Grain-Size Effect on the Magneto caloric Properties of the DyCo$_3$B$_2$ Compound

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The compound DyCo$_3$B$_2$ has been recently found to show a significant magneto caloric effect (MCE) at the ferromagnetic ordering temperature $T_{C} = 22$ K. In the present study we verify the influence of the mechanical milling, i.e. the grains size effect on the characteristic parameters describing MCE. The grain size has been determined after each milling time by X-ray diffraction. MCE has been extracted from both the isothermal magnetization and the specific heat measurements. It is found that even a long milling does not spoil significantly the MCE parameters and only $t_{m} > 5$ h reduces noticeably the value of the magnetic susceptibility, the isothermal magnetic entropy change and the relative cooling power.

1. Introduction

DyCo$_3$B$_2$ belongs to the family of the intermetallic compounds represented by the general formula $R_{1+n}Co_{5+3n}B_{2n}$ (R = rare earth), where RCo$_3$B$_2$ corresponds to $n = \infty$. The crystallographic structure is hexagonal and the general formula originates from the boron substitution for Co in the RCo$_3$ compounds.

The R-R sublattice of DyCo$_3$B$_2$ orders ferromagnetically at $T_{C} = 22$ K and the magnetic moment on Co is absent for R = Y; however, a small antiparallel magnetic moment is induced at the presence of the rare earth ion. Around the ordering temperature of 22 K a significant magneto caloric effect (MCE) has recently been observed [1, 2]. A maximum isothermal magnetic entropy change $\Delta S_M = 17.5$ J kg$^{-1}$K$^{-1}$ and the adiabatic temperature change $\Delta T_{ad} = 14$ K at the magnetic field change of 9 T have been determined. From the point of view of the practical applicability the MCE materials are usually classified using the relative cooling power, RC$P_T$ and RC$P_S$ [3], which is a product of the maximum values and the full width at half maximum of the $\Delta T_{ad}(T)$ or $\Delta S_M(T)$ curves, respectively. It has been found for DyCo$_3$B$_2$ [1, 2] that RC$P$ is relatively large if compared with MCE materials of similar ordering temperature.

In the present studies we have investigated the influence of the mechanical milling on the structural, magnetic and thermodynamic properties of DyCo$_3$B$_2$, with special emphasis on the evolution of the MCE parameters, i.e. $\Delta S_M(T)$, $\Delta T_{ad}(K)$ and RC$P$, with the size of the grains. The grains size has been verified by the analysis of the X-ray diffraction patterns.

2. Experimental

The DyCo$_3$B$_2$ compounds were prepared by induction melting of the constituent elements under an argon atmosphere. The samples of different grains size were obtained by mechanical milling performed in a conventional horizontal ball mill rotated at a speed of 80 rev/min. Stainless steel vial and balls were used.

Measurements of the $M(H,T)$ curves were carried out on the commercial Quantum Design Physical Property Measurement System (PPMS) equipped with the vibrating sample magnetometer (VSM) option.

The heat capacity data were collected by the relaxation method (two-$\tau$ model) using the same PPMS apparatus in the temperature range 2-300 K and magnetic fields up to 9 T.

Full-pattern Rietveld refinements (program FULLPROF) of the X-ray diffraction measurements have confirmed the hexagonal structure, space group $P6/mmm$. The exemplary analysis is presented in Fig. 1.

![Fig. 1. X-ray pattern for milling time of 2 h fitted by FULLPROF (solid line). Bottom line: difference between the model and the experiment.](image_url)

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Grain-Size Effect on the Magneto-ocaloric Properties of the DyCo$_3$B$_2$...

Fig. 2. Zero-field cooled (ZFC) magnetic susceptibility. Inset: low temperatures range.

Fig. 3. The magnetic entropy change $-\Delta S_M$ and the adiabatic temperature change $\Delta T_{ad}$, determined from the heat capacity for magnetic field change of 5 T.

3. Results and discussion

The milling process has been carried out for up to $t_m = 25$ hours and the magnetic susceptibility has been measured to verify the changes in the magnetic properties. It is visible from Fig. 2 that the ordering temperature does not change noticeably, whereas the low temperature value of the susceptibility $\chi$ reduces only for $t_m > 5$ h. This behaviour is reversed for temperatures $T > T_C$, i.e. $\chi$ is increased for $t_m > 5$ h, showing also a deviation from the Curie-Weiss law, which may be due to the beginning of the amorphization or a composition modification of the grains surface.

Similar courses of the magneto-ocaloric effect have been determined both from the isothermal magnetization curves (not shown) and the specific heat measurements in various magnetic field values. Figure 3 shows the magnetic entropy change $-\Delta S_M$ and the adiabatic temperature change $\Delta T_{ad}$ for magnetic field change of 5 T. In spite of a long milling time the maximum of MCE drops rather weakly. The small sensitivity of MCE to the powdering is important if one considers the powdered form in future applications.

In Fig. 4 RCP$_S$ and RCP$_T$, corresponding to the $\Delta S_M(T)$ and $\Delta T_{ad}(T)$ curves, respectively, are plotted as a function of $t_m$ and the grain size. RCP$_S$ has been additionally extracted for $\Delta S_M(T)$, determined from the magnetization curves $M(H)$. It is seen from Fig. 4 that only reduction of the grain size by 50% starts to deteriorate significantly the RCP values.

Fig. 4. Relative cooling power RCP$_S$ and RCP$_T$ as a function of the grain size and the milling time.

4. Conclusions

It has been found that the studied compound is very resistant to the undertaken mechanical milling process and the characteristic parameters are stable even after long-lasting milling. For example, the magnetic entropy change $-\Delta S_M$ is reduced by 22% after 15 h milling, corresponding to the grain size reduction by 44%.

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References