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Magnetic properties of $\text{Sm}_2\text{Fe}_{17}\text{N}_y$ with Al substituted for Fe

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Abstract

By means of X-ray diffraction analysis, it is shown for $x < 0.4$ that all the interstitial $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}\text{N}_y$ nitrides and the parent compounds crystallize with $\text{Th}_2\text{Zn}_{17}$ -type structure. The lattice constants of the parent compounds increase linearly with Al concentration. The introduction of nitrogen atoms leads to a further increase in the lattice constants, but the increase becomes smaller with increasing Al concentration; this can be related to the fact that the nitrogen content introduced into the parent compounds decreases nearly linearly with increasing Al concentration. The dependence on composition of T_C of the parent compounds exhibits a maximum, whereas T_C of the nitrides decreases monotonically with Al content from 750 K for $x=0$ to 313 K for $x=0.4$. The introduction of nitrogen leads to enhancement of the average magnetic moment of Fe in $\text{Sm}_2\text{Fe}_{17}$, whereas the substitution of Al for Fe leads to a decrease in the average magnetic moment of Fe in both the nitrides and the parent compounds. The anisotropy field B_a of nitrides is almost independent of the Al concentration for $x \leq 0.3$, then decreases very fast and becomes zero at about $x=0.4$.

Keywords: Magnetic properties; Aluminium; Iron; X-ray diffraction

1. Introduction

The R_2Fe_{17} intermetallic compounds ($\text{R} \equiv$ rare earth) crystallize in the rhombohedral $\text{Th}_2\text{Zn}_{17}$ -type structure for the light R elements and in the hexagonal $\text{Th}_2\text{Ni}_{17}$ -type structure for R heavier than Dy; both structure types may coexist for Gd, Tb and Dy [1,2]. The magnetic properties of the series have been investigated in great detail [3,4]. Although the R_2Fe_{17} compounds are the most Fe rich of all binary rare-earth–Fe intermetallics, owing to their low Curie temperatures and their non-uniaxial magnetocrystalline anisotropy, the R_2Fe_{17} compounds have not been used as practical permanent magnetic material.

In 1990, Coey and Sun [5] successfully improved the magnetic properties of the R_2Fe_{17} compounds by introducing nitrogen to form interstitial nitrides $\text{R}_2\text{Fe}_{17}\text{N}_y$ with $y \approx 2.3$. The introduction of nitrogen into R_2Fe_{17} compounds leads not only to a large increase in Curie temperature to about 400 K higher than that of the R_2Fe_{17} parent compounds, and to an increase in the magnetic moment of Fe, but also to a change in the anisotropy of $\text{Sm}_2\text{Fe}_{17}$ from planar to uniaxial over the

whole temperature range up to the Curie temperature. These outstanding intrinsic magnetic properties make $\text{Sm}_2\text{Fe}_{17}\text{N}_y$ a most promising candidate for permanent magnets. Therefore, the $\text{R}_2\text{Fe}_{17}\text{N}_y$ nitrides have recently attracted considerable interest in both fundamental and applied research.

Ion-substitution is usually carried out not only to improve the performance of the magnetic materials, but also to examine the fundamental magnetic properties of the rare-earth–transition-metal compounds, because much information about magnetic interactions can be obtained from investigation of the quasi-ternary compounds formed by substitution of magnetic or non-magnetic atoms for R or Fe atoms.

Some of the magnetic properties of the $\text{R}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ compounds are reported in Refs. [6–11]. It has been shown that magnetic properties such as the saturation magnetization, the Curie temperature and the anisotropy depend strongly on the Al concentration. It has been found [6] that the substitution of Al for Fe leads to an increase in the uniaxial anisotropy of the Sm sublattice in the $\text{Sm}_2\text{Fe}_{17-x}\text{Al}_x$ compounds. However, Al is also considered an important element for im-

provement of the magnetic performance of permanent magnetic materials. For example, an outstanding value of magnetic hardness can be achieved at cryogenic temperature in both powder and bulk materials of SmCo_5 by substitution of Al for Co [8].

As mentioned above, both substituting a third element (such as Al) for Fe and introducing interstitial atoms (such as N, C) lead to a remarkable enhancement of the Curie temperature and the uniaxial anisotropy in the R_2Fe_{17} series with R having a positive second-order Stevens coefficient α_J . Here, in an attempt to maximize these enhancements, we studied the $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)\text{N}_y$ series to investigate the effect of the substitution of Al for Fe on the structural and magnetic properties of the interstitial $\text{R}_2\text{Fe}_{17}\text{N}_y$ nitrides. In this study such an effect was determined and the results are presented.

