MAGNETIC PROPERTIES OF NITRIDES Sm_2Fe_{17} COMPOUND AFTER SEVERE PLASTIC DEFORMATION BY TORSION AT 77K

[1]Igor SHCHETININ, [1]Igor BORDYUZHIN, [1]Vladimir MENUSHENKOV, [2]Roman SUNDEEV, [1,3]Anton KAMYNIN, [4]Viktor VERBETSKII, [1]Alexander SAVCHENKO

[1]*National University of Science and Technology «MISiS», Moscow, Russian Federation, ingvar@misis.ru*

[2]*Moscow Technological University, «MIREA», Moscow, Russian Federation*

[3]*JSC "Spetsmagnit", Moscow, Russian Federation*

[4]*Lomonosov Moscow State University, Moscow, Russian Federation*

https://doi.org/10.37904/metal.2019.857

Abstract

Using X-ray diffraction analysis, scanning electron microscopy and magnetic properties analysis the Sm_2Fe_{17} compound nitrides after severe plastic deformation by torsion at a temperature of 77K were studied. It was shown that severe plastic deformation led to the structure refinement without the formation of new phases. A decrease in grain size led to coercivity increase up to 235.2 kA/m/2.94 kOe and a residual magnetization increase up to 53 A×m^2/kg.

Keywords: Magnetic properties, nitride, intermetallic, permanent magnets, severe plastic deformation

1. INTRODUCTION

Since the discovery of the Sm_2Fe_{17} nitrides [1], they have attracted much researchers attention because of a high Curie temperature [2], a high constant of magnetocrystalline anisotropy [3], better resistance to oxidation, a lower content of rare-earth (RE) metals and lower cost of Sm than other RE metals, first of all Nd and Dy. All this makes the Sm_2Fe_{17} compound nitrides promising for the production of permanent magnets with better performance and economic characteristics than the $Nd_2Fe_{14}B$ compound [3]. However, over the past thirty years, permanent magnets based on the Sm_2Fe_{17} nitrides with properties higher than those based on the Nd-Fe-B system have not succeeded.

The main research ways in this area are methods for producing nitride particles of the Sm_2Fe_{17} compound with dimensions of not more than 1 µm for obtaining high values of the coercivity, as well as preferential orientation of the particles for obtaining a rectangular hysteresis loop. For obtaining these materials the reduction-diffusion methods [5] have been used. Methods of ball millimg [6,7] are also often used to obtain dispersed particles for the exchange-coupled state [8,9]. Usually the process is carried out at low temperatures [10] to suppress the decomposition of nitrides. For sintering powder materials, spark plasma sintering [11,12], explosive pressing [13], sintering with low-melting additives [14] and eutectics [15] have been used. However, all sintering processes lead to the decrease of the coercivity and residual magnetization. One of the methods for obtaining a bulk state represents severe plastic deformation, which can lead to welding effects [16] and texture formation [17], which was observed in other systems based on RE elements for permanent magnets. In this regard, the study of magnetic properties changes in the process of severe plastic deformation in order to obtain bulk materials with high values of coercivity is an aktual task.

2. MATERIALS AND METHODS

The alloys of the Sm-Fe system were obtained by the induction melting from pure components Sm (99.9 wt.%) and Fe (99.9 wt.%). After melting, the ingots were subjected to homogenization annealing at 1100 °C for 40 hours. Next, the ingots were subjected to grinding and repeated hydrogenation-dehydrogenation procedure in order to increase the free surface. Hydrogenation was carried out at room temperature and a hydrogen pressure 15 atm. After the hydrogenation-dehydrogenation procedures, the alloys were subjected to nitriding in a nitrogen atmosphere at a temperature 450 °C for 40 hours before the cessation of gas absorption. The nitrides obtained after nitriding were subjected to severe plastic deformation by torsion in the Bridgman anvil with a pressure of 6 GPa at a temperature -196 °C (77 K) and a punching speed of N = 3 and 5. Materials were studied by X-ray diffraction on a Rigaku Ultima IV diffractometer using CoK_α radiation and graphite monochromator. The analysis of the spectra including the analysis of the broadening of diffraction lines was performed using the PDXL2 software package (Rigaku). To study the structure of materials, scanning electron microscopy was used on a TescanVega 3SB microscope. Studies of magnetic properties were carried out at a physical quantity measurement (PPMS, EverCool II, Quantum Design) facility in fields up to 7.2 MA/m (90 kOe) and at temperatures of -268 and 27 °C (5 and 300 K).

