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Mössbauer spectrometric study of $Sm_2Fe_{17}N_x$ (x=0–8)

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Ternary rare-earth–iron–nitrogen compounds of $Sm_2Fe_{17}N_x$ with x ranging from 0 up to 8, which have a rhombohedral structure of Th_2Zn_{17} and a high Curie temperature up to 475–480 °C depending on the degree of nitrogenation, were prepared by the nitrogenation of arc-melted Sm_2Fe_{17} in mixed ammonia and hydrogen gas atmospheres of various ratios, and Mössbauer spectra of these compounds were observed at room temperature in order to analyse the physicochemical state of the nitrogenated products. The obtained data were analysed by focusing main attention on the effect of degree of nitrogenation on the variation of spectral profiles. Paramagnetic peaks due to an amorphous compound became prevalent as x became higher than ~ 2.3.

1. Introduction

Samples of $Sm_2Fe_{17}N_x$ with x ranging from 0 to 8, prepared by nitrogenation of Sm_2Fe_{17} alloy in an NH_3–H_2 atmosphere [1–3], showed different magnetic properties from those prepared by the nitrogenation of Sm_2Fe_{17} in N_2 atmosphere. The nitrogenation in NH_3–H_2 atmosphere can produce $Sm_2Fe_{17}N_x$ compounds with x greater than 3.0, whereas the nitrogen gas method [4–6] cannot produce $Sm_2Fe_{17}N_x$ with x more than 2.8. The best magnetic properties, such as the saturation magnetization ($4\pi I_s$), intrinsic coercive force (iH_c) and magnetic anisotropy, were observed for $Sm_2Fe_{17}N_{3.0-3.2}$ as reported previously [1].

The saturation magnetization and anisotropy field of these magnetic materials were clearly increased with the progress of nitrogenation, and exhibited maxima of $4\pi I_s$ at 15.7 kG and H_a at 260 kOe for the compound with $x = 3.0$ [7]. Peaks due to α-Fe phase are found neither in the X-ray diffraction patterns nor in Mössbauer spectra of $Sm_2Fe_{17}N_x$ produced by an ammonia–hydrogen nitrogenation process.

Buschow [8, 9] proposed 9e sites as positions of nitrogen atoms included in $Sm_2Fe_{17}N_x$, which has the crystal structure of Th_2Zn_{17}. We noticed, however, that an increase of x increased the lattice constant along both a and c axes up to 0.875 and 1.270 nm, respectively, for the compound with $x = 3.0$ [1, 10]. We therefore, investigated the structural change of $Sm_2Fe_{17}N_x$ with increase of x by means of X-ray diffractometry and Mössbauer spectrometry in more detail, which revealed that the elevation of x to more than 2.3 increased the intensity of the paramagnetic doublet due to an amorphous phase.

2. Experimental procedure

The host alloy of Sm_2Fe_{17} was prepared by induction melting of Sm and Fe (99.9%). Sm was added slightly in excess of stoichiometry to exclude the precipitation of α-Fe. The cast ingot was annealed in an argon atmosphere at 1520 K for 3 h. The alloy was pulverized in a coffee mill in a nitrogen atmosphere to obtain particles with a size distribution of 20 to 106 μm, and then nitrogenated in a furnace at 693–768 K with a mixed gas of NH_3 and H_2. The value of x was regulated by variation of the partial pressure ratio of hydrogen to ammonia in the nitrogenating atmosphere. The nitrogenated alloy was annealed at 465 °C in argon in order to diffuse nitrogen atoms into the crystal grains.

The apparent number of nitrogens in the $Sm_2Fe_{17}N_x$ was determined by inert gas fusion of samples at 2800 °C and subsequent detection of evolved nitrogen by gas chromatography at room temperature.

Mössbauer spectra were observed at room temperature with a transmission Mössbauer spectrometer (Austin Science Associates). A γ-ray source of Co^{57} in a Rh matrix was used in a constant acceleration mode.

