

## REVIEW ARTICLE

Research on the magnetic material of Sm-Fe matrix nitrides<sup>\*</sup>CUI Chunxiang<sup>\*\*</sup>, SUN Jibing, ZHANG Ying, WANG Ru, LI Lin and LIANG Zhimei

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**Abstract** In this paper, the types of Sm-Fe matrix compounds and their correlations are introduced, and progress of research on the magnetic materials of Sm-Fe matrix nitrides is also reviewed. Possible research trends of future permanent magnetic materials of Sm-Fe matrix nitrides are briefly predicted.

**Keywords:** Sm-Fe matrix, nitrides, dual-phase nano-grain rare earth permanent magnetic materials

In 1990, Coey et al.<sup>[1]</sup> developed a series of  $R_2Fe_{17}N_x$  compounds by using gas-solid reaction, in which  $Sm_2Fe_{17}N_x$  compound has strong uniaxial anisotropy at room temperature, and its anisotropy field is 140—220 kOe, twice larger than  $Nd_2Fe_{14}B$ , its Curie temperature is 749 K, and its saturation magnetization is about 1.5 T. In 1993, Skomski and Coey et al.<sup>[2]</sup> using micromagnetics calculated the theoretical magnetic energy product of  $Sm_2Fe_{17}N_3$  (2.5 nm)/ $Fe_{65}Co_{35}$  (9 nm) multi-layer orientation double phase nano-composite magnetics, which can reach the maximum of  $1 MJ/m^3$  (120 MG Oe), twice higher than that of sintered  $NdFeB$ , the best permanent magnet at present. From then on, studies on Sm-Fe matrix compounds became one of the hot topics in the magnetic material field. A lot of studies on Sm-Fe matrix compounds have been carried out in recent 10 years, but Sm-Fe matrix compounds are easy to be volatilized and oxidized in the melting process, and there are still some problems in theory and fabrication technology to be solved in the current studies, which limit the industrial application of Sm-Fe compound magnetic materials.

## 1 Types of Sm-Fe matrix compounds

The Sm-Fe matrix compounds obtained at present include:  $2:17$ ,  $1:12$ ,  $3:29$ ,  $1:7$ ,  $1:11$ ,  $1:5$ ,  $1:2$ ,  $1:3$ ,  $1:9$  and  $6:23$ -type. Detailed introduction of them is as follows:

### 1.1 $Sm_2Fe_{17}$ -type compound

$Sm_2Fe_{17}$  compound has both  $Th_2Zn_{17}$ -type and  $Th_2Ni_{17}$ -type crystal structures<sup>[3-6]</sup>. Generally speaking,  $Th_2Ni_{17}$ -type exists at high temperature, and can be transformed into  $Th_2Zn_{17}$ -type by allotropic change at low temperature. Both  $R_2Fe_{17}$  compounds come from  $CaCu_5$ -type compound  $RT_5$  stacking along  $c$ -axis, namely  $3RT_5-R + 2T \rightarrow R_2T_{17}$  or three  $RT_5$  cells stacking along  $c$ -axis, and  $Sm_2Fe_{17}$  compound is formed while an R atom is replaced by an atom of transition metal.

$Th_2Ni_{17}$ -type belongs to hexagonal crystal system, and its space group is  $P63/mmc$ . One cell unit is composed of two  $Th_2Ni_{17}$  molecules, which contains 38 atoms. Among them, Th (or R) atoms occupy the  $b$  crystal sites and the other two Th (or R) atoms occupy the  $d$  crystal sites. In the other 34 Ni (or Co or Fe etc.) atoms, six of them occupy the  $g$  crystal sites, twelve occupy the  $k$  crystal sites, four occupy the  $f$  crystal sites, and twelve occupy the  $j$  crystal sites.  $4f$  is a dumbbell crystal site and is occupied by a pair of Ni, or Co, or Fe, which is equal to the situation that rare earth atoms at the  $c$  crystal sites of  $CaCu_5$ -type structure are occupied by a pair of Ni, or Co, or Fe atoms. The formation of  $Th_2Ni_{17}$ -type structure can be considered to be the stacking of the four atom layers at  $z=0, 1/4, 1/2, 3/4$  ( $c=1$ ) along  $[0001]$  axis.

