Structure and Magnetic Properties of Mechanically Alloyed Sm(Fe,Ti)$_7$ Compounds and Their Nitrides

H. T. Kim

Department of Metallurgical Engineering, Chungnam National University, Taejon 306-764, Korea

Mechanically alloyed TbCu$_7$-type Sm$_{12.5}$Fe$_{87.5-x}$Ti$_x$ ($x=0$, 2.5, 5, 7.5), and their nitrides have been studied systematically by X-ray diffraction, A.C. initial susceptibility, and pulsed magnetization measurement. In this series, the volume expansion by nitriding is 5.6%~7.3%, and the increment of the Curie temperature is in the range of 210 °C~350 °C. With increasing Ti content, the remanence decreases linearly due to the substitution of non-magnetic Ti, and the coercivity decreases rapidly from 34.6 kA/cm (43.5 kOe) for $x=0$ to 14.3 kA/cm (18 kOe) for $x=7.5$. In the Sm$_{12.5}$Fe$_{87.5-x}$Ti$_x$N$_y$ series, the best magnetic properties were obtained from Sm$_{12.5}$Fe$_{87.5}$N$_y$ ($x=0$) with $_iH_c=34.6$ kA/cm (43.5 kOe), $B_r=0.75$ T, and $(BH)_{max}=113.8$ kJ/m^3 (10.9 MGOe).

1. Introduction

Sm containing iron-rich nitrides have been considered as potential candidates for permanent magnet applications due to the strong uniaxial anisotropy contributed from the Sm sublattice. Since the discovery of Sm$_2$Fe$_{17}$N [1] much attention has been focussed on the study of nitrides introduced into the Sm-Fe system. Katter *et al.* [2] reported that the magnetic properties of Th$_2$Zn$_{17}$-type Sm$_{12}$Fe$_{88}$N$_d$ made by rapid solidification were $_iH_c=16.7$ kA/cm (21.0 kOe), $B_r=0.73$ T, and $(BH)_{max}=65.6$ kJ/m^3 (8.2 MGOe), and those of TbCu$_7$-type Sm$_{10.6}$Fe$_{89.4}$N$_d$ were $_iH_c=4.9$ kA/cm (6.2 kOe), $B_r=0.86$ T, and $(BH)_{max}=69.6$ kJ/m^3 (8.7 MGOe). Liu *et al.* [3] reported that the best magnetic properties of TbCu$_7$-type Sm$_{10}$Fe$_{90}$N made by mechanical alloying were $_iH_c=35.0$ kA/cm (44 kOe), $B_r=0.86$ T, and $(BH)_{max}=$ 113.8 kJ/m^3 (14.3 MGOe). And Zhao *et al.* [4] reported the properties of Sm$_2$Fe$_{17}$N$_y$ made by the hydrogenation-disproportionation-desorbtion-recombination (HDDR) process, to be $_iH_c=16.7$ kA/cm (20.1 kOe), $B_r=0.81$ T, and $(BH)_{max}=103.5$ kJ/m^3 (13.0 MGOe).

In this work we have systematically studied mechanically alloyed Sm$_{12.5}$Fe$_{87.5-x}$Ti$_x$ ($x=0$, 2.5, 5, 7.5), and their nitrides, and report the structure and magnetic properties depending on the Ti content.

2. Experimental

The nominal compositions of Sm$_{12.5}$Fe$_{87.5-x}$Ti$_x$ ($x=0$, 2.5, 5, 7.5) were mechanically alloyed for 4 hours under an Ar atmosphere using a modified high-energy ball mill, with raw materials of 99.9% and 99.6% purity for Sm and Fe,

respectively. The mechanically alloyed powders were annealed at 600 °C~850 °C for 0.5 hour in an Ar atmosphere. Nitrides were prepared by heating the mechanically alloyed fine powders at 450 °C for 3 hours in a N$_2$ atmosphere. Crystal structure was examined by X-ray diffraction using Cu-K_a radiation with a graphite monochrometer. A.C. initial susceptibility measurements were performed to determine the Curie temperature. In order to measure the magnetic properties, fine particles were embedded in epoxy-resin and solidified to form cylindrical isotropic magnets about 2 mm-diameter and 20 mm-length. Magnetic properties were measured by a pulsed-field magnetometer in fields up to 10 T.

