Study of phase composition, structure and magnetic properties of high-coercivity alloys based on Sm$_2$Fe$_{17}$ system depending on technology of their manufacture.

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Abstract. The article presents technologies of production and treatment of sintered magnetically hard alloys based on the Sm$_2$Fe$_{17}$ system with the subsequent nitriding of the powder. Methods of an electronic microscopy, X-ray and metallography were used to study the microstructure and phase composition of the alloys immediately after smelting and after homogenizing. The optimum homogenizing regime was established. The influence was investigated of nitriding regimes on the phase composition of the synthesized Sm$_2$Fe$_{17}$N$_x$ nitride. The optimum regime of a nitriding was found. The optimum regime of powder grinding and the optimum size of particles were established.

1. Introduction

Permanent magnets based on the Rare Earth-3d-metal intermetallic are widely used a long time ago as elements of modern high-precision smart systems for radiolocation, aircraft and missile controlling, electro-drive and actuators, etc. During recent years there is a widespread meaning concerning the weak prospects in improving of the magnetic property level for existing permanent magnet materials. Therefore, the development of the said industry branches is possible with the provision of new materials for permanent magnets. The increase of permanent magnet energy product has a significant impact on the possible application fields. In order to achieve minimal weight/dimension parameter of device or equipment the permanent magnet must show the highest magnetic energy (maximal energy product). Aiming to that one must seek for new materials possessing high magnetic crystal anisotropy and high magnetic induction, since these two characteristics are determining the value of area under magnetic hysteresis loop, i.e. the magnetic field energy stored by given permanent magnet.

Nowadays permanent magnets based on SmCo$_5$ [1, 2], Sm$_2$Co$_{17}$ и Nd$_2$Fe$_{14}$B [3, 4] compositions are the most widely in various applications. Since 1984 (the appearance of Nd$_2$Fe$_{14}$B) there are no fundamentally new intermetallic compounds or alloys which could be proposed for industry. The highest magnetic energy product has been obtained in the sintered magnets based on the Nd$_2$Fe$_{14}$B boride. From the other hand, material having optimal combination of characteristics is still the SmCo$_5$ compound: the coercive force of the SmCo$_5$ is essentially the same as for Nd$_2$Fe$_{14}$B magnets, while Curie point is significantly higher for SmCo$_5$ magnets. During recent years the search of new prospective compounds with high magnetic anisotropy are conducting, these researches are focused mainly in the field of carbides, nitrides, and borides of transition metals by the similarity with the
Nd$_2$Fe$_{14}$B boride. Among the investigated compounds, the ternary Sm$_2$Fe$_{17}$N$_x$ nitride ($2<x<3$) is the prospective candidate [1].

This nitride is concurred with Nd$_2$Fe$_{14}$B, first of all due to higher Curie point (749 K instead of 588 K) with comparable magnetic saturation $\mu_0M_s$ values (1.52 T for nitride and 1.61 T for boride). Magnetic anisotropy constant, which is determining a possible value of coercive force, much higher for nitride (8.6 MJ/m$^3$ against 4.9 MJ/m$^3$). In comparing with SmCo$_5$ and Sm$_2$Co$_{17}$ magnets the Sm$_2$Fe$_{17}$N$_x$ nitride is prevailing by saturation magnetization (1.05, 1.3 and 1.52 T accordingly), and has a lower cost due to the Co absence and lower content of the rare earth metal by formula unit.

The main obstacle to create the permanent magnet based on the Sm-Fe-N system is then low thermodynamic stability of the Sm$_2$Fe$_{17}$N$_x$ nitride: above 500°C Sm$_2$Fe$_{17}$N$_x$ is decomposing into a-Fe and the stable SmN$_3$ nitride. Due to this, the sintering operation of powder compact is completely excluded, and nowadays only plastic bonded magnets with the obviously low magnetic induction are fabricated from this nitride. Consequently, timely problem is the search of new compacting and densification techniques for fine powders without high temperature sintering operation is of current importance. In addition, relevant objective is the development of technology for the synthesis of Sm$_2$Fe$_{17}$N$_x$ compound in powder form, and basic technology for processing powder into finished magnetic products, since in the world so far permanent magnets are not produced from this compound except resin-bonded magnets in Japan.

Nitrogen forms a solid interstitial solution with a solvent, which leads to the creation of uniaxial magnetic anisotropy in zone of its introduction and thus allows obtaining a material with high coercive force and magnetic texture. For hard-magnetic materials, residual magnetization reaches the highest values along the axis of the magnetic texture.

