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FMR study of crystallization in the amorphous alloy $Fe_{67}Co_{18}B_{14}Si_1$ (Metglas 2605CO)

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Abstract

The crystallization kinetics of the amorphous alloy $Fe_{67}Co_{18}B_{14}Si_1$ (Metglas 2605CO) has been studied using the FMR technique. The Avrami exponent, n, and the effective activation energy, E_c, were determined for the primary and polymorphic crystallization stages. The results for the primary stage ($n=1.00$, $E_c=230$ kJ mol^{-1}) are consistent with diffusion-controlled growth with a nucleation rate close to zero; for the polymorph stage, the results ($n=1.55$, $E_c=365$ kJ mol^{-1}) are consistent with diffusion-controlled growth with a constant nucleation rate. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Metglas; Amorphous alloys; Ferromagnetic resonance

1. Introduction

The thermal stability of metallic glasses is a subject of considerable interest, since the properties of these engineering materials may be significantly changed by the onset of crystallization. Ferromagnetic resonance (FMR) spectroscopy seems to be [1–8] a convenient method to study the crystallization of metallic glasses, because it is a fast, sensitive and nondestructive technique. In the present work, the FMR technique was used to investigate the annealing behaviour of the amorphous alloy Metglas 2605CO, manufactured by AlliedSignal Inc.

2. Background

Previous studies, using differential scanning calorimetry (DSC), have shown [9] that this metallic glass crystallizes in two stages: primary crystallization followed by polymorphic crystallization. The peak of the primary crystallization exotherm is separated from the peak of the polymorphic crystallization exotherm by a temperature interval of 74 K at a heating rate of 20 K min^{-1}. The Avrami exponent, n, was found to be about 2 for the primary crystallization and 2.8 for the polymorph crystallization. The first value is in disagreement with the results of Criado et al. [10], who found a value of about 1 for the Avrami exponent for the primary crystallization using the resistivity technique; the second value is difficult to interpret in terms of a nucleation and growth mechanism, since the Avrami exponent is expected to be [11] in the range from 1 (zero nucleation rate) to 2 (increasing nucleation rate). Recently, a DSC study of the crystallization kinetics of two Fe–Bi–Si metallic glasses [12] also yielded unreasonably high values for the Avrami parameter. The use of a third technique to study both crystallization stages was expected to yield new information about this system and also about the reliability of the DSC technique in this kind of study.

3. Experimental

The alloy, of nominal composition $Fe_{67}Co_{18}B_{14}Si_1$, was supplied in the form of ribbons 25 mm wide and 30 μm thick. Isothermal heat treatments were carried out in air on small pieces of the ribbon (typical dimensions 4 mm×3 mm) in a tube furnace with a temperature accuracy of ±1 K. First-derivative FMR spectra were recorded at room temperature using an X-band Varian E-12 spectrometer.

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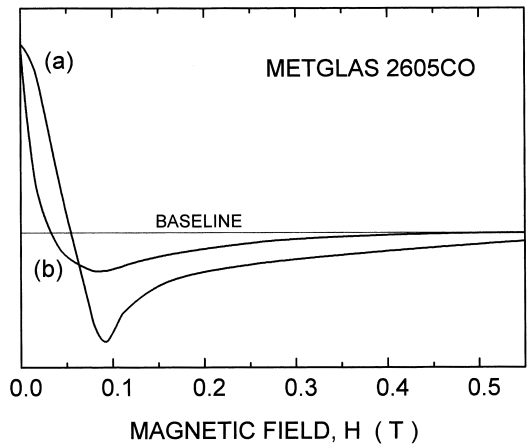

Fig. 1. FMR spectra of Metglas 2605CO samples. (a) As-received; (b) annealed for 4 h at 757 K.

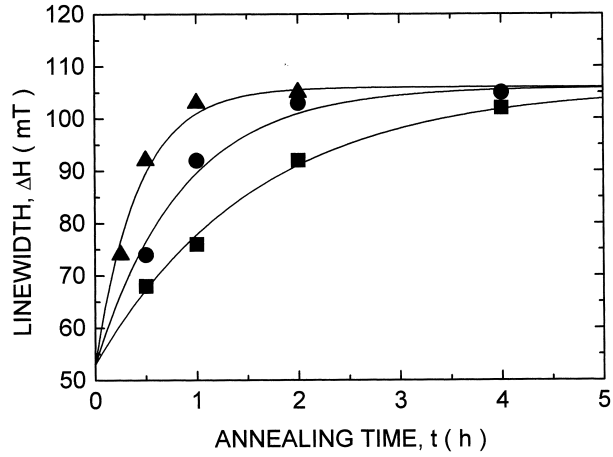

Fig. 3. Linewidth parameter as a function of annealing time, for three different annealing temperatures: (■) 635 K, (●) 645 K, (▲), 655 K.

All measurements were taken with the static field parallel to the sample surface and along the long axis of the ribbon.

