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ADVANCED MATERIALS AND TECHNOLOGIES

Phase Composition and Magnetic Properties of $Nd_2Fe_{14}B/\alpha$-Fe Nanocomposites Prepared by Mechanical Alloying

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Abstract—Combined studies of hard magnetic $Nd_2Fe_{14}B/\alpha$-Fe nanocomposites are performed. They were prepared by mechanical alloying of melt-quenched $Nd_{7.4}Pr_{2.0}Fe_{76.6}Co_{4.2}Zr_{3.4}B_{6.4}$ and $Nd_{5.8}Fe_{80}Co_{4.9}Ti_{1.5}Si_{2.5}B_{5.3}$ alloys taken in mass proportions of 90/10 and 70/30. It is found that, after mechanical alloying, an amorphous–crystalline structure is formed; it consists of the hard magnetic $Nd_2Fe_{14}B$ and soft magnetic (amorphous and α-Fe) phases. Subsequent annealing at ~500°C initiates the decomposition of the amorphous phase and the formation of the nanocrystalline $Nd_2Fe_{14}B$ and α-Fe phases. This leads to an increase in the coercivity and the residual magnetization-to-saturation magnetization ratio ($\sigma_r/\sigma_s \geq 0.5$). It is assumed that the magnetic hardening of powders is due to the formation of an exchange-coupled state, which results from the exchange interaction between α-Fe nanocrystals and the $Nd_2Fe_{14}B$ phase.

Keywords: magnetic $Nd_2Fe_{14}B/\alpha$-Fe nanocomposites, mechanical alloying, phase composition, magnetic properties, exchange-coupled state

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INTRODUCTION

Hard magnetic $Nd_2Fe_{14}B/\alpha$-Fe nanocomposites are of ever-growing interest of investigators because of the potentiality of reaching high maximum magnetic product $(BH)_{max}$. This is due to the exchange interaction of the magnetic moments of the soft magnetic nanocrystalline (α-Fe) and the hard magnetic ($Nd_2Fe_{14}B$) phases, which results in the alignment of the moments of the soft-magnetic phase along the averaged magnetic moment of adjacent hard-magnetic phase grains [1, 2]. The initiation of such an interaction is possible when the grain sizes of the $Nd_2Fe_{14}B/\alpha$-Fe phases are 20–50 [3, 4] and 10 nm [4], respectively.

The main magnetization-reversal mechanism of Nd–Fe–B alloys with a nanocrystalline structure is the uniform (or nonuniform) magnetization rotation of grains, the sizes of which are from 10 nm to the critical single-domain size [5]. As a result of uniform magnetization rotation of nanosized grains, the residual magnetization of the exchange-coupled composite increases and becomes higher than the limit $M_r = 0.5M_s$ [6] predicted in accordance with the Stoner–Wohlfarth theory.

However, according to experimental data, the realization of the potential of hard magnetic composites in practice is limited by difficulties in forming a nanocomposite state [7–9]. Mechanical alloying [10–12] is among the most promising methods used for the preparation of $Nd_2Fe_{14}B/\alpha$-Fe nanocomposites. This method also allows one to increase the coercivity of prepared composites [13]. It is of interest to determine the optimum structural and phase states of the $Nd_2Fe_{14}B/\alpha$-Fe nanocomposite prepared by mechanical alloying, which determines high magnetic properties of the material.

EXPERIMENTAL

The powder compositions consisting of the $Nd_{7.4}Pr_{2.0}Fe_{76.6}Co_{4.2}Zr_{3.4}B_{6.4}$ (RQ1) and $Nd_{5.8}Fe_{80}Co_{4.9}Ti_{1.5}Si_{2.5}B_{5.3}$ (RQ2) alloys were taken in mass proportions of 90/10 and 70/30 and subjected to mechanical alloying. The alloys were prepared by melt-quenching using a copper wheel 200 mm in diameter and a rotation speed of 1800 rpm. Ribbon samples were crushed by hand using an agate mortar to prepare powders 1 mm in particle size. The powder mixtures were subjected to mechanical alloying in a helium atmosphere for 3 h in a Retsch PM400 planetary ball mill. To prevent the aggregation of powder particles, a surface-active agent (0.05 mL oleic acid)

