

Effect of the Milling Time on the Magnetic Properties of Powder Compositions of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ Intermetallic Compound and an Nd–Fe–B Alloy

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Abstract—The effect of the wet milling time on the magnetic properties of powder compositions consisting of the hard magnetic $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ ($x = 2.9\text{--}3.0$) nitride and a rapidly quenched $\text{Nd}_{9.6}\text{Fe}_{76.3}\text{Co}_{4.3}\text{Zr}_{3.4}\text{B}_{6.4}$ (at %) alloy, which are taken in different mass proportions, is studied. The compositions containing no more than 20 wt % alloy are found to exhibit a substantial increase in the magnetic characteristics as compared to those of the nitride. It is shown that the determining effect on the coercivity is related to the degree of structural imperfection of Nd–Fe–B powders, whereas the specific remanent magnetization and the specific magnetization in a field of 2 T are determined by the corresponding characteristics of the alloy. The optimum composition and efficient treatment conditions for powder mixtures are determined.

Keywords: $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ intermetallic compound, hard magnetic nitride, rapid quenching, wet milling, hysteresis loop, coercivity, remanent magnetization

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INTRODUCTION

For several recent decades, hard magnetic $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ nitrides ($x > 2.8$) are of interest for investigators owing to their specific functional properties. It was shown by numerous experimental studies that the maximum magnetic properties of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ intermetallic compound are comparable with or even exceed those of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound [1–5]. In particular, the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$ compounds exhibit almost the same saturation magnetization; at the same time, the nitrides have a higher Curie temperature (750 K), anisotropy field (15.6 T), and corrosion resistance and are characterized by thermal stability [6, 7].

The prospects of using $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ for composite permanent magnets has determined the development of a wide range of methods for the preparation of intermetallic-based magnetic powders. Moreover, it is known that the powder blending method [8] allows one to improve the hysteretic characteristics of each powder mixture component, in particular, to increase the coercivity of Nd–Fe–B alloys and the remanent magnetization of $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ powders. Such properties

of materials cannot be reached by direct methods, such as melting and rapid quenching.

It is known that milling allows one to vary the properties of milled materials over wide ranges [9]. In particular, the coercivity of isotropic $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ -based alloys subjected to milling in a planetary ball mill to a powder-particle size of 100–800 nm is 800 kA/m (~10 kOe) [10]. However, no data on the effect of the degree of milling on the properties of magnetic powder mixtures of various compositions are available. The aim of the present study is to investigate the effect of the wet milling time on the phase composition and the hysteretic properties of powder compositions based on the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ nitride and a rapidly quenched Nd–Fe–B alloy.

EXPERIMENTAL

We studied the phase composition and the magnetic properties of powder compositions consisting of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ ($x = 2.9\text{--}3.0$) intermetallic compound and 10 or 20 wt % rapidly quenched $\text{Nd}_{9.6}\text{Fe}_{76.3}\text{Co}_{4.3}\text{Zr}_{3.4}\text{B}_{6.4}$ (at %) alloy.

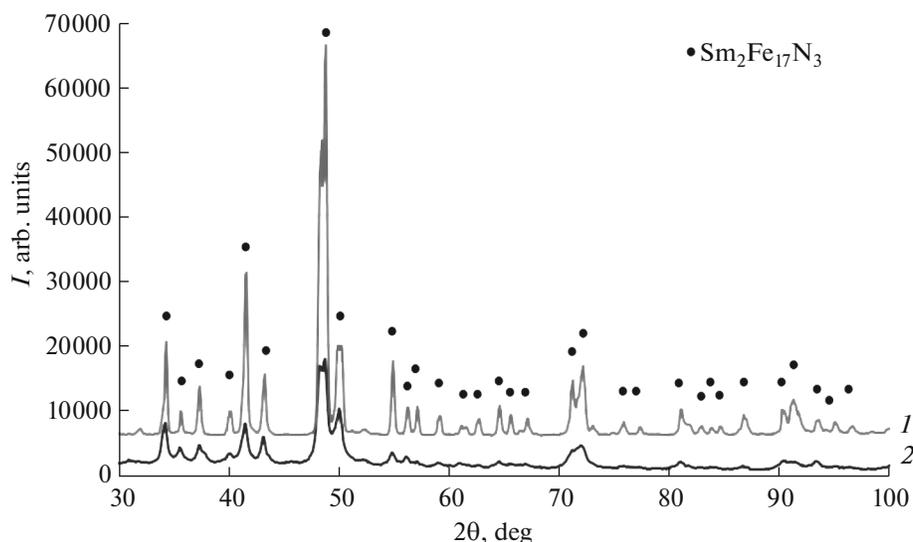


Fig. 1. X-ray diffraction patterns of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ nitride (1) in the initial state and (2) after milling for 60 min.

