Nitrogen Absorption by $\text{Sm}_2\text{Fe}_{17}$

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This paper reviews typical and significant behaviours of the $\text{Sm}_2\text{Fe}_{17}\text{-N}_2$ system which is potentially of significance as a nitromagnetic material (metal nitride magnetic material). This paper is focusing on the processes of the N_2 absorption by the $\text{Sm}_2\text{Fe}_{17}$ and summarises results: (i) the crystal structure of $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ and the significance of N atoms as an interstitial in the alloy, (ii) thermodynamic properties and a partial phase diagram of the $\text{Sm}_2\text{Fe}_{17}\text{-N}_2$ system based on pressure-composition-temperature (PCT) measurements, and (iii) the mechanism of N_2 absorption by the $\text{Sm}_2\text{Fe}_{17}$ based on kinetic measurements and on catalytic behaviours on the alloy surface.

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1. Introduction

A NUMBER of investigations of the synthesis of a nitromagnet material $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ and their magnetic properties have been intensively made in a last decade, motivating by its theoretical potential as a permanent magnet material.^{1)–4)} The interstitial N atoms play an important role for the changes of Fe–Fe distance in the parent compound, which leads to the significant rises of Curie temperature.^{4)–6)}

Noticeable feature of the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ magnet is particularly to fabricate it through solid–gas reaction processes. $\text{Sm}_2\text{Fe}_{17}$ nitrides are normally synthesised by N uptake by the intermetallic $\text{Sm}_2\text{Fe}_{17}$ compound in the exposure to the N_2 gas. The significant improvement in the behaviour of N uptake by the $\text{Sm}_2\text{Fe}_{17}$ is made with $\text{N}_2 + \text{H}_2$, NH_3 , $\text{NH}_3 + \text{H}_2$ gases or plasma nitrogenation process.^{7)–11)} Although the formation of nitrides is achieved through the gas–solid reaction processes, such view does not seem to have been taken into account in most of published works.

This paper reviews the interaction of the $\text{Sm}_2\text{Fe}_{17}$ with the N_2 gas, followed by the gas–metal reaction point of view covering the structure, thermodynamics, kinetic behaviours and surface characteristics.

2. Crystal structure

The $\text{Sm}_2\text{Fe}_{17}$ intermetallic compound adopts the rhombohedral $\text{Th}_2\text{Zn}_{17}$ -type structure (space group R-3 m), which takes up considerable amounts of N atoms without any structural transition. Generally, the isostructural compounds $\text{Pr}_2\text{Fe}_{17}\text{N}_x$ or $\text{Nd}_2\text{Fe}_{17}\text{N}_x$, for instance, are used for neutron scattering study instead of $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ because of the large absorption cross section of Sm.^{12)–14)} N atoms fully occupy the 9e type octahedral Sm_2Fe_4 site, and the crystal structure of $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ can be described as a stacking of three $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ slabs along c [001] as shown in Fig. 1, providing the overall stoichiometry $3 \times \text{Sm}_2\text{Fe}_{17}\text{N}_3$.

Bonding lengths correlate to the relative stability of compounds. The interatomic distances Fe–N in Sm_2Fe_4 tetrahedra are 1.91 and 1.94 Å, respectively, indicating rather strong Fe–N bond (similar to the closest Fe–N distance 1.90 Å in

Fig. 1. The crystal structure of $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ (Space group R-3 m (No. 166)).¹³⁾ The composed net-layer and the stacking of slabs are shown. 6 Sm in 6c: 0, 0, 0.3431; 6 Fe(1) in 6c: 0, 0, 0.0947; 9 Fe(2) in 9d: 1/2, 0, 1/2; 18 Fe(3) in 18f: 0.2818, 0, 0; 18 Fe(4) in 18h: 0.5059, 0.4936, 0.1532; 9 N in 9e: 1/2, 0, 0.

Fe_4N calculated based on Ref. 15)). The bonding distance Sm–N (2.52 Å) in $\text{Sm}_2\text{Fe}_{17}$ is also close to that in SmN (2.52 Å calculated based on Ref. 16)). These imply that Sm–N and Fe–N bonding are in parallel responsible for the stability of $\text{Sm}_2\text{Fe}_{17}$ nitrides [Note: the stability of isostructural $\text{Pr}_2\text{Fe}_{17}$ nitrides is strongly dominated by Fe–N bonding contribution¹³⁾].