3. Results and Discussion

In the Sm$_{12.5}$Fe$_{87.5-x}$Ti$_x$ ($x=0$, 2.5, 5, 7.5) compounds, the dependence of magnetic phases and Curie temperature depending on the Ti content were examined. The magnetic phases were analyzed by X-ray diffraction in combination with A.C. initial susceptibility measurements. Fig. 1 shows the X-ray diffraction patterns for the mechanically alloyed Sm$_{12.5}$Fe$_{87.5-x}$Ti$_x$ ($x=0$, 2.5, 5, 7.5) samples before (a) and after (b) nitrogenation. In the patterns of Fig. 1(a), the whole sample consists of the TbCu$_7$-type phase with a small amount of a-Fe. The amount of the minor a-Fe phase decreases with increasing Ti content, due to the substitution of Ti for Fe. For the Sm$_{12.5}$Fe$_{87.5}$ ($x=0$) sample, we can see small (204), (211), (216), and (413) peaks which are related to the Th$_2$Zn$_{17}$-type phase. But the Curie temperature (T_c) of the Sm$_{12.5}$Fe$_{87.5}$ sample shown in Fig. 2 is 140 °C, which indicates the existence of a metastable TbCu$_7$-type phase as

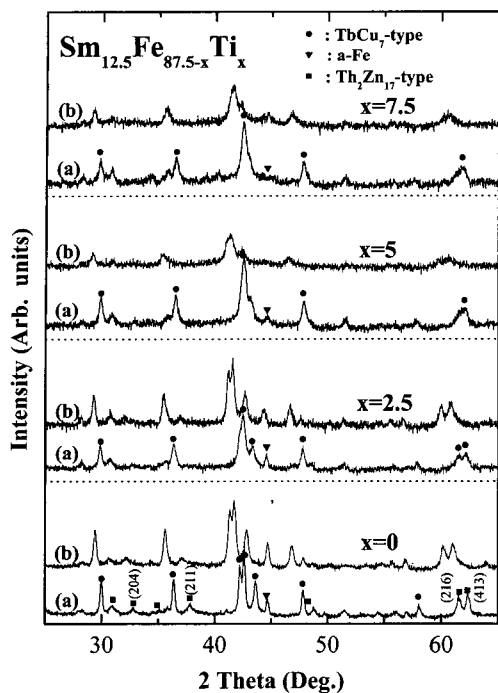Fig. 1. X-ray diffraction patterns of $Sm_{12.5}Fe_{87.5-x}Ti_x$ (x=0, 2.5, 5, 7.5) compounds mechanically alloyed for 4 h. (a) annealed at 750 °C for 30 min., and (b) subsequently nitrogenated at 450 °C for 3 h.

Fig. 2. The temperature dependence of A.C. initial susceptibility for $Sm_{12.5}Fe_{87.5-x}Ti_x$ (x=0, 2.5, 5, 7.5) compounds (a) before and (b) after nitrogenation.

previously reported by Liu *et al.* [3]

It is well known that the Th_2Zn_{17}-type structure can be derived from the $CaCu_5$ structure by replacing some of the rare-earth (R) atoms by transition metal (TM) dumbbells. [5] Judging from the pattern of X-ray diffraction in Fig. 1(a) and the value of the Curie temperature (140 °C in Fig. 2(a)) which is extremely close to the Curie temperature (120 °C) of Sm-Fe compound having a Th_2Zn_{17}-type structure, we assume that partial substitution of R by TM dumbbells has occurred, resulting in a mixture of the $TbCu_7$-type and the Th_2Zn_{17}-type phases. Similar behavior has been observed by Shield *et al.* [6] that the partially ordered Sm_2Fe_{17}, closer to the $SmFe_7$ structure, formed upon melt-spinning $Sm_{11}Fe_{99}$. And in comparison with the previous report [3] that only the $TbCu_7$-type phase exists in the composition $Sm_{12.5}Fe_{87.5}$, my sample of $Sm_{12.5}Fe_{87.5}$ has substantial a-Fe, which results from the different thermal history. The different thermal history may contribute to be formed the $TbCu_7$-type phase having the partial formation of the Th_2Zn_{17}-type phase. Meanwhile, the $Sm_{12.5}Fe_{80}Ti_{7.5}$ (x=7.5) compound having a main phase of the $TbCu_7$-type as shown in Fig. 2(a), show a second phase of the $ThMn_{12}$-type with T_c of 310 °C.

