, London, 1978, Vol. 1, p. 424.
10. *Idem*, in Proceedings of 3rd International Conference on Rapidly Quenched Metals, London, 1978, Vol. 1 (Metals Society) p. 428.
11. B. J. ZELDOVICH, *J. Exp. Theor. Phys.* **12** (1942) 525.
12. I. GUTZOW and D. KASHCEV, *Commun. Bulg. Acad.* 3(4) (1970) 645.
13. I. GUTZOW, V. DOCHEV, E. PANCHEVA and K. DIMOV, *J. Polym. Sci. Polym. Phys. Ed.* **6** (1978) 1155.

Received 15 August
and accepted 26 September 1985