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Measurement of N and C diffusion in Sm_2Fe_{17} by magnetic relaxation

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Abstract

Magnetic after-effect (MAE) measurements of nitrided and carburized Sm_2Fe_{17} compounds were performed in the temperature range of 140 K to 480 K. Both nitrided and carburized compounds show relaxation maxima at 285 and 300 K, respectively, which are absent in pure Sm_2Fe_{17} compounds. Therefore, these relaxation maxima are attributed to jumps of interstitially dissolved nitrogen or carbon atoms. Numerical evaluation yielded an activation enthalpy Q^{N} (0.84 ± 0.05) eV and a pre-exponential factor $\tau_0^{\mathrm{N}}=3\cdot10^{-15\pm1}$ s for the short-range diffusion of N atoms. The corresponding values for the carbon diffusion are $Q^{\mathrm{C}}=(0.91\pm0.05)$ eV and $\tau_0^{\mathrm{C}}=1\cdot10^{-15\pm1}$ s. The carbon and nitrogen content of the samples was determined from the increase in mass during nitrogenation or carburization to $Sm_2Fe_{17}N_{1.2}$ and $Sm_2Fe_{17}C_{2.6}$. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Intermetallic compound; Sm_2Fe_{17}; N-diffusion; C-diffusion; Magnetic after-effect

1. Introduction

The intermetallic compound Sm_2Fe_{17}, which is of rhombohedral Th_2Zn_{17} structure, exhibits a planar magnetic anisotropy with a Curie temperature, T_C, below 400 K. By nitriding [1] or carburizing [2] Sm_2Fe_{17} the anisotropy can be changed into a uniaxial one with a simultaneous increase of the Curie temperature by more than 250 K caused by the lattice expansion [3]. Owing to the high values of anisotropy field and Curie temperature the nitrides [4] and carbides [5] of Sm_2Fe_{17} are promising candidates for a new class of permanent magnets. Nitrogenation and carburization can be achieved by direct reaction of Sm_2Fe_{17} powder particles with N_2, NH_3 or CH_4 gas. The reaction involves a slow diffusion of C or N atoms from the surface to the center of the particles. Therefore measurements of nitrogen and carbon diffusion in Sm_2Fe_{17} compounds are of considerable interest and technological importance. The highly sensitive method of magnetic after-effect (MAE) is ideally suited for this task because it yields direct results about diffusion in the bulk [6]. Therefore, processes like surface penetration or phase changes which often affect measurements of nitrogen uptake from the gas phase have not to be considered. In this paper we systematically investigated the short-range C and N diffusion by MAE measurements of $Sm_2Fe_{17}C_{2.6}$ and $Sm_2Fe_{17}N_{1.2}$ compounds.

2. Experimental details

2.1. Specimen preparation and characterization

The Sm_2Fe_{17} alloys were prepared by arc melting in argon atmosphere using high-purity metals (Sm 99.9 at.%, Fe 99.98 at.%). To ensure homogeneity the alloys were remelted several times and annealed in argon atmosphere at 1350 K for 8 days (Sm_2Fe_{17}). Fig. 1 shows the X-ray diffraction (XRD) patterns of the Sm_2Fe_{17} alloys before and after nitrogenation or carburization using Cu K_α radiation. Reasonable homogeneity was achieved, although the small line at about 44° shows that precipitates of bcc Fe could not be completely avoided in all cases.

The samples were crushed into coarse powder and charged with nitrogen by placing them in a high-purity N_2 atmosphere of 70 kPa at 820 K for 20 h. The nitrogen content of the samples was determined from their increase in mass during nitrogenation to $Sm_2Fe_{17}N_{1.2}$. After nitrogenation the sample showed an increase in the Curie temperature of about 80 K to 470 K, a value well within the expected range for a nitrogen content of about 1.2 atoms per formula unit [7].