Further nitrogen is filling in the 18g tetrahedral Sm_2Fe_2 site using NH_3 , $\text{NH}_3 + \text{H}_2$ or $\text{N}_2 + \text{H}_2$ mixture gases.¹⁷⁾ The tetrahedral Sm_2Fe_2 shares two triangular Sm_2Fe faces each other. Similarly to metal–hydrogen systems, a possible simultaneous occupation of the site can be assumed using the suggestion that the N atoms do not occupy interstices that share common faces at same time,¹⁸⁾ and which gives the maximum possible occupation number = 0.5. This provides a possible model: 9 N

Fig. 2. Pressure-Composition Isotherms at 623, 648 and 673 K for the $\text{Sm}_2\text{Fe}_{17}\text{-N}_2$ system.

in $9e+9$ N in $18g=3 \text{ Sm}_2\text{Fe}_{17}\text{N}_6$. If H atoms simultaneously occupy the 18g site with N atoms,¹⁹⁾ the maximum N content may be $x < 6$ in $\text{Sm}_2\text{Fe}_{17}\text{N}_x$.^{7),8),20)} The maximum N capacity $\text{N}/\text{Sm}_2\text{Fe}_{17} > 6$ has been also reported.^{9),10),21)} The available polyhedral site of N and reasonable model, however, are unknown. More detailed information on the N coordination in the $\text{Sm}_2\text{Fe}_{17}$ sublattice is required.

3. Thermodynamic property of $\text{Sm}_2\text{Fe}_{17}\text{-N}_2$ system

3.1 Pressure-Composition-Temperature relationship

Absorption Pressure-Composition-Temperature (P-C-T) relationships for $\text{Sm}_2\text{Fe}_{17}\text{-N}_2$ system at temperature between 623 K and 673 K were measured volumetrically using a Sieverts-type apparatus.²²⁾⁻²⁵⁾ The measured isotherms are shown in Fig. 2. Homogeneous distribution of N atoms in the alloy particles was confirmed by electron probe microanalysis (EPMA) observation.^{26),27)} Clear plateau pressures were reproducibly seen between approximately $0.7 < x < 1.6$ and $2.1 < x < 2.8$ in $\text{Sm}_2\text{Fe}_{17}\text{N}_x$, indicating the formation of two different nitride phases; $\text{Sm}_2\text{Fe}_{17}\text{N}_2$ and $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ in addition to N solid solution phase, as follow:

Zhang et al. observed the obeying Sieverts' law $C_N \propto P_{\text{N}_2}^{1/2}$, where C_N is the N concentration and P_{N_2} is the N_2 pressure, for chemically related $\text{Sm}_2(\text{Fe}_{0.75}\text{Co}_{0.25})_{17}\text{-N}_2$ system at 823 K.²⁸⁾ It is of evidence that nitrogen atomically dissolves into the metal matrices.

The particle size of a sample of an intermetallic compound strongly affects the solubility or chemical potential of an interstitial atom such as hydrogen.^{29),30)} In the present study, no significant change has been observed for the isotherms with different particle sizes of the sample, implying that the contri-

Fig. 3. Change in the lattice parameters as a function of N content.

bution of surface energy, or internal stresses of the particles with different particle sizes to N chemical potentials is negligible.

Figure 3 shows the change in the lattice parameters as a function of the amount of N uptake. The lattice parameters a and c rapidly increase when the formation of $\text{Sm}_2\text{Fe}_{17}\text{N}_2$ occurs from N solid solution phase around $\text{N}/\text{Sm}_2\text{Fe}_{17} = 0.7$. Further N uptake leads gradual increases of the parameters by $\Delta a/a = 2.3\%$ and $\Delta c/c = 1.6\%$ at 298 K at a N concentration of around $\text{N}/\text{Sm}_2\text{Fe}_{17} = 2.8$. The change in the lattice parameter between $\text{Sm}_2\text{Fe}_{17}\text{N}_2$ and $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ seems to be rather small, where well agreed, as reported earlier,³¹⁾ no distinct splitting of XRD peaks was found in the region of $\text{Sm}_2\text{Fe}_{17}\text{N}_2/\text{Sm}_2\text{Fe}_{17}\text{N}_3$ coexistence.