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Sm<sub>2</sub>Co<sub>17</sub> and Sm<sub>2</sub>Fe<sub>17</sub> compounds are mostly Th<sub>2</sub>Zn<sub>17</sub>-type structure at low temperature, which has similar crystal structure to Th<sub>2</sub>Ni<sub>17</sub>. Th<sub>2</sub>Zn<sub>17</sub>-type crystal structure belongs to rhombohedral structure of the rhombohedral crystal system (or trigonal system) and its space group is  $R\bar{3}m$  (166). Each cell unit includes 57 atoms, among which, six Sm (Th) atoms occupy the *c* crystal sites, nine atoms of the other 51 Fe (or Zn) atoms occupy the *d* crystal sites, 18 atoms occupy the *f* crystal sites, 18 atoms occupy the *h* crystal sites, and six atoms occupy the *c* crystal sites. 6*c* are dumbbell crystal sites. The formation of Th<sub>2</sub>Zn<sub>17</sub>-type structure can be considered to be the stacking of the six atom layers at  $z=0, 1/6, 1/3, 1/2, 2/3, 5/6$  ( $c=1$ ) along [0001] axis. The structure has two different interstitial sites, in which the bigger one is the 9*e* crystal site of octahedron and the smaller one is the 18*g* crystal site of tetrahedron.

## 1.2 ThM<sub>n12</sub>-type

Yang et al.<sup>[7-9]</sup> first found NdFe<sub>12-x</sub>M<sub>x</sub>N<sub>y</sub> (M = Ti, Mo, W, etc.  $x=1-2$ ) had strong uniaxial anisotropy, and they fabricated a rare-earth permanent magnet material NdFe<sub>10.5</sub>Mo<sub>1.5</sub>N<sub>y</sub> interstitial compound with the magnet performance of  $B_r=1.02$  T,  $H_g=477.6$  kA/m,  $(BH)_{max}=168.75$  kJ/m<sup>3</sup> by a gas-solid reaction.

The molecular formula of 1:12-type rare-earth and iron system compound can be written as R(Fe, M)<sub>12</sub> or R(Fe<sub>12-x</sub>M<sub>x</sub>). Here, M represents a special metal element, which is a prerequisite for 1:12-type compound to exist steadily, so M is a stable element for 1:12-type compound, in which M=V, Mo, and Ti. 1:12-type compound with tetragonal system ThM<sub>n12</sub>-type crystal structure and space group IA/mmm<sup>[10]</sup> has five different crystal sites named 2*a*, 8*f*, 8*i* (8*i*-1, 8*i*-2), 8*j* crystal sites. One cell unit is composed of two R(Fe, M)<sub>12</sub> molecules, in which R atoms occupy the angular point and the 2*a* crystal sites of center, and Fe and M occupy the 8*i*, 8*j*, 8*f* crystal sites. ThM<sub>n12</sub>-type structure can be derived from the CaCu<sub>5</sub> structure in which a fraction of Ca atoms in CaCu<sub>5</sub> are replaced by a pair of dumbbell metal atoms. It can be considered that 1:12-type compound is composed of four CaCu<sub>5</sub> units, in which two R atoms are replaced by metal M atoms. In the CaCu<sub>5</sub> unit, the crystal sites replaced by M atoms are 000, 101, 110 and 011. The relationship of lattice parameters between 1:5-type and

1:12-type is as follows:  $a_{1:12}=2a_{1:5}=2c_{1:5}$ ;  $c_{1:12}=a_{1:5}=1/2a_{1:12}$ , and *c*-axis of 1:12-type is perpendicular to that of 1:5-type. Neutron-diffraction analysis indicates that the stable element atoms mostly occupy the 8*j* and 8*f* crystal sites.

