Magnetic properties of $(RSm)_2(FeCo)_{17}N_x$ alloys (R= La/Ce/Pr)

J.M. Yau, T.S. Chin and K.H. Cheng

Department of Materials Science and Engineering, Tsing Hua University,
Hsinchu, 300, TAIWAN, Republic of China

$(R_xSm_{1-x})_2(Fe_{1-y}Co_y)_{17}N_z$ intermetallic compounds (R= Ce,Pr and La, x= 0, 0.1, 0.3, 0.5, 0.8 and 1, y= 0 and 0.2, z= 1.9 to 2.1) were prepared by arc-melting, pulverization and nitrogenation. Structure and magnetic properties of the nitrogenated alloys as a function of x and y were studied by x-ray diffractometer, vibrating sample magnetometer and thermomagnetic balance. Single 2:17 phase sustains for the whole range of x for Ce and Pr, while $x \leq 0.3$ for La substitution, all with a small amount of free Fe, after nitrogenation. The Curie temperatue, anisotropy field and magnetization decreased monotonically with increasing x. However signficant improvement after nitrogenation is noticed, $(R_{0.5}Sm_{0.5})_2Fe_{17}N_z$ alloys (R= Ce, Pr) show saturation magnetization of 155 to 170 emu/g and Curie temperature of 475 to 495°C.

1. INTRODUCTION

Large saturation magnetization (Ms), high stability against environment (high enough Curie temperature, Tc, good corrosion resistance, etc), strong uniaxial anisotropy field (HA) and low cost are four basic requirements, among other things, for permanent magnets[1]. The discovery of the Nd-Fe-B magnet opens a new era in the development of permanent magnets[2]. However, its Curie temperature, about 310°C, and the corrosion resistance, aren't high as compared to Alnico or SmCo magnets and hence efforts have been paying on the improvements on these aspects. These in turn led to many researchers for novel compounds for permanent magnet applications.

The R_2Fe_{17} compounds are the possible candidates due to their high iron content hence high saturation magnetization. The crystal structure is the Th_2Zn_{17} type when R is light rare earth elements except R= La, in which no 2:17 phase exists, and the Th_2Ni_{17} type when R is heavy rare earth elements. But the Curie temperature of R_2Fe_{17} is too low. They show a plannar anisotropy at room temperature that is fatal for permanent magnet application.

Recently Coey and Sun proposed a nitrogenation method for R_2Fe_{17} [3-6]. The saturation magnetization increases by greater than 30% and the Curie temperature increases from 380K to 750K after the nitrogen atoms is absorbed into interstitial sites without changing their parent structure. Most significatly, the easy magnetization direction (EMD) changes to c-axis from basal plane, and the anisotropic field is about 140 kOe at room temperature for $Sm_2Fe_{17}N_2$ [3-6].

2. EXPERIMENTAL PROCEDURES

Samples of $(R_xSm_{1-x})_2(Fe_{1-y}Co_y)_{17}$ (R= Ce, Pr, x= 0, 0.1, 0.5, 0.8 and 1, y= 0 and 0.2) and $(La_xSm_{1-x})_2(Fe_{1-y}Co_y)_{17}$ (x= 0, 0.1, 0.2 and 0.3, y= 0 and 0.2) were prepared by arc-melting starting from elemental metals of high purity (99.9% or higher) in a water cooled copper hearth under Ar atmosphere and the alloys were remelted at least five times to insure homogeneity. Excessive Sm losses during melting were compensated by adding 5 wt% more Sm with respect to the stoichiometric Sm content. Then, the samples were homogenization-annealed under Ar protection at 1150°C for 4 hour with an additional piece of Sm to provide compensating Sm vapor. Table I shows the nomenclature of the alloys and their composition.

Table I. The nomenclature of the studied $(R_xSm_{1-x})_2Fe_{17}$, alloys, and the corresponding composition

Alloys	C0	C1	C5	C8	C10
$(Ce_xSm_{1-x})_2Fe_{17}$	x= 0	0.1	0.5	0.8	-
Alloys	P0	P1	P5	P8	P10
$(Pr_xSm_{1-x})_2Fe_{17}$	x= 0	0.1	0.5	0.8	1
Alloys	L0	L1	L2	L3	L4
$(La_xSm_{1-x})_2Fe_{17}$	x= 0	0.1	0.2	0.3	-

The nitrogenation process of the samples were carried out at 450°C for 4 hours under a flowing nitrogen gas. Magnetization measurements were performed in a vibrating sample magnetometer (VSM), with a maximum field strength up to 20 kOe and were calibrated by pure Ni. Anisotropy field (HA) was estimated from extropolated magnetization

curves measured parallel and perpendicular to alignment field of paraffin-fixed powders cooled under a magnetic field. Curie temperature (Tc) was determined by a thermomagnetic balance under a field of 400 Oe. X-ray diffraction (XRD) was used to study the crystal structure by using a RIGAU D-MAX-B diffractometer with Cu-kα radiation.

