JOURNAL OF MATERIALS SCIENCE 27 (1992) 2468–2472

Structural relaxations in Fe–Co–Si–B amorphous alloys

G. A. STERGIOUDIS*, J. YANKINTHOS‡, P. J. RENTZEPERIS*, Z. BOJARSKI§, T. J. PANEK§
*Laboratory of Applied Physics, Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece
‡Laboratory of Physics, Department of Electrical Engineering, Democritos University of Thrace, 67100 Xanthi, Greece
§Institute of Physics and Chemistry of Metals, Silesian University, 40-007 Katowice, Bankowa 12, Poland

The structural relaxation involved in the thermal treatment of Fe–Co–Si–B metallic glasses and the crystallization process as a function of Co content have been investigated. Magnetic measurements and the Mössbauer temperature scanning method for measuring the Curie temperature were used. One stage of structural relaxation above 570 K in metallic glasses with composition $Fe_{78-x}Co_xSi_9B_{13}$ was observed. This stage is characterized by a change of the chemical short-range ordering. The crystallization process detected by the magnetic measurements proceeds in two and in some cases in three steps.

1. Introduction

Heating of metallic glasses at temperatures considerably below the crystallization temperature produces various irreversible changes in the material. The structure of the material relaxes wherever the atoms are mobile. Many of the physical properties change, some drastically and others only to a moderate degree.

The structural relaxation effects in metallic glasses are difficult to observe directly by test techniques, but many of the changes taking place in the physical properties can be examined indirectly [1]. An example of the use of differential thermal analysis (DTA) for studying thermally induced structural relaxation, by determining the Curie temperature in metallic glasses with a nominal composition $Fe_{78}Si_9B_{13}$ (Metglass 2605 S-2, Allied Corporation), is given by Taylor *et al.* [2].

DTA showed the existence in $(Co_xFe_{1-x})_{78}Si_9B_{13}$ metallic glasses (with $0 < x < 1$) of two or more exothermic maxima, which are associated with primary crystallization of α-(Fe, Co) and also crystallization of eutectic intermetallic phases $(Fe, Co)_3(Si, B)$ [3–5]. Depending on the chemical composition of these metallic glasses, a suitable sequence for the crystallization process was proposed and also the activation energy of the first (2.5–3.5 eV) and second (3.5–5 eV) crystallization stages was estimated. The results of Mössbauer examination indicated the existence in this material, in the as-quenched state, of short-range atomic ordering (SRO) which differs from the SRO in the precipitated crystalline phases formed during the crystallization process. Thus this would be a material of amorphous structure II [6].

Again, the variation of the mean magnetic field at ^{57}Fe nuclei as a function of cobalt concentration, x, in the naturally aged Fe–Co–Si–B alloys indicates that the structure of this material could correspond to amorphous structure I [7]. Very probably a significant influence on the state of the material is exerted by the low-temperature structure relaxation occurring at ambient temperature.

In our present study the method of Mössbauer temperature scanning (MTS) was used for detailed determination of low-temperature structural relaxation in $Co_xFe_{78-x}Si_9B_{13}$ metallic glasses. The MTS method was supplemented by classical magnetic measurements.

2. Experimental procedure

$Co_xFe_{78-x}Si_9B_{13}$ ($0 < x < 78$) metallic glasses were obtained by the melt-spinning method in air, in the form of strips of width from 8 to 10 mm and thickness from 23 to 40 mm. The state after solidification was analysed in detail by X-ray diffraction methods (Philips diffractometer), transmission electron microscopy (JEM 200B) and Mössbauer transmission spectroscopy [3, 5]. The amorphous state of these materials after solidification from the liquid was confirmed, while no significant changes were observed relative to the initial state of this material after natural ageing for 1 year.

