The influence of the kinetics of the hydrogenation of Nd–Fe–B alloys on hydrogen distribution in the alloy phases

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Abstract

We present results of experiments on hydrogenation of Nd₆Fe₁₅B₂ controlled by two parameters: the amount of hydrogen and the rate of feeding the sample with hydrogen at low pressures. By proper combination of these parameters four different schemes for the hydrogenation process were generated: (1) selective hydrogenation of the Nd-rich phase, (2) hydrogenation of the Nd-rich phase followed by diffusion of hydrogen into the Nd₆Fe₁₅B phase, (3) simultaneous partial hydrogenation of both phases, (4) simultaneous complete hydrogenation of both phases. For the first two cases the results of measurements of equilibrium pressure versus hydrogen concentration at room temperature are presented in the form of a $p$–$c$ diagram with three phase regions: (1) Nd₆NdHₓNd₆Fe₁₅B, (2) NdHₓ + Nd₆Fe₁₅B $\rightarrow$ Nd₆Fe₁₅BHₓ, (3) NdHₓ + Nd₆Fe₁₅BHₓ $\rightarrow$ NdHₓ + Nd₆Fe₁₅BHₓ

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1. Introduction

The magnetic Nd–Fe–B alloys have become of much importance since the first permanent magnets were manufactured of them in 1984. These magnets were continuously improved and became a significant part of the permanent magnets market due to their advantageous magnetic properties and relatively low costs of manufacturing. The ferromagnetic phase Nd₆Fe₁₅B ($\phi$) is the carrier of the high saturation magnetisation of the materials. It comprises 85% of the magnet volume and is mostly accompanied by two paramagnetic phases, a Nd-rich one (about 10% vol.) and Nd₁₅Fe₁₅B₄ ($\eta$) (about 2% vol.) [1]. The latter phases produce an optimal microstructure that strongly enhances the magnets coercivity.

Due to hydrogenation, hydrogen atoms penetrate into the interstitial sites of the Nd₆Fe₁₅B lattice and Nd hydride is produced from the Nd-rich phase. The materials become brittle and decrepitate into a powder as a result of the large volume expansion of the lattice of both the matrix and the intergranular phases. This way of powdering known as hydrogen decrepitation (HD) is a well-established stage of manufacturing technologies of sintered [2,3] and bonded [4] Nd–Fe–B magnets. The interstitial hydrogen in the ferromagnetic Nd₆Fe₁₅B phase reduces significantly its anisotropy field $H_A$. That is why desorption of hydrogen is necessary in order to recover the high values of the intrinsic magnetic coercivity of the magnets. It is possible to avoid the hydrogenation of the ferromagnetic phase by selective intergranular HD [5]. This process, in which only the intergranular Nd-rich phase absorbs hydrogen, is carried out at low values of hydrogen pressure compared to the pressures necessary to enforce absorption of hydrogen by the matrix phase. The intergranular hydrogenation occurs also at high pressures at the initial stages of the solid–gas reaction [6] but its selective character is quickly covered up by the hydrogenation of the ferromagnetic phase at the later stages of the process.

As the solubility of hydrogen in Nd drops with pressure [7], the way of the hydrogen diffusion into the alloy may change. Indeed, it will be shown in this work that simultaneous hydrogenation of the Nd-rich phase and the $\phi$ phase occurs if one wishes to limit considerably the
sample feeding with hydrogen or to slow down the reaction kinetics. We show also the influence of the reaction kinetics on the proportions of phases present in material.

2. Experimental

The experiments were performed on irregular and elongated pieces of as-cast ingots manufactured by John-son Matthey & Co. The composition of this material was nominally Nd_{16}Fe_{75.6}B_{8.2}.

The kinetics of hydrogen diffusion was measured by use of a tensometric analyser [8]. The alloy specimen of about 1 g was placed in a reaction chamber of the analyser, where the specimen was heated in vacuum at a temperature of 300°C for about 1 h to remove the absorbed gases and to relieve the strain in the sample. The hydrogenation process was performed after cooling the sample in the reaction space of a known volume filled with dry hydrogen at various pressures.