The nitrogen content was analyzed by a N-O gas analyzer. In order to compare the structure and magnetic properties before/after nitrogenation. All nitrogenation parameters were kept the same and led to a nominal formula $(R_xSm_{1-x})_2Fe_{17}N_z$, z=1.9 to 2.1.

3. RESULTS AND DISCUSSION

3.1 Crystal Structure

The x-ray diffraction patterns showed that all the studied alloys, $(R_xSm_{1-x})_2(Fe_{1-y}Co_y)_{17}$, at whole range of x for R= Ce, Pr; while x≤ 0.3 for R= La, have the rhombohedral Th_2Zn_{17} structure. The x-ray patterns of the nitrogenated compounds were shifted to lower angles as a result of the unit cell volume expansion with the same Th_2Zn_{17} structure.

The volume expansion of unit cell increases as the replacement amount (x) of R for Sm in the $(R,Sm)_2Fe_{17}$ increases. It is largest for the Ce-substituted compounds. Several explainations have been proposed for the exceptional expansion of the $(Ce_xSm_{1-x})_2Fe_{17}$ alloys on nitrogenation. The most possible consequence is attributed to the conversion of the non-magnetic valence state in Ce during nitrogenation; the strongly intermediate valency state (eg., close to 4+) of Ce may be shifted to a lightly intermediate valency state (eg., close to 3+) [7,8].

Because the stable $La_2(Fe,Co)_{17}$ compound doesn't exist in the binary La-Fe system, we were interested to know what is the solubility of La in Sm_2Fe_{17} compound. As shown in Fig.1, the Th_2Zn_{17} type structure retains in $(La_xSm_{1-x})_2Fe_{17}$ or $(La_xSm_{1-x})_2$-$(Fe_{0.8}Co_{0.2})_{17}$ alloys x≤ 0.3. When x= 0.4, the 2:17 structure seems to become unstable since the free iron becomes the major phase in the XRD pattern, and the 2:17 reflctions are very low in intensity. Hence, the solubility of La in $(La,Sm)_2Fe_{17}$ is estimated to be 30 to 40 at%.

It was found that 20 at% Co substitued for Fe in $(R_xSm_{1-x})_2(Fe_{0.8}Co_{0.2})_{17}$, R= Ce/Pr/La, shows a smaller volume expansion in unit cell after nitrogenation. The possible consequence is due to the fact that the Co atoms in RE-TM alloy may reduce the reaction

rate of nitrogenation to result in slightly lower nitrogen contents in the compounds.

3.2 Magnetic properties

There are two sublattices in the R_2Fe_{17} compounds, the rare-earth sublattice (plannar anisotropy except Sm sublattice which is uniaxial) and the 3d sublattic (axial anisotropy). They compete each other in determining the EMD of the compounds. Both the rare-earth sublattice anisotropy and 3d sublattice anisotropy are much stronger in nitrogenated samples than un-nitrogenated ones and results in a large increase of H_A in nitrogenated alloys as shown in
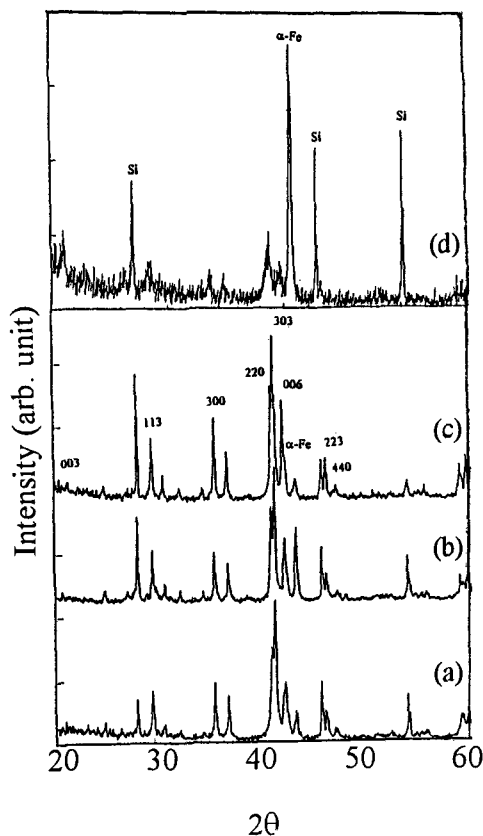

