

Letter

Pressure–composition–temperature relation of the $\text{Sm}_2\text{Fe}_{17}\text{–N}$ system

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Abstract

The pressure–composition isotherm of the $\text{Sm}_2\text{Fe}_{17}\text{–N}$ system was measured volumetrically at 823 K. The data strongly suggest the formation of a nitrogen solid solution with the solubility limit lying at a nitrogen concentration $[\text{N}]/[\text{Sm}_2\text{Fe}_{17}] = 3$ in mole ratio and a nitride phase with the composition $\text{Sm}_2\text{Fe}_{17}\text{N}_6$. More marked anisotropic changes in the lattice structure seem to take place in the formation of the solid solution phase at $[\text{N}]/[\text{Sm}_2\text{Fe}_{17}] < 3$ than at $3 < [\text{N}]/[\text{Sm}_2\text{Fe}_{17}] < 6$, where two phases, namely a nitrogen-saturated solid solution and a nitride, would seem to coexist.

1. Introduction

Recent findings about the nitromagnet $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ have provoked intensive studies world wide to search for new types of hard magnetic materials via interstitial modification [1]. So far, many research groups have confirmed that the nitrogenation of $\text{Sm}_2\text{Fe}_{17}$ yields markedly improved magnetic properties such as Curie temperature, saturation magnetization and magneto-crystalline anisotropy which are equivalent or somewhat superior to those of Nd–Fe–B-type magnets [1, 2]. Most work on nitrogenation measurement reports that $\text{Sm}_2\text{Fe}_{17}$ absorbs nitrogen at nitrogen concentrations up to $[\text{N}]/[\text{Sm}_2\text{Fe}_{17}] = 3$ in mole ratio or $x = 3$ in the form $\text{Sm}_2\text{Fe}_{17}\text{N}_x$. On the basis of a gas analysis method, one group has reported the possibility that $\text{Sm}_2\text{Fe}_{17}$

might absorb nitrogen up to $[N]/[\text{Sm}_2\text{Fe}_{17}] = 6$ if the alloy is nitrogenated using an $\text{H}_2\text{-NH}_3$ gas mixture [3].

However, no information is available on the phase relation of the $\text{Sm}_2\text{Fe}_{17}\text{-N}$ system, although such knowledge is essential to understand the mechanisms of occurrence of the magnetic properties exhibited by $\text{Sm}_2\text{Fe}_{17}\text{N}_x$. Actually, the following question needs to be urgently answered: whether $\text{Sm}_2\text{Fe}_{17}$ forms only a nitrogen solid solution phase or whether a nitride phase also exists.

In this letter we report our latest data on the pressure–composition–temperature ($P\text{-}C\text{-}T$) relation of the $\text{Sm}_2\text{Fe}_{17}\text{-N}$ system and the effect of nitrogenation on the lattice parameters of $\text{Sm}_2\text{Fe}_{17}$ in the range of nitrogen concentration $0 \leq [N]/[\text{Sm}_2\text{Fe}_{17}] \leq 5.2$.

2. Experimental details

$\text{Sm}_2\text{Fe}_{17}$ samples were prepared by arc melting samarium with iron and annealing in argon at 1400 K for 4 h. The formation of the single phase of $\text{Sm}_2\text{Fe}_{17}$ peritectically was controlled with respect to structure, stoichiometric composition and morphology using X-ray diffraction (XRD), energy-dispersive X-ray (EDX) spectroscopy, induction-coupling plasma (ICP) emission spectrochemical analysis, secondary electron microscopy (SEM) and optical microscopy.

The $P\text{-}C\text{-}T$ relation was measured volumetrically using a Sieverts-type apparatus with a high vacuum system. Nitrogen absorption was carried out at 823 K by exposure of the alloy to N_2 gas at pressures between 0.1 and 100 bar with and without prior cyclic hydriding–dehydriding pretreatments. Details of Sieverts system used and the measurement method are described elsewhere [4–7]. The amount of nitrogen absorbed by the sample was examined also by the weight change after the $P\text{-}C\text{-}T$ measurement.

3. Results and discussion

Figure 1 shows the measured $P\text{-}C$ isotherm at 823 K (solid curve). The equilibrium pressure increases with increasing nitrogen content in $\text{Sm}_2\text{Fe}_{17}$ and the isotherm exhibits a plateau region around an N_2 equilibrium pressure $P = 36$ bar and nitrogen concentrations between $[N]/[\text{Sm}_2\text{Fe}_{17}] = 3$ and 6. The equilibrium pressure tends to increase again at $[N]/[\text{Sm}_2\text{Fe}_{17}] = 6$. This change in the isotherm suggests that a nitrogen solid solution phase may be formed at nitrogen concentrations up to $[N]/[\text{Sm}_2\text{Fe}_{17}] = 3$ and that a nitride phase with the composition $\text{Sm}_2\text{Fe}_{17}\text{N}_6$ may begin to precipitate at $[N]/[\text{Sm}_2\text{Fe}_{17}] = 3$. The plateau region may indicate the coexistence of the two phases.

