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A magnetic and crystallographic study of $(Sm/Gd)_2(Fe/Si)_{17}C_z$ solid solutions

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The crystallographic and magnetic properties of $Sm_yGd_{2-y}Fe_{17-x}Si_x$ ($0 \leqslant x \leqslant 3$ and $y = 1$ and 1.5) solid solutions and their interstitial carbides have been investigated using x-ray diffraction and magnetic measurements. The $Sm_yGd_{2-y}Fe_{17-x}Si_x$ samples crystallized in the rhombohedral Th_2Zn_{17} structure with less than 5 mol % of impurities. The unit cells of the mixed rare-earth (R) samples are smaller than those of Sm_2Fe_{17} and Gd_2Fe_{17}. The carbided samples contain up to a total of 15 mol % of free iron, an iron silicide, and/or cubic Si_5C_3. The unit cells of the carbided samples are 1%–4% larger than those of the parent samples. For a given silicon concentration, the Curie temperatures (T_c) of $Sm_yGd_{2-y}Fe_{17-x}Si_x$ intermetallics are higher than those of the two end members. For example, the T_c of $SmGdFe_{17}$ (280 °C) is approximately 160° and 80° higher than that of Sm_2Fe_{17} and Gd_2Fe_{17}, respectively. The T_c measured for the $Sm_yGd_{2-y}Fe_{17-x}Si_x$ samples, 280–290 °C, are among the highest values observed for a $R_2Fe_{17-x}M_x$ intermetallic where M is a substituent other than cobalt. Except in the case of $SmGdFe_{16}SiC_z$ (z unknown), the T_c of the carbided samples are 20%–25% higher than those of the parent samples. A T_c of 426 °C and a magnetization of 120.6 emu/g observed for $SmGdFe_{16}SiC_z$ are the highest values measured for the intermetallics investigated herein. As determined by x-ray diffraction studies of magnetically aligned samples, the easy axis of magnetization is parallel to the c axis. © *2000 American Institute of Physics.* [S0021-8979(00)77208-2]

INTRODUCTION

Presently, all leading candidates for the next generation of permanent magnets belong to the family of rare-earth–transition-metal (R/T) intermetallics.[1] Unfortunately, existing theoretical models that describe the magnetic behavior of these materials are unable to predict the magnetic properties of a given intermetallic. Consequently, researchers must synthesize and characterize R/T intermetallics of varying compositions in order to identify potential candidates. The present study is expected to contribute to the existing database on the magnetic properties of these intermetallics.

The magnetic behavior of R/T intermetallics depends on the type of the rare earth (R). For example, the T_c of Gd_2Fe_{17} is approximately 80° higher than that of Sm_2Fe_{17}.[2] In addition, as has been observed for intermetallics such as $R_2Fe_{17-x}Si_x$,[3,4] partial substitution of the iron sublattice by silicon can lead to remarkable improvements in certain magnetic properties.[3] Another process by which the magnetic properties of these materials, especially the R_2Fe_{17} intermetallics, can be improved is interstitial nitrogenation or carbiding.[5] In order to investigate the combined affects of mixing rare earths, partially substituting the iron sublattice, and insertion of interstitial atoms, we have studied the crystallographic and magnetic properties of $Sm_yGd_{2-y}Fe_{17-x}Si_xC_z$ ($y = 1$ and 1.5, $0 \leqslant x \leqslant 3$, and z unknown) solid solutions.

