Effect of solid solution treatment and nitrogenation on magnetic properties of Sm$_{2+\delta}$Fe$_{17}$N$_x$ powders

To cite this article: D Kolodkin et al 2019 J. Phys.: Conf. Ser. 1389 012125

View the article online for updates and enhancements.
Effect of solid solution treatment and nitrogenation on magnetic properties of Sm$_{2+\alpha}$Fe$_{17}$N$_x$ powders

D Kolodkin$^1$, A Popov$^{1,2}$, A Protasov$^{1,2}$, V Gaviko$^{1,2}$, S Kavita$^3$, D B Prabhu$^3$, R Gopalan$^3$

$^1$ M.N. Mikheev Institute of Metal Physics of Ural Branch of Russian Academy of Sciences, Ekaterinburg, Russia
$^2$ Institute of Natural Sciences and Mathematics, Ural Federal University, Ekaterinburg, Russia
$^3$ International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI), Chennai, India
E-mail: kolodkin@imp.uran.ru

Abstract. The effect of solid solution treatment (SST) of Sm-Fe alloys and conditions of the nitrogenation on the structure and magnetic properties of the Sm$_{2+\alpha}$Fe$_{17}$N$_x$ ($\alpha = 0 \div 0.6$) powders has been investigated. It is observed that the nitrided powders with the best hysteresis properties can be prepared from the Sm$_{2.4}$Fe$_{17}$ alloy after the SST at a temperature of 1050°C (5 h) and heat treatment at 525°C in a H$_2$:N$_2$ = 1:1 gas mixture with a pressure of 2.5 atm. The additional ball milling of the powder enhances the coercivity to 6.4 kOe.

1. Introduction
Since their discovery [1], the Sm$_2$Fe$_{17}$N$_x$ compounds have attracted attention because of the high values of their Curie temperature $T_C$, anisotropy field $H_a$, and room-temperature saturation magnetization $4\pi M_s$, i.e., 475°C, 250 kOe, and 15.7 kG, respectively. The interstitial nitride Sm$_2$Fe$_{17}$N$_x$ compounds are prepared via the gas-solid phase nitrogenation of the Sm$_2$Fe$_{17}$ powder, ground to an average particle size of several units or tens of micrometers. The diffusion of nitrogen atoms occurs at a temperature of 350–550°C and at N$_2$ pressure in the range from 0.01 to tens of atmospheres as follows [2]:

\[
\frac{1}{2}xN_2 + \text{Sm}_2\text{Fe}_{17} \rightarrow \text{Sm}_2\text{Fe}_{17}N_x (1)
\]

At the same time, at a temperature above 450°C, the enhanced diffusion of Fe atoms initiates the thermal decomposition of the Sm$_2$Fe$_{17}$N$_3$ nitride, as follows:

\[
\text{Sm}_2\text{Fe}_{17}N_3 \rightarrow 2\text{SmN} + \text{Fe}_4\text{N} + 13\text{Fe} (2)
\]

Preparation of high-quality Sm$_2$Fe$_{17}$N$_x$ powders involves several technological problems. The first task is to obtain a single-phase Sm$_2$Fe$_{17}$ alloy. Since the Sm$_2$Fe$_{17}$ compound forms via the peritectic reaction of primary Fe crystals with a liquid enriched in Sm, solidification of the melt inevitably ends with the formation of a multiphase system containing $\alpha$-Fe, Sm$_2$Fe$_{17}$, SmFe$_3$, and SmFe$_2$. The subsequent nitriding of such a multiphase system leads to the formation of numerous magnetically soft nuclei of magnetization reversal, which significantly decreases the hysteresis properties. Only prolonged solid solution treatment (SST) of ingots at temperatures below 1280°C helps removing additional phases. Samarium rapidly evaporates in the course of melting and SST of...
of the alloys, because of its high vapor pressure. The loss of samarium can be counteracted by having its excess content in the original Sm$_2$Fe$_{17}$ alloys. The value of the excess $\alpha$ is selected empirically, taking into account the melting, SST and nitrogenation, thus to ensure the formation of the single-phase Sm$_2$Fe$_{17}$N$_x$ powder.

Another crucial task for the production of highly anisotropic Sm$_2$Fe$_{17}$N$_x$ powders is the optimization of the nitriding process. The problem originates from both the low diffusion mobility of nitrogen atoms in the Sm$_2$Fe$_{17}$ lattice and the instability of the Sm$_2$Fe$_{17}$N$_x$ nitride resulting in its decomposition into $\alpha$-Fe and SmN [3]. Despite the wide range of studies of the diffusion of the nitrogen atoms into the rhombohedral lattice of the Sm$_2$Fe$_{17}$ compound [4-15], the practical task of synthesizing the anisotropic single-phase Sm$_2$Fe$_{17}$N$_x$ powder can be reduced to optimization of the multiparameter nitrogenation for the specific conditions of its realization [16-19].

