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Magnetocaloric Effect in Amorphous and Partially Crystallized Fe–Zr–Nb–Cu–B Alloy

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This paper presents the results of an investigation into the: microstructure, magnetic properties and influence of annealing temperature on the magnetocaloric effect of $Fe_{82}Zr_7Nb_2Cu_1B_8$ alloy in the as-quenched and partially crystalline state. The microstructure was investigated using Mössbauer spectroscopy. The magnetocaloric effect was observed as a change in the magnetic entropy, which was calculated from isothermal magnetization curves. Fully-amorphous $Fe_{82}Zr_7Nb_2Cu_1B_8$ alloys, in the as-quenched state, exhibit a Curie temperature equal to (340 ± 5) K. The transmission Mössbauer spectrum for the as-quenched $Fe_{82}Zr_7Nb_2Cu_1B_8$ alloy is typical for weak ferromagnets with the average hyperfine field of 9.86(2) T. For this alloy in the as-quenched state, the changes in maximum magnetic entropy occur near the Curie points and are equal to 0.95 J/(kg K). Also, the maximum magnetic entropy changes decrease after partial crystallization.

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1. Introduction

The appropriate selection of the chemical composition and the applied heat treatment can have a considerable effect on the magnetic structure of a manufactured alloy. The combination of these two factors allows materials to be obtained which possess a given set of desired magnetic properties. The resulting materials are very suitable for application in industry. In particular, the soft magnetic iron-based alloys have great application potential; especially the group in which the Curie temperatures are close to room temperature [1, 2]. Suitable thermomagnetic properties of these alloys allow their application in the production of magnetic refrigerators, which are a promising alternative to conventional refrigerators.

The rare earth alloys show a large magnetocaloric effect near room temperature. However, these materials require a large change of magnetic field, and, in addition, the relatively high cost of raw materials makes these alloys less attractive when compared with transition metal alloys. In the latter alloys, a large magnetocaloric effect can be achieved with a significantly lower magnetic field.

In this paper, investigations are presented into the: microstructure, magnetic ordering and magnetocaloric effect occurring in samples of amorphous and partially-crystallized, multicomponent, $Fe_{82}Zr_7Nb_2Cu_1B_8$ alloy.

2. Experimental procedure

Amorphous ribbons of the alloy, of nominal composition $Fe_{82}Zr_7Nb_2Cu_1B_8$, were prepared with dimensions: width 3 mm and thickness 20 μm; this fabrication process was achieved using a rapid-quenching method involving a single roller under a protective argon atmosphere. The microstructure and magnetic properties of the sample both in the as-quenched state and after annealing were investigated. This was achieved at room temperature by means of a "POLON" Mössbauer spectrometer, equipped with a ^{57}Co (Rh) source with an activity of 50 mCi. The transmission Mössbauer spectra were analysed using "NORMOS" [3] software. The isothermal magnetization curves were measured over a wide range of temperatures, and under the influence of a maximal magnetic field of 0.75 T, using a force magnetometer. From these curves, the magnetic entropy change (ΔS_M) was calculated — which is a measure of the magnetocaloric effect [4, 5].

All of the investigations were performed on samples of the $Fe_{82}Zr_7Nb_2Cu_1B_8$alloy in both the as-quenched and partially-crystallized states, the latter being obtained using additional annealing processes at temperatures of 750 K and 773 K over a time duration of 15 min.

3. Results and discussion

In the as-quenched state, the investigated ribbons were found to be fully amorphous with their Curie points equal to 340 ± 5 K. In Fig. 1, the following results for the $Fe_{82}Zr_7Nb_2Cu_1B_8$ samples are shown: the transmission Mössbauer spectra (a, c, e) and corresponding hyperfine field distributions (b, d, f) in the as-quenched state (a, b) and after annealing at 750 K (c, d) and then 773 K (e, f).

The spectrum of the alloy in the as-quenched state is characteristic for that of amorphous materials with ferromagnetic ordering (Fig. 1a). There are components of the low- and high-field induction in the distribution of hyperfine fields. This is a result of the inhomogeneous distributions of iron atoms throughout the sample volume. The average hyperfine field, B_{hf}, for the amorphous $Fe_{82}Zr_7Nb_2Cu_1B_8$alloy, in the as-quenched state, is equal to 9.86(2) T. Theincrease in heat treatment temperature resulted in an increase in volume fraction of the crystalline phase [6], which is observed as an increase in the area (Fig. 1e).