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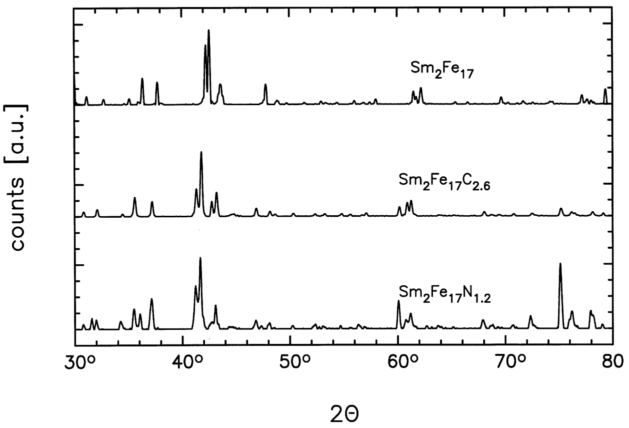

Fig. 1. XRD patterns (Cu K_α) of Sm_2Fe_{17}, $Sm_2Fe_{17}C_{2.6}$, and $Sm_2Fe_{17}N_{1.2}$.

Carburization was performed on powder with particle sizes below 100 microns in a high-purity methane atmosphere, CH_4, of 60 kPa at 770 K for 16 h leading to a carbon content of $Sm_2Fe_{17}C_{2.6}$ and a Curie temperature of 670 K.

2.2. Magnetic after-effect

The microscopic mechanism of the magnetic after-effect is based on the dependence of the magnetic interaction energy between the directions of spontaneous magnetization within a domain wall and the symmetry axis of anisotropic C or N interstitial configurations or anisotropic structural vacancies [8]. Owing to thermally activated jumps, the reorientation of interstitial atoms or vacancies lowers this interaction energy and after demagnetization leads to a decrease in the initial susceptibility $\chi(t)$, i.e. an increase in the reluctivity $r(t)=1/\chi(t)$. The reluctivity was measured using an automated a.c. device [9], where the sample is placed in the coil of an LC-oscillator. The susceptibility was calculated from the resonance frequency of this oscillator. Prior to measuring the magnetic after-effect the sample was demagnetized by sending an amplitude-modulated ac-current of 250 Hz with a maximum current of 99 mA for one second through the coil leading to a maximum demagnetization field of 15 kA m^{-1}, well above the coercive field of the samples.

The experimental results are represented as isochronal relaxation curves, where the change of the reluctivity between the times t_1 and t_2, defined as

$$\frac{\Delta r(t_1, t_2, T)}{r(t_1, T)} = \frac{r(t_2, T) - r(t_1, T)}{r(t_1, T)}, \tag{1}$$

is plotted versus temperature. In the measurements presented, $t_1 = 0.5$ s and t_2 varies from 1.5 s to 179.5 s. The relaxation processes are characterized by spectra of relaxation times, where each relaxation time was assumed to obey an Arrhenius law, corresponding to a box-like distribution of activation enthalpies with a common pre-exponential factor τ_0.

3. Experimental results

The nitrogenated compound $Sm_2Fe_{17}N_{1.2}$ shows a MAE relaxation maximum at about 285 K which is absent in the nitrogen-free compound. Likewise the carburized compound shows a MAE relaxation maximum at about 300 K. The nitrogenated compound shows an additional MAE relaxation maximum at about 180 K, which is related to the short-range diffusion of hydrogen [10]. Small amounts of hydrogen are almost unavoidable since Sm_2Fe_{17} is known to absorb hydrogen from air humidity [11].

The relaxation maxima at 285 K and 300 K can be described by an Arrhenius law and are assigned to jumps of interstitially dissolved nitrogen or carbon atoms, respectively. Owing to the small initial susceptibilities of hard magnetic materials these measurements are very difficult. Therefore, the fluctuations of the experimental data for longer times are due to experimental uncertainties. Numerical evaluation yielded an activation enthalpy $Q^{N} = (0.84 \pm 0.05)$ eV and a pre-exponential factor $\tau_0^{N} = 3 \cdot 10^{-15 \pm 1}$ s for the short-range diffusion of nitrogen. Fig. 2 shows this nitrogen-induced MAE relaxation maximum together with the numerical fit as well as the hydrogen induced relaxation maximum at 180 K. The inset in Fig. 2 shows the spectrum of activation enthalpies. The upper half of the enthalpy spectrum corresponds to the 285 K relaxation maximum while the lower half corresponds to the hydrogen diffusion.