Fig. 1 XRD patterns of (a) $(La_{0.1}Sm_{0.9})_2Fe_{17}$, (b) $(La_{0.3}Sm_{0.7})_2Fe_{17}$, (c) $(La_{0.3}Sm_{0.7})_2(Fe_{0.8}Co_{0.2})_{17}$, (d) $(La_{0.4}Sm_{0.6})_2Fe_{17}$

Table II. The EMD for R_2Fe_{17} lies in the basal plane, while that of $Sm_2Fe_{17}N_2$ compound is switched to the c-axis after nitrogenation but that of $Ce_2Fe_{17}N_2$ and $Pr_2Fe_{17}N_2$ alloys is still in the basal plane. The EMD

Table II.
Anisotropy field (T) of $(R_xSm_{1-x})_2Fe_{17}$ alloys after nitrogenation

Alloys	C0	C1	C5	C8	C10
$(Ce_xSm_{1-x})_2Fe_{17}$	2.5*	2.5*	2.5*	1*	-
$(Ce_xSm_{1-x})_2Fe_{17}N_2$	14	12	11.5	2.5	-
Alloys	P0	P1	P5	P8	P10
$(Pr_xSm_{1-x})_2Fe_{17}$	2.5*	2.8*	2.0*	2.5*	2.5*
$(Pr_xSm_{1-x})_2Fe_{17}N_2$	14	10.6	4	5	2.5
Alloys	L0	L1	L2	L3	L4
$(La_xSm_{1-x})_2Fe_{17}$	2.5*	3.4*	3.0*	3.5*	-
$(La_xSm_{1-x})_2Fe_{17}N_2$	14	14.4	15	-	15.4

*This denotes the extrapolated intercept value of M-H curves, not the true anisotropy field (planar anisotropy)

of all the studied $(R,Sm)_2Fe_{17}N_2$ alloys is uniaxial. Table II shows that the anisotropy field of the uniaxially anisotropic $(R_xSm_{1-x})_2Fe_{17}$, R= Ce, Pr and La, decreases with the increasing substitution amounts of Sm by R. However, since the maximum field of measurement was only 2T, the extrapolation to 15 T is not precise at all. These values are of semi-quantitative nature only for comparison purposes.

Hurley et al. reported that 3d sublattice anisotropy dominates the whole lattice anisotropy in $Y_2(Fe,Co)_{17}$, since Y is nonmagnetic, and it is enhanced on nitrogenation [10]. In our study, the Ce-containing alloys showed the similar behavior because Ce is in an intermediate valence non-magnetic state as described above [7,8,10].

Table III shows the variation of Curie temperature before and after nitrogenation. As x increases in $(R_xSm_{1-x})_2Fe_{17}$, R= Ce and Pr, the lattice parameters and unit cell volume decrease monotonically due to smaller radii of Ce and Pr than that of Sm. Since the Curie temperature is generally known to be sensitive to the interatomic Fe-Fe distances, the $(R_xSm_{1-x})_2Fe_{17}$ compounds showed a decreasing tendency of Tc with the contraction of unit cell volume when Sm is replaced by Pr or Ce, especially for Ce_2Fe_{17} with a Tc below zero.

After the nitrogen atoms enter the interstitial sites of R_2Fe_{17} lattice, it leads to a large increase in Curie temperature by about 400°C in average occurs due to lengthening the interatomic Fe-Fe distances which in turn lead to a strengthening of Fe-Fe exchange interaction according to the Bethe-Slater curve [8]. The $(Ce_xSm_{1-x})_2Fe_{17}N_2$ compounds show the largest increment in Tc as compared to $(Ce_xSm_{1-x})_2Fe_{17}$ accompanied by the largest expansion in unit cell.

This is probably due to the conseqence of conversion of Ce^{4+} into Ce^{3+} during nitrogenation.