The purpose of this work is to study structure and magnetic properties of powder alloys based on the Sm$_2$Fe$_{17}$ system, followed by nitriding of the powder, at various stages of their manufacture to create an economical hard-magnetic alloy with high magnetic characteristics.

2. Methods

Magnets based on rare-earth metals was manufactured using powder metallurgy technology, involving the following steps:

- ingot melting from pure components or with a ligature by induction melting methods;
- homogenization of ingots with subsequent cooling at different rates;
- crushing of ingots into pieces, and then into powder to size of 0.5 - 1 mm;
- milling of powders in a liquid medium - isopropyl alcohol, freon-113 or toluene;
- nitriding of powder;
- pressing of powder in a magnetic field;
- magnetization and measurement of magnetic characteristics.

The alloy was melted by induction melting method in argon atmosphere. Elementary Sm and Fe of 99.99% purity were used as charge materials. Samarium in the form of pieces 20-50 mm in size was added in prepared iron melt. Three compositions (table 1) of peristoichiometric and two preostoichiometric (24.2, 26.8 and 29.4 wt. %) were melted. After melting, the alloys were homogenized in vacuum at a single-phase temperature of 1100°C for 30 hours with subsequent cooling at different conditions.

After milling, powders were nitrated at different temperatures and nitriding times. The powder was placed in a vacuum furnace, heated to temperature of 100°C, and the samples were dried from the milling medium for 2 hours. To remove residual vapors, the furnace was heated to 200°C and held for one hour with pumping by fore vacuum and diffusion pumps.

The chemical composition of ingots was measured by the plasma method on “OAE-MSA-SMR” spectrometer and a Rigaku X-ray fluorescence spectrometer.
Metallographic analysis was carried out using ZEISS AXIO SCOPE A1 light microscope and JSM-6610LV scanning electron microscope to study microstructure of the melted and homogenized Sm$_2$Fe$_{17}$ alloy.

Samples were ground roughly by grinding wheel, afterwards they were carried to state, where scratches were not visible on non-etched sample, by emery paper of different roughness (from 400 to 1500).

Metallographic analysis were carried out using Neophot 30 light microscope. Metallographic sections were made by standard methods using an automatic press from Struers-ProntoPress-2 and a grinding and polishing machine from Struers-Planopol-2.

The microstructure was detected by etching sections in a 3% alcoholic solution of nitric acid; the etching time was 5–15 sec.

Phase identification and quantitative phase analysis were performed using X-ray diffraction analysis using the Rietveld method on a DRON-3M diffractometer in monochromatic CoKα radiation (wavelength λKα = 0.1790 nm) at angles of 20–120 °, exposure time – 3 s.

Magnetic properties were measured using a MH-50 hysteresis graph.

| Melting No. | X-ray diffraction method | Spectral method |
|------------|--------------------------|-----------------|
|            | Sm                      | Fe              | Sm           | Fe           |
| 1          | 24,2 ± 2                 | 75,8 ± 2        | 23,68 ± 0,5  | 76,32 ± 0,2  |
| 2          | 26,1 ± 2                 | 73,9 ± 2        | 25,35 ± 0,5  | 74,65 ± 0,2  |
| 3          | 29,8 ± 2                 | 70,2 ± 2        | 29,00 ± 0,5  | 71,00 ± 0,2  |
|            | Stoichiometric compound  | 24,06           | 75,94        |
|            | of Sm$_2$Fe$_{17}$        |                 |              |

3. Results and discussion

The intermetallic compound Sm$_2$Fe$_{17}$ was melted in induction furnace in an argon atmosphere. Charge composition was calculated from stoichiometry of compound Sm$_2$Fe$_{17}$ and the need to obtain three alloys of a given composition (table 1). Due to the high volatility of samarium, it is possible to evaporate it from loading material, so when charge calculation was carried out, its 5% excess for burning was taken into account. The large difference in the melting points of the components (for Fe – 1539°C, for Sm – 1072°C) makes it necessary to carefully design the process of melting Sm$_2$Fe$_{17}$ ingots.

In this work, we used a scheme that found application in melting of KS25DC permanent magnets in JSC “Spetsmagnit” – pieces of iron 10-20 mm in size are loaded into the crucible, they are melted, and after a short delay samarium is added to the melt.

After multiple remelting, homogenizing annealing was performed, since the Sm$_2$Fe$_{17}$ compound is formed by peritectic reaction between Sm-Fe liquid phase and γ-Fe phase at a temperature of 1177°C (figure 1).
Figure 1. Phase diagram of the Fe-Sm system.