3. RESULTS AND DISCUSSION

According to the XRD phase analysis data the alloys after melting and homogenization were single-phase state containing Sm_2Fe_{17} phase (R-3m). The results of the determination of the lattice spacing and the main magnetic characteristics are given in **Table 1**. The nitriding of the alloys led to a strong change in the lattice periods of the Sm_2Fe_{17} (R-3m) phase without changing the phase composition. The volume effect of the Sm_2Fe_{17} (R-3m) phase associated with nitriding before and after nitriding was 7.6 % (by measuring the lattice spacing), which according to literature corresponds to the formation of $Sm_2Fe_{17}N_x$ nitride (where x ≈ 2.8) [18,19]. According to the measurement of magnetic properties (**Table 1**), nitriding did not lead to the coercivity increase. However, the anisotropy field of the $Sm_2Fe_{17}N_{2.8}$ phase and saturation magnetization increased [18], by the analysis of of the magnetization curve form (**Figure 1**).

Table 1 The results of phase analysis and the magnetic properties measurements of the alloys after smelting and homogenization, nitriding.

Sample	Phase composition, %	Lattice spacing, Å	H_c, kA/m (Oe)	σ_r, A·m²/kg	σ_s, A·m²/kg
Sm2Fe17	Sm2Fe17 - 100	a = 8.552 ± 0.001 c = 12.444 ± 0.001	2.0 ± 0.8 (25 ± 10)	3 ± 1	138 ± 1
Sm2Fe17N2.8	Sm2Fe17 - 98 ± 1	a= 8.739 ± 0.001 c = 12.685 ± 0.001	16 (200 ±)	10 ± 1	149 ± 1
	α-Fe - 2 ± 1	2.866 ± 0.001			

Alloy powders were used as raw materials for severe plastic deformation. Severe plastic deformation by torsion led to the formation of disks with a diameter of 10 mm and a thickness of 0.5 - 1 mm.

According to the XRD phase analysis data severe plastic deformation at -196 °C (77 K) did not led to a change in the phase composition and decrease in the lattice periods of the phase (**Table 2** and **Figure 2**). According to the analysis of the broadening of diffraction lines, severe plastic deformation led to a strong decrease in crystallite size to 20 nm for n = 3 and 15 nm for n = 5 (**Table 2**). There were no texture or predominant grain orientation detected on XRD patterns after severe plastic deformation.

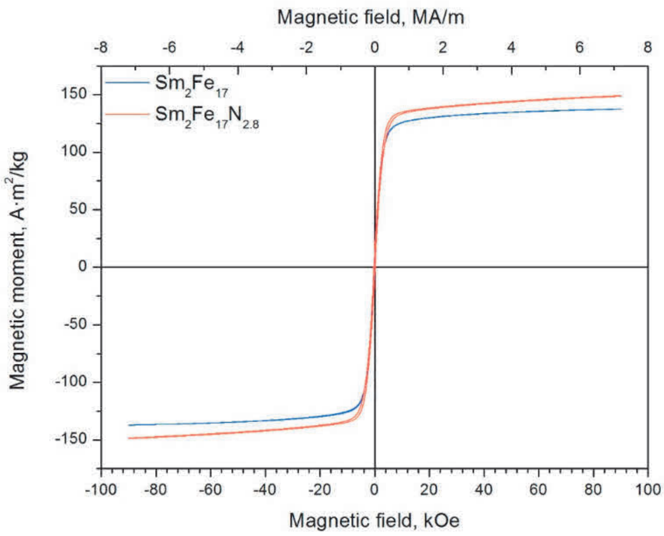

Figure 1 Magnetic hysteresis loops of alloys after melting and homogenization, nitriding

