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Applicability of FMR for crystallization studies in metallic glasses

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It has been shown theoretically that the peak-to-peak ferromagnetic resonance (FMR) linewidth (ΔH_{pp}) should be proportional to the volume fraction (f) of the crystalline phase formed during annealing in ferromagnetic glasses. However, in the case of zero-magnetostrictive cobalt-based glasses ($\lambda = 0$), ΔH_{pp} should remain constant due to very low values of anisotropy. In $Co_{68}Fe_4Mo_1Si_{17}B_{10}$ glass ($\lambda = 0$), ΔH_{pp} has been found to remain unaffected upon progressive crystallization. In $Fe_{65}Cr_8B_{27}$ glass, ΔH_{pp} has been found to be linearly proportional to f. Using this dependence, the activation energy of crystallization (E_a) has been calculated. The value of E_a obtained from the FMR technique (248 kJ mol^{-1}) agrees quite well with those from DTA studies using Kissinger's or Ozawa's technique.

1. Introduction

Crystallization behaviour of metallic glasses is a subject of practical interest, because the properties of amorphous materials are significantly changed by the onset of crystallization. The resistance to crystallization in a metallic glass can be estimated by its crystallization temperature and activation energy for crystallization. Recently, de Biasi and co-workers [1, 2] have shown that in ferromagnetic resonance (FMR), linewidth (ΔH_{pp}) changes on annealing for $Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$ (Metglas 2826 A) and $Fe_{40}Ni_{40}P_{14}B_6$ (Metglas 2826), and can be used to study the structural relaxation and crystallization kinetics. However, they assumed that ΔH_{pp} is proportional to the volume fraction transformed (f). The main objectives of the present work were;

(i) to prove theoretically as well as experimentally the linear dependence of f on ΔH_{pp},

(ii) to show that FMR is not likely to be sensitive to the crystallization process in the case of zeromagnetostrictive metallic glasses, and

(iii) to compare the activation energy for crystallization obtained by FMR technique with those estimated by differential thermal analysis (DTA) using non-isothermal kinetics. For this purpose, the crystallization kinetics of $Fe_{65}Cr_8B_{27}$ and $Co_{68}Fe_4Mo_1Si_{17}B_{10}$ (VITROVAC 6025) glasses were investigated by FMR. The basic principle behind this method has been explained by analysing the various contributions to the linewidth of the FMR [3].

2. Experimental details

The metallic glass $Fe_{65}Cr_8B_{27}$ was prepared by rapidly solidifying the premelted mother alloy in an argon atmosphere on the surface of single copper roller using following parameters: nozzle diameter = 0.6 mm; linear velocity of the copper roller = 25 m sec^{-1}; ejection pressure of argon gas = 2.0 kgf cm^{-2}; angle of ejection = 14° from the normal. The resulting ribbons were approximately 2 mm wide and 40 μm thick. The amorphous structure of the alloy was confirmed by X-ray diffraction performed on a Phillips PW1140 X-ray diffractometer using Fe$K\alpha$ radiation. The alloy $Co_{68}Fe_4Mo_1Si_{17}B_{10}$ (VITROVAC 6025) was obtained from Vacuumschmelze, Hanau, West Germany.

Room-temperature FMR spectra were recorded in the X-band (~9.5 GHz) using a Varian E-12 ESR Spectrometer. Samples (1 mm × 1 mm) were mounted horizontally on a flat end of a quartz rod and all the measurements were taken with the static magnetic field parallel to the sample surface and along the easy axis of magnetization of the ribbon. Annealing of the samples was carried out on straight lengths of ribbons inside the tubular furnace at various temperatures in an argon atmosphere for various lengths of time ranging from 5 min to 2 h. The X-ray diffraction studies on the annealed samples were performed. The crystallization temperatures were determined by Shimazdu's Differential Thermal Analyser at the heating rates of 10, 15, 20, 30 and 50° C min^{-1}. The volume fractions of the crystalline phase (f) in the annealed metallic glass were estimated by quantitative metallography.

