

Structural and Magnetic Studies of the Fe–Co–Zr–Mo–W–B Amorphous Alloy

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The paper presents a characterization of the phase structure by X-ray diffraction and isothermal magnetic entropy changes for the amorphous Fe₅₈Co₁₀Zr₁₀Mo₅W₂B₁₅ alloy sample in the as-quenched state. An ingot sample was obtained by arc-melting. The ribbon sample was obtained by the melt-spinning technique. The magnetic measurements at various temperatures allowed for the study of the Curie temperature T_C and magnetic entropy changes $|\Delta S_M|$. In order to determine the Curie temperature T_C of amorphous phase, three independent methods were used. Determination of the Curie temperature T_C for the amorphous alloys is not a trivial problem, as magnetization does not decrease rapidly around T_C . Therefore it is essential issue to establish T_C using few complementary methods. X-ray diffraction analysis revealed a fully amorphous structure of the ribbon samples.

DOI: [10.12693/APhysPolA.131.1204](https://doi.org/10.12693/APhysPolA.131.1204)

PACS/topics: 61.43.Dq, 75.50.Kj, 75.30.Sg, 75.30.Kz, 75.40.–s

1. Introduction

Magnetic refrigerators based on magnetocaloric effect (MCE) working below room temperature are currently attracting much interest. The MCE offers an energy efficient and environmental friendly alternative to the traditional refrigeration or heat pumps [1–3]. The development of Fe-based amorphous soft magnetic materials with a wide supercooled liquid region and good glass formability has become an important research topic in recent years [4–6].

The MCE is significant mostly at around the phase transition temperature. The search for new magnetocaloric material for commercial applications has concentrated mainly around the tunable T_C and reasonable changes of magnetic entropy (ΔS_M) [7].

Iron based metallic glasses have attracted great attention of researchers, due to their good magnetic and mechanical properties, as well as the possibility of utilizing the magnetocaloric effect. There are three main factors allowing to estimate the potential of magnetocaloric materials: the magnetic entropy change (ΔS_M), the adiabatic temperature change (ΔT_{ad}) and the relative cooling power (RCP) [8]. An ideal magnetic refrigerant material has to possess large values of both ΔS_M and ΔT_{ad} as well as high RCP around room temperature at a low magnetic field [9]. The RCP is actually considered to be the most important factor for assessing the usefulness of magnetic refrigerant material [10, 11]. The investigation of the $-\Delta S_M$ is one of the method which allows one to obtain information about the magnetic phase transition in these materials as well as to assess the MCE. *

The Fe₆₀Co₈Zr₁₀Mo₅W₂B₁₅ alloy attracts a lot of attention, due to the wide supercooled liquid region before crystallization, a high glass-forming ability (GFA), thermal stability, strength and corrosion resistance. It reveals however low Curie temperature [4, 12, 13]. A promising iron based alloy with good GFA seems to be the Fe₅₈Co₁₀Zr₁₀Mo₅W₂B₁₅. By changing the Fe and Co ratio it is possible to modify T_C for this type of material to get its value around room temperature.

The aim of the present work was to determine the phase structure and magnetic properties of the rapidly solidified ribbons of the Fe₅₈Co₁₀Zr₁₀Mo₅W₂B₁₅ alloy and discuss the possibility of their application as the magnetic refrigerant.

2. Experimental

The Fe₅₈Co₁₀Zr₁₀Mo₅W₂B₁₅ alloy ingot was prepared by arc-melting technique of the high purity (99.98%) constituent elements Fe, Co, Zr, Mo, W with the addition of pre-alloyed Fe–B. Ingot was re-melted at least seven times to guarantee the homogeneity of the alloy.

The ribbon was prepared by the melt-spinning technique at the surface velocity of the copper roller of 40 m/s. Both the arc-melting and melt-spinning were performed under Ar atmosphere to avoid oxidation.

The phase structure was investigated by X-ray diffraction (XRD) using Bruker D8 Advance with Cu K_α radiation and the LynxEye dimensional compound strip detector. The data were recorded using the step-scanning method in 2θ range from 25 to 100 degrees.

Temperature dependences of magnetization were measured by VersaLab (Quantum Design) system. Magnetic measurements $M(H)$ in the temperature range 225–325 K were performed and the magnetocaloric effect (MCE) was estimated by calculation of the temperature and field dependences of magnetic entropy change $-\Delta S_M$. The magnetic entropy change $-\Delta S_M$ was calculated using the Maxwell thermodynamic formula [14]:

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$$\Delta S_M(T,H) = \int_0^H \left(\frac{\partial M(T,H)}{\partial T} \right)_H dH, \quad (1)$$

where T — temperature, $M(T,H)$ — magnetization, H — external magnetic field.

From thermomagnetic curves the Curie temperature of the $\text{Fe}_{58}\text{Co}_{10}\text{Zr}_{10}\text{Mo}_5\text{W}_2\text{B}_{15}$ alloy was determined. Furthermore, the isothermal Arrott plots were constructed and the magnetic entropy changes were calculated [15, 16].