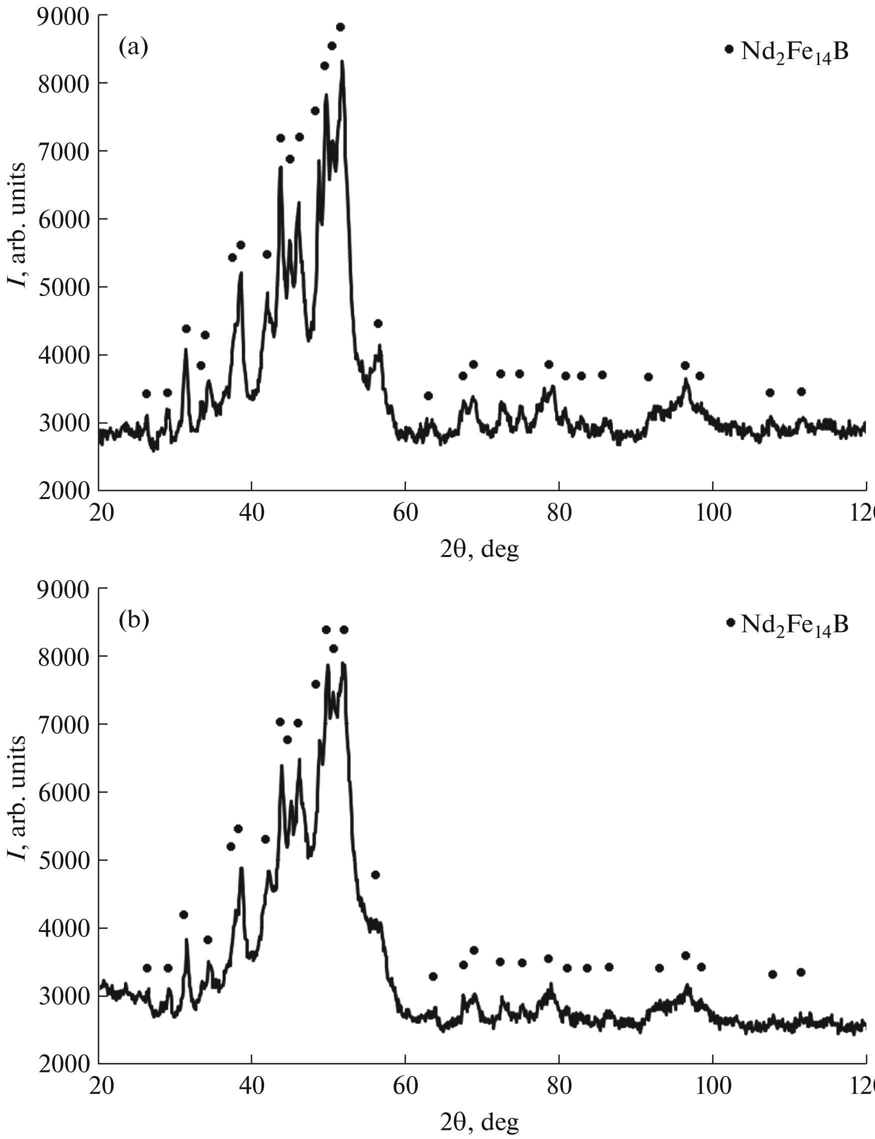

Fig. 1. X-ray diffraction patterns of the nanocomposite powders mechanically alloyed with (a) 10 and (b) 30% RQ2 alloy.

was introduced into each vial. The charge and discharge of powders from vials were performed in an argon atmosphere. The powder-to-milling ball mass ratio was 1 : 10, and the mass of material loaded in each of milling vials was 30 g. After mechanical alloying, the powders were subjected to annealing in an argon atmosphere at 480–650°C for 20 min.

X-ray diffraction (XRD) analysis was performed in a 2θ angle range of 20°–120° using a DRON-4 diffractometer, a graphite monochromator, and Co*K*α radiation (λ = 1.07921 Å). Quantitative phase analysis was performed by the Rietveld method with the Phan% software [14]. The sensitivity of the phase analysis was 1 vol % and the statistical error of determining the phase content was no more than 2%. The phase analysis of alloys with the mixed amorphous–crystalline structure was performed using the procedure described in [15]. The magnetic properties of the samples were measured at room temperature in a magnetizing field up to 2 T (1600 kA/m) on a VSM-250 vibrating-sample magnetometer.