2. Experimental details

$\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ parent compounds with $x=0, 0.01, 0.02, 0.04, 0.07, 0.1, 0.2, 0.3$ and 0.4 were prepared by arc melting the constituent elements of at least 99.9% purity in an argon atmosphere. To obtain homogeneous materials, the samples were remelted several times in the arc furnace. The alloys were homogenized by annealing in vacuum at 1100°C for 10 h. The $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}\text{N}_y$ nitrides were prepared by heat treating pulverized $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ in purified N_2 gas at a pressure of 1 atm at 500°C for four different times, depending on the Al content in the parent compound, to achieve sufficient nitrogenation. The nitrogen content was determined by weighing to be 2.6 for the compound with $x=0$.

X-ray diffraction with $\text{Cu K}\alpha$ radiation was used to check the crystal structure and to determine lattice constants. Thermomagnetic analysis (TMA) was performed in the temperature range from room temperature to above the Curie temperature in a field of 0.8 T using an extracting-sample magnetometer. The Curie temperatures were derived from σ^2 - T plots. The magnetization curves of samples consisting of powder that was free to be oriented by an applied magnetic field were measured at 4.2 K in an extracting-sample magnetometer using a field of 7 T produced by a superconducting magnet. Values of saturation magnetization were derived from σ - $1/B$ plots.

The high-field magnetization was measured in the high-field installation at the University of Amsterdam [12]. The magnetic isotherms were recorded at 4.2 K in external fields up to 21 T applied either parallel or perpendicular to the alignment direction of the cylindrical samples which were prepared by aligning powder particles at room temperature in a field of 1 T and fixing the direction with epoxy resin. For every compound, the anisotropy field B_a was determined as the

intersection point of the two curves (or their extrapolations) measured with the field parallel and perpendicular to the alignment direction.

3. Results and discussion

X-ray powder diffraction and TMA show that all investigated ternaries and their nitrides are single phase except for a small amount of α -Fe in some of the samples as second phase. The $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ compounds crystallize in the rhombohedral $\text{Th}_2\text{Zn}_{17}$ -type structure. Substitution of Al for Fe does not change the structure of the $\text{Sm}_2\text{Fe}_{17}$ compound. All investigated nitrides have the same structure as the parent compounds.

The values of the lattice constants a and c and the expansion of the unit-cell volume are given in Table 1. The lattice constants a and c as a function of the Al concentration are also shown in Fig. 1. It can be seen that the substitution of Al for Fe results in a linear increase in the lattice constants a and c with increasing Al concentration. This may be associated with the larger radius of the Al atoms compared with the Fe atoms. The introduction of interstitial nitrogen atoms in the $\text{Sm}_2\text{Fe}_{17}$ compound leads to a further increase in the lattice constants and the expansion of the unit-cell volume reaches about 8%, but the amplitude of this increase is smaller for increasing Al concentration. It is noteworthy that the values of lattice constants a and c of the interstitial nitrides

Table 1

The lattice constants a and c , expansion of the unit cell volume $\Delta V/V$, saturation magnetization σ_s and Curie temperature T_C for $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}\text{N}_y$ compounds; the data in parentheses pertain to the compounds before nitriding; errors, a and $c \pm 0.005 \text{ \AA}$, $T_C \pm 5^\circ\text{C}$, $\sigma_s \pm 2 \text{ A m}^2 \text{ kg}^{-1}$

x	a ($\text{\AA}$)	c ($\text{\AA}$)	$\Delta V/V$ (%)	σ_s ($\text{A m}^2 \text{ kg}^{-1}$)	T_C (K)
0.00	8.730 (8.494)	12.650 (12.343)	8.0	162.5 (141.4)	750 (412)
0.01	8.748 (8.569)	(12.663) (12.415)	6.3	167.2 (137.0)	739 (420)
0.02	8.744 (8.579)	12.641 (12.407)	5.8	159.4	733 (429)
0.04	8.750 (8.580)	12.640 (12.423)	5.8	160	718 (436)
0.07	8.768 (8.600)	12.652 (12.464)	5.5	150.0 (131.3)	675 (455)
0.10	8.754 (8.605)	12.636 (12.458)	5.0	144.0 (127.2)	646 (462)
0.20	8.748 (8.651)	12.649 (12.566)	3.0	129.2 (116.6)	529 (486)
0.30	8.721 (8.693)	12.689 (12.622)	1.2	106.3 (96.8)	452 (433)
0.40	8.750 (8.745)	12.694 (12.682)	0.2	82.1 (80.9)	313 (313)

Fig. 1. Lattice constants a and c as a function of Al concentration for $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}\text{N}_y$ and $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$.