As mentioned earlier, higher amounts of N can be absorbed by the $\text{Sm}_2\text{Fe}_{17}$ using NH_3 or $\text{NH}_3 + \text{H}_2$ atmospheres up to around $\text{N}/\text{Sm}_2\text{Fe}_{17} > 3$. Thermodynamic calculation shows that the activity of N in NH_3 is several orders of magnitude higher than that of N in N_2 .¹⁰⁾ Nitrogenation in NH_3 can be assumed as an equivalent to nitrogenation in N_2 at much higher pressures, which may drive a higher N capacity in the $\text{Sm}_2\text{Fe}_{17}$ than those in N_2 .

3.2 Thermodynamic property

The relative partial molar thermodynamic functions for the formation of the $\text{Sm}_2\text{Fe}_{17}$ nitrides can be characterised based on measured P-C-T relationships from the thermodynamic relation

$$\Delta\mu_N = \frac{1}{2} RT \ln P_{\text{N}_2} = \Delta H_N - T\Delta S_N \quad (3)$$

where $\Delta\mu_N$ is the change in the relative partial molar free energy, ΔH_N is the change of the relative partial molar enthalpy, and ΔS_N is the change in the relative partial molar entropy. The calculated values of the thermodynamic functions for the formation of $\text{Sm}_2\text{Fe}_{17}$ nitrides are $\Delta H_N = -26.5 \pm 0.8 \text{ kJ}(\text{mol}_N)^{-1}$, $\Delta S_N = -7.0 \pm 0.2 \text{ J}(\text{K} \cdot \text{mol}_N)^{-1}$ for $\text{Sm}_2\text{Fe}_{17}\text{N}_2$, and $\Delta H_N = -23.5 \pm 1.2 \text{ kJ}(\text{mol}_N)^{-1}$, $\Delta S_N = -12.7 \pm 0.7 \text{ J}(\text{K} \cdot \text{mol}_N)^{-1}$ for $\text{Sm}_2\text{Fe}_{17}\text{N}_3$, respectively. The enthalpy value of $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ formation well agrees with that obtained by different technique.³²⁾

Fig. 4. Calculated isotherms for the $\text{Sm}_2\text{Fe}_{17}\text{-N}_2$ system.

3.3 Partial phase diagram

A lattice-gas model given by Lacher³³⁾ was applied to estimate the P - C - T relationship for wider ranges for pressure and temperature. And from this the partial phase diagram for the $\text{Sm}_2\text{Fe}_{17}\text{-N}$ system was constructed. The calculation was made for two regions: $0.54 < [\text{N}]/[\text{Sm}_2\text{Fe}_{17}] < 1.96$ for the $\text{Sm}_2\text{Fe}_{17}\text{N}_2$ formation, and $1.92 < [\text{N}]/[\text{Sm}_2\text{Fe}_{17}] < 2.98$ for the $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ formation, respectively. And then these solubility limits were normalised as $0 < \theta < 1$ for each regions (θ is the fraction of the occupied sites). The equilibrium pressure P can be expressed as

$$\frac{1}{2} \ln \frac{P}{P_{0.5}} = \ln \frac{\theta}{1-\theta} - \frac{(\theta - 1/2) W_{\text{NN}}}{RT} \quad (4)$$

in which, $P_{0.5}$ is the pressure in the mid point of each region mentioned above, W_{NN} is the N-N interaction energy, R is the gas constant and T is the reaction temperature.^{23)-25),34)}

By fitting the measured P - C - T diagrams, the critical temperatures were estimated as $T_c = 834 \pm 25$ K for $\text{Sm}_2\text{Fe}_{17}\text{N}_2$ and 793 ± 30 K for $\text{Sm}_2\text{Fe}_{17}\text{N}_3$, respectively. The interaction energies between neighbouring N atoms in metal matrices were obtained from the relation $W_{\text{NN}} = T_c/4R$ as 12.7 ± 0.7 kJ(mol_N)⁻¹ for $\text{Sm}_2\text{Fe}_{17}\text{N}_2$, and 13.2 kJ(mol_N)⁻¹ for $\text{Sm}_2\text{Fe}_{17}\text{N}_3$, respectively. Based on the obtained thermodynamic functions, the isotherms were calculated for different temperatures as shown in Fig. 4. From the calculated isotherms, a partial phase diagram was constructed as shown in Fig. 5. These results indicate a relatively low decomposition temperature of the $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ phase, and this leads to a difficult sintering process in manufacturing the $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ magnet.