RESULTS AND DISCUSSION

According to XRD data, the composite powders subjected to mechanical alloying have an amorphous–crystalline structure. XRD patterns exhibit well-resolved reflections of the hard magnetic $Nd_2Fe_{14}B$ phase, which are observed above the background of an amorphous halo (Fig. 1). The fraction of amorphous phase in the powders prepared with 10 and 30% RQ2 alloy is about 25 and 40 vol %, respectively.

The magnetic properties of the mechanically alloyed powders are low. The magnetization coercivity

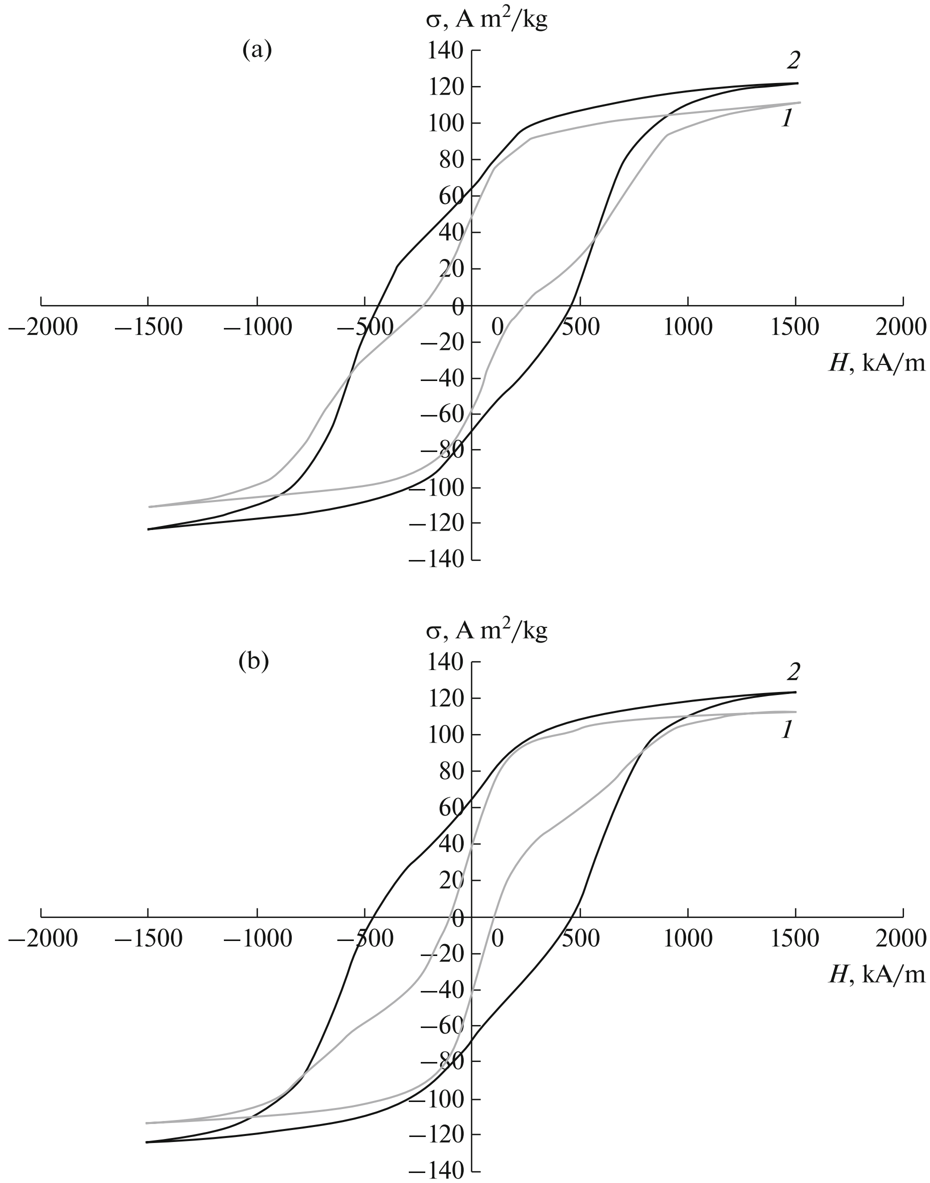

Fig. 2. Magnetic hysteresis loops for the nanocomposite powders prepared with (a) 10 and (b) 30% RQ2 alloy: (*1*) after mechanical alloying and (*2*) after mechanical alloying and annealing at 500°C for 20 min.

