Proceedings of the 15th Czech and Slovak Conference on Magnetism, Košice, Slovakia, June 17–21 2013

Grain-Size Effect on the Magnetocaloric Properties of the $DyCo_3B_2$ Compound

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The compound $DyCo_3B_2$ has been recently found to show a significant magnetocaloric 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.

DOI: 10.12693/APhysPolA.126.160

PACS: 71.20.Lp, 75.30.Sg, 75.40.Cx, 81.20.Ev

1. Introduction

$DyCo_3B_2$ 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_3B_2 corresponds to $n = \infty$. The crystallographic structure is hexagonal and the general formula originates from the boron substitution for Co in the RCo_5 compounds.

The R-R sublattice of $DyCo_3B_2$ 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 magnetocaloric 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, RCP_T and RCP_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 $DyCo_3B_2$ [1, 2] that RCP 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 $DyCo_3B_2$, with special emphasis on the evolution of the MCE parameters, i.e. $\Delta S_M(T)$, ΔT_{ad}(K) and RCP, with the size of the grains. The grains size has been verified by the analysis of the X-ray diffraction patterns.

2. Experimental

The $DyCo_3B_2$ 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-τ 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.

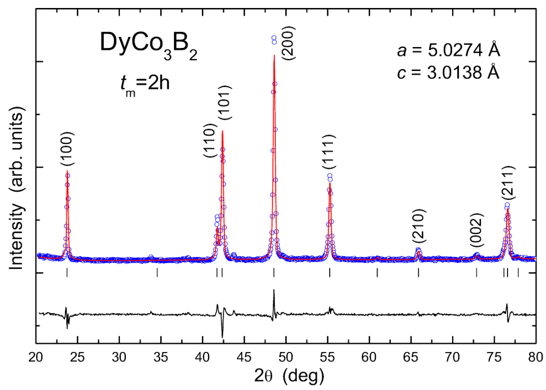

Fig. 1. X-ray pattern for milling time of 2 h fitted by FULLPROF (solid line). Bottom line: difference between the model and the experiment.

The grain size has been derived from the X-ray patterns using the standard Scherrer's formula $D = 0.89\lambda/B\cos\theta$, where D is the grain thickness, λ is the X-ray wavelength, B =FWHM, and θ is the Bragg angle.

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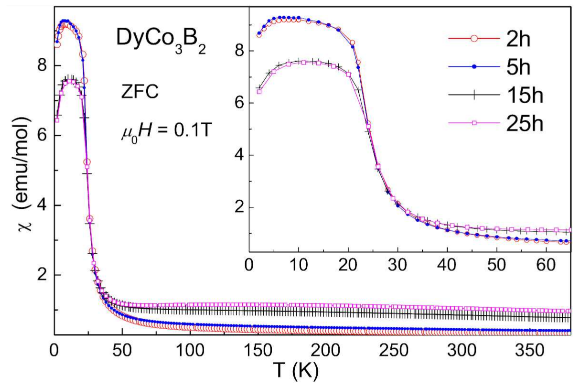

Fig. 2. Zero-field cooled (ZFC) magnetic susceptibility. Inset: low temperatures range.

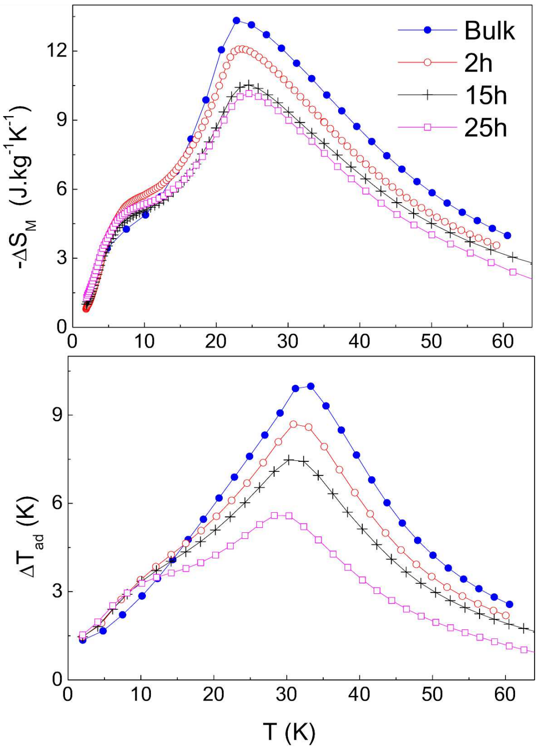

Fig. 3. The magnetic entropy change $-\Delta S_M$ and the adiabatic temperature change ΔT_{ad}, determined from the heat capacity for magnetic field change of 5 T.

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 χ reduces only for $t_m > 5$ h. This behaviour is reversed for temperatures $T > T_C$, i.e. χ 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 amorphisation or a composition modification of the grains surface.

Similar courses of the magnetocaloric 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 ΔT_{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.

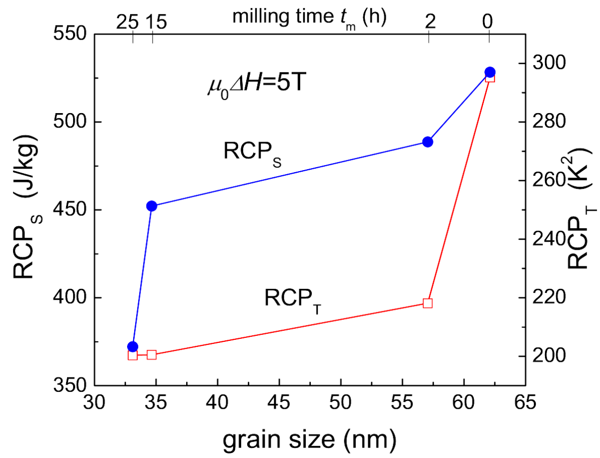

Fig. 4. Relative cooling power RCP_S and RCP_T as a function of the grain size and the milling time.

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 grains size reduction by 44%.

Acknowledgments

This work was supported by the funds of the National Science Centre as a research project no. N N507 219540 in years 2011-2013.

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