Therefore, to increase the amount of Sm$_2$Fe$_{17}$ phase in the ingot, alloys were subjected to prolonged homogenizing annealing in a vacuum furnace SNVE-1.3.1/16 in argon atmosphere at a temperature of 1100ºС for 10 hours, cooling from the homogenization temperature was performed at different rates (cooling in water, helium or in calm air).

Table 2 presents results of X-ray structural phase analysis of three alloys after homogenization.

| Sample No. | Volume percentage of phases, % | Sm$_2$Fe$_{17}$ | α-Fe | SmFe$_2$ | SmFe$_3$ |
|------------|--------------------------------|----------------|------|---------|---------|
| Air cooling |                               |                |      |         |         |
| 1          | 96,5 ± 3                       | 3,5 ± 1        | -    | -       | -       |
| 2          | 98,8 ± 3                       | 1,2 ± 1        | -    | -       | -       |
| 3          | 81,1 ± 3                       | -              | 10,5 ± 1 | 8,4 ± 1 |
| Quenching in helium |                       |                |      |         |         |
| 1          | 97,3 ± 3                       | 2,7 ± 1        | -    | -       | -       |
| 2          | 99,0 ± 3                       | 1,0 ± 1        | -    | -       | -       |
| 3          | 82,6 ± 3                       | -              | 9,5 ± 1 | 7,9 ± 1 |
| Water quenching |                       |                |      |         |         |
| 1          | 98,1 ± 3                       | 1,9 ± 1        | -    | -       | -       |
| 2          | 99,1 ± 3                       | 0,9 ± 1        | -    | -       | -       |
| 3          | -                              |                |      |         |         |
From table 2 it can be seen that even in the alloy of stoichiometric composition from charge, the elementary iron remains regardless of the method of cooling after homogenization. In alloys of prestoichiometric and stoichiometric compositions, the elementary iron always remains regardless of the time of the homogenizing annealing.

In the highly enriched Sm alloy, phases SmFe$_3$ (8.4 vol %) and SmFe$_2$ (10.5 vol.%) are observed, which are formed by peritectic reactions at temperatures of 1010°C and 900°C, respectively. In [5], it was found that in such alloys areas of metallic samarium, which are the last portions of liquid between solidified dendrites, could remain.

Solving the problem of the presence of pure samarium in samples after homogenization is possible by quenching the alloy from the homogenization temperature in He atmosphere or in water. There is also the option of obtaining the initial ingot using low-melting ligatures. In this case, a ligature of eutectic composition (72.5 at. % of Sm) was used. The microstructure of the eutectic alloy are shown in figures 2-4.

**Figure 2.** The microstructure of alloy Sm-Fe eutectic composition at different magnifications.

Two-phase alloy contains a bright area of eutectic and dark inclusions. Composition of each phase was measured by VEGA3 TESCAN scanning electron microscope, hereafter the average results of measurements series (at least three) for each component are given, the error of the method is 5%. Dark inclusions (figure 3a) are the phase of pure elementary Sm. The presence of insignificant amount of Cl and S in all inclusions (figure 3b) is not critical and is associated with etching during sample preparation; this also explains the large amount of oxygen (0.3 wt. %) in pure samarium area. The presence of aluminum in the sample is caused by its diffusion into the melt from the crucible during the melting of charge materials.
Figure 3. Local chemical analysis of dark inclusions of Sm-Fe eutectic composition: a) the microstructure of ingot and survey area; b) energy dispersive spectrum from selected area.

Figure 4. Local chemical analysis of dark inclusions of Sm-Fe eutectic composition: a) the microstructure of ingot and survey area (pink square); b) energy dispersive spectrum from selected area.

Melting of the alloy, slightly enriched in samarium with obtained ligature, showed absence of a pure Sm phase (figure 5). Microstructure analysis of alloy and the determination of the elemental composition were carried out on Tescan Vega LMU electron microscope using DryCool and X-max 80 Oxford Instruments energy dispersive spectrometers.

Three structural phase components (table 2) were observed: α-Fe (dark gray dendrites), intermetallic compound SmFe₃ (light crystallites) and Sm₂Fe₁₇ (light gray matrix).
Figure 5. Microstructure images of Sm-Fe alloy with a pre stoichiometric composition melted with a ligature: a) SEM, magnification x500; b) SEM, magnification x1900.

