

MAGNETOCALORIC EFFECT IN AMORPHOUS AND NANOCRYSTALLINE FeCrNbBCu ALLOYS

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Abstract. The magnetocaloric effect in series of amorphous and nanocrystalline $\text{Fe}_{73.5}\text{Cr}_5\text{Nb}_{4.5}\text{B}_{16}\text{Cu}$ and $\text{Fe}_{72}\text{Cr}_8\text{Nb}_3\text{B}_{16}\text{Cu}$ samples has been studied by evaluating the magnetic entropy changes, ΔS_m , from magnetization data. An addition of different amount of chromium to the FeNbBCu and the subsequent heat treatment were used to shift the Curie temperature of amorphous phase, $T_c(am)$, to the vicinity of room temperature. Upon a 0.6 T magnetic field change, the maximum entropy change $\Delta S_m \sim 0.5$ J/kgK is found at the Curie temperature $T_c(am) \approx 310\text{K}$ of the amorphous $\text{Fe}_{72}\text{Cr}_8\text{Nb}_3\text{B}_{16}\text{Cu}$ alloy. Hence, the FeCrNbBCu alloys could be considered as potential low cost magnetic refrigerants near room temperature.

Magnetic refrigeration based on the magnetocaloric effect, (MCE), has attracted a lot of attention of researchers and technologists during several decades. The first MCE applications took place at low temperatures; however, nowadays there is a very intensive search for new magnetic materials that show sufficiently large magnetic entropy change at ambient temperatures [1]. Recently, several Fe-based amorphous and/or nanocrystalline alloys prepared in the form of metallic ribbons by rapid quenching from the melt have been identified as promising magnetic refrigerants capable of the operation in the vicinity of room temperature [2-4].

In this work, the MCE in series of amorphous and nanocrystalline $\text{Fe}_{73.5}\text{Cr}_5\text{Nb}_{4.5}\text{B}_{16}\text{Cu}$ and $\text{Fe}_{72}\text{Cr}_8\text{Nb}_3\text{B}_{16}\text{Cu}$ samples has been studied by evaluating the magnetic entropy changes, ΔS_m , from magnetization data. We show that an addition of different amount of chromium to the FeNbBCu and the subsequent thermal processing could be used for tailoring of the Curie tempera-

ture of amorphous phase, $T_c(am)$, within broad temperature range near room temperature, which makes the FeCrNbBCu alloys an interesting material for room temperature magnetic refrigeration.

Amorphous ribbons of $\text{Fe}_{73.5}\text{Cr}_5\text{Nb}_{4.5}\text{B}_{16}\text{Cu}$ and $\text{Fe}_{72}\text{Cr}_8\text{Nb}_3\text{B}_{16}\text{Cu}$ alloys were prepared by the method of planar flow casting. Pieces of these ribbons were annealed under protective argon atmosphere for 1 hour at temperatures ranging from 573 to 723K. The magnetization has been measured by vibrating sample magnetometer (VSM) in the temperature range from 240 to 410K. The magnetic entropy changes ΔS_m induced by an isothermal magnetization from $H=0$ to 0.6 T were determined using the following equation associated with the Maxwell thermodynamic $(\partial S/\partial H)_T = (\partial M/\partial T)_H$ relationship:

$$\begin{aligned} \Delta S_m(T, H) &= S_m(T, H) - S_m(T, 0) \\ &= \int_0^H (\partial M / \partial T)_H dH. \end{aligned} \quad (1)$$

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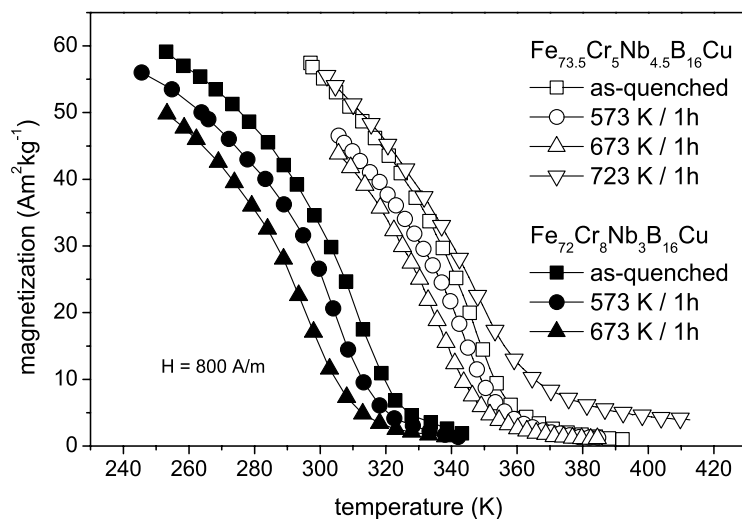


Fig. 1. Temperature dependences of the magnetization for the amorphous and annealed samples measured in an applied field 800 A/m.

