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Qualitative Analysis of Magnetization versus Temperature Curves in Amorphous $\mathrm{Fe_{70-x}Co_xMn_{10}Mo_5B_{15}}$ $(0 \le x \le 0.5)$ Alloys at Low Magnetizing Field

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The Curie temperature is usually obtained by differentiating of the temperature magnetization curves ($\sigma(T)$) or by analyzing the critical behavior of magnetization at temperature, close to but lower than the Curie point. The paper presents magnetization versus temperature curves in the range 50–400 K for amorphous $\mathrm{Fe_{70-x}Co_xMn_{10}Mo_5B_{15}}$ $(0 \le x \le 0.5)$ alloys, applying external magnetizing field of 2.5, 5, and 25 mT, after earlier demagnetization and cooling of samples in the presence (field cooled) and without magnetic field (zero field cooled). The complicated runs of magnetization versus temperature curves for low magnetizing fields is the result of several processes: freezing of spins, different temperature dependence of magnetization and magnetic anisotropy constant and antiferromagnetic coupling in iron–manganese and cobalt– manganese pairs.

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1. Introduction

Theoretical and experimental determination of magnetization versus temperature, magnetizing fields and composition of alloys is the most fundamental task of magnetism. From the sets of isothermal magnetization curves as a function of magnetizing field the isothermal magnetic entropy change can be computed [1–3], which exhibits maximum value at temperature close to the temperature of ferromagnetic-paramagnetic phase transition [1]. From the application point of view in refrigerant technology searching for materials with the Curie point (T_{C}) near the ambient one is very important. T_{C} is usually derived by differentiation of the magnetization versus temperature curve recorded at small magnetizing field or by analysis of magnetization critical behavior in temperature near but lower than T_{C}. The aim of this paper is qualitative analysis of magnetization versus temperature curves in amorphous $\mathrm{Fe_{70-x}Co_xMn_{10}Mo_5B_{15}}$ $(0 \le x \le 0.5)$ alloys in low external magnetizing fields of 2.5, 5, and 25 mT. In the parent alloy $\mathrm{Fe_{70}Mn_{10}Mo_5B_{15}}$ some Fe atoms are replaced by Co ones.

2. Experimental procedure

The amorphous ribbons of the $\mathrm{Fe_{70-x}Co_xMn_{10}Mo_5B_{15}}$ $(0\le x \le0.5)$ alloys was prepared by rapid quenching on a single roller. The width of the ribbons was 2 mm and their thicknesses, determined from mass and density measurements, were about 20 μm. The amorphicity of the samples in the as-quenched stage and after the accumulative annealing within the amorphous state at 723 K for 0.5 h and then at 753 K for 0.5 h was checked by X-ray diffraction. The specific magnetization (σ, magnetization per unit mass) versus temperature in 50–400 K range in the external magnetizing field induction of 2.5, 5, and 25 mT was measured by a VersaLab (Quantum Design) system, for samples in the as-quenched state and after accumulative annealing at 723 K and at 753 K for 0.5 h. The sample were in the form of single stripes 8 mm long. After the demagnetization external magnetic field was applied parallel to the axis of the ribbon in its plane. Magnetization measurements were made after cooling the samples in the magnetic field (field cooled FC mode I) and without the presence of the field (zero field cooled ZFC mode II). The Curie temperature of amorphous alloys in the as-quenched and after annealing was determined from curves describing the magnetization derivative with respect to temperature $\mathrm{d}\sigma/\mathrm{d}T$.

