



Hydrogenation effect on the hysteresis properties of rapidly quenched Nd–Ho–Fe–Co–B alloys

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ABSTRACT

The hydrogenation effect on the hysteresis properties of rapidly quenched (RQ) $(\text{Nd}_{0.55}\text{Ho}_{0.45})_{2.7}(\text{Fe}_{0.8}\text{Co}_{0.2})_{14}\text{B}_{1.2}$ compound obtained by melt-spinning is studied. A comparative study of RQ alloy and its hydride $(\text{Nd}_{0.55}\text{Ho}_{0.45})_{2.7}(\text{Fe}_{0.8}\text{Co}_{0.2})_{14}\text{B}_{1.2}\text{H}_{2.5}$ has shown that hydrogenation resulted in the increase of magnetization without significant effect on the Curie temperature. In contrast to hydrogen-free alloy having a maximum on the $H_c(T)$ curve, the H_c of the hydrogen-charged compound increased monotonously with decreasing temperature. Among the factors affecting H_c in hydrogenated sample are the increase of the grain size of the crystalline phase and the decrease of both the iron and the rare earth contributions to the magnetocrystalline anisotropy. High-field hysteretic distortions of the magnetization/demagnetization curves of RQ and RQ + hydrogen samples are observed at 4.2 K in fields up to 90 kOe indicating the existence of a magnetic phase with very high local coercivity.

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1. Introduction

Most of the high-performance permanent magnet materials based on rare-earth intermetallic compounds absorb large amounts of hydrogen readily and form stable hydrides at room temperature [1,2]. The changes in magnetic properties occurring due to hydrogen absorption are of great fundamental and practical interest. In particular, in $\text{R}_2\text{Fe}_{14}\text{B}$ compounds hydrogenation increases the iron sublattice magnetization and Curie temperature; at the same time, hydrogenation has the effect of reducing and modifying the anisotropy of both the Fe and the rare earth sublattice anisotropy resulting in variations of the spin reorientation transition temperatures (SRT) [3–8].

In spite of extensive studies of hydrogenation effects in R–Fe–B, little is known on how hydrogen absorption affects hysteresis properties important for permanent magnet applications. The present work is devoted to the study of magnetic properties of a high coercive rapidly quenched $(\text{Nd}_{0.55}\text{Ho}_{0.45})_{2.7}(\text{Fe}_{0.8}\text{Co}_{0.2})_{14}\text{B}_{1.2}$ alloy and

its hydride. The motivation for the choice of this composition is that a partial Co substitution for Fe in the 3d-sublattice and Ho for Nd in the rare-earth (RE) sublattice of $\text{Nd}_2\text{Fe}_{14}\text{B}$ for attainment of a material with a very low (0.01–0.05%/K) temperature coefficient of remanence in the –50 to +100 °C temperature range [9]. In addition, high coercive flakes suitable for the production of bonded magnets may be prepared by melt-spinning of this alloy.

The aim of the present work was to investigate the influence of hydrogen content on the hysteresis properties of rapidly quenched $(\text{Nd}_{0.55}\text{Ho}_{0.45})_{2.7}(\text{Fe}_{0.8}\text{Co}_{0.2})_{14}\text{B}_{1.2}$ and its hydride both at high and at low temperatures where the change of magnetic anisotropy type due to SRT is expected.

2. Experimental

The starting alloy was melted in the induction furnace using fused quartz crucibles. The ingot pieces were then re-melted in quartz ampoules with an orifice and subjected to centrifugal melt spinning on a chilling iron wheel with a surface speed of V_s of 15–30 m/s. The resulting ribbon fragments (flakes) were ~10 to 20 mm long, 2–5 mm wide, and 0.03 mm thick. A structural analysis was performed by X-ray diffraction (Cu K α radiation, DRON-3 diffractometer) and by the scanning electron microscopy (SEM) using LEO 430i and QUANTA-200 microscopes. The interaction with hydrogen was studied under the pressure of up to 13 atm. To initiate the reaction, the sample was preheated to 250 °C. No incubation period was required to start the hydrogenation process which resulted in the formation of $(\text{Nd}_{0.55}\text{Ho}_{0.45})_{2.7}(\text{Fe}_{0.8}\text{Co}_{0.2})_{14}\text{B}_{1.2}\text{H}_{2.5}$ hydride at the end of reaction. The com-

