

Synthesis and Study of Influence of Mechanical Activation Processing on the Structure and Magnetic Properties of $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x\text{N}_y$ Nitride Powders

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Abstract— $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x$ ($x = 0.1, 0.2, 0.3$ and 0.4) alloys and alloy-based nitrides were synthesized. The chemical and phase composition, microstructure of cast and homogenized alloys, and the hysteresis properties were studied by scanning electron microscopy, local microanalysis, and X-ray diffraction analysis. It was established that nitriding of pseudobinary $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x$ compounds leads to the increase in lattice parameters and simultaneous increase in the specific saturation magnetization. Mechanical activation processing of the nitriding products revealed the different nature of their magnetic behavior depending on aluminum concentration in the alloys. Mechanical activation leads to the increase in coercive force and simultaneous decrease in the values of specific saturation magnetization and the average size of particles at small content of aluminum (18.6 at %). The coercive force of nitride also increases after mechanical activation at high aluminum content (38.3 at %); however, the specific saturation magnetization also increases. Generally, the increase in aluminum content in Sm–Fe–Al–N alloy leads to the decrease in their hysteresis characteristics after mechanical activation processing.

Keywords: Sm–Fe–Al alloys, nitrides, mechanical activation, crystal structure, SEM, magnetic properties

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INTRODUCTION

It is known that $\text{Sm}_2\text{Fe}_{17}\text{N}_y$ nitrides synthesized by Coey and Hong Sun in 1990 for the first time [1, 2] are very promising hard magnetic phases characterized by outstanding magnetic properties. These properties open new prospects for the elaboration of a new generation of highly coercive hard magnetic materials [3–5].

Poor thermal stability is the main drawback of $\text{Sm}_2\text{Fe}_{17}\text{N}_{3-\delta}$ compounds. In practice, it was established that $\text{Sm}_2\text{Fe}_{17}\text{N}_{3-\delta}$ nitrides can be decomposed into soft magnetic SmN and α -Fe phases; this fact significantly restricts the possibility of using them for the fabrication of high-energy permanent magnets and determines the need to continue the studies in this direction.

The search for a highly efficient and economically sound hard magnetic material based on 2 : 17 substituted compounds (by varying the chemical composition at constant stoichiometry) characterized by properties which are not inferior to the ones of $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ nitride has continued in the last decades. For example, in a series of studies [6–8], it is mentioned that partial replacement of atoms of iron with nonmagnetic ele-

ments $M = \text{Si}, \text{Ga}, \text{Al}$ in the crystal lattice of the initial intermetallic compound $\text{Sm}_2\text{Fe}_{17}$ provides the increase in the parameters and the volume of the unit cell, causes the increase in its Curie temperature (first of all, owing to the increase in Fe–Fe distance at 6c sites of the rhombohedral structure), and leads to the change of the sign of the first constant of magnetocrystalline anisotropy (similar to the addition of light atoms to the crystal lattice). However, the Curie temperature and saturation magnetization of such compounds significantly depend on the concentration of substituent nonmagnetic atoms M , because the mentioned transformation of properties is determined by the changes in electron structure of the initial compound which are related to volume and chemical effects as well as to the common dilution [9].

The studies of nitrides based on quasi-binary $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x$ compounds were performed in [8, 10–12]. X-ray diffraction analysis (XRD) showed that these nitrides are characterized by the same $\text{Th}_2\text{Zn}_{17}$ type of structure ($R\bar{3}m$ space group) typical of $\text{Sm}_2\text{Fe}_{17}$ compound. The introduction of nitrogen atoms into the lattice of $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x$ compounds leads to the increase

Table 1. Elemental and phase composition of $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ after homogenizing annealing at 1000°C for 40 h

No.	Calculated content of components, at %			Average integrated chemical composition, at %			Phase composition (according to XRD and EDX data)	Phase content in the sample (according to XRD), wt %
	Sm	Fe	Al	Sm	Fe	Al		
1	10.5	80.5	8.9	10.0	82.8	10.4	$\text{Sm}_2\text{Fe}_{14.9}\text{Al}_{1.9}$ α -(Fe, Al)	49 51
2	10.5	71.6	17.9	9.2	72.2	18.6	$\text{Sm}_2\text{Fe}_{13.3}\text{Al}_{3.8}$ α -(Fe, Al)	72 28
3	10.5	62.6	26.8	9.2	63.6	27.2	$\text{Sm}_2\text{Fe}_{10.7}\text{Al}_{6.3}$ α -(Fe, Al)	75 25
4	10.5	53.7	35.8	10.1	51.6	38.3	$\text{Sm}_2\text{Fe}_{9.9}\text{Al}_{7.1}$ α -(Fe, Al)	96 4

in the parameters of the elementary cell and expected increase in the Curie temperature and specific saturation magnetization. However, the amplitude of this increase decreases as the value of x increases as compared to the undoped compound. In other words, $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x\text{N}_z$ nitrides are characterized by lower values of the main magnetic characteristics as compared to $\text{Sm}_2\text{Fe}_{17}\text{N}_3$. It should be mentioned that the magnetic experiments on intermetallic compounds and their nitrides were carried out in magnetic fields characterized by the intensity of 1 T [10] and 2–6.5 T [8] at room temperature and only in few cases [11, 12] at the magnetic field intensity up to 7 T at 4.2 K. The results of X-ray studies and magnetic measurements are given in the studies dedicated to $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x\text{N}_z$ nitrides; however, the content of nitrogen is given only for the samples characterized by the minimum and maximum concentrations of aluminum among the studied concentrations; the general regularity of its negative influence on the properties of the compound is mentioned.