3. Results and discussion

The internal magnetizing field induction, $\boldsymbol{B}$, is the vector sum of external magnetic field induction $\boldsymbol{B}_0$ applied to the sample, magnetic anisotropy field induction $\boldsymbol{B}_A$, and demagnetizing field induction $\boldsymbol{B}_D$ [4]:

$$\boldsymbol{B} = \boldsymbol{B}_0 + \boldsymbol{B}_A + \boldsymbol{B}_D, \tag{1}$$

where $\boldsymbol{B}_D = -\mu_0 N \boldsymbol{M}_S$, $\boldsymbol{B}_A = (2K_{\mathrm{eff}}/M_S)\boldsymbol{e}_A$, μ_0 — vacuum magnetic permeability, N — demagnetizing factor, $\boldsymbol{M}_S$ — the saturation magnetization (the magnetic moment per volume unit), K_{eff} — effective magnetic anisotropy constant and $\boldsymbol{e}_A$ — unit vector of the magnetic anisotropy field direction. Taking into account the shape of the sample, the ratio of length to

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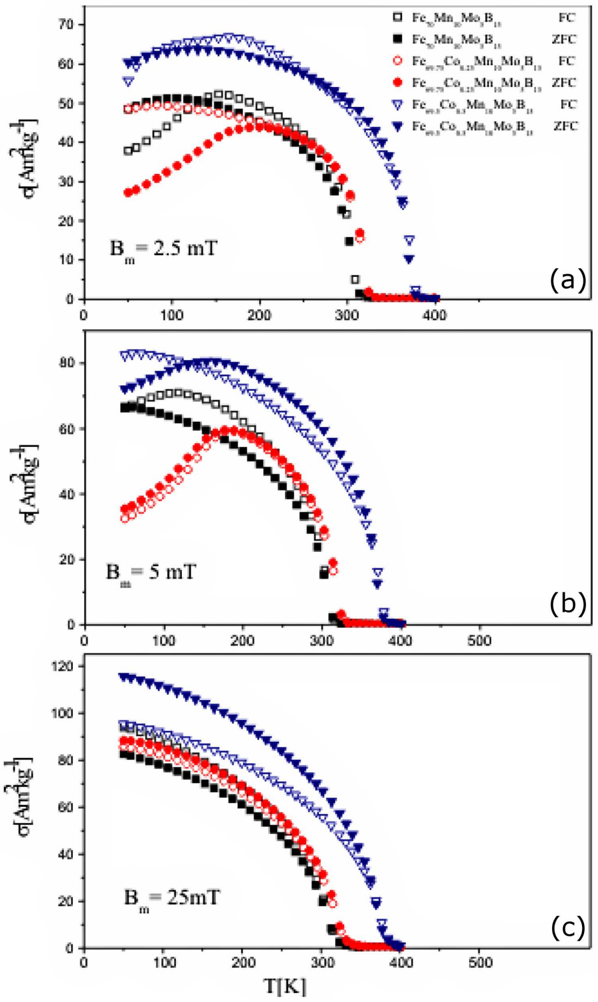

Fig. 1. Specific magnetization (σ) as a function of temperature for amorphous $Fe_{70}Mn_{10}Mo_5B_{15}$, $Fe_{69.75}Co_{0.25}Mn_{10}Mo_5B_{15}$ and $Fe_{69.5}Co_{0.5}Mn_{10}Mo_5B_{15}$ alloys in the as-quenched state measured in the external magnetizing field induction of 2.5, (a), 5 (b) and 25 mT (c).