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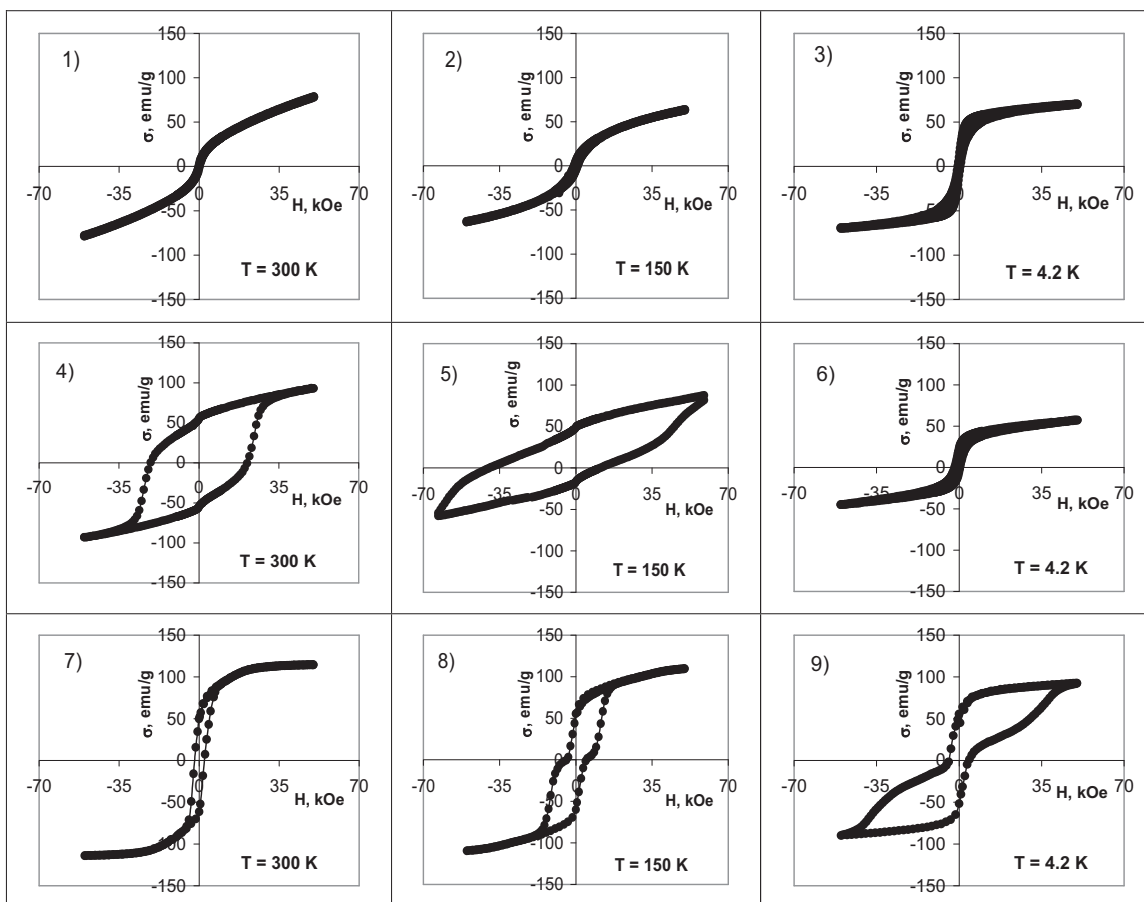


Fig. 1. Hysteresis loops of the initial as-cast $(\text{Nd}_{0.55}\text{Ho}_{0.45})_{2.7}(\text{Fe}_{0.8}\text{Co}_{0.2})_{14}\text{B}_{1.2}$ (1–3), RQ $(\text{Nd}_{0.55}\text{Ho}_{0.45})_{2.7}(\text{Fe}_{0.8}\text{Co}_{0.2})_{14}\text{B}_{1.2}$ obtained at $V_q = 15$ m/s (4–6) and the RQ hydride $(\text{Nd}_{0.55}\text{Ho}_{0.45})_{2.7}(\text{Fe}_{0.8}\text{Co}_{0.2})_{14}\text{B}_{1.2}\text{H}_{2.5}$ (7–9) at various temperatures and fields up to 55 kOe.

position of the hydride phase was determined volumetrically making use of the high pressure hydrogen state equation based on the experimental data on hydrogen compressibility and theoretical p – V – T expressions [10,11] ensuring an accuracy of 0.1–0.5%.