3. Results and discussion

A typical FMR spectrum of the $Fe_{65}Cr_8B_{27}$ metallic glass sample is shown in Fig. 1. It can be seen that the FMR lines are broad with a typical peak-to-peak linewidth, ΔH_{pp}, of few hundred Gauss. ΔH_{pp} can be expressed as [3]

$$\Delta H_{pp} = \Delta H_u + \Delta H_I \quad (1)$$

where ΔH_u is the contributions to the linewidth from porosity, pits, eddy currents and intrinsic fields, and ΔH_I is the line broadening due to anisotropy in the inhomogeneous phase with the simultaneous presence of amorphous and crystalline phases.

ΔH_I can be written as [4]

$$\Delta H_I = \langle H_d^2 \rangle / 4M \quad (2)$$

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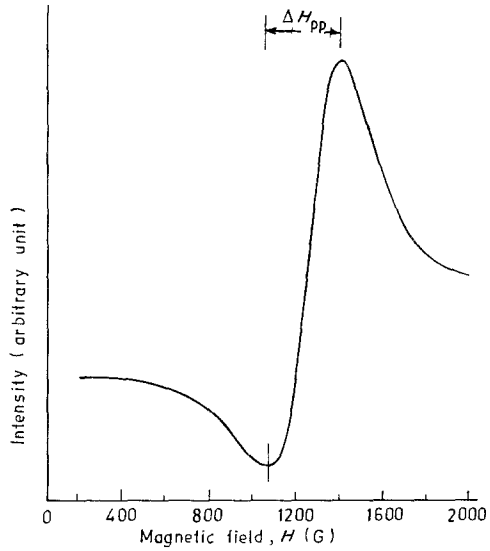

Figure 1 A typical FMR spectrum of a metallic glass.

where M is the magnetization of the sample and $\langle H_d^2 \rangle$ comprises the contribution from the crystalline and amorphous regions in the sample which can be expressed as

$$\langle H_d^2 \rangle = [(K/2M)^2 V_i + H_a^2(V - V_i)]/V \quad (3)$$

where K is the uniaxial anisotropy constant for the crystalline phase, H_a is the anisotropy field of the amorphous phase, V_i the volume of the crystalline phase formed, and V the total volume of the sample. Substituting the values of $\langle H_d^2 \rangle$ and ΔH_l from Equations 3 and 2, respectively, in Equation 1, it can be shown that

$$\Delta H_{pp} = \Delta H_u + \frac{H_a^2}{4M} + \left(\frac{K^2}{16M^3} - \frac{H_a^2}{4M}\right) f \quad (4)$$

where f is the volume fraction of the crystalline phase, $= V_i/V$. The first term ΔH_u does not change significantly with annealing as compared to the other terms in Equation 4 [3]. Thus Equation 4 predicts that ΔH_{pp} should be linearly dependent on f.

In the zeromagnetostrictive $Co_{68}Fe_4Mo_1Si_{17}B_{10}$ metallic glass, $H_a = 0$. Hence Equation 4 reduces to

$$\Delta H_{pp} = \Delta H_u + \frac{K^2}{16M^3} f \quad (5)$$

Substituting the values of K (of the order 10^5 erg cm^{-3}) and M (of the order 10^3 G) for the crystalline phases

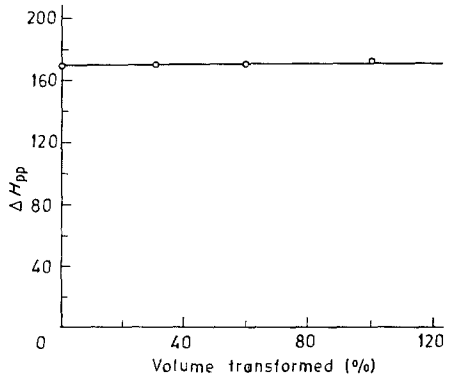

Figure 2 Dependence of FMR linewidth, ΔH_{pp}, on volume transformed (f) for $Co_{68}Fe_4Mo_1Si_{17}B_{10}$ metallic glass.