Thus, alloy melting with ligature solves the problem of residual samarium, however it is still necessary to carry out the process of homogenization. The phase composition of stoichiometric composition alloy melted with ligature is $\text{Sm}_2\text{Fe}_{17} = 99.3 \pm 3 \text{ wt.} \%$, $\alpha$-Fe $= 0.7 \pm 1 \text{ wt.} \%$. The increase in number of the target phase compared with homogenizing annealing followed by quenching in water is insignificant. Further, all technological operations and investigations were carried out on alloy 2, melted using a low-melting alloy of eutectic composition and annealed at temperature of 1100ºС for 10 hours with subsequent quenching in water.

After carrying out homogenizing annealing, samples were milled in M-35 ball vibratory mill in ethyl alcohol medium for various milling times. Determination of the average particle size was performed by laser diffraction and gas permeability using Fritsch Analysette-22 Nanotech and PSKh-1, PSKh-10a, respectively. The graphical dependence of change in average particle size on milling time is shown in figure 6.

Figure 6. Dependence of average particle size of powder on milling time in ethyl alcohol medium.
As can be seen from figure 6, the average particle size of the powder (dav) is intensively reduced during the first 20 minutes, with further milling, a slight decrease in dav is observed.

Differences in values of average particle diameter at the point prior to the start of milling on PSKh-type devices are explained by differences in methods of creating a vacuum in the measuring volume. PSH-1 device uses scheme with a water-jet pump, which has greater efficiency, and, as a consequence, the ability to pump out the measuring chamber with a coarsely dispersed powder. PSH-10a pumps out the working volume with a low-power vacuum pump, which greatly increases pumping time and gives slightly overestimated values in the case of measuring coarsely dispersed powder. By virtue of the above, it can be assumed that measurement values of average particle diameter before milling should be taken from the values obtained on PSKh-1.

In general, the indicated values of devices based on the principle of gas permeability, have a satisfactory convergence between themselves, especially in the range of low values of average diameter.

The dav value curve taken on Fritsch Analysette-22 Nanotech shows higher values than gas permeability method (darkened area in figure 6). Detailed analysis of the Mie theory and differences between methods suggests that spontaneous magnetization of powders and their partial agglomeration occur during milling process. Such agglomerates do not disintegrate during sonication and they are recorded in the laser diffraction method as a single particle having the size of the agglomerate. To confirm this hypothesis, study of powder microstructure after grinding them on scanning electron microscope was made. Photos of microstructures are presented in figure 7.

For more detailed picture of the distribution of powders in size, samples were photographed with different magnifications. Powder particles have angular high-energy edges, which theoretically facilitates nitrogen adsorption to surface, and, as a result, accelerates the process of nitriding.

The photographs presented in figure 7 show clusters of particles and their partial agglomeration. Smaller powder particles adhere to larger particles — in figure 7 (a) (milling for 20 minutes), particles of about 12–20 nm in size are seen, formed agglomerate particles around a larger particle is about 50 nm.

![Figure 7. Agglomeration of nanoparticles on particles of micron scale: (a) magnification x1500; (b) magnification x2000.](image)

It should be noted that indicated values of devices like PSKh do not depend on agglomeration phenomena, since the “adhering” of particles does not affect gas permeability of measured sample.

The process of nitriding is more efficient if particle distribution have monosize nature and the dispersion values of particles are minimal. Histograms of particle size distribution for different milling times were obtained using method of laser diffraction based on Mie theory.
It is important to note that above studies refer to the material from tumbling milling equipment. On any type of mill, after carrying out the process, unmilled alloy particles with sizes ranging from 40 to 300 \( \mu \text{m} \) remain on the walls of the inner surface. With increase in milling time, these particles do not change much in their size, and some of them fall into sample amount of future pressed compact. Solution of this problem is possible by using a special particle classifier used in some manufacturers of permanent magnets. However, the volume fraction of such particles is small and the presence of an insignificant amount in sample is recognized as acceptable.

The change in phase composition of the samples after nitriding is shown in Figure 8. It can be seen that samples containing elementary \( \alpha \)-Fe, after nitriding, have a smaller volume fraction of the \( \text{Sm}_2\text{Fe}_{17}N_x \) phase than in the sample with a prestoichiometric composition. Perhaps \( \alpha \)-Fe acts as a catalyst for decomposition of already formed \( \text{Sm}_2\text{Fe}_{17}N_x \) nitride by a chemical reaction:

\[
2\text{Sm}_2\text{Fe}_{17}N_3 \rightarrow 2\text{SmN} + \text{Fe}_4N + 13\text{Fe}
\]

(1)

The products of this reaction (1) in form of \( \alpha \)-Fe, \( \text{Fe}_4N \) and \( \text{SmN} \) adversely affect magnetic properties of obtained samples.