In this work, we studied the effect of SST of Sm-Fe alloys and the conditions of the nitrogenation on the structure and magnetic properties of the Sm$_{2+\alpha}$Fe$_{17}$N$_x$ nitrides ($\alpha=0 \div 0.6$) powders.

2. Experimental
The initial Sm$_{2+\alpha}$Fe$_{17}$ ($\alpha=0 \div 0.6$) alloys were prepared by the induction melting in a vacuum furnace. The alloys were subjected to the SST at 1000–1100°C for 1–20 h. Nitrogenation of the powders was carried out at 450–550°C for 4 h in the H$_2$ + N$_2$ gas mixture under pressure of up to 2.5 atm. The Curie temperatures were determined from the first derivatives of the temperature dependences of magnetic susceptibility $\chi(T)$, which were measured by the method of compensated transformer in an alternating magnetic field with an amplitude of 4 Oe and frequency of 800 Hz in the temperature range of 18–800°C. Magnetization-reversal curves of the nitrogenated powders which were prior aligned in the magnetic field of 10 kOe were measured along and perpendicular to the texture direction using a vibrating sample magnetometer (VSM, Lake Shore 7407) with the maximum field of 17.5 kOe. X-ray diffraction patterns were taken with an Empyrean (PANanalytical) diffractometer in CuK$_\alpha$-radiation. Microstructures were observed with a Neophot 2 optical microscope.

3. Results and discussion
3.1. Solid solution treatment of as-cast alloys
Figure 1 (a - d) shows the dendritic microstructure of the as-cast Sm$_{2+\alpha}$Fe$_{17}$ ($\alpha=0 \div 0.6$) alloys. It consists of the matrix Sm$_2$Fe$_{17}$ phase and the significant inclusions of the $\alpha$-Fe and SmFe$_3$ phases (figure 1a). The SST at temperatures of 1000–1100°C promotes a decrease in the fraction of the $\alpha$-Fe and SmFe$_3$ inclusions. Figure 2 shows the temperature dependences of magnetic susceptibility $\chi(T)$ of the Sm$_{2+\alpha}$Fe$_{17}$ alloys. The weak peaks at 360°C, which correspond to the Curie temperature $T_c$ of the SmFe$_3$ phase almost completely disappear after the SST at 1000–1100°C for 5 h. The relative contribution of the $\alpha$-Fe and Sm$_2$Fe$_{17}$ phases to the total susceptibility gradually increases in favor of the latter with increasing SST time. For example, only a small amount of $\alpha$-Fe phase inclusions is observed in the matrix Sm$_2$Fe$_{17}$ phase after the SST at 1050°C for 20 h as can be seen from the micrographs in figure 1 (e–h).

The X-ray diffraction patterns of the Sm$_{2+\alpha}$Fe$_{17}$ powders prepared from the alloys after the SST at 1050°C for 20 h are presented in figure 3. The alloys mainly consist of the rhombohedral modification (R-3m) of Sm$_2$Fe$_{17}$ phase and the small amount of the $\alpha$-Fe phase, i.e, 4.7; 10.1; 3.4 and 4.5% for $\alpha=0; 0.2; 0.4$ and 0.6, respectively.

3.2. Nitrogenation of powders
To prepare uniformly nitrided powder, it is required to carefully control the particle size, temperature, and heating time in N$_2$ atmosphere. In order to obtain high quality nitrides, lower temperature and longer nitrogenation time is required. Fukuno et al. [20, 21] reported that the hydrogenation before the nitrogenation significantly increased the gas-solid reaction area by inducing many cracks in the
Sm$_2$Fe$_{17}$ particles. Thus, this hydrogenation promoted nitrogenation at lower temperature minimizing the impurity formation.

In this work, we studied the effect of nitrogen and hydrogen ratios in the gas mixture on properties of the nitrogenated Sm$_{2+\alpha}$Fe$_{17}$N$_x$ powders. Figure 4 represents the temperature dependences of the ac magnetic susceptibility of the Sm$_{2+\alpha}$Fe$_{17}$N$_x$ powders, nitrogenated at 475°C for 4 h in the H$_2$ gas mixture.

**Figure 1.** Microstructure of the cast Sm$_{2+\alpha}$Fe$_{17}$ alloys (a-d) before and after the SST at 1050 °C for 20 hours (e-h).

**Figure 2.** Temperature dependences of magnetic susceptibility of the Sm$_{2+\alpha}$Fe$_{17}$ alloys with $\alpha = 0$ (a) and $\alpha = 0.6$ (b) in as cast state (1) and after the SST at 1000, 1050, and 1100°C for 1 h (2), 5 h (3), and 20 h (4).

