Magnetic Field Effect on Nitrogenation of Sm$_2$Fe$_{17}$

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Nitrogenation of Sm$_2$Fe$_{17}$ powder was performed under a zero field and a magnetic field of 5 T at 623, 673 and 743 K to clarify the magnetic field effect on nitrogenation. Applying a magnetic field of 5 T induced nitrogenation compared with zero-field nitrogenation, and almost fully nitride Sm$_2$Fe$_{17}$N$_3$ was obtained at 743 K. Mössbauer spectroscopy results suggested that a 5-T magnetic field promoted the phase transformation to the fully-nitride Sm$_2$Fe$_{17}$N$_3$ phase. The magnetic field effect was discussed based on the magnetic energy gain and magnetic properties of host Sm$_2$Fe$_{17}$ and fully nitride Sm$_2$Fe$_{17}$N$_3$. [doi:10.2320/matertrans.MT-MN20190012]

(Keywords: magnetic field effect, nitrogenation, gas-solid reaction, Sm$_2$Fe$_{17}$N$_3$

1. Introduction

Ferromagnetic (FM) nitride Sm$_2$Fe$_{17}$N$_x$ ($0 < x \leq 3$) with a rhombohedral Th$_2$Zn$_{17}$ type structure (space group R3m) was synthesized using the N$_2$ gas-solid reaction technique on host Sm$_2$Fe$_{17}$.$^1$ The host’s cell volume expands by 6%–7% to accommodate three nitrogen atoms at the 9e-interstitial sites.$^2$ The fully-nitride (FN) Sm$_2$Fe$_{17}$N$_3$ has high Curie temperature $T_C$ of 746 K, high saturation magnetization $\mu_0M_S$ of 1.51 T and large anisotropy field of 21 T at room temperature (RT).$^3$ Therefore, FN Sm$_2$Fe$_{17}$N$_3$ is a candidate for permanent magnets.$^2,3$ However, Sm$_2$Fe$_{17}$N$_3$ decomposes to $\alpha$-Fe and SmN above 720 K.$^4,5$

Magnetic field stabilizes the FM phase by gaining large magnetic energy (Zeeman energy) $G_M$. For example, magnetic fields induced FM phases of LaCo$_4$H$_6$,$^6,7$ MnBi$_8$$^{8-12}$ and MnAl.$^{13,14}$ Therefore, it is expected that magnetic fields will promote nitrogenation for Sm$_2$Fe$_{17}$. However, to the best of our knowledge, the magnetic field effect (MFE) on nitrogenation of the Sm$_2$Fe$_{17}$ system had not been reported in detail. Recently, to clarify the MFE on nitrogenation, we developed an in-field heat treatment furnace utilized for a 5-T cryocooled superconducting magnet with a 50 mm room-temperature bore.$^{15}$ In this paper, we describe a review of MFE on nitrogenation of Sm$_2$Fe$_{17}$, which suggests competition between enhancement of phase transformation and suppression of diffusion processes by applying a magnetic field.

2. Experimental Procedure

The host Sm$_2$Fe$_{17}$ compound was prepared by induction melting of the constituent elements under an argon atmosphere and then annealed at 1423 K for 24 h in an argon atmosphere for homogeneity treatment.$^{16}$ The Sm$_2$Fe$_{17}$ ingot was crushed and pulverized into powder with particle size less than 53 μm in diameter. The lattice parameters $a$ and $c$ of Sm$_2$Fe$_{17}$ were 0.856 nm and 1.24 nm, respectively. The zero-field nitrogenation (ZFN) and in-field nitrogenation (IFN) of 5 T (IFN-5T) for the Sm$_2$Fe$_{17}$ powder were performed under a nitrogen gas pressure $P_n$ of 0.1 MPa at nitrogenation temperature $T_n$ of 623, 673 and 743 K for 24 hours in an applied magnetic field $\mu_0H$ of 5 T. The IFN equipment is described in Ref. 15) in detail. The nitrogen content $x$ in the nitrided powders was estimated from the increased sample mass after nitrogenation. Detailed sample preparation is reported in Ref. 17).