Data on structural and magnetic properties of finely dispersed Sm–(Fe, Al)–N nitrides (for example, after mechanical activation (MA) are absent in the literature. However, according to numerous published sources, the magnetic properties of $\text{Sm}_2\text{Fe}_{17}\text{N}_y$ powders, in particular, the coercive force, can be significantly improved by additional mechanical disintegration. Thus, in the study [13], it was shown that the low coercive force of nitride after nitriding (<100 kA/m) increases to 540 kA/m after 60 min of disintegration. The influence of powder size on its coercive force is related to the change in the domain structure. The authors of the study [14] suppose that single-domain particles which are switched in the intense fields and provide higher values of coercive force are formed during disintegration. In view of the aforesaid, the goal of the present research was to synthesize $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x\text{N}_{3-\delta}$ nitrides, where $x = 0.1, 0.2, 0.3$ and 0.4, and to study the influence of mechanical activation processing on their structure and magnetic properties.

EXPERIMENTAL

The smelting of alloys of $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ nominal composition, where $x = 0.1, 0.2, 0.3$, and 0.4, was carried out by vacuum arc remelting (VAR) (alloys 1–3) and vacuum induction melting (VIM) (alloy 4) from extrapure metals taking into account the addition of 5% excess of samarium owing to its evaporation during smelting under an argon atmosphere. The designations and the elemental (calculated and found) and phase composition of the alloy according to the X-ray and SEM studies are given in Table 1. Homogenizing annealing was performed in vacuum-processed quartz ampoules at 1000°C for 40 h. The phase composition of alloys 1–4 before and after annealing was studied on polished samples using a LEO EVO-50 XVP scanning electron microscope (Carl Zeiss, Germany). The measurement error was ± 0.3 at %.

Nitriding of alloys was carried out under an extrapure nitrogen atmosphere, pressure of 5 MPa, temperature of $490 \pm 5^\circ\text{C}$, and for duration 48 h after their preliminary hydride disintegration. The relative error of the determination of hydrogen and nitrogen content in the alloys did not exceed $\pm 0.1 \text{ H(N)/Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$.

X-ray diffraction analysis (XRD) of the initial alloys and products of their nitriding was carried out on a DRON-4-07 diffractometer ($U = 40 \text{ kV}$, $I = 30 \text{ mA}$); monochromatized $\text{CoK}\alpha$ radiation was used; the scanning angle range was $2\theta = 20^\circ\text{--}120^\circ$; the step was 0.05° ; the storage time was 5 s at every point. The approximation of X-ray diffraction patterns was performed according to the Rietveld refinement. The accuracy of determination of lattice parameters was $\pm(0.01\text{--}0.05)\%$; the accuracy of determination of mass fractions of phases was $\pm(5\text{--}10)\%$.

Mechanical activation processing of nitrides was carried out in a high-energy planetary mono mill Pulverisette 6 (Fritsch, Germany). The milling bodies and nitride powder were placed into tungsten carbide milling glasses; 100 metal spheres (tungsten carbide, diameter of 5 mm) were used as milling bodies. The milled sample (up to 15 g) was loaded into the 225 mL

Table 2. Conditions of nitriding and results of phase analysis of nitrided alloys of $\text{Sm}_2(\text{Fe, Al})_{17}$

Sample no.	2 : 17 phase	P_{N_2} , MPa	T , °C	Phase composition of alloys after nitriding; fractions of phases (wt % $\pm$ 1).
5	$\text{Sm}_2\text{Fe}_{14.9}\text{Al}_{2.1}$	50.0	$490 \pm 5^\circ\text{C}$	$\text{Sm}_2\text{Fe}_{14.9}\text{Al}_{2.1}\text{N}_{2.4} - 41$; $\text{SmN} - 2$; $\alpha\text{-(Fe, Al)} - 57$
6	$\text{Sm}_2\text{Fe}_{13.2}\text{Al}_{3.8}$			$\text{Sm}_2\text{Fe}_{13.2}\text{Al}_{3.8}\text{N}_{2.1} - 68$; $\text{SmN} - 2$; $\alpha\text{-(Fe, Al)} - 30$
7	$\text{Sm}_2\text{Fe}_{10.7}\text{Al}_{6.3}$			$\text{Sm}_2\text{Fe}_{10.7}\text{Al}_{6.3}\text{N}_{1.6} - 63.5$; $\text{SmN} - 3.5$; $\alpha\text{-(Fe, Al)} - 33$
8	$\text{Sm}_2\text{Fe}_{9.9}\text{Al}_{7.1}$			$\text{Sm}_2\text{Fe}_{9.9}\text{Al}_{7.1}\text{N}_{0.3} - 93$; $\text{SmN} - 1$; $\alpha\text{-(Fe, Al)} - 6$.

grinding bowl; grinding bowl ~35 mL of heptane and 2–3 drops of oleic acid (surfactant preventing the coalescence of particles) were added. Milling was carried out under an argon atmosphere to avoid the oxidation of the studied compounds during milling. Milling lasted for 15, 30, 45 and 60 min; the rotation velocity of planetary disk was set to 300 rpm. A Supra 40 scanning electron microscope (Carl Zeiss, Germany) was used to obtain SEM images of nitride powders before and after mechanical processing and determine the size of particles of nitrided powders.