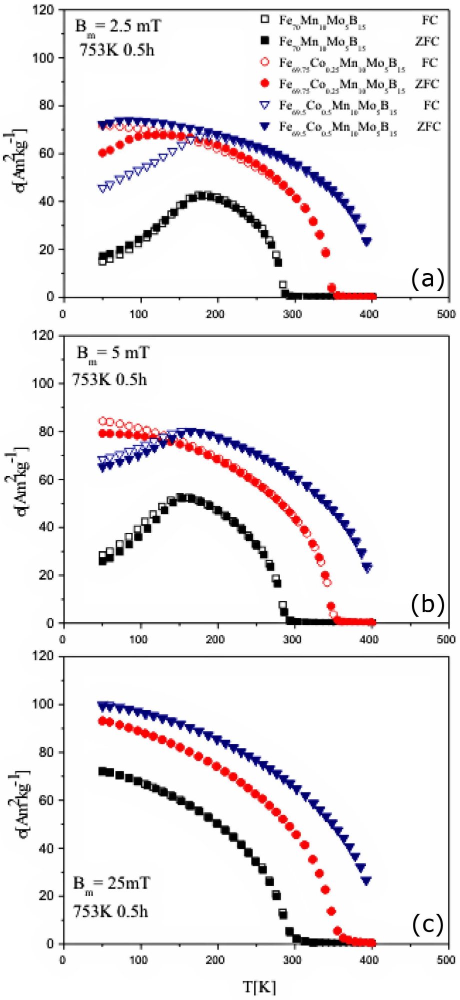

Fig. 2. Specific magnetization (σ) as a function of temperature for amorphous $Fe_{70}Mn_{10}Mo_5B_{15}$, $Fe_{69.75}Co_{0.25}Mn_{10}Mo_5B_{15}$ and $Fe_{69.5}Co_{0.5}Mn_{10}Mo_5B_{15}$ alloys after the accumulative annealing at 723 K and 753 K for 0.5 h measured in the external magnetizing field induction of 2.5 (a), 5 (b) and 25 mT (c).

width of the strip is 4 and hence demagnetizing factor N is very small and consequently the demagnetizing field can be neglected. The effective magnetizing field then is the vector sum of external and anisotropy fields. Figure 1 shows the specific magnetization (σ) versus temperature for all investigated amorphous $Fe_{70}Mn_{10}Mo_5B_{15}$, $Fe_{69.75}Co_{0.25}Mn_{10}Mo_5B_{15}$ and $Fe_{69.5}Co_{0.5}Mn_{10}Mo_5B_{15}$ alloys in the as-quenched state. Magnetization curves in the low temperature range for ZFC and FC modes obtained in the lower magnetizing fields of 2.5 mT and 5 mT do not overlap and confirm the existence of the so-called states of "frozen spins" inside the investigated materials [5]. The magnetization recorded in mode I and II for all samples increases initially until the local maximum value is reached, after which a monotonic decrease is observed. Such behavior results from different dependence of specific magnetization and magnetic anisotropy constant on temperature. The latter diminishes faster than the former one with temperature and consequently the local maximum is obtained. Near the phase transition temperature the magnetization drops very fast. The specific magnetization measured at magnetizing field of 25 mT do not show local maxima and decreases monotonically in the whole temperature range. It means that the external magnetization field of 25 mT is higher than the magnetic anisotropy field. Generally, in ferromagnetic materials exhibiting "spin freezing" the magnetization obtained in FC mode is higher than in ZFC one. In our case we observe opposite behavior of $\sigma(T)$ curves at low temperature and at the external magnetizing fields of 2.5 mT and 5 mT (Fig. 1a, b). Such situation is more pronounced for the curves measured at 25 mT. The amorphous $Fe_{70}Mn_{10}Mo_5B_{15}$ alloy behaves like typical ferromagnet with "spin freezing". The discrepancy of magnetization increases with Co content (Fig. 1c).