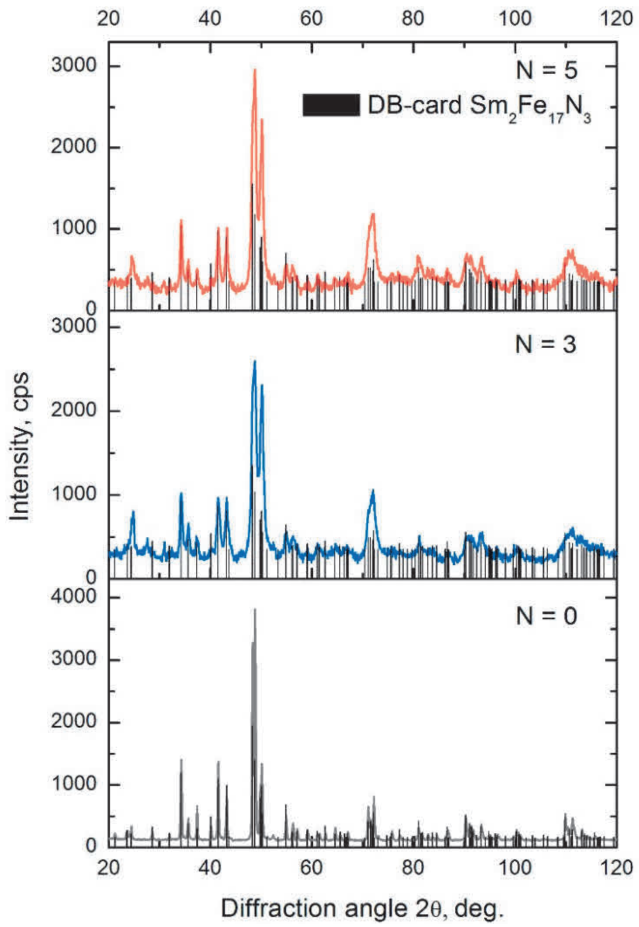

Figure 2 XRD patterns of $Sm_2Fe_{17}N_{2.8}$ alloys after severe plastic by torsion with N = 0, 3, 5

Table 2 The results of XRD analysis and the magnetic properties measurements of the alloys severe plastic deformation at 5 and 300K

Sample	Phase composition	Lattice spacing, Å	Crystalline size, nm/strain, %	Temperature, K	H_c, kA/m (Oe)	σ_r, A·m²/kg	σ_s, A·m²/kg
N = 3	$Sm_2Fe_{17}N_{2.8}$ 100 %	A = 8.747± 0.003 c = 12.685 ± 0.003	20 ± 1/ 0.15±0.01	5	728.0 ± 2.4 (9.10 ± 0.03)	64 ± 1	109 ± 1
				300	171.2 ± 0.8 (2.14 ± 0.01)	42 ± 1	112 ± 1
N = 5	$Sm_2Fe_{17}N_{2.8}$ 100 %	A = 8.741 ± 0.003 c = 12.675 ± 0.003	15 ± 1/ 0.20 ± 0.01	5	817.6 ± 2.4 (10.22 ± 0.03)	71 ± 1	111 ± 11
				300	235.2 ± 0.8 (2.94 ± 0.01)	53 ± 1	115 ± 1

A decrease in crystallite size led to a the coercivity and residual magnetization increase (**Table 2** and **Figure 3**). An increase in the degree of deformation led to an increase in both the coercivity and the residual magnetization. Magnetic hysteresis loops of the samples after severe plastic deformation had features associated with the presence of kink on the back of the loop. The presence of kink may be due to the fact that the deformation process does not proceed evenly throughout the material volume, so there remain areas with low deformation that behave like magnetic phases. Measurement of magnetic hysteresis loops at -196 °C (5 K) indicates that cooling causes an increase of the coercivity up to 817.6 kA/m (10.22 kOe) and the residual magnetization (up to 71 A×m²/kg) of the alloys for N = 5. It also preserved the features and a kink of the magnetic hysteresis loops, which indicates the absence of transformations in the temperature range -196 - 27 °C (5 - 300 K). The ratio of the residual magnetization to the saturation magnetization had a level lower than 0.5, which confirms the absence of texture and preferential grain orientation in the alloys after severe plastic deformation by torsion.