To examine the phases of ZFN and IFN-5T samples, X-ray powder diffraction (XRD) measurements were performed using Cu-Kα radiation at RT. Magnetization $M$ data were corrected using a superconducting quantum interference device magnetometer and a vibrating sample magnetometer. $T_C$ of the sample was determined by differential scanning calorimetry under a zero field.$^5$ Fe Mössbauer spectroscopy experiments with a 1.85 GBq $^{57}$Co(Rh) source were performed using a conventional constant acceleration method at RT. The velocity scale was calibrated with $\alpha$-Fe which had a hyperfine field of 33.1 T. The values of the hyperfine parameters were refined using NORMOS.$^{18}$

3. Results

The estimated $x$ in the Sm$_2$Fe$_{17}$N$_x$ powder prepared by ZFN and IFN-5T are listed in Table 1. In this table, the data for host Sm$_2$Fe$_{17}$ are also shown. It is clear that $x$ of IFN-5T is larger than that of ZFN for all $T_n$. By applying a magnetic field of 5 T, $x$ increased by 0.4–0.6 nitrogen atoms per formula unit. For condition of $T_n = 743$ K, almost FN Sm$_2$Fe$_{17}$N$_{2.9}$ was obtained using IFN-5T, while $x$ was only 2.3 using ZFN. Magnetic field promotes nitrogenation for the temperature $T$ range of 623–743 K. From XRD analysis for ZFN and IFN-5T samples,$^{17}$ we confirmed that the poor-nitride (PN) and FN phase coexisted in the nitride sample with $x \leq 1.9$. However, the XRD patterns for $x = 2.3$ and 2.9 did not show clearly the two phase coexistence of the PN and FN phases but a single nitride phase with a very small amount of $\alpha$-Fe phase.$^{15}$ The determined lattice parameters for the nitride with $x = 2.3$ and 2.9 are listed in Table 1. The parameters of the nitride with $x = 2.9$ are comparable to the data for FN Sm$_2$Fe$_{17}$N$_3$ reported in previous literature.$^{2}$

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Table 1 Conditions of zero-field nitrogenation (ZFN) and 5 T in-field nitrogenation (IFN-5T) for 24 h, nitrogen content $x$, lattice parameters, Curie temperature, relative fraction of poor-nitride phase (PN) and fully-nitride phase (FN), and average hyperfine field ($B_{hf}$).

<table>
<thead>
<tr>
<th></th>
<th>$T_n$ (K)</th>
<th>$x$</th>
<th>$a$ (nm)</th>
<th>$c$ (nm)</th>
<th>$T_C$ (K)</th>
<th>rel. fraction</th>
<th>$&lt;B_{hf}&gt;$</th>
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<tbody>
<tr>
<td>ZFN</td>
<td>623</td>
<td>0.6</td>
<td>two phase</td>
<td>two phase</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>IFN-5T</td>
<td>623</td>
<td>1.0</td>
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<td>two phase</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZFN</td>
<td>673</td>
<td>1.3</td>
<td>two phase</td>
<td>two phase</td>
<td>-</td>
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<tr>
<td>IFN-5T</td>
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<td>1.9</td>
<td>two phase</td>
<td>two phase</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZFN</td>
<td>743</td>
<td>2.3</td>
<td>0.874</td>
<td>1.27</td>
<td>0.157</td>
<td>0.843</td>
<td>25.5 33.3</td>
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<tr>
<td>IFN-5T</td>
<td>743</td>
<td>2.9</td>
<td>0.874</td>
<td>1.27</td>
<td>0.082</td>
<td>0.918</td>
<td>25.7 33.2</td>
</tr>
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</table>

The determined $T_C$ of Sm$_2$Fe$_{17}$N$_{2.9}$ was 746 K, which is almost the same as that of FN Sm$_2$Fe$_{17}$N$_{3.2}$. Figure 2 shows $m_S$ at 10 K for the ZFN (open circles) and IFN-5T (solid circles). The magnetic field of 5 T enhanced the nitrogen content $x$ and magnetic properties of Sm$_2$Fe$_{17}$N$_x$ at each $T_n$.

The thermomagnetization ($M$-$T$) curves of host Sm$_2$Fe$_{17}$, Sm$_2$Fe$_{17}$N$_{x}$ (ZFN) and Sm$_2$Fe$_{17}$N$_{x}$ (IFN-5T) in a magnetic field of 1 T were measured in the $T$ range of 10–830 K, which was shown in Ref. 15). The $M$-$T$ curves for 0.6 $\leq x \leq 2.3$ did not show the Brillouin-function like curve but a superposition of two $M$-$T$ curves, suggesting that the PN and FN phase coexisted in the sample. The $M$-$T$ curve of Sm$_2$Fe$_{17}$N$_{x}$ showed a single Brillouin-function curve. The determined $T_C$ of Sm$_2$Fe$_{17}$N$_{2.9}$ was 746 K, which is almost the same as that of FN Sm$_2$Fe$_{17}$N$_{3.2}$. Figure 2 shows $m_S$ at 10 K for the ZFN (open circles) and IFN-5T (solid circles). The magnetic field of 5 T enhanced the nitrogen content $x$ and magnetic properties of Sm$_2$Fe$_{17}$N$_x$ at each $T_n$.