Measurements of Curie temperature, T_c, and crystallization temperature, T_k, were conducted using the MTS method. The schematic layout for these is shown in Fig. 1. The gamma quanta passing through the absorbent (S, the tested material) placed in the furnace (F) were recorded by the detector (D). Control of furnace operation permitted a linear rate of temperature increase with heating rate $\alpha = dT/dt$ from about

0022–2461

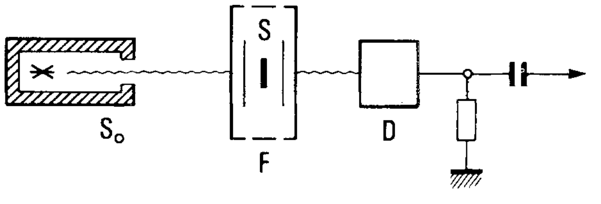

Figure 1 Schematic diagram of the Mössbauer temperature scanning set: (S) target, (F) furnace, (D) proportional counter, (S_0) Mössbauer source.

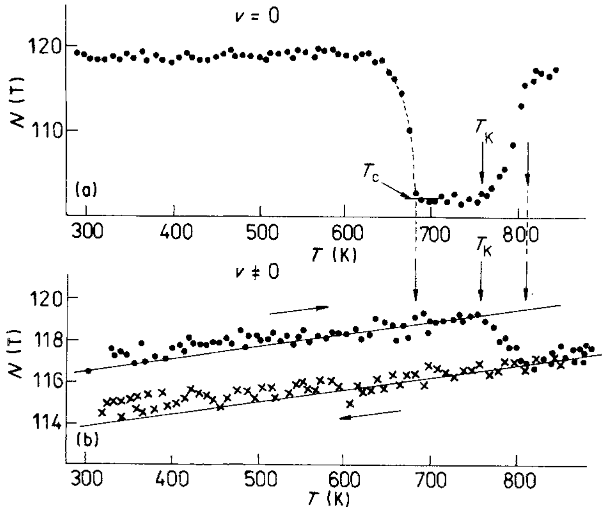

Figure 2 Count rate $N(T)$ of gamma quanta detected after the absorbent (target) as a function of the heating temperature T: (a) Doppler velocity of the Mössbauer source $v = 0$, (b) results for non-zero source velocity. The solid line represents the results obtained from Equation 1.

3 to 80 K min^{-1}. The operative control element was a platinum sensor (Pt-100). The temperature of the samples was measured with a Chromel–Alumel thermocouple.

Magnetic measurements using a vibrating sample magnetometer with an external field of 1 T were performed. The saturation magnetization and Curie temperature were measured.

3. Results and discussion

The measured number of gamma quanta $N_0(T)$ recorded after penetrating the absorbent, with constant source velocity equal to zero ($v = 0\,\mathrm{mm\,s^{-1}}$), as a function of temperature, T, is shown in Fig. 2a as an example of curves obtained for the $Fe_{78}Si_9B_{13}$ alloy.

A sharp drop of the $N_0(T)$ curve at the Curie point is observed, while above this point there is a plateau followed by a sharp rise in the curve at the moment of commencement of the crystallization process. For a non-zero source velocity $(-10\,\mathrm{mm\,s^{-1}} < v < +10\,\mathrm{mm\,s^{-1}})$ the N_v curve does not exhibit any significant variations at the Curie temperature (Fig. 2b), while a clear drop in this curve after the start of the crystallization process can be observed. Lowering the temperature gives a form of the $N_v(T)$ curve similar to that for the amorphous state with a distinct lowering of the level. The MTS curves measured with a moving Mössbauer source provide data on changes in the area, P_f, under the Mössbauer effect spectrum as a function of temperature. For a thin absorbent this field is approximately proportional to the probability of recoilless absorption of gamma quanta, f'. The Debye temperature of the metallic glasses tested lies in the interval from 300 to 400 K, depending on the cobalt concentration [8]. This indicates that at temperatures from about 450 K upwards, the following equation holds with good approximation:

$$f' = 1 - \frac{6R}{ke_D^2}T \qquad (1)$$

where e_D is the Debye temperature, R the recoil energy of the Mössbauer nucleus at the moment of emission of the gamma quantum and k the Boltzmann constant.

As may be seen from the example shown on Fig. 2b, $N_v(T)$ is described by a straight line for the material in the amorphous state at temperatures above 560 K, and again after crystallization, at temperatures above 620 K.

