NON-EQUILIBRIUM GAS-PHASE NITROGENATION

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Abstract - Non-equilibrium nitrogenation of transition-metal rich rare-earth intermetallics can be used to increase the nitrogen content beyond its equilibrium concentration. For example, nitrogenation of Sm_2Fe_{17} using ammonia yields volume expansions up to 8.3 vol %, which correspond to a composition $Sm_2Fe_{17}N_x$ with $x \approx 4$. This effect is related to catalytic action at the metal surface where ammonia is decomposed into nitrogen and hydrogen, with nitrogen absorption on a site where it is weakly bound, as an intermediate step. For overloaded $Sm_2Fe_{17}N_x$ with $x>3$ the net reaction energy $U_0 = 5 \pm 10$ kJ/mole indicates a nearly temperature-independent occupation of the non-9e sites.

I. INTRODUCTION

There is much evidence that quasi-equilibrium nitrogenation of Sm_2Fe_{17}, conducted at 400 - 500 °C in about one bar N_2, yields a nitride $Sm_2Fe_{17}N_{3-\delta}$ with useful hard-magnetic properties [1-4]. Neutron diffraction measurements indicate a practically exclusive occupation by nitrogen of the octahedral 9e interstices in the rhombohedral Th_2Zn_{17} structure [5], when these nitrogenation conditions are used.

On the other hand, some authors report nitrogen contents $x \approx 6$ after treatment in ammonia or hydrogen which are incompatible with an exclusive occupation of the Sm_2Fe_{17} 9e octahedra. No structural data are yet available, but the observed volume expansion (about 7.5 % in [6]) is little greater than that for $Sm_2Fe_{17}N_3$.

Here we discuss the possibility of a nitrogen content $x > 3$ within the framework of *non-equilibrium* thermodynamics and statistics. We present data indicating the catalytic action of Sm_2Fe_{17} for ammonia decomposition, which is attributed to occupancy of sites other than 9e octahedra.

II. STATISTICAL BACKGROUND

Neglecting interatomic interaction effects, the equilibrium nitrogen solubility on the 9e sites is given by [3,4]

$$x = 3\left(1 + \sqrt{\frac{p_0}{p}}\, e^{U_0/kT}\right)^{-1} \qquad (1)$$

with p_0 constant ≈ 100 kbar and U_0 the net reaction energy (nitrogen absorption energy). The sign and magnitude of U_0 determine whether the nitrogen uptake is high or low. The

experimental value $U_0 = -57$ kJ/mole for Sm_2Fe_{17} [3,4] indicates a high solubility, whereas the value for α-Fe, $U_0 = 30$ kJ/mole [7], means a very low solubility.

From the point of view of equilibrium thermodynamics there is no advantage in using ammonia instead of molecular nitrogen. The formation of ammonia from nitrogen and hydrogen is exothermic ($U_0 \approx -45$ kJ/mole [8,9]), but the large entropy contributions from the hydrogen and nitrogen gases outweigh the energetic effect. Correspondingly, the concentration of ammonia under typical nitrogenation conditions (1 bar pressure and 500 °C), if it were in equilibrium with hydrogen and nitrogen, would be negligibly small (less than 1 %).

The situation changes, however, if the ammonia partial pressure is kept artificially high. Ammonia then decomposes catalytically at the metal surface, which involves the formation of an intermediate nitride. Note that nitrogen desorption and adsorption are known to be the rate-limiting steps in ammonia catalysis [8,10]. This intermediate nitrogenation is a possible way to produce overloaded nitrides having $x > 3$.

III. RESULTS

To investigate the catalytic activity and the nitrogenation behaviour of the intermtallics, ingot samples were milled for 15 minutes under cyclohexane. After drying and sieving, a narrow particle size distribution, typically 10 - 15μm, was obtained. To monitor the gas pressure as a function of time and temperature, the reaction was conducted in the quartz sample tube (volume = 6.3 cm^3), of a thermopiezic analyser (TPA), connected to mass spectrometer. Fig 1 shows the ammonia concentration deduced from the total pressure. X-ray powder diffraction with Cu K_α radiation was used for phase analysis and determination of the lattice parameters.

Fig. 2 shows the effect of Sm_2Fe_{17} on the catalytic decomposition of ammonia. The catalyzed decomposition starts at about 300 °C, compared to about 550 °C in an empty quartz tube. Other experimentally determined onset temperatures are 450 °C for Y_2Co_{17}, 400 °C for $Y_6Fe_{11}Ga_3$, 350 °C for Fe, Co, and $SmCo_5$, and 300 °C for Y_2Fe_{17}.

To investigate the initial stage of the reaction, the isothermal decomposition curves were fitted to the solution of the Temkin equation [9].

