Advanced Materials '93, I / B: Magnetic, Fullerene, Dielectric, Ferroelectric,
Diamond and Related Materials, edited by M. Homma et al.
Trans. Mat. Res. Soc. Jpn., Volume 14B

Nitrogen Absorption by Sm_2Fe_{17}

H.Uchida[a],S.Kise[a],T.Yanagisawa[a],S.Tachibana[a],H.H.Uchida[b],V.Koeninger[c],Y.Matsumura[c],T.Kurino[d] and H.Kaneko[d]

[a]Dept. of Applied Physics, [b]Dept. of Resources and Environmental Science, Tokai University, 1117 Kitakaname, Hiratsuka, Kanagawa 259-12, Japan

[c]Kanagawa Academy of Science and Technology (KAST), 3-2-1 Sakado, Takatsu-ku, Kawasaki, Kanagawa 213, Japan

[d]The Society of Non-Traditional Technology (SNTT), 1-2-8 Toranomon, Minato-ku, Tokyo 105, Japan

The characteristics of the nitrogen absorption by Sm_2Fe_{17} were investigated from the view points of both equilibrium and reaction kinetics. In pressure-composition isotherm measurements, a pressure plateau was found between nitrogen concentrations x=2 and x=3 in $Sm_2Fe_{17}N_x$. A consistent behavior was found for the lattice constants. If the nitrogen content is x<2, the lattice parameters increase with concentration, while at x>2 they reach a saturation. These results suggest a phase transformation or an order-disorder transformation either between Sm_2Fe_{17}-N(solid solution) and $Sm_2Fe_{17}N_3$(nitride) or between an other phase $Sm_2Fe_{17}N_{2-x}$ and $Sm_2Fe_{17}N_3$(nitride).

1.INTRODUCTION

$Sm_2Fe_{17}N_x$ compounds have been extensively investigated as a new type of hard magnetic material, with possibly better properties than Nd-Fe-B type magnets [1]. The interstitial modification of the Sm_2Fe_{17} alloy with nitrogen atoms gives an improvement of the saturation magnetization and the magnetic anisotropy and a large increase of the Curie temperature. However, the phase relationships in the Sm_2Fe_{17}-N system and the kinetic mechanisms of N_2 absorption by Sm_2Fe_{17} are not yet well understood. Actually, the following question needs to be urgently answered: whether Sm_2Fe_{17} forms only a nitrogen solid solution phase or whether a nitride phase also exists. In this paper, we report the characteristics of nitrogen absorption by Sm_2Fe_{17} from the viewpoints of both equilibrium and reaction kinetics.

2.EXPERIMENTAL

The Sm_2Fe_{17} alloy was prepared from 99.9% pure Sm and 99.99% pure Fe by arc melting and annealed in an Argon atmosphere at 1373K for 14400s. Then it was ground and meshed to powder with particle sizes smaller than 38μm. The chemical composition, microstructure and phase distribution were determined by inductively coupled plasma emission spectroscopy (ICP), energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy and optical microscopy.

The nitrogen absorption equilibrium and the rate of the reaction were measured by a volumetric method using a Sieverts' type apparatus with high vacuum system. Nitrogen absorption was carried out at 623K by exposing Sm_2Fe_{17} powder to 99.9995% nitrogen at pressures between 10^2 and 10^7Pa. Details of the Sieverts' system used and the measurement method are described elsewhere[2]. After nitriding, the structure and lattice constants of the sample were examined using XRD. The amount of absorbed nitrogen was also confirmed gravimetrically.

