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Crystallization of the amorphous alloy $Fe_{40}Ni_{40}B_{20}$: a ferromagnetic resonance study

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The ferromagnetic resonance (FMR) technique was used to study the crystallization of the metallic glass $Fe_{40}Ni_{40}B_{20}$ (Vitrovac 0040). The line intensity of the amorphous phase was measured for several isothermal annealing times in the temperature range 360 to 375° C. The transformed fraction, as derived from FMR data, satisfies the Johnson–Mehl–Avrami equation with the exponent *n* between 1.49 and 1.70. The activation energy for crystallization is estimated from the times to 25% to 75% transformation to be 364 kJ mol^{-1}.

1. Introduction

The thermal stability of metallic glasses is a subject of considerable interest, because the properties of these engineering materials may be significantly changed by the onset of crystallization. Ferromagnetic resonance (FMR) spectroscopy seems to be a convenient method to study the crystallization of metallic glasses, because it is a fast, sensitive and non-destructive technique. In the present work, the FMR method was used to investigate the annealing behaviour of the commercial alloy Vitrovac 0040, manufactured by Vacuumschmelze GmbH, Hanau, Germany.

2. Experimental procedure

The alloy, of nominal composition $Fe_{40}Ni_{40}B_{20}$, was supplied in the form of ribbons 5 mm wide and 40 μm thick. Isothermal heat treatments were carried out in air, on small pieces of the ribbon (typical dimensions 3 mm × 2 mm), in a tube furnace with a temperature accuracy of $\pm 1°$C.

First-derivative FMR spectra were recorded at room temperature using an X-band Varian E-12 spectrometer. All measurements were taken with the static field parallel to the sample surface and along the long axis of the ribbon.

3. Experimental results

3.1. FMR spectra

The FMR spectra of a virgin sample and of samples annealed for various times at 375° C are shown in Fig. 1. The resonance curve of the amorphous phase AB in Figs 1a to d is the only one that can be seen for short ageing times. For ageing times longer than about 20 min, a second curve appears, whose positive peak is indicated by C in Figs 1c to f and whose negative peak is indicated by D in Figs 1e and f. The negative peak cannot be observed in Figs 1c and d because it is masked by peak B of the amorphous phase. The amplitude of this second curve increases with ageing time up to about 1 h and remains constant for longer ageing times, as shown in Figs 1e and f.

3.2. Line intensity measurements

The relative intensity, I/I_0, of curve AB, where I_0 is the intensity of the curve in untreated samples, is shown in Fig. 2 as a function of annealing time, for three ageing temperatures. For each curve, the intensity, *I*, was calculated using the equation

$$I = A/pG \qquad (1)$$

where *A* is the curve amplitude, *p* is the sample weight and *G* is the spectrometer gain (there was no need to take the linewidth into account because it was approximately the same for all samples).

4. Analysis

For all four annealing temperatures, the intensity of curve AB is described well by equations of the form

$$I = I_0 \exp[-(kt)^n], \qquad (2)$$

where *t* is the ageing time. This confirms that curve AB is due to the amorphous phase. The second, broader curve that appears for medium ageing times is attributed to a crystalline phase with composition $(Fe, Ni)_3B$ [1]. In that case, the transformed fraction, *f*, in each sample is given by

$$f = 1 - I/I_0 \qquad (3)$$

where *f* is the transformed fraction and I/I_0 is the relative intensity of curve AB.

Once the relationship between I/I_0 and *f* is known, it is possible to determine the Avrami exponent, *n*, for the transformation. To do that, the parameters *n* and

TABLE I Experimental values of the Avrami exponent, *n*, and the reaction rate, *k*, for the crystallization of the metallic glass $Fe_{40}Ni_{40}B_{20}$