The X-ray diffraction patterns of powder samples were taken in a Philips PW 1700 automated powder diffractometer using CuK_α radiation.

The thermogravimetric (TG) data were obtained with a SINKU-RIKO 7000 TG analyser by elevating the temperature of the samples at a rate of 5 °C min^{-1}.

Mass spectrometric thermal analyses were carried out with an NICHIDEN-ANELVA AQA 360 quadrupole-type mass spectrometer by elevating the temperature of the sample at a rate of 5 °C min^{-1}.

3. Results and discussion

Fig. 1 shows an idealized crystal structure of $Sm_2Fe_{17}N_x$. Otani *et al.* [4] and Capehart *et al.* [11] examined the sites of nitrogen in $Sm_2Fe_{17}N_x$ by EXAFS and XANES, and reported that the interatomic distance between Sm and N is about 0.25 nm, concluding that the nitrogen atoms are present at 9e sites. Typical examples of the powder X-ray diffraction patterns of powder samples (2–3 μm in depth) are shown in Fig. 2. All of the nitrogenated specimens except for $x = 8$ showed the same Th_2Zn_{17} structure as Sm_2Fe_{17}. It should be noted that the coarse powder sample with $x = 1.7$ showed only a single set of diffraction lines corresponding to $x = 3.2$, because the un-nitrogenated phase existed at an inner sphere of particles where the X-rays could not penetrate [7]. The specimen with $x = 5.1$, on the other hand, showed a set of slightly broad diffraction lines with a large background. This specimen is revealed to contain a fair amount of an amorphous phase which prevailed in the specimen with $x = 8$.

The existence of the amorphous phase is also confirmed by Mössbauer study. The Mössbauer spectra of Sm_2Fe_{17}, $Sm_2Fe_{17}H_y$ and $Sm_2Fe_{17}N_x$ are shown in Fig. 3. The Mössbauer spectra of these compounds were resolved into four subspectra associated with the four non-equivalent iron atoms occupying 6c, 9d, 18f and 18h sites. It is revealed that both hydrogen and nitrogen atoms intruded into the crystal lattice of Sm_2Fe_{17} and that the intrusion of hydrogen and nitrogen increased the magnitude of the internal magnetic field. The intrusion of hydrogen atoms in the crystal lattice of $Sm_2Fe_{17}N_x$ affects the wave function of the 1s electron of neighbouring iron atoms, resulting in a variation in isomer shift (IS) to the positive direction. It also increased the internal magnetic field of $Sm_2Fe_{17}N_x$ by 25%. The nitrogenation of Sm_2Fe_{17}

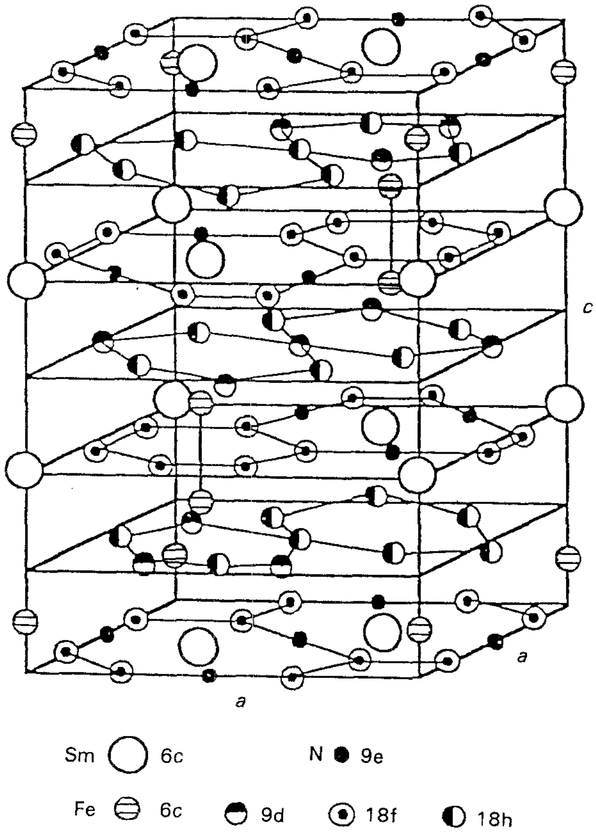

Figure 1 Crystal structure of Th_2Zn_{17}.