The values for the short-range diffusion of carbon are $Q^{C} = (0.91 \pm 0.05)$ eV and $\tau_0^{C} = 1 \cdot 10^{-15 \pm 1}$ s. The C-induced

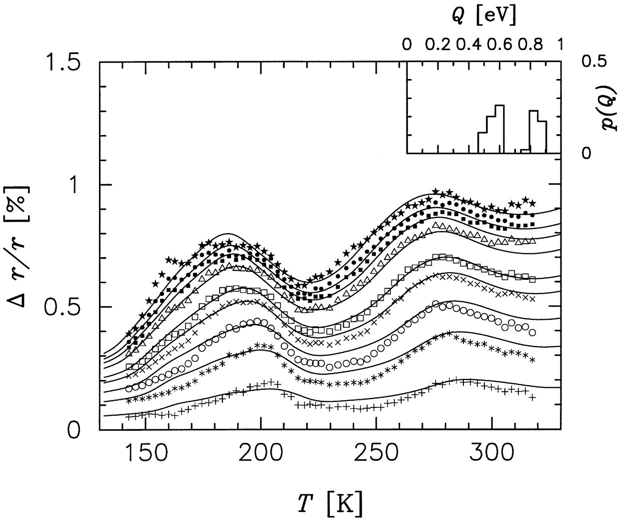

Fig. 2. MAE spectra of $Sm_2Fe_{17}N_{1.2}$ Experimental data are represented by symbols ($t_1 = 0.5$ s, $t_2 = +1.5$, * 4.5, ○ 9.5, × 19.5, □ 29.5, △ 59.5, ■ 89.5, ● 119.5, ★ 179.5 s) and the solid lines correspond to the numerical fit. The insert shows the distribution of activation enthalpies.

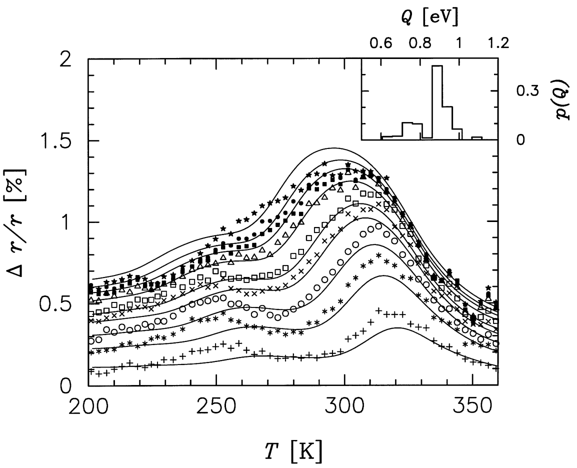

Fig. 3. MAE spectra of $Sm_2Fe_{17}C_{2.6}$, symbols as in Fig. 2.

MAE relaxation maximum and its numerical fit are shown in Fig. 3. As can be seen this maximum shows a small shoulder at about 250 K and is in fact a double maximum. The small maximum at about 250 K is assigned to jumps of C atoms in α-iron precipitates, as the carbon induced MAE relaxation maximum temperature in pure α-iron is about 265 K [12].

4. Discussion

MAE measurements of nitrided and carburized Sm_2Fe_{17} compounds show relaxation maxima at 285 K and 300 K, respectively, which do not appear in pure Sm_2Fe_{17} compounds. The C-induced MAE relaxation maximum shows a small additional shoulder at about 250 K which is attributed to the short-range diffusion of carbon in precipitates of α-iron detected by XRD (Fig. 1) for this sample.