T (° C)	*n*	*k* (h^{-1})
360	1.70	0.53
365	1.49	0.91
370	1.49	1.48
375	1.62	2.65

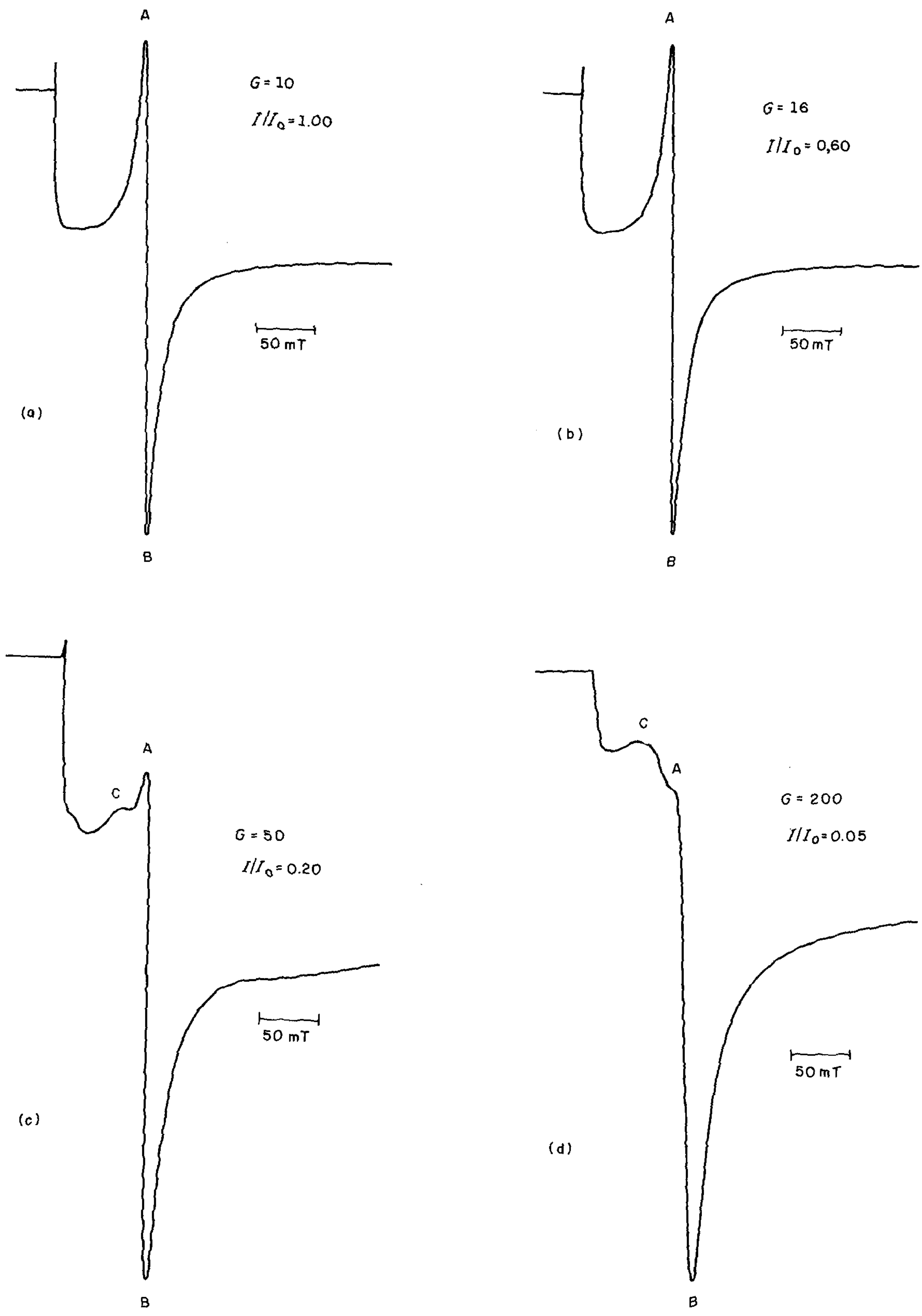

Figure 1 FMR spectra of $Fe_{40}Ni_{40}B_{20}$ samples. (a) As-received; (b) annealed for 15 min at 375° C; (c) annealed for 30 min at 375° C; (d) annealed for 45 min at 375° C; (e) annealed for 90 min at 375° C; (f) annealed for 120 min at 375° C.

k in the Johnson–Mehl–Avrami equation

$$f = 1 - \exp[-(kt)^n] \quad (4)$$

were chosen so as to give the best fit to the experimental points, using Equation 3 to determine the transformed fraction from line intensity data. The results are shown in Fig. 3 and Table I. The average value of n is 1.58.

The apparent energy for crystallization, E_c, was calculated from the temperature dependence of the time to a certain transformed fraction, according to the equation

$$t_f = A\exp(-E_c/kT) \quad (5)$$

where A is a constant and the transformed fraction may be determined using Equation 3. Plots of ln (t_f) as a function of $1/T$ are shown in Fig. 4 for three different values of the transformed fraction. The corre-

