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Study of the thermal effects during microstructural changes of metastable alloys by means of temperature-modulated thermomagnetometry

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Abstract

Thermomagnetometry (TM) with modulated temperature has been employed to study the dynamics of the nanophase forming from amorphous alloys. A sinusoidal type of modulation in combination with saw-tooth and quasi-isothermal allow for separation reversible and irreversible processes during crystallization in the regions of the Curie temperature of precursor glasses $T_c(am_1)$, the remainder of amorphous phase $T_c(am_2)$ and bcc nanophase T_c(n-Fe). The results are compared with those obtained from standard TM and differential scanning calorimetry of $Fe_{80}B_{20}$ and $Fe_{86}B_{14}$ alloys. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Thermomagnetometry; Temperature modulation; Amorphous–crystalline transformation; Curie temperature

1. Introduction

Nanocrystalline magnetic alloys obtained by partial devitrification of the amorphous precursor have extremely soft magnetic properties with high saturation magnetic flux density and high permeability. The origin of these properties are from the homogeneous microstructure with the occurrence of nanometer size crystalline grains (10–20 nm) embedded with a residual amorphous matrix [1]. Nanocrystalline structure can be obtained from the amorphous state via crystallization process under appropriately controlled annealing [2].

In the technology of nanocrystalline materials, the crystallization process is monitored by complementary methods: differential scanning calorimetry (DSC), X-ray diffraction, thermomagnetometric measurement (TM). For hypo-eutectic alloys of Fe–B, two exothermic peaks are detected by DSC when crystallization takes place [3]. First maximum corresponds to the precipitation of bcc-Fe solid solution grains, the second is associated with the crystallization of the intermetallic compounds from the remainder part of the amorphous phase (am_2), which is attributed to the Fe_3B precipitation. The basic scheme of this reaction is:

$$\text{(I)} \quad am_1 \rightarrow \text{bcc-Fe} + am_2 \qquad (1)$$

$$\text{(II)} \quad am_2 \rightarrow Fe_3B$$

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While the amorphous–crystalline transformation is recognized by two exothermic peaks in DSC, this process appears as a single uprise of the magnetization in TM.

In the present work the TM measurement is employed where the temperature is modulated. The method allows to obtain more details about processes which take place in the region of crystallization. The results are compared with the DSC results previously reported [3].

2. Experimental

The TM measurements were carried out using the ac susceptometer/magnetometer described elsewhere [4]. The temperature of the sample is controlled by furnace current in a feedback via software. This solution together with small masses of furnace and sample allows for arbitrary heating program with heating rates up to 640°C/min.

Temperature modulated TM measurement is accomplished by adding to a linear heating ramp $\langle q \rangle$ a modulating component (Fig. 1):

$$T_s = T_0 + \langle q \rangle t + A_{T_s} \sin \omega t \qquad (2)$$

with T_0 representing the isotherm at the beginning of the scanning. The modulation frequency ω is equal to $2\pi/p$ in units of reverse time, with p representing the length of one cycle (min). $\langle q \rangle$ indicates an average heating rate over modulation period (°C/min).

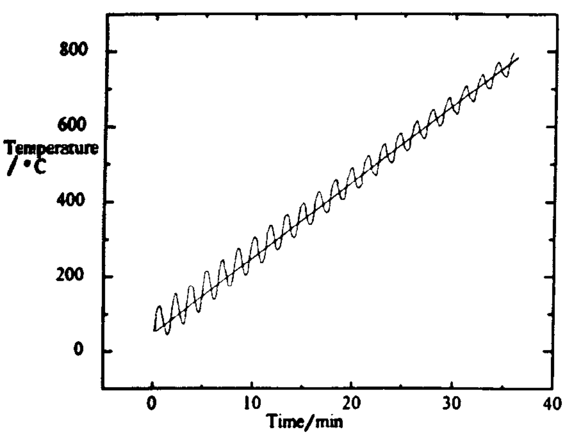

Fig. 1. Modulated temperature of the sample during heating with rate of 20°C/min. Modulation period $p = 2$ min, temperature deviation $A_{T_s} = +/- 20$°C.