EXPERIMENT

The samples were synthesized as ingots by induction melting stoichiometric amounts of elements of purity 99.99% or better in a copper cold boat. Sample compositions are shown in Table I. A weight allowance (~3%) was made for possible loss of samarium during melting. The ingots were wrapped in tantalum foil and annealed at 950 °C for 7 days under flowing argon. The carbided samples were obtained by reacting 325 mesh powders of the parent samples with methane at temperatures ranging from 300 to 350 °C. The phase purity was verified by x-ray diffraction (XRD) using a SCINTAG diffractometer with Cu $K\alpha$ radiation. The presence of samarium in these samples prevents the use of neutron diffraction techniques to determine the site occupancies. Consequently, the compositions of the samples listed in Table I, especially the Sm:Gd and Fe:Si ratios, may be some-

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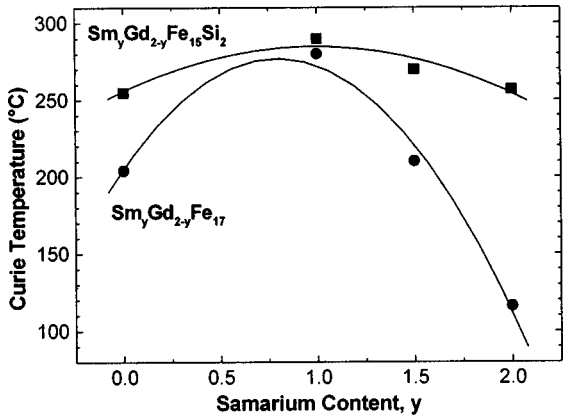

FIG. 1. Dependence of the Curie temperature of $Sm_yGd_{2-y}Fe_{17}$ and $Sm_yGd_{2-y}Fe_{15}Si_2$ on the samarium content. The data for $y=0$ and $y=2$ have been taken from Ref. 7. The curves are provided only as a guide to the eye.

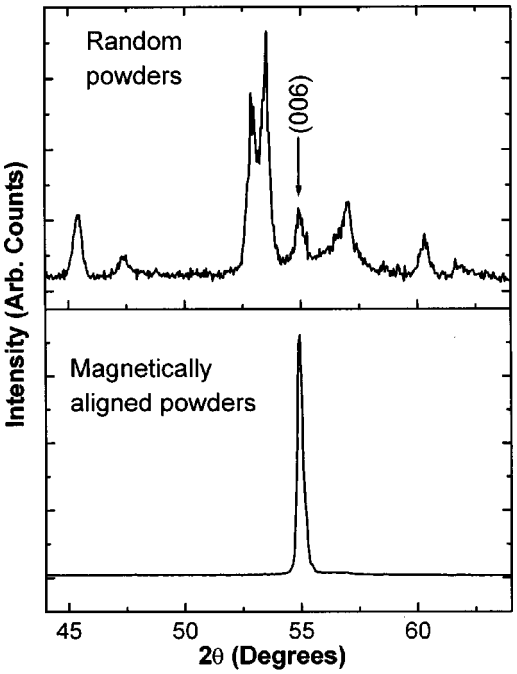

FIG. 2. X-ray diffraction patterns measured for $SmGdFe_{16}Si_1C_z$ from random powders (top) and a magnetically aligned sample (bottom).

what different from the actual compositions. The lattice parameters were obtained by Rietveld analysis[6] of powder XRD patterns. The thermomagnetic behavior was investigated using a vibrating-sample magnetometer and/or a Faraday-type balance. The magnetization versus applied field curves were obtained by extraction between 10 and 14.5 T, at decreasing field, at 1.5 K using a magnetometer at the Louis Néel Laboratory, Grenoble, France. The saturation magnetization at infinite field was obtained by extrapolation from the M vs $1/H^2$ plots using a second-order polynomial. The easy direction of magnetization of the carbided samples was investigated by measuring Fe $K\alpha$ XRD data for samples which were magnetically oriented perpendicular to the specimen surface.

RESULTS AND DISCUSSION

The XRD data suggest that all of the parent (prior to carbiding) samples crystallized in the rhombohedral Th_2Zn_{17}-type structure[2] with only a small amount (<5 mol %) of impurities. The impurity content increased with the silicon content. The carbided samples, however, contain up to approximately 15 mol % of impurity phases. The most prominent impurity phases were α-iron, an iron silicide, and/or Si_5C_3. The presence of Si_5C_3 suggests that elemental silicon was present in the parent sample. Consequently, the silicon content in certain samples is quite likely somewhat less than that shown in Table I.