4. Results and discussion

The FMR spectra of a virgin sample and of a sample annealed for 4 h at 757 K are shown in Fig. 1. Although the linewidth is definitely larger in the annealed sample, it cannot be measured in terms of the peak-to-peak linewidth, as it has been done for other metallic glasses [1–3,6,7] because the low-field side of the derivative curve is partially absent (Fig. 1). Since we are interested only in the relative change of the linewidth due to crystallization, we can measure instead the full width at half-height of the high-field part of the derivative curve, ΔH, as shown in Fig. 2. This linewidth parameter appears in Fig. 3 as a function of annealing time for three annealing temperatures (635, 645 and 655 K) in the range where primary crystallization is expected to occur. It is described well by equations of the form $\Delta H = A + B[1 - \exp(-kt^n)]$ with $A =$ 53 mT and B = 53 mT. This suggests that, as for other metallic glasses [1–3,6,7], the linewidth increases linearly with the transformed fraction of the sample. A plot of Fig. 4 was done using the data shown in Fig. 3 to determine the value of the Avrami exponent, n. The transformed fraction, f, was calculated from the linewidth data assuming the linear relation $f = (\Delta H - 53)/53$ to hold for all temperatures investigated. The value of n is 1.00 for the three temperatures. The apparent energy E_c for crystallization was calculated from the temperature dependence of the time to a certain value of the linewidth, $t_{\Delta H}$, according to the equation $t_{\Delta H} = A \exp(-E_c/kT)$. Plots of $\ln t_{\Delta H}$ as a function of $1/T$ are shown in Fig. 5 for several values of the linewidth. The corresponding values of E_c, as obtained from the slopes of straight-line fits to the experimental data, are also shown. The average value of E_c is 230 kJ mol^{-1}. Both the Avrami exponent and the activation

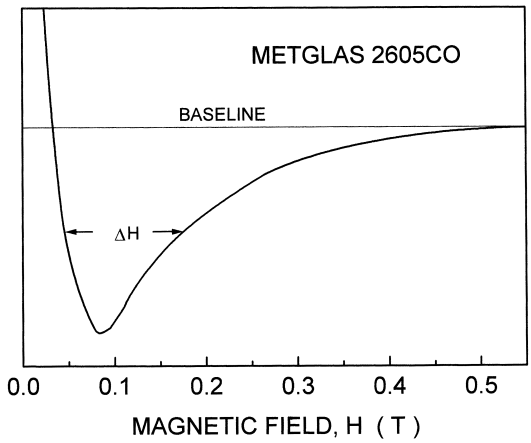

Fig. 2. High-field part of the FMR spectrum of a Metglas 2605CO sample annealed for 4 h at 757 K, showing the method used to determine the linewidth parameter.

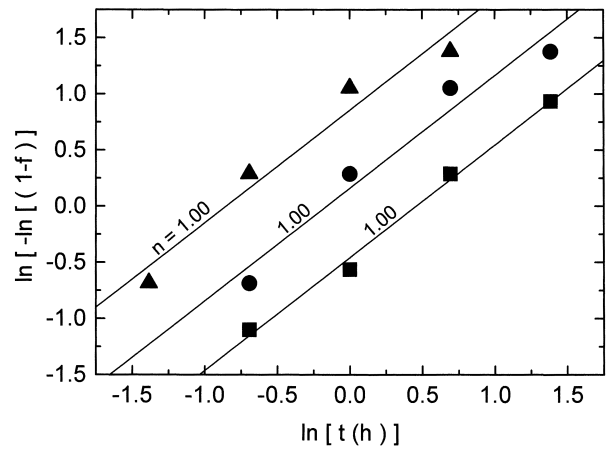

Fig. 4. Avrami plots for three different temperatures: (■) 635 K, (●) 645 K, (▲) 655 K.

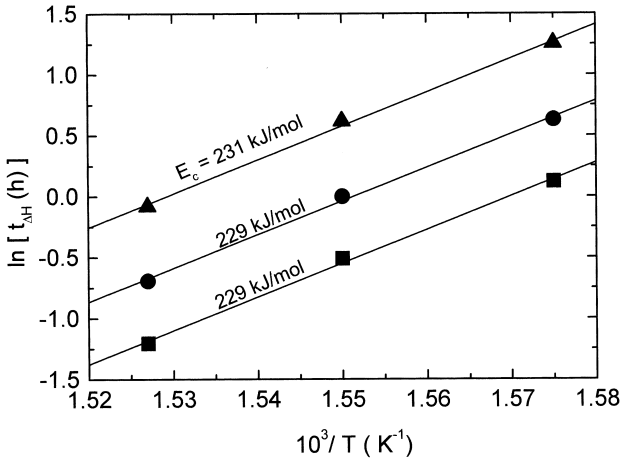

Fig. 5. Plot of $\ln t_{\Delta H}$ as a function of the annealing temperature. The straight lines are least-squares fits to the experimental data. ΔH=(■) 80 mT, (●) 90 mT, (▲) 100 mT.

