Journal of Thermal Analysis, Vol. 32 (1987) 9–16

INVESTIGATION OF STRUCTURAL RELAXATION OF $Fe_{85}B_{15}$ AMORPHOUS METALLIC ALLOY BY THERMOMAGNETIZATION

E. Illeková, P. Ambrovič* and *K. Czomorová*

*INSTITUTE OF PHYSICS, EPRC, SLOVAK ACADEMY OF SCIENCES, BRATISLAVA
INSTITUTE OF POLYMERS, CCHR, SLOVAK ACADEMY OF SCIENCES, BRATISLAVA, CZECHOSLOVAKIA

(Received February 18, 1986)

Thermomagnetometry was used to determine the Curie temperature of $Fe_{85}B_{15}$ amorphous alloy. Measurements were made with a TGS-1 Perkin–Elmer thermobalance in a permanent magnetic field. Armosphous material with a thickness of ~25 μm was prepared by melt spinning.

In the temperature region 300 to 800 K the sample is characterized by one Curie transformation in the amorphous matrix at $T_c \sim 570$ K. A broad region of primary crystallization of α-Fe begins at approximately 660 K, followed closely by the rapid crystallization of Fe_3B phase with maximum at T_{cr2} 750 K. Amorphous material which is unstable due to quenching is relaxed by annealing. The structural relaxation causes ageing of the Curie temperature in the metallic glass.

The observed phenomena might be explained in terms of certain changes in local atomic arrangement.

Fe-based metallic glasses are investigated from the aspects of cheap production technology and technical application and also their interesting magnetic and mechanical properties. Metallic glasses are produced by rapid quenching ($> 10^6$ deg s^{-1}) of multicomponent melts with chemical compositions close to the eutectic one. Usually, they are either highly supersaturated solid solutions or multiphase systems; they are characterized by substantial topological and chemical inhomogeneities. The specific frozen-in configuration depends on the thermal history of the sample.

The annealing of glasses causes pronounced changes in the physical properties, which may be due to (a) the quenched-in internal stresses, which occur in the early stages of annealing, (b) the structural relaxation of the glassy state, or (c) the onset of crystallization or of separation into two glassy phases in the later stages of annealing.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Metallic glasses containing a high (typically around 80%) atomic fraction of magnetic components are ferromagnetic and therefore exhibit a Curie transition. Recent results suggest that in general the Curie temperature T_c of ferromagnetic material is drastically reduced upon glassification of the material [1]. On annealing, the T_c of a glass changes significantly, even at times and temperatures substantially below those necessary to cause crystallization. T_c is a useful parameter for studying the structural relaxation of the glass. The only disadvantages of using T_c are that it cannot be monitored continuously, and if T_c is too high, unavoidable relaxation may occur during its determination, thereby obscuring any effects of pre-annealing.

The T_c-s of metallic glasses have generally been determined by differential scanning calorimetry as described in the papers of Greer [2–4] or So [5], and rarely via magnetic data obtained, for example, with a vibrating sample magnetometer [1], because of the complicated and time-consuming experimental arrangement. The drawback of DSC is that, after a particular annealing time at some intermediate and high annealing temperatures, the T_c of the amorphous matrix is not detectable by DSC [2–5] because there is not enough amorphous matrix left after the primary crystallization and/or because the magnetic transition is blurred by substantial composition gradients in the matrix.

In the present work a thermomagnetometric method is reported for the determination of the T_c of $Fe_{85}B_{15}$ amorphous alloy. A Perkin–Elmer TGS–1 thermobalance in a permanent magnetic field was used. The apparatus ensured automatic, program-controlled measurements, high stability of temperature or of heating rate and a large variability of heating rates, from 0.5 to 160 deg min^{-1}. The magnitude and character of the external magnetic field can be tested. The information content yielded by magnetic measurements concerning the structural relaxation of ferromagnetic materials is higher than that obtained from thermal measurements.

Experimental

The "effective magnetic mass" of the investigated material was determined by thermomagnetometry (TM) using a Perkin–Elmer TGS–1 thermobalance. The standard rate of heating was 10 deg min^{-1} and the sample temperature varied between 300 and 800 K. The atmosphere used was nitrogen. The one-piece square-shaped samples of ~0.15 mg mass cut from the amorphous foil were placed in a reproducible manner on the thermobalance pan in the centre of the permanent magnet. The sensitivity of the apparatus is about 0.1 mg/full-scale deflection (full scale = 25 cm). A set of materials with defined Curie points was used for temperature scale calibration. These were both alloys and synthetized garnets with

variable content of scandium. Calibration was performed at a heating rate of 10 deg min^{-1}. The accuracy of the calibration was ± 1.5 K. Because of the identical nature of the process of calibration and measurement, we did not take into account proposed corrections for temperature lag [3].