The hysteresis properties of nitrides before mechanical activation processing were determined using the vibration magnetic add-on to the PPMS-9 system (Ever Cool II, Quantum Design) in magnetic fields with H reaching 9 T at room temperature. The hysteresis properties of nitride powders after mechanical activation were determined in magnetic fields with H reaching 2 T at room temperature; a VSM-250 vibrating magnetometer was used. The error of the determination of the specific saturation magnetization (σ_s), specific residual magnetization (σ_r), and coercive force with respect to magnetization (jH_c) was $\pm 0.3\%$ (PPMS-9) and $\pm 2.0\%$ (VSM-250).

RESULTS AND DISCUSSION

Characteristics of Cast and Homogenized Sm–Fe–Al Alloys

The X-ray fluorescence (XRF) analysis of the cast alloys showed that the bars obtained by VAR are significantly depleted in samarium despite the addition of 5% of this metal into the furnace charge sample. According to the X-ray spectral analysis, in particular, energy-dispersive spectroscopy (EDX), and XRD of the homogenized alloys, the $\alpha\text{-(Fe, Al)}$ phase is also present in the alloys besides the main quasi-binary $\text{Sm}_2(\text{Fe, Al})_{17}$ phase of $\text{Th}_2\text{Zn}_{17}$ ($R\bar{3}m$ space group) structure. The mass fractions of the mentioned phases in the alloys are given in Table 1.

The images of the microstructure of Sm–Fe–Al alloys after homogenizing annealing at 1000°C for 40 h

are given in the study [15]. It is seen that the type of iron distribution is similar to the one observed for the cast alloy. SEM images of alloys 1–4 after homogenization showed that dendritic structure is more or less typical of all samples; however, it is most pronounced in case of alloy 3, which apparently is due to the significant difference between the rates of cooling of the different parts of a bar. Sample 4 does not contain any traces of dendritic segregation probably because of a more uniform distribution of the initial components during the VIM process.

Characteristics of $\text{Sm}_2(\text{Fe}_{1-x}\text{Al})_{17}$ Alloys after Nitriding: Structure and Magnetic Properties

Highly dispersed powders were obtained as a result of nitriding of Sm–Fe–Al alloys after their preliminary hydride disintegration. According to the X-ray analysis of the nitride phases, absorption of nitrogen was followed by a characteristic increase in the unit cell volume of 2 : 17 type without any changes of its structural type and by a significant broadening of the corresponding diffraction lines. It was found that nitride phases were partially decomposed: firstly, a drastic increase in intensity of the lines of the $\alpha\text{-(Fe, Al)}$ phase was observed in the diffraction patterns of all four alloys, while the intensity of the main phase did not change; secondly, the SmN phase was identified as the product of thermal decomposition.

The conditions of nitriding and the results of phase analysis after nitriding are given in Table 2.

The temperature regime of nitriding of Sm–Fe–Al alloys was selected taking into account the data given in [11, 12], where $T_{\text{N}_2} = 500^\circ\text{C}$, $t = 4$ h; in our study, $T_{\text{N}_2} = 490^\circ\text{C}$, $t = 48$ h (such a long exposure under a nitrogen atmosphere is determined by the heterogeneity of the initial material). It should be mentioned that decomposition of the nitride phase at high temperature ($T \geq 450^\circ\text{C}$) was not mentioned in the sources given above.

The results given in Table 3 show that the value of $\Delta V/V$ tends to decrease from 4.9 to 0.4% as the con-

Table 3. Structural parameters and magnetic characteristics of quasi-binary intermetallics $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ before and after nitriding (structure of $\text{Th}_2\text{Zn}_{17}$ type, $R\bar{3}m$ space group, no. 166)

