

Physical properties of $R_2Fe_{17}N_{3+\delta}$ (R=Y, Ce and Sm) prepared under high-pressure nitrogen gas

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We review our recent results on nitrogen diffusion process in bulky Sm_2Fe_{17} under high pressure N_2 -gas, on the structural and magnetic properties of high-quality $R_2Fe_{17}N_{3+\delta}$, our attempt to magnetically harden Sm-Fe-C melt-quenched ribbons by nitrogenation and finally prospective view for bonded magnets based on R-Fe-N systems.

1. INTRODUCTION

One of the methods fabricating new advanced materials is to interstitially introduce non-metallic atoms with small atomic-radius into host compounds. In 1990, Coey and Sun [1] have discovered that a new family of interstitially modified rare earth iron nitride $Sm_2Fe_{17}N_{3-\delta}$ exhibits excellent magnetic characteristics similar to the based compound $Nd_2Fe_{14}B$ in Nd-Fe-B permanent magnets. After then, special attention has been paid on developing it into new high-performance bonded-magnets.

Recently, we succeeded in fabricating the high-quality nitride $R_2Fe_{17}N_{3+\delta}$ with $\delta=0.1\sim 0.6$ (R=Y, Ce and Sm) under high-pressure nitrogen gas up to 10 MPa [2]. In that event, the reaction at relatively lower temperature offers two advantages: The first is to suppress the surface

segregation of α -Fe phase on the powder samples during nitrogenation process and the second is to reach higher nitrogen contents (≥ 3.0) than nitrogenation in a moderate N_2 -gas atmosphere. In this paper, we report our results on nitrogen absorption process in the bulky Sm_2Fe_{17} under high pressure N_2 -gas, the basic magnetism, magnetically hardening of Sm-Fe-C melt-quenched ribbons with several 100 μm in thickness by nitrogen uptake and prospects for bonded-magnets based on R-Fe-N systems.

2. NITROGEN ABSORPTION PROCESS UNDER HIGH PRESSURE N_2 -GAS

For clarifying the nitrogen diffusion process in bulky Sm_2Fe_{17} with ~ 1 mm in thickness, we nitrogenated it by changing the charging periods from 12 to 144 hrs, under N_2 -gas pressure of 6 MPa at 738K.

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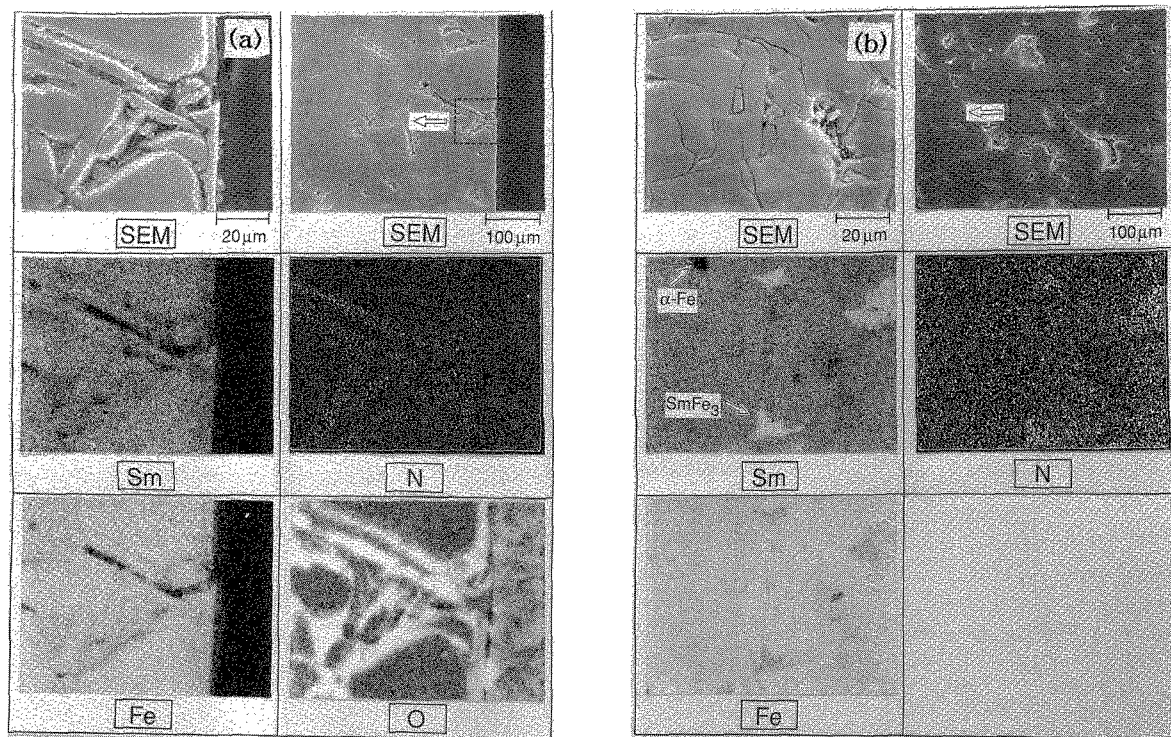