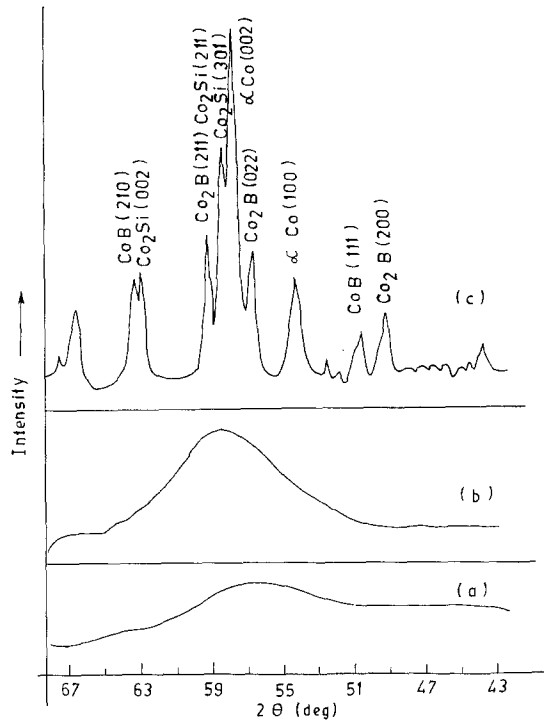

Figure 3 XRD patterns of $Co_{68}Fe_4Mo_1Si_{17}B_{10}$ alloy (a) in the as-spun state, (b) after annealing at 450° C, 1 h, (c) after annealing at 550° C, 1 h.

formed, the second term is estimated to be a few Gauss, the contribution is negligible when compared to the initial linewidth of 170 G. Thus one should not expect a change in linewidth even after crystallization. This has been confirmed experimentally as shown in Fig. 2. The corresponding X-ray diffraction spectra for various annealed states for $Co_{68}Fe_4Mo_1Si_{17}B_{10}$ glass have been shown in Fig. 3. Thus, the FMR technique is not suitable for studying the crystallization kinetics of cobalt-based zeromagnetostrictive metallic glasses.

The dependence of ΔH_{pp} on and for $Fe_{65}Cr_8B_{27}$ glass at various annealing stages is shown in Fig. 4. The linear nature of the curve in Fig. 4, shows the validity of Equation 4 for the $Fe_{65}Cr_8B_{27}$ metallic glass. Figure 5 shows the variation of ΔH_{pp} with the annealing time intervals at various annealing temperatures. The initial dip in the curve, at the annealing temperature of 430° C, is due to the reduction in anisotropy of the sample during structural relaxation. The linewidth can be well described [1, 2] by the equation similar to that of John–Mehl–Avrami equation which describes the

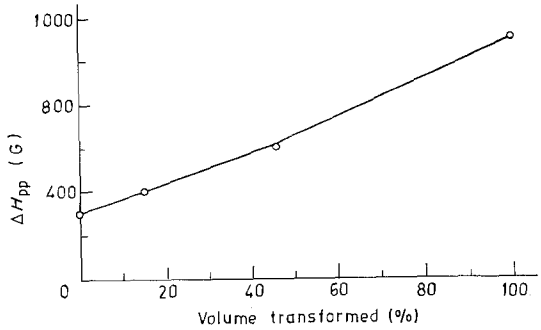

Figure 4 Dependence of FMR linewidth, ΔH_{pp}, on the volume transformed in $Fe_{65}Cr_8B_{27}$.