Composition of 2 : 17 phase in the initial state and after nitriding	a , Å	c , Å	c/a	V , Å ³	$\Delta V/V$, %	σ_s , A m ² /kg
$\text{Sm}_2\text{Fe}_{16}\text{Al}$ [10]	8.574	12.530	1.461	798	—	—
$\text{Sm}_2\text{Fe}_{15.3}\text{Al}_{1.7}$ [12]	8.605	12.458	1.448	—	—	127.2**
$\text{Sm}_2\text{Fe}_{15.3}\text{Al}_{1.7}\text{N}_{2.6}$ [12]	8.754	12.636	1.443	—	5	144**
$\text{Sm}_2\text{Fe}_{15.1}\text{Al}_{1.9}$ (sample 1)	8.603 (4)	12.522 (3)	1.456	802.7	—	95.9*
$\text{Sm}_2\text{Fe}_{15.1}\text{Al}_{1.9}\text{N}_{2.4}$ (sample 5)	8.751 (9)	12.717 (3)	1.453	842.3	4.9	82.1*
$\text{Sm}_2\text{Fe}_{15}\text{Al}_2$ [10]	8.610	12.546	1.457	805	—	—
$\text{Sm}_2\text{Fe}_{13.6}\text{Al}_{3.4}$ [12]	8.651	12.566	1.453	—	—	116.6**
$\text{Sm}_2\text{Fe}_{13.4}\text{Al}_{3.4}\text{N}_2$ [12]	8.748	12.649	1.446	—	3	129.2**
$\text{Sm}_2\text{Fe}_{13.6}\text{Al}_{3.4}$ [11]	8.641	12.554	1.453	811.8	—	—
$\text{Sm}_2\text{Fe}_{13.4}\text{Al}_{3.4}\text{N}_{2.7}$ [11]	8.789	12.750	1.451	852.9	5.1	—
$\text{Sm}_2\text{Fe}_{14}\text{Al}_3$ [10]	8.629	12.541	1.453	809	—	—
$\text{Sm}_2\text{Fe}_{13.2}\text{Al}_{3.8}$ (sample 2)	8.643 (7)	12.596 (3)	1.457	815.6	—	70.6*
$\text{Sm}_2\text{Fe}_{13.2}\text{Al}_{3.8}\text{N}_{2.1}$ (sample 6)	8.770 (8)	12.765 (1)	1.456	848.4	4	74*
$\text{Sm}_2\text{Fe}_{13}\text{Al}_4$ [10]	8.659	12.598	1.455	818	—	—
$\text{Sm}_2\text{Fe}_{11.9}\text{Al}_{5.1}$ [12]	8.693	12.622	1.452	—	—	96.8**
$\text{Sm}_2\text{Fe}_{11.9}\text{Al}_{5.1}\text{N}_m$ [12]	8.721	12.689	1.455	—	1.2	106.3**
$\text{Sm}_2\text{Fe}_{10.7}\text{Al}_{6.3}$ (sample 3)	8.695 (3)	12.670 (5)	1.457	829.5	—	62.4*
$\text{Sm}_2\text{Fe}_{10.7}\text{Al}_{6.3}\text{N}_{1.6}$ (sample 7)	8.780 (5)	12.759 (8)	1.454	852.6	2.8	37*
$\text{Sm}_2\text{Fe}_{10.2}\text{Al}_{6.8}$ [12]	8.745	12.682	1.450	—	—	80.9**
$\text{Sm}_2\text{Fe}_{10.2}\text{Al}_{6.8}\text{N}_k$ [12]	8.750	12.694	1.451	—	0.2	82.1**
$\text{Sm}_2\text{Fe}_{9.9}\text{Al}_{7.1}$ (sample 4)	8.774 (0)	12.695 (4)	1.456	849.8	—	22.1*
$\text{Sm}_2\text{Fe}_{9.9}\text{Al}_{7.1}\text{N}_{0.3}$ (sample 8)	8.781 (8)	12.779 (1)	1.456	854	0.4	37.8*

* The values of σ_s measured in magnetic fields of 9 T intensity at room temperature were calculated using Eq. (1).

** The values of σ_s were measured at 4.2 K in magnetic fields of 7 T.

centration of aluminum in the alloys is increased; a simultaneous decrease in the absorption capacity with respect to nitrogen is observed. The ratio c/a of the initial phases changes weakly; it hardly depends on the content of aluminum in the sample. Therefore one can conclude that the increase in parameters of the unit cell is isotropic.

The introduction of nitrogen atoms into the $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ compound leads to the increase in the parameters of the unit cell; their amplitude decreases as the content of aluminum in the alloys is raised (Fig. 1). Therefore, one can suppose that replacement of iron with aluminum impedes the dissolution of nitrogen in the 2 : 17 phase.

The hysteresis loops of nitrated alloys 1–4 measured at room temperature in a field with the intensity of 7.164 MA/m are given in Fig. 2.

The values of the specific saturation magnetization σ_s of the 2 : 17 phase in these alloys before and after nitriding was calculated according to the equation

$$\sigma_s(2 : 17) = [\sigma_s(\text{sample}) - \sigma_s(\sigma\text{-Fe})\omega(\alpha\text{-(Fe,Al)})]/\omega(2 : 17), \quad (1)$$

where $\sigma_s(\alpha\text{-Fe}) = 210 \text{ A m}^2/\text{kg}$ [16] and ω is the phase content in a sample (wt %).