Fig. 1 SEM and EPMA-image figures (a) near surface and (b) at center in a cross section of the sheet $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.7}$ with 1 mm in thickness, where the N content of 2.7 was gravimetrically determined on average.

After nitriding, we have performed the morphological and microscopic composition analyses using scanning electron microscope (SEM) and electron probe micro-analyser (EPMA).

Fig. 1 shows the SEM and EPMA-image figures in a cross section of the sheet of $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.7}$ with 1 mm in thickness. As is seen in Fig. 1(a) near the surface of the $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.7}$ sheet, there are many cracks with various shapes and sizes along the grain boundaries, which may be caused by nitrogen absorption. Countering to our expectation, we notice that nitrogen atoms are absorbed along the grain boundaries near the cracks but is not observed inside of grains near the sheet surface. This may be originated in poisoning of the grain boundaries near the surface by remaining gases in the nitriding pressure systems. In the center of the

cross section of the $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.7}$ sheet, the nitrogen atoms are introduced homogeneously in the grain interiors, as is seen in the EPMA-figure of N element in Fig. 1(b). This indicates that a clean surface is essential for homogeneous and faster nitrogenation. There, we can also observe many cracks along the grain boundaries from the SEM-figure in Fig. 1(b) and slight segregation of $\alpha\text{-Fe}$ and SmFe_3 phases from the EPMA-image figures of Sm and Fe-elements. They remain as soft magnetic phases even after nitriding, which lead to small H_c , and its large temperature dependence.

In Fig. 2, are shown the X-ray diffraction patterns of $\text{Sm}_2\text{Fe}_{17}$ and $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ obtained by nitriding at 738K for 96 hrs under 0.1 MPa and 6 MPa, which were pulverized to powder with particle size of several 10 μm .

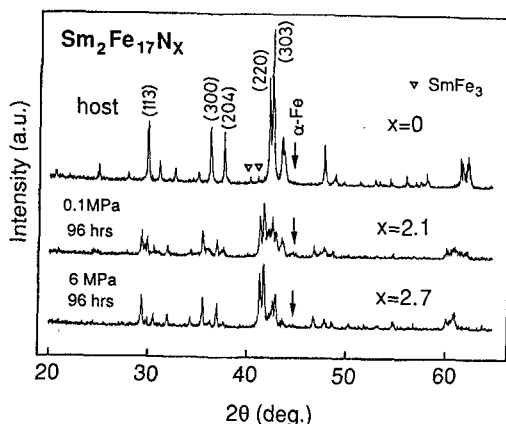


Fig. 2 X-ray diffraction patterns using Cu K α radiation of $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ obtained by heating at 738K for 96 hrs under 0.1 and 6 MPa.