In the $Sm_{12.5}Fe_{80}Ti_{7.5}$ compound formed with the $TbCu_7$-type structure, the solubility of Ti in the Fe sublattice reaches 8.6 at. %. This value is double the solubility of 4.2 at. % in the Sm-Fe compound with the Th_2Zn_{17}-type structure reported by one group [7]. This means that the solubility of Ti atoms in an Fe sublattice for the $TbCu_7$-type

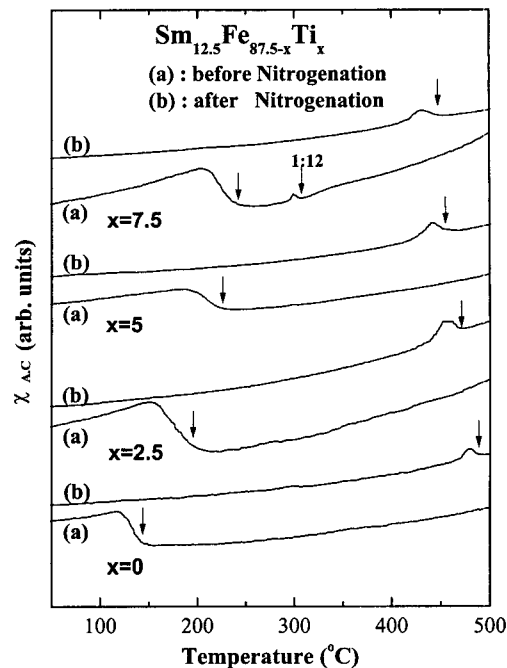structure is higher than that for the Th_2Zn_{17}-type structure, which seems to be the reason that the $TbCu_7$-type is closer to the non-equilibrium phase.

In the A.C. initial susceptibility curves of Fig. 2(a), the results show the same trend which is in good agreement with those of X-ray diffraction. The Curie temperature, T_c of the $TbCu_7$-type $Sm_{12.5}Fe_{87.5-x}Ti_x$ (x=0, 2.5, 5, 7.5) compounds is in the wide range of 140 °C~240 °C, implying the
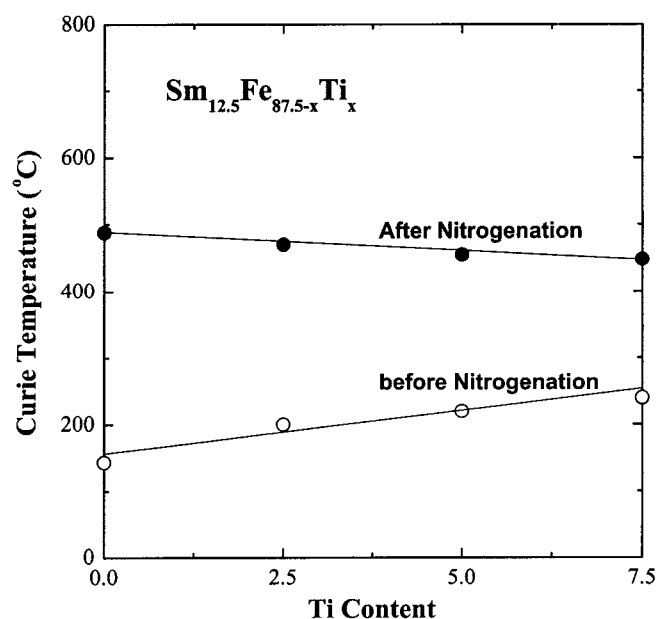

Fig. 3. The Curie temperature dependence on Ti content for $Sm_{12.5}Fe_{87.5-x}Ti_x$ (x=0, 2.5, 5, 7.5) compounds (a) before and (b) after nitrogenation.

