Vol. **135** (2019) *ACTA PHYSICA POLONICA A* No. 2

Proceedings of XIX International Scientific Conference "New Technologies and Achievements in Metallurgy, Material Engineering, Production Engineering and Physics", Częstochowa, Poland, June 7–8, 2018

Impact of Annealing on Flattening of Magnetic Entropy Change versus Temperature Curves in Amorphous and Partially Crystallized $\mathrm{Fe_{76}Mo_{10}Cu_1B_{13}}$ Alloy

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"Table-like" shape of the magnetic entropy change versus temperature, $\Delta S_M(T)$, curve in amorphous and partially crystallized $\mathrm{Fe_{76}Mo_{10}Cu_1B_{13}}$ alloy has been investigated. The single ribbons in the as-quenched state and after annealing within the amorphous state exhibit "caret-like" behavior of $\Delta S_M(T)$ near the Curie point, T_C, of the amorphous phase. Amorphous $\mathrm{Fe_{76}Mo_{10}Cu_1B_{13}}$ alloy shows the Curie point of 277 K in the as-quenched state. According to the invar effect T_C decreases to 272 K and increases to 284 K after the annealing at 623 K and 673 K for 0.5 h, respectively. Layered composite consisting of annealed ribbons shows almost flat mathematically modeled $\Delta S_M(T)$ curve in the temperature range from 262 K to 288 K. The temperature span $\Delta T = 26$ K is rather modest but takes place exactly in the ambient temperature range. The modeled values of ΔS_M do not differ a lot from the maximum values of the single constituent. After the annealing at 823 K for 0.5 h $\Delta S_M(T)$ curve for a single ribbon is flat in much wider temperature range than in the layered composite due to diversity of magnetic phases presented in the heat treated sample but ΔS_M values drastically decrease.

DOI: 10.12693/APhysPolA.135.212

PACS/topics: 75.50.Bb, 75.50.Kj, 75.60.Ej, 75.30.Sg

1. Introduction

Requirements made for magnetic refrigerant materials depend on the thermodynamic cycles they should undergo [1]. For the refrigerant appliances working near the room temperature the magnetic Ericsson cycle consisting of two isothermal and two isofield magnetization steps seems to be the most adequate. The Ericsson cycle is the most energetically efficient if the magnetic entropy change versus temperature ($\Delta S_M(T)$) is almost constant in the temperature span $\Delta T = T_{\mathrm{hot}} - T_{\mathrm{cold}}$, where T_{hot} and T_{cold} correspond to the temperatures of hot and cold sinks, respectively [2]. Single magnetic phases usually do not exhibit such "table-like" behavior but a "caret-like" one with the peak value of $\Delta S_M(T)$ near the Curie point of the alloy, so for this reason the composite materials consisting of at least two magnetic phases are considered [1]. In the case of amorphous ferromagnets the composite is formed by two ribbons with different composition and consequently different Curie temperature. In this way the working temperature range is widened as compared to single phased refrigerant material [3]. The Curie temperature of the amorphous ferromagnet can be easily tuned not only by changes in chemical composition but by proper annealing within the amorphous state [4]. In this paper we present the thermomagnetic properties of amorphous $\mathrm{Fe_{76}Mo_{10}Cu_1B_{13}}$ alloy in the as-quenched state and after annealing below and above the primary crystallization temperature. The properties of layered composite obtained from two amorphous ribbons with the same chemical composition but subjected to different heat treatments are discussed.