The significant content of the soft magnetic phase of $\alpha\text{-(Fe, Al)}$ and the presence of the SmN phase in the studied nitrides determine the low values of the specific magnetization σ_s of the alloys. In particular, the fraction of the hard magnetic phase drastically decreases owing to the thermal decomposition of nitride of the main phase based on alloys 1 and 3 leading to the increase in the mass fraction of $\alpha\text{-(Fe, Al)}$ as compared to the initial sample and because of the formation of the nonmagnetic SmN phase. As a result,

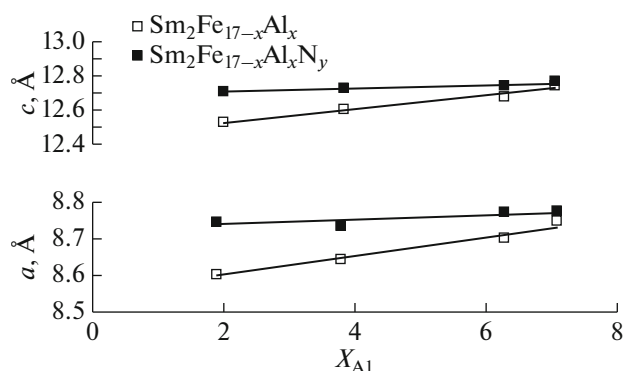


Fig. 1. Concentration dependence of parameters a and c of $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x$ and $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x\text{N}_y$ compounds.

the values of specific saturation magnetization of $\text{Sm}_2\text{Fe}_{15.1}\text{Al}_{19}$ and $\text{Sm}_2\text{Fe}_{10.7}\text{Al}_{63}$ appeared to be lower than those before the interaction with nitrogen. The introduction of nitrogen into the lattice of $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ compounds usually leads to the increase in σ_s ; the amplitude of this increase decreases as the aluminum concentration is raised. In case of samples 1 and 3, this regularity is not fulfilled owing to the simultaneous influence of several factors: (1) the presence of heterogeneities in the microstructure of the homogenized alloys leading to the heterogeneous volume nitriding of the alloys; (2) high content of the soft magnetic phase (and corresponding decrease in content of the hard magnetic phase); (3) high amount of aluminum atoms which substitute iron (simple dilution). Insignificant thermal decomposition of the nitride phase in alloy 4 exhibited the lowest influence on the magnetic properties.

The areas of loops of magnetic hysteresis of all nitrated alloys monotonically decrease. The insets in Figure 2 show that the coercive force in magnetic fields with intensity of -7.164 to $+7.164$ MA/m decreases along the magnetization at room temperature as the number of the sample (i.e., Al content in alloys) becomes higher; this is probably related to the increase in the number of nonmagnetic aluminum atoms in the products of nitriding. The same tendency is typical of the specific saturation magnetization of the 2 : 17 phase in homogenized alloys before and after nitriding: σ_s becomes higher in nitrides as compared to the initial phase owing to the introduction of nitrogen into the 2 : 17 phase. However, it monotonically decreases in both cases as the aluminum concentration is raised.

Influence of Mechanical Activation Processing on the Size of Particles of Nitride Powders, Their Structure and Properties

The study of the influence of time of mechanical activation was carried out on nitride samples 6 and 8