![Figure 8](image)

**Figure 8.** Dependence of change in content of nitride \( \text{Sm}_2\text{Fe}_{17}N_x \) on nitriding temperature.

The X-ray diffraction patterns of samples with the highest percentage of \( \text{Sm}_2\text{Fe}_{17}N_x \) nitride and fully decomposed \( \text{Sm}_2\text{Fe}_{17}N_x \) on \( \alpha \)-Fe, \( \text{Fe}_4N \) and \( \text{SmN} \) are shown in Figures 9 and 10, respectively. The diffraction pattern of completely decomposed samples is simple and it is calculated with greater accuracy. The spectra of powders containing \( \text{Sm}_2\text{Fe}_{17}N_x \) phase have a large number of peaks and it is calculated with accuracy of \( \pm 3\% \) for \( \text{Sm}_2\text{Fe}_{17}N_x \) phase and \( \pm 1\% \) for residual phases.
The highest nitrogen content was achieved on samples nitrided at temperature of 400ºС for 7 hours; the volume fraction of Sm$_2$Fe$_{17}$N$_x$ nitride was 94.3%.

Sm$_2$Fe$_{17}$ compound is a soft magnetic material; the introduction of nitrogen atoms changes the phase anisotropy type from planar to uniaxial, which transform the material to hard-magnetic one. The Sm$_2$Fe$_{17}$N$_x$ phase is interstitial solution; when nitrogen introduced into the lattice, Sm$_2$Fe$_{17}$ increases lattice parameters (figure 11). The change in periods of unit cell can show average number of nitrogen atoms per formula unit of Sm$_2$Fe$_{17}$.

From figure 11, it is clear that the larger average number of nitrogen atoms per formula unit Sm$_2$Fe$_{17}$, the greater the increase in lattice periods (and the increase in value of crystal anisotropy, respectively), the c/a ratio remains almost unchanged. Average number of nitrogen atoms per Sm$_2$Fe$_{17}$ formula unit depending on the nitriding temperature was determined using periods of Sm$_2$Fe$_{17}$N$_x$ crystal lattices determined during the X-ray diffraction analysis (Figure 12). The greatest number of nitrogen atoms x was reached at nitriding temperature of 470–480ºС for 7 hours and equals 2.8 atoms per unit cell of Sm$_2$Fe$_{17}$, the error in determining x value was ±0.005 nm (±0.05 Å). In samples with the highest
x, the best combination of magnetic properties should be expected with the same phase composition and microstructure.

![Figure 12](image-url)

**Figure 12.** The effect of nitriding temperature on the average number of nitrogen atoms in the Sm$_2$Fe$_{17}$ unit cell

Measurements of magnetic properties were carried out on compacts obtained by isostatic pressing in a polyurethane sleeve. When pressing, the powders were textured with a magnetic field of 1.1 T, direction of application of magnetic field in the scheme was coaxial to direction of pressing. After precompaction, sample was additionally compacted in a special press mold with a polyurethane sleeve, which allows isostatic compression of samples with simultaneous axial deformation along the direction of magnetization of samples.

The best combination of hysteresis properties was achieved on samples nitrated at a temperature of 470°C for 7 hours, which are characterized by the maximum nitrogen content (x=2.8) in Sm$_2$Fe$_{17}$N$_x$ compound. Following magnetic properties were obtained on magnets pressed with a hydrostatic pressure of 14000 atm.: $H_{cb} = 4.6$ kOe, $B_r = 4.3$ kGs.

4. Conclusions

1. After melting alloys using a low-melting ligature of eutectic composition and carrying out homogenizing annealing at a temperature of 1100°C for 10 hours, in structure of stoichiometric and stoichiometric alloys, metallic Sm and SmFe$_2$ and SmFe$_3$ phases do not remain; insignificant content of primary iron secretion remains.

2. With an increase in the duration of milling, average particle size of powder ($d_{av}$) decreases rapidly during the first 20 minutes to a value of 5.1 μm; with further milling slight decrease in $d_{av}$ up to 3 microns after 70 min milling is observed.

3. The highest content of the phase Sm$_2$Fe$_{17}$N$_x$ (94.3 vol. %) is achieved at nitriding temperature of 450°C for 7 hours.

4. The best combination of hysteresis properties was achieved on samples nitrated at temperature of 470°C for 7 hours, which corresponds to the maximum nitrogen content (x=2.8) in Sm$_2$Fe$_{17}$N$_x$ compound. For the first time, the following magnetic properties were obtained on compact magnets without alloying elements: $H_{cb} = 4.6$ kOe (366 kA/m), $B_r = 4.3$ kGs (0.43 T).

5. References:

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