$\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}\text{N}_y$ are almost independent of the Al concentration. According to Wei *et al.* [13], the lattice constants a and c are proportional to the nitrogen content for smaller nitrogen content y . When $y > 2$ the value a remains almost constant, while c increases linearly in the range $2 < y < 6.4$. So from inspection of our data it can be reasonably assumed that the amount of nitrogen introduced in the parent compounds decreases approximately linearly with increasing Al concentration. According to neutron diffraction and Mössbauer effect studies of the $\text{Nd}_2\text{Fe}_{17-x}\text{Al}_x$ compounds [14], the Al fractional occupancy on the 18f sites in $\text{Nd}_2\text{Fe}_{17-x}\text{Al}_x$ increases uniformly with increasing Al content. The occupancy of the large Al atoms on the 18f sites results in a decrease in the 9e spatial volume and may prevent the introduction of nitrogen atoms.

Fig. 2 shows the effect of substitution of Al for Fe on the Curie temperatures T_C for $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}\text{N}_y$ and for the parent compounds. The values of T_C are also listed in Table 1. It can be seen that the effect is distinctly different for the two series. In the parent compounds, T_C clearly increases with a small amount of Al substitution, goes through a maximum at $x \leq 0.2$, then decreases with further Al substitution. A similar dependence of T_C on the Al concentration has been reported for other rare-earth compounds [10,11].

Narasimhan and Wallace [11] explained this observation by assuming preferential substitution of Al atoms for Fe atoms; probably the Al atoms substitute preferentially for Fe atoms at the sites responsible for negative interaction. X-ray diffraction peak-intensity analysis [15] and a Mössbauer study [16] on

Fig. 2. Curie temperature T_C for $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}\text{N}_y$ and $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ as a function of Al concentration.

$\text{R}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ compounds indicate such a tendency for preferential substitution of Al atoms on the 6c and 9d sites. Because substitution of Al for Fe leads to an increase in the lattice constants, the initial increase in T_C may also include a contribution from expansion of the unit-cell volume due to Al substitution. At higher Al concentrations, the decrease in the magnetic moment leads to a decrease in T_C (see later).

The introduction of nitrogen in $\text{Sm}_2\text{Fe}_{17}$ leads to a distinct increase in T_C . This may be associated with expansion of the unit-cell volume after nitrogenation. Jaswal *et al.* [17] ascribed the increase in T_C to both the increase in magnetization and a decrease in the spin-up density of states at E_f associated with narrowing of the 3d band. T_C of the nitrides decreases monotonically with Al concentration. This may be attributed to the smaller amount of nitrogen that can be introduced into $\text{Sm}_2\text{Fe}_{17}$ owing to the substitution of Al for Fe.

Fig. 3 shows the magnetization curves of (a) $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ and (b) $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}\text{N}_y$ with different Al concentrations, measured on samples consisting of powder particles free to be oriented in external fields up to 7 T at 4.2 K. Comparing Fig. 3(a) with (b), it can be seen that the introduction of nitrogen leads to an increase in the saturation magnetization, but the amplitude of the increase decreases with Al concentration. Values of the saturation magnetization σ_s were derived from the easy direction magnetization curves by σ vs. $1/B$ plots as shown in Fig. 4. The σ_s values have been corrected for the contribution of the α -Fe impurity phase to the magnetization which could

(a)

(b)

Fig. 3. Magnetization curves for (a) $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ and (b) $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}\text{N}_y$ with different Al concentrations.

be deduced from high temperature magnetization measurements. The values are given in Table 1. The dependence on concentration of the saturation magnetization σ_s at 4.2 K for both the nitrides and the parent compounds is presented in Fig. 4. The saturation magnetization of both nitrides and the parent compounds decreases monotonically with increasing Al concentration, but the decrease is much faster than in the case of simple magnetic dilution. In order to obtain more information about the influence of Al substitution on the magnetization, the average Fe magnetic moment μ_{Fe} was calculated on the basis of the saturation magnetization measured at 4.2 K, shown in Fig. 5. For evaluation of the magnetic moment per Fe ion it was assumed that the magnetic moment of Sm is independent of the Al concentration, and the value found is the

Fig. 4. Saturation magnetization σ_s as a function of Al concentration for $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}\text{N}_y$ and $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$.