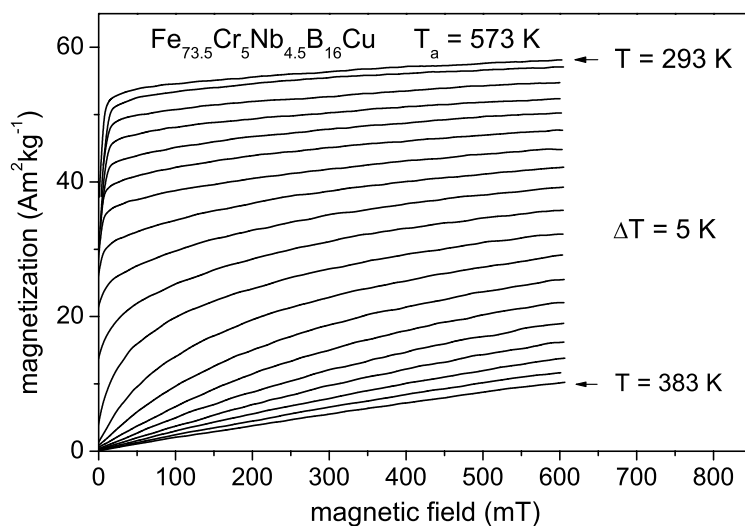


Fig. 2. Field dependences of the magnetization for the sample $\text{Fe}_{73.5}\text{Cr}_5\text{Nb}_{4.5}\text{B}_{16}\text{Cu}$ annealed for 1 hour at 573K measured at 5K steps.

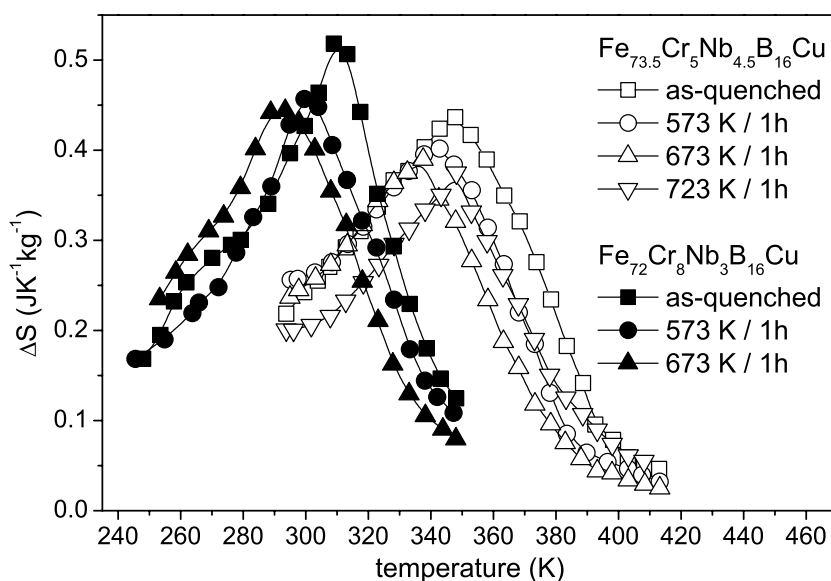


Fig. 3. Temperature dependences of the ΔS_m calculated from the magnetization data for a field change of 0.6 T.

Using this equation the values of $\Delta S_m(T, H)$ were calculated numerically from the corresponding $M(H, T)$ magnetization data sets.

Fig. 1 shows the temperature dependencies of the magnetization for the as-quenched and heat treated samples measured in an applied field 800 A/m. The experimental curves show behavior expected for the single-phase amorphous ferromagnetic material except of $M(T)$ curve for Fe_{73.5}Cr₅Nb_{4.5}B₁₆Cu annealed at 723 K/1 hour, which shows the presence of small amount of nanocrystalline particles with higher Curie temperature. The decrease of $T_c(am)$ with increase of annealing temperature is clearly seen for all thermally relaxed amorphous samples. However, for Fe_{73.5}Cr₅Nb_{4.5}B₁₆Cu sample containing small amount of nanocrystalline particles, the value of $T_c(am)$ has increased. This feature can be connected either with a penetration of the exchange field caused by the nanocrystalites into residual matrix and/or with the enrichment of the residual amorphous phase by boron [5].

The magnetocaloric behaviour of the amorphous as-quenched and heat treated samples was studied by evaluating the magnetic entropy changes ΔS_m from the magnetization data. A special attention is focused on the temperature region, where the amorphous phase displays a transition from a ferromagnetic to a paramagnetic state. Fig. 2 shows a family of $M(H)$ curves for the sample Fe_{73.5}Cr₅Nb_{4.5}B₁₆Cu annealed at 573K. The ΔS_m values calculated by using relationship (1) are depicted in Fig. 3. For all samples, the magnetic entropy changes clearly show a peak at temperature close to $T_c(am)$. The largest magnetic entropy changes are observed for amorphous samples. The ΔS_m values are comparable to those reported recently for other multi-component Fe-rich amorphous ribbons [2-4]. The advantage of the

Fe₇₂Cr₈Nb₃B₁₆Cu alloys is a close proximity of its $T_c(am)$ to the room temperature. The nanocrystallization causes a decrease of the magnetic entropy change. Hence, the partially crystallized samples are less suitable for use in magnetic refrigeration [3].

In conclusion, the amorphous FeCrNbBCu-type alloys could be considered as potentially interesting magnetic refrigerants near room temperature. Among the attractive properties of these alloys are relatively low fabrication costs, easily controllable magnetic entropy change in the presence of relatively low magnetic fields and easily tuned Curie temperature. Moreover, the addition of Cr is known to increase the corrosion resistance of this kind of melt-spun alloys.

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