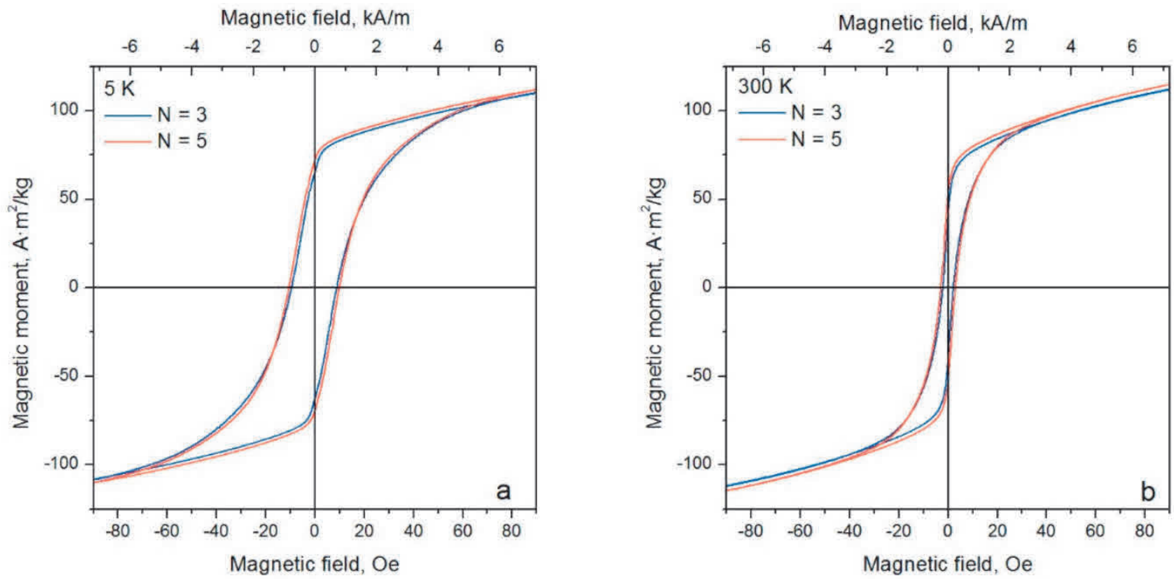

Figure 3 Magnetic hysteresis loops of $Sm_2Fe_{17}N_{2.8}$ alloys after severe plastic deformation (N = 3, 5) by torsion at 5 (a) and 300K (b)

4. CONCLUSION

In this work the nitrides of $Sm_2Fe_{17}N_x$ compound were obtained; it was established by measuring the lattice periods that the nitrogen content is $x \approx 2.8$. Volumetric discs with a diameter of 10 mm and a thickness of 0.5 - 1 mm were obtained by the method of severe plastic deformation. Intense plastic deformation led to the significant crystallite size decrease, which led to an increase in the coercivity up to 235.2 kA/m (2.94 kOe) and residual magnetization up to 53 A×m²/kg for N = 5. However, there are features on the magnetic hysteresis loops that are associated with the presence of areas with low deformation. For obtaining higher values of the coercivity, greater degrees of deformation are needed. Measurements of magnetic hysteresis loops at -196 °C (5 K) showed an increase in the coercivity, which is associated with the anisotropy field increase and the absence of transformations in the temperature range -196 - 27 °C (5 - 300 K). Measurements of magnetic properties showed the absence of texture formation and preferential orientation after severe plastic deformation, which was confirmed by X-ray diffraction data.

ACKNOWLEDGEMENTS

This research was funded by the Russian Science Foundation (RSF), grant number 18-72-00249.

REFERENCES

[1] COEY, J.M.D. and SUN, H. Improved magnetic properties by treatment of iron-based rare earth intermetallic compounds in ammonia. *Journal of Magnetism and Magnetic Materials.* 1990. vol. 87, pp. L251-L254.

[2] KOBAYASHI, K., KANEKO, K. and HAYAKAWA, K. Curie temperatures of $Sm_2Fe_{17}N_x$ (0<x<3) of intermediate nitrogen concentrations. *Journal of Alloys and Compounds*. 2006. vol. 408-412, pp. 1363-1367.

[3] LI, H.-S., HU, B.-P., COEY, J.M.D., GAVIGAN, J.P., MARUSI, G., PARETI, L. CZJZEK, G. and KMIEC, R. Large anisotropy fields in hexagonal $R_{2-x}T_{17+2x}$. *Journal of Magnetism and Magnetic Materials*. 1990. vol. 83, pp. 251-253.

[4] COEY, J.M.D., STAMENOVA, P., PORTERA, S.B., VENKATESANA, M., ZHANGA, R. and IRIYAMA, T. Sm-Fe-N revisited; remanence enhancement in melt-spun Nitroquench material. *Journal of Magnetism and Magnetic Materials*. 2019. vol. 480, pp. 186-192.

[5] OKADA, S., SUZUKI, K., NODE, E., TAKAGI, K., OZAKI, K. and ENOKIDO, Y. Preparation of submicron-sized Sm2Fe17N3 fine powder with high coercivity by reduction-diffusion process. *Journal of Alloys and Compounds*. 2017. vol. 695, pp. 1617-1623.

[6] AKDOGAN, N.G., HADJIPANAYIS, G.C. and SELLMYER, D.J. Anisotropic Sm-(Co,Fe) nanoparticles by surfactant-assisted ball milling. *J. Appl. Phys.* 2009. vol. 105, p. 07A710.

