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Magnetocaloric Properties of $Fe_{75}Mo_8Cu_1B_{16}$ and $Fe_{81}Mo_8Cu_1B_{10}$ Metallic Glasses

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Microstructure and thermomagnetic properties for the $Fe_{75}Mo_8Cu_1B_{16}$ and $Fe_{81}Mo_8Cu_1B_{10}$ metallic glasses in the as-quenched state and after heat treatment at 643 K and 723 K are studied. The inverse change of the Curie point was observed for $Fe_{75}Mo_8Cu_1B_{16}$ metallic glass after annealing below the onset of crystallization. It is attributed to structural relaxation of the amorphous phase. The maximum of magnetic entropy change calculated for magnetic field of 1.0 T occurs for the $Fe_{75}Mo_8Cu_1B_{16}$ alloy annealed at 643 K at temperature close to the Curie point and equals 0.74 J kg^{-1} K^{-1}.

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1. Introduction

NANOPERM alloys exhibit interesting magnetic properties [1] through which they have found a variety of practical applications [2]. Especially, magnetic materials with the ferromagnetic–paramagnetic phase transition near room temperature are important for practical use in refrigerators [3]. Consequently, the studies of crystallization, which affects their magnetic features, are very abundant. Little is known, however about their behaviour after low temperature annealing below the onset of crystallization [4]. In this work we concentrate on magnetocaloric effects in a Fe–Mo–Cu–B system that also belong to this family of alloys. We are interested in the influence of structural relaxation upon magnetic parameters. Moreover, the change of the Curie point after annealing was also considered.

2. Experimental procedure

$Fe_{75}Mo_8Cu_1B_{16}$ and $Fe_{81}Mo_8Cu_1B_{10}$ metallic glasses were prepared by rapid quenching. Their chemical composition was checked by optical emission spectrometry with inductively coupled plasma (Mo, B) and flame atomic absorption spectrometry (Fe, Cu). As-quenched and annealed (at 643 K and 723 K for 0.5 h) samples were studied by Conversion Electron Mössbauer Spectrometry (CEMS). DC magnetic measurements versus temperature and magnetic field were carried out by a VersaLab (Quantum Design) system. The magnetocaloric effect was studied as magnetic entropy changes versus temperature.

3. Results and discussion

CEMS spectra of both alloys are shown in Fig. 1 in a narrow velocity range. While the $Fe_{75}Mo_8Cu_1B_{16}$ is fully amorphous even after annealing at moderate temperatures, the $Fe_{81}Mo_8Cu_1B_{10}$ exhibits a presence of surface crystallization already in the as-quenched state. Moreover, crystallites are unambiguously identified in the annealed samples. For clarity, only fits to experimental data are shown in Fig. 1. The spectra were normalized to a unit area in order to allow their mutual quantitative comparison.

The shapes of CEMS spectra of both as-quenched alloys indicate close-to-room Curie temperature. The $Fe_{75}Mo_8Cu_1B_{16}$ alloy undergoes structural relaxation after annealing as it is demonstrated by narrowing of the 642 K Mössbauer spectrum. At the same time, its intensity rises. Further increase in annealing temperature (to 743 K), however exhibits a tendency of the system to acquire the original amorphous stage. Consequently, changes in the Curie temperature are expected. The $Fe_{81}Mo_8Cu_1B_{10}$ system is partially crystallized even after the preparation [5] and shows further progress of crystallization after annealing. Therefore, in the following we will concentrate our attention to the $Fe_{75}Mo_8Cu_1B_{16}$ alloy.

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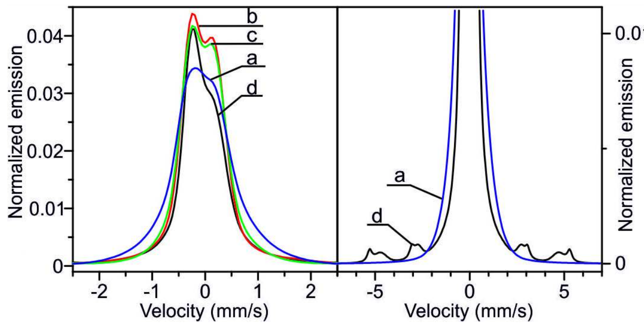

Fig. 1. CEMS spectra measured for as-quenched (a, d) and annealed sample at 643 K (b) and 723 K (c) of $Fe_{75}Mo_8Cu_1B_{16}$ (a, b, c) and $Fe_{81}Mo_8Cu_1B_{10}$ (d) alloys.