2. Experimental procedure

The amorphous ribbons, 10 mm wide and 20 μm thick, with the nominal composition of $\mathrm{Fe_{76}Mo_{10}Cu_1B_{13}}$ were prepared by melt spinning method. The microstructure was studied by X-ray diffraction and the Mössbauer spectroscopy. A Brucker-AXS, type D8 Advanced X-ray diffractometer and a conventional constant acceleration spectrometer with a ^{57}Co(Rh) radioactive source were used. Transmission Mössbauer spectra were fitted using NORMOS package. The specific magnetization (magnetization per unit mass, σ) versus temperature in 50–400 K range at the magnetizing field induction of 5 mT by a VersaLab (Quantum Design) system was measured for disc samples. The isothermal magnetization curves $\sigma(B)$ (where B is the magnetizing field induction) were obtained in 205–355 K temperature and 0–2 T of B ranges. The amorphous transition metals based amorphous alloys exhibit the second order ferromagnetic–paramagnetic phase transition. Therefore, from the sets of isothermal magnetization curves $\sigma(B)$ the magnetic entropy change ($\Delta S_M(T)$) can be calculated from the Maxwell thermodynamic equation [1] according to the procedure described in details in [5]. All measurements

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were performed and $\Delta S_M(T)$ were computed for samples in the as-quenched state and after the conventional annealing within the amorphous state and at temperature above the onset of primary crystallization. The annealing temperatures were determined from differential scanning calorimetry (DSC) curve recorded by means of a NETZSCH STA 449F1 setup at the heating rate of 10 K/min.

3. Results and discussion

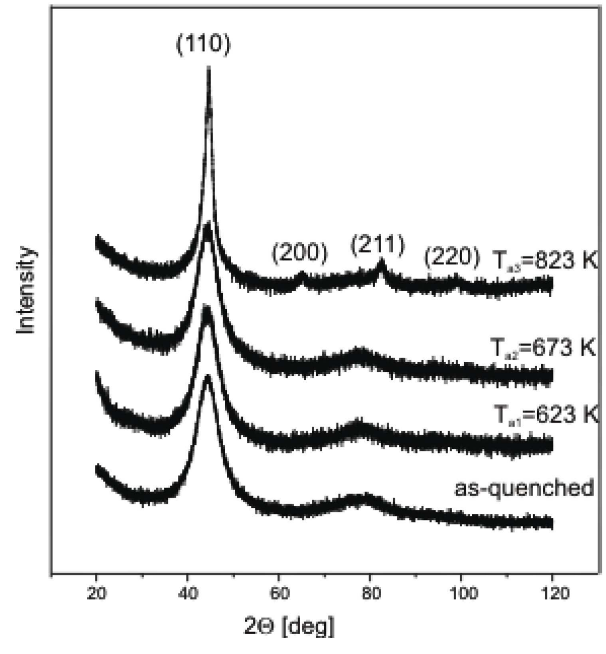

Fig. 1. X-ray diffraction patterns for the as-quenched and annealed at T_{a1}, T_{a2}, and T_{a3} for 0.5 h $Fe_{76}Mo_{10}Cu_1B_{13}$ amorphous ribbons.

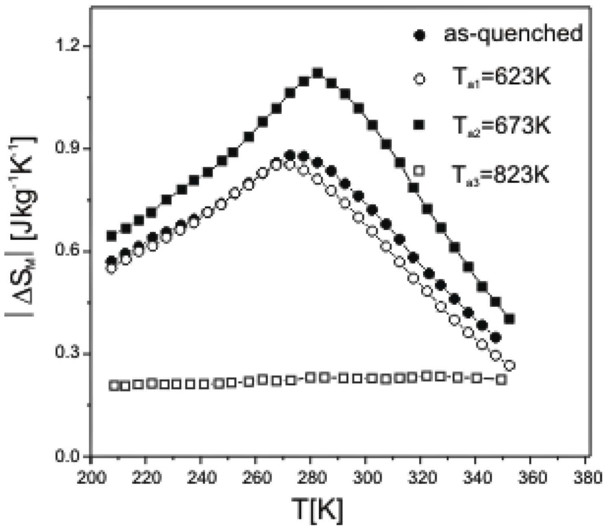

Fig. 2. Isothermal magnetic entropy change, ΔS_M versus temperature for the as-quenched and annealed at T_{a1}, T_{a2}, and T_{a3} for 0.5 h $Fe_{76}Mo_{10}Cu_1B_{13}$ amorphous ribbons.