for the powders prepared with 10 and 30% RQ2 alloy (H_{ci}) is 226 and 99 kA/m, respectively; the specific magnetization (σ_r) is 53 and 41 A m^2/kg; and the magnetization in a field of 2 T is 111 and 114 A m^2/kg, respectively. The presence of a soft magnetic amorphous phase determines the kink on the hysteresis loops (Fig. 2) and nonmonotonic change of magnetization in low remagnetization fields, which is typical for magnetic multiphase materials [16].

Subsequent annealing of the powders at 480–650°C for 20 min leads to the decomposition of the amorphous phase and an increase in the volume fraction of the hard magnetic ($Nd_2Fe_{14}B$) and soft magnetic (α-Fe) phases. Moreover, a small amount of the Nd_2O_3 oxide (of no more than 5 vol %) appears. In particular, after annealing at 500°C, the content of the hard and soft magnetic phases in the compositions with 10% RQ2 alloy is 57 and 40 vol %, respectively; in the case of 30% RQ2 alloy, their content is 54 and 42 vol %, respectively. After annealing, the coercivity H_{ci} of the compositions increases to 436 and 443 kA/m, respectively; the ratios σ_r/σ_{2T} for the compositions with 10 and 30 vol % RQ2 alloy are almost similar, i.e., they are 0.53 and 0.52, respectively (for the initial RQ1 and RQ2 alloys, the ratio is 0.48 and 0.36, respectively). In this case, the shape of hysteresis loops substantially changes and they become typical