3. Results and discussion

In Fig. 1 the XRD pattern of the as-cast $\text{Fe}_{58}\text{Co}_{10}\text{Zr}_{10}\text{Mo}_5\text{W}_2\text{B}_{15}$ ribbon is presented. The ribbon exhibits a typical broad diffraction maximum characteristic for the amorphous structure without any crystalline reflexes, suggesting that the alloy can be melt-spun into the fully amorphous ribbon with a thickness of about 20 μm .

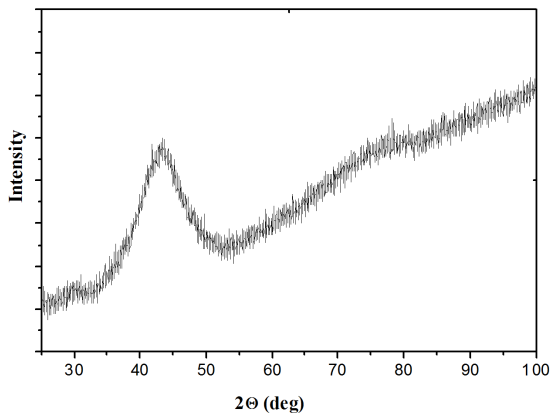


Fig. 1. The XRD pattern measured for the $\text{Fe}_{58}\text{Co}_{10}\text{Zr}_{10}\text{Mo}_5\text{W}_2\text{B}_{15}$ sample in the as-cast state.

The temperature dependences in FC mode magnetization measured for the $\text{Fe}_{58}\text{Co}_{10}\text{Zr}_{10}\text{Mo}_5\text{W}_2\text{B}_{15}$ alloy were recorded at 2.5, 5, and 15 mT and the corresponding dM/dT curves were presented in Fig. 2. With increasing temperature, a drop of magnetization is observed below T_C . The Curie temperature T_C is determined from the condition $dM/dT = \text{minimum}$ and its value T_C reaches 263 K.

The Curie temperature T_C can be determined using the equation [17]:

$$M(T) = M(0) \left(1 - \frac{T}{T_C} \right)^\beta, \quad (2)$$

where $M(0)$ is the saturation magnetization at 0 K and β is constant of 0.36. The Curie temperature was determined from $M^{1/\beta}$ vs. T curves measured at various external magnetic fields (Fig. 3) and extrapolated to zero field (inset in Fig. 3). The values of T_C determined using this method reaches 263 K.

From the magnetization isotherms presented in Fig. 4, the Arrott plots were constructed in order to determine T_C and confirm the order of phase transition (Fig. 5). For the linear parts of $M^2(\mu_0 H/M)$ curves the relation

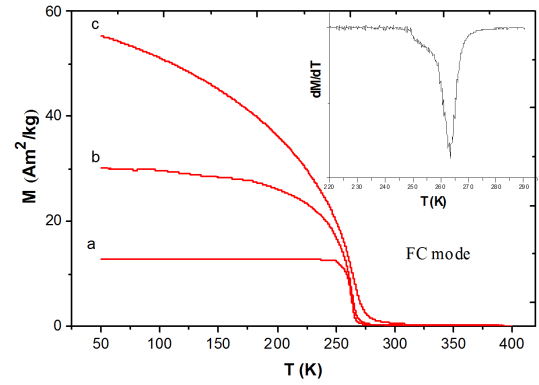


Fig. 2. The temperature dependence of the field cooled (FC) magnetization for the $\text{Fe}_{58}\text{Co}_{10}\text{Zr}_{10}\text{Mo}_5\text{W}_2\text{B}_{15}$ alloy ribbon at external magnetic fields: (a) 2.5 mT, (b) 5 mT, and (c) 15 mT. The inset shows a derivative curve of dM/dT .

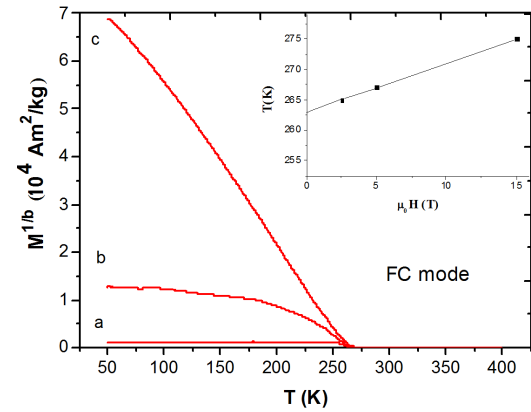


Fig. 3. The modified the curve of $M^{1/\beta}(T)$ with a critical parameter ($\beta = 0.36$) for magnetization for the $\text{Fe}_{58}\text{Co}_{10}\text{Zr}_{10}\text{Mo}_5\text{W}_2\text{B}_{15}$ alloy ribbon at external magnetic fields: (a) 2.5 mT, (b) 5 mT, and (c) 15 mT.