Table I also gives lattice parameters and unit-cell volumes. Note that the unit cell of $SmGdFe_{17}$ is smaller than that of Sm_2Fe_{17} and Gd_2Fe_{17}. However, in contrast to most $R_2Fe_{17-x}Si_x$ intermetallics for which the unit cell contracts with increasing silicon content,[3,4] the unit cell of the $SmGdFe_{17-x}Si_x$ samples is larger than that of $SmGdFe_{17}$. In the case of the $Sm_yGd_{2-y}Fe_{17-x}Si_x$ samples, however, the cell volume increases very slightly with increasing samarium content.

The percent change of the cell volume upon carbiding is a measure of the amount of carbon absorbed by the samples. Near complete interstitial carbiding of $R_2Fe_{17-x}Si_x$ intermetallics leads to ~6% expansion of the unit cell.[7,8] Based on the percent volume expansions shown in Table I that are much less than 6%, we conclude that the samples are only partially carbided. Most likely, the carbon content in the samples investigated herein was limited not by their structural or chemical properties but by the carbiding conditions utilized.

It is interesting to note that, (see Table I) in spite of its smaller unit cell, the 280 °C Curie temperature of $SmGdFe_{17}$ is approximately 160° and 80° higher than that of Sm_2Fe_{17} and Gd_2Fe_{12}, respectively. It appears that the Curie temperature of $Sm_yGd_{2-y}Fe_{17}$ intermetallics may vary through a maximum as the samarium content is increased. In contrast to other $R_2Fe_{17-x}Si_x$ intermetallics,[3,4] partial substitution of iron by silicon in $SmGdFe_{17-x}Si_x$ does not have a significant effect on the Curie temperature. However, the T_cs of the $SmGdFe_{17-x}Si_x$ intermetallics reported herein are among the highest values observed for a $R_2Fe_{17-x}M_x$ intermetallic where M is a substituent other than cobalt. Note that the Curie temperatures of the $Sm_yGd_{2-y}Fe_{15}Si_2$ samples are higher than that of $Gd_2Fe_{15}Si_2$ and $Sm_2Fe_{15}Si_2$.[7] In fact, the dependence of the Curie temperature of $Sm_yGd_{2-y}Fe_{15}Si_2$ on the samarium content is similar to that described above for $Sm_yGd_{2-y}Fe_{12}$, see Fig. 1.

As seen in Table I, carbiding resulted in elevated Curie temperatures. However, the increase in the Curie temperature for most of the samples is only in the 20%–25% range. As expected, the $SmGdFe_{16}Si_1C_z$ sample whose unit cell expanded the most (4%) due to carbon insertion experienced the largest increase (146°) in Curie temperature. Note that the 426 °C Curie temperature of $SmGdFe_{16}Si_1C_z$ is higher than those of $Sm_2Fe_{17}C_3$ (395 °C),[4] $Sm_2Fe_{16}Si_1C_2$ (332 °C),[8] and $Gd_2Fe_{16}Si_1C_2$ (366 °C).[8] In addition, the Curie temperature of $SmGdFe_{16}Si_1C_z$ is only ~50° less than that of $Sm_2Fe_{17}N_3$.[4] Taking into account that complete carbiding of

TABLE I. Crystallographic and magnetic properties of $Sm_yGd_{2-y}Fe_{17-x}Si_xC_z$ intermetallics.