Different from R<sub>2</sub>Fe<sub>17</sub> series, the ion crystal sublattice of Sm (Fe, Ti)<sub>12</sub> with a small and negative crystal field  $A_2^0$  has a strong magnetocrystalline anisotropy, so it has better hard magnet performance. After nitrogenation, the ion crystal sublattice still keeps uniaxial anisotropy, but rare-earth crystal sublattice changes greatly because two nitrogen atoms around rare-earth atoms along *c*-axis make  $A_2^0$  positive and  $A_2^0 \approx 300ka_0^{-2}$ , which makes SmFe<sub>12</sub>-type compounds have *a* plane anisotropy. Similar to Sm<sub>2</sub>Fe<sub>17</sub>, nitrogen atoms exist at octahedron interstitial sites in 1:12-type rare-earth and iron system, and theoretical maximum nitrogen content is one atom per molecule. For example as for SmFe<sub>11</sub>Ti, the cell volume of the nitride expands 2%—4%, and the Curie temperatures for Sm(Fe<sub>11</sub>Ti)N<sub>y</sub> and Sm(Fe<sub>11</sub>Mo)N<sub>y</sub> are 740 K and 480—700 K, respectively.

## 1.3 R<sub>3</sub>(Fe, M)<sub>29</sub>-type

In 1968, Johnson and Smith<sup>[11]</sup> predicted the existence of 3:29-type in R-Fe-M compound by geometric crystallography. In 1992, Collocott et al.<sup>[12]</sup> found a new type of Nd(Fe, Ti)<sub>19</sub> compound at Fe-rich corner when studying the Nd-Fe-Ti ternary phase diagrams. In 1994 Li et al.<sup>[13]</sup> using X-ray diffraction and Hu et al.<sup>[14]</sup> using neutron diffraction verified that the correct molecular formula of Nd(Fe, Ti)<sub>19</sub> compound was Nd<sub>3</sub>(Fe, Ti)<sub>29</sub>. Nd<sub>3</sub>(Fe, Ti)<sub>29</sub> belongs to monoclinic crystal structure with space group A<sub>2</sub>/m, and its structure can be derived by replacing the CaCu<sub>5</sub> structure<sup>[15]</sup> by a pair of dumbbell metal atoms, which can be represented by the following formula:  $5(RFe_5)-2R+4(Fe, M)$  (2-dumbbell)  $\rightarrow R_3(Fe, M)_{29}$ . 3:29 structure can be considered to be a medial structure between rhombohedral Th<sub>2</sub>Zn<sub>17</sub> structure and tetragonal ThM<sub>n12</sub> structure. The relationship of crystal structure parameters between 3:29-type and 1:5-type can be shown as follows:  $a_{3:29}=[(2a_{1:5})^2+(c_{1:5})^2]^{1/2}$ ;  $b_{3:29}=a_{1:5}$ ;  $c=[(a_{1:5})^2+(2c_{1:5})^2]^{1/2}$ ;  $\beta=\arctan[(2a_{1:5})/c_{1:5}+\arctan[a_{1:5}/(2c_{1:5})]$ . One cell unit is composed of two molecules with 64 atoms, and six of them are R atoms, the other 58 are Fe(M) atoms. Two R atoms

occupy the 2*a* crystal sites, and 4 R atoms occupy the 4*i* crystal sites, two Fe atoms occupy *c* crystal sites, 32 Fe atoms occupy four different 8*j* crystal sites, 16 Fe atoms occupy four different 4*i* crystal sites, four Fe atoms occupy the 4*g* crystal sites, four Fe atoms occupy four different 4*e* crystal sites, and M atoms occupy a fraction of 4*i* crystal sites and 4*g* crystal sites. Nitrogen atoms occupy two big octahedron interstitial sites after nitrogenation, there are four nitrogen atoms in each formula to form Sm<sub>3</sub>(Fe, Ti)<sub>29</sub>N<sub>4</sub>, and the increasing of cell volume is 6%. The infiltration of nitrogen changes the Fe-Fe bond length (increases or decreases), but the total effect is to get positive exchange action, and to increase the Curie temperature and saturation magnetization. Anisotropy of R<sub>3</sub>(Fe, M)<sub>29</sub> is estimated to be in the range of 10–13 T, so it increases a little after nitride. In addition, preparation of R<sub>3</sub>(Fe, M)<sub>29</sub> compound is not easy to control. The element M can be V, Cr, Mo, W, etc., or be M, but 3:29-type is not always obtained by adding these elements, and the content, cooling velocity and annealing technology are still required to control. For these control conditions, there is still no consistent conclusion. The magnetic properties of Sm<sub>3</sub>(Fe<sub>0.933</sub>Ti<sub>0.067</sub>)<sub>29</sub>N<sub>4</sub> at 300 K by Koyama et al. are:  $M_s = 140 \text{ Am}^2/\text{kg}$ ,  $\mu_0 H_A = 12.8 \text{ T}$ ,  $T_c = 750 \text{ K}$ .