Figure 1 shows the magnetization ($M$-$H$) curves of Sm$_2$Fe$_{17}$ (a), Sm$_2$Fe$_{17}$N$_2.3$ (ZFN) (b) and Sm$_2$Fe$_{17}$N$_2.9$ (IFN-5T) (c) at room temperature.

![Figure 1](image_url) Magnetization curves of Sm$_2$Fe$_{17}$ (a), Sm$_2$Fe$_{17}$N$_2.3$ (ZFN) (b) and Sm$_2$Fe$_{17}$N$_2.9$ (IFN-5T) (c) at room temperature.

![Figure 2](image_url) Saturation moment for ZFN, IFN-5T and Sm$_2$Fe$_{17}$ at 10 K.

Figure 3 shows the Mössbauer spectra of Sm$_2$Fe$_{17}$, Sm$_2$Fe$_{17}$N$_{x}$, and Sm$_2$Fe$_{17}$N$_{x}$ at RT. In this figure, dots and solid curves indicate experimental data and fitting curves, respectively. Since Fe atoms occupy 6c, 9d, 18f and 18h sites in the Th$_2$Zn$_{17}$-type structure, the spectrum of Sm$_2$Fe$_{17}$ was fitted with four sub-spectra using hyperfine interaction parameters: site-occupation, isomer shift, quadruple splitting and hyperfine field $B_{hf}$. The determined average $B_{hf}$ was 21.5 T for Sm$_2$Fe$_{17}$, which is in good agreement with reported data (21.8 T) for Sm$_2$Fe$_{17}$. The spectra of Sm$_2$Fe$_{17}$N$_{x}$ and Sm$_2$Fe$_{17}$N$_{x}$ were fitted with eight sub-spectra due to the PN and FN phases. The determined parameters of relative fraction and $<B_{hf}>$ of Sm$_2$Fe$_{17}$N$_{x}$.
Sm$_2$Fe$_{17}$N$_{2.9}$ were shown in Table 1. The relative fraction of the FN phase of $x = 2.9$ (IFN-5T) was $92\%$, which is larger than that of $x = 2.3$ (ZFN). In contrast, the relative fraction of the PN phase of IFN-5T is smaller than that of ZFN. ($B_{eq}$) of the PN phase was determined to be 25.7 T for $x = 2.3$ (ZFN) and 24.9 T for $x = 2.9$ (IFN-5T), which were larger than that of Sm$_2$Fe$_{17}$. The determined ($B_{eq}$) of the FN phase was 33.3–33.4 T, which is in good agreement with reported data (33.3 T) of Sm$_2$Fe$_{17}$N$_{3.19}$. From Mössbauer spectroscopy experiments, it was found that both PN and FN phases existed in the nitrides with $x = 2.3$ and 2.9. The obtained results indicate that $m_s$ of the PN phase is smaller than that of the FN phase but slightly larger than that of Sm$_2$Fe$_{17}$.

The results of this study showed that magnetic fields promoted phase transformation from the PN to the FN phase under at same $T_n$. That is, the equilibrium state of the N$_2$ gas-solid reaction probably was changed by applying a magnetic field to form the FN phase with large $m$.

4. Discussion

In this section, MFE on the nitridation of Sm$_2$Fe$_{17}$ is discussed. The gain of $G_M$, $\Delta G_M$, can be driving force of the gas-solid reaction. $\Delta G_M$ of the Gibbs free energy tends to be more stable of a FM state with large $m$ and promotes ferromagnet synthesis. So far, it has been reported that the reaction or phase transformations from the non-FM to FM phase was accelerated by magnetic fields.\(^{10,11,14,20}\)

Our results showed the two-phase coexistence of the FN and PN phases in Sm$_2$Fe$_{17}$N$_x$ ($x < 3$), so that the field-induced phase transformation by $\Delta G_M$ is a possible mechanism. Assuming a simple model with only the Zeeman effect, $\Delta G_M$ under $H$ can be written as

$$\Delta G_M = \mu_0 H \Delta m_S,$$

where $\mu_0$ is the permeability of a vacuum and $\Delta m_S$ is the change of the saturation moment.\(^{21,22}\) In the present case, $\Delta m_S$ is expressed by

$$\Delta m_S = m_{PN} - m_{FN},$$

where $m_{PN}$ and $m_{FN}$ are the magnetic moments for the PN and FN phases, respectively. The MFE direction is found by the sign of $\Delta m_S$.\(^{22}\) As shown in Fig. 3 of Ref. 15, FN Sm$_2$Fe$_{17}$N$_3$ is ferromagnetic, but the PN phase is paramagnetic at $T_n = 623$ K, 673 K and 743 K, so that the sign of $\Delta m_S$ and $\Delta G_M$ is negative in this $T_n$ range. This indicates that the MFE promotes the phase transformation from the PN to FN phase.\(^{22}\)