If we assume that

$$P_f = Af' \qquad (2)$$

where A is a proportionality coefficient, then

$$N_v(T) = N_b - Af' \qquad (3)$$

where N_b is the area under the background of the Mössbauer spectrum. Substituting from Equation 1 we obtain

$$N_v(T) = B + \frac{6AR}{ke_D^2}T \qquad (4)$$

where $B = N_b - A$, a constant.

The slope of both straight lines (Fig. 2b) does not change, which signifies that in these metallic glasses at temperatures greater than 560 K a structural relaxation process takes place and a chemical short order is present for which the characteristic value $(e_D^2/A)_{\mathrm{amorphous}}$ is the same as that for the crystalline phases, $(e_D^2/A)_{\mathrm{crystal}}$, appearing after the temperature T_k (Fig. 2a). A distinct jump in the $N_v(T)$ curve at the crystallization point is clear evidence that the mean square amplitude of the thermal vibrations of the atoms forming the crystalline phase is less than that of the atoms in the amorphous phase at the same temperature. The behaviour of the $N_v(T)$ curves as a function of cobalt concentration is of similar type.

During the course of the present investigations it was observed that there are no visible changes in the probability of the Mössbauer effect at the Curie point, which made possible a correct determination of temperature T_c as a function of the cobalt concentration, x.

The values of the Curie temperature for the initial material and after one year's natural ageing are shown in Fig. 3. The plot of $T_c(x)$ has a similar form to that for the $Co_xFe_{78-x}Si_{10}B_{12}$ material studied by Kuentzler and Williams [8]. After prolonged natural ageing at room temperature a very small (on the average of less than 20°) drop in the Curie temperature was found. On the other hand, the Curie temperature increased with the time of heating to higher temperatures [2, 3]. This contradictory T_c behaviour could lead to the conclusion that structural relaxation at room temperature is caused by a different mechanism from the one taking place at higher temperatures, or that T_c strongly depends on the heating rate.

The existence of two stages of structural relaxation in Fe–Ni–B metallic glasses was observed by Gerling and Wagner [9]. This was attributed to the reduction and redistribution of frozen excess free volume during the heating of the metallic glass and also to the annihilation of p and n-type defects. In order to elucidate this problem, measurements were made of the MTS curve, at zero source velocity, as a function of time of isothermal heating (during 1 h) at two different temperatures. The results are shown in Fig. 4. It is clear that no changes of $T_c(x)$ as a function of the isothermal heating temperatures are observed. The Curie temperatures dependence on the heating rate, α, for the material under investigation is shown in Fig. 5. The following empirical relation is used to describe $T_c(t)$:

$$T_c(t) - T_c(\infty) = [T_c(0) - T_c(\infty)] \times \exp\left[-\left(\frac{t}{\tau}\right)^n\right] \qquad (5)$$

where $T_c(t)$, $T_c(0)$ and $T_c(\infty)$ are the values of T_c (T is constant) at times t, $t = 0$ and $t \to \infty$. The power exponent n ranges from zero to unity; in the present study the value $n = 1$ was taken.

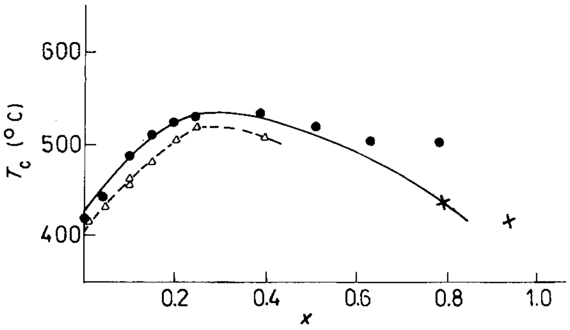

Figure 3 Curie temperature T_c versus cobalt concentration (x) for $Fe_{78-x}Co_xSi_9B_{13}$ metallic glasses: (●, ×) as-quenched materials with measurements at heating rate $\alpha = 3.4$ K min^{-1}, (△) material after natural ageing for one year and measurements performed at $\alpha = 5$ K min^{-1}.