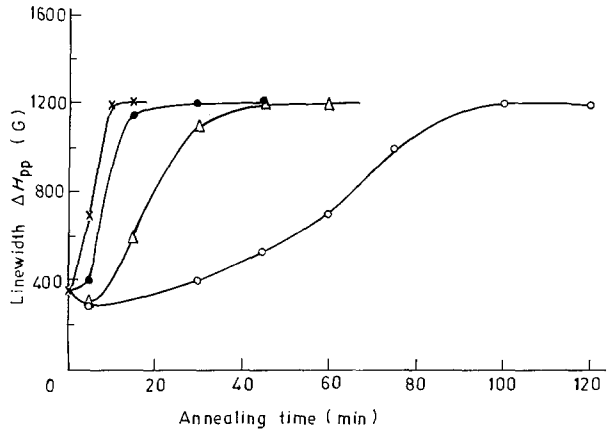

Figure 5 Dependence of FMR linewidth, ΔH_{pp}, on annealing time, at (○) 430° C, (△) 450° C, (●) 460° C, x 470° C.

overall crystallization kinetics as

$$\Delta H_{pp} = A + B[1 - \exp(kt^n)] \quad (6)$$

with $A = 290$ G and $B = 910$ G. Thus

$$\frac{\Delta H_{pp} - 290}{910} = 1 - \exp(kt^n) = f \quad (7)$$

Thus one can calculate f from the linewidth data as

$$f = \frac{\Delta H_{pp} - 290}{910} \quad (8)$$

The Avrami plot of $\ln[-\ln(1 - f)]$ against $\ln t$ is shown in Fig. 6 and from the slope the Avrami exponent n is obtained. The value of n is found to be 1.51. This suggests the diffusion-controlled bulk crystallization due to the growth of a fixed number of nuclei [5]. This value of n also agrees with the earlier reported values for some other metallic glasses [5, 6].

The activation energy of crystallization was calculated from the temperature dependence of the time to a certain value of the linewidth, $t_{\Delta H}$, according to the equation

$$t_{\Delta H} = A_1 \exp(-E_a/kT) \quad (10)$$

The average activation energy was estimated from the slopes of the Arrhenius curves (Fig. 7). This lies in the range of 240 to 255 kJ mol^{-1}.

The activation energy can also be determined from non-isothermal DTA kinetic experiments by following

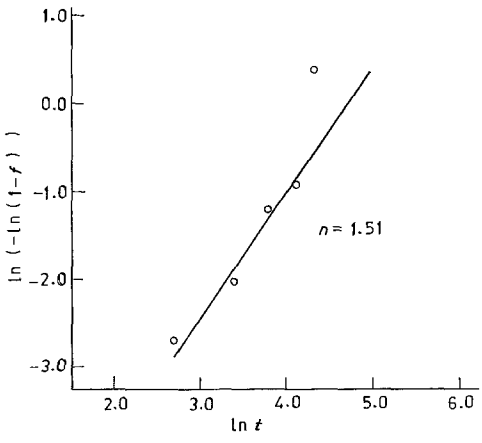

Figure 6 Avrami's plot for $Fe_{65}Cr_8B_{27}$.

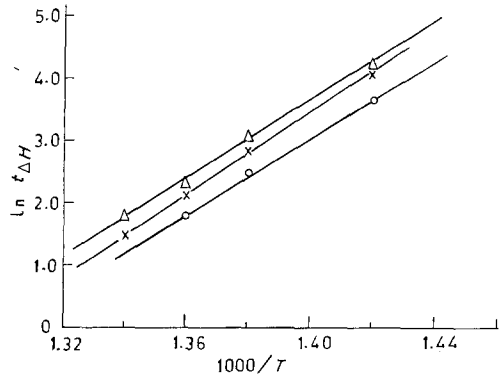

Figure 7 Arrehenius plot for $Fe_{65}Cr_8B_{27}$: (○) 500 G, (x) 700 G, (△) 900 G.