At low pressures, all the hydrogen is absorbed by the sample and the final pressure in the chamber is nearly zero. However, when the pressure starts to be higher than a certain pressure $p_B$, only a portion of hydrogen is absorbed from the chamber. The $p_B$ separates two pressure regimes: $p<p_B$ and $p>p_B$, i.e., with deficiency and excess of hydrogen respectively. The gas can be introduced into the chamber in two ways:

1. by expansion with a rate $v_B$ much larger than the rate of gas diffusion into the sample,
2. by exuding with a rate $v_x$ 20–50 times slower than the rate of the gas absorption by the sample.

Consequently there were four combinations of pressure and reaction rate applied in this work: $(p_{D1}, v_5)$; $(p_{D2}, v_5)$; $(p_{D1}, v_6)$ and $(p_{D2}, v_6)$.

The mass gain of the sample during the reaction was estimated from the hydrogen pressure changes with an accuracy of 20 ppm, whereas the entire relative mass increase was about 0.5%. The temperature of the sample was monitored during the experiment. The highest increase of the sample temperature was about 30 K and it did not cause noticeable rise of hydrogen pressure.

The structures of the samples hydrogenated at the different rates under the various pressures were investigated by X-ray diffraction. The Rietveld analysis of the diffraction patterns [9] and the insertion scheme of hydrogen in Nd_{14}Fe_{14}B lattice [10] were used to find the hydrogen content in the matrix phase. The progress of hydrogenation of the Nd-rich phase was deduced from analysis of X-ray patterns and oxidation curves of the hydrogenated samples [11].

3. Results and discussion

3.1. Hydrogen distribution in the alloy phases

Changes of the phase relations in the investigated Nd–Fe–B alloy caused by the different runs of its reactions with hydrogen are sketched in Fig. 1. This figure has been divided into four parts that correspond to four combinations of the initial hydrogen pressures and the reaction rates as described above. The process runs and the resultant phase relations are imaged in each part. The images summarise graphically the results of the analyses of both the X-ray diffraction patterns and the oxidation curves of the hydrogenated samples. Fig. 1b and Fig. 1d image hydrogenation runs known from literature [6,12–14]. Fig. 1a and Fig. 1c display runs performed by the authors at significantly lowered rates. Fig. 1a and 1b can be conceived as images of the initial stages of the reactions described in parts 1c and 1d, respectively.

The reaction speed in the typical hydrogenation run (Fig. 1b, 1d) is limited only by the rate of the gas diffusion into the sample. When the reaction proceeds in deficiency of hydrogen (Fig. 1b) only a part of the Nd transforms into neodymium hydride NdH, as it follows from the diffraction pattern displayed in Fig. 2d. That pattern includes peaks of Nd-rich phase, NdH, and Nd_{14}Fe_{14}B. Hence the Nd-rich phase coexists with NdH, and the pure phase $\phi$ in the sample.

When the reaction proceeds rapidly in excess of hydrogen at 750 hPa, the (004) peak of Nd disappears from the diffraction pattern and the (111) peak of NdH appears (Fig. 2e). The $\phi$ phase pattern shifts toward lower scattering angles, which means an increase of the $\phi$ phase cell parameters. It is a result of incorporation of the hydrogen atoms into the tetrahedral interstices in the Nd_{14}Fe_{14}B lattice and formation of Nd_{14}Fe_{14}BH_{1.21} [10]. Summarising, the whole intergranular Nd-rich phase transforms to NdH, hydrogen atoms diffuse throughout the $\phi$ grains and a phase Nd_{14}Fe_{14}BH_{1.21} is formed.

The phase composition changes when lowering the hydrogenation rate. Peaks of Nd_{14}Fe_{14}BH_{1.25} are visible close to the $\phi$ phase peaks (see Fig. 2b), which indicates only partial hydrogenation of this phase. A similar conclusion on the partial hydrogenation of the Nd-rich phase can be derived from a comparison of the oxidation curves measured on virgin, partially and fully hydrogenated samples, shown in Fig. 3. The weight gains indicated by these curves result from the transformation of Nd-rich phase and/or NdH$_3$ into Nd(OH)$_3$ [1,15]. As it follows from the comparison of curves (a) and (d) in Fig. 3 the oxidation rate of NdH$_3$ is much higher than that of the Nd-rich phase. The oxidation rate of the partially hydrogenated sample (Fig. 3c) is intermediate between (a) and (d). It means that in this case oxidation of both Nd-rich phase and NdH$_3$ contribute to the observed weight gain.
Fig. 1. Phase relations in the Nd–Fe–B alloy during the hydrogenation. (a) Slow reaction in deficiency of hydrogen, (b) rapid reaction in deficiency of hydrogen, (c) slow reaction in excess of hydrogen, (d) rapid reaction in excess of hydrogen.