[7] MA, X.B., LI, L.Z., LIU, S.Q., HUA, B.Y., HAN, J.Z., WANG, C.S., DUA, H.L., YANG, Y.C. and YANG, J.B. Anisotropic Sm-Fe-N particles prepared by surfactant-assisted grinding method. *Journal of Alloys and Compounds.* 2014. vol. 612, pp. 110-113.

[8] O'DONNELL, K. and COEY, J. M. D. Characterization of hard magnetic two-phase mechanically alloyed Sm2Fe17N3/α-Fe nanocomposites. *J. Appl. Phys*. 1997. vol. 81, p. 6310.

[9] ITO, M., YOSHIOKA, H., MAJIMA, K., KATSUYAMA, S. and NAGAI, H. $Sm_2Fe_{17}N_x$ / a-Fe anisotropic composite powders prepared by Sm evaporation and mechanical grinding in NH_3. *Scripta Materialia.* 2002. vol. 46, pp. 695-698.

[10] FANG, Q., AN, X., WANG, F., LI, Y., DU, J., XIA, W., YAN, A., LIU, J.P. and ZHANG J. The structure and magnetic properties of Sm-Fe-N powders prepared by ball milling at low temperature. *Journal of Magnetism and Magnetic Materials*. 2016. vol. 410, pp.116-122.

[11] SAITO, T. and KIKUCHI, K. Production of SmFeN bulk magnets by the spark plasma sintering method with dynamic compression. *Journal of Alloys and Compounds*. 2016. vol. 673, pp. 195-198.

[12] ZHANG, D. T., YUE, M. and ZHANG, J. X. Study on bulk $Sm_2Fe_{17}N_x$ sintered magnets prepared by spark plasma sintering. *Powder Metallurgy*. 2007. vol. 50, No. 3, pp. 215-218.

[13] KASZUWARA, W., LEONOWICZ, M., JANUSZEWSKI, D., MENDOZA, G., DAVIES, H.A. and PASZULA, J. Consolidation of magnetic powders by shock compression, *J. Mater. Sci. Mater. Electron.* 1998. vol. 9, pp. 17-23.

[14] MATSUURA, M., SHIRAIWA, T., TEZUKA, N., SUGIMOTO, S., SHOJI, T., SAKUMA, N. and HAGA, K. High coercive Zn-bonded Sm-Fe-N magnets prepared using fine Zn particles with low oxygen content. *Journal of Magnetism and Magnetic Materials*. 2018. vol. 425, pp. 243-248.

[15] OTOGAWA, K., TAKAGI, K. and ASAHI, T. Consolidation of $Sm_2Fe_{17}N_3$ magnets with Sm-based eutectic alloy binder. *J. Alloys Compd*. 2018. vol. 746, pp. 19-26.

[16] ROMANKOV, S., HAYASAKA, Y., SHCHETININ, I.V. and YOON J.M. Joining and microstructural development of Ni-Al-Ti sheets under ball collisions. *Acta Materialia*, 2012. vol. 60, issue 5, pp. 2196-2208.

[17] MENUSHENKOV, V.P., SHCHETININ, I.V., CHERNYKH, S.V., SAVCHENKO, A.G., GORSHENKOV, M.V. and ZHUKOV, D.G. Structure and magnetic properties of the $Nd_{9.5}Fe_{84.5}B_6$ alloy subjected to severe plastic deformation and annealing. *Russian Metallurgy (Metally)*. 2017. vol. 2017, NO. 10, pp. 801-806.

[18] MENUSHENKOV, A.P., SAVCHENKO, A.G., IVANOV, V.G., IVANOV, A.A., SHCHETININ, I.V., MENUSHENKOV, V.P., RUDNEV, I.A., RAFAL'SKII, A.V., ZHUKOV, D.G., PLATUNOV, M., WILHELM, F. and ROGALEV, A. Effect of nitrogenation and hydrogenation on the magnetic properties and structure of the Sm_2Fe_{17} alloy: Analysis of XMCD data. *JETP Letters*. 2018. vol. 107, no. 4, pp. 228-232.

[19] SAVCHENKO, A.G., MENUSHENKOV, V.P., PLASTININ, A.Y., SHCHETININ, I.V., BORDYUZHIN, I.G., RYAZANTSEV, V.A., VERBETSKII, V.N. and MOVLAEV, E.A. Effect of the milling time on the magnetic properties of powder compositions of the $Sm_2Fe_{17}N_x$ intermetallic compound and an Nd-Fe-B alloy. *Russian Metallurgy (Metally)*. 2017. vol. 2017, no. 10 pp. 807-812.