#### 1.4 SmFe<sub>7</sub>-type

SmFe<sub>7</sub>-type compound belongs to rhombohedral structure, which is considered to be a medial structure between Th<sub>2</sub>Zn<sub>17</sub> structure and CaCu<sub>5</sub> structure. Its space group is  $R\bar{3}m$  (166), and its typical lattice constants are  $a = 0.8554 \text{ nm}$ ,  $c = 1.2441 \text{ nm}$  [JCPDS card 190621]. Wang et al. [16, 17] studied Sm<sub>10</sub>Fe<sub>90-x</sub>Ti<sub>x</sub> ( $x = 4.5$  and  $6$ ) and got the TbCu<sub>7</sub>-type structure. They found that parent alloy plane is anisotropic. In addition, they gave the test data as follows: The Curie temperature of nitride  $T_c = 733 \text{ K}$ , anisotropic  $\mu_0 H_A = 10.5 \text{ T}$ ,  $M_s = 140 \text{ J/T kg}$ , and coercivity  $\mu_0 H_{cj} = 1.8\text{--}2.3 \text{ T}$  at room temperature. The relationship of lattice constants among 1:7-type, 2:17-type, and 1:12-type is as follows:

$$\begin{aligned} a(\text{TbCu}_7) &= a(\text{Th}_2\text{Zn}_{17})/\sqrt{3} = c(\text{ThMn}_{12}), \\ c(\text{TbCu}_7) &= c(\text{Th}_2\text{Zn}_{17})/3 = a(\text{ThMn}_{12})/2. \end{aligned}$$

Suzuki [18] studied Sm<sub>10</sub>(Fe, V)<sub>90</sub>N<sub>4</sub> by rapid solidification and found that it was TbCu<sub>7</sub> structure when the roll velocity was in the range of 15–50 m/s. The magnetic properties such as  $J_r =$

$0.71 \text{ T}$ ,  $H_{cj} = 535 \text{ kA/m}$  (6.7 kOe),  $(BH)_m = 63.7 \text{ kJ/m}^3$  were obtained when Sm<sub>10</sub>(Fe, V)<sub>90</sub>N<sub>4</sub> was nitrided at 773 K for six hours.

#### 1.5 SmTiFe<sub>10</sub>-type (1:11-type)

SmTiFe<sub>10</sub>-type compound belongs to tetragonal structure with body-centered lattice and space group  $R\bar{3}m$  (166), and its typical lattice constants are  $a = 0.8566 \text{ nm}$ ,  $c = 0.4796 \text{ nm}$  [JCPDS card 451202]. Yang et al. [19] found that SmTiFe<sub>10</sub> still belonged to ThMn<sub>12</sub>-type with uniaxial anisotropy. They gave the magnetic properties of SmTiFe<sub>10</sub> as follows: Susceptibility is 123 emu/g at room temperature, anisotropy field intensity  $H_A = 104.5 \text{ kOe}$ ,  $K_1 = 4.27 \times 10^7 \text{ erg/cm}^3$ , Curie temperature  $T_c = 610 \text{ K}$ , and potential maximum magnetic energy product is 38 MGOe. The other 1:11-type SmFe<sub>9.5</sub>Ti<sub>1.5</sub> was nonferromagnetic phase.

