Magnetocaloric Effect in Amorphous and Partially Crystallized Fe$_{80}$Zr$_7$Cr$_6$Nb$_2$Cu$_1$B$_4$ Alloy

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In the present work the microstructure and thermomagnetic properties of Fe$_{80}$Zr$_7$Cr$_6$Nb$_2$Cu$_1$B$_4$ ribbon in the as-quenched state and after the accumulative annealing in the temperature range 600–800 K for 10 min were studied using Mössbauer spectroscopy and vibrating sample magnetometry. The second order phase transition from ferromagnetic to paramagnetic state is observed. The Curie temperature $T_C$ defined as inflection point on the magnetization versus temperature curve recorded on zero-field cooled mode equals 262.5 K for the as-quenched material. With increasing the annealing temperature increase of $T_C$ is observed. The maximum value of the magnetic entropy change $(-\Delta S)$ observed in the vicinity of the Curie point is equal to 0.85 J/(kgK) for the alloy in the as-quenched state. Moreover, for the samples annealed up to 750 K for 10 min the low intensity maximum at about 190 K related to the supplementary magnetic phase is observed. The presence of this phase was confirmed as additional component visible on hyperfine field distributions of Mössbauer spectra.

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1. Introduction

Amorphous metallic materials are characterized by unique mechanical, electrical, corrosion resistance and magnetic properties [1-4]. Some of them are very soft magnetic materials and their Curie temperature $T_C$ could be easily tuned by the change of the chemical composition or/and proper heat treatment [5]. It allows to produce materials with $T_C$ near room temperature which could be used as an active magnetic regenerator in magnetic refrigerator [6].

The aim of the present work is to study the structure and thermomagnetic properties (espacially magnetic entropy change) of the Fe$_{80}$Zr$_7$Cr$_6$Nb$_2$Cu$_1$B$_4$ alloy fabricated in the form of ribbon. The investigation was carried out for determining its suitability for magnetic refrigeration.

2. Experimental procedure

The Fe$_{80}$Zr$_7$Cr$_6$Nb$_2$Cu$_1$B$_4$ alloy was prepared by arc melting under a protective argon atmosphere using high purity elements. Obtained ingot was remelted several times in order to achieve a good homogeneity. The amorphous ribbon 3 mm wide and 20 $\mu$m thick was produced by a single roller melt-spinning technique.

The microstructure of the investigated sample was studied using Brucker D8 Advanced X-ray diffractometer with CuK$_\alpha$ radiation and conventional Mössbauer spectrometer with $^{57}$Co(Rh) radioactive source of 25 mCi activity. From transmission Mössbauer spectra analysis, the average value of the quadrupole splitting $QS$, hyperfine field distributions $P(E)$ and phase composition of the samples in the as-quenched state and after annealing were determined by a Normos package according to the procedure developed in [7].

The magnetization measurements as a function of temperature (temperature range 50–400 K) and external magnetic field (up to 1 T) were carried out by the vibrating sample magnetometer (VSM) VersaLab system (Quantum Design). Magnetocaloric effect, studied as magnetic entropy change according to the Maxwell formula [8], was calculated basing on isothermal magnetization versus magnetic field.

To compare more precisely obtained results all investigations were carried out for the same piece of sample. Therefore, measurements were performed for as-quenched amorphous precursor and after the accumulative heat treatment at 600 K and then 700 K, 750 K and 800 K for 10 min. The conditions of the annealing were chosen according to the Differential Scanning Calorimetry (DSC) measurements (NETSCH STA 449F1 Jupiter) set at the heating rate of 10 K/min.

3. Results and discussion

Figure 1 shows the temperature dependence of heat flow for the as-quenched Fe$_{80}$Zr$_7$Cr$_6$Nb$_2$Cu$_1$B$_4$ alloy recorded with the help of Differential scanning calorimetry. It is seen that primary crystallization temperature is equal to 810 K. In diffraction patterns recorded for the Fe$_{80}$Zr$_7$Cr$_6$Nb$_2$Cu$_1$B$_4$ samples in the as-quenched state and after the annealing for 10 min at 600 K and then 700 K and 750 K only a broad hallo, characteristic of amorphous materials, is observed. As an example, in Fig. 2a the X-ray diffraction pattern of the sample annealed at 600 K and then 700 K and 750 K is shown.
Mössbauer spectrum for this sample is present in Fig. 3a. Similar Mössbauer spectra measured at room temperature were obtained for samples in the asquenched state and after the accumulative annealing at 600 K and then 700 K [9]. These spectra are characteristic of amorphous paramagnets and have a form of asymmetric broad doublets. Further annealing at 800 K for 10 min leads to the partial crystallization of the investigated alloy. In X-ray diffraction pattern for Fe$_{80}$Zr$_7$Cr$_6$Nb$_2$Cu$_1$B$_4$ alloy after the annealing at 800 K for 10 min additional sharp peaks appear which correspond to the crystalline phases (Fig. 2b). It was also confirmed by Mössbauer studies (Fig. 3e). This Mössbauer spectrum, characteristic of paramagnetic partially crystalline material, was decomposed into three components corresponding to the amorphous matrix, interfacial zone and crystalline phase.