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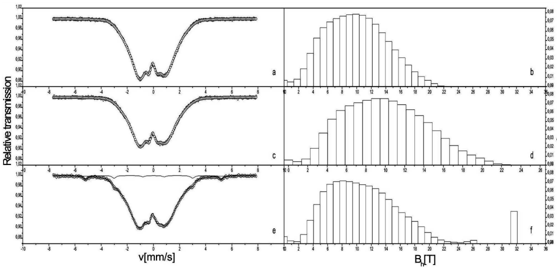

Fig. 1. Transmission Mössbauer spectra (a, c, e) and corresponding hyperfine field distributions (b, d, f) for $Fe_{82}Zr_7Nb_2Cu_1B_8$alloy: in the as-quenched state (a, b), after annealing at 750 K (c, d) and then at 773 K (e, f) for 15 min.

The magnetocaloric effect, observed as the change of the magnetic entropy, was calculated in accordance with following formula for isothermal magnetization curves measured over a wide temperature range.

The isothermal magnetic entropy changes ΔS_{M} were obtained from the relation (Ref. [5]):

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

The isothermal magnetic entropy changes versus temperature were computed and are presented in Fig. 2, for the $Fe_{82}Zr_7Nb_2Cu_1B_8$ samples in the as-quenched state and after annealing at 750 K and then at 773 K for 15 min. The $-\Delta S_{\mathrm{M}}(T)$ curves can be seen to exhibit distinct maxima. For all of the curves, the broad maxima are observed at temperatures close to the Curie point for the investigated alloy. Moreover, along with the appearance of a substantial quantity of grains of the crystalline phase, a reduction in the maximum height is seen to be taking place on the $-\Delta S_{\mathrm{M}}(T)$ curves. This result proves that grains of the crystalline phase do not contribute practically to the observed magnetocalorific effect. The investigated alloy is a two-phase material, and the Curie temperature of the crystalline phase is much higher than the Curie temperature of the amorphous matrix. Given a magnetic field change of 0 to 0.75 T, the maximum entropy change located at T_{c} for

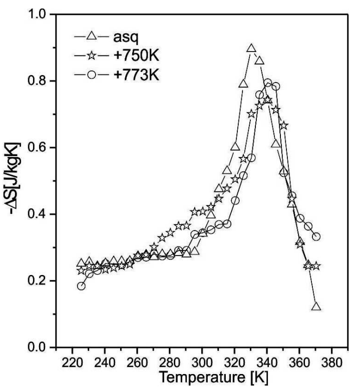

Fig. 2. Magnetic entropy changes versus temperature for $Fe_{82}Zr_7Nb_2Cu_1B_8$ alloy in the as-quenched state and after annealing.

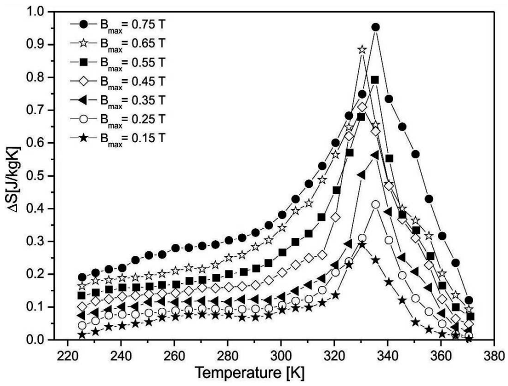

Fig. 3. Temperature dependence of isothermal magnetic entropy changes for seven different maxima of the magnetizing field in the as-quenched $Fe_{82}Zr_7Nb_2Cu_1B_8$ alloy.

amorphous ribbons has been found to be approximately 0.8 J/(kg K). In the sample after annealing the nanocrystalline grains were present, which leads to a more dispersed ferro-paramagnetic passage [7]. As a result, a reduction in the ΔS curve magnetic entropy change has been observed (Fig. 2).

In the as-quenched $Fe_{82}Zr_7Nb_2Cu_1B_8$alloy, the magnetic entropy changes depend on the temperature but also on the maximum magnetizing field (Fig. 3).

It can be seen that the magnetic entropy change is greatest for the largest magnetic field and is 0.95 J/(kg K) whereas that for the smallest the maximum magnetic field (0.15 T) is 0.3 J/(kg K). As can be seen from Figs. 2 and 3 the magnetic entropy change depend both on the temperature and the maximum magnetic field as well.

4. Conclusions

In conclusion, it may be stated that the multicomponent $Fe_{82}Zr_7Nb_2Cu_1B_8$ alloy in the as-quenched state was fully amorphous. The largest change in the magnetic entropy was exhibited by the sample of the investigated alloy in the as-quenched state, and was found to be 0.95 J/(kg K). After partial crystallization, the magnetic entropy changes were found to decrease. The change in the magnetic entropy is highly influenced by the magnetic field; the peak on the curve of ΔS was found to increase with increasing magnetic field.

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