#### 1.6 SmFe<sub>5</sub>-type (1:5-type)

SmFe<sub>5</sub> compound belongs to CaCu<sub>5</sub>-type hexagonal structure with P6/mmm (191) space group, and its typical lattice constants are  $a = 0.496 \text{ nm}$ ,  $c = 0.415 \text{ nm}$  [JCPDS card 251099]. Its magnetic properties has not been reported till now.

#### 1.7 SmFe<sub>2</sub> and SmFe<sub>3</sub>

SmFe<sub>2</sub> belongs to Cu<sub>2</sub>Mg-type cubic structure with space group Fd3m (227), and its typical lattice constant is  $a = 0.7415 \text{ nm}$  [JCPDS card 251152]. Japanese TDK company [20] studied SmFe<sub>2</sub> and SmFe<sub>3</sub>, and found that these materials were ferromagnetic, the saturation magnetization intensity of SmFe<sub>2</sub> was 60 emu/g, and the Curie temperature was 425 °C; while the saturation magnetization of SmFe<sub>3</sub> was 80 emu/g, and the Curie temperature was 410 °C. After nitrogenation, these two compounds were decomposed into SmN and α-Fe, and the soft magnetic phase destroyed the magnetic properties of Sm<sub>2</sub>Fe<sub>17</sub>N<sub>4</sub>. Yau [21] studied the magnetic properties of SmFe<sub>3</sub> and found that it had PuNi<sub>3</sub> structure with space group R3m, and the lattice constants were  $a = 0.519 \text{ nm}$ ,  $c = 2.483 \text{ nm}$ . Yau found that the magnetic properties of SmFe<sub>3</sub> were:  $M_s = 59.1 \text{ emu/g}$ ,  $iH_c = 0.21 \text{ kOe}$ , and  $4\pi M_r = 11.6 \text{ emu/g}$ . After nitrogeation, when the nitrogen content reached 5.69wt%, the magnetic properties of SmFe<sub>3</sub> were:  $4\pi M_s = 53.1 \text{ emu/g}$ ,  $4\pi M_r = 29.3 \text{ emu/g}$ ,  $H_A = 56 \text{ kOe}$ ,  $iH_c = 1.3 \text{ kOe}$ , and  $T_c = 380 \text{ °C}$ . After hy-

drogenation,  $\text{SmFe}_3\text{H}_y$ , when  $y=1.78$ ,  $4\pi M_s=72.5 \text{ emu/g}$ ,  $4\pi M_r=6.3 \text{ emu/g}$ ,  $H_A=32 \text{ kOe}$ ,  $H_c=0.15 \text{ kOe}$ , possessed the uniaxial anisotropy, and its anisotropy field was:  $H_A=61 \text{ kOe}$ ,  $T_c=378 \text{ }^\circ\text{C}$  (651 K), while for  $\text{SmFe}_2$ ,  $T_c=395 \text{ }^\circ\text{C}$ .

### 1.8 $\text{Sm}_{10}\text{Fe}_{90}$ -type

$\text{Sm}_{10}\text{Fe}_{90}$  compound belongs to  $\text{Cu}_7\text{Tb}$ -type hexagonal structure with space group  $\text{P6}/\text{mmm}$  (191), its typical lattice constants are  $a=0.49056 \text{ nm}$ ,  $c=0.41886 \text{ nm}$  [JCPDS card 43131], and its magnetic performance has not been reported till now.

### 1.9 $\text{Sm}_6\text{Fe}_{23}$ -type

Samata et al. [22] studied  $\text{SmFe}$  alloy with the ratio of atoms  $\text{Sm}:\text{Fe}=65:35$  and found that it was  $\text{Th}_6\text{Mn}_{23}$ -type structure with space group  $\text{Fm}\bar{3}\text{m}$ , and its lattice constant was  $a=1.2178 \pm 0.006 \text{ nm}$ . The results calculated from B-H curve were indicated as follows: the magnetic moment per molecular formula is  $59 \mu_B$  (at 5 K), the anisotropy field intensity is  $6.1 \text{ kOe}$ , the anisotropy constants  $K_1=-2.7 \times 10^6 \text{ erg/cm}^3$ , and  $K_2=6.3 \times 10^5 \text{ erg/cm}^3$ .