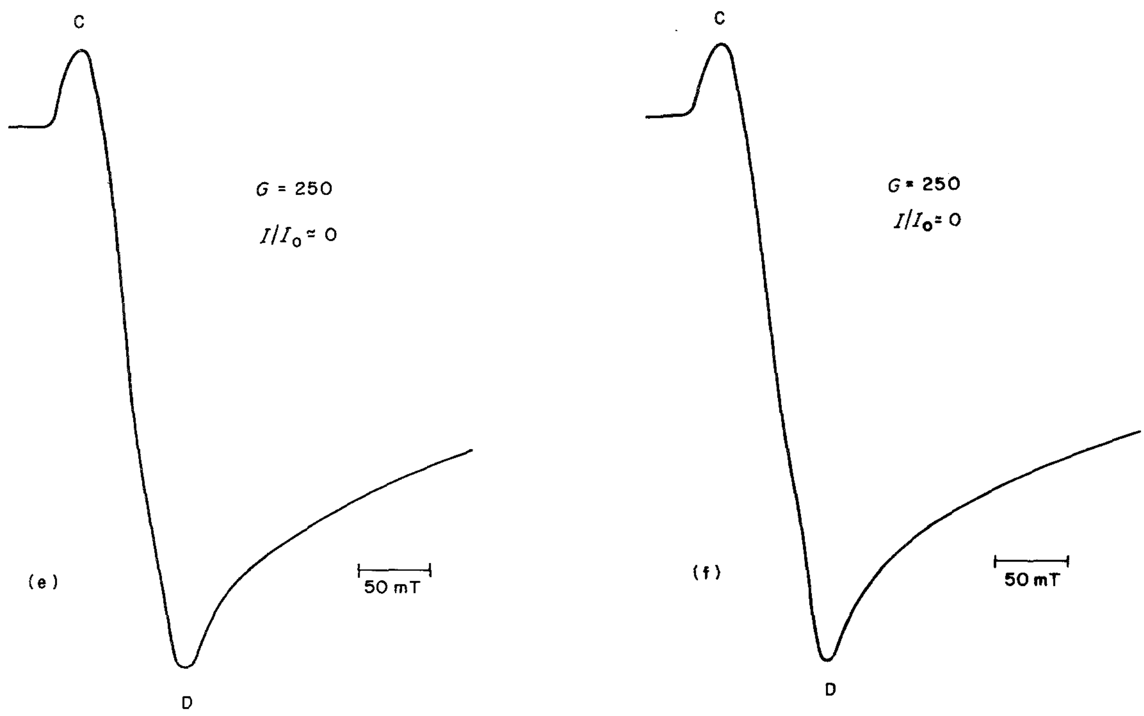

Figure 1 Continued.

sponding values of E_c, as obtained from the slopes of straight-line fits to the experimental points, are shown in Table II. The average value of E_c is $364\,kJ\,mol^{-1}$.

5. Discussion and conclusions

Previously reported values for the activation energy for crystallization of the Vitrovac 0040 alloy range from 289 to $444\,kJ\,mol^{-1}$ [2–5]. The experimental values of E_c obtained in the present work lie within this range (see Table II). The values of the Avrami exponent, n (Table I), are smaller than the values of 2.6 to 3.8 reported by Gobran *et al.* [5], which, however, were measured at higher temperatures (387 to 407° C) and thus cannot be compared directly to the

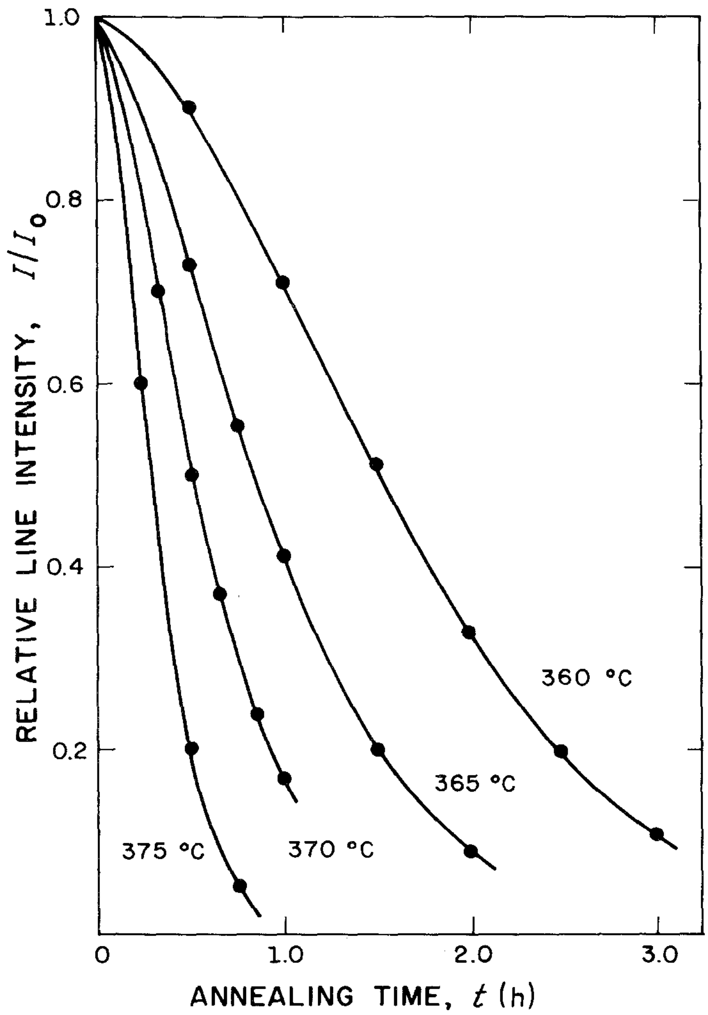

Figure 2 Relative intensity of line AB as a function of annealing time, for four annealing temperatures.

