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Magnetocaloric Effect and Magnetic Phase Transitions in Nanocrystalline Rare-Earth Metals: Tb, Dy, and Gd

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Abstract—The magnetocaloric effect of rare-earth metals (REMs) Gd, Tb, and Dy in the nanostructured state is investigated. The ranges of working temperatures and cool capacity for materials based on nanocrystalline REMs are calculated from the experimental data. These results enable us to evaluate in detail the magnetic properties of REMs in a nanocrystalline state. It is shown that nanocrystalline Dy possesses the largest cool capacity, making this material most effective for magnetic cooling in the temperature range of 82–134 K.

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INTRODUCTION

The technology of magnetic cooling, which is based on the magnetocaloric effect (MCE), considerably improves power efficiency compared to usual refrigerating engineering, which is based on the compression and expansion of gases. The MCE manifests itself as reversible heat liberation or absorption, accompanied by variations in magnetic entropy (ΔS_M) with rapid (adiabatic) variations in the magnetic field [1–3]. To date, no investigations of the effect of crystallite size, which varies within limits of millimeters to tens of nanometers, on the magnetocaloric characteristics of rare-earth metals (REMs) have been performed.

There are three main parameters that characterize magnetocaloric materials: *RC*, the cool capacity (relative cooling power); $\Delta S_{M\max}$, the maximum variation in magnetic entropy; and ΔT, the adiabatic variation in temperature. *RC* shows the suitability of a material as a working body for magnetic refrigerators and is determined from the temperature dependences of ΔS_M as

$$RC = \int_{T_{\text{col}}}^{T_{\text{hot}}} \Delta S_M(T)\, dT. \quad (1)$$

Where $\delta T = T_{\text{hot}} - T_{\text{col}}$ is the width of the temperature range with the half-maximum of the magnitude of ΔS_M. An increase in ΔS_M and broadening of temperature range δT is required to optimize magnetocaloric materials. Magnetic materials with a narrow peak in the $\Delta S_M(T)$ curve are therefore not optimal magnetic cooling agents as a rule.

The aim of this work was to investigate the influence of rapid quenching on the magnetocaloric properties of and size of crystallites in Gd, Dy, and Tb, in which magnetic ordering upon cooling is observed [4, 5].

EXPERIMENTAL

Nanocrystalline Gd, Tb, and Dy samples were obtained by rapid quenching using initial metals with purities no lower than 99.9% and the technique validated in [6]. As a result of rapid quenching from a melt on a copper disc, our samples were obtained in the form of fragments of thin ribbons.

To confirm that the samples were of satisfactory quality, we performed an X-ray structural analysis on a DRON-3M diffractometer with FeK_α radiation that showed the samples contained no second phases. Their microstructure was observed on the surface of metallographic cross-sections using Axiovert 200MAT and Neophot-31 metallographic optical microscopes (Zeiss).

The character of the surface and the crystallite sizes were determined by atomic force microscopy (AFM) using a Solver P47 unit.

The MCE was determined directly from measurements of temperature variation with adiabatic magnetization in the temperature range of 78–310 K in magnetic fields of up to 12 kOe with absolute accuracies no worse than 10^{-3} K [7].

RESULTS AND DISCUSSION

Analysis of our X-ray diffraction patterns confirmed that rapidly quenched REMs have crystal lattices with space group $P6_3/mmc$. Results from our AFM studies (Fig. 1a) show that grains with linear sizes of up to 250 nm are formed after rapid quenching with no preferential orientation of the grains. Based on a static analysis of various segments of the surface, we constructed histograms (Fig. 1b) and determined the average grain size (table). It was found that all rapidly