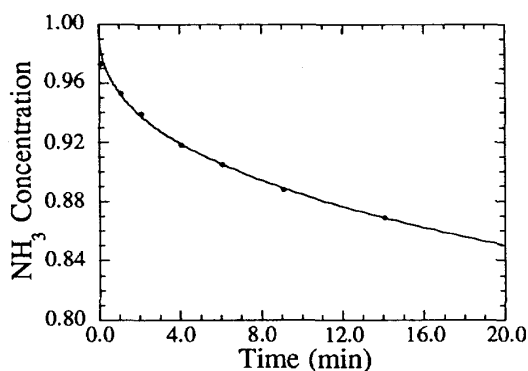$$\frac{dN_A}{dt} = k_1\, p_N \left(\frac{p_H^3}{p_A^2}\right)^\alpha - k_2 \left(\frac{p_A^2}{p_H^3}\right)^{1-\alpha} \qquad (2)$$

Fig. 1 Reduced ammonia concentration as a function of time for a short isothermal experiment at 425°C with a Sm_2Fe_{17} catalyst.

Here N_A is the total number of hydrogen atoms in the system, and p_A, p_N, and p_H, are the partial pressures of the three gasses involved. Results are $\alpha = 0.75 \pm 0.10$ for Y_2Co_{17}, $\alpha = 0.75 \pm 0.20$ for Fe, and $\alpha = 0.77 \pm 0.15$ for Sm_2Fe_{17}. Though preliminary, these results, as well as the corresponding catalytic activities k_2 [11], indicate a similiar catalytic behaviour for all the compounds investigated [12].

To obtain materials with nitrogen contents $x > 3$, Sm_2Fe_{17} powder was heated in pure ammonia (Table 1). The volume expansion of 8.3 % (cf. Fig. 3) clearly indicates that nitrogen occupancy is not restricted to the 9e sites. Assuming a unit cell expansion of about 2.1 % per per nitrogen atom (cf. the corresponding consideration for hydrogen in metals [13]), we obtain a nominal composition $Sm_2Fe_{17}N_4$. Higher nitrogen uptake (up to $x = 6.25$) leads to the formation of Fe_4N and SmN. Other intermetallics, such as $SmCo_5$, become amorphous upon ammonia treatment.

Neglecting interatomic interaction effects and nitrogen outgassing, the nitrogen concentration on the non-9e sites is given by [11]

$$c = \left(1 + \sqrt{\frac{p_H^3}{p_A^2 p_c}} \, e^{(U_o-U_A)/kT}\right)^{-1} \quad (3)$$

Compound	Sm_2Fe_{17}	$Sm_2Fe_{17}N_{3-\delta}$	$Sm_2Fe_{17}N_{3+\delta}$
a (Å)	8.535	8.719	8.745
c (Å)	12.434	12.635	12.832
$\Delta a/a\%$	0.0	2.2	2.5
$\Delta c/c\%$	0.0	1.6	3.2
v (Å^3)	784.4	831.8	849.9
$\Delta v/v\%$	0.0	6.0	8.3

Table 1. Crystallographic data for nitrides of Sm_2Fe_{17} produced by gas phase interstitial modification with N_2 and NH_3.

where $p_c \approx 70$ kbar and U_o is the net reaction energy for the non-9e site. Note that this equation, though formally related to Eq. (1) by the equilibrium reaction constant $k = (p_N \, p_H^{1.5})/p_A$ (cf. e.g. [14]), does *not* describe an equilibrium process - the equilibrium solubility is given by Eq. (1). The use of ammonia is equivalent to a huge effective nitrogen pressure, $p_{eff} \approx 3Mbar$ in Eq. (1). p_H and p_A are controlled by the reaction conditions so Eq. (3) can be used to estimate U_o. Based on the data given in Table 2, the value $U_o = 5 \pm 10$ kJ/mole, is obtained from Eq. (3) taking $c=[(\Delta v/v)-6.3]/2.1$, which indicates a weakly endothermic reaction. Table 2 compares the observed volume expansions $(\Delta V/V)_{ex}$ with values calculated $(\Delta V/V)_{th}$, using $U_o = 5$ kJ/mole - the agreement is reasonably good.

IV. DISCUSSION

The data shows that the catalytic decomposition of ammonia by transition-metal rich rare-earth intermetallics, in particular R_2Fe_{17}, strongly influences the interstitial modification
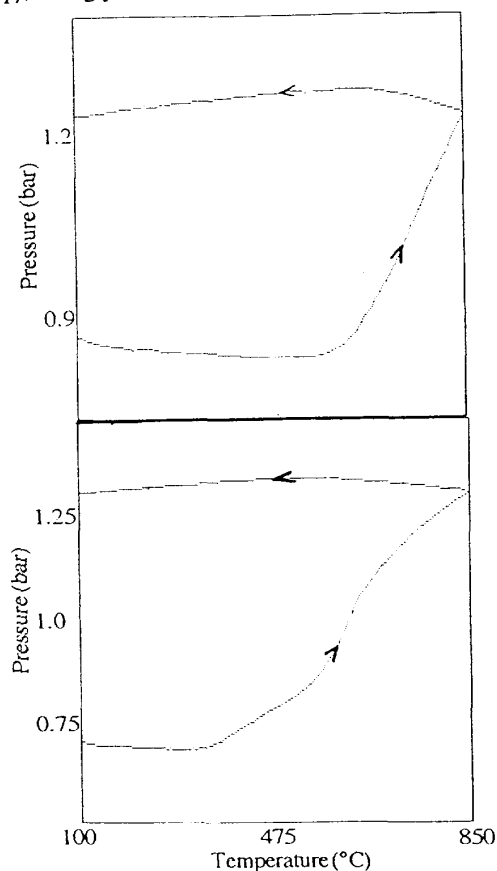