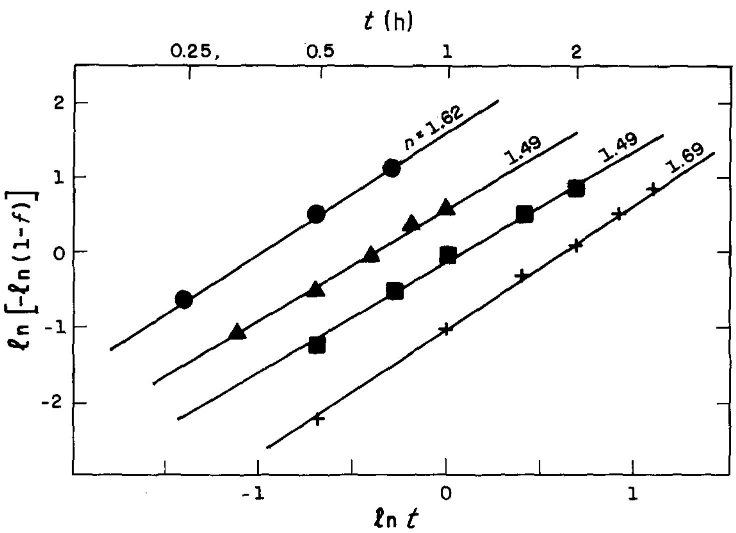

Figure 3 Avrami plots for four annealing temperatures. The straight lines are least-squares fits to the experimental points. (●) 375° C, (▲) 370° C, (■) 365° C, (+) 360° C.

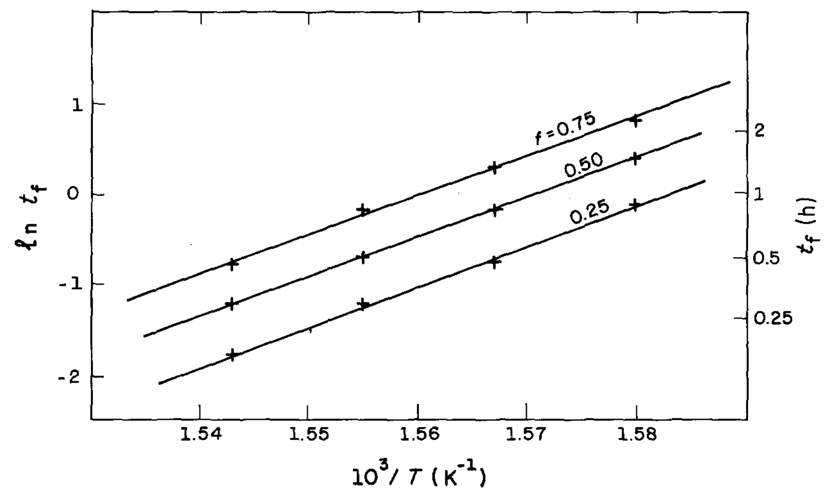

Figure 4 Plot of ln (t_f) as a function of inverse annealing temperature. The straight lines are least-squares fits to the experimental points.

present results. The average value of n for all annealing temperatures is 1.58, reasonably close to the values of 1.65 and 1.67 reported for the first crystallization in the Fe–Ni amorphous alloys $F_{32}Ni_{36}Cr_{14}P_{12}B_6$ (Metglas 2826A) [6] and $Fe_{40}Ni_{40}P_{14}B_6$ (Metglas 2826) [7] and to the theoretical value of 1.67 proposed by Ilschner [8] for parabolic growth with a constant nucleation rate. This suggests that the crystallization of the $(Fe, Ni)_3B$ phase in the Vitrovac 0040 alloy is a process involving the diffusion-controlled growth of crystals nucleating at a constant or slightly decreasing rate.

TABLE II Experimental values of the apparent activation energy, E_c, for the crystallization of the metallic glass $Fe_{40}Ni_{40}B_{20}$, for three different values of the transformed fraction, f

f	E_c (kJ mol^{-1})
0.25	362
0.50	362
0.75	368

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