Fig. 5. Average magnetic moment μ_{Fe} of Fe as a function of Al concentration for $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}\text{N}_y$ and $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$.

same as that derived from the saturation magnetization of $\text{Sm}_2\text{Fe}_{17}$ by comparing it with that of Y_2Fe_{17} [18]. The number of nitrogen atoms in one molecular formula can be estimated by assuming that the nitrogen content introduced into the compounds decreases linearly with Al concentration from 2.6 for $x=0$ to 0 for $x=0.4$ as

mentioned above. Our results imply that in both the nitrides and the parent compounds, the average Fe moment decreases monotonically with Al concentration. In the case of nitrides the moment decreases with Al concentration from $2.23 \mu_B$ for $x=0$ to $1.5 \mu_B$ for $x=0.4$. This indicates quenching of the Fe moment by the substitution of Al and is very similar to various analogous systems based on Al, rare-earth and magnetic transition metals [7]. Plusa *et al.* [19] explained the decrease in σ_s with Al concentration in $Y_2(Fe_{1-x}Al_x)_{17}$ pseudobinary compounds by assuming that all the Al valence electrons populate the 3d band of the Y_2Fe_{17} compound and one spin sub-band is completely full. Zhen *et al.* [20] explained the increase in the average Fe moment in $Sm_2Fe_{17}N_y$ on nitrogenation by assuming that the introduction of nitrogen gives rise to electron transfer from 4s electrons of Fe (h), Fe (f) and electron transfer of 6s Sm atoms to the 2p orbital of neighboring nitrogen atoms. The increase in the average magnetic moment of Fe in the nitrides on nitrogenation decreases monotonically with the Al concentration. This can be explained by taking into account the decrease in the nitrogen content in Sm_2Fe_{17} compounds in which Al has been substituted for Fe.

The introduction of nitrogen leads to a change in the magnetic anisotropy of Sm_2Fe_{17} from planar to uniaxial over the whole temperature range up to T_C . The anisotropy field B_a is 32 T at 4.2 K [21]. The substitution of Al for Fe also has a significant influence on the anisotropy of the nitrides. Fig. 6 shows the anisotropy field B_a as a function of Al concentration for the $Sm_2(Fe_{1-x}Al_x)_{17}N_y$ compounds. It can be seen that the anisotropy field of the nitride is approximately independent of the Al concentration for $x \leq 0.3$, then decreases very fast with increasing Al concentration, and becomes zero at about $x=0.4$. Such behavior of the anisotropy of $Sm_2(Fe_{1-x}Al_x)_{17}N_y$ compounds results from the contribution of the substitution of Al for Fe

Fig. 6. Magnetic anisotropy field B_a for $Sm_2(Fe_{1-x}Al_x)_{17}N_y$ as a function of Al concentration.

to the uniaxial anisotropy. It has been found [6] that the substitution of Al for Fe causes an increase in the uniaxial anisotropy which results from Sm substitution. X-ray diffraction of the aligned powder samples shows that the Al substituted for Fe leads to the appearance of uniaxial anisotropy at room temperature in the $Sm_2(Fe_{1-x}Al_x)_{17}$ compounds in the Al concentration range 0.15–0.3.

4. Conclusions

We have shown that all the $Sm_2(Fe_{1-x}Al_x)_{17}N_y$ nitrides and the parent compounds crystallize with Th_2Zn_{17} -type structure for $x \leq 0.4$. The lattice constants of the parent compounds increase linearly with Al concentration. The introduction of nitrogen leads to a further increase in lattice constants, but the amplitude of this increase is smaller for increasing Al concentration. The dependence on concentration of the Curie temperatures T_C of the parent compounds shows a maximum. The introduction of nitrogen leads to an increase in T_C , but the T_C values of the nitrides decrease monotonically with Al concentration from 750 K for $x=0$ to 313 K for $x=0.4$. The substitution of Al for Fe prevents the introduction of nitrogen atoms. The average magnetic moment of Fe in both the nitrides and the parent compounds decreases monotonically with Al concentration. The anisotropy field of the nitrides is almost independent of Al concentration for $x \leq 0.3$, then decreases very fast with increasing Al concentration, which results from the contribution of the Al substituted for Fe to the uniaxial anisotropy of the Sm sublattice.

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