## 2 Existing problems in the research of Sm-Fe matrix nitride compounds

At present the potential Sm-Fe matrix nitride compounds used for permanent magnets are  $2:17$ -type,  $3:29$ -type, and  $1:12$ -type. The structure of  $2:17$ -type with good magnetic properties is stable, while  $3:29$ -type and  $1:12$ -type need the addition of stable elements and are easy to be restricted by the condition of smelting and heat treatment. However, generally, these three types of compounds will still the research focuses in the next few years, because there are still some problems in the process of preparing these nitride powders and magnet. There is a long way to go to make the practical fourth-generation permanent-magnet materials.

### 2.1 Technical problems of fabrication process of Sm-Fe matrix nitride compounds

Compared with the third-generation permanent-magnet material  $\text{NdFeB}$ , the fabrication technology of Sm-Fe matrix nitride compounds is relatively complex. Firstly, tetragonal phase  $\text{NdFeB}$  can be obtained directly by casting, but  $3d-4f$  nitride needs to choose a proper nitrogenation process to get perfect

magnetic properties. The reaction kinetics of nitrogenation for  $\text{Sm}_2\text{Fe}_{17}$  parent alloy is slow, and the magnetic properties are closely related to nitrogen content and homogeneity of nitrogen, so all the particles are expected to be fully nitrated from surface to the core, otherwise the soft magnetic core without nitrogenation will decrease its coercivity. So the parent alloy needs to be crushed into fine powder ( $<40 \mu\text{m}$ ) [23]. In addition, the coercivity increases with the decrease of the size of particles in the range of  $1-10 \mu\text{m}$ . The single domain particle size of  $\text{Sm}_2\text{Fe}_{17}$  is about  $300 \text{ nm}$ , and its magnetization is consistent with the magnetization reversal of single domain, when the particle size is about  $1-3 \mu\text{m}$ . So it is good for the size of  $\text{Sm}_2\text{Fe}_{17}\text{N}_y$  particles in this range. In order to get the fine and homogeneous powder, it is necessary to grind the nitride, but the process will increase its inner stress and destroy its crystal structure. Generally, when the octahedron  $9e$  crystal sites of  $\text{Sm}_2\text{Fe}_{17}$  are totally taken up by nitrogen, its molecular formula is  $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ , but the content of nitrogen over 3 atoms is harmful to the magnetic properties, and it can decrease  $K_1$  [24-26] and reduce  $T_c$  by  $10 \text{ K}$  [3]. Secondly, compared with Nd and Fe, the melting point ( $1345.2 \text{ K}$ ) and the boiling point ( $2073 \text{ K}$ ) of Sm are low, so Sm will be volatilized in the process of melting and annealing even nitrating, which makes the composition of Sm-Fe alloy unstable. Otherwise, the volatilized Sm does harm to the vacuum system during these processes running in a vacuum condition. Thirdly, the whole fabrication process greatly affects the magnetic properties, so the fabrication process needs to be further optimized, and at the same time new measurements to prevent powder from oxidizing are needed.

### 2.2 Nitrogenation mechanism of Sm-Fe matrix nitride compounds needs further study

At present, there are mainly two mechanisms about nitrogenation. One is free diffusion mechanism [27-29], with nitrogen continuous diffusing nitrogen atoms from the surface to the core of the particle, and the nitrogen content varies continuously. Nitrogen only occupies the  $9e$  crystal sites, and nitrogen can exist steadily at the  $9e$  crystal sites because of high bond energy. The other mechanism [30-36] is trapping diffusion or chemical reaction diffusion, which makes nitrogen diffuse in the  $18g$  crystal sites with the energy for hard diffusing. Nitrogen at the  $9e$  crystal sites, which is the result of chemical reac-

tion, cannot be moved once it enters  $9e$ .