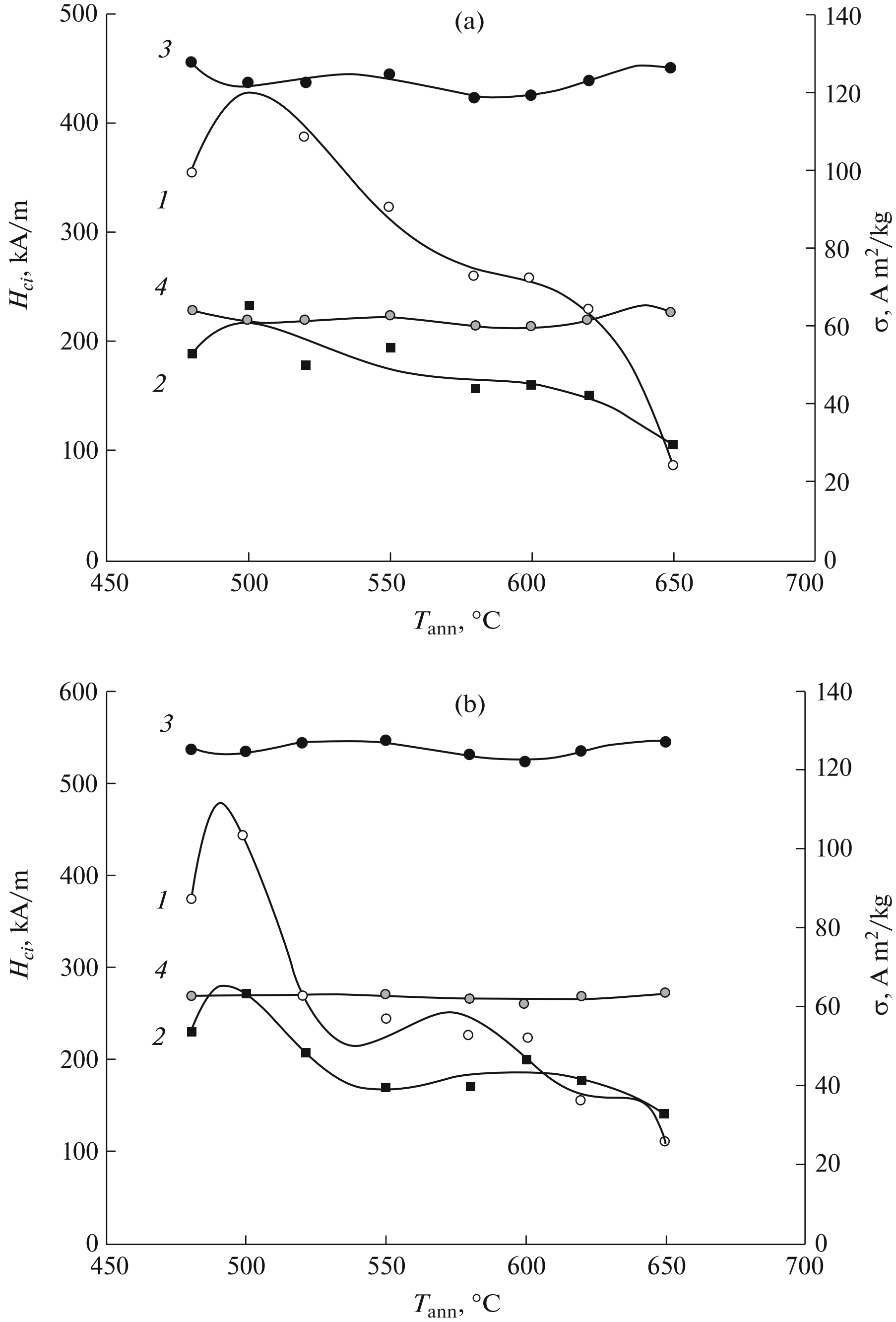

Fig. 3. Magnetic properties of the mechanically alloyed powders with (a) 10 and (b) 30% RQ2 alloy vs. the annealing temperature: (*1*) coercivity H_{ci}, (*2*) remanence σ_r, (*3*) magnetization in a field of 2 T σ_{2T}, and (*4*) magnetization in a 2-T field $\sigma_{2T}/2$.

for those observed for single-phase hard magnetic materials (see Fig. 2). This fact indicates the formation of an exchange-coupled state in the powders.

Figure 3 shows the dependences of the magnetic properties of the mechanically alloyed powders from the annealing temperature. We can note that the σ_{2T} magnitude for both powder systems demonstrates a weak and nonmonotonic dependence from the annealing temperature. This fact indicates a relatively constant phase composition of the powders after crystallization. At the same time, the dependences of the structurally sensitive characteristics (H_{ci}, σ_r) from the annealing temperature demonstrate an extreme character. In this case, the dependences $\sigma_r(T_{ann})$ of the compositions vary almost simultaneously, whereas the dependences $H_{ci}(T_{ann})$ differ substantially.

The volume fraction of the soft magnetic phase in the powders with 30% RQ2 alloy is higher. Therefore, taking into account the crystallization kinetics, we can assume that the coarsening of the structure and, therefore, the decay of exchange-coupled state in such compositions occurs at relatively low temperatures. This explains the abrupt decrease in their coercivity H_{ci} at $T_{ann} > 500°C$. The analogous decrease in H_{ci} for the powders with 10% RQ2 alloy is observed only after annealing at $T_{ann} > 550°C$. According to XRD data, a decrease in the coercivity H_{ci} after annealing at $T_{ann} < 500°C$ is related to partial crystallization of the soft magnetic amorphous phase.

CONCLUSIONS

A powder blending procedure combined with mechanical alloying shows promise as a method for preparing high-performance hard magnetic materials. In particular, the mechanical alloying of powder mixtures of a hypostoichiometric $Nd_{7.4}Pr_{2.0}Fe_{76.6}Co_{4.2}Zr_{3.4}B_{6.4}$ alloy with 30 wt % low-neodymium $Nd_{5.8}Fe_{80}Co_{4.9}Ti_{1.5}Si_{2.5}B_{5.3}$ alloy and subsequent annealing at 500°C for 20 min allowed us to reach the following properties: the coercivity was $H_{ci} = 443$ kA/m, the residual magnetization was $\sigma_r = 64$ A m^2/kg, the magnetization in a field of 2 T was $\sigma_{2T} = 125$ A m^2/kg, and $\sigma_r/\sigma_{2T} > 0.5$. In this case, it is obvious that the further optimization of the mechanical alloying and crystallization conditions and purposeful alloying will allow us to increase the magnetic properties of the hard magnetic nanocomposites.

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