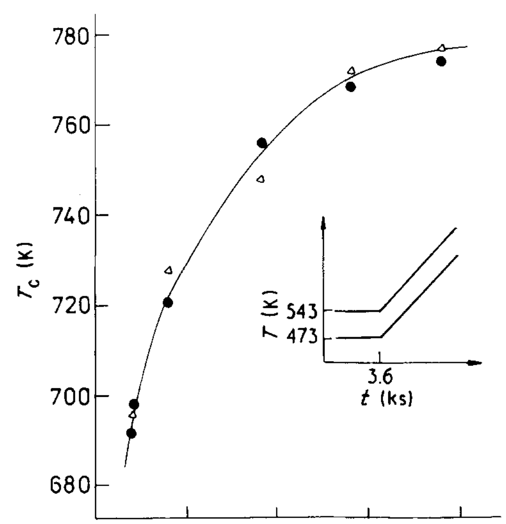

Figure 4 Curie temperatures T_c for $Fe_{78-x}Co_xSi_9B_{13}$ metallic glasses measured after isothermal annealing at two different temperatures: (●) 473 K, (△) 543 K. $dT/dt = 13$ K min^{-1}.

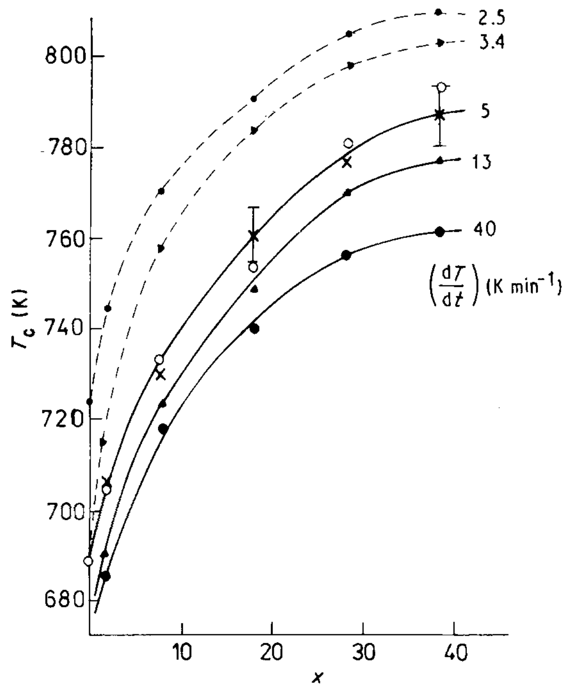

Figure 5 Curie temperature dependence on the heating rate for investigated alloys.

Values obtained for relaxation time $\tau(T)$ allowed the estimation of the mean activation energy for the relaxation process. Asssuming

$$\tau = \tau_0 \exp\left(-\frac{\langle E_a \rangle}{kT}\right)$$

then $\langle E_a \rangle = (2.20–2.25)$ eV. The values of the activation energy for the crystallization process in $Co_xFe_{78-x}Si_9B_{13}$ were found to be from about 3 to 5 eV [3, 5]. This E_a temperature dependence reflects a fairly wide activation energy spectrum in the case of structural relaxation in the metallic glasses tested.

In Fe–Co–B alloys the Curie temperature is governed by the boron content. Increase in boron concentration causes a rise in T_c [10]. It has also been concluded that T_c is strictly related to the amorphous $(Fe, Ni)_3B$ phase in $Fe_{40}Ni_{40}B_{20}$ metallic glasses [9]. Hence for $Co_xFe_{78-x}Si_9B_{13}$ glasses at temperatures above 573 K, the recorded variations in T_c may be associated with local redistribution of boron and the formation of an amorphous $(Fe, Co)_3B$ cluster. The diffusion of Fe and Co atoms causes the occurrence of SRO corresponding to the α-Fe(Co) phase.

In the amorphous alloys with $28 < x < 78$, except for $Fe_{20}Co_{58}Si_9B_{13}$, the magnetization decreases with increasing x (cobalt concentration) at a given temperature. This may be due to the decrease of iron concentration, the average magnetic moment per Fe atom being higher than that per Co atom as observed elsewhere [11] for an FeSi amorphous alloy. The rate of magnetization decreases with temperature and is smaller than that of the $0 < x < 28$ series. According to Chen and Tai [12] the field-induced anisotropy at the same temperature increases with x in $(Fe_{1-x}Co_x)_{78}Si_{10}B_{12}$ alloys, and consequently the decrease of magnetization must be slower for the Co-rich amorphous alloys.

