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The crystallization kinetics of Fe-Ni based metallic glasses

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Differential scanning calorimetry is used to study the crystallization kinetics of two commerical Fe–Ni metallic galsses near their glass transition point. For $0.01 < x < 0.85$ the fraction transformed, x, as a function of time, t, satisfies the Johnson–Mehl–Avrami equation with exponent n varying from 2.8 to 4.3 as the annealing temperature is increased. The activation energies for the crystallization process are estimated from the time to 50% transformation as close to 100 kcal mol^{-1} and are interpreted as arising from viscous flow.

1. Introduction

Metallic glasses have been produced in a large number of alloys of the type $M_{80}X_{20}$ where M represents one or more noble or transition metals and X any or several of a number of metalloids [1]. Particular interest has centred on Fe–Ni based alloys since these glasses combine high strength [2], interesting ferromagnetic properties [3] and good corrosion resistance [4]. Despite the considerable attention that has been paid to the physical and mechanical properties of these alloys little appears to be known about their crystallization behaviour. Aside from the obvious academic interest in studying the growth of crystals in a highly undercooled melt, an understanding of the crystallization process is of considerable importance since, if such alloys are to find commercial applications, their thermal stability must be well documented. Moreover, by partial or total crystallization of metallic glasses, it may prove possible to produce useful microstructures unobtainable by other means; in such cases a knowledge of the kinetics of the process is a prerequisite.

Since the crystallization of a metallic glass is a highly exothermic process, differential scanning calorimetry (DSC) is a very suitable means of studying the kinetics of the process. The technique has been applied to a number of glassy alloys produced by splat-quenching [5–7] and to Ni–P and Co–P produced by electroless deposition [8]. Recently Coleman [9] used the method to follow the isothermal crystallization of Fe–Co based glasses and suggested that the process obeyed standard phase change kinetics with an Avrami exponent between 7 and 11. It will be shown later, however, that these values are thought to be artificially high. In this paper DSC is used to study the crystallization kinetics of two commerical Fe–Ni based glasses: Metglas* 2826 and 2826B.

2. Experimental

The alloys, which were supplied by Allied Chemical Corporation, were in the form of tapes with cross-sections 50 μm x 2 mm (2826) and 70 μm x 0.75 mm (2826B). The nominal compositions were $Fe_{40}Ni_{40}P_{14}B_6$ (2826) and $Fe_{29}Ni_{49}P_{14}B_6Si_2$ (2826B) although other investigators have reported small traces of Cr and Al [10].

Differential scanning calorimetry was performed on a Perkin–Elmer DSC 2; specimens of mass 1 to 5 mg were annealed in aluminium containers under a pure argon atmosphere. The temperature and power axes of the instrument were calibrated from the melting endotherms of pure zinc and tin. Continuous heating experiments were conducted at 10 K min^{-1} from room temperature to beyond the crystallization exotherms. Isothermal anneals were performed between 645 and 667.5 K for the 2826 alloy and between 670 and 700 K for the 2826B. In these experiments the specimen was heated at 320 K min^{-1} to the annealing temperature. Previous experience with this equipment has suggested that

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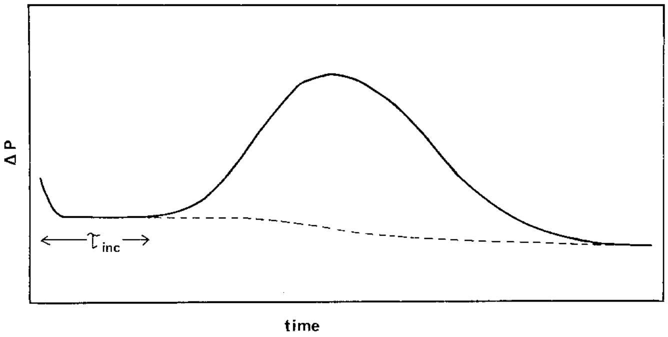

Figure 1 Typical DSC curve for an isothermal anneal, showing the baseline construction under the peak.

overshoot of the annealing temperature is negligible. Transients in the recording equipment, however, made it impossible to make measurements until about 15 sec after the specimen had reached the annealing temperature. This limitation determined the upper temperature at which isothermal anneals could be conducted.

3. Results

On continuous heating at $10\,\mathrm{K\,min^{-1}}$ both alloys crystallized with a single heat evolution. The crystallization temperatures, taken as the peak onset, were 667 ± 1 K and 710 ± 1 K for 2826 and 2826B respectively.