The maximum amount of hydrogen that can be absorbed by these compounds is 5 H atoms/f.u. [8]. In our studies we limited the hydrogen uptake by a value of 2.5 H atoms/f.u. With this provision the hydrided flakes retained their shape and were not disintegrated. The formation of the single-phase hydride was checked by the standard X-ray diffractograms. Segregation of α -Fe was not observed.

Magnetic measurements in the 4.2–550 K temperature range were performed using Quantum Design SQUID and PPMS magnetometers in magnetic fields up to 55 and 90 kOe, respectively. The hydrogenated samples with dimensions of ~ 4 mm \times 1 mm \times 0.03 mm were fixed in the sample holder and measured along the largest side.

3. Results and discussion

The X-ray diffraction and SEM analysis of rapidly quenched $(\text{Nd}_{0.55}\text{Ho}_{0.45})_{2.7}(\text{Fe}_{0.8}\text{Co}_{0.2})_{14}\text{B}_{1.2}$ have shown that the samples contain grains of the crystalline 2-14-1 phase of different size (hard magnetic phase) and the amorphous phase (soft magnetic) [9]. In the ribbon core the main 2-14-1 phase (an average grain size of about 30–40 nm) is separated by very thin layers of a rare-earth-rich nonmagnetic phase of undetermined composition. The ribbon surface layer being in contact with the chilling wheel is characterized by a very fine nearly amorphous nanostructure, while relatively coarse grains of the 2-14-1 phase are observed at the opposite (so-called “free”) side of the ribbon.

As distinct from the core both of these layers possess low coercivity. Accordingly the demagnetization curves exhibit typical

flexures in the 2nd and 4th quadrants of the low field regions of the hysteresis loop. At room temperature the coercive field maximum corresponds to the sample quenched at $V_q = 15$ m/s.

The structure of the $(\text{Nd}_{0.55}\text{Ho}_{0.45})_{2.7}(\text{Fe}_{0.8}\text{Co}_{0.2})_{14}\text{B}_{1.2}\text{H}_{2.5}$ hydride was also investigated by X-ray diffraction and SEM. Hydrogenation was found to increase the average grain size of the 2-14-1 phase (by 2.5–3 times), probably due to sample heating during the hydrogen treatment. However, the ratio between the crystalline and amorphous phases and the sample micromorphology were not changed significantly.

The comparative investigation of the magnetic properties of the as-cast (coarse-grained) $(\text{Nd}_{0.55}\text{Ho}_{0.45})_{2.7}(\text{Fe}_{0.8}\text{Co}_{0.2})_{14}\text{B}_{1.2}$, rapidly quenched (RQ) samples and their hydrides $(\text{Nd}_{0.55}\text{Ho}_{0.45})_{2.7}(\text{Fe}_{0.8}\text{Co}_{0.2})_{14}\text{B}_{1.2}\text{H}_{2.5}$ was performed at various temperatures (Fig. 1). In the unprocessed initial alloy, the coercive field is near to zero at all temperatures studied (Fig. 1, curves 1–3). On the contrary for the RQ sample, a high coercive field ($H_c = 20$ kOe) is obtained at room temperature (curve 4). Lowering the temperature results in a strong distortion of the hysteresis loop shape accompanied by a large decrease of the coercive field (Fig. 1, curves 5 and 6 for 150 and 4.2 K, respectively). Fig. 2 (curve 1) demonstrates the temperature dependence of the coercive field $H_c(T)$ for the RQ sample in more detail. It is seen that the initial increase of the coercive force with decreasing temperature is changed by a rapid fall at temperatures below 100 K.