Sample	a (Å)	c (Å)	V (Å^3)	$\Delta V/V$[a] (%)	T_c (°C)	ΔT[b]	M_s (emu/g)[c]
Sm_2Fe_{17}[2]	8.540	12.430	785.08	···	116	···	···
Gd_2Fe_{17}[2]	8.524	12.414	781.18	···	204	···	···
$GdFe_{15}Si_2$[7]	8.480	12.360	769.72	···	255	···	···
$SmGdFe_{17}$	8.478	12.469	766.08	···	280	···	···
$SmGdFe_{16}Si$	8.483	12.474	777.36	···	280	···	···
$SmGdFe_{15}Si_2$	8.488	12.470	777.86	···	290	···	···
$SmGdFe_{14}Si_3$	8.478	12.450	772.51	···	280	···	···
$Sm_{1.5}Gd_{0.5}Fe_{15}Si_2$	8.499	12.452	778.93	···	270	···	···
$Sm_2Fe_{17}C_{2.2}$[2]	8.750	12.57	833.4	6.2	395	···	···
$Sm_2Fe_{16}SiC_2$[2]	8.650	12.451	806.74	···	332	···	···
$Gd_2Fe_{16}SiC_2$[2]	8.658	12.455	808.66	···	366	···	83.8
$SmGdFe_{17}C_z$	8.560	12.373	785.20	1.18	350	70(25%)	103.3
$SmGdFe_{16}SiC_z$	8.646	12.486	808.35	3.99	426	146(52%)	120.6
$SmGdFe_{14}Si_3C_z$	8.554	12.336	781.65	1.18	337	57(20%)	93.1
$Sm_{1.5}Gd_{0.5}Fe_{15}Si_2C_z$	8.625	12.407	799.35	2.62	337	67(25%)	114.3

[a]Fractional change in the unit-cell volume due to carbon insertion.
[b]Change in T_c due to carbiding. Percent change is given in parenthesis.
[c]Measured at 1.2 K.

a 2:17 intermetallic causes an ~6% expansion of the unit cell and an ~280° increase in the Curie temperature, one can envision a fully carbided or nitrided $SmGdFe_{16}Si_1C_3$ sample whose Curie temperature equals or exceeds that of $Sm_2Fe_{17}N_3$.

The saturation magnetization values given in units of emu/g in Table I have not been adjusted for the weight of the impurity phases. Consequently, the actual saturation magnetization of the $Sm_yGd_{2-y}Fe_{17-x}Si_xC_z$ phase in each sample must be somewhat different from that given in Table I. In any case, note that the sample with the highest Curie temperature, $SmGdFe_{16}Si_1C_z$, also has the highest saturation magnetization (120.6 emu/g).

Figure 2 compares the XRD pattern for random powders of $SmGdFe_{16}Si_1C_z$ with that for the magnetically aligned counterpart. The rapid growth of the (006) reflection upon alignment indicates that the basal planes are preferentially oriented parallel to the reflecting surface of the x-ray specimen. Taking into account that the samples were aligned perpendicular to the surface, we conclude that the net moment of the sample is perpendicular to the basal plane, or parallel to the c axis of the unit cell.[8] The easy directions of magnetization of all of the carbided samples investigated herein are parallel to the c axis.

CONCLUSIONS

For a given silicon concentration, the Curie temperatures (T_c) of the mixed-rare-earth $Sm_yGd_{2-y}Fe_{17-x}Si_x$ intermetallics are higher than those of the two end members. Furthermore, the T_c measured for $Sm_yGd_{2-y}Fe_{17-x}Si_x$ samples are observed for a $R_2Fe_{17-x}M_x$ intermetallic not containing cobalt. Interstitial carbiding of these samples resulted in expanded unit cells and higher T_cs. The effects of carbiding were most prominent for $SmGdFe_{16}Si_1C_z$ for which the unit-cell volume and T_c increased by 4% and 52%, respectively. Even though $SmGdFe_{16}Si_1C_z$ is only partially carbided, its T_c is only ~50° lower than that of $Sm_2Fe_{17}N_3$. It is quite likely that the T_c of certain fully carbided/nitrided $Sm_yGd_{2-y}Fe_{17-x}Si_x(C/N)_z$ samples may be comparable to, or exceed those of, most $R_2Fe_{17}N_3$ intermetallics. Of the samples studied herein, the highest saturation magnetization of 120 emu/g was observed for $SmGdFe_{16}Si_1C_z$. The easy direction of magnetization for all of the carbided samples investigated herein is the c axis.

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