According to the DSC curve the primary crystallization of the amorphous $Fe_{78}Mo_{10}Cu_1B_{13}$ alloy starts at 703 K and the secondary at 937 K, so the annealing temperatures $T_{a1} = 623$ K and $T_{a2} = 673$ K are far below the onset of crystallization, whereas $T_{a3} = 823$ K is in the span of the primary crystallization. In Fig. 1 X-ray diffraction patterns for the as-quenched and annealed at T_{a1}, T_{a2}, and T_{a3} $Fe_{78}Mo_{10}Cu_1B_{13}$ amorphous ribbons are shown. The patterns for the as-quenched and annealed T_{a1} and T_{a2} for 0.5 h samples are typical of amorphous alloys with no traces of crystallization, although α-Fe medium range ordered (MRO) regions 1–2 nm in size with small volume fraction (about 3%) were revealed by transmission high-resolution electron microscopy and the Mössbauer spectroscopy [4]. After the annealing at T_{a3} the presence of peaks originating from the (110), (200), (211), and (220) planes in α-Fe(Mo) crystalline grains are shown. By derivation of $\sigma(T)$ curves measured at $B = 5$ mT the Curie points are derived and equal to $T_C = (277 \pm 1)$ K, $T_{C1} = (272 \pm 1)$ K and $T_{C2} = (284 \pm 1)$ K in the as-quenched state and after the annealing at T_{a1} and T_{a2}, respectively. T_C for the as-quenched amorphous phase makes the material very interesting for magnetic refrigeration. The decrease of T_C after annealing at T_{a1} may be attributed to the annealing out of free volumes. Consequently, the average distance between Fe atoms and the exchange interaction between them decrease resulting in lowering of T_C. During annealing at higher temperature (T_{a2}) two mechanisms play the role — the mentioned above annealing out of free volumes and diffusion of atoms which may lead to strengthening of the exchange interaction between magnetic atoms and the enhancement of the Curie temperature is observed. Therefore, the Curie point of the amorphous phase due to invar effect can be easily tuned by proper conventional annealing. In Fig. 2 ΔS_M versus temperature for the as-quenched and annealed samples is depicted. In the as-quenched state and after the annealing within the amorphous state (T_{a1} and T_{a2})$\Delta S_M(T)$ exhibits the "caret-like" behavior with the peak value close to the Curie temperature of the amorphous phase. After annealing at T_{a3}, as revealed by transmission Mössbauer spectroscopy [6], the amorphous paramagnetic and ferromagnetic phases, interface zone, and crystalline α-Fe grains are presented in the samples at room temperature. The diversity of the magnetic phases with different Curie points causes the distinct flattening of $\Delta S_M(T)$ curve and drastic decrease of ΔS_M value (Fig. 2). If the composite from two adherent ribbons subjected to the heat treatments at T_{a1} and T_{a2} is considered, neglecting magnetic dipolar interactions between ribbons ΔS_M of the composite can be mathematically modeled by:

$$\Delta S_M(T) = \alpha \Delta S_{M1}(T) + (1 - \alpha)\Delta S_{M2}(T), \qquad (1)$$

where $\Delta S_{M1}(T)$ and $\Delta S_{M2}(T)$ are magnetic entropy change of composite constituents, α is the mass fraction of the first constituent. Such composite has the temperature span of the Curie point equal to 12 K.