A middle heating rate of 20°C/min was applied in our experiment. It was found that the character of the thermomagnetic curve is practically not affected by heating rate between 5°C/min and 80°C/min. The temperature was modulated sinusoidal with the period of 2 min and deviation of $+/-20$°C. The magnetization was detected at 68 Hz in synchronizm with applied alternating magnetic field of 30 Oe in amplitude.

3. Measurement results

Thermal and thermomagnetic properties of amorphous $Fe_{80}B_{20}$ and $Fe_{86}B_{14}$ alloys were investigated elsewhere [5], and these materials are considered as reference. It is known that crystallization of the amorphous $Fe_{80}B_{20}$ alloys takes place in one step, bcc-Fe and Fe_3B crystals being its products [6]. The TM curve (Fig. 2) shows Curie temperature (*1*) of the amorphous

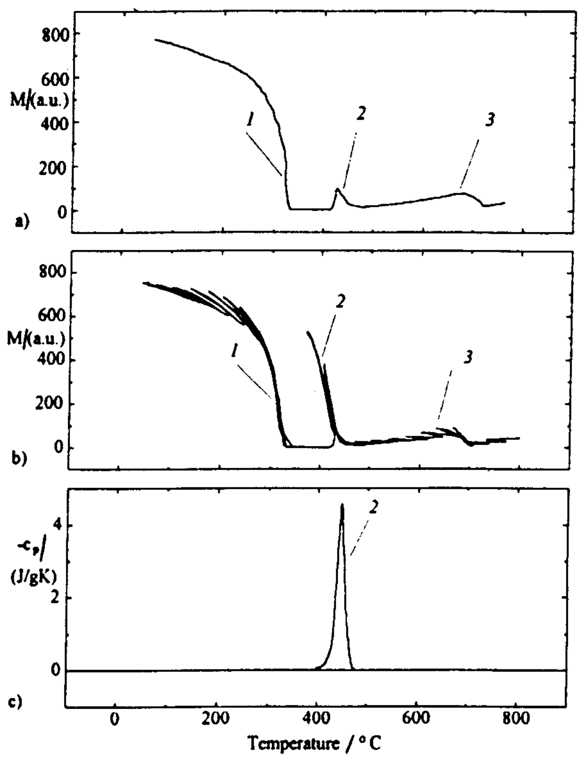

Fig. 2. The conventional TM curves for amorphous–crystalline transformation of $Fe_{80}B_{20}$: linear (a) and temperature modulated (b), standard DSC curve (c). Heating rate 20°C/min.

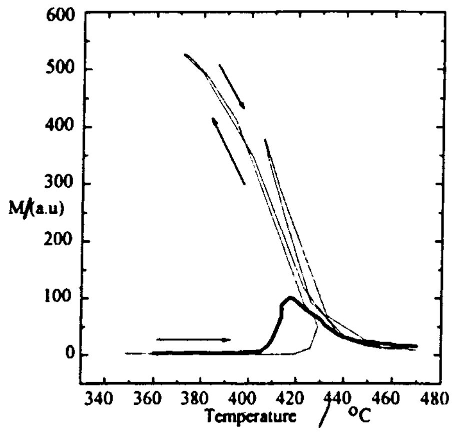

Fig. 3. The TM curves from Fig. 2a and b between 360°C and 470°C. The thick line corresponds to conventional TM; thin line is obtained by temperature modulated TM.

phase at 320°C and one peak (*2*) in crystallization region at 420°C. The flat uprise between 600°C and 700°C (*3*) is attributed to the decomposition $Fe_3B \rightarrow Fe_2B$ + bcc-Fe during heating. The temperature modulated TM curve is shown in Fig. 2b. The ferro-paramagnetic transition (*1*) at Curie temperature of the amorphous phase is stable and reversible over many periods. In the crystallization region is observed irreversible behaviour of the magnetization (*2*). This region for both linear and modulated temperature is magnified in Fig. 3. With the increasing temperature, when temperature crosses over 420°C and then decreases below 400°C, the magnetization increases several times in comparison with linear heating rate. The para–ferro transition first is observed in opposite direction, from high towards low temperature. Then the transition is reversible and stable over the next period. The corresponding maximum of exothermic peak of DSC lies a little above this transiton (Fig. 2c).