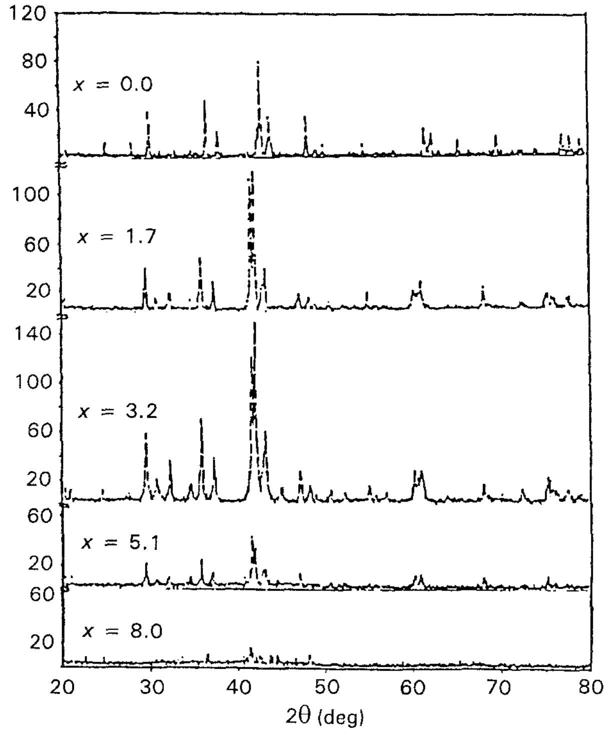

Figure 2 X-ray diffraction pattern (CuK_α) of the powder sample $Sm_2Fe_{17}N_x$.

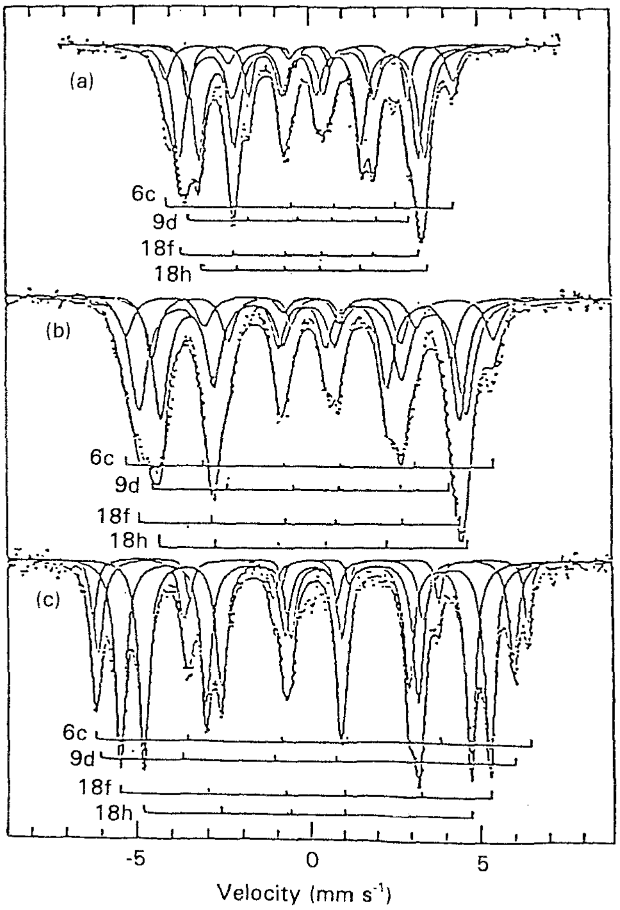

Figure 3 Mössbauer spectra of (a) Sm_2Fe_{17}, (b) $Sm_2Fe_{17}H_y$, (c) $Sm_2Fe_{17}N_{3.2}$.