The DSC trace from a typical isothermal anneal is shown in Fig. 1. After an initial transient lasting about 15 sec there was an incubation period, τ_0, before the start of the crystallization exotherm. Values of the incubation time for each temperature are listed in Table I and their significance will be discussed later. 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 taken as proportional to the fractional area under the peak up to this time. The peak areas were derived by measuring the ordinates at closely spaced values of t and using a Simpson-type integration. Up to 150 points were analysed for each annealing. The extrapolation of the baseline under the peak is shown in Fig. 1 and was estimated using the assumption that the contributions of the glassy and crystalline phases to the specific heat of the partially transformed specimen were in direct proportion to their volume fractions. Full details of this construction are given elsewhere [11].

TABLE I Incubation time, τ_0, and slope of Avrami plots, n, for various annealing temperatures, T.

	T(K)	n	τ_0 (min)
2826	645	3.5 ± 0.2	16.0 ± 0.1
($Fe_{40}Ni_{40}P_{14}B_6$)	650	3.8 ± 0.2	8.0 ± 0.1
	652.2	4.0 ± 0.2	5.1 ± 0.1
	655	3.7 ± 0.2	4.2 ± 0.1
	657.5	3.9 ± 0.2	3.0 ± 0.1
	662.5	4.1 ± 0.2	1.7 ± 0.1
	665	4.4 ± 0.2	1.1 ± 0.1
	667.5	4.3 ± 0.2	0.9 ± 0.1
2826B	670	2.8 ± 0.2	27.0 ± 0.1
($Fe_{29}Ni_{49}P_{14}B_6Si_2$)	675	3.0 ± 0.2	13.8 ± 0.1
	680	3.5 ± 0.2	6.1 ± 0.1
	682.5	3.4 ± 0.2	4.4 ± 0.1
	685	3.4 ± 0.2	4.1 ± 0.1
	687.5	3.4 ± 0.2	3.3 ± 0.1
	690	3.6 ± 0.2	2.3 ± 0.1
	695	4.1 ± 0.2	1.3 ± 0.1
	697.5	4.2 ± 0.2	1.1 ± 0.1
	700	4.3 ± 0.2	0.9 ± 0.1

The x versus t relationships for each temperature are shown in Fig. 2 and are of the familiar sigmoidal type. The kinetics of the transformation were analysed in terms of the generalized theory of phase transformations: [12]

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

where b is a rate constant and n is an exponent which need not be an integer.

This may be written as the well-known Johnson–Mehl–Avrami equation:

$$\log(-\log(1-x)) = \log(b/2.303) + n\log t.$$

Plots of $\log(-\log(1-x))$ against $\log t$ for each annealing temperature are shown in Fig. 3. For $0.01 < x < 0.85$ the plots approximate to straight lines. Deviations from linearity for $x < 0.10$ are thought to be due to termination errors in the expression whereas above $x = 0.85$ grain growth of already crystallized material probably becomes significant. The values of the Avrami exponent, n, given by the slope of the graphs are listed in Table I. For both alloys the value of n tends to rise with increasing annealing temperature, ranging between 3.5 to 4.3 (±0.2) for the 2826 alloy and 2.8 and 4.3 (±0.2) for the 2826B.