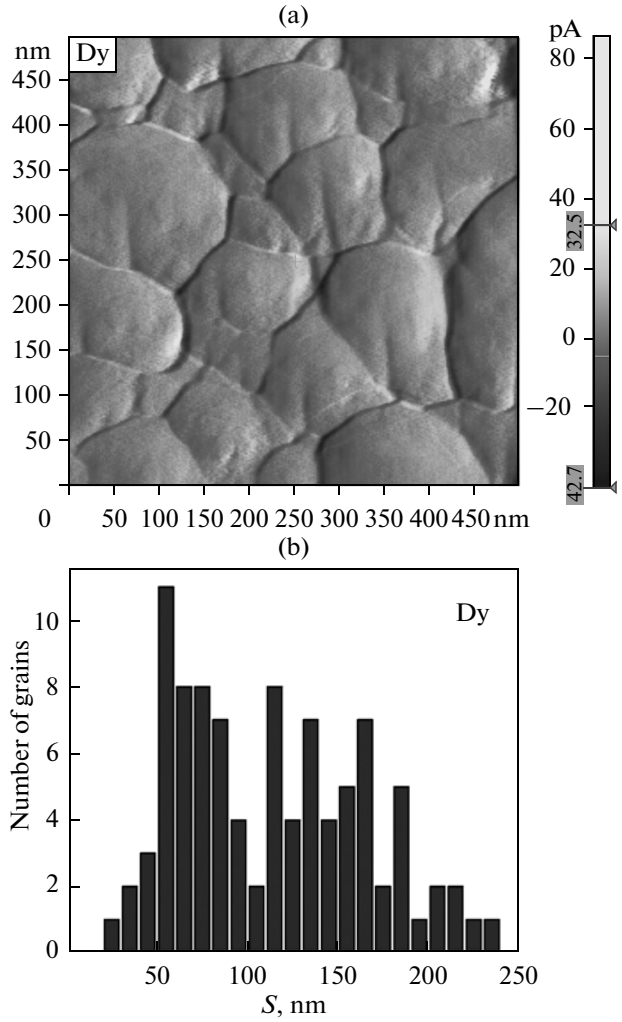

Fig. 1. (a) Structure of the surface of nanocrystalline dysprosium and (b) histogram of the grain size distribution (D) in nanocrystalline dysprosium.

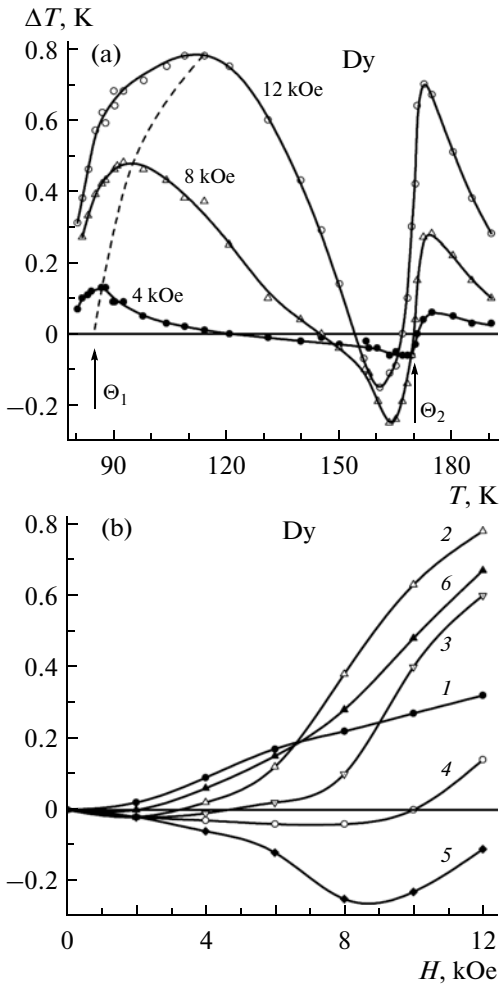

Fig. 2. (a) Temperature dependences of the MCE in fields of 4, 8, and 12 kOe; and (b) field dependences of the MCE for nanocrystalline dysprosium at temperatures of (*1*) 83, (*2*) 110, (*3*) 132, (*4*) 150, (*5*) 163, and (*6*) 175 K.

quenched REM ribbons had a nanodimensional structure.

Figure 2 shows temperature $\Delta T(T)$ and field $\Delta T(H)$ dependences of the MCE for nanocrystalline dysprosium. The broad maximum in the $\Delta T(T)$ curves in the range of 78–130 K corresponds to the ferromagnetism–antiferromagnetism phase transition and the maximum temperature and ΔT_{max} for an increased MCE as the field grew (Fig. 2a). The MCE isotherms in the phase transition region display an abrupt rise to magnitude $\Delta T_{max} = 0.8$ K (curves *1* and *2* in Fig. 2b). The phase transition temperature $\Theta_1 = 83.2$ K for

Parameters of the crystal lattices (a and c), unit cell volumes (V), average grain sizes (S), and MCE maxima (ΔT_{max}) in a field of 10 kOe and cool capacity (RC) in fields of 10 and 12 kOe for nanocrystalline rare-earth metals Gd, Dy, and Tb

Composition	a, nm	c, nm	V, nm^3	S, nm	T_{max}, K (10 kOe)	RC, J kg^{-1} K^{-1}	
						10 kOe	12 kOe
Gd	0.3634	0.5782	0.1981	105	1.98	44	–
Dy	0.3590	0.5648	0.1889	110	0.64	73	96
Tb	0.3601	0.5694	0.1916	108	1.46	37	49