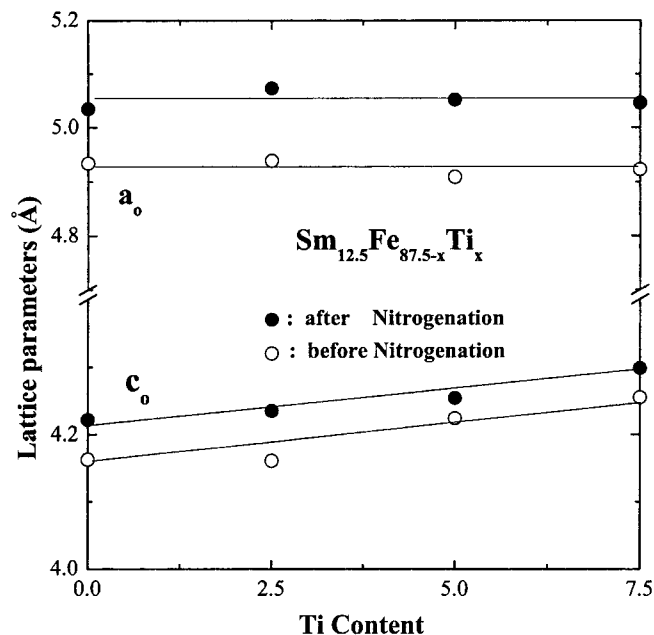Fig. 4. The lattice parameter dependence on Ti content for $Sm_{12.5}Fe_{87.5-x}Ti_x$ (x=0, 2.5, 5, 7.5) compounds before ($\circ$) and after ($\bullet$) nitrogenation.

solid solubility of compounds. The linear increase of T_c with increasing Ti content, as shown in Fig. 3(a), results from the increase of the lattice parameter c as plotted in Fig. 4, which may be due to the substitution of Ti atoms having larger atomic radius than Fe atoms.

In the study of $Sm_{12.5}Fe_{87.5-x}Ti_xN_y$ (x=0, 2.5, 5, 7.5) compounds, compared to the non-nitrides, the structures are not changed and still remain the $TbCu_7$-type phase, but the diffraction peaks are shifted to lower angles as shown in Fig. 1(b), indicating an expansion of the lattice. The lattice parameters a and c vs. Ti content before ($\circ$) and after ($\bullet$) nitrogenation are plotted in Fig. 4. With increasing Ti content, the lattice parameter c increases linearly resulting from the substitution of Ti atoms having larger atomic radius than Fe atoms, while the lattice parameter a remains almost constant. Comparing the chnange of lattice constants a and c before and after nitrogenation, the increment of a is larger

than that of c. They are approximately 2.5% and 1.5%, respectively, and the corresponding volume expansion due to the nitrogenation is in the range of 5.6%~7.3% as shown in Table 1. It is well known that the increase of Curie temperature owing to the nitrogenation is due to the volume expansion resulting from the introduced nitrogen atoms. In the curves of Fig. 2(b), the T_c of whole samples are considerably increased after nitrogenation. The increment of T_c owing to the nitrogenation is in the range of 210 °C~ 350 °C, and decreases with increasing Ti content. The increase of T_c has been ascribed to the variation of some interatomic Fe-Fe distances. Although the lattice volume is increased with increasing Ti content, the Curie temperature is decreased, which is attributed to the higher Ti content hindering the introduction of nitrogen, which can contribute
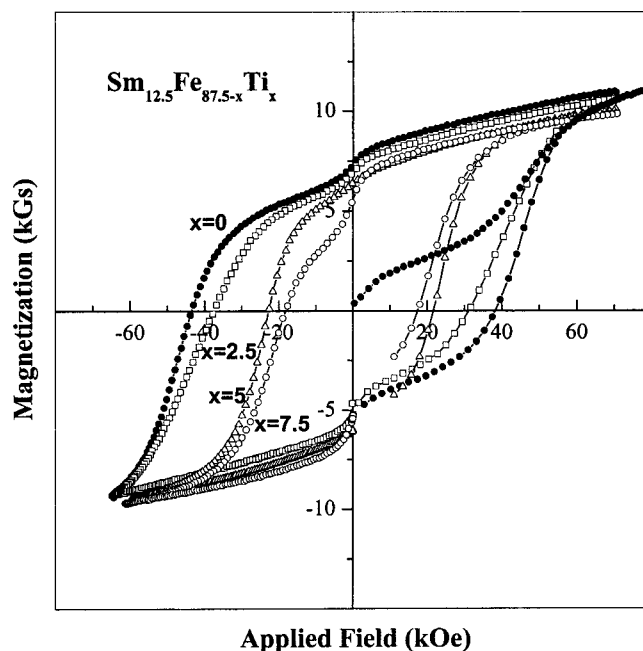