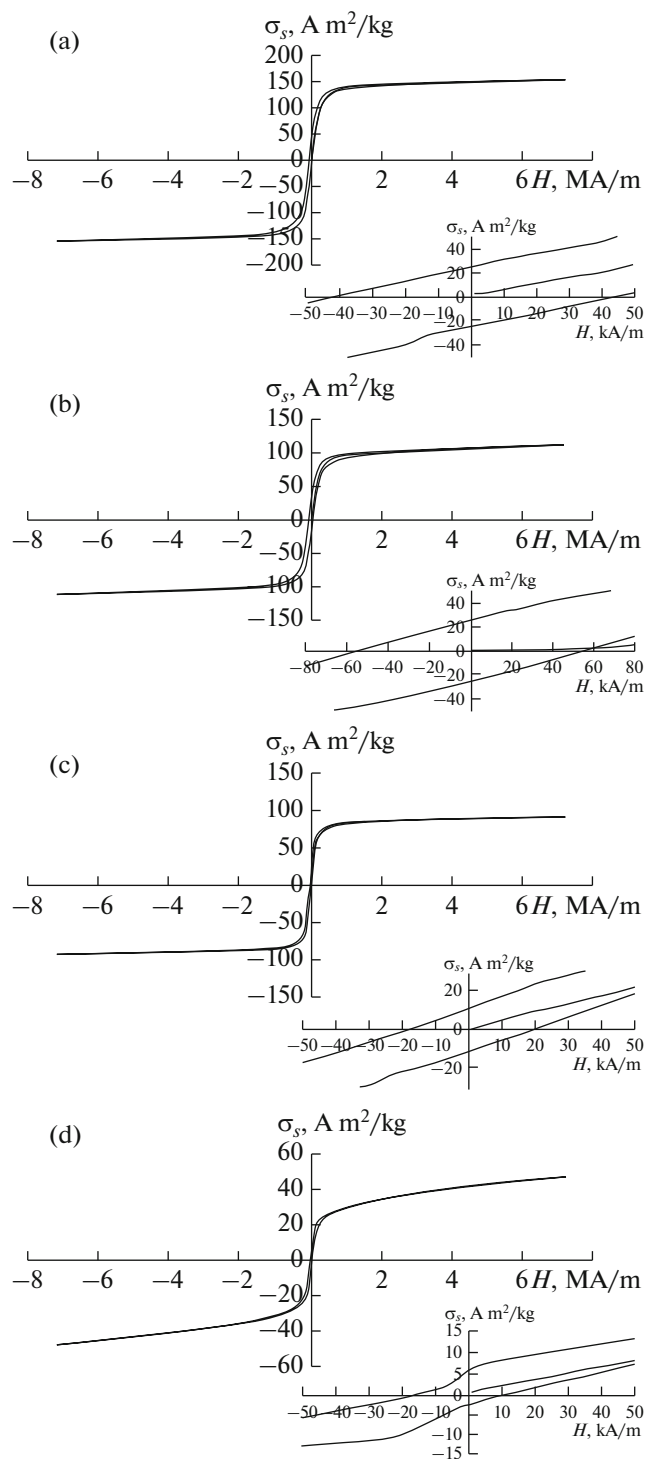


Fig. 2. Loops of magnetic hysteresis of nitrated material based on samples 1–4 (curves in Figs. 2a–2d, top down, respectively) measured in a magnetic field of 7.164 MA/m at room temperature; the dependence of σ_s on H is given in the insets to estimate the coercive force of nitrides.

(initial homogenized alloys 2 and 4, respectively) because the most significant thermal decomposition was observed in nitrated alloys 5 and 7 (see Table 2)

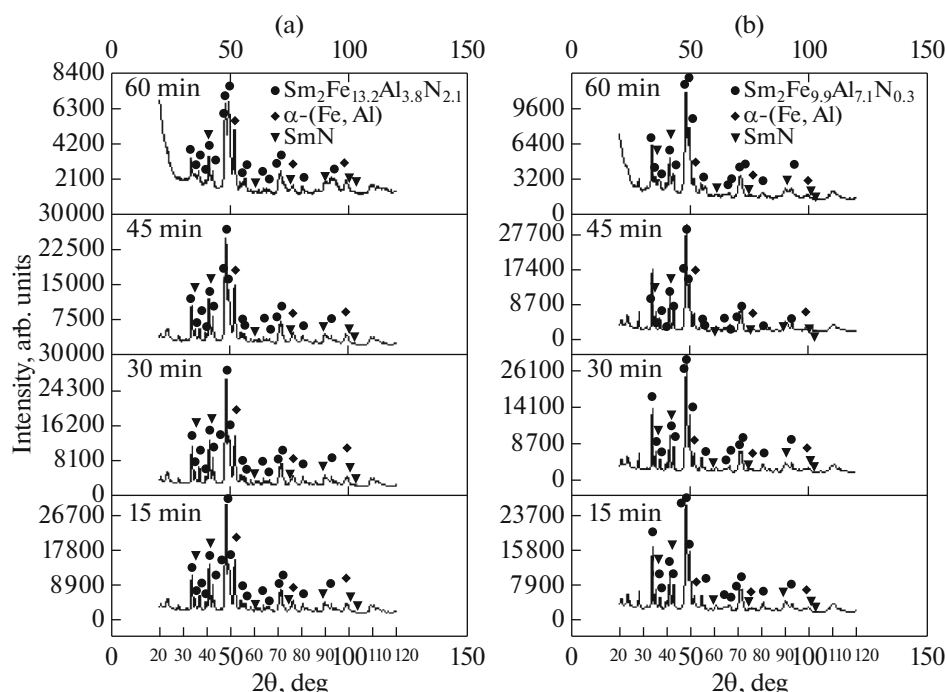


Fig. 3. Diffraction patterns of samples 6 (a) and 8 (b) after milling for 15, 30, 45, and 60 min at room temperature.

which correspond to homogenized alloys 1 and 3 and because of the high content of the soft magnetic α -Fe-based phase.

No signs of amorphization are observed in the diffraction patterns of both series of nitride powders after mechanical activation which lasted for 15, 30, and 45 min (Fig. 3). The shape of spectra does not change significantly: the peak/background ratio of the diffraction patterns generally does not change and the intensity of lines of the basic 2 : 17 : N phase does not

change as the time of mechanical activation is raised; their half-width also changes insignificantly. The most pronounced changes are observed for the intensities of the lines of the α -Fe-based phase: it slightly changes in the milling series of alloy 6 and exhibits a weakly pronounced tendency to decrease in the case of alloy 8; however, the changes in its mass fraction lie within the margin of the experimental error.

Mechanical activation for 60 min led to a significant change in the shape of diffraction spectra of both

Table 4. X-ray characteristics of $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x\text{N}_y$ nitrides in the initial state and after various modes of mechanical activation processing

Sample no.	Time of mechanical activation, min	Phase content in the nitriding product, wt %			Parameters of the unit cell of 2 : 17 : N phase, Å		Volume of the unit cell of 2 : 17 : N phase, Å ³
		2:17:N	SmN	α -(Fe, Al)	<i>a</i> , Å	<i>c</i> , Å	
6	0	68	2	30	8.770 (8)	12.765 (1)	848.4
	15	72	2.5	25.5	8.771 (3)	12.764 (6)	849.1
	30	72.5	3	24.5	8.770 (7)	12.767 (2)	848.5
	45	73	2	25	8.771 (3)	12.766 (1)	848.9
	60	70.5	1.5	28	8.772 (1)	12.765 (5)	849.3
8	0	93	1	6	8.781 (8)	12.779 (1)	854
	15	94	1	5	8.781 (4)	12.778 (5)	853.8
	30	95	1	4	8.782 (9)	12.777 (2)	853.2
	45	92.5	1.5	6	8.782 (5)	12.778 (6)	852.8
	60	92	1.5	6	8.781 (3)	12.778 (4)	853