4. Kinetic behaviour

From a gas-metal interaction point of view, in general, the reaction rate is determined by one or several of the partial steps for N_2 absorption by $\text{Sm}_2\text{Fe}_{17}$.^{35),36)} Of the N_2 uptake by $\text{Sm}_2\text{Fe}_{17}$, two distinctly different rate-determined steps are of

Fig. 5. Calculated isobars for the $\text{Sm}_2\text{Fe}_{17}\text{-N}_2$ system.

presence.^{37),38)}

4.1 Dissociative chemisorption on $\text{Sm}_2\text{Fe}_{17}$ surface

The N_2 absorption rate can be expressed as the following empirical equation:³⁹⁾ $v = kP^n$ where v is the rate of N_2 absorption, k is the proportional constant depending on temperature and n is the exponent factor of pressure. The rate determining-step can be estimated by the value of $n = 0-1$.^{35),39)}

Figure 6 shows the pressure dependence $n=1.0$ of N_2 absorption at initial stage of reaction, indicating that the overall reaction is dominated by the dissociation of covalent N_2 molecules into N atoms on the surface of $\text{Sm}_2\text{Fe}_{17}$.^{35),39)} The trend of linear relation with the exponent factor seems to be independent of the prior H_2 treatment. On the other hand, the rate of N_2 absorption by H_2 pre-treated sample was lower than that by untreated sample. Generally, the electron transfer between gas molecules and the alloy surface is the essential step for the molecule dissociation.^{36),40),41)} A reasonable suggestion is that chemisorbed H leads rather non-metallic state at the surface, and which inhibits the electron exchange between N_2 molecules and the alloy surface.

4.2 N diffusion in $\text{Sm}_2\text{Fe}_{17}\text{N}_x$

As N concentration increases, the rate of N_2 absorption was found independent of the pressure, and this indicates that the rate-determining step shifts to the N diffusion in $\text{Sm}_2\text{Fe}_{17}\text{N}_x$.³⁷⁾ Typical N_2 absorption characteristics by $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ are shown in Fig. 7 as a square root of reaction time t versus N content in $\text{Sm}_2\text{Fe}_{17}$. The linear relationships are clearly seen, implying that N_2 absorption kinetics is controlled by N diffusion process.

Figure 8(a) shows the dependence of the apparent N diffusion coefficient on N concentration. A strong N content dependency of the N diffusivity D can be seen. The N diffusivity seems to be closely related to the stress field led by N uptake. In-situ XRD measurements on the nitrogenation processes showed marked lattice deformations during the N absorption.⁴²⁾ In addition, D was found to be strongly dependent on the particle size of alloy samples as shown in Fig. 8

Fig. 6. Pressure dependence of the N_2 absorption rate by Sm_2Fe_{17} at initial stage. The trend with and without prior H_2 absorption-desorption cycle are shown at 773 and 823 K.

Fig. 7. The N amount of absorbed vs the square root of the reaction time at 673 K.

(b), where marked contributions of the frequency factor of D rather than the activation energy for N diffusion were found.³⁸⁾ The smaller particle readily reduces the stresses induced by volume expansions since dislocations may easily pass through the particle.^{29),30),43)} Under such less constrained samples, the diffusion processes would readily proceed. In nitrogenation process, anomalously high N concentrations

Fig. 8. (a) Change in N diffusion coefficient D in Sm_2Fe_{17} as a function of the N content. (b) Change in N diffusion coefficient D in Sm_2Fe_{17} as a function of the particle size of Sm_2Fe_{17} sample.

were observed as at surface regions of each sample particle before an equilibrium state with uniform distributions of N atoms in each particle.^{26),27)} A further study may be required to understand this kinetic behaviour.