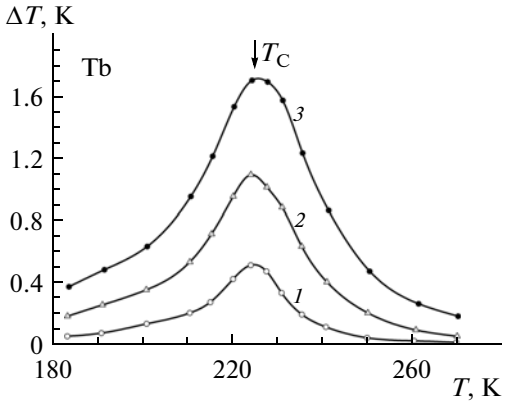

Fig. 3. Temperature dependences of the MCE for nanocrystalline terbium in magnetic fields of (*1*) 4, (*2*) 8, and (*3*) 12 kOe.

nanocrystalline Dy was determined from extrapolation using the formula $H = A\sqrt{t}$ (where $t = T/\Theta_1 - 1$ is the reduced temperature and $A = 17.23$ kOe) at $H \to 0$ (the dashed curve in Fig. 2a).

Curves *4* and *5* in Fig. 2b show that antiferromagnetic ordering induces a negative MCE ($\Delta T_{min} = -0.27$ K). As the magnetic field rises above the critical value (H_{cr}), an increase in the MCE is observed as a result of the destruction of the antiferromagnetic and the induction of ferromagnetic ordering. As the temperature grows, H_{cr} increases, tending to zero at the Néel temperature (Θ_2). The phase transition temperature at $H > 0$ corresponds to the point in dependence $\Delta T(T)$ at $\Delta T = 0$ and $d(\Delta T)/dT > 0$. Value $\Theta_2 = 171$ K is calculated from extrapolation to the zero field by formula $H = A\sqrt{t} + Bt$ (where $t = 1 - T/\Theta_2$ is the reduced temperature; $A = 112.2$ kOe; and $B = -237.5$ kOe). Figure 2b shows that the negative MCE is completely suppressed in the region of the order–disorder phase transition as the temperature rises, and second maximum $\Delta T = 0.74$ K is observed at 175 K. This maximum is caused by heat liberation during the destruction of the antiferromagnetic structure under the effect of a magnetic field exceeding H_{cr}.

It was shown that the temperatures of magnetic phase transitions fall in nanocrystalline but not polycrystalline dysprosium: the drop in the Néel temperature was 8 K, and the reduction in the temperature of the ferromagnetism–antiferromagnetism phase transition was ~2 K.

The MCE in nanocrystalline terbium (Fig. 3) reaches its largest value near the ordering temperature (T_C). The maximum MCE $\Delta T_{max} = 1.75$ K was attained in the field of 12 Oe at $T_C = 225$ K. In nanocrystalline Tb, the transition temperature fell by 5 K, relative to polycrystalline Tb.

In nanocrystalline gadolinium [7], as in Tb, the MCE abruptly increases as we approach the Curie temperature $T_C = 286$ K. The drop in T_C relative to polycrystalline Gd was 7 K.

The substantial decline in transition temperatures in nanocrystalline REMs could be due to an increase in the number of atoms on the surfaces of crystallites with a smaller number of neighboring sites in the nearest coordination spheres. An increase in the number of surface atoms would lower the exchange interaction energy and, as a consequence, reduce the energy of thermal vibrations of the crystal lattice needed to destroy the magnetic order.

From the temperature dependence of the MCE for nanocrystalline Dy, Gd, and Tb, we can assess the region of working temperatures δT for which ΔT declines by a factor of 2, compared to ΔT_{max}. The range of working temperatures is 81–140 K for Dy, 208–241 K for Tb, and 277–298 K for Gd. Using the thermodynamic relation

$$\Delta S_M = \frac{C_p}{T}\Delta T, \qquad (2)$$

where C_p is heat capacity [2, 5], we can estimate ΔS_M and *RC* using formula (1). Our values for ΔT_{max} and *RC* are presented in the table. Even though the MCE for nanocrystalline Tb and Gd exceeds the corresponding value for Dy by a factor of approximately 2, the appreciably wider working temperature range in which the greater MCE manifests itself for nanocrystalline Dy allows us to obtain material with notably higher cool capacity.

CONCLUSIONS

Nanocrystalline alloys of heavy rare-earth metals Gd, Dy, and Tb were obtained for the first time by rapid quenching from a melt. It was established that the nanostructured state substantially lowers the temperatures of the magnetic phase transition and reduces the maximum MCE in heavy REMs. The broadening of the temperature region in which large MCEs are observed in nanocrystalline REMs allows us to increase the range of working temperatures for a composite (polycrystalline and nanocrystalline) working body.

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