The magnetization at 300 K under a field of $B = 1$ T varies between 85 and 140 e.m.u. g^{-1}, except for that of $Fe_{20}Co_{58}Si_9B_{13}$ which is equal to 190 e.m.u. g^{-1}, the highest in all the series. For $62 < x < 78$ the alloys present the lowest magnetization. In this case, with the decrease of the iron content a filling of the 3d band of cobalt may occur, decreasing the 3d moment.

The Curie temperature, T_c, takes its highest values for the Co concentration $28 < x < 58$ in contrast with unpublished results obtained for $Fe_{78-x}Co_xSi_{10}B_{12}$ and supplied to Kuentzler and Williams [8]. The behaviour of T_c in that observation is quite the same except for the displacement of T_c towards higher Co contents (higher x). At the highest cobalt concentration T_c drops off substantially and follows the remarks and the rules mentioned elsewhere [13].

Two- or three-step crystallization with broad and sharp changes occurs in these alloys (Figs 6 and 7). For $x = 0$, 4, and 8 the crystallization occurs near the paramagnetic region of the amorphous while for $x = 18$ and 28 it starts far from the paramagnetic region.

The crystallization process is a kinetic one and T_k is difficult to define, especially for the heating rate chosen in this work. Usually a rate of 10 K min^{-1} or higher is sufficient for a well-defined T_k [14, 15]. Prolonged heating at a temperature much lower than T_k would eventually induce crystallization [16], so its behaviour is very complicated and tends to be different from sample to sample depending on the chemical composition and heat treatment [17]. However, some useful deductions could be extracted by following the crystallization process from sample to sample:

1. In the alloy $Fe_{78}Si_9B_{13}$ crystallization sets in with α-Fe precipitation and the unstable Fe_3B phase.
2. All four alloys with $x = 4$, 8, 18 and 28 exhibit similar behaviour of crystallization, with gradual appearance of the Fe_3B phase and diminution of the α-Fe precipitation.
3. The Fe_3B phase transforms rapidly into Fe_2B and α-Fe at elevated temperatures and under low heating rate does not appear at all [16].
4. A remarkable behaviour has been observed in the alloy with composition $Fe_{20}Co_{58}Si_9B_{13}$ which exhibits just one crystallization peak, at a temperature near 830 K.
5. In the richer cobalt samples with $x = 66$, 70, 74 and 78 an equilibrium is reached and the crystallization process described elsewhere dominates [18, 19].
6. By extrapolating the last region of magnetization a T_c around (1030) K is reached, lying between 1015 K [20] and 1043 K [21], the Curie temperature values of the crystalline Fe_2B and α-Fe phases, respectively. For the $Fe_{74}Co_4Si_9B_{13}$ compound a third crystallization peak is observed at about 835 K with a corresponding T_c higher than 1020 K.

4. Conclusions

The existence of one stage of structural relaxation above 570 K in Fe–Co–Si–B metallic glasses after natural ageing for four years at room temperature was observed. Depending on the Co concentration, x, the Curie temperature versus x curve shows three distinct regions. For $0 < x < 28$ the Curie temperature increases steeply with x, in the $28 < x < 66$ region its variation is not appreciable within the experimental errors, and finally it drops abruptly for $66 < x < 78$. The magnetization versus x for as-quenched amorphous state increases with x in the low Co concentration