The $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ intermetallic compound was prepared by vacuum induction melting in an argon atmosphere using pure components. The ingot was subjected to homogenizing annealing at 1050°C for 30 h, crushing, hydrogenation (at 120°C at a hydrogen pressure of 1.2 MPa), and subsequent dehydrogenation (at 450°C in a vacuum) and nitriding (at $410\text{--}430^\circ\text{C}$ at a nitrogen pressure of 1.5 MPa).

The $\text{Nd}_{9.6}\text{Fe}_{76.3}\text{Co}_{4.3}\text{Zr}_{3.4}\text{B}_{6.4}$ alloy was prepared by rapid quenching using a copper wheel 200 mm in diameter and a rotation speed of 1800 rpm. Ribbon samples were crushed by hand using a mortar. To ensure a high-coercivity state, the crushed alloy was subjected to crystallization annealing under optimum conditions, namely, annealing at 520°C for 20 min. The following properties of annealed milled alloy were reached. The coercivity was $H_{\text{ci}} = 679$ kA/m, the remanent magnetization was $\sigma_r = 85.4$ A m²/kg, and the magnetization ratio in a field of 2 T was $\sigma_r/\sigma_s = 0.73$ (σ_s is the saturation magnetization).

Powder mixtures were prepared using an Aktivator 2S planetary ball mill, a toluene environment, and a speed of vial rotation of 800 rpm; the powder-to-milling ball mass ratio was 1 : 10; and the mass of material loaded in each of milling vials was 30 g.¹ The milling process consisted of two stages: preliminary milling of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ intermetallic compound (for 20–60 min (t_1)) and its milling together with the $\text{Nd}_{9.6}\text{Fe}_{76.3}\text{Co}_{4.3}\text{Zr}_{3.4}\text{B}_{6.4}$ alloy for 20 min (t_2); the amounts of powder components were calculated to obtain 10 or 20% mass fractions of the alloy in a composition. The powders unloaded from the mill vials were dried in air for 2 h.

¹ The use of wet milling was due to the need to exclude amorphization of the milled powders, which can occur in the course of dry milling (which is also a high-energy process).

X-ray diffraction (XRD) analysis was performed in a 2θ angle range of $20^\circ\text{--}120^\circ$ using a DRON-3M diffractometer, a graphite monochromator, and $\text{CoK}\alpha$ radiation ($\lambda = 1.07921$ Å). A quantitative phase analysis was performed by the Rietveld method with the Phan% software [11]. The sensitivity of the phase analysis was 1 vol % and the statistical error of determining the phase content was no more than 2%. The magnetic properties of the prepared powders were measured at room temperature in a magnetizing field of to 2 T on a VSM-250 vibrating-sample magnetometer.

RESULTS AND DISCUSSION

According to XRD data, the intermetallic compound before and after milling contains only the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ phase (Fig. 1). The magnetization coercivity of the intermetallic compound before milling is $H_{\text{ci}} = 36$ kA/m and the remanent magnetization is $\sigma_r = 10.9$ A m²/kg; the ratio is $\sigma_r/\sigma_s = 0.11$ (see Table 1). After milling, the coercivity of the intermetallic compound H_{ci} monotonically increases to 704 kA/m (see Table 1 and Fig. 2). In this case, as the milling time (t_1) increases, remanent magnetization σ_r varies non-monotonically, namely, demonstrates about a fourfold increase after milling for 20 min and decreases by 1.3 times after subsequent milling for 60 min (Fig. 3, curve 3). As a result, specific magnetization σ_s of the intermetallic compound decreases by one and a half time (see Table 1). In this case, the ratio σ_r/σ_s first increases by 5.5 times at $t_1 = 20$ min and, subsequently, as the milling time increases, also decreases and reaches 0.54 at $t_1 = 60$ min (Fig. 3, curve 6).