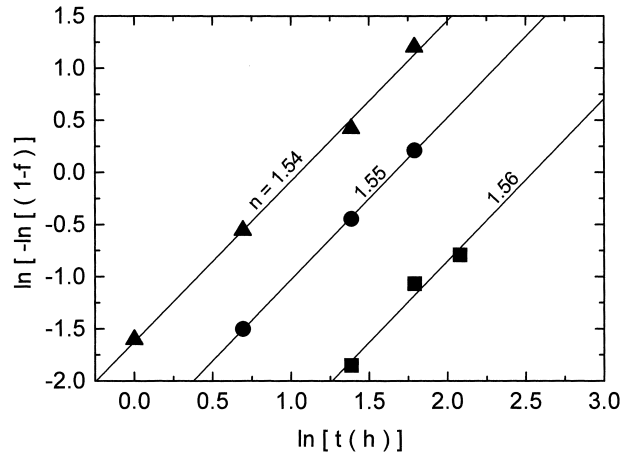

Fig. 7. Avrami plots for three different temperatures: (■) 747 K, (●) 757 K, (▲) 767 K.

energy are in excellent agreement with the resistivity results [10] but not with the DSC results [9]. The value of the Avrami exponent, 1.00, suggests that primary crystallization is a diffusion-controlled process with a nucleation rate close to zero [11].

The linewidth parameter appears in Fig. 6 as a function of annealing time for three annealing temperatures (747, 757 and 767 K) in the range where polymorph crystallization is expected to occur. It is described well by equations of the form $\Delta H=A+B[1-\exp(-kt^n)]$ with $A=$ 106 mT and $B=55$ mT. A plot of Fig. 7 was done using the data shown in Fig. 6 to determine the value of the Avrami exponent, n. The transformed fraction, f, was calculated from the linewidth data assuming the linear relation $f=(\Delta H-106)/55$ to hold for all temperatures investigated. The average value of n is 1.55. The apparent energy E_c for crystallization was calculated from the temperature dependence of the time to a certain value of the linewidth, $t_{\Delta H}$, according to the equation $t_{\Delta H}=A\exp(-E_c/kT)$. Plots of $\ln t_{\Delta H}$ as a function of $1/T$ are shown in Fig. 8 for several values of the linewidth. The corresponding values of E_c, as obtained from the slopes of straight-line fits to the experimental data, are also shown. The average value of E_c is 365 kJ mol^{-1}, slightly larger than the activation energy for the second crystallization of Metglas 2826MB [8], another iron-based amorphous alloy. The value of the Avrami exponent, 1.55, is consistent with a diffusion-controlled process with a constant nucleation rate [11].

The present results are consistent with resistivity results [10] and with known crystallization models [11], but not with DSC results [9]. This suggests that analysis of non-isothermal processes such as those used to collect DCS data should be done with care, since it can yield misleading results.

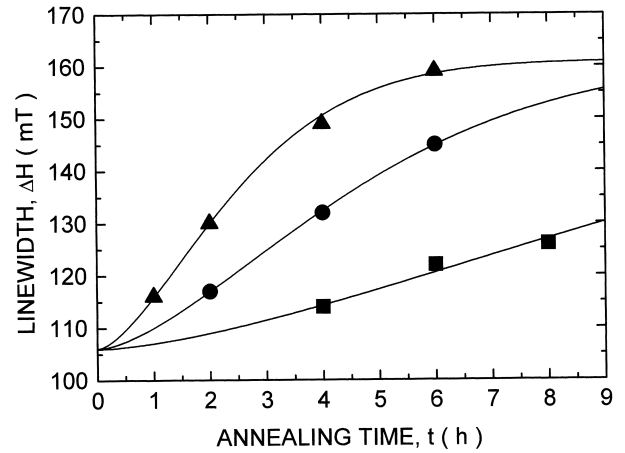

Fig. 6. Linewidth parameter as a function of annealing time, for three different annealing temperatures: (■) 747 K, (●) 757 K, (▲), 767 K.

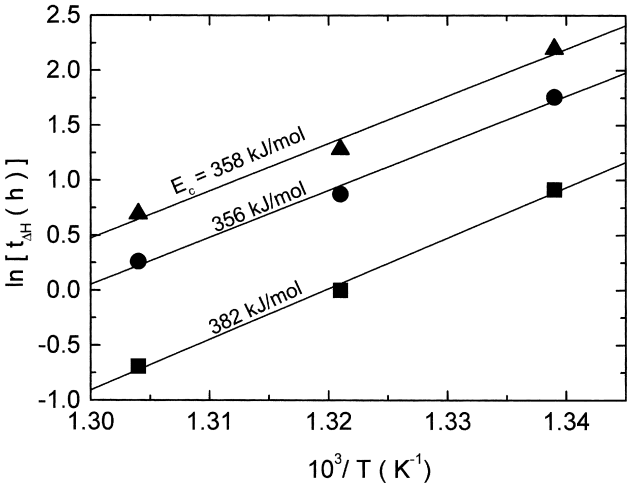

Fig. 8. Plot of $\ln t_{\Delta H}$ as a function of the annealing temperature. The straight lines are least-squares fits to the experimental data. ΔH=(■) 110 mT, (●) 120 mT, (▲) 130 mT.

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