As is evident from Fig. 2, the X-ray pattern of the $\text{Sm}_2\text{Fe}_{17}$ host compound is almost a single phased $\text{Th}_2\text{Zn}_{17}$ -type structure with no trace of α -Fe but only a very small (noticeable) trace of SmFe_3 . Even after nitriding the bulky $\text{Sm}_2\text{Fe}_{17}$ at 738K for as long as 96 hrs under an atmospheric pressure of N_2 -gas, nitrogen concentration determined from the increase in mass only reaches to $x=2.1$. The

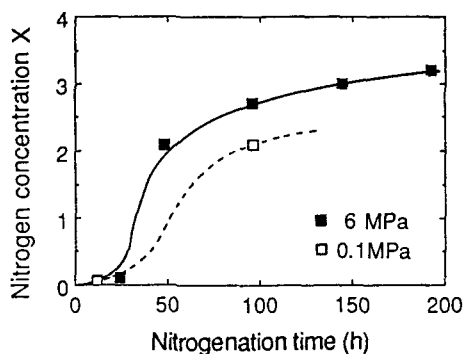


Fig. 3 Nitrogen concentration x as a function of charging periods at 738K under N_2 -gas pressures of 0.1 and 6 MPa.

X-ray diffraction pattern reveals multi-phases consisting of the host compound ($\text{Sm}_2\text{Fe}_{17}$), fully charged nitride ($\text{Sm}_2\text{Fe}_{17}\text{N}_3$) and α -Fe phases. When nitrogenated it under N_2 -gas of

6 MPa, x reaches to 2.7, leading to almost single-phased nitride without α -Fe segregation as shown in Fig. 2. From the time dependence of nitrogen concentration in the bulky $\text{Sm}_2\text{Fe}_{17}$ obtained by nitriding in the N_2 -gas (see Fig. 3), we notice that high pressure nitrogenation process is effective to complete nitriding in $\text{Sm}_2\text{Fe}_{17}$ reaching to $x=3.0$. Whenever we use pure N_2 -gas of 0.1 MPa for nitrogenation, the N content x in bulky sample does not reach 3.0, being incomplete nitrogenation.

3. STRUCTURAL AND MAGNETIC PROPERTIES OF $\text{R}_2\text{Fe}_{17}\text{N}_{3+6}$ ($\text{R}=\text{Y}$, Ce and Sm)

After confirming that all the host compounds R_2Fe_{17} were almost single-phased with a rhombohedral $\text{Th}_2\text{Zn}_{17}$ -type structure, they were

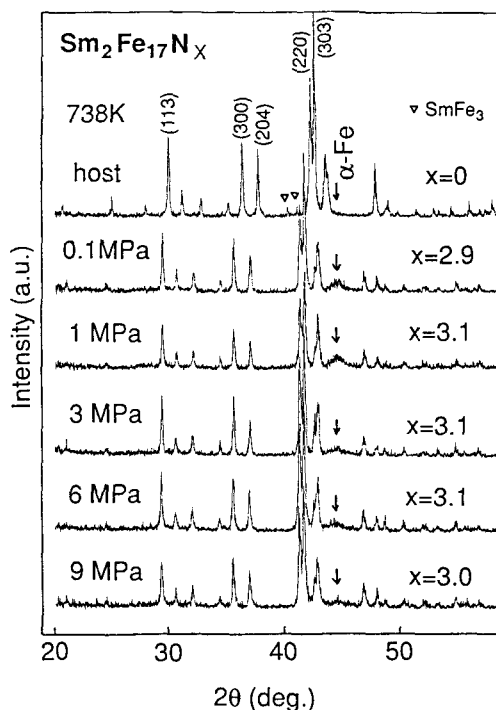


Fig. 4 X-ray diffraction patterns of $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ obtained by heating at 738K for 12 hrs under various N_2 -gas pressures

pulverized into powder with particle sizes less than 20 μm in an argon atmosphere. Nitrogenation was carried out by heating them at temperatures from 723K to 773K for 12 hrs under high-pressure N_2 -gas of 6 MPa. As is evident from Fig. 4, the reaction under high pressure N_2 -gas is quite effective for suppressing the segregation of σ -Fe on the surface of the $\text{Sm}_2\text{Fe}_{17}$ nitride. The composition image-figure of N element due to EPMA indicated that N-atoms distribute uniformly in the nitrides on the microscopic scale [2]. The structural data are summarized in Table I