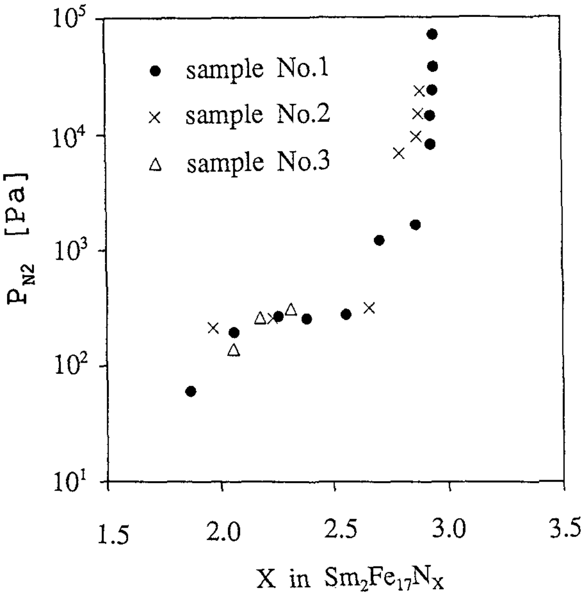

Figure 1. *Pressure-composition isotherm of the Sm_2Fe_{17}-N system at 623K*

3.RESULTS AND DISCUSSION

Fig.1 shows the pressure-composition isotherms of the Sm_2Fe_{17}-N system at 623K. To confirm the reproducibility of the experiments, the experiment was repeated 3 times. The absorbed nitrogen contents were also confirmed by measuring the weight of the samples before and after nitriding. In Fig.1, a pressure plateau can be seen at an equilibrium pressure of p_{N2}=2.5x10^{2}Pa, between N concentrations x=2 and 3 in $Sm_2Fe_{17}N_x$.

XRD-spectra for nitrided samples between $Sm_2Fe_{17}N_{0.95}$ and $Sm_2Fe_{17}N_{2.95}$ are shown in Fig.2. The diffraction data indicates almost no change in the basic patterns of Sm_2Fe_{17} but some small precipitation of α-iron. The lattice constants, shown in Fig.3, exhibit a large expansion of the a and c-axis between x=0 and x=2, but a much smaller expansion between x=2 and x=3, indicating a different way of absorption of nitrogen at these high concentrations.