Table III. Variation in Curie temperature (°C) in $(R_xSm_{1-x})_2Fe_{17}$ alloys before and after nitrogenation

Alloys	C0	C1	C5	C8	C10
$(Ce_xSm_{1-x})_2Fe_{17}$	156	150	87	103	-3
$(Ce_xSm_{1-x})_2Fe_{17}N_2$	489	499	493	468	442
Alloys	P0	P1	P5	P8	P10
$(Pr_xSm_{1-x})_2Fe_{17}$	156	145	113	102	17
$(Pr_xSm_{1-x})_2Fe_{17}N_2$	489	-	476	487	437
Alloys	L0	L1	L2	L3	L4
$(La_xSm_{1-x})_2Fe_{17}$	156	176	166	162	164
$(La_xSm_{1-x})_2Fe_{17}N_2$	489	498	499	-	492

The substitution of Co for Fe is found to increase effectively the Curie temperature of the R_2Fe_{17} compounds. Tc's of all the samples with y= 0.2, $(R_xSm_{1-x})_2(Fe_{0.8}Co_{0.2})_{17}$ alloys, are higher than 550°C after nitrogenation. The Co can also compensate partly the decrease in anisotropy field due to the replacement of Sm by Ce, Pr and La.

The replacement of Sm by Ce or Pr leads to a decrease in the saturation magnetization (σ_{20K}, measured at a maximum field of 20 kOe) despite of the fact that the effective Bohr magneton of Ce^{3+} and Pr^{3+} are higher than that of Sm^{3+}ion. It is probably due in one respect to the possibility that Ce or Pr ions are not totally in the 3+ valency state; and on the other hand, the fact that the inclusion of Ce or Pr leads to a decrease in Curie temperature, hence the room temperature saturation magnetization value is lowered by the law of correspondence. After nitrogenation of these samples, the saturation magnetization was found to increase greatly, 28% to 86%, as shown in Table IV. The x= 0.5 alloys have the highest σ_{20K} among the nitrogenated alloys of the C-alloys or P-alloys. The change in valency state of Ce and Pr ions during nitrogenation may play a role.

Table IV. Saturation magnetization (σ_{2T}, emu/g) of $(R_xSm_{1-x})_2Fe_{17}$ alloys before and after nitrogenation

Alloys	C0	C1	C5	C8	C10
$(Ce_xSm_{1-x})_2Fe_{17}$	109	-	88.9	71.1	(a)
$(Ce_xSm_{1-x})_2Fe_{17}N_2$	140	140	154	132	121
Alloys	P0	P1	P5	P8	P10
$(Pr_xSm_{1-x})_2Fe_{17}$	109	93.7	107	84.5	97
$(Pr_xSm_{1-x})_2Fe_{17}N_2$	140	151	170	152	147

(a): Curie temperature of Ce_2Fe_{17} is Tc= -3°C

4. CONCLUDING REMARKS

We have shown that the Th_2Zn_{17}-type structure exists in $(R_xSm_{1-x})_2Fe_{17}$ alloys, x= 0 to 1 for R= Ce or Pr, while x≤ 0.3 for R= La. The solubility limit of La in Th_2Zn_{17}-type Sm_2Fe_{17} matrix was estimated to be about 30 to 40 at% total rare-earths from XRD patterns and metallography data. The replacement of Sm by Ce, Pr or La in $(R_xSm_{1-x})_2Fe_{17}$ results in the decrease in H_A, Tc and σ_{20K}. Nitrogenation of these alloys results in great improvement in H_A, Tc (by 400°C more) and σ_{20K} (by 28 to 86% more). The results are interpreted in terms of enhancement in 3d-sublattice and R-sublattice anisotropies on nitrogenation. The EMD changes from basal plane to c-axis in the nitrogenated $(R_xSm_{1-x})_2Fe_{17}$ samples, R= Ce, Pr and La. The Ce-substituted alloys showed the largest improvement in this study. It is probably due to the conversion in part of Ce^{4+} into Ce^{3+} during nitrogenation.

The substitution of Co for Fe enhance H_A, σ_{20K} and Tc. The Curie temperatures of Co-substituted compounds are all higher than 550C, and that of $(La_{0.3}Sm_{0.7})_2(Fe_{0.8}Co_{0.2})_{17}N_2$ is as high as 610°C. The Co can also partly compensate the decrease of anisotropy field due to the replacement of Sm by Ce, Pr and La.

Since Ce, and La are abundant and relatively inexpansive as compared to Sm, and the magnetic properties of the nitrogenated $(Ce_xSm_{1-x})_2Fe_{17}$ and $(La_xSm_{1-x})_2Fe_{17}$ alloys are reasonably good, they were potential for applications as bonded magnets.

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