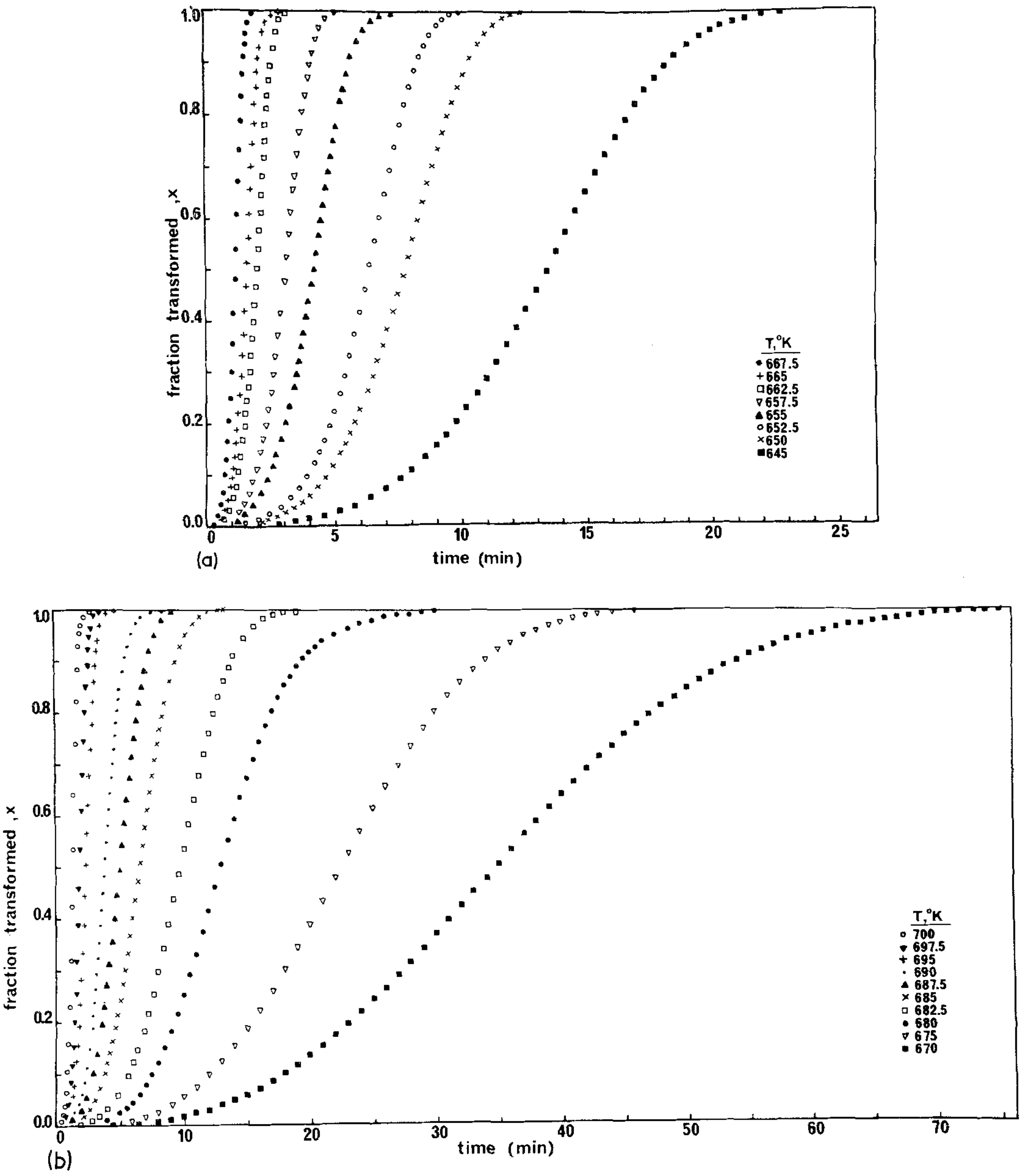

Figure 2 Fraction transformed (x) as function of time (t) for (a) alloy 2826 and (b) alloy 2826B.

Activation energies for the process were deduced from the temperature dependence of the time to 50% crystallization ($t_{0.5}$) i.e. from

$$t_{0.5} = A \exp -E/kT,$$

where A is a constant and E the activation energy.

Plots of $\log t_{0.5}$ against $1/T$ are shown in Fig. 4. For both alloys straight lines resulted; from the slopes activation energies of $92 \pm 2\,\mathrm{kcal\,mol^{-1}}$ ($4.0 \pm 0.1\,\mathrm{eV}$) for 2826 and $102 \pm 2\,\mathrm{kcal\,mol^{-1}}$ ($4.4 \pm 0.1\,\mathrm{eV}$) for 2826B were determined.

4. Discussion

The spontaneous crystallization temperatures of the alloys are in agreement with those reported elsewhere. These two alloys are somewhat unusual in that they crystallize in one stage; most amorphous alloys pass through one or more metastable intermediate phases before the equilibrium crystalline phases are obtained. Indeed the replacement of some of the iron and nickel with chromium (Metglas alloy 2826A) causes the crystallization exotherm to divide into two peaks separated by