Therefore these MAE maxima at 285 K and 300 K can evidently be assigned to the short-range diffusion of interstitial N or C atoms within the Sm_2Fe_{17} phase. Nitrogen in Sm_2Fe_{17} occupies, like carbon and hydrogen, the octahedral 9e interstices [13]. Diffusion of interstitial atoms in Sm_2Fe_{17} compounds happens via 9e–9e jumps within the basal plane and via 9e–18g–9e jumps perpendicular to it [14]. The unit cell of the $Sm_2Fe_{17}(C, N)_3$ phase is shown in Fig. 4. The method of MAE cannot distinguish between these jumps, but in any case the long-range diffusion path will consist of these jumps and therefore the activation enthalpy of short-range diffusion will be relevant for the long-range diffusion as well. The present results of activation enthalpies of $Q^N = (0.84 \pm 0.05)$ eV for nitrogen diffusion and $Q^C = (0.91 \pm 0.05)$ eV for carbon diffusion with pre-exponential factors $\tau_0^N = 3 \cdot 10^{-15 \pm 1}$ s and $\tau_0^C = 1 \cdot 10^{-15 \pm 1}$ s compare favorably with diffusion data for nitrogen and carbon in α-iron of $Q_{Fe}^N = (0.82 \pm 0.01)$ eV and $Q_{Fe}^C = (0.87 \pm 0.01)$ eV [15]. As in α-iron the greater size of a carbon atom (0.77 as compared to 0.75 for nitrogen) leads to higher activation enthalpies for carbon diffusion than for nitrogen diffusion in Sm_2Fe_{17} as well.

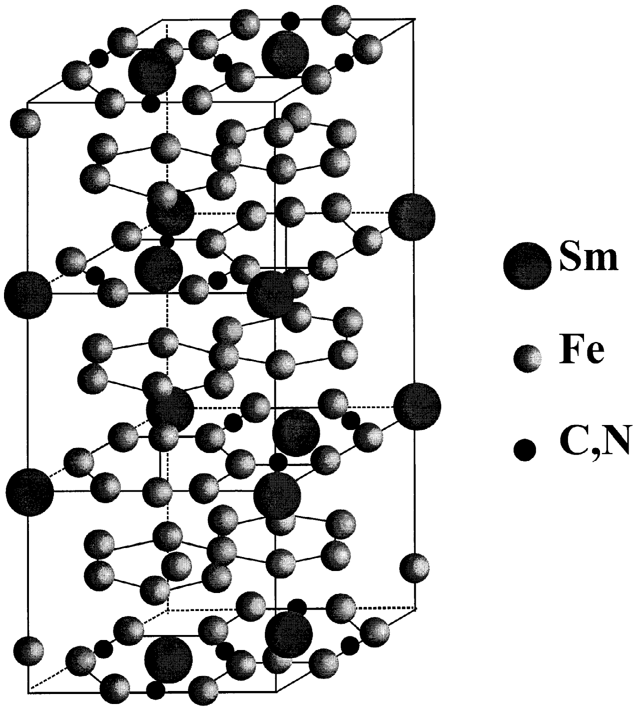

Fig. 4. Crystal structure of $Sm_2Fe_{17}(N, C)_3$. Large, medium-sized and small circles refer to Sm atoms, Fe atoms and N or C atoms in 9e interstitial sites, respectively.

The present MAE results of an activation enthalpy of $Q^N = (0.84 \pm 0.05)$ eV for nitrogen diffusion in Sm_2Fe_{17} compare favorably with results from Coey et al. giving $Q^N = (0.81 \pm 0.03)$ eV measured by gas phase absorption of nitrogen [16]. Considerably higher activation enthalpies of $Q^N = (1.38 \pm 0.05)$ eV [7] and $Q^N = (1.48 \pm 0.1)$ eV [17] were also reported in literature. These results were obtained either directly by nitrogen absorption measurements of Sm_2Fe_{17} particles from gas phase [7] or by measuring the growth of a nitrogen-rich Sm_2Fe_{17} phase upon nitrogen uptake from gas phase [17]. Besides a possible concentration dependence of the nitrogen diffusion it has to be kept in mind that in such measurements diffusion is not necessarily the rate controlling step. Other possibilities include surface penetration, dissociation of nitrogen molecules into atoms or even formation of a metastable $Sm_2Fe_{17}N_3$ phase. To complicate matters further a unique rate controlling step not necessarily exists and nitrogen uptake might be controlled by a combination of several processes [18].

For an improvement of the nitrogenation or carburization process in future applications for the production of permanent magnets it is important to note that our MAE diffusion data in comparison with nitrogen absorption measurements from literature suggest that the nitrogenation process is not diffusion controlled.

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