Hydrogenation of the RQ sample resulted in the coercive field decrease in the whole temperature interval studied. At the same time the maximal magnetization values in high fields are significantly augmented (Fig. 1, curves 7–9), although the Curie

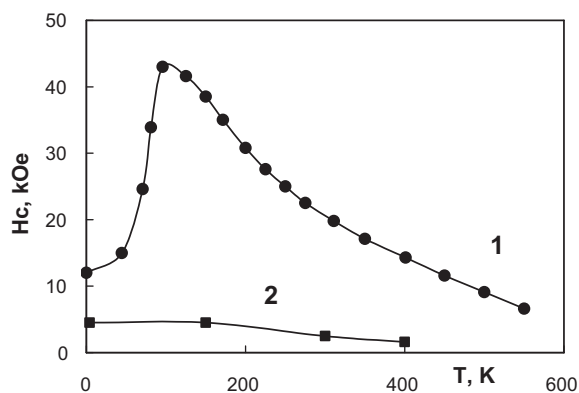


Fig. 2. Temperature dependence of the coercive field of $(\text{Nd}_{0.55}\text{Ho}_{0.45})_{2.7}(\text{Fe}_{0.8}\text{Co}_{0.2})_{14}\text{B}_{1.2}$ alloy (1) and its hydride $(\text{Nd}_{0.55}\text{Ho}_{0.45})_{2.7}(\text{Fe}_{0.8}\text{Co}_{0.2})_{14}\text{B}_{1.2}\text{H}_{2.5}$ (2).

temperature remains almost unchanged (similar behavior was previously observed in Ref. [12]).

At room temperature the demagnetization curve of the hydrogenated RQ sample (Fig. 1, curve 7) exhibits behavior typical of a single-phase material, while at lower temperatures hysteresis loop flexures arrive serving as an indicator of magnetic non-uniformity of the material (curves 8 and 9 for 150 and 4.2 K) (the latter point needs some more discussion.) Shown in Fig. 3 are the hysteresis loops of the RQ samples measured at 4.2 K before and after hydrogenation in higher (up to 90 kOe) fields, because it was evident from Fig. 1 (curves 5 and 6) that 55 kOe are insufficient for full magnetization. A remarkable feature of the hysteresis loop of the RQ sample presented by the curve 1 in Fig. 3 is that even in fields as large as 90 kOe the magnetization reversal process is still of hysteretic character, i.e. there is no univocal correspondence between the values of external magnetic field and magnetization.

An even more striking feature of this sample is its dependence on the measurement procedure. Shown in Fig. 4 are the hysteresis loops of the RQ sample measured at 300 (curve 1) and 4.2 K after zero-field cooling (ZFC) (curve 2) and cooling under the action of the external field (FC) (curve 3). It is seen that FC results in an extraordinary large vertical shift of the hysteresis loop. This means that at room temperature the field of 55 kOe was sufficient to saturate the sample, i.e. the coercivity was low enough to be surmounted in all parts of the sample, while at 4.2 K a considerable volume of the sample acquired local coercivities larger than the maximum available applied field.

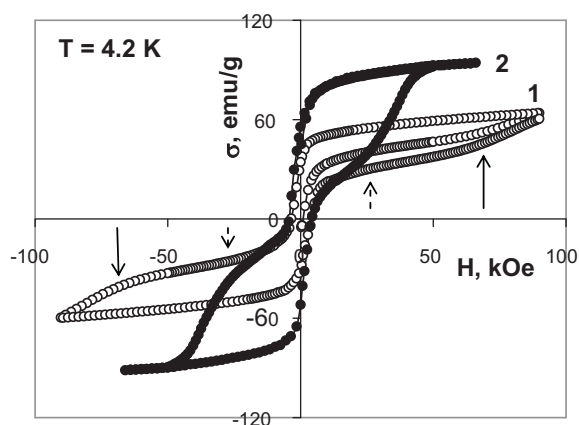


Fig. 3. Hysteresis loops of RQ $(\text{Nd}_{0.55}\text{Ho}_{0.45})_{2.7}(\text{Fe}_{0.8}\text{Co}_{0.2})_{14}\text{B}_{1.2}$ (1) and its hydride (2) measured at $T = 4.2$ K in magnetic fields of ± 90 kOe.