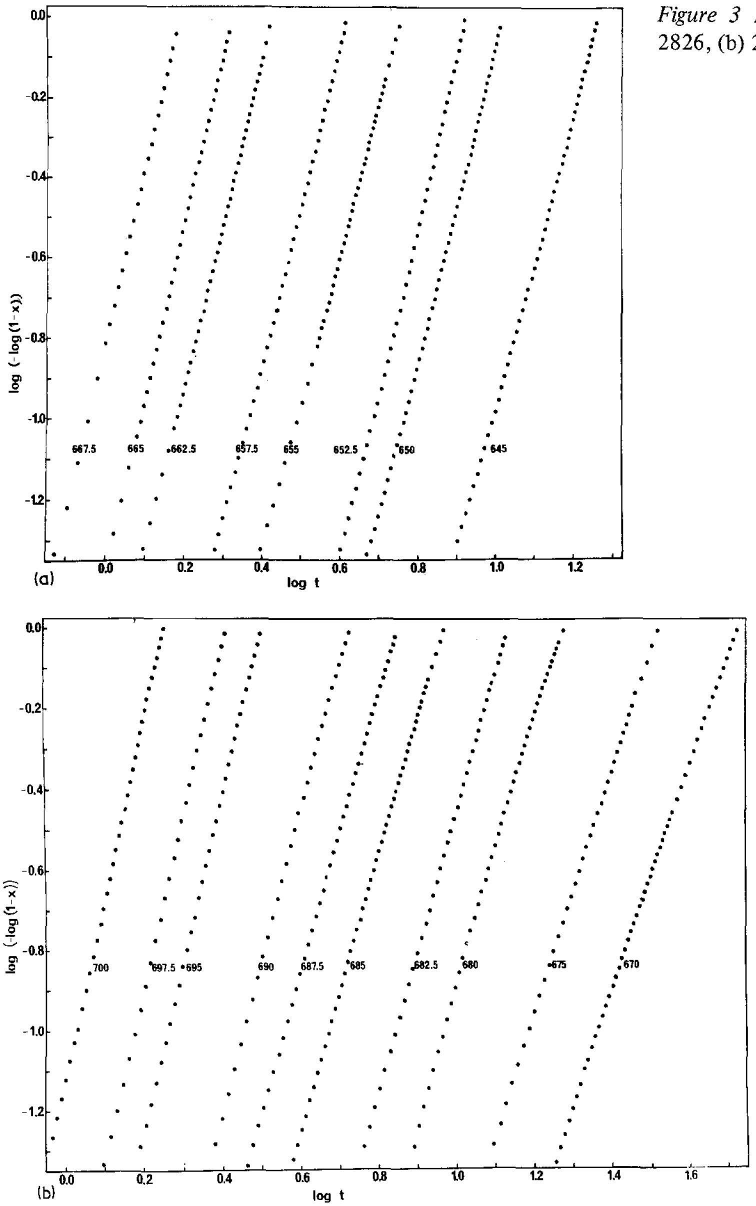

Figure 3 Avrami plots for $0.01 < x < 0.85$ (a) 2826, (b) 2826B.

about 40 K. The two alloys discussed in this paper were chosen specifically since the one-stage crystallization eliminated the problems associated with interpreting overlapping peaks in the isothermal DSC plots.

Within experimental limits the values of the Avrami exponent, n, lie between 3 and 4, consistent with the values obtained in similar studies of splat-quenched Pd–Si [6, 7, 13] and chemically deposited Ni–Co–P alloys [8]. Such values may represent either interface controlled growth of crystals or diffusion limited growth of a cellular product [14]. In both cases n would vary from 3 at zero nucleation rate to 4 at constant nucleation rate. Cellular decomposition has been observed in Pd–Cu–Si [15] glasses but electron microscopy of these Fe–Ni based alloys indicated only the growth of single phase crystals [10].

Any postulation as to the precise mechanisms of the crystallization process, however, requires detailed microscopic evidence; consequently an electron microscope study of the crystallization process is under way. In both alloys the value of n increases with increasing annealing temperature, suggesting that at higher temperatures the rate of decrease of nucleation rate during the transform-

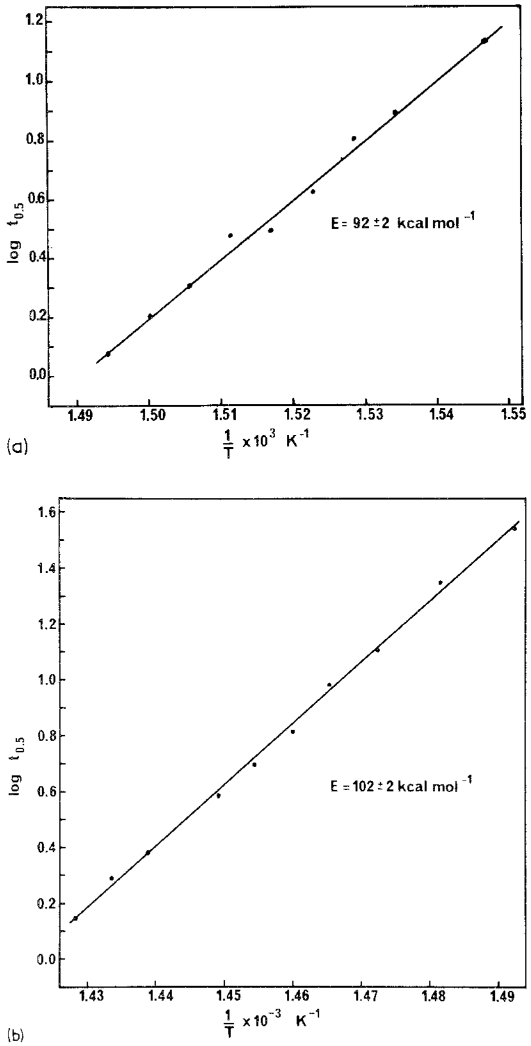

Figure 4 Determination of activation energy from time to 50% transformation (a) 2826, (b) 2826B.