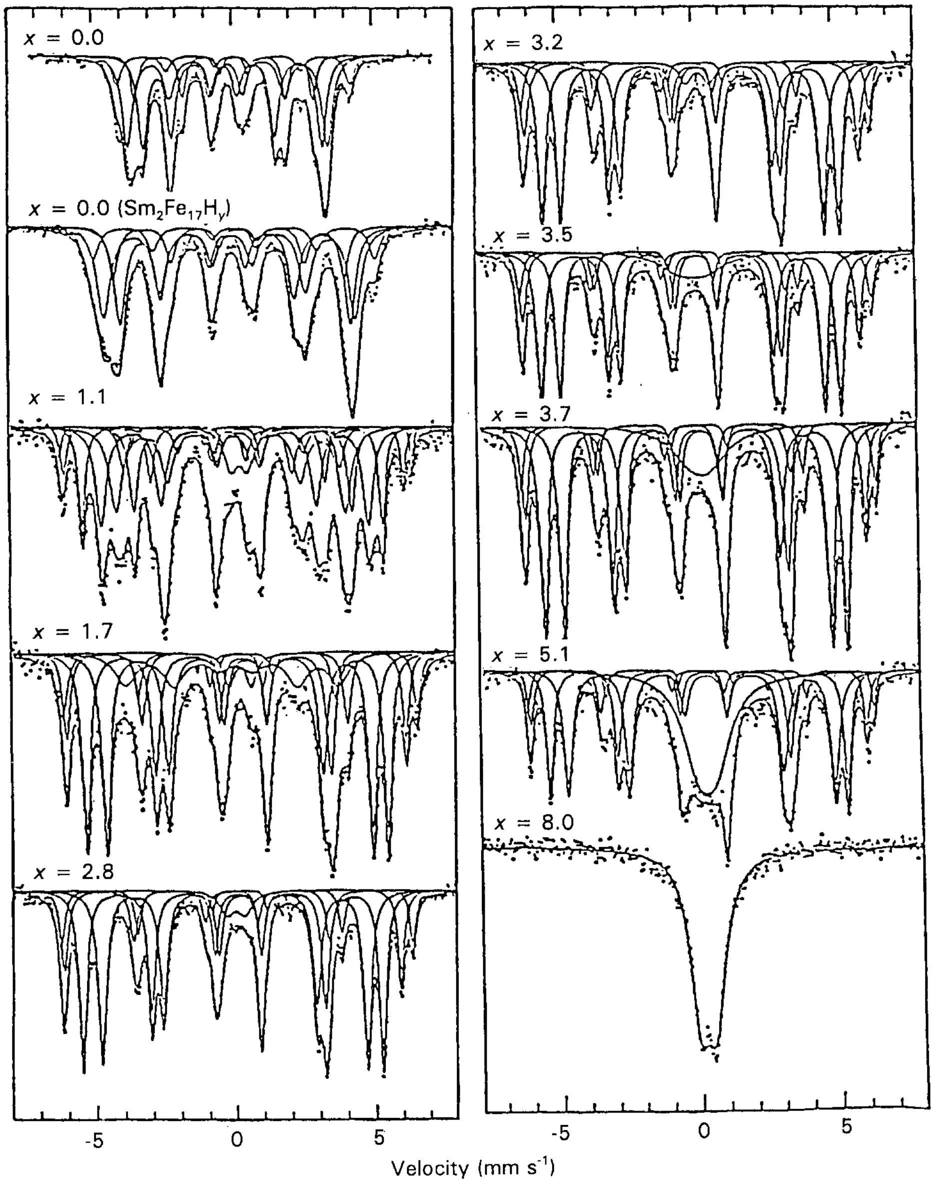

Figure 4 Mössbauer spectra of $Sm_2Fe_{17}N_x$ ($x = 0$–8).

increased the internal magnetic field of 18h from 20.2 to 29.8 T, 18f from 22.5 to 33.5 T, 9d from 20.2 to 37.7 T, and 6c from 26.3 to 39.4 T. These variations were definite evidence of interaction between neighbouring iron and nitrogen atoms. Nitrogen atoms were considered to locate preferably in the 9e site of the *c* plane.