It is difficult to evaluate magnetic moment of the FN phase in the $M$-$T$ curve of Sm$_2$Fe$_{17}$N$_x$ ($x < 3$) sample because of a superposition of two $M$-$T$ curves.\(^{13}\) Since present IFN was conducted under a magnetic field of 5 T, we estimated $m(T,H)$ of Sm$_2$Fe$_{17}$ as the PN phase and Sm$_2$Fe$_{17}$N$_3$ as the FN phase for $\mu_0 H = 5$ T based on a mean field theory for a simple two-sublattice model.\(^{2,22}\) The mean-field calculation is described in the appendix.

Figure 4 shows the temperature dependence of the magnetic moments (a) and calculated moment $m(T,H)$ of Sm$_2$Fe$_{17}$ and Sm$_2$Fe$_{17}$N$_3$ for $\mu_0 H = 1$ T (broken curves) and 5 T (solid curves). The open circles present the experimental data of $\mu_0 H = 1$ T.

Fig. 3 Mössbauer spectra of Sm$_2$Fe$_{17}$ (a), Sm$_2$Fe$_{17}$N$_{2.3}$ (ZFN) (b) and Sm$_2$Fe$_{17}$N$_{2.9}$ (IFN-5T) (c) at room temperature.

Fig. 4 Temperature dependence of the magnetic moments (a) and calculated moment $m(T,H)$ of Sm$_2$Fe$_{17}$ and Sm$_2$Fe$_{17}$N$_3$ for $\mu_0 H = 1$ T (broken curve) and 5 T (solid curve). The open circles present the experimental data of $\mu_0 H = 1$ T.
calculated $m$-$T$ curves represent the experimental data. The difference between the experimental data of $\mu_0 H = 1 \, \text{T}$ and calculated data of $\mu_0 H = 5 \, \text{T}$ is small. Therefore, we considered that the field-induced $m$ was negligibly small within the present IFN-5T condition, and $m_{\text{PN}}$ and $m_{\text{FN}}$ under $\mu_0 H = 5 \, \text{T}$ were regarded as the experimental $m$ of Sm$_2$Fe$_{17}$ and Sm$_2$Fe$_{17}$N$_3$ for $\mu_0 H = 1 \, \text{T}$, respectively. Since $\Delta G_M$ of an electron spin of $1\mu_0$ in $\mu_0 H = 1 \, \text{T}$ corresponds to thermal energy of 0.67 K, $T_n$ dependence of $\Delta G_M$ for $\mu_0 H = 5 \, \text{T}$ was obtained, as shown in Fig. 5, which was evaluated using eqs. (1) and (2). Here, $\Delta m_3$ was deduced from Fig. 4(a) (broken arrows), which is presented in the inset of Fig. 5. With decreasing $T_n$ from $T_n = 743 \, \text{K}$, $\Delta G_M$ decreases: the gain of $G_M$ becomes larger.

In Fig. 6, the field-induced nitrogen content $\Delta x$ is shown as a function of $T_n$. Here, the experimental $\Delta x$ (open circles) was evaluated from the inset of Fig. 6: $\Delta x = x(\text{IFN-5T}) - x(\text{ZF N})$. If the field-induced nitrogen content ($\Delta x = 0.6$) from $x(\text{ZF N}) = 2.3$ to $x(\text{IFN-5T}) = 2.9$ is only due to $\Delta G_M$ (approximately 35 K) at $T_n = 743 \, \text{K}$, the change of the nitrogen content $x$ was calculated to be $\Delta x = 1.0$ at $T_n = 673 \, \text{K}$ and $\Delta x = 1.2$ at $T_n = 623 \, \text{K}$, as shown by the solid circles in Fig. 6. The experimental $\Delta x$ at $T_n = 623 \, \text{K}$ and 673 K were smaller than $\Delta x$ estimated from $\Delta G_M$. This result suggests that only phase transformation mechanism from the paramagnetic PN phase to ferromagnetic FN phase is hard to explain the field-induced nitrogenation. As seen in Fig. 6, the nitrogenation due to the field-induced phase transformation is probably suppressed at lower $T_n$. We should consider other MFE mechanisms as well as the field-induced phase transformation in Sm$_2$Fe$_{17}$N$_x$ powder.