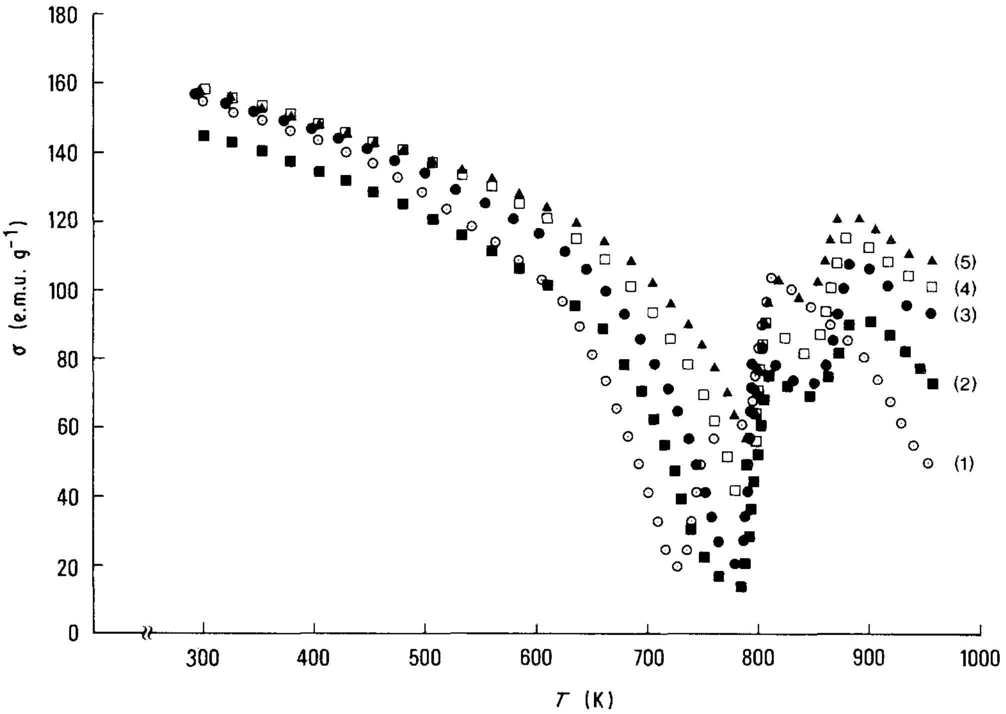

Figure 6 Magnetization curves for $Fe_{78-x}Co_xSi_9B_{13}$ metallic glasses: (○) $x = 0$, (■) $x = 4$, (●) $x = 8$, (□) $x = 18$, (▲) $x = 28$.

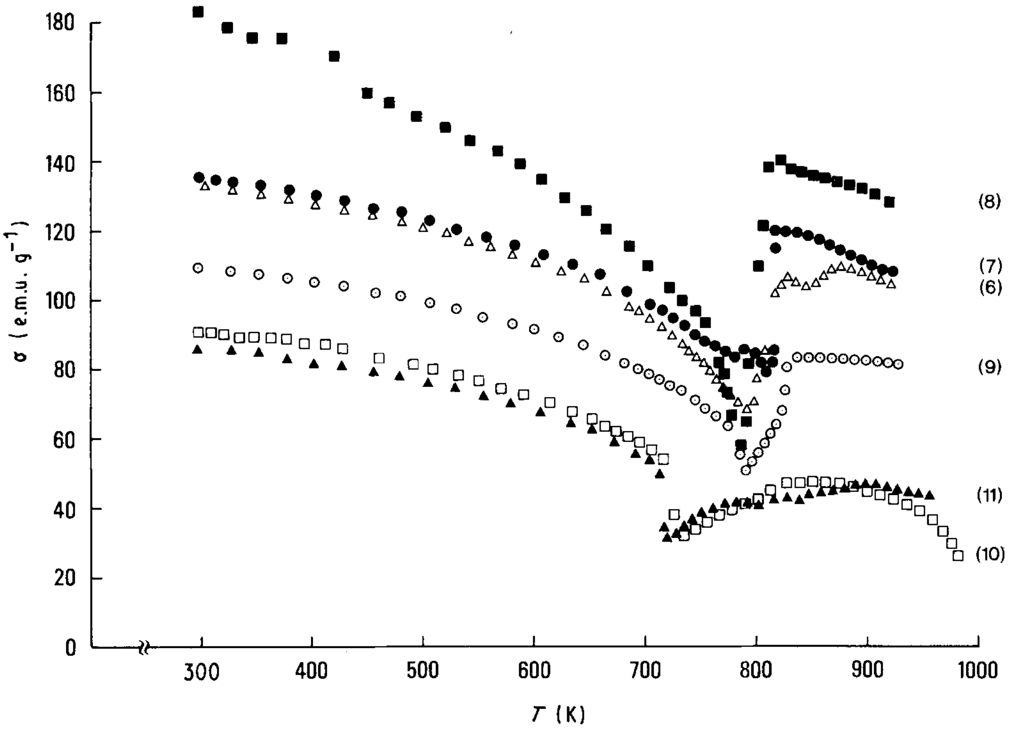

Figure 7 Magnetization curves for $Fe_{78-x}Co_xSi_9B_{13}$ metallic glasses: (△) $x = 38$, (●) $x = 58$, (■) $x = 66$, (○) $x = 70$, (□) $x = 74$, (▲) $x = 78$.