Temperature dependences of mass magnetization for the as-quenched $Fe_{75}Mo_8Cu_1B_{16}$ and $Fe_{81}Mo_8Cu_1B_{10}$ alloys presented in Fig. 2 show typical behaviour observed

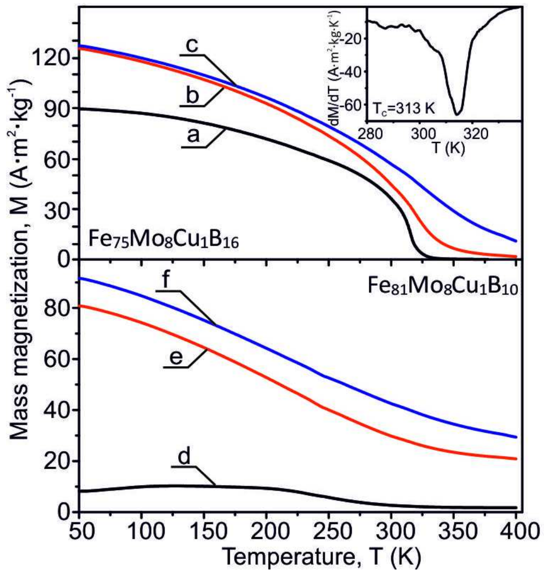

Fig. 2. The mass magnetization versus temperature for the as-quenched $Fe_{75}Mo_8Cu_1B_{16}$ (a, b, c) and $Fe_{81}Mo_8Cu_1B_{10}$ (d, e, f) alloys measured at the magnetic field of 2.5 mT (a, d), 0.1 T (b, e) and 1 T (c, f). The derivative $\mathrm{d}M/\mathrm{d}T$ close to the Curie temperature for the curve (a) is shown in the inset.

for ferromagnetic materials. Magnetization rapidly decreases at the temperature close to the Curie point of the investigated alloys. With increasing the magnetic field up to 0.1 T and 1.0 T an increase of magnetization is observed for both $Fe_{75}Mo_8Cu_1B_{16}$ and $Fe_{81}Mo_8Cu_1B_{10}$ alloys. Moreover, the as-quenched sample with higher content of B (16 at.%) shows higher values of mass magnetization than the sample with 10 at.% of B. The Curie temperature (T_C) for the as-quenched $Fe_{75}Mo_8Cu_1B_{16}$ alloy calculated as derivative $\mathrm{d}M/\mathrm{d}T$ versus temperature equals to $T_C = 313$ K. With increasing temperature of annealing up to 643 K and 723 K, which is

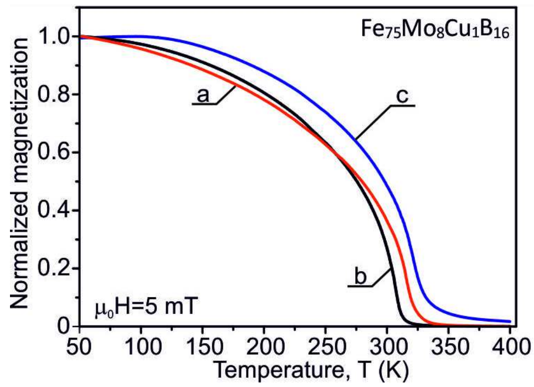

Fig. 3. The normalized magnetization versus temperature for the $Fe_{75}Mo_8Cu_1B_{16}$ alloys in the as-quenched state (a) and after heat treatment for 0.5 h at 643 K (b) and 723 K (c).

still below the onset of crystallization, the decrease and then increase in T_C was observed and equal to 306 K and 315 K, respectively. This behaviour is related to structural relaxation of the investigated samples that is accompanied by annealing out of some free volumes. This tendency was also confirmed by the Mössbauer studies. The sample of the $Fe_{81}Mo_8Cu_1B_{10}$ alloy after preparation shows presence of crystalline α-Fe phase with Curie point higher than 400 K (see in Fig. 1, right part). More visible changes of T_C after heat treatment of the amorphous $Fe_{75}Mo_8Cu_1B_{16}$ alloy are also presented in Fig. 2. Lower T_C value for the sample annealed at 643 K is seen on the dependence of normalized magnetization versus temperature taken at constant magnetic field of 5 mT in Fig. 3.

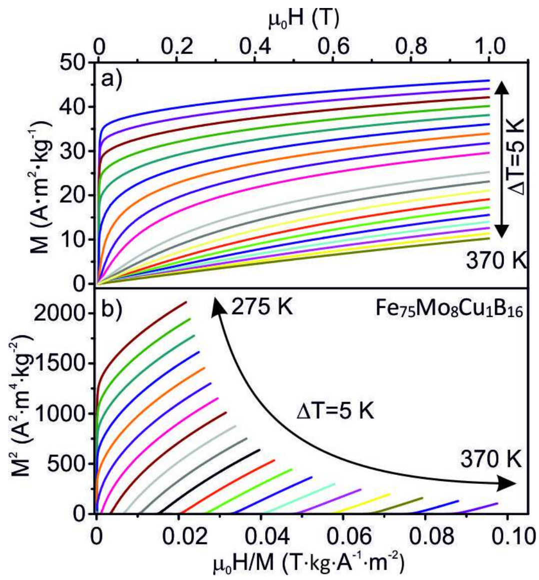

Fig. 4. Sets of isothermal magnetization curves in the temperature range 275 – 370 K (a) and Arrott plots, i.e. M^2 as a function of $\mu_0 H/M$ for the $Fe_{75}Mo_8Cu_1B_{16}$ alloy after annealing at 643 K for 0.5 h.