2.3 A big difference between magnetic properties of Sm-Fe matrix nitride compounds and theoretical values

Generally, coercivity of nitride powder should not be lower than  $550\text{--}800\text{ kA/m}^{[3]}$ , and studies are mostly at laboratory level. The magnetic energy product of isotropy polycrystal  $\text{Sm}_2\text{Fe}_{17}\text{N}_y$  obtained by different methods is  $100\text{ kJ/m}^3$ , and the maximum is estimated to be  $160\text{ kJ/m}^{3[3]}$ , far from the theoretical value of  $472.0\text{ kJ/m}^3$ , without displaying the perfect magnetic properties of  $\text{Sm}_2\text{Fe}_{17}\text{N}_y$ . The coercivity is about  $2\text{ MA/m}$ , and its maximum record is  $3.5\text{ MA/m}$ . The remnant magnetism is  $0.7\text{--}0.8\text{ T}$ , lower or equal to  $M_s/2$ . In most cases only the maximum variable is given, such as high remnant magnetism with low coercivity, or high coercivity with low remnant magnetism. In addition, different investigators give different magnetic properties for the same composition because of the different experimental condition, so the repeatability of the experiment is low.

2.4 Sm-Fe matrix nitride compounds can be used only for bonding magnets

The nitrogenation process is irreversible, and vacuum pumping cannot make nitrogen deviate from the interstitial crystal sites once the nitrides are formed. The nitrogenation temperature is about  $350\text{--}500\text{ }^\circ\text{C}$ . It is difficult to nitride at too low a temperature, and at too high a temperature,  $\text{Sm}_2\text{Fe}_{17}\text{N}_y$  will decompose into  $\text{SmN}$ ,  $\alpha\text{-Fe}$  and  $\text{Fe}_4\text{N}$ , without permanent magnetic properties. However, the sintering temperature is mostly higher than  $500\text{ }^\circ\text{C}$ , so  $\text{Sm}_2\text{Fe}_{17}\text{N}_y$  cannot be used for sintering magnets but only for bonding magnets. At present the magnetic energy product of  $15\text{--}25\text{ wt}\%$  Zn bonding  $\text{Sm}_2\text{Fe}_{17}\text{N}_y$  is lower than  $80\text{--}90\text{ kJ/m}^3$ , because cohesive material diluting effects can strongly decrease the remnant magnetism. The strength of bonding magnet will decrease greatly with the further decrease of the Zn content. The magnetic energy product of  $\text{Sm}_2\text{Fe}_{17}\text{N}_y$  bonded by polymers can be over  $150\text{ kJ/m}^3$ , but the softening temperature of polymer is too low, and the superiority of stable magnetic properties at high temperature for  $\text{Sm}_2\text{Fe}_{17}\text{N}_y$  cannot be used. So the problems of how to get bonding magnets with strong strength, high softening tempera-

ture, and strong magnetic properties are hard to be solved. A greater press strength is needed to apply in the orientation pressing, so the strength of the non-magnetic steel mold needs to be improved, and the density after cold static pressing should be lower (about  $5.0\text{ g/cm}^3$ ).

2.5 New preparation ways to obtain Sm-Fe matrix nitride compounds need optimizing

At present, in all the fabrication processes to get Sm-Fe matrix nitride compounds, traditional powder metallurgy is the main method in experiment and industry for its simplicity. However, its disadvantage is big corner angle discrete field effect for polygon particles after rubbing or milling, and the particle size distribution range is relatively large<sup>[35, 36]</sup>. The deoxidizing diffusion method is hard to develop for its inevitable bathing makes powders be oxidized even though the raw material is cheap. Although studies on mechanical alloying, HDDR, and rapid solidification have seen much progress, there is no well-accepted explanation about the action mechanism, the powders are mainly isotropic, and the remnant magnetism is hard to increase. So to obtain anisotropic powders by changing the composition and heat treatment condition is the main research work in the future. In addition, for the phenomenon that amorphous phase appears in both mechanical alloying and rapid solidification, different investigators draw different conclusions in the method to control crystalline temperature, time and  $\alpha\text{-Fe}$  contents during crystalline treatment, which makes it hard to manufacture<sup>[37]</sup>. Hydrogenation, disproportionation, desorption and recombination (HDDR) treatment, which can crush particles before nitrogenation, is beneficial to nitriding. But HDDR is only a process of decomposition and superposition, and  $\alpha\text{-Fe}$  can be produced during this process. No well agreed explanation about HDDR and desorption-recombination (HD) is given till now. The effects of nitrogen press, liquidity, and purity during nitrogenation on the nitrogen content and magnetic properties have not been extensively studied.