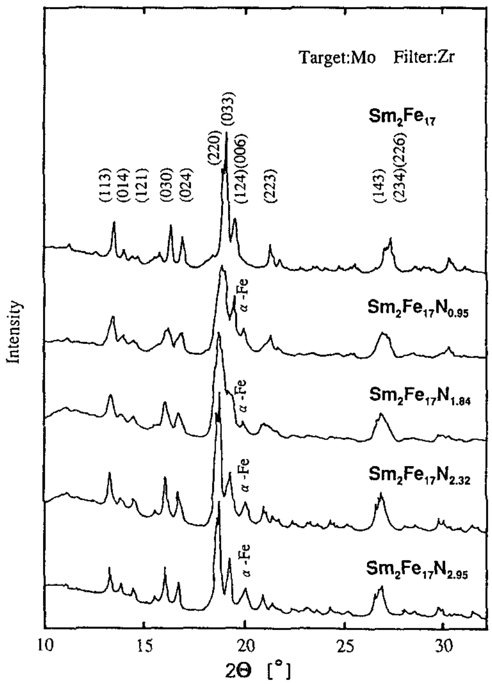

Figure 2. *XRD patterns for the Sm_2Fe_{17}-N system at 623K*

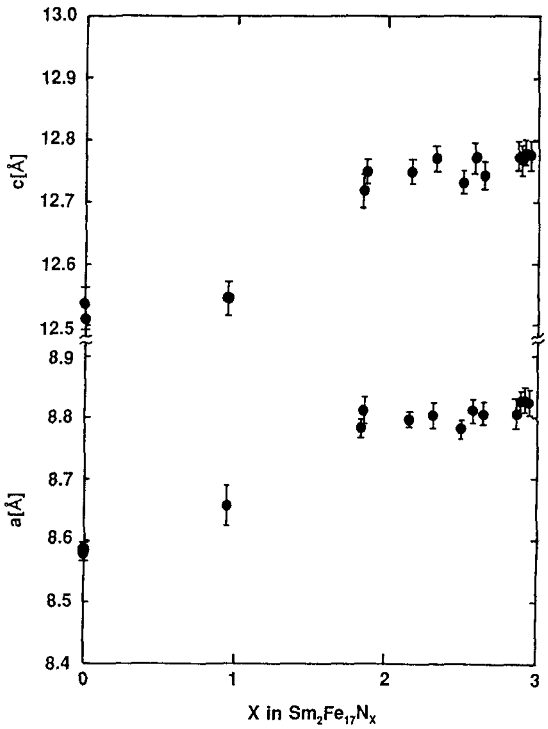

Figure 3. *Lattice constants in the Sm_2Fe_{17}-N system at 623K*

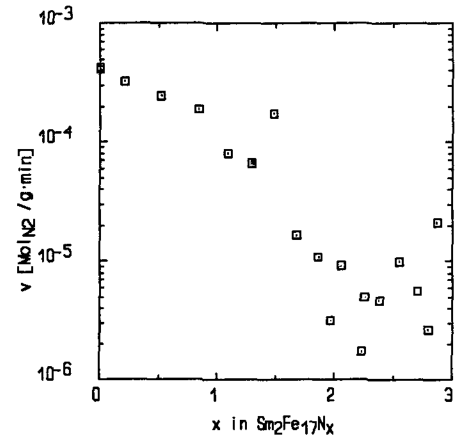

Figure 4. *Nitrogen absorption rate of the Sm_2Fe_{17}-N system at 623K*

Fig.4 shows the change in nitrogen absorption rate as a function of nitrogen content. The absorption rate decreases with increasing nitrogen content. We reported previously, that there is only a weak dependence of reaction rate and pressure [3]. So the kinetic data suggest a diffusion controlled rather than a surface reaction controlled absorption mechanism.

A pressure plateau is a strong indication for a two phase state e.g. a phase transformation. The behavior of the lattice parameters also shows a different absorption mechanism at x>2. This can be explained by a transformation either between Sm_2Fe_{17}-N(solution) and $Sm_2Fe_{17}N_3$ (nitride) or between a new phase $Sm_2Fe_{17}N_{2-x}$ and $Sm_2Fe_{17}N_3$(nitride). The first explanation would be a solid solution of nitrogen in a lattice with a limited amount of interstitial sites, as described by the Lacher-model [4]. If the partial reaction enthalpy ΔH of the nitrogen solution reaction becomes more negative with increasing N-content, and the temperature is sufficiently low, a pressure plateau is formed. In an ideal case, the center of the plateau should be at x=1.5 and the PCT curve for low pressures and low concentrations should follow Sieverts law, with $x \sim p^{0.5}$. As seen in Fig.1, the plateau is at higher concentrations. Sieverts law can not be confirmed nor rejected because the equilibrium pressures there are much too low to measure with our apparatus. The second explanation involves another phase or an ordered state with an upper concentration limit of about x=2 and therefore another two phase region (pressure plateau) at lower concentrations and pressure. But the XRD spectra (Fig.3) show no significant change in lattice structure except of lattice expansion. So this phase transformation may be possibly an order–disorder transformation or a transformation between rhombohedral and hexagonal structure, which are difficult to separate with XRD. Until now, we can not decide, which transformation really occurs.

4.CONCLUSION

The pressure composition isotherm of the Sm_2Fe_{17}-nitrogen system at 623K shows a plateau between concentrations x=2 and x=3 in $Sm_2Fe_{17}N_x$ and so indicates the existence of a phase transformation or an order-disorder transformation there. This is confirmed by the change of the lattice constants, which increase steeply up to x=2 and then stay almost constant. The phase transition can be either between Sm_2Fe_{17}-N(solid solution) and $Sm_2Fe_{17}N_3$(nitride) or between another phase $Sm_2Fe_{17}N_{2-x}$ and $Sm_2Fe_{17}N_3$(nitride).

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