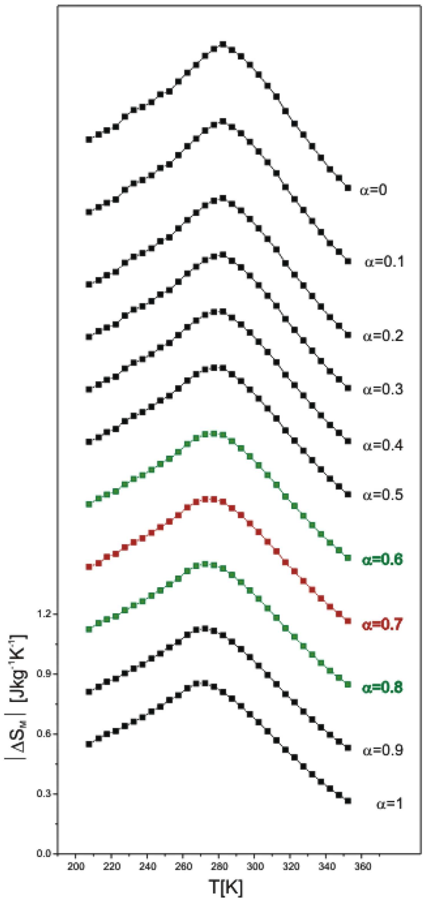

Fig. 3. Mathematically modeled magnetic entropy change as a function of temperature for the layered composite consisted of two $Fe_{76}Mo_{10}Cu_1B_{13}$ amorphous ribbons subjected to the annealing within the amorphous state with different mass fraction of the constituents (α). The scale of the vertical line refers only to the ribbon annealed at $T_{a1} = 623$ K for 0.5 h ($\alpha = 1$).

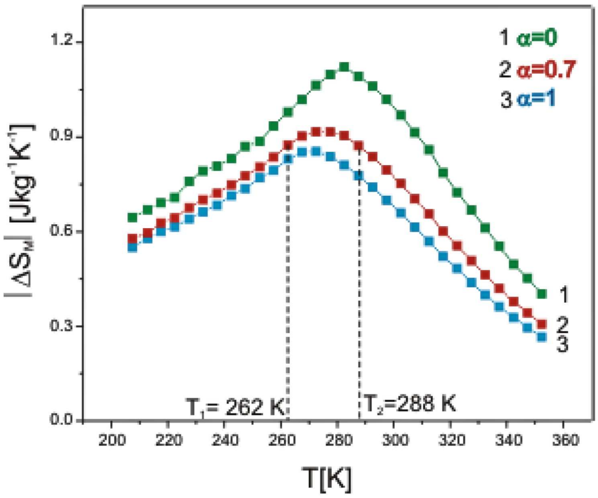

Fig. 4. Temperature dependence of the mathematically modeled magnetic entropy change for the composite ($\alpha = 0.7$) and measured single components ($\alpha = 1$ and $\alpha = 0$).

$\Delta S_M(T)$ curves for the composite for different values of α are presented in Fig. 3. The most flattened maximum is obtained for $\alpha = 0.7$ but the shape of maxima for $\alpha = 0.6$ and $\alpha = 0.8$ does not differ a lot. For the comparison in Fig. 4 $\Delta S_M(T)$ for the single ribbons of the $Fe_{76}Mo_{10}Cu_1B_{13}$ alloy subjected to the heat treatment at T_{a1} and T_{a2} ($\alpha = 1$ and $\alpha = 0$) and for the composite with the mass fraction $\alpha = 0.7$ are shown. The almost flat maximum for the composite is obtained in the temperature range from 262 K to 288 K ($\Delta T = 26$ K) and is higher than the difference in the Curie points of the constituents. The temperature span is rather modest but is very interesting because is obtained by annealing the amorphous ribbons with the same chemical composition within the amorphous state and lies in the room temperature range. Additionally, the maximum value of ΔS_M of the composite does not differ a lot from these of the constituents contrary to the single ribbon heat treated in the primary crystallization range for which the distinct increase of flattening temperature span is accompanied by drastic decrease of ΔS_M value (Fig. 2).

4. Conclusions

The values of the magnetic entropy change and the temperature span $\Delta T = 26$ K of almost flat $\Delta S_M(T)$ curve for the composite formed by two adherent ribbons annealed at T_{a1} and T_{a2} for 0.5 h are rather modest. Taking into account the prices of raw elements, possibility to tune the Curie point not only by changes in chemical composition but by the proper conventional annealing the ribbons with the same composition, as well and considering the fact that ΔT is in the vicinity of room temperature, the investigated material may be interesting for magnetic refrigeration technology.

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