Since only the differences in "magnetic mass" were examined, conversion of the readings to absolute values of susceptibility was unnecessary. Therefore, direct thermobalance scale readings were used throughout this study. Each measurement was relative to the "magnetic mass" of the amorphous sample at room temperature (a scale reading of 1.00).

The annealing of amorphous samples was carried out in the Perkin–Elmer DSC–2 differential scanning calorimeter. The apparatus was calibrated to ± 0.5 K and has a temperature control of ± 0.1 K. The degree of crystallinity was also determined by DSC, at a heating rate of 10 deg min^{-1}.

Amorphous foils ~ 25 μm thick were produced by a melt spinning technique. It is known that the physical parameters of amorphous ribbons several metres long change along the length of the ribbon [6]. For this reason the value of T_c was taken as the average of five measurements under the same conditions. Samples were examined as received. A correction was made for spontaneous long-lasting room temperature relaxation of the material under investigation.

Samples were annealed during given time intervals, then taken out from the furnace (air-quenched), and the "magnetic-mass" was measured during the linear heating cycle. Because of the occurrence of additional annealing effects (see point (2) in the Discussion) during the determination of the T_c of samples, the heating times were not cumulative.

The "effective magnetic mass" of the glass studied as a function of temperature exhibited a curve typical of the magnetization of a conventional ferromagnet. TM data and the simultaneous DSC curve taken upon heating of the sample are exemplified in Fig. 1. The Curie point is defined as the temperature where ferromagnetism disappears completely. However, the termination and the culmination of any process as observed from the scan are rather fictive. Accordingly, the Belov–Goriaga–Arrot method was used to determine T_c. The maximum in the abrupt increase of the "magnetic mass" was taken to characterize the crystallization transformation of the glass above T_c to the ferromagnetic crystalline phase.

The amorphous nature of samples was checked both by X-ray diffraction and by transmission electron microscopy. With an atomic emission spectrometer, the content of boron in the $Fe_{85}B_{15}$ amorphous samples was checked to be $15.15 \pm 0.15\%$.

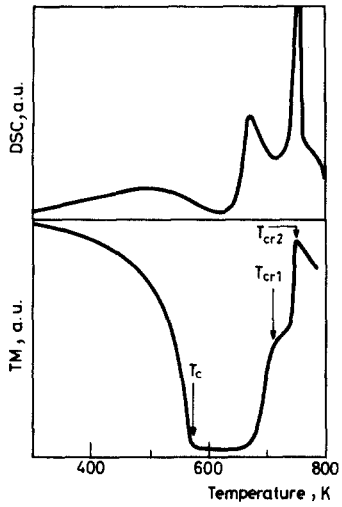

Fig. 1 Differential scanning calorimetry and thermomagnetization traces of amorphous $Fe_{85}B_{15}$ at a heating rate of 10 deg min^{-1}; T_c = Curie temperature, T_{cr1}, T_{cr2} = crystallization temperatures

Results

Annealing was done for six different annealing times, t_a, and at six annealing temperatures, T_a, for the $Fe_{85}B_{15}$ amorphous samples. Two sets of relaxation curves were determined.

In the first set, T_c *vs.* time isotherms were constructed. The first 160 min of these isotherms is shown in Fig. 2. It can be seen that, as a consequence of annealing at $T_a \leqslant 580$ K, T_c levels off in a reasonable time (e.g. 120 min at 580 K). The absolute change in T_c is a few degrees. The final value attained by T_c varies with T_a. Annealing at $T_a > 580$ K causes abrupt changes of some ten degrees in T_c. The magnitude and character of these changes can hardly be interpreted in terms of the structural relaxation of the glass. The reason for these changes might be some qualitative change in the local atomic arrangement of the ferromagnetic phase.