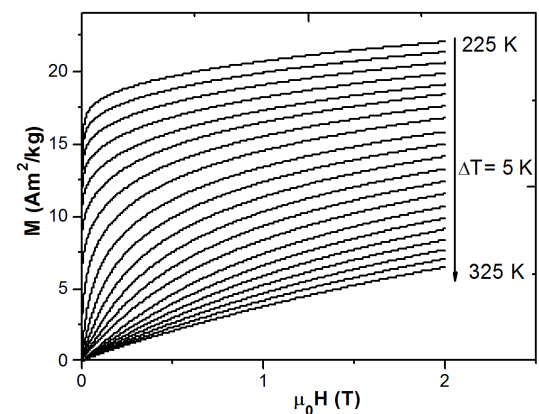


Fig. 4. The magnetization isotherms for the $\text{Fe}_{58}\text{Co}_{10}\text{Zr}_{10}\text{Mo}_5\text{W}_2\text{B}_{15}$ alloy ribbon from 225 to 325 K.

M_{sp}^2 vs. T (where M_{sp} — spontaneous magnetization) was drawn and T_C was determined as an interception of this line with T axis (inset in Fig. 5). The T_C value obtained using this method reached 270 K. The character of the Arrott plots is typical for the second order phase transition in the amorphous sample [16].

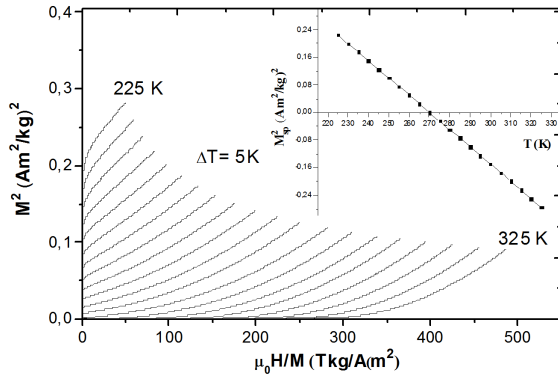


Fig. 5. Arrott plots, i.e. M^2 versus $\mu_0 H/M$ for $\text{Fe}_{58}\text{Co}_{10}\text{Zr}_{10}\text{Mo}_5\text{W}_2\text{B}_{15}$ alloy. Inset: linear fit of M_{sp}^2 versus T to determine the Curie point.

Furthermore, the temperature changes of $-\Delta S_M$ were also determined from magnetization isotherms (Fig. 6). The maximum value of $-\Delta S_M$ reached $0.44 \text{ J kg}^{-1} \text{ K}^{-1}$ for the maximum change of the external magnetic field up to 2 T.

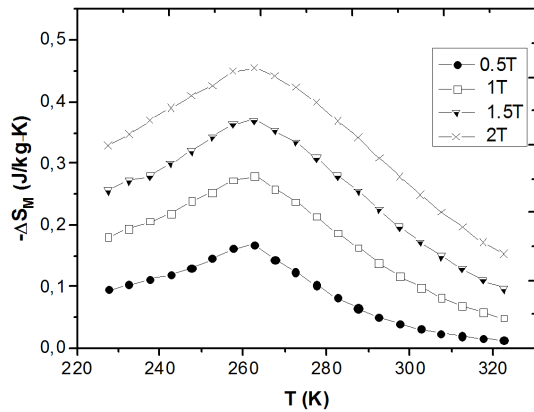


Fig. 6. Magnetic entropy change $-\Delta S_M$ around the Curie temperature T_C measured for $\text{Fe}_{58}\text{Co}_{10}\text{Zr}_{10}\text{Mo}_5\text{W}_2\text{B}_{15}$ alloy at magnetic field changes from 2 (top) to 0.5 T (bottom).

4. Conclusions

In the present studies the magnetic and structural properties in $\text{Fe}_{58}\text{Co}_{10}\text{Zr}_{10}\text{Mo}_5\text{W}_2\text{B}_{15}$ alloy ribbon have been investigated. Characteristic of the XRD studies confirmed the amorphous structure of melt-spun ribbons.

The Curie temperature of the amorphous ribbon was determined using three techniques. In the first one, T_C was obtained from the measurements of temperature dependences of the FC magnetization. Using this method

T_C reached 263 K. In the second approach, the T_C was obtained from a derivative curve of dM/dT and values of T_C reached 263 K. In the third approach, the Arrott plots were derived from the initial magnetization curves measured at various temperatures. The determined value of T_C reached 270 K.

The maximum magnetic entropy change $\Delta S_{M \max} = 0.44 \text{ J kg}^{-1} \text{ K}^{-1}$ at the change of external magnetic field at 2 T is not very high, but the range of temperatures at which $-\Delta S_M$ maintain a significant level seems to be promising for application. Therefore, further studies focused on doping the base alloy with Gd are in progress. Furthermore an appropriate admixture of the base alloy will result in the shift of T_C to the higher temperatures. The tunable T_C around room temperature makes this alloy potentially useful for the development of magnetocaloric regenerators.

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