Milling of the intermetallic compound with addition of the 10% Nd–Fe–B alloy leads to an increase in coercivity H_{ci} of the mixture in the case of preliminary

Table 1. Magnetic properties of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ intermetallic compound and the $\text{Nd}_{9.6}\text{Fe}_{76.3}\text{Co}_{4.3}\text{Zr}_{3.4}\text{B}_{6.4}$ alloy before and after milling

Material	State	H_{ci} , kA/m	σ_r , (A m ²)/kg	σ_s , (A m ²)/kg	σ_r/σ_s
Alloy	After annealing	679	85.4	117.0	0.73
Intermetallic compound	Initial (before milling)	36	10.9	96.0	0.11
	After milling:				
	$t_1 = 20$ min	413	44.7	74.4	0.60
	$t_1 = 40$ min	573	36.6	74.5	0.49
Powder mixture	After milling:				
	$t_1 + t_2 = 40$ min	521/592*	81.8/71.4	109/99	0.75/0.72
	$t_1 + t_2 = 60$ min	611/522	69.8/57.3	102/93	0.68/0.62
	$t_1 + t_2 = 80$ min	551/444	61.7/55.4	102/92	0.60/0.60

* Numerator and denominator indicate the values for the mixtures containing 10 and 20 wt % Nd–Fe–B alloy, respectively.

milling of the intermetallic compound at $t_1 \leq 40$ min and to a decrease in the coercivity at $t_1 = 60$ min ($t_1 + t_2 = 80$ min) (see Fig. 2, curve 2). The coercivity of the milled powder mixture consisting of the intermetallic and 20% alloy linearly decreases (see Fig. 2, curve 3). In this case, it should be noted that, after preliminary milling of the intermetallic compound at $t_1 = 20$ min and subsequent milling of the alloy-containing mixture at $t_2 = 20$ min ($t = t_1 + t_2 = 40$ min), the coercivity of the mixture is higher than that of the intermetallic compound milled at $t_1 = 40$ min; i.e., the coercivity is 592 and 573 kA/m, respectively. This fact indicates a determining effect of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ intermetallic compound on the coercivity of the powder composition.

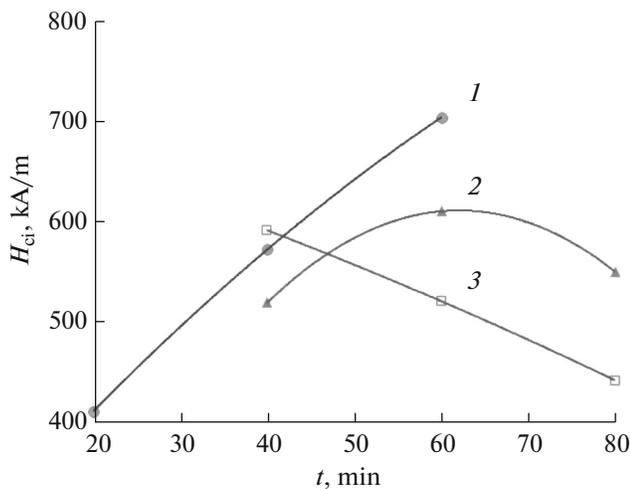


Fig. 2. Coercivity of (1) the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ intermetallic and its mixture with (2) 10 and (3) 20 wt % Nd–Fe–B alloy vs. the milling time.

As the milling time increases, a monotonic decrease in remanent magnetization σ_r and the ratio σ_r/σ_s is observed (see Fig. 3); in all cases, the ratio σ_r/σ_s for the powder mixtures with 10 and 20 wt % of alloy substantially exceeds the Stoner–Wohlfarth limit ($\sigma_r/\sigma_s = 0.5$) [12].

The magnetic hysteresis loops of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ intermetallic compound before and after milling differ substantially in appearance (Fig. 4). Moreover, the simply connected hysteresis loops (which are typical of magnetically single-phase materials) that are obtained for the intermetallic compound before milling and after short-time ($t_1 = 20$ min) milling transform, at $t_1 \geq 40$ min, into the hysteresis loops charac-

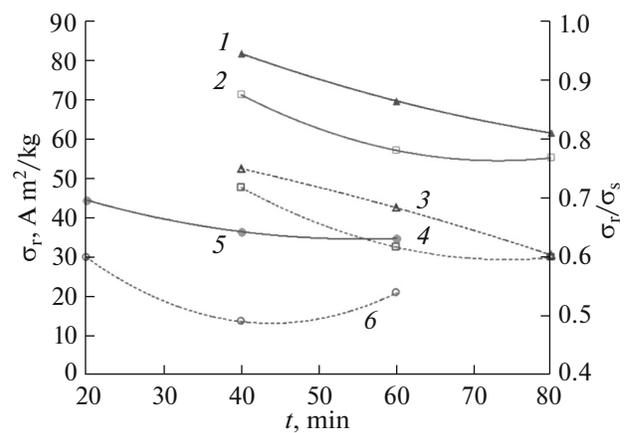


Fig. 3. (1–3) Remanent magnetization σ_r and (4–6) σ_r/σ_s ratio vs. the milling time for the powder compositions consisting of $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ and Nd–Fe–B alloy: (1, 3) intermetallic with 10 wt % Nd–Fe–B alloy, (2, 4) intermetallic with 20 wt % Nd–Fe–B alloy, and (5, 6) pure intermetallic.