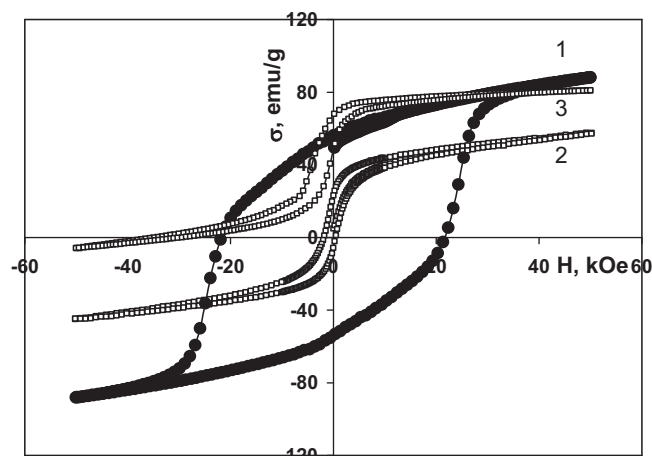


Fig. 4. Hysteresis loops of ZFC (2) and FC (3) RQ $(\text{Nd}_{0.55}\text{Ho}_{0.45})_{2.7}(\text{Fe}_{0.8}\text{Co}_{0.2})_{14}\text{B}_{1.2}$ at 4.2 K and at 300 K (1) in magnetic fields of ± 55 kOe.

Interpretation of the temperature dependence of coercivity of these materials is inevitably connected with the fact that $\text{R}_2\text{Fe}_{14}\text{B}$ ($\text{R} = \text{Nd}, \text{Ho}$) compounds undergo the spin-reorientation transition (SRT) at low temperatures ($T_{\text{SRT}} = 135$ K for $\text{Nd}_2\text{Fe}_{14}\text{B}$ and 58 K for $\text{Ho}_2\text{Fe}_{14}\text{B}$ [8]). In the quasibinary $(\text{Nd}_{0.55}\text{Ho}_{0.45})_{2.7}(\text{Fe}_{0.8}\text{Co}_{0.2})_{14}\text{B}_{1.2}$ the SRT also exists ($T_{\text{SRT}} \approx 120$ K), as determined from ac-susceptibility $\chi(T)$ measurement and from the temperature dependence of the residual specific magnetization $\sigma_{\text{R}}(T)$ [9].

The experimental results on the temperature dependence of the coercive field of hydrogenated compound are in qualitative agreement with the fact that the magnetocrystalline anisotropy energy of the 2-14-1 phase decreases due to the effect of hydrogen atoms insertion into the lattice [13,14]. This circumstance was also confirmed in our study of the $\text{Y}_2(\text{Fe},\text{Co})_{14}\text{B}$ hydrides with Y as a nonmagnetic analog of rare earth element [15].

Although at 4.2 K both the RQ and the RQ+hydrogen samples are characterized by relatively low (4–12 kOe) coercive fields (as measured in the 2nd and 4th quadrant), the specific widening of the hysteresis loops in the 1st and 3rd quadrant are indicative of the existence of regions with very high local coercivities values in the material under study.

4. Conclusion

Comparative study of the structure and magnetic hysteresis properties of rapidly quenched Nd–Ho–Fe–Co–B alloys with and without hydrogen was performed. Hydrogenation of the RQ melt-spun samples was found to increase the magnetization without significant effect on the Curie temperature. In contrast to hydrogen-free alloys having a maximum on the $H_c(T)$ curve, the coercive force of the hydrogen-charged compounds with $H = 2.5$ at./f.u. increases monotonously with decreasing temperature. Among the factors affecting the coercive force are an increase of the grain size (decreasing intergrain exchange interaction) of the crystalline phase of hydrogenated samples and decrease of both the iron and the rare earth contributions to the magnetocrystalline anisotropy. Unexpected high-field hysteretic distortions of the magnetization/demagnetization curves are observed at 4.2 K indicating the existence of magnetic phase with very a high local coercivity and spin reorientation transition [9].

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