Fig. 5. An initial magnetization curve of $Sm_{12.5}Fe_{87.5}$ (x=0) and hysteresis loops of $Sm_{12.5}Fe_{87.5-x}Ti_xN_y$ (x=0, 2.5, 5, 7.5) compounds mechanically alloyed for 4 h, annealed at 750 °C for 0.5 h, and subsequently nitrogenated at 450 °C for 3 h.

Table 1. Structure, lattice parameters a and c, unit cell volume v, volume expansion Dv/v, and axial ratio c/a for mechanically alloyed $Sm_{12.5}Fe_{87.5-x}Ti_x$ (x=0, 2.5, 5, 7.5) annealed at 750 °C for 0.5 h, and subsequently nitrogenated at 450 °C for 3 h

| Compound	Structure	Lattice parameter			Δv/v (%)	c/a
		a (Å)	c (Å)	v (Å^3)		
$Sm_{12.5}Fe_{87.5}$ (x=0)	hexa.-$TbCu_7$-type	4.934	4.163	87.77		0.845
$Sm_{12.5}Fe_{87.5}N_y$	hexa.-$TbCu_7$-type	5.035	4.222	92.69	5.6	0.839
$Sm_{12.5}Fe_{85}Ti_{2.5}$ (x=2.5)	hexa.-$TbCu_7$-type	4.939	4.161	87.90		0.843
$Sm_{12.5}Fe_{85}Ti_{2.5}N_y$	hexa.-$TbCu_7$-type	5.073	4.235	94.38	7.3	0.835
$Sm_{12.5}Fe_{82.5}Ti_5$ (x=5)	hexa.-$TbCu_7$-type	4.909	4.224	88.15		0.860
$Sm_{12.5}Fe_{82.5}Ti_5N_y$	hexa.-$TbCu_7$-type	5.052	4.254	94.02	6.7	0.842
$Sm_{12.5}Fe_{80}Ti_{7.5}$ (x=7.5)	hexa.-$TbCu_7$-type	4.923	4.255	89.31		0.864
$Sm_{12.5}Fe_{80}Ti_{7.5}N_y$	hexa.-$TbCu_7$-type	5.046	4.298	94.77	6.1	0.852
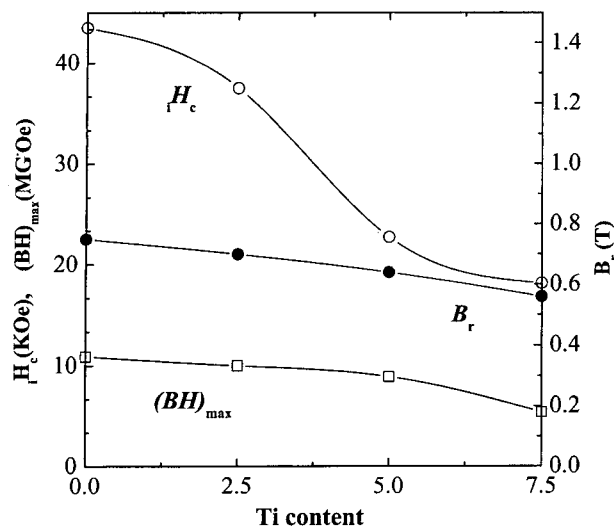
Fig. 6. Variation of the coercivity, $_iH_c$, the remanence, B_r, and the maximum energy product, $(BH)_{max}$ as a function of Ti content for $Sm_{12.5}Fe_{87.5-x}Ti_xN_y$ (x=0, 2.5, 5, 7.5) compounds.

to the Curie temperature more than Ti. The increasing ratio of T_c with respect to the Ti content is about 13 °C per at.% of Ti.