Without the cyclic hydriding–dehydriding pretreatment the nitrogen absorption proceeded at nitrogen concentrations only up to $[N]/[\text{Sm}_2\text{Fe}_{17}] = 3$.

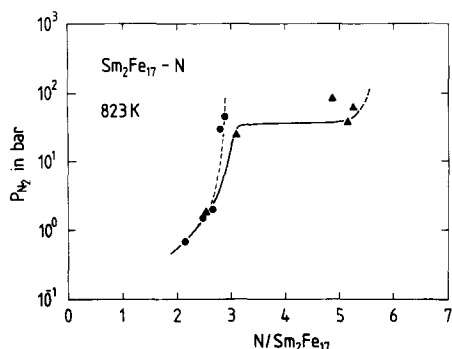


Fig. 1. Pressure-composition isotherm of the $\text{Sm}_2\text{Fe}_{17}\text{-N}$ system at 823 K: \blacktriangle with a solid line; samples pretreated by cyclic hydriding-dehydriding; \bullet with a dotted line; samples without hydriding pretreatment.

The corresponding isotherm is shown as the dotted curve in Fig. 1. The samples pretreated by cyclic hydriding absorbed nitrogen at nitrogen concentrations above $[\text{N}]/[\text{Sm}_2\text{Fe}_{17}] = 3$. Irrespective of the pretreatment, the initial rates exhibited a pressure dependence, $n = 1$ ($V \propto P^n$), and the subsequent reaction rates exhibited no pressure dependence, $n = 0$. This means that the initial rates measured were controlled not by bulk diffusion but rather by some surface processes. At present it is not clear how surface processes of nitrogen can be influenced by the presence of hydrogen. Further work needs to be done regarding the reaction kinetics, which is of great importance to the industrial production of nitromagnets.

With increasing nitrogen content the XRD lines of $\text{Sm}_2\text{Fe}_{17}$ were shifted to lower diffraction angles. Neither separation of the XRD lines of $\text{Sm}_2\text{Fe}_{17}$ nor the additional lines was observed up to the nitrogen concentration $[\text{N}]/[\text{Sm}_2\text{Fe}_{17}] = 5.2$ within the accuracy of measurement. The nitrogen solid solution and nitride phase, if they actually exist, might have quite similar structures and thus will not give distinct separations of the XRD lines in spite of the coexistence of the two phases. A similar observation is reported for the $\text{Ho}_2\text{Fe}_{17}\text{-C}$ system in which a phase transformation from hexagonal to rhombohedral takes place with increasing carbon content [8]. By analogy with this, the phase transformation for the $\text{Sm}_2\text{Fe}_{17}\text{-N}$ system might be predicted to occur with increasing nitrogen content from a nitrogen-saturated solid solution $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ with a rhombohedral structure to $\text{Sm}_2\text{Fe}_{17}\text{N}_6$ with a hexagonal structure because samarium belongs to the light rare earth group [9].

The lattice parameters a and c of $\text{Sm}_2\text{Fe}_{17}$ with the $\text{Th}_2\text{Zn}_{17}$ structure are listed in Table 1 as a function of nitrogen concentration. The a and c axes expand with increasing nitrogen content: $\Delta a/a = 2\%$ and $\Delta c/c = 1.4\%$ between $[\text{N}]/[\text{Sm}_2\text{Fe}_{17}] = 0$ and 2.7 and $\Delta a/a = 0.7\%$ and $\Delta c/c = 0.6\%$ between $[\text{N}]/[\text{Sm}_2\text{Fe}_{17}] = 2.7$ and 5.2. The expansion of a axis is more drastic for $[\text{N}]/[\text{Sm}_2\text{Fe}_{17}] < 3$ than for $3 < [\text{N}]/[\text{Sm}_2\text{Fe}_{17}] < 6$, implying that more marked

TABLE 1

Lattice parameters a and c of $\text{Sm}_2\text{Fe}_{17}$ ($\text{Th}_2\text{Zn}_{17}$ type) as a function of nitrogen content

| Parameter | $\text{Sm}_2\text{Fe}_{17}$ | $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.7}$ | $\text{Sm}_2\text{Fe}_{17}\text{N}_{5.2}$ |
|-----------|-----------------------------|---|---|
| a (nm) | 0.8609 | 0.8778 | 0.8838 |
| c (nm) | 1.257 | 1.274 | 1.282 |

changes in the magnetocrystalline anisotropy might be induced at nitrogen concentrations below $[\text{N}]/[\text{Sm}_2\text{Fe}_{17}] = 3$.

If any plateau region is present at nitrogen concentrations lower than $[\text{N}]/[\text{Sm}_2\text{Fe}_{17}] = 3$, these should also be investigated. In our group, additional P-C-T, reaction kinetics and XRD measurements are in progress in extended ranges of N_2 pressure and temperature.

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