Table I Structural data

Compound	a (nm)	c (nm)	$\Delta a/a$ (%)	$\Delta c/c$ (%)	$\Delta V/V_0$ (%)
Y_2Fe_{17}	0.851	1.238			
$\text{Y}_2\text{Fe}_{17}\text{N}_{3.4}$	0.868	1.275	2.0	2.9	6.9
$\text{Ce}_2\text{Fe}_{17}$	0.848	1.241			
$\text{Ce}_2\text{Fe}_{17}\text{N}_{3.6}$	0.873	1.281	2.9	3.2	9.3
$\text{Sm}_2\text{Fe}_{17}$	0.855	1.243			
$\text{Sm}_2\text{Fe}_{17}\text{N}_{3.1}$	0.874	1.265	2.3	1.5	6.2

V_0 : the volume of the host compound

for R_2Fe_{17} and their nitrides with $\text{R}=\text{Y}, \text{Ce}$ and Sm . The unusual volume expansion ($\Delta V/V_0 \sim 9\%$) for $\text{Ce}_2\text{Fe}_{17}$ upon nitrogenation could be due to the conversion of Ce^{4+} into Ce^{3+} states, showing that the character of $4f$ -electrons changes from itinerant to localized states by nitriding [2].

The magnetic characteristics obtained are summarized in Figs. 5 to 6, and Table II for all the R_2Fe_{17} and their nitrides. As is listed in Table II, the saturation magnetization of Y_2Fe_{17} per formula unit M_s increases from 1.54 T to 1.65 T at 4.2K upon nitrogenation, which could be explained by the increase of Fe moments accompanied by nitrogenation as calculated using self-consistent LMTO method by Asano et al [3] for a rhombohedral $\text{Th}_2\text{Zn}_{17}$ -type Y_2Fe_{17} . The

Table I Magnetic data

Compound	M_s (T)		$\mu_0 H_k$ (T)		T_c (K)
	300K	4.2K	300K	4.2K	
Y_2Fe_{17}		1.54	plane		300
$\text{Y}_2\text{Fe}_{17}\text{N}_{3.4}$		1.65	plane		701
$\text{Ce}_2\text{Fe}_{17}$		1.55	complex		*210
$\text{Ce}_2\text{Fe}_{17}\text{N}_{3.6}$	1.49	1.88	plane		712
$\text{Sm}_2\text{Fe}_{17}$	1.10	1.78	plane		389
$\text{Sm}_2\text{Fe}_{17}\text{N}_{3.1}$	1.58	1.81	≥ 15	≥ 35	752

* corresponding to Neel temperature T_N

Curie temperature increases by $\sim 400\text{K}$ from 300K to 701K upon nitrogenation which might be explained by suppression of spin-fluctuation [4].

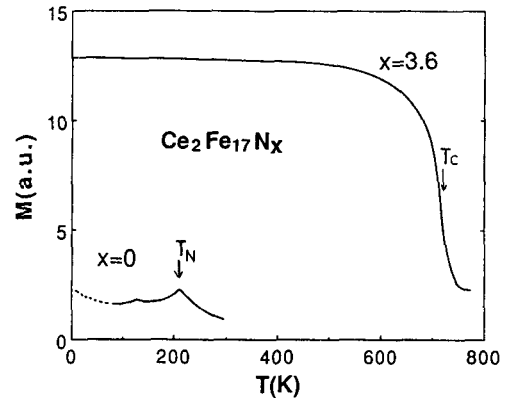


Fig. 5 Magnetization vs. temperature curves for $\text{Ce}_2\text{Fe}_{17}$ and $\text{Ce}_2\text{Fe}_{17}\text{N}_{3.6}$.