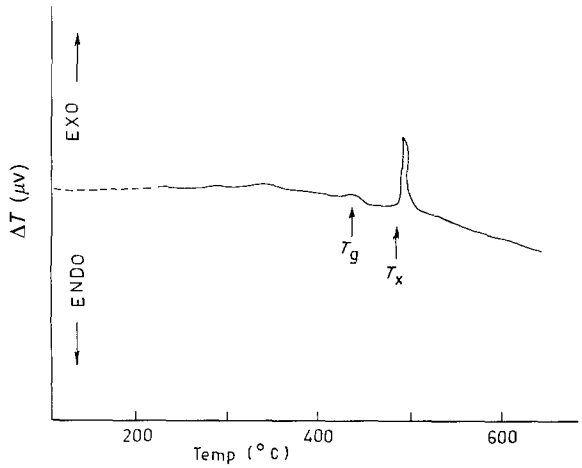

Figure 8 A typical DTA curve for $Fe_{65}Cr_8B_{27}$ metallic glass.

the methods due to Kissinger [7] or Ozawa [8]. The original Kissinger's relation is

$$[\mathrm{d}\ln(T_x^2/\alpha)]/[\mathrm{d}(1/T_x)] = (E_a/R) \quad (11)$$

and the Ozawa's relation gives

$$[\mathrm{d}(\ln\alpha)]/[\mathrm{d}(1/T_x)] = -(E_a/R) \quad (12)$$

where α is the heating rate, T_x the crystallization temperature and R the gas constant.

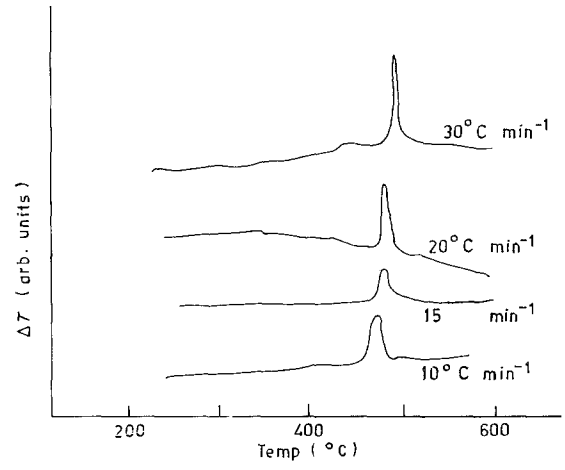

Figure 9 Effect of heating rates on the crystallization temperatures in $Fe_{65}Cr_8B_{27}$ metallic glass.

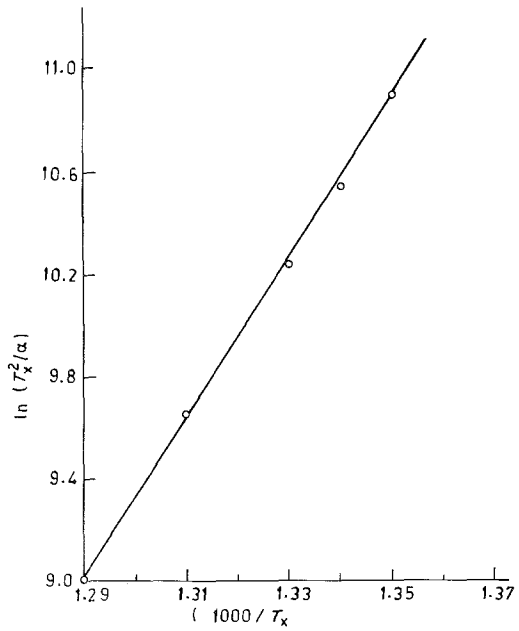

Figure 10 Kissinger's plot for $Fe_{65}Cr_8B_{27}$ metallic glass.

Thus by plotting ln (T_x^2/α) or ln α against $(1/T_x)$ one can obtain the activation energy of crystallization. Figure 8 shows the DTA curve obtained for $Fe_{65}Cr_8B_{27}$ metallic glass at the heating rate of 20° C min^{-1}. The variation in crystallization temperature (T_x) with the heating rate (α) is shown in Fig. 9. From these data, Kissinger's plot of ln (T_x^2/α) against $(1/T_x)$ and Ozawa's plot of ln α against $(1/T_x)$ were made and are shown in Figs 10 and 11. From the slope of the straight lines, the activation energy of crystallization was calculated and was found to be 252 and 249 kJ mol^{-1}, respectively.