For $Fe_{86}B_{14}$ two exothermic peaks are observed by DSC (Fig. 4c). The conventional TM measurement (Fig. 4a) shows Curie temperature of the amorphous phase at 230°C (*1*) and one peak in crystallization region at 420°C (*2*). The temperature modulated TM curve is shown in Fig. 4b. The Curie transition of amorphous phase at 230°C (*1*) is stable and reversible. With the increasing temperature the uprise at 400°C (*4*) is observed. This uprise is observed, when the temperature crosses over 420°C and then decreases

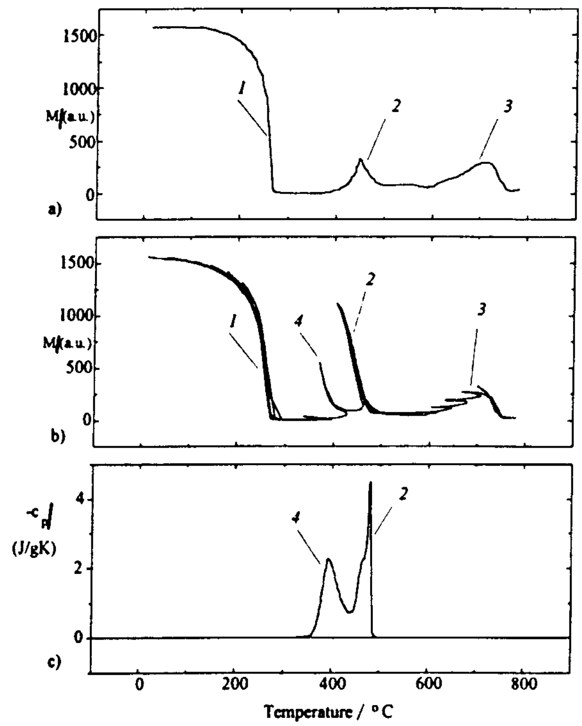

Fig. 4. TMAG curves for amorphous–crystalline transformation of $Fe_{86}B_{14}$: linear (a) and temperature modulated (b), standard DSC curve. Heating rate and modulation like in Fig. 2.

below 400°C. In comparison with the DSC curve, this uprise of magnetization indicates on the Curie point of nanocrystalline phase. It corresponds to a first exothermal maximum which lies above the temperature of magnetic transition. During further temperature increase the effect of crystallization, in analogy to $Fe_{80}B_{20}$ alloy, is observed.

4. Discussion

The crystallization process of the amorphous $Fe_{80}B_{20}$ alloy takes place in one step. In Fig. 2a it is shown that the magnetization peak (*2*) corresponds to a temperature when crystallization starts, between 400°C and 420°C. Maximal speed of the crystallization is above this temperature and is observed as the exothermic peak of DSC curve (Fig. 2c). From the above and from temperature modulated TM measurement it is seen that crystallization of $Fe_{80}B_{20}$ takes place at the Curie temperature of its product Fe_3B.

Two processes during crystallization of amorphous $Fe_{86}B_{14}$ are observed by DSC. The TM with linear heating rate has the same character as for $Fe_{80}B_{20}$ alloy (Fig. 2a and Fig. 4a) – only the process of formation of Fe_3B is visible (*2*). From the TM with the modulated temperature the significant increase of magnetization (*4*) is observed when temperature reaches 420°C and then decreases below 400°C (Fig. 4b). This indicates that between 400°C and 420°C a process took place which is identified as the precipitation of bcc-Fe solid solution grains. In this temperature range the exothermic peak is observed by DSC. In contrast to Fe_3B crystallization, the nanocrystalline phase is forming above its Curie temperature since it is not observed using linear temperature increase.

5. Conclusions

The modulation of temperature added to the standard TM method allows for investigation of magnetic properties of amorphous alloys whose crystallization temperature is higher than their Curie transition. The method does not take more measurement time than the conventional one.

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