As an example, the set of isothermal magnetization curves recorded in temperature range 275–370 K with $\Delta T = 5$ K, as well as the Arrott plots [6], i.e. M^2 versus $\mu_0 H/M$ constructed for the $Fe_{75}Mo_8Cu_1B_{16}$ alloy annealed at 643 K are depicted in Fig. 4a and Fig. 4b, respectively. The positive slope of the presented Arrott curves at T_C in Fig. 4b confirms the second order ferromagnetic to paramagnetic phase transition [7]. The same phenomenon was observed for the samples with 16 at.% of B content after annealing at 643 K and 723 K. Magnetocaloric effect can be calculated according to the Maxwell thermodynamic relation [8]:

$$\Delta S_{\mathrm{M}} = \mu_0 \int_0^{H_{\mathrm{m}}} \left(\frac{\partial \sigma(T,H)}{\partial T} \right)_H \mathrm{d}H = \int_0^{B_{\mathrm{m}}} \left(\frac{\partial \sigma(T,B)}{\partial T} \right)_B \mathrm{d}B,$$

where $B_{\mathrm{m}} = \mu_0 H_{\mathrm{m}}$. The changes of entropy ($-\Delta S_{\mathrm{M}}$) versus temperature in Fig. 5 were calculated using numerical approximation according to the above equation. Figure 5 shows magnetocaloric effect investigation of the $Fe_{75}Mo_8Cu_1B_{16}$ alloy: annealed at 643 K (upper figure) measured for different values of maximum magnetizing field; and in the as-quenched state and after heat treatments (lower figure) at 643 K and 723 K. The increase of magnetizing field from 0.25 T to 1.0 T leads to increase of the maximum value of ($-\Delta S_{\mathrm{M}}$) from 0.21 to 0.57 J kg^{-1} K^{-1} (Fig. 5, curves *a*–*d*). Moreover, the maximum value of magnetic entropy changes of 0.74 J kg^{-1} K^{-1} at $T = T_C = 313$ K was observed for the $Fe_{75}Mo_8Cu_1B_{16}$ alloy in the as-quenched state (Fig. 5, curve *e*).

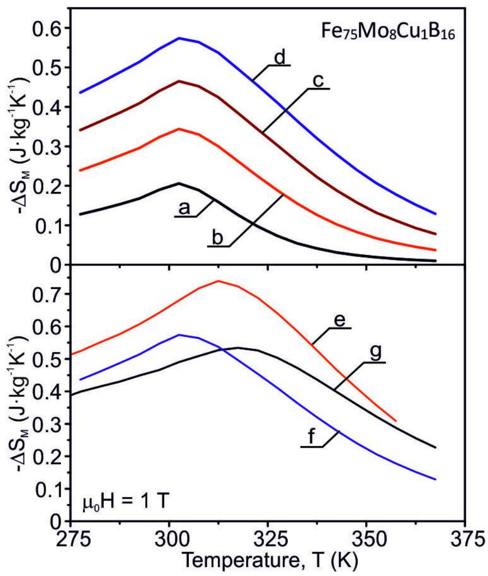

Fig. 5. The magnetic entropy ($-\Delta S_{\mathrm{M}}$) changes versus temperature measured for sample annealed at 643 K at the maximum magnetizing field of 0.25 T (a), 0.5 T (b), 0.75 T (c), 1.0 T (d) — upper figure, and the magnetic entropy changes ($-\Delta S_{\mathrm{M}}$) versus temperature measured at magnetizing field of 1.0 T — lower figure, for the as-quenched (e) and after annealing for 0.5 h at 643 K (f) and 723 K (g) $Fe_{75}Mo_8Cu_1B_{16}$ alloy.

4. Conclusions

- Magnetic parameters of $Fe_{75}Mo_8Cu_1B_{16}$ and $Fe_{81}Mo_8Cu_1B_{10}$ alloys in their as-quenched state and after heat treatment at moderated temperatures (below the onset of crystallization) were investigated. The value of mass magnetization is higher for the alloy with 16 at.% B. Its Curie temperature can be modified using appropriate annealing that resulted in either its decrease or increase with respect to T_C observed in the as-quenched state.
- The positive slope of Arrott plots at T_C confirmed the second order ferromagnetic to paramagnetic phase transition and magnetocaloric effect for different values of $\mu_0 H$ in the temperature range 275–370 K. The changes of magnetic entropy exhibit maximum at room temperature for the $Fe_{75}Mo_8Cu_1B_{16}$ alloy when measured under different magnetizing fields irrespective of their structural state (as-quenched and/or annealed). However, the latter govern not only T_C but also the maximum of entropy changes.
- Employing Mössbauer spectrometry, which provides simultaneous information about the structural arrangement and magnetic states, the role of structural relaxation upon the magnetic parameters was confirmed.

Acknowledgments

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