Table 5. Magnetic properties of the powders of samples 8 and 9 before (*) and after (**) mechanical activation

Sample no.	Time of mechanical activation, min	Particle size (SEM), μm	jH_c , kA/m	σ_r , A m ² /kg	σ_s , A m ² /kg	σ_r/σ_s	σ_s of 2 : 17 : N*** phase, A m ² /kg
6	0	up to 70–90 and less	56	—	112	—	74
	15	≤ 6	89	26	90	0.29	50.6
	30	≤ 10	101	27.5	89.6	0.30	52.6
	45	≤ 8	106	27.7	88.1	0.31	48.8
	60	≤ 7	91.4	19.6	62.7	0.31	5.5
8	0	up to 200 and less	12.5	—	47.2	—	37.8
	15	≤ 5	20.5	4.4	33.4	0.13	39.5
	30	≤ 7	21.7	5.3	36	0.15	40.8
	45	≤ 6.5	23.7	6	37	0.16	37.4
	60	≤ 6	23	5.7	31.5	0.18	20.5

* The values of σ_s were measured in magnetic fields of 9 T at room temperature.

** The values of σ_s were measured in magnetic fields with intensity reaching 2 T at room temperature.

*** The values of σ_s were calculated using Eq. (1).

nitrides; in particular, the lines of the main phase became broader. However, certain differences between them are observed. Thus, in the case of sample 6, the intensities of lines at $2\theta = 48.3^\circ$ and 49.6° became equal. At the same time, almost no changes in the SmN and α -(Fe, Al) phases are observed: their mass fractions and intensities of lines became a bit lower as compared to the nitrides after mechanical activation during a lower processing time (Table 4).

Mechanical activation for 60 min led to the increase in coercive force (owing to the decrease in the average size of particles) at the simultaneous decrease in the specific saturation magnetization (Fig. 4, Table 5), which is in accordance with the existing concepts of the influence of milling of Sm–Fe–N nitrides on the processes of nucleation and growth of the domains of the reverse magnetization [13, 14]. However, the further increase in the time of mechanical activation leads to the worsening of the magnetic properties of nitrides: the value of jH_c starts to drastically decrease.

In case of powders of sample 8, the tendency to amorphization registered according to the emergence of halo and broadening of diffraction lines of the 2 : 17 phase is also observed after mechanical activation lasting for more than 45 min. However, generally, it hardly influenced the intensity of the lines of the alloy's phases. Mechanical activation leads to the increase in saturation magnetization and coercive force of the powders as the time of mechanical activation is raised and the average size of the particles becomes smaller. However, the coercive force of sample 8 starts increasing at a simultaneous decrease in the specific magnetization as opposed to sample 6. It is interesting to mention that this inverse effect is observed even at a low content of the soft magnetic α -Fe-based phase. One can suppose that this phenomenon is related to the high concentration of nonmagnetic aluminum in

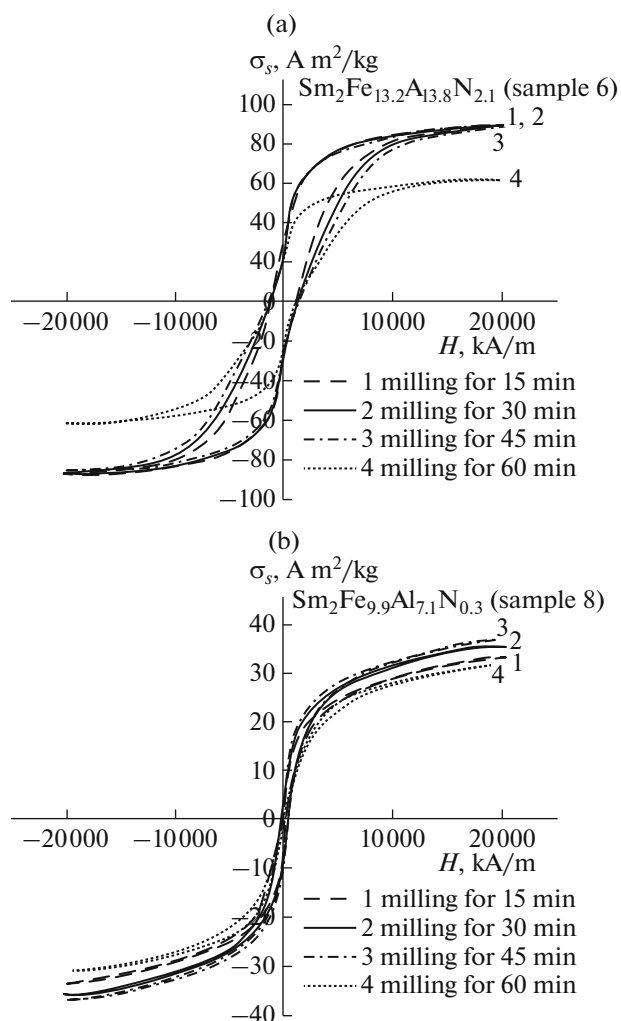


Fig. 4. Loops of magnetic hysteresis of nitride samples 6 (a) and 8 (b) after disintegration in the mill for 15, 30, 45, and 60 min measured in a field of 20 000 kA/m at room temperature.