In the second set of relaxation curves, the dependence of the relaxation of the glass on T_a is demonstrated. The T_c *vs.* T_a curves for various t_a are plotted in Fig. 3. At low T_a, T_c increases mildly with t_a and temperature and passes through a maximum value. At higher temperatures above the peak, however, instead of dropping off to a smaller value, T_c increases abruptly. This is a good argument for assuming the presence of two different processes. These are probably to be interpreted as structural relaxation and partial crystallization of the sample (see point (1) in the Discussion).

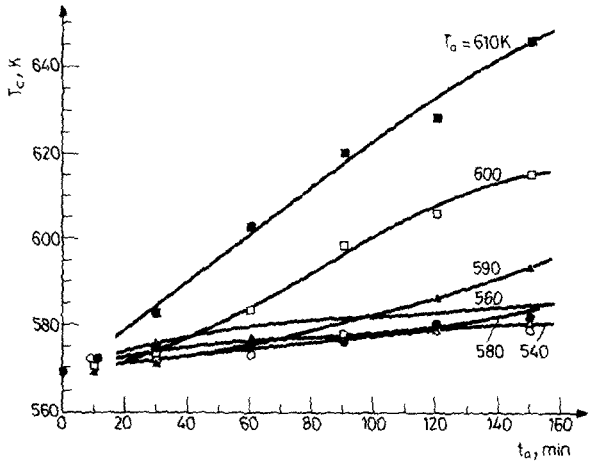

Fig. 2 Effect of isothermal annealing on Curie temperature, T_c, of amorphous $Fe_{85}B_{15}$, annealing temperature as parameter (T_c determined in a 10 deg min^{-1} run)

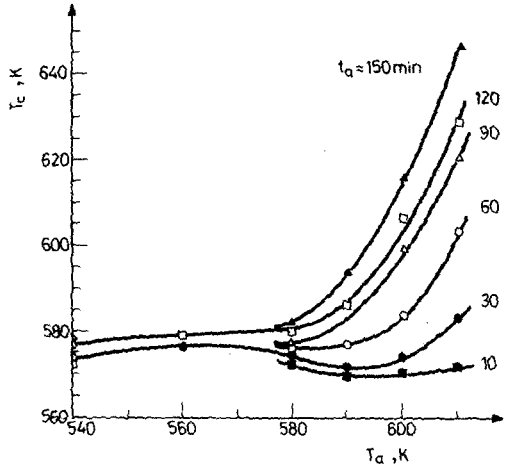

Fig. 3 Curie temperature as a function of isochronal annealing of $Fe_{85}B_{15}$ glass, determined in a 10 deg min^{-1} run

Discussion

(1) Effect of crystallization

The investigated samples were heated in the differential scanning calorimeter. In all cases two peaks were found in the trace, as illustrated in Fig. 1. It was found [7] that α-Fe precipitates during the first reaction, and crystallization of the remaining

amorphous phase to the Fe_3B phase follows during the second reaction. Both DSC and TM measurements revealed that annealing at $T_a > 580$ K did not significantly change the temperatures of these two crystallizations as compared with the relaxation of T_c, but the first crystallization became very broad due to the resulting inhomogeneity in the amorphous matrix, and proceeded to completion gradually. For example, as seen from the relative decrease in the area of the first DSC peak, ~40% of the α-Fe crystalline phase was annealed-out at 610 K after 120 min.

It is known [3] that for metallic glasses the sharpness of the Curie transition is dependent on the concentration of magnetic components. If this concentration decreases, the transition becomes more smeared.

At comparatively high T_a, it is expected (compared with the results at lower temperature) that any rise in T_c due to structural relaxation will be over quickly. Thus, the continuous rise in T_c at longer times follows the onset of crystallization of α-Fe and can be interpreted as being due to some changes within the remaining amorphous phase.

(2) Annealing effects on heating

If T_c is sufficiently high with respect to relaxation effects, the heating necessary to perform its determination may have an additional annealing effect. It can be seen that the apparent Curie and crystallization temperatures vary strongly with the heating rate. The crystallization temperature obeys the Kissinger relation [8]. Assuming that the actual temperature of the Curie transformation is unaffected by the heating rate, the apparent Curie temperature determined through the procedure of linear heating of the sample must be corrected with respect to the annealing effects on heating.

In the case of amorphous $Fe_{85}B_{15}$, the variation in the measured T_c against the heating rate Φ was

$$\Delta T_c = 3.49 \cdot 10^{-1} \Phi$$

in linear approximation.