**Figure 3.** X-ray diffraction patterns of the Sm$_{2+\alpha}$Fe$_{17}$ powders after SST at 1050°C for 20 h ($\alpha = 0$; 2 - 0.2; 3 - 0.4; 4 - 0.6).

In this work, we studied the effect of nitrogen and hydrogen ratios in the gas mixture on properties of the nitrogenated Sm$_{2+\alpha}$Fe$_{17}$N$_x$ powders. Figure 4 represents the temperature dependences of the ac magnetic susceptibility of the Sm$_{2+\alpha}$Fe$_{17}$N$_x$ powders, nitrogenated at 475°C for 4 h in the H$_2$ gas mixture.
and N₂ atmosphere with different H₂:N₂ ratio under the pressure 2.5 atm. The intensity of peaks in the vicinity of \( T_C \) in Sm\(_2\)Fe\(_{17}\)N\(_3\) phase increased in comparison with the intensity of the Sm\(_2\)Fe\(_{17}\) peaks as H₂:N₂ ratio is equal to 1:1. Thus, as shown in figure 4b we obtained the largest amount of the interstitial nitrogen for \( x = 2.7 \). The Sm\(_{2.6}\)Fe\(_{17}\)N\(_{2.7}\) powder had the maximal specific magnetization \( \sigma_{17} \), which was measured in the field 17 kOe, and coercivity \( H_c \).

The nitrogenation of Sm\(_{2.6}\)Fe\(_{17}\) powder with 28 µm size particles at 475°C for 4 h did not result in the complete phase transformation from Sm\(_2\)Fe\(_{17}\) to Sm\(_2\)Fe\(_{17}\)N\(_3\) as can be seen in figure 4a. Thus, effects of the nitrogenation temperature \( T_{nitr} \) on the properties of Sm\(_{2-\alpha}\)Fe\(_{17}\)N\(_{\alpha}\) (\( \alpha = 0÷0.6 \)) powder was studied in detail. For example, figure 5a demonstrates the temperature dependences of the ac magnetic susceptibility of the Sm\(_{2}\)Fe\(_{17}\) powders, nitrogenated at \( T_{nitr} = 450 – 550 ^{\circ} \)C. With increasing \( T_{nitr} \) from 475 to 525°C, the relative intensity of the high anisotropic Sm\(_3\)Fe\(_{17}\)N\(_3\) phase significantly increases. The Sm\(_2\)Fe\(_{17}\) phase peak gradually disappears. However, the formation of Sm\(_2\)Fe\(_{17}\)N\(_x\) phase with \( x < 3 \) broadens the peak in the temperature range 250-350°C in the \( \chi(T) \) curve. Increasing \( T_{nitr} \) up to 525 °C increases anisotropy of the magnetization measured along and across the texture direction of the powder aligned with the magnetic field (figure 5b).

**Figure 4.** (a) Temperature dependences of the ac magnetic susceptibility of the Sm\(_{2}\)Fe\(_{17}\)N\(_{x}\) powders, nitrogenated at \( T_{nitr}=475^\circ \)C under pressure of 2.5 atm in H₂ and N₂ atmosphere with different H₂:N₂ ratio: 1 – N₂, 2 – N₂:H₂=3:1, 3 – N₂:H₂=1:1, 4 – N₂:H₂=1:3; (b) the effect of the H₂:N₂ ratio in the gas mixture on the amount of interstitial nitrogen \( x \) (1), magnetization \( \sigma_{17} \) (2) and coercivity \( H_c \) of the nitrogenated Sm\(_{2}\)Fe\(_{17}\)N\(_{x}\) powders.

**Figure 5.** (a) Temperature dependences of the ac magnetic susceptibility, and (b) demagnetization curves, measured along and across alignment of textured powders, prepared from Sm\(_{2.6}\)Fe\(_{17}\) alloy after SST (1100°C, 5 h) and nitrogenation at different temperature \( T_{nitr}: 1 - 450, 2 - 475, 3 - 500, 4 - 525, 5 - 550^\circ \)C.

The dependences of properties of the Sm\(_{2-\alpha}\)Fe\(_{17}\)N\(_{\alpha}\) nitride with \( \alpha = 0 \) and 0.6 on the nitrogenation temperature (450-550°C) are shown in figure 6. The amount of interstitial nitrogen \( x \) monotonically increases with increasing \( T_{nitr} \). However, the values of \( \sigma_{17} \) and \( H_c \) reach maximum at \( T_{nitr} = 525^\circ \)C. Further increasing \( T_{nitr} \) up to 550°C drastically decreases \( \sigma_{17} \) and \( H_c \), which is caused by the accelerated decomposition of the Sm\(_3\)Fe\(_{17}\)N\(_3\) nitride at elevated temperatures.