Although the preparation of $Sm_2Fe_{17}N_x$ compounds having x more than 3.0 is not achieved by nitrogenation in N_2, they were readily obtained by the nitrogenation in mixed NH_3–H_2 gas. Hydrogen atoms intrude into crystalline grains to form hydrides of unit cell size, followed by the substitution of hydrogen by nitrogen atoms. This sequential nitrogenation is the main cause of the acceleration of the reaction rate. The reason for the increase of lattice constants with degree of nitrogenation was interpreted as the intrusion of nitrogen atoms to the 9e site up to $x = 2.3$ and partial amorphization of the crystalline phase, but the details were left for further discussion. The nitrogen atoms in the resultant compounds are presumably present not only at the 9e site but also at other locations.

Mössbauer spectra of $Sm_2Fe_{17}N_x$ with $x = 0$, 1.1, 1.7, 2.8, 3.2, 3.5, 3.7, 5.1 and 8 are shown in Fig. 4. A doublet appeared at the centre of the spectrum when x increased to more than 2.3, and dominated the spectrum as x approached 7–8. The quadrupole splitting (QS) and IS of the unknown paramagnetic doublet are 0.87 and 0.34 mm s^{-1}, respectively. Observation of the Mössbauer spectrum of $Sm_2Fe_{17}N_8$ at liquid nitrogen temperature revealed that the doublet is resolved into a doublet and a broad singlet. This evidence indicates that the amorphous phase is composed of two components, one being small particles and another an amorphous phase of some iron nitrides or $Sm_2Fe_{17}N_x$ compounds. The previous discussion suggests that the number of nitrogen atoms included in a 9e site of Sm_2Fe_{17} is about $x = 2.3$, so that the possibility of nitrogen atoms existing in other locations as well as 9e, for example in the 18g site of an $Sm_2Fe_{17}N_x$ crystal or in an amorphous phase of $Sm_2Fe_{17}N_x$ compound, can be suggested for samples above $x = 2.3$. The presence of these amorphous and minute crystalline phases is inferred to contribute to amelioration of the magnetic properties of $Sm_2Fe_{17}N_x$ compounds.

The variations of Mössbauer parameters (IS, QS and H_{int}) are shown in Fig. 5. The Mössbauer parameters of the nitrogenated particles are constant and the constancy of all Mössbauer parameters suggests that these spectra were the sum of spectra from the hydrogenated and the nitrogenated Sm_2Fe_{17}. In other words, the nitrogenation proceeds from the surface layer of $Sm_2Fe_{17}H_x$, substituting hydrogen atoms by nitrogen atoms toward the centre.