Thus, the values obtained from the non-isothermal kinetic data using Kissinger's and Ozawa's relation correlates well with that of the value obtained from the isothermal kinetic study using the FMR technique.

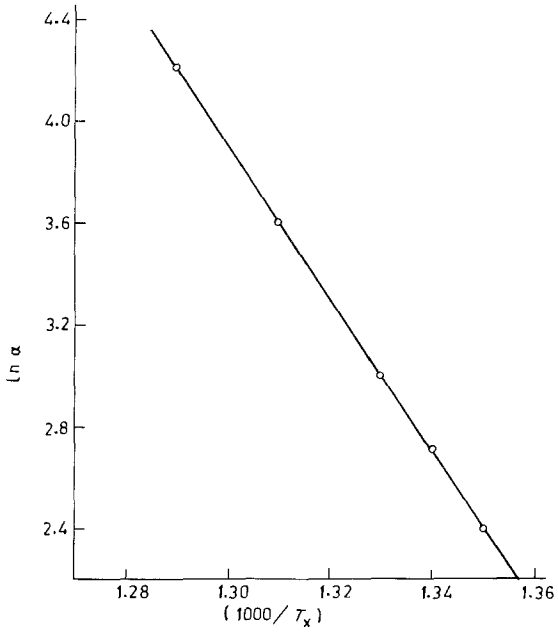

Figure 11 Ozawa's plot for $Fe_{65}Cr_8B_{27}$ metallic glass.

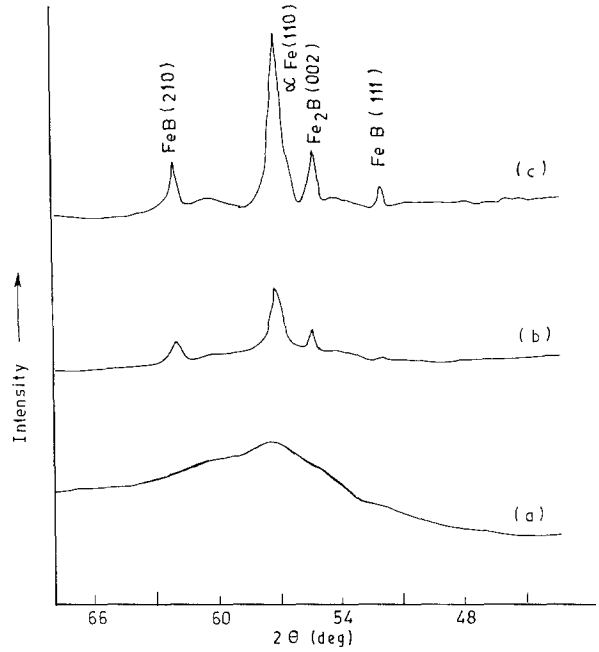

Figure 12 XRD patterns of $Fe_{65}Cr_8B_{27}$ (a) in the as-spun state, (b) after annealing at 450° C, 1 h, (c) after annealing at 500° C, 1 h.

The X-ray diffraction spectra are shown in Fig. 12 for the samples annealed at 450° C. The X-ray diffraction intensities were also found to increase with annealing time. From the diffraction peaks the crystalline phases were identified as α-Fe, Fe_2B and FeB.

4. Conclusions

We have shown that the FMR linewidth, ΔH_{pp} varies linearly with the volume fraction of the crystalline phase, f, in ferromagnetic metallic glasses. However, for zeromagnetostrictive cobalt-based metallic glasses, ΔH_{pp} remains almost independent of f.

The activation energy for the crystallization process of $Fe_{65}Cr_8B_{27}$ metallic glass using the FMR technique has been found to be 245 kJ mol^{-1}. This agrees quite well with those obtained from DTA studies using Kissinger's and Ozawa's methods.

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