Magnetic Properties of Tb(Ni$_{1-x}$Fe$_x$)$_3$ ($x = 0.2$, 0.6) Crystalline Compounds and Powders

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In the paper we present and discuss magnetic properties of the Tb(Ni$_{1-x}$Fe$_x$)$_3$ ($x = 0.2$, 0.6) crystalline compounds and their ball-milled powders. The investigated samples are polycrystalline and crystallize in the rhombohedral PuNi$_3$ type of crystal structure. The Curie temperature of the material seems to be independent of particle size and is constant. The coercivity depends on the amount of iron dopant. The saturation magnetization decreases after mechanical grinding which is connected with the reduction in particle size. After 6 h milling time the SEM results show the presence of nanoflakes with thickness up to 100 nm or even smaller. Moreover, the pulverization leads to the observed decrease of magnetocaloric effect.

1. Introduction

Ball milling is an effective technique for production of mechanically alloyed materials and powder particles [1]. In recent years this technique has been widely applied to preparation of nanostructured hard magnetic powder, with very fine particle and grain size, based on rare earth and transition metal elements [2-6]. One of the previously studied series which was prepared in such a way is Gd(Ni$_{1-x}$Fe$_x$)$_3$ [3]. The mechanical grinding of the Gd(Ni$_{1-x}$Fe$_x$)$_3$ compounds causes an increase of the Curie temperature (T$_C$), a decrease of the saturation magnetization (M$_S$) and a decrease of the magnetic entropy (ΔS_m) on average by about 50%. The observed changes were explained by the appearance of structural disorder and the demagnetization factor. It is worth to analyze the influence of the milling time and the amount of iron doping on the magnetic properties of chosen compounds. It is useful in determining the best application parameters and designing the nanoscale magnetic materials.

The aim of presented work was to study magnetic properties and magnetocaloric effect in Tb(Ni$_{1-x}$Fe$_x$)$_3$ ($x = 0.2$, 0.6) compounds, in bulk crystalline and ball-milled powder form.

2. Experimental

The polycrystalline Tb(Ni$_{1-x}$Fe$_x$)$_3$ ($x = 0.2$, 0.6) compounds were prepared by arc melting of the high purity elements 99.9 wt.% under argon atmosphere. To ensure homogeneity the samples were remelted several times. The melted samples were then wrapped in tantalum foil, placed in quartz tubes and annealed at temperature of 1173 K for 8 days. The samples were milled for 6 h at frequency of 30 Hz using Mixer Mill MM 400 (Retsch). The milling was carried out in dimethylformamide for 6 h employing zirconia balls of 0.5 mm diameter and weight ratio of 10:1. The samples were characterized

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before and after mechanical grinding by X-ray powder diffraction (SIEMENS D5000 diffractometer using Cu K$_\alpha$ radiation, $\lambda = 1.541$ Å). The morphology and size of the obtained particles were examined using Laser Scattering Particle Size Distribution Analyzer LA−950 and JEOL−JSM 6480 scanning electron microscope (SEM). Magnetization measurements were performed using a superconducting quantum interference device (MPMS XL7 Quantum Design) magnetometer in the temperature range $2 \div 400$ K and applied magnetic field up to 7 T.

3. Results

The ball-milled samples of Tb(Ni$_{1-x}$Fe$_x$)$_3$ ($x = 0.2$, 0.6) were analysed using XRD before and after 6 h milling time (see Fig. 1).
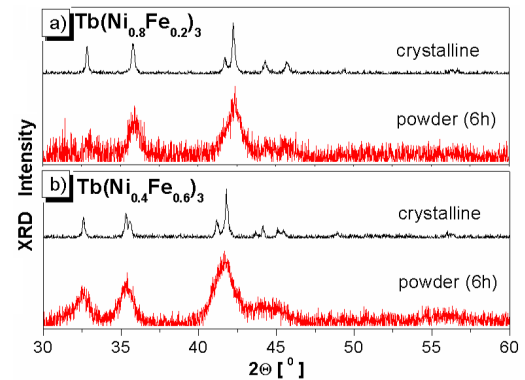

Fig. 1. XRD pattern at 300 K for the Tb(Ni$_{1-x}$Fe$_x$)$_3$ crystalline compound and powders after 6 h milling time: (a) for $x = 0.2$, (b) for $x = 0.6$.