Fig. 2. Diffraction patterns of the Nd₆Fe₇₋ₓBₓ samples with different hydrogen content: (a) rapidly hydrogenated to saturation, (b) slowly hydrogenated to saturation, (c) slowly, partially hydrogenated, (d) virgin.

Fig. 3. Oxidation curves of the Nd₆Fe₇₋ₓBₓ samples with different hydrogen content: (a) rapidly hydrogenated to saturation, (b) slowly hydrogenated to saturation, (c) slowly, partially hydrogenated, (d) virgin.

The analysis of the X-ray patterns and the oxidation curves leads to the image of diffusion displayed in Fig. 1a, in which hydrogen atoms locate simultaneously in some areas of both the Nd-rich and the Φ phase, most
excess of hydrogen (Fig. 1c). Since the X-ray diffraction pattern contains only peaks of the hydrogenated $\phi$ phase ($\text{Nd}_3\text{Fe}_{14}\text{BH}_{19.4}$) (Fig. 2c) the conclusion as to full hydrogenation of the Nd-rich phase follows from comparison of the oxidation curves (a) and (b) in Fig. 3. The oxidation curve (b) of the sample fully hydrogenated at low rate is almost the same like the curve (a) of the fully hydrogenated sample at high rate.

3.2. Metastable $p-c$ diagram

The hydrogenation curves measured in this work are shown in Fig. 4. The hydrogenation curves (a)–(f) display the weight gains obtained via the rapid process caused by an hydrogen gas expansion at the rate $v$. The curves (g)–(h) were recorded for the much slower reaction with hydrogen exuding at the rate $v$. The curves (a)–(f) can be well described on the basis of diffusion theory and a decrepitation model presented previously [8].

Since the maximum total mass gain $\delta_m$ read out from the curves mentioned above is only 0.45% the total mass gains are within good approximation equal to equilibrium concentrations $c_{\text{equ}}$ of the hydrogen absorbed by the samples. These concentrations together with the equilibrium pressures $p_{\text{equ}}$ are arranged in the $p-c$ diagram at room temperature shown in Fig. 5. It is to be recalled that the diagram was constructed only for the rapid type of hydrogenation reactions.

Three regions can be distinguished in the diagram. The equilibrium pressure is constant in the first two regions and it rises rapidly in the third one. The first region corresponds to the situation displayed in the Fig. 1b with only the Nd-rich phase absorbing hydrogen. Since the solubility of the hydrogen in Nd is in the range 2.7–3 H/Nd [1,14,16,17] and the content of the Nd-rich phase in the alloy is about 12% [1], the equilibrium concentration is between 0.22 and 0.25%. The latter uncertainty is indicated by the shaded area at the border between regions I and II. In region II, hydrogen starts to penetrate the $\phi$ phase. We have no X-ray evidence for this region but we can speculate what happens there from the hydrogenation degree of Nd$_3$Fe$_{14}$BH$_{19.4}$ for the regions I and III displayed in Fig. 6. Indeed the line $x_{\text{H}}(c_{\text{equ}})$ extrapolated from region III to II crosses the abscissa at $c_{\text{equ}} = 0.21$. Most likely region II corresponds to the situation displayed as stage 2 in Fig. 1(d). Region III corresponds to the situation displayed in Fig. 1(d).

The net gas model [18] was applied to fit the absorption curve in region III in Fig. 5. Both phases reacting with hydrogen, i.e. the Nd-rich and the $\phi$ phase, were regarded as one ‘average phase’ for the fitting purposes. The highest concentration of hydrogen in the sample and the formation energy of ‘average hydride’ of 0.502(1)% and 47.8(2) kJ/mol, respectively, were calculated with the model.
but the physics of the hydrogenation process is still poorly understood.

References