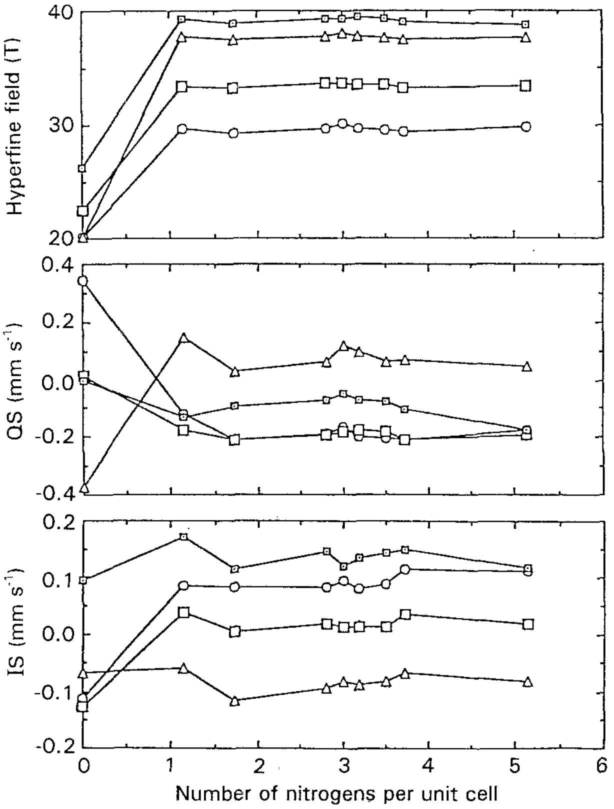

Figure 5 Mössbauer parameters of $Sm_2Fe_{17}N_x$: (⊡) 6c, (△) 9d, (□) 18f, (○) 18h.

The relative area intensity ratios of $Sm_2Fe_{17}N_x$ to Sm_2Fe_{17} increases with the progress of nitrogenation as shown in Fig. 6. Examination of Fig. 6 suggests that $Sm_2Fe_{17}N_{2.2}$ and $Sm_2Fe_{17}N_{2.3}$ are the most plausible and stable compounds produced respectively, i.e. the nitrogenation proceeded up to the formation of $Sm_2Fe_{17}N_{2.3}$ and then the nitrogen atoms seem to enter unidentified positions in the crystal.

In order to get experimental evidence that nitrogen atoms evolve from $Sm_2Fe_{17}N_{3.2}$ by heating at two different temperatures, we applied mass spectrometric thermal analysis of nitrogen to $Sm_2Fe_{17}N_{3.2}$ and got the result shown in Fig. 7a. Nitrogen evolved at 520–720 °C and 720–770 °C. The result revealed that

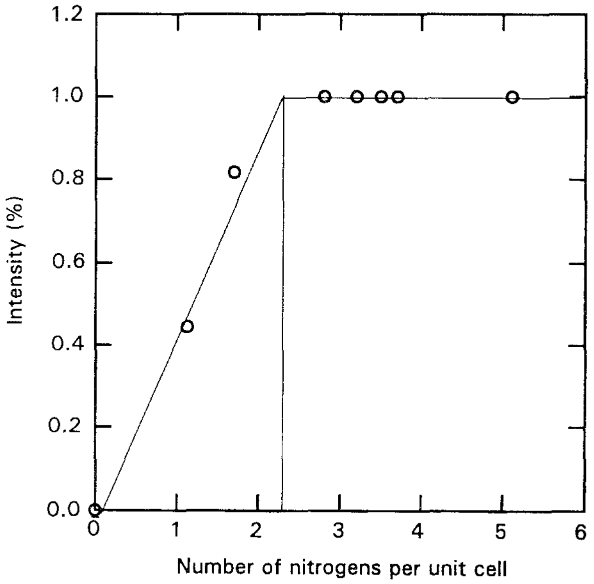

Figure 6 Relative area intensity in Mössbauer spectra of nitride.