Conclusions

The main conclusions from the above work are: (i) The Curie temperature, T_c, of metallic glasses can be measured rapidly by using the Perkin–Elmer TGS–1 system with an external magnetic field. The reproducibility is satisfactory (± 1.0 deg). The use of thermomagnetometry to investigate the relaxation of T_c is superior to other methods, because of its productivity and high sensitivity (0.1 mg/full-scale

deflection) and because its heating rate is high enough and can be changed in a large enough interval to minimize any annealing effects during the deterination. (ii) T_c is in general a good parameter for studying the stability of $Fe_{85}B_{15}$ glass. In the as-quenched samples, T_c was observed to be 570 K. The annealing causes the relaxation of the glass. T_c initially rises sharply by a few degrees and then gradually levels off to the equilibrium value. However, at T_a = 580 K another process, which becomes more pronounced at higher temperatures and longer annealing times, is superimposed on the latter. This process can be identified as partial crystallization of the α-Fe phase. (iii) The origin of the increase in T_c on the relaxation of $Fe_{85}B_{15}$ glass is not well understood. It might be explained in terms of some changes in local atomic arrangement. The relaxation of the glassy structure becomes nearly complete within 120 min at 580 K. However, progressive crystallization of α-Fe at higher temperatures and times is accompanied by much more pronounced changes in coordination, which, from the point of view of macrostructure, probably represent a qualitative change in topology.

* * *

We wish to thank P. Duhaj for the preparation of glassy ribbons.

References

1 R. Hasegawa and R. Ray, J. Appl. Phys., 49 (7) (1978) 4174.
2 A. L. Greer and J. A. Leake, J. Non-Cryst. Sol., 33 (1979) 291.
3 A. L. Greer, Thermochim. Acta, 42 (1980) 193.
4 A. L. Greer, J. Mat. Sci., 17 (1982) 1117.
5 F. F. So, R. Kaplow and R. C. O'Handley, J. Non-Cryst. Sol., 58 (1983) 285.
6 Ľ. Kubičár, E. Illekováand Mrafko, in Rapidly Quenched Metals, ed. by S. Steeb and H. Warlimont, Elsevier Science Publ. B. V., 1985, p. 655.
7 P. Duhaj and F. Hanic, Phys. Stat. Sol., (a) 76 (1983) 467.
8 H. E. Kissinger, Anal. Chem., 29 (1957) 1702.

Zusammenfassung — Die thermomagnetometrische Methode wurde zur Bestimmung der Curie-Temperatur der amorphen Legierung $Fe_{85}B_{15}$ herangezogen. Die Messungen wurden mit einer Perkin–Elmer-Thermowaage des Typs TGS-1 unter Anwendung eines permanenten Magnetfeldes ausgeführt. Das ~25 μm dicke amorphe Material wurde nach dem Schmelzspinnverfahren dargestellt. Im Temperaturbereich von 300 bis 800 K ist für die Probe eine Curie-Transformation in der amorphen Matrix bei $T_c \sim 570$ K charakteristisch. Ein breiter Bereich der primären Kristallisation von α-Fe beginnt bei etwa 660 K, dem sofort eine schnelle Kristallisation der Fe_3B-Phase mit maximaler Geschwindigkeit bei $T_{cr2} \sim 750$ K folgt. Die durch Abschrecken eintretende Instabilität des amorphen Materials wird durch Tempern aufgehoben. Die strukturelle Relaxation verursacht eine Alterung der Curie-Temperatur im metallischen Glas. Die beobachteten Phänomene können durch Veränderungen der lokalen Anordnung der Atome erklärt werden

Резюме — Термомагнетометрический метод был использован для определения температуры Кюри аморфного сплава $Fe_{85}B_{15}$. Измерения были проведены с помощью термовесов ТГС–1 Перкин–Эльмер, используя постоянное магнитное поле. Аморфные пленки толщиной ~25 мкм были получены методом обкатки расплава. В области температур 300–800 К аморфный образец характеризуется одной точкой Кюри. Широкая область первичной кристаллизации α-Fe начинается приблизительно при температуре 660 К, за которой сразу же начинается быстрая кристаллизация фазы Fe_3B с максимумом при T_{cr2} ~ 750 К. Аморфный сплав, являясь неустойчивым вследствии закаливания, укрепляется тушением. Структурная релаксация вызвана старением температуры Кюри в металлическом стекле. Наблюдаемое явление может быть объяснено на основе определенных изменений локального атомного окружения.