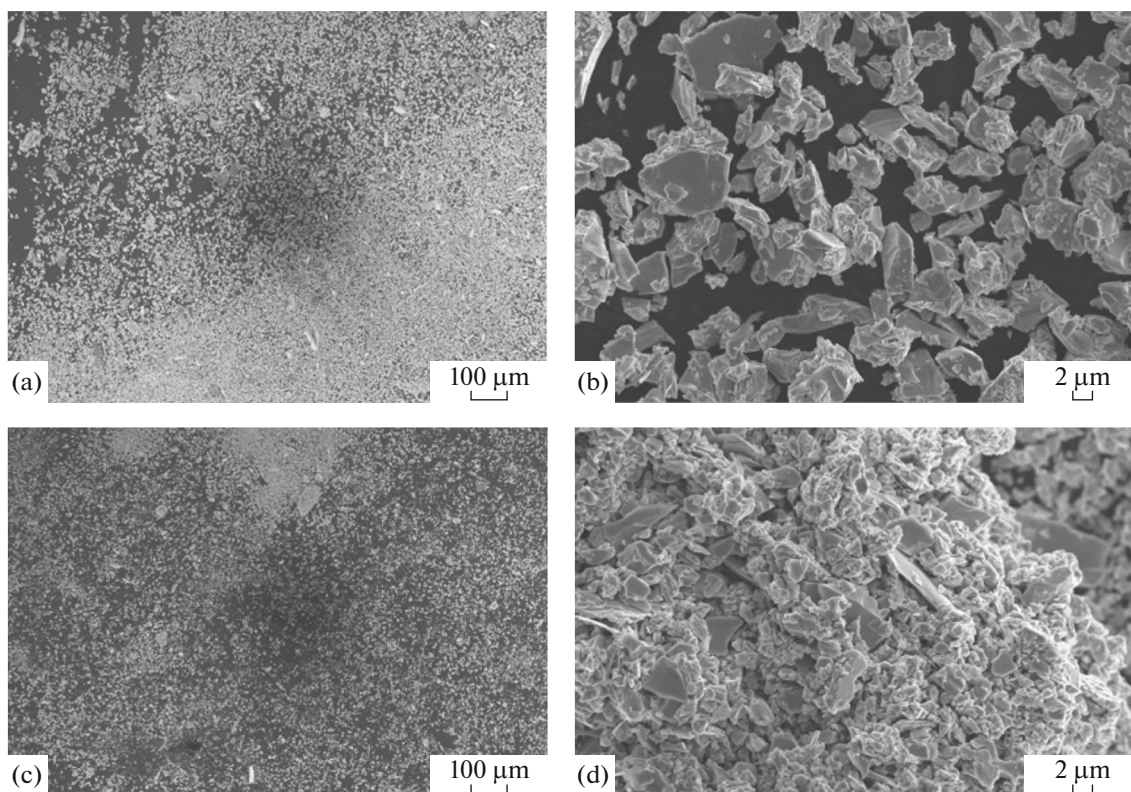


Fig. 5. SEM images of samples 6 (a, b) and 8 (c, d) after ball-milling for 60 min.

the sample, which predominantly determines the decrease in hysteresis properties of the initial and mechanically activated nitrated alloy, providing the deviation of the behavior of hysteresis properties of powders of $\text{Sm}_2\text{Fe}_{17}\text{N}_{3-\delta}$ alloys from the typical one after increasing the time of mechanical activation.

Figure 5 shows SEM images of the powders of nitrides 6 and 8 mechanically activated for 60 min obtained with a scanning electron microscope. It is seen that the samples are composed of agglomerates formed by a huge amount of chaotically oriented particles contacting each other.

Generally, the parameters and volume of the unit cell remain almost constant as the milling time is raised. No structure modification is observed.

CONCLUSIONS

The completed studies made it possible to establish the following:

(1) Replacement of iron with aluminum in $\text{Sm}_2\text{Fe}_{17}$ leads to the increase in the unit cell volume; introduction of nitrogen into the lattice of quasi-binary $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x$ intermetallics provides an additional increase in the lattice parameters. However, the amount of absorbed nitrogen and the value of the relative increase in the unit cell volume $\Delta V/V$ decrease as

the concentration of aluminum in the 2 : 17 phase is raised.

(2) Mechanical activation of Sm–(Fe, Al) nitrides does not cause any modification of the structure of the material but affects their magnetic properties. An insignificant increase in jH_c along with a tendency toward the decrease in the specific saturation magnetization and particle sizes as the time of mechanical activation is raised is observed in the sample containing 18.6 at % Al. The increase in aluminum concentration in the sample containing a lower amount of soft magnetic α -Fe phase leads to the emergence of magnetic behavior which is not typical of ferromagnetic: the coercive force increases at the simultaneous increase in the values of the specific saturation magnetization.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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