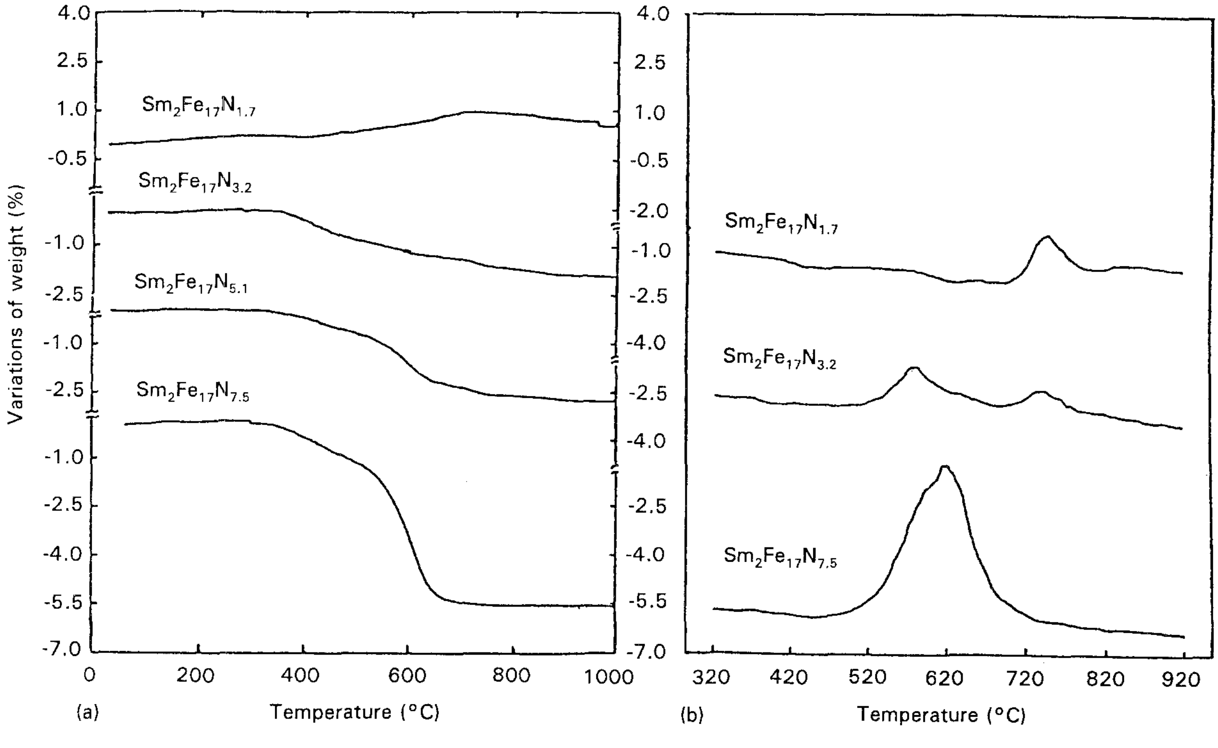

Figure 7 (a) Thermogravimetry and (b) mass-spectroscopic thermal analysis.

the nitrogen atoms exist in two states, one being tightly bound to the 9e site and other being relatively loosely bound in a different lattice site, possibly attributed to the amorphous $Sm_2Fe_{17}N_x$ compound. The loosely bound nitrogen atoms may dissociate at about 520 °C as shown for $Sm_2Fe_{17}N_{7.5}$ and remain tightly bound to the 9e site evolved at 720 °C as shown for $Sm_2Fe_{17}N_{1.7}$ (Fig. 7b). The accumulated knowledge suggests that the evolution of nitrogen in the first and second stages could be the result of the following thermochemical process:

$$Sm_2Fe_{17}N_x \longrightarrow SmN + FeN \longrightarrow SmN + \alpha\text{-}Fe$$

Discrimination of the reactions pertinent to each decomposition step will be discussed and reported in a subsequent publication.

4. Conclusion

$Sm_2Fe_{17}N_x$ compounds with x up to 8 were prepared by the NH_3–N_2 nitrogenation procedure and Mössbauer spectra of these compounds were observed. We can conclude that the major portion of nitrogen atoms occupy 9e sites to form stable $Sm_2Fe_{17}N_{2.3}$ and the remaining nitrogen may occupy another site in the crystal to form an amorphous and paramagnetic substance. An increase of x to more than 2.3 increased the intensity of the doublet. Since the best magnetic properties are observed for $Sm_2Fe_{17}N_{3.2}$, these magnetic particles have an internal structure dependent on the nitrogen concentration, and the internal structure may play a role in improving the magnetic characteristics. Experiments to identify the proposed amorphous, paramagnetic substance by various analyses are being carried out now, and details will be reported in the near future.

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