The Curie temperatures obtained with numerically calculated derivatives from $\sigma$(T) curves (Fig. 4) are presented in Table I. As it is shown in this table, the Curie temperature decreases after annealing at 600 K and slightly increases after the next stage of the heat treatment. Similar tendency is observed for average values of QS collected in Table 2. This behaviour is characteristic of materials exhibiting the invar effect [10].

The amount of heat transferred between the hot and cold reservoirs of a thermodynamic cycle, RCP was calculated from the formula:

$$RCP = -(-\Delta S)_{max}\delta T,$$

where $\delta T$ is full width at half maximum of the $(-\Delta S)$ versus T curves [11].

In Fig. 5 $\sigma^2$ versus $\mu_0H/\sigma$ i.e. the Arrott plots are depicted. In the present case, the slopes remain positive, indicating that the phase transition (from ferromag-
The Curie temperature $T_C$, the maximum magnetic entropy change $-\Delta S_{\text{max}}$, the temperature of the maximum entropy change $T_p$ and relative cooling power $RCP$ of the major peak for investigated Fe$_{80}$Zr$_7$Cr$_6$Nb$_2$Cu$_1$B$_4$ alloy in the as-quenched state and after the accumulative annealing for 10 min at 600 K and then 700, 750, and 800 K.

| Heat treatment | $T_C$ [K] | $-\Delta S_{\text{max}}$ [J/(kg K)] | $T_p$ [K] | $RCP$ [J/(kg K)] |
|----------------|----------|-----------------------------------|----------|--------------|
| as-quenched    | 262.5    | 0.85                              | 263      | 62           |
| 600 K          | 253.0    | 0.69                              | 252      | 48           |
| 700 K          | 256.0    | 0.83                              | 255      | 57           |
| 750 K          | 258.0    | 0.54                              | 256      | 40           |
| 800 K          | 259.0    | 0.33                              | 260      | 38           |

The magnetic entropy change achieves the highest value $-\Delta S_{\text{max}}$ for the investigated alloy in the as-quenched state and decreases after the annealing at 750 K and then at 800 K. The temperature of the maximum entropy change $T_p$ is observed near the Curie point and shifts toward temperatures scale like the $T_C$. It is worth noticing that the second, low intensity maximum, near 180 K is also visible. Furthermore, in $\sigma(T)$ curves the bifurcation between ZFC and FC results in this temperature range disappears (Fig. 4).

The average value of the quadrupole splitting distribution $QS$ and its standard deviation $\langle QS \rangle$, isomer shift of the single line $I_{S_L}$ and its relative intensity $I_{S_L}$ of Fe$_{80}$Zr$_7$Cr$_6$Nb$_2$Cu$_1$B$_4$ alloy in the as-quenched state and after the accumulative heat treatment for 10 min at 600 K and then 700 and 750 K.

| Heat treatment | $QS$ [mm/s] | $\langle QS \rangle$ [mm/s] | $I_{S_L}$ | $I_{S_{SL}}$ [mm/s] |
|----------------|------------|-----------------------------|--------|-------------------|
| as-quenched    | 0.482      | 0.256                       | 0.14     | -0.027            |
| 600 K          | 0.478      | 0.249                       | 0.14     | -0.111            |
| 700 K          | 0.482      | 0.246                       | 0.18     | -0.101            |
| 750 K          | 0.482      | 0.250                       | 0.16     | -0.099            |

This maximum on $\Delta S(T)$ curves observed for samples annealed up to 750 K is related to low intensity components on $P(B)$ and $P(QS)$ distributions. The hyperfine field distribution obtained from the Mössbauer spectrum, collected at the liquid nitrogen temperature, consists of two continuous components with average hyperfine field $B_1 = 15.8$ T, $B_2 = 17.0$ T and relative intensities $I_1 = 0.82$, $I_2 = 0.16$, respectively. The similar components, with the same intensities, we distinguished in the quadrupole splitting distribution for the spectrum measured at room temperature (Fig. 3b) and one of them (the single line for $QS=0$) is ascribed to Fe sites with the cubic symmetry of atoms arrangement in the nearest neighbourhood [10].

4. Conclusions

The Curie temperature for the Fe$_{80}$Cr$_6$Zr$_7$Nb$_2$Cu$_1$B$_4$ alloy in the as-quenched state equals to 263 K. After annealing at 600 K the Curie temperature drops down and then monotonically increases for the investigated samples annealed up to 800 K. This behaviour is connected to the invar effect.

For the investigated Fe$_{80}$Zr$_7$Cr$_6$Nb$_2$Cu$_1$B$_4$ alloy the highest value of the magnetic entropy change of 0.85 J/(kg K) is observed in the as-quenched state and occurs in the vicinity of the Curie point.
The additional maximum in $\Delta S(T)$ curve, visible at low temperatures, indicates the biphasic structure of the material. Such structure consists of areas with different concentration of Fe atoms, what is visible as low and high field components on hyperfine field distributions of Mössbauer spectra.

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