2.6 Contributions of substituted elements

At present, alloy elements added to Sm-Fe alloy are mainly IV B, V B, VI B group elements: Ti ( $Z=22$ ), V ( $Z=23$ ), Cr ( $Z=24$ ), Zr ( $Z=40$ ), Nb ( $Z=41$ ), Mo ( $Z=42$ ), Hf ( $Z=72$ ), Ta ( $Z=73$ ), W ( $Z=74$ ); VIII B group element: Mn ( $Z=25$ ); VIII B

group elements: Co ( $Z=27$ ), Ni ( $Z=28$ ), and I B group element Cu ( $Z=29$ ). In recent ten years, the exact explanation about magnetic properties and structure of Sm-Fe(M) alloy has been accepted, but there are many divergences about the contribution of substituted elements to different Sm-Fe matrix nitride compounds, which needs to be researched further, especially for the relationship between phase and structure of nitride and magnetic properties in different methods.

## 2.7 Characteristics of Sm-Fe matrix nitride compounds need further studies

The relationship among magnetic properties and structure, composition and fabrication method needs perfect experimental data, especially for 2:17-type, 3:29-type and 1:12-type.

## 2.8 Inconsistent testing methods for magnetic properties affect the testing accuracy

At present the instruments to test magnetic properties are mainly Superconducting Quantum Interference Device (SQUID, the maximum applied magnetic field is over 5 T), Vertical Sliding Sample Magnetometer (the maximum applied magnetic field can be over 20 T), magnetic balance, impulse magnetometer (the applied magnetic field can be over 7–12 T), Vibrating Sample Magnetometer (VSM, the maximum applied magnetic field is 2–3 T), hysteresiscope (2 T), fluxgraph, and permanent magnetic measuring instrument, etc. The powders cannot be tested directly, but the magnetic properties of powders can only be tested after mixing with ceresin wax and orienting after pressing, so the magnetic properties may be different for different instruments and applied magnetic fields. SQUID and VSM belong to open circuit test, and can directly obtain the powders' moment or magnetization, but some investigators obtain the magnetization values by calculating the theoretical density. Hard magnetic materials cannot be saturated in the applied magnetic field of 2 T during the tests of magnetic properties, so the remnant magnetization and coercivity are low. Some permanent measuring instruments belong to closed-circuit test used only for oriented massive samples, and the magnetization intensity can be obtained. At present, there are still no uniform testing instruments for magnetic properties, because the difference of experimental condition among different laboratories is big and intercomparison for the same property is bad.

## 3 Perspectives

(1) Single phase Sm-Fe matrix magnetic material with nearly theoretical magnetic properties prepared by any new fabrication method, is the research focus at present. Main methods used for the fabrication of Sm-Fe matrix magnetic material are powder metallurgy, mechanical alloying, HDDR and a rapid solidification, but there is a definite difference between the magnetic properties and theoretical values. Effective combination of different fabrication methods should be taken into consideration, such as the combination of rapid solidification with HDDR, airflow milling, and the combination of powder metallurgy with HDDR, etc. Non-oxygen production line for continuous manufacture is the key factor to determine the magnetic properties of these types of magnetic materials.

(2) Another important aspect is Sm-Fe-N/ $\alpha$ -Fe dual-phase nano-grain magnetic material. At present Sm-Fe matrix magnetic material is easy to obtain by rapid solidification, but total crystallization of amorphous phase is difficult to do especially for theoretically real coupling of Sm-Fe-N/ $\alpha$ -Fe dual-phase. In addition, how to measure the reciprocity of dual-phase nano-grain coupling and control the ratio of dual-phase and crystal stability will affect the ultimate coupling results.

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