The mechanically alloyed powders were shown to be amorphous by X-ray diffraction, and the optimum annealing temperature for obtaining high coercivity was 750 °C. All the annealed samples have coercivity lower than 0.3 kA/cm before nitrogenation. Fig. 5 shows the hysteresis loops of $Sm_{12.5}Fe_{87.5-x}Ti_xN_y$ (x=0, 2.5, 5, 7.5) compounds and an initial magnetization curve of the $Sm_{12.5}Fe_{87.5}$ compound. The shape of the initial magnetization curve for the $Sm_{12.5}Fe_{87.5}N_y$ (x=0) compound suggests that the coercivity mechanism in this sample is a combination of domain nucleation and wall pinning. The step in the demagnetization curves near zero field is attributed to the magnetically soft a-Fe phase as revealed in Fig. 1.

The coercivity $_iH_c$, the remanence B_r, and the maximum energy product $(BH)_{max}$ are plotted as a function of the Ti content in Fig. 6. The remanence is 0.56 T~0.75 T, and decreases almost linearly with increasing Ti content due to the addition of non-magnetic Ti. And the coercivity decreases rapidly in the range of 34.6 kA/cm (43.5 kOe) ~14.3 kA/cm (18 kOe), where the deterioration of the coercivity with increasing Ti content is ascribed to the dramatic variation of the anisotropy of the Sm compound [7]. Espe-

cially in the compound $Sm_{12.5}Fe_{80}Ti_{7.5}N_y$ (x=7.5), the formation of a minor phase such as the ThMn$_{12}$-type phase having lower anisotropy field, gives rise to the deterioration of the coercivity as well.

4. Conclusions

The mechanically alloyed $Sm_{12.5}Fe_{87.5-x}Ti_x$ ($0 \le x \le 7.5$) samples consist of the TbCu$_7$-type phase as a main phase with a small amount of a-Fe. The $Sm_{12.5}Fe_{87.5}$(x=0) sample shows the evidence for the partially ordered Th$_2$Zn$_{17}$-type phase, and the ThMn$_{12}$-type phase starts to be formed in $Sm_{12.5}Fe_{80}Ti_{7.5}$ (x=7.5). The T_c of the TbCu$_7$-type $Sm_{12.5}Fe_{87.5-x}Ti_x$ (x=0, 2.5, 5, 7.5) is in the range of 140 °C~240 °C, implying the solid solubility of the compounds. After nitrogenation, the structure of $Sm_{12.5}Fe_{87.5-x}Ti_xN_y$ ($0 \le x \le 7.5$) is not changed and still remains the TbCu$_7$-type, but the increments of T_c are 210 °C~350 °C resulting from the considerable volume expansion of 5.6%~7.3%. The amount of the increment, however, is decreased with increasing Ti content. The magnetic properties of the $Sm_{12.5}Fe_{87.5-x}Ti_xN_y$ ($0 \le x \le 7.5$) show that with increasing Ti the remanence decreases almost linearly due to the addition of non-magnetic Ti. And the coercivity decreases rapidly, especially at the composition $Sm_{12.5}Fe_{80}Ti_{7.5}N_y$ (x=7.5) which is ascribed to the formation of a minor phase such as ThMn$_{12}$-type having lower anisotropy field.

References

[1] J. M. D. Coey and Hong Sun, J. Magn. Magn. Mater., **87**, L251 (1990).

[2] M. Katter, J. Wecker and L. Schultz, J. Appl. Phys., **70**, 3188 (1991).

[3] Wei Liu, Qun Wang, X. K. Sun, Xin-guo Zhao, Tong Zhao, Zhi-dong Zhang, Y. C. Chuang, J. Magn. Magn. Mater., **131**, 413 (1994).

[4] Xin-guo Zhao, Zhi-dong Zhang, Wei Liu, Qun-feng Xiao and X. K. Sun, J. Magn. Magn. Mater., **148**, 419 (1995).

[5] H. H. Stadelmaiser, Z. Metallkder., **75**, 227 (1984).

[6] J. E. Shield, C. P. Li, and D. J. Branagan, J. Magn. Magn. Mater., **188**(3), 353 (1995).

[7] A. Paoluzi, L. Pareti, J. Magn. Magn. Mater., **189**, 89 (1998).