ation is slower. A similar behaviour has been noted in Pd–Si alloy glasses [13]. One factor that has been overlooked in previous work is the possibility of self heating causing the crystallization rate to accelerate to a value characteristic of a temperature higher than that of the programmed annealing temperature. The slight upward curve of the Avrami plots during the transformation may be a consequence of this effect.

The values of n obtained in this work are considerably at variance with those of up to 11 obtained by Coleman [9] for similar (Fe, Co, Ni) P–B–Al alloys. The cause of this discrepancy is, however, obvious when one notices that in his analysis of the kinetics Coleman has taken $t = 0$ as the start of the anneal rather than as the end of the incubation period. It is normal to subtract incubation times from such data and if this is done to Coleman's results values of $n \sim 4$ are obtained which are more consistent with this work. Further support for this point is obtained by noting that when he examined a "pre-annealed" specimen, Coleman obtained a value $n = 4.7$. Pre-annealing is equivalent to subtracting part of the incubation period. Incubation periods are a common feature of isothermal phase transformations and may be considered as the time taken for a population of nuclei characteristic of the annealing temperature to be achieved [16]. Normally the phenomenon is associated with the formation of a critical nucleus concentration on down-quenching from above the equilibrium transformation temperature. In the present case annealing is carried out at a temperature below the nose of the TTT curve and consequently in a regime where nucleation rate increases with increasing temperature. The existence of an incubation period therefore implies that no suitable sized nuclei exist in the as-quenched glass. The values of the incubation time listed in Table I are in agreement with those quoted by Luborsky [17] for alloy 2826. The same author has pointed out that these times give a measure of the stability of the glass for practical purposes.

Metallic glasses have been observed to crystallize in two ways. At temperatures well below the glass transition some alloys transform to a single phase solid solution with an activation energy of 10 to 20 kcal mol^{-1} (0.4 to 0.8 eV) [18]. No such crystallization has been reported in the alloys under discussion and specimens annealed up to 20 h at 450 K still appeared amorphous by X-ray diffraction. However it is well known that structural rearrangements in the amorphous state do occur on annealing for short times at as low as 400 K. These processes give rise to the stress relief, magnetic annealing and embrittlement effects reported elsewhere [19–21]. On heating rapidly to near the glass transition temperature, as in the present work, these low temperature processes may be avoided and crystallization occurs with activation energies of ~100 kcal mol^{-1} (4.3 eV). The values obtained in the present work are close to those reported for a number of other metallic glasses, and in the case of 2826 agree with that determined by Luborsky (3.9 eV) [17]. No data are available for the activation energies of diffusion in these glasses, although if that for Fe and P in glassy Fe–P–C [22] is any guide values considerably lower than those measured here would be expected. The activation energies of crystallization of these and other metallic glasses are of the same order as those expected for the viscous flow of these materials near their glass transition [23] and it is widely thought that the crystallization process is viscosity controlled, i.e. it requires some co-ordinated motion of all atomic species rather than the diffusion of a single species. This interpretation is consistent with the observation of Ast and Krenitsky [10] that on annealing of alloy 2826 inside the electron microscope the sharp edges of the foil become rounded by viscous flow coincidentally with the start of crystallization. The decrease in activation energy from 102 kcal mol^{-1} for 2826B to 92 kcal mol^{-1} for 2826 corresponds with the decrease in spontaneous crystallization temperature from 710 K for 2826B to 667 K for 2826 and supports previous observations that the stability of these glasses decreases as Ni is replaced by Fe [9].

5. Conclusions

The crystallization of two commercial Fe–Ni based metallic glasses follows classical nucleation and growth kinetics with an Avrami exponent of n between 2.8 and 4.3. The value of the exponent increases with increasing annealing temperature. Activation energies deduced from the time of 50% transformation are 92 ± 2 kcal mol^{-1} (2826) and 102 ± 2 kcal mol^{-1} (2826B); these values are close to those predicted for viscous flow.

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