Fuji et al. reported that the FN-phase grain growth (phase transformation) becomes dominant at the later stage in nitrogenation at 733 K under $P_n \geq 0.1 \, \text{MPa}$, exceeding the nitrogen diffusion process, which is important at the earlier stage. That is, at first, nitrogen atoms diffuse into the Sm$_2$Fe$_{17}$ powder from the surface, which forms the PN phase. After that, the PN phase transforms into the FN phase. This means that the amount of the PN phase is important for progressing the grain growth of the FN phase (phase transformation).

It was reported that the carbon diffusion in $\gamma$-iron and the diffusion process in Fe/Ga diffusion couples were suppressed by applying magnetic fields. If the nitrogen diffusion process for forming the PN phase is suppressed by applying a magnetic field, the competition of MFE between the enhancement of the phase transformation and suppression of the diffusion processes will occur. The nitrogen diffusion process is regarded as an activation type, so that thermal effect of the diffusion is dominant at higher $T_n$ such as 743 K, compared with the nitrogen diffusion process suppressed by MFE. In contrast, the field-induced suppression of the nitrogen diffusion process becomes more effective at lower $T_n$ such as 623 K. This leads to smaller $\Delta x$ than that estimated from the phase transformation from the PN to FN phase by $\Delta G_M$. Now, further IFN experiments in fields up to 15 T are in progress to verify this scenario, which will be reported soon elsewhere. However, it should be noted that the present results clearly show the promotion of nitrogenation of the Sm$_2$Fe$_{17}$ magnet by applying a magnetic field under our IFN condition.

5. Conclusions

ZF N and IFN-5T for Sm$_2$Fe$_{17}$ powder were conducted under nitrogen gas pressure of 0.1 MPa at 623, 673 and 743 K for 24 h to investigate the magnetic field effect on the nitrog enation to Sm$_2$Fe$_{17}$N$_x$. Nitrogenation of the Sm$_2$Fe$_{17}$ magnet was promoted by applying a magnetic field. Mössbauer spectroscopy results suggested that magnetic fields promoted the phase transformation from the poor-nitride to fully-nitride Sm$_2$Fe$_{17}$N$_x$ phase. It was hard to explain the magnetic field effect on nitrogenation in Sm$_2$Fe$_{17}$ by only mechanism of the field-induced phase transformation due to gain of magnetic free energy.

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Mössbauer spectroscopy experiments were carried out at the Division of Isotope Science, Research Support Center, Institute for Research Promotion, Kagoshima University.

Appendix

In the simple model, \( m(T, H) \) is expressed by

\[
m(T, H) = 2m_{Sm}(T, H) + 17m_{Fe}(T, H),
\]

where \( m_{Sm}(T, H) \) and \( m_{Fe}(T, H) \) are the magnetic moments of Sm and Fe atoms, respectively. Then, \( m_{Sm}(T, H) \) and \( m_{Fe}(T, H) \) are written by

\[
m_{Sm}(T, H) = g(J)\mu_B
\]

and

\[
m_{Fe}(T, H) = 2(S)\mu_B,
\]

where \( g \) is the Lande g-factor, \( (J) \) and \( (S) \) are thermal averages of the total angular momentum \( J \) of Sm and the total spin momentum \( S \) of Fe, respectively. The molecular field \( H_m \) acting on \( m_{Sm}(T, H) \) and \( m_{Fe}(T, H) \) can be written by

\[
H_m(\text{Sm}) = \frac{(g - 1)^2}{8\mu_B} j^{\text{SmSm}}(J) + \frac{g - 1}{8\mu_B} j^{\text{SmFe}}(S)
\]

and

\[
H_m(\text{Fe}) = \frac{1}{2\mu_B} j^{\text{FeFe}}(S) + \frac{(g - 1)}{2\mu_B} j^{\text{FeSm}}(J),
\]

respectively. Here, \( j^{\text{SmSm}} \), \( j^{\text{SmFe}} \) and \( j^{\text{FeFe}} \) are the exchange effective parameters of the Sm–Sm, Sm–Fe and Fe–Fe interaction, respectively, and \( z^0 \) is the number of nearest neighbor \( j \)-atoms of an i-atom. In the Th₂Zn₁₇-type structure, Sm occupies the 6c site and Fe occupies the 6c, 9d, 18f sites.

REFERENCES