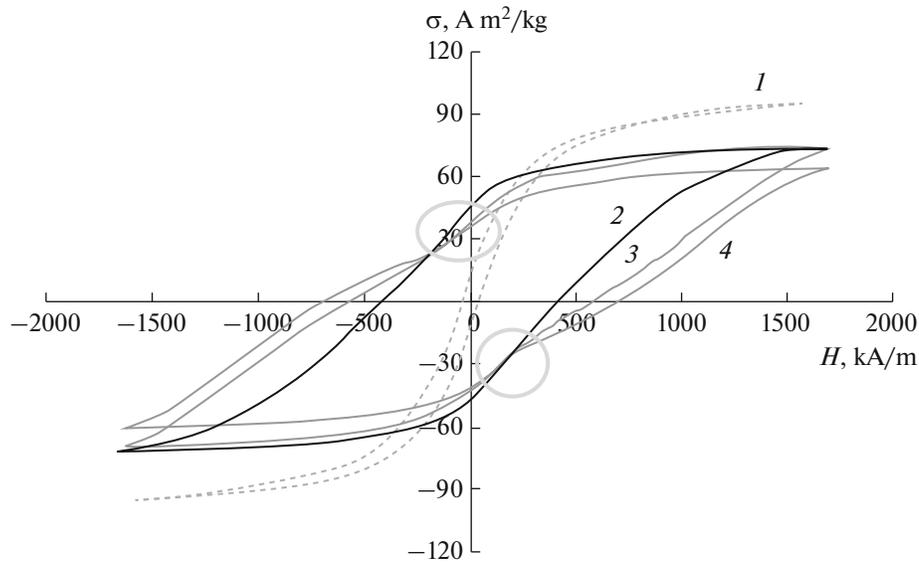


Fig. 4. Magnetic hysteresis loops for the powder $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ intermetallic compound (1) in the initial (before milling) state and after milling for (2) 20, (3) 40, and (4) 60 min.

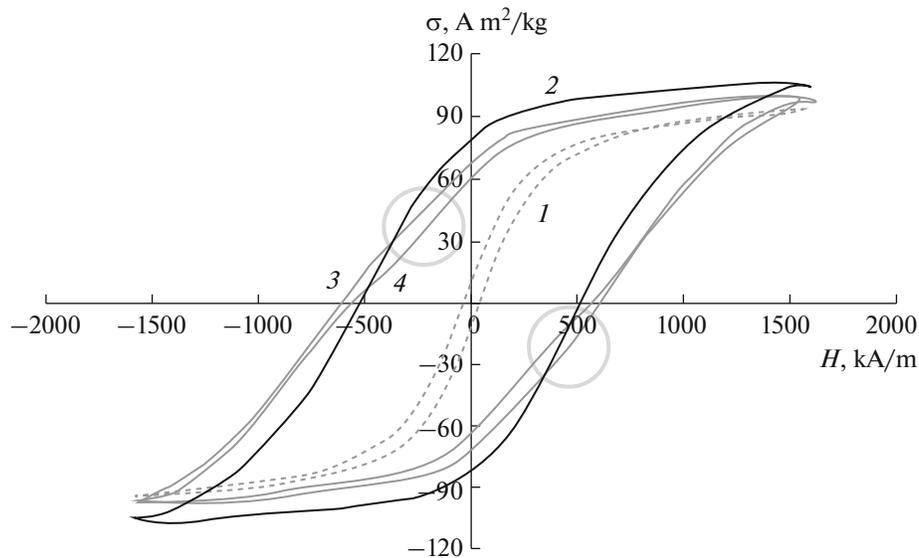


Fig. 5. Magnetic hysteresis loops for the powder $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ intermetallic compound and its mixture with 10 wt % Nd–Fe–B alloy: (1) $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ intermetallic before milling and the mixture after milling for (2) 20, (3) 40, and (4) 60 min.

terized by nonmonotonic variations of magnetization in demagnetizing fields, which are typical of magnetically multiphase materials [13, 14]. Portions of such anomalous variations of magnetization are shown by circles in hysteresis loops 3 and 4 (see Fig. 4).