An ordinary sintering technique cannot be applied for the fabrication of nitromagnet since T_c of the nitrides is as low as 800 K (see Fig. 4)⁴⁴⁾ as discussed earlier. However, based on the N diffusivity data, if the sintering time can be controlled within a time of order of microseconds (faster than N diffusivities^{38),45)–48)}, a shock compaction technique⁴⁹⁾ may be applied to consolidate the $Sm_2Fe_{17}N_3$ powder. We have tried to sinter the nitride powders by a shock compaction method. The sintering itself was successful, however, the formed sample exhibited a much lower magnetization than expected, because high strains were induced throughout the sample by the shock compaction.

4.3 Synthesis of NH_3 on the surface of Sm_2Fe_{17}

The presence of H atoms on the Sm_2Fe_{17} surface retards the reaction rate of N uptake, and an excess N absorption exceeding $x > 3$ in $Sm_2Fe_{17}N_x$ is well known from $N_2 + H_2$ or prior exposure to H_2 gases.^{8),50)} These suggest the possibility of NH_3 synthesis on Sm_2Fe_{17} surface. Such catalytic behaviours can be determined by highly sensitive technique called a volumetric Wagener method.^{51),52)} With this method, a clean surface of a metal sample can be prepared under ultra high vacuum condition. And quantitative reactivity, reaction probability, of a gas, and reacted gas amount can be measured, where reaction probability is defined as the ratio of reaction rate to impinging rate of a gas.

Figure 9 shows the change in N_2 reaction probability r_{N_2} on

Fig. 9. (a) Change in r_{N_2} on SmH_x surface as a function of N_{N_2} at 298 K. (b) The change in partial pressure of N_2 , H_2 and NH_3 as a function of N_{N_2} .

the surface of SmH_{2+x} in (a) and the change in the partial pressure of detected gases in (b) as a function of adsorbed or absorbed gas molecules N_{N_2} . The increase of partial pressure of NH_3 was obvious during the exposure to N_2 (see Fig. 9 (b)). Usually, the hydride of rare earth metals poses the metallic state without some higher hydrides.⁵³⁾ The surface of Sm hydride may be still metallic, and N_2 molecules can dissociate and form NH_3 on the surface. The appearance of NH_3 synthesis was observed also for the SmH_x with N_2 pre-adsorbed layers as the sample exposes to N_2 .⁵⁴⁾

The formation of NH_3 was detected for Fe with H_2 and N_2 pre-adsorbed sample under H_2 atmosphere as shown in Fig. 10. This suggests that the dissociative chemisorption of N_2 takes place on the H_2 adsorbed surface of Fe during N_2 adsorption process. On the other hand, no NH_3 formation was detected when the sample with H_2 pre-adsorption exposed to N_2 .⁵⁴⁾ The fact that $\Delta H = -134 \text{ kJ}(\text{mol}_{\text{H}_2})^{-1}$ for H_2 dissociative chemisorption on Fe is negatively much higher than $\Delta H = -60 \text{ kJ}(\text{mol}_{\text{N}_2})^{-1}$ for the N_2 chemisorption on Fe⁵⁴⁾ suggests the NH_3 can be synthesised only by the reaction of chemisorbed N on Fe with dissociative H from H_2 gas phases.

The results above indicate that the Sm or Fe segregates in the $\text{Sm}_2\text{Fe}_{17}$ surface contribute to the catalytic synthesis of NH_3 in the alternate exposures to H_2 and N_2 gases.

5. Conclusion

Nitrogenation processes on the $\text{Sm}_2\text{Fe}_{17}$ intermetallic compound are reviewed from a point of view of solid-gas interaction. From the measurement of the equilibrium reaction of the $\text{Sm}_2\text{Fe}_{17}\text{-N}$ system, we constructed a partial phase diagram of this system. From kinetic measurements of nitrogenation of the $\text{Sm}_2\text{Fe}_{17}$, a strong dependence of the N diffusivity on the

Fig. 10. (a) Change in r_{H_2} on Fe surface with H_2 and N_2 pre-adsorbed layers as a function of N_{H_2} at 298 K. (b) The change in partial pressures of H_2 , N_2 and NH_3 as a function of N_{H_2} .

alloy particle size was found. This seems to be related with strains induced by increasing N content in the alloy. Catalytic synthesis of NH_3 on the surface of $\text{Sm}_2\text{Fe}_{17}$ gives a reasonable explanation for the marked enhancement of N_2 absorption kinetics using N_2 and H_2 gases. Many phenomena staying behind are still hidden and not well understood. Further investigations are required.

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