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, nitro-
genation of Sm2Fe17 using ammonia yields volume expansions up to 8.3 vol %, which correspond to a composition Sm2Fe17N x with x = 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 Sm2Fe17N x with x > 3 the net reaction energy U0 = 5 ± 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 Sm2Fe17, conducted at 400 - 500 °C in about one bar N2, yields a nitride Sm2Fe17N5.8 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 Th2Zn17 structure [5], when these nitrogenation conditions are used.

On the other hand, some authors report nitrogen contents x = 6 after treatment in ammonia or hydrogen which are incompatible with an exclusive occupation of the Sm2Fe17 9e octahedra. No structural data are yet available, but the observed volume expansion (about 7.5 % in [6]) is little greater than that for Sm2Fe17N3.

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 Sm2Fe17 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]

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

with p0 constant ∼ 100 kbar and U0 the net reaction energy (nitrogen absorption energy). The sign and magnitude of U0 determine whether the nitrogen uptake is high or low. The experimental value U0 = - 57 kJ/mole for Sm2Fe17 [3,4] indicates a high solubility, whereas the value for α-Fe, U0 = 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 (U0 = - 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 intermetallics, 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 cm3), 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 Kα radiation was used for phase analysis and determination of the lattice parameters.

Fig. 2 shows the effect of Sm2Fe17 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 Y2Co17, 400 °C for Y6Fe11Ga3, 350 °C for Fe, Co, and SmCo5, and 300 °C for Y2Fe17.

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

$$\frac{dN_A}{dt} = k_1 p_N \left( \frac{p_{H_2}}{p_A^3} \right)^\alpha - k_2 \left( \frac{p_{H_2}}{p_H^3} \right)^{1-\alpha} \quad (2)$$

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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 gases 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 \( Sm_2Fe17 \). Though preliminary, these results, as well as the corresponding catalytic activities \( k_2 \) [11], indicate a similar catalytic behaviour for all the compounds investigated [12].

To obtain materials with nitrogen contents \( x > 3 \), \( Sm_2Fe17 \) 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 \( Sm_2Fe17N_4 \). 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]

\[
c = \left(1 + \sqrt{\frac{p_H^3}{p_A^3} e^{(U_0-U_A)/kT}}\right)^{-1}
\]

Table 1. Crystallographic data for nitrides of \( Sm_2Fe17 \) produced by gas phase interstitial modification with \( N_2 \) and \( NH_3 \).

<table>
<thead>
<tr>
<th>Compound</th>
<th>( Sm_2Fe17 )</th>
<th>( Sm_2Fe17N_{3.5} )</th>
<th>( Sm_2Fe17N_{3+\delta} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a (\text{Å}) )</td>
<td>8.535</td>
<td>8.719</td>
<td>8.745</td>
</tr>
<tr>
<td>( c (\text{Å}) )</td>
<td>12.434</td>
<td>12.635</td>
<td>12.832</td>
</tr>
<tr>
<td>( \Delta a/a% )</td>
<td>0.0</td>
<td>2.2</td>
<td>2.5</td>
</tr>
<tr>
<td>( \Delta c/c% )</td>
<td>0.0</td>
<td>1.6</td>
<td>3.2</td>
</tr>
<tr>
<td>( v (\text{Å}^3) )</td>
<td>784.4</td>
<td>831.8</td>
<td>849.9</td>
</tr>
<tr>
<td>( \Delta v/v% )</td>
<td>0.0</td>
<td>6.0</td>
<td>8.3</td>
</tr>
</tbody>
</table>

Fig. 2: TPA data, showing the ammonia decomposition in (a) an empty quartz tube, and (b) in a quartz tube containing \( Sm_2Fe17 \) 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 accommodated 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 dumbbell distance which is consistent with the observed small decrease in \( T_c (\Delta T_c = -10 \text{K}) \), 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, furthermore, even hydrogen atoms, which are much smaller than nitrogen, occupy no more than two 18g sites per hexagon \([15]\).

The net reaction energy \( U_0 = 5 \pm 10 \text{kJ/mole} \) indicates that the occupation of non-9e site is energetically much less favourable than occupancy of the 9e sites where \( U_0 = -57 \pm 5 \text{kJ/mole} \). Putting the value 5 kJ/mole into Eq. (1) we find that under typical nitrogenation conditions (1 bar \( \text{N}_2 \), 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 \( \text{Sm}_2\text{Fe}_{17}\text{N}_3 \). We can expect a reduction in anisotropy energy for \( x > 3 \). The anisotropy energy gain, compared to the parent compound \( \text{Sm}_2\text{Fe}_{17} \), in \( \text{Sm}_2\text{Fe}_{17}\text{N}_4 \) is only 1/3 of that in \( \text{Sm}_2\text{Fe}_{17}\text{N}_3 \), 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 \( U_0 = 5 \pm 10 \text{kJ/mole} \).

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REFERENCES


Table 2: Volume expansions for different \( \text{Sm}_2\text{Fe}_{17}\text{N}_3+\delta \) samples (\( T = 425 \text{ °C}, t = 50 \text{ min} \)).