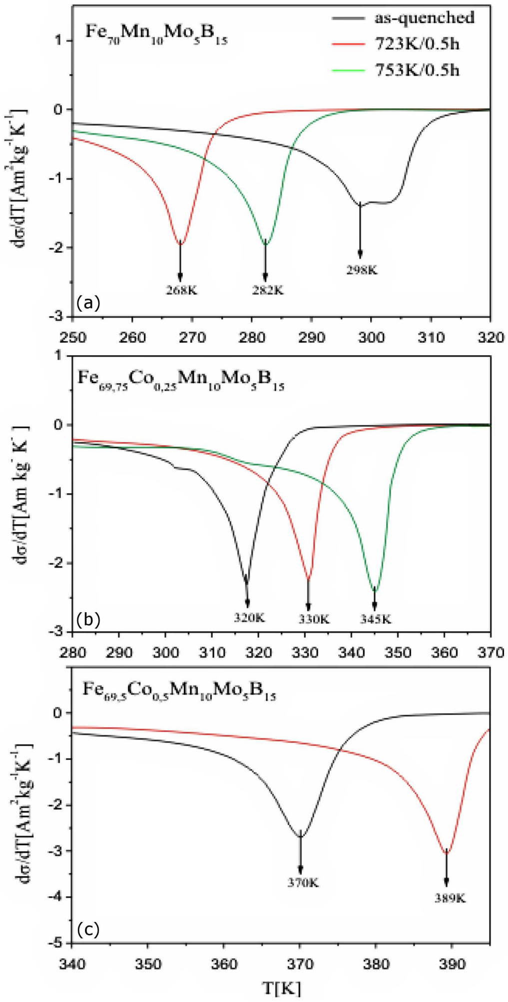

Fig. 3. The derivatives dσ/dT for amorphous $Fe_{70}Mn_{10}Mo_5B_{15}$, $Fe_{69.75}Co_{0.25}Mn_{10}Mo_5B_{15}$ and $Fe_{69.5}Co_{0.5}Mn_{10}Mo_5B_{15}$ alloys in the as-quenched state (a) and after the accumulative annealing at 723 K (b) and 753 K (c) for 0.5 h to derive the Curie point.

It results from the fact that Co atoms pronounced the antiferromagnetic coupling in Fe–Mn or Co–Mn pairs. Moreover, it can be seen that the magnetization curves converge near the Curie points independently of the mode of cooling, so the Curie points derived from differentiation of $\sigma(T)$ in both modes will be the same. In Fig. 2 the magnetization curves versus temperature at the external magnetizing field induction of 2.5, 5, and 25 mT for the annealed samples are exemplary shown for the specimen subjected to the accumulative heat treatment at 723 K and 753 K for 0.5 h. In the case of annealed samples (Fig. 2), as well as in the as-quenched state, the same mechanism of initial magnetization increase occurs, up to a certain maximum value, and then its monotonic decrease. The magnetization curves obtained in ZFC and FC modes at the magnetizing field of 25 mT (Fig. 2c) overlap and do not show a local maximum, which as mentioned above indicates that the magnetic anisotropy field is significantly lower than the external magnetizing field and therefore the magnetization decreases monotonically with increasing temperature. The magnetization curves obtained in FC and ZFC modes coincide and the "freezing of spins" effect is not observed. The Curie temperatures of the amorphous $Fe_{70}Mn_{10}Mo_5B_{15}$, $Fe_{69.75}Co_{0.25}Mn_{10}Mo_5B_{15}$ and $Fe_{69.5}Co_{0.5}Mn_{10}Mo_5B_{15}$ alloys in the as-quenched state are equal to 298, 320, 370 K, respectively (Fig. 3) [6]. After the annealing at 723 K for 0.5 h the Curie point of the amorphous $Fe_{70}Mn_{10}Mo_5B_{15}$ alloy significantly diminishes to 268 K and then increases to 282 K after the accumulative heat treatment at 723 K and 753 K for 0.5 h (Fig. 3a). Similar tendency in specific magnetization is observed (Figs. 1c and 2c) Such behavior is attributed to the invar effect. The annealing out of the free volumes during the heat treatment decreases the average distance between Fe atoms and according to the Bethe–Slater curve lowers the exchange interactions between them and consequently T_C. Moreover, the magnetic moment configuration is less collinear and magnetization decreases [6]. During annealing at higher temperature, apart from mentioned above annealing out of free volumes, a diffusion of atoms is activated and the mean distance between Fe atoms increases because B atoms may be placed between them strengthening the exchange interaction which, in turn, enhances T_C and magnetization. In alloys containing cobalt atoms the successive increase of the Curie temperature is observed after the annealing within the amorphous state due to destruction of invar effect by Co atoms (Fig. 3b,c). It is evidently shown that the Curie points in amorphous $Fe_{70-x}Co_xMn_{10}Mo_5B_{15}$ $(0 \leq x \leq 0.5)$ alloys can be tuned by the annealing within the amorphous state.

4. Conclusions

The runs of the magnetization versus temperature curves at low magnetizing field induction are governed mainly by different temperature dependence of the magnetization and magnetic anisotropy field. The Curie temperature can be easily modified not only by changes in chemical composition but by the annealing within the amorphous state, as well.

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