The XRD pattern reveals that both compounds are single phase with the rhombohedral PuNi$_3$-type crystal structure (space group *R-3m*). After 6 h of milling this structure is still visible but broadening of the diffraction peaks is observed. It may be ascribed to crystallite size reduction as it was reported for many other intermetallics [2, 4–6]. After 6 h of milling the average particle size was estimated as 3.0 μm ($x = 0.2$) and 1.7 μm ($x = 0.6$). However, both samples indicate a

quite large shape anisotropy, confirmed by SEM measurements. Representative SEM image obtained after 6 h mechanical grinding shows the presence of nanoflakes with thickness of up to 100 nm or even smaller (see Fig. 2).
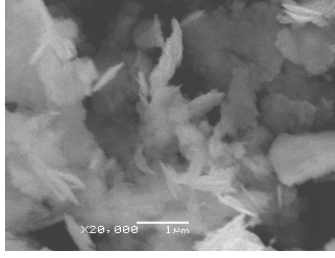

Fig. 2.   SEM micrographs of the Tb(Nie$_{0.8}$Fe$_{0.2}$)$_3$ particles after mechanical grinding for 6 h.

Figure 3 presents the magnetic hysteresis loops measured at 2 K for the Tb(Ni$_{1-x}$Fe$_x$)$_3$ (x = 0.2, 0.6) samples before and after 6 h milling time. The dependence of the saturation magnetization (estimated after extrapolation to the infinite field) M_S versus x may suggest the ferrimagnetic arrangement of Tb(4f) as well as T(3d) magnetic moments for all studied samples. The magnetic properties exhibit quite different behaviour for $x = 0.2$ and 0.6 in the bulk and ball-milled form. After 6 h milling time the M_S values are lower than in the case of crystalline compounds (see Table I). However for $x = 0.6$ the decrease of the M_S value is nearly two times larger. Moreover, after 6 h milling time the decrease in coercivity (H_C) is observed, whereas for $x = 0.2$ the value of H_C increases.

TABLE I

Magnetic parameters for the Tb(Ni$_{1-x}$Fe$_x$)$_3$ (x = 0.2, 0.6) system obtained from magnetic measurements.

x	T_C (K)	M_s (μ_B/f.u.)	H_C (T) at 2 K	M_R (μ_B/f.u.) at 2 K	$-\Delta S_M$ (J/kg/K) at 1 T
0.2	325	4.88	0.25	3.25	0.24
0.2 (6 h)	325	4.37	0.66	2.03	0.08
0.6	–	4.21	0.58	3.81	–
0.6 (6 h)	–	2.46	0.40	0.77	–

Additionally, for $x = 0.2$ the value of the magnetic entropy $|\Delta S_m|$ was calculated from a family of magnetic isotherms, measured at different temperatures from 2 to 300 K. The maximum of $|\Delta S_m|$ in $\mu_0 \Delta H = 1$ T, occurring at T_C, decreases from 0.24 to 0.08 J/kg/K (for the bulk samples and samples after 6 h milling, respectively). The observed variation of the magnetic parameters can be explained, taking into account the reduction of grain size and simultaneous significant increase of the surface contribution [5]. The increase in H_C value is related to the decrease in of the grain size. It is well known that H_C exhibits an increase up to the certain particle size reduction (poly domain structure), and then with further reduction of the particle size it exhibits a decrease (thermally blocked domains or single domain structure) [7].
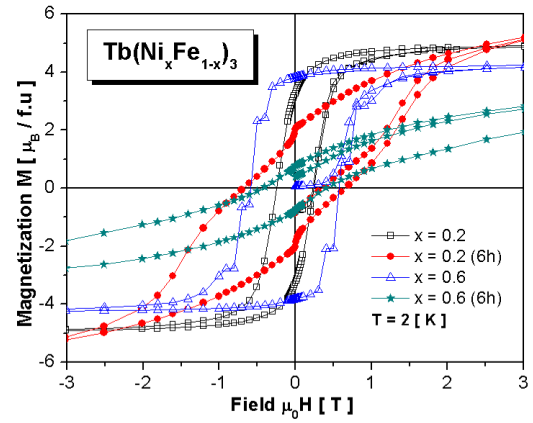

Fig. 3.   Hysteresis loops at 2 K for the Tb(Ni$_{1-x}$Fe$_x$)$_3$ (x = 0.2, 0.6) crystalline compound and powders after 6 h milling time.

For $x = 0.6$, smaller particles have been obtained and than a lower H$_C$ has been derived. In addition, a visible impact of iron content on the magnetic properties may be noticed. Probably such a behaviour may be related with the change within $4f - 3d$ interactions and their connection with the change of the 3d-electrons number.

4. Conclusions

The compounds Tb(Ni$_{1-x}$Fe$_x$)$_3$ (x = 0.2, 0.6) crystallize in the PuNi$_3$ rhombohedral type of crystal structure. The analysis of XRD for ball-milled powders shows broadening of the observed peaks, related to the reduction of the crystallites size. The T_C value does not depend on the sample form and on the milling time. Moreover, with the increasing pulverization degree, the magnetic hardening and the decrease of magnetocaloric effect were also observed.

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