We assume that the decrease in σ_r remanent magnetization and σ_s magnetization in a field of 2 T, which are observed for the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ powders with increasing milling time, can be related to the appearance of 2–14–1 phase grains characterized by a higher content of structural imperfections and, therefore, a lower effective uniaxial-anisotropy constant, which facili-

tates their magnetization reversal. An analogous result was obtained in [15]. According to [15], as the milling time increases, the composition of $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ remains unchanged and close to $\text{Sm}_2\text{Fe}_{17}\text{N}_3$. To a certain degree, this is confirmed by XRD data (see Fig. 1, curve 2). The XRD patterns exhibit no additional reflections related to other phases; however, as the milling time increases, the reflections of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ phase become smeared. Thus, the powder intermetallic compound remains structurally stable in the course of milling but becomes nonuniform in a magnetic-moment distribution. This fact was observed in [16].

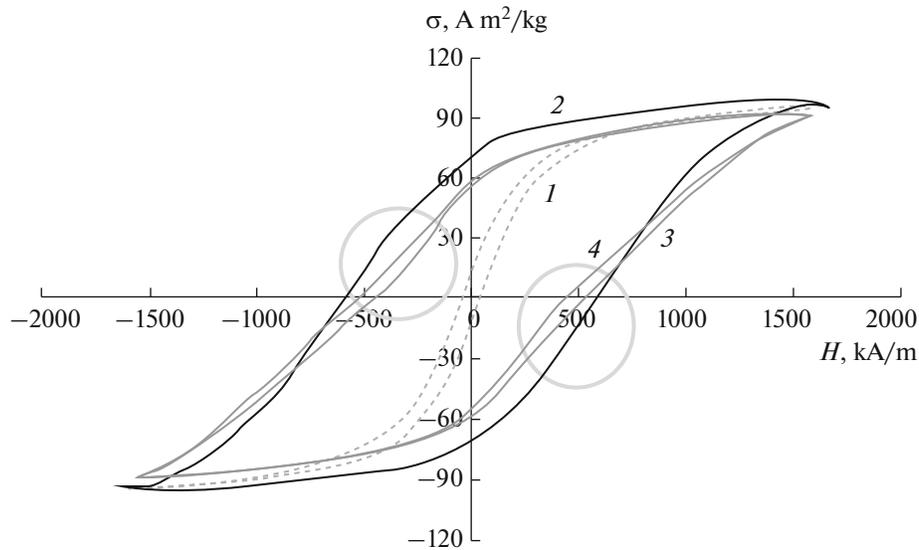


Fig. 6. Magnetic hysteresis loops for the powders of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ intermetallic compound and its mixture with 20 wt % Nd–Fe–B alloy: (1) $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ intermetallic before milling and the mixture after milling for (2) 20, (3) 40, and (4) 60 min.

The magnetic hysteresis loops of the powder compositions prepared by milling at $t = t_1 + t_2 = 40$ min are smooth (see Figs. 5, 6; curves 2). In the case of prolonged milling, the hysteresis loops demonstrate bends (Figs. 5, 6; curves 3, 4), although they are less pronounced than those observed in the hysteresis loops measured for the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ intermetallic compound subjected to milling for $t_1 \geq 40$ min (see Fig. 4, curve 4). This fact confirms the determining effect of the hard magnetic nitride on the magnetization reversal processes in the powder compositions.

CONCLUSIONS

It was experimentally shown that the powder mixture method allowed us to form powder compositions of magnetic, in particular, magnetically anisotropic, materials for high performance permanent magnets. The maximum magnetic properties (magnetization coercivity $H_{ci} = 521$ kA/m, remanent magnetization $\sigma_r = 81.8$ A m²/kg, the ratio of remanent magnetization to the magnetization in a magnetizing field of 2 T $\sigma_r/\sigma_s = 0.75$) were observed for the powder composition, which consisted of 90 wt % of $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ nitride and 10 wt % rapidly quenched $\text{Nd}_{9.6}\text{Fe}_{76.3}\text{Co}_{4.3}\text{Zr}_{3.4}\text{B}_{6.4}$ alloy and was subjected to certain treatment. It includes milling of the intermetallic compound for 20 min and 20 min joint milling with 10 wt % rapidly quenched alloy.

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