Nitrogenated powder with average grain size 28 µm and the best hysteresis properties (\( \sigma_{17} = 152 \) emu/g and \( H_c = 0.87 \) kOe) was obtained from the Sm\(_{2.4}\)Fe\(_{17}\) alloy after annealing at 1050 °C for 5 h and
subsequent heat treatment at $T_{nitr}=525$°C in the mixture of gases H$_2$:N$_2$ =1:1 under the pressure 2.5 atm. In order to enhance coercivity, the powder was additionally milled in a ball mill in toluene with ratio of powder to balls mass $m_p/m_b = 1/15$. Figure 7 represents monotonic increase of $H_c$ up to 6.4 kOe with increasing milling time up to 24 h.

4. Conclusion

By means of metallography, X-ray diffraction, measurements of the temperature dependences of the ac magnetic susceptibility and hysteresis magnetic properties of as-cast and homogenized Sm$_{2+\alpha}$Fe$_{17}$ ($\alpha = 0 \div 0.6$) alloys it have been shown:

1) The addition of excess Sm with $\alpha = 0.4$ to the initial Sm$_{2+\alpha}$Fe$_{17}$ alloys is required in order to compensate for its loss during melting and SST for 20 h at 1050 °C contributed to homogeneous starting alloy without Sm-rich phases and the minimum amount of $\alpha$-Fe phase.

2) Magnetically anisotropic powder with average grain size of 28 µm and the best hysteresis properties ($\sigma_{17} = 152$ emu/g and $H_c = 0.87$ kOe) was prepared by nitrogenation at $T_{nitr}=525$°C in a mixture of gases H$_2$:N$_2$ =1:1 under pressure 2.5 atm.

3) Grinding the nitrogenated powder in a ball mill increases the coercivity up to 6.4 kOe.

The work is supported by RFFI-BRICS project No.17-52-80072 and DST-BRICS under Proposal 258.

References

[1] Coey J M D, Sun H 1990 *J. Mag. Mag. Mater.* **87** L251
[2] Skomski R, Coey J M D 1993 *J. Appl. Phys.* **73** 7602
[3] Christodoulou C N, Takeshita T 1993 *J. Alloys Compd.* **202** 173
[4] Coey J M D, Lawler J F, Sun H, Allan J E M 1991 *J. Appl. Phys.* **69** 3007
[5] Skomski R, Coey J M D 1993 *J. Mater. Eng. Perform.* **2** 241
[6] Christodoulou C N, Komada N 1994 *J. Alloys Compd.* **206** 1
[7] Christodoulou C N, Komada N 1994 *J. Appl. Phys.* **76** 6041
[8] Brennan S, Skomski R, Qi Q, Coey J M D 1995 *J. Magn. Magn. Mater.* **140** 999
[9] Christodoulou C N, Komada N 1995 *J. Alloys Compd.* **222** 27
[10] Hu J, Zhao T, Guo H, Shen B, Wang Z, Liu G, Wang K, Wang Y, Hu B 1995 *J. Alloys Compd.* **222** 113
[11] Uchida H, Yanagisawa T, Kise S, Tachibana S, Kawanabe T, Matsumura Y, Koeninger V, Uchida H H, Miyamoto Y, Kaneko H, Kurino T 1995 *J. Alloys Compd.* **222** 33
[12] Inoue T, Ishikawa K, Suzuki T, Uchida H 1995 *J. Adv. Sci.* **7** 116
[13] Uchida H, Tachibana S, Kawanabe T, Matsumura Y, Koeninger V, Uchida H H, Kaneko H, Kurino T 1995 *J. Alloys Compd.* **222** 107
[14] Sun H, Tomida T, Makita K, Maehara Y 1996 *J. Alloys Compd.* **237** 108
[15] Zhang Y D, Budnick J I, Hines W A, Yang D P 1996 *J. Appl. Phys.* **79** 4596
[16] Ma X B, Li L Z, Liu S Q, Hu B Y, Han J Z, Wang C S, Du H L, Yang Y C, Yang J B 2014 *J. Alloys Compd.* **612** 110
[17] Yue M, Li Y Q, Liu R M, Liu W Q Guo, Z H, Li W 2015 *J. Alloys Compd.* **637** 297
[18] S Okada, K Suzuki, E Node, K Takagi, K Ozaki, Y Enokido 2017 *J. Alloys Comp.* **695** 1617
[19] M Matsuura, Y Nishijima, N Tezuka, S Sugimoto, T Shoji, N Sakuma 2018 *J. Magn. Magn. Mater.* **467** 64
[20] Fukuno A, Ishizaka C, Yoneyama T 1991 *J. Appl. Phys.* **70** 6021
[21] Fukuno A, Ishizaka C, Chihara H, Yoneyama T 1992 *IEEE Trans. Magn.* **28** 2575