Below 210K, $\text{Ce}_2\text{Fe}_{17}$ exhibits a helical structure and transforms to a fan-structure at 110K (see Fig. 5). Before nitriding, the valence of Ce in $\text{Ce}_2\text{Fe}_{17}$ is considered to be a tetravalent state. In other words, the $4f$ -electrons behave as itinerant electrons in the crystal with a heavy mass [5]. Nitrogenation leads to strong ferromagnetism, suggesting the conversion of the $4f$ -electron character from itinerant to localized states [2]. As a result, $\text{Ce}_2\text{Fe}_{17}\text{N}_{3.6}$ reveals $T_c=704\text{K}$ and $M_s=1.49\text{T}$ at 300K, but it shows no uni-

axial anisotropy behavior at 300K, being unsuitable for permanent magnets.

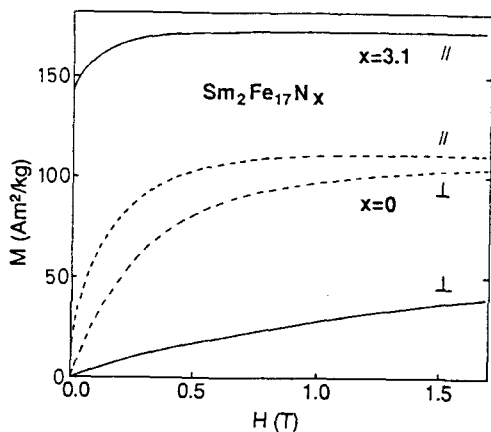


Fig. 6 Magnetization vs. magnetic field curves at 300K along the directions parallel and perpendicular to aligned-axis for $\text{Sm}_2\text{Fe}_{17}$ and $\text{Sm}_2\text{Fe}_{17}\text{N}_{3.1}$.

In Fig. 6, are shown magnetization versus magnetic field curves for aligned powder of $\text{Sm}_2\text{Fe}_{17}$ and $\text{Sm}_2\text{Fe}_{17}\text{N}_{3.1}$ at 300K. We notice appearance of strong uniaxial anisotropy upon nitrogenation (2). The magnetization along the direction perpendicular to the aligned axis is nearly linear against magnetic field indicating almost no soft magnetic impurity like $\alpha\text{-Fe}$.

4. MAGNETIC HARDENING OF AMORPHOUS RIBBON UPON NITROGENATION

The ingot $\text{Sm}_2\text{Fe}_{17}\text{C}$ was prepared by arc-melting and then amorphous $\text{Sm}_2\text{Fe}_{17}\text{C}$ ribbons were obtained by a single-roller quenching technique under a substrate surface velocity of 51 m/s. The amorphous flake-shape ribbons with several $100\mu\text{m}$ thickness were, in situ, crystallized and nitrogenated under N_2 -gas of 1 MPa in the high-pressure reactor cell.

After confirming that the crystallization temperature is $\sim 855\text{K}$ by DTA-trace in N_2 -gas, we examined to crystallize the amorphous ribbons at

several temperatures from 793K to 933K for 2 hrs, and then to nitrogenate at 723K for 4 hrs. Fig. 7 shows M_s , remanent magnetization M_r and intrinsic coercivity $\mu_0 H_{c1}$, as a function of crystallization temperature for $\text{Sm}_2\text{Fe}_{17}\text{CN}_{1.5}$. Here, all the data except triangle symbols are the results obtained by magnetizing in a field of 1.7 T. The triangles in-