region ($0 < x < 28$) and then decreases steeply for $28 < x < 74$ except for the alloy $Co_{78}Si_9B_{13}$. The crystallization process detected by magnetic measurements proceeds by two and in some cases three steps and exhibits no remarkable differences from those observed by X-ray or DSC analysis.

Acknowledgements

The Institute of Materials Engineering, Warsaw Polytechnic, supplied the test materials and also partially financed this project. One author (T.J.P.) thanks Mr Meczynski for his technical assistance during the MST measurements.

References

1. H. S. CHEN, in "Amorphous Metallic Alloys", edited by F. E. Luborsky (Butterworths, Boston, 1983) p. 169.
2. T. J. TAYLOR, Y. P. KHANNA and H. H. LIEBERMANN, *J. Mater. Sci.* **23** (1988) 2613.
3. Z. BOJARSKI, T. J. PANEK, J. LELATKO, L. PAJAK and R. MECZYNSKI, in Proceedings of 13th Conference on Applied Crystallography, Cieszyn, Poland, 1988, edited by Z. Bojarski, T. Bold and H. Krzton, Vol. 1 (IMX, Gliwice) p. 36.
4. M. KOPCEWICZ, M. El ZAYAT and U. GONSER, *J. Magn. Magn. Mater.* **72** (1988) 119.
5. J. KWARCIAK, L. PAJAK, and J. LELATKO, *Z. Metallkde* **79** (1988) 712.
6. R. C. O'HANDLEY, *J. Appl. Phys.* **62** (1987) R15.
7. K. WITANSKI and T. J. PANEK, *Acta Phys. Pol.* **A75** (1989) 137.
8. R. KUENTZLER and D. E. G. WILLIAMS, *J. Phys. F: Met. Phys.* **15** (1985) 2283.
9. R. GERLING and R. WAGNER, *Scripta Metall.* **17** (1983) 1129.
10. C. L. CHEN and K. M. UNRUH, *Phys. Rev. B* **24** (1981) 1556.
11. G. MARCHAL, Ph. MANGIN, M. PIECUCH, Ch. JANOT and J. HUBSCHI, *J. Phys. F: Metal Phys.* **7** (1977) L165.
12. D.-X. CHEN and L.-C. TAI, *J. Magn. Magn. Mater.* **50** (1985) 329.
13. K. HAYASHI, K. HOTAI, M. HAYAKAWA, Y. OCHIAI, H. MATSUDA, S. UEDAIRA and K. ASO, *ibid.* **36** (1983) 237.
14. P. K. RASTOGI and P. DUWEZ, *J. Non-Cryst. Solids* **5** (1978) 1.
15. F. E. LUBORSKY, *Mater. Sci. Eng.* **28** (1977) 139.
16. C. L. CHIEN, *Phys. Rev. B* **18** (1978) 1003.
17. Y. KHAN, *Z. Metallkde.* **74** (1983) 385.
18. Y. KHAN, T. ABBAS and S. A. SHAHEEN; *J. Mater. Sci. Lett.* **3** (1984) 319.
19. J. ZACHARIDOVA, V. ANCHEV and M. YAPRAKOVA, in Proceedings of 13th Conference on Applied Crystallography, Cieszyn, Poland, 1988, edited by Z. Bojarski, T. Bold and H. Krzton, Vol. 1 (IMX, Gliwice) p. 147.
20. C. L. CHIEN and D. MUSSER, *Phys. Rev. B* **20** (1979) 283.
21. A. K. MAJUMBAR, V. OERTREICH, D. WECHLENFELDER and F. E. LUBORSKY, *ibid.* **21** (1983) 5618.

Received 16 January
and accepted 7 June 1991