Fig. 2: TPA data, showing the ammonia decomposition in (a) an empty quartz tube, and (b) in a quartz tube containing Sm_2Fe_{17} powder. The decomposition of ammonia is seen as pressure increase on the heating curve (heating rate 10°C/min).

reaction. Ammonia decomposition enhances nitrogen uptake, leading to overloaded nitrides.

The additional nitrogen atoms are likely to be accomodated on the hexagon of 18g tetrahedral interstitial sites or on the 3b site at the centre of the hexagon, midway between two rare-earths. The nominal composition with x = 4 corresponds to occupation of three 9e sites and *one* of the 18g sites per formula unit. The possibility of nitrogen atoms on the 3b site may reduce the dumbell distance which is consistant with the observed small decrease in T_c ($\Delta T_c =$ 10K), for a sample with 7.7% unit cell volume expansion.

The occupation of two or more sites per 18g hexagon [6,14] is unlikely as the observed volume expansion does not support nitrogen occupancies larger than four, futhermore, even hydrogen atoms, which are much smaller than nitrogen, occupy no more than two 18g sites per hexagon [15].

The net reaction energy $U_o = 5 \pm 10$ kJ/mole indicates that the occupation of non-9e site is energetically much less favourable than occupancy of the 9e sites where $U_o = -57 \pm 5$ kJ/mole. Putting the value 5 kJ/mole into Eq. (1) we find that under typical nitrogenation conditions (1 bar N_2, 500 °C) there are only 0.005 nitrogen atoms per formula unit on the non-9e sites.

As far as the magnetic properties of the material are concerned, there is not much hope that the performance of the

magnet can be improved with respect to $Sm_2Fe_{17}N_3$. We can expect a reduction in anisotropy energy for x > 3. The anisotropy energy gain, compared to the parent compound Sm_2Fe_{17}, in $Sm_2Fe_{17}N_4$ is only 1/3 of that in $Sm_2Fe_{17}N_3$, if the excess nitrogen atom is centered at the 3b site. Note that this result is qualitatively confirmed by measurements on samples with x < 6 [6,14].

CONCLUSIONS

Non-equilibrium nitrogenation using ammonia, which from a thermodynamic viewpoint is closer to ion implantation than to conventional gas-phase interstitial modification using molecular nitrogen, can be used to produced overloaded nitrides. Nitrogen absorption is an intermediate step during ammonia decomposition and it assures a nitrogen flux through the particle surface. Once in the lattice, nitrogen is subject to bulk diffusion and yields volume expansions up to 8.3 %, corresponding to a nitrogen content of about 4 nitrogen atoms per formula unit. The net reaction energy for the excess nitrogen atoms, which may be situated on distorted 3b sites is $U_o = 5 \pm 10$ kJ/mole.

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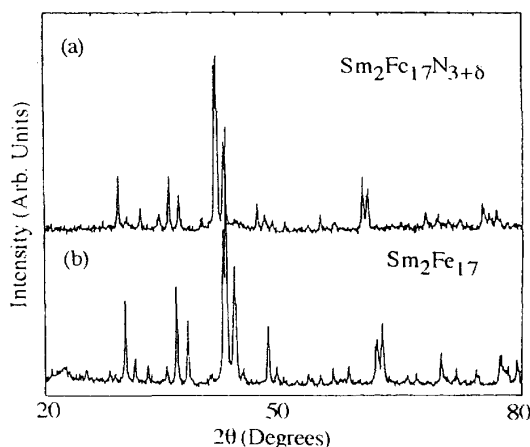[15] O. Isnard *et al.*, Physica B **180&181** (1992) 629-631.

Fig 3. X-ray diffraction pattern of (a) $Sm_2Fe_{17}N_{3+\delta}$ ($\delta \approx 1$) and (b) Sm_2Fe_{17}.

p_A[mbar]	m[mg]	$(\Delta V/V)_{ex}$[%]	$(\Delta V/V)_{th}$[%]
110	9.8	6.7	6.6
192	10.0	6.7	6.8
375	8.9	6.8	7.2
720	10.3	7.4	7.5
1007	12.2	7.7	7.6
1450	13.5	8.3	7.7

Table 2: Volume expansions for different Sm2Fe17N3+δ samples (T = 425 °C, t = 50 min).