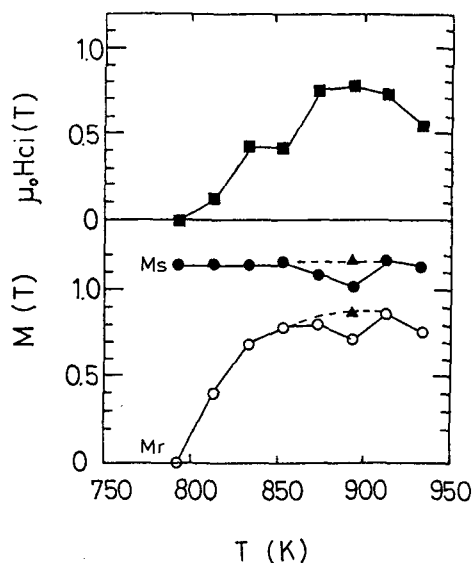


Fig. 7 Crystallization temperature dependence of $\mu_0 H_{c1}$, M_s and M_r under a field of 1.7T for the flake-shape $\text{Sm}_2\text{Fe}_{17}\text{CN}_{1.5}$. The triangles shows the data when magnetized at a high field of 7 T.

dicating those when magnetized in a higher field of 7.0 T. The difference between them suggests the existence of hard magnetic phases, which could not be fully magnetized under a weaker field of 1.7 T. Both $\mu_0 H_{c1}$ and M_r take a maximum around $T=893\text{K}$, while M_s remains almost constant. The rapid increase of $\mu_0 H_{c1}$ and M_r from 793K to 855K is due to crystal growth of magnetically isotropic microcrystalline $\text{Sm}_2\text{Fe}_{17}\text{CN}_{1.5}$ whereas both of the decreases above 893K are caused by the grain growth of the matrix phase. In this work,

the best hard magnetic properties were obtained by crystallizing the amorphous $\text{Sm}_2\text{Fe}_{17}\text{C}$ ribbon at 893K for 2 hrs and then nitriding it at 773K for 4 hrs.

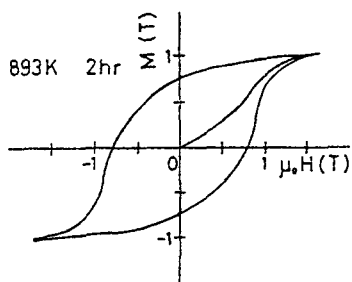


Fig. 8 Magnetic hysteresis loop after magnetized under a pulse field of 7T for the best isotropic flake-shape ribbon.

Fig. 8 shows the full hysteresis loop of the isotropic flake-shape magnet obtained under the above condition. From this figure, we obtained the following isotropic-permanent magnetic properties of $\mu_0 H_c = 0.80$ T, $M_r = 0.87$ T and $(BH)_{max} = 93$ kJ/m³ (12 MGOe). We can expect higher $\mu_0 H_c$, by completing fully nitrogenation in this system, but have to pay efforts to develop anisotropic permanent magnets composed of microcrystalline $\text{Sm}_2\text{Fe}_{17}\text{CN}_2$.

5. PROSPECTS

Since the discovery of new hard magnetic compounds $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ [1] and $\text{NdFe}_{11}\text{TiN}$ [6], special attention has been paid on developing them into new high-performance bonded magnets. As both of the nitrides are very resistant to corrosion compared to the Nd-Fe-B magnets [7], they are more suitable for bonded-magnets. The energy product has reached $(BH)_{max} = 160$ kJ/m³ in a bonded-magnet based on $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ by improving nitrogenation processes [7-9], the value of which is almost satisfactory for applications. However, the intrinsic coercive force $\mu_0 H_c$ is ~ 1 T and the temperature variation is rela-

tively large compared to the Sm-Co bonded magnets. Consequently, the Sm-Fe-N bonded-magnets have to be further improved so as to obtain higher H_c , and weaker temperature dependence for useful applications.

For improving the hard magnetic characteristics, we believe that it is important (1) to make sample characterization more careful, (2) to stabilize 2-17 and/or 1-12 phases by some small-substitutions, and (3) to synthesize the single-phased host compounds. In addition, it is also necessary (4) to understand why the α -Fe phase segregates during nitrogenation process even at temperature lower than the decomposition temperature, and (5) to clarify the mechanism of nitrogen absorption process. These fundamental problems still remain to be elucidated. As a result of resolving these problems, we can expect that much better bonded magnets with higher H_c and its weaker temperature variation are realized and become useful for various applications.

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