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Hydrogenation process of Nd–Dy–Fe–B alloy

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The influence of the alloy granulation grade, temperature and surface oxidation on the kinetics and the course of the fracture processes during the hydrogenation of $Nd_{16-x}Dy_xFe_{76}B_8$ ($x = 0$–3) alloy was studied. The average particle sizes of the alloy were 1 mm, 5 mm and 3 cm and the temperature range between 20 and 200 °C. Pre-oxidation times of the alloy were 0, 5, 10, 20, 30, 120 and 1200 min. No influence of the alloy composition on the kinetics and fracture processes during the hydrogenation was observed. An influence of the granulation grade of the alloy particles on the reaction rate was established and an influence of increasing temperature on the shortening of the incubation period was observed. It was also shown that the incubation time is influenced by surface oxidation. A tentative model of the hydrogenation-decrepitation process is suggested.

1. Introduction

One of the processes used for the preparation of Nd–Fe–B alloy is arc-melting of the basic alloys [1]. Nd–Fe–B alloy exhibits extremely high toughness due to the presence of free iron and neodymium. Therefore, the preparation of the powder for the production of sintered magnets by the conventional crushing and milling process is difficult. This difficulty can be avoided by using the so-called hydrogenation-decrepitation process which is an alternative process for powder preparation in the processing of sintered Nd–Fe–B magnets [2, 3]. When used in conjunction with conventional milling techniques, this method is most effective. The hydrogenation-decrepitation process works at room temperature and a hydrogen pressure of 1 bar [4, 5]. It is known that under these conditions hydrogen absorption takes place in two stages. First, the Nd-rich phase reacts on the grain boundaries, and secondly this reaction promotes the hydrogenation of the $Nd_2Fe_{14}B$ (T_1) phase [5]. The hydrogenated Nd-rich phase contains 13.9 hydrogen atoms per mole and the composition of the matrix phase is $Nd_2Fe_{14}BH_{2.7}$ [4]. The hydrogenation process is influenced by surface oxidation of the alloy [6], the hydrogen pressure [2] and the temperature [7].

The purpose of our work was to investigate the influence of the granulation grade of Nd–Dy–Fe–B alloy, the hydrogenation temperature, and the surface oxidation on the progress of hydrogenation of the basic alloy. The hydrogenation-decrepitation process during the reaction was followed.

2. Experimental procedure

Samples were prepared by arc-melting of basic alloys in a pure Ar atmosphere. Basic alloys were Nd–Fe, Dy–Fe and Fe–B (Treibacher Chemische Werke AG) and Fe (Koch-Light 99.9%). The alloy composition was $Nd_{16-x}Dy_xFe_{76}B_8$ ($x = 0$–3). In addition, a commercial alloy with the composition $Nd_{14}Dy_2Fe_{76}B_8$ (Treibacher Chemische Werke AG) was used. The oxygen content in the basic alloys was about 0.03 wt %. Most of the experimental work was performed in glove-boxes in a high-purity Ar atmosphere. Samples for further experiments were prepared by crushing the alloy to different granulations in the glove-boxes. The average particle sizes were: samples A 1 mm, samples B 5 mm and sample C about 3 cm.

Some of the samples with granulation B were exposed to atmospheric conditions at room temperature and 40% relative humidity for a period of 5, 10, 20, 30, 120 or 1200 min.

Samples were hydrogenated in a reactor with about 5 l volume at 1 bar in the temperature range from 20 to 200 °C. Hydrogen used was of high-grade purity additionally cleaned through molecular sieves (Linde X13) at the temperature of liquid nitrogen. The hydrogenation process was followed by measuring the pressure and the temperature in the reactor.

The microstructures were analysed by means of optical microscopy and scanning electron microscopy (SEM) (Leitz Amray 1600 T) equipped with an energy-dispersive X-ray (EDX) system (γ PGT). The oxygen content was determined by a Ströhlein oxygen analyser.

3. Results and discussion

Fig. 1 shows a typical microstructure of the Nd–Fe–B alloy with columnar grain morphology after melting in the arc furnace. This microstructure is also known as the Neomax structure [1]. Solidification takes place very rapidly from overheated melt and with a sharp temperature gradient. Consequently, column-shaped

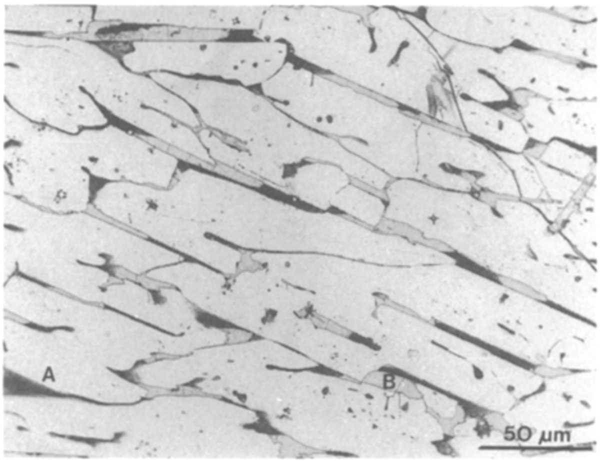

Figure 1 Microstructure of melted Fe–Nd–B alloy (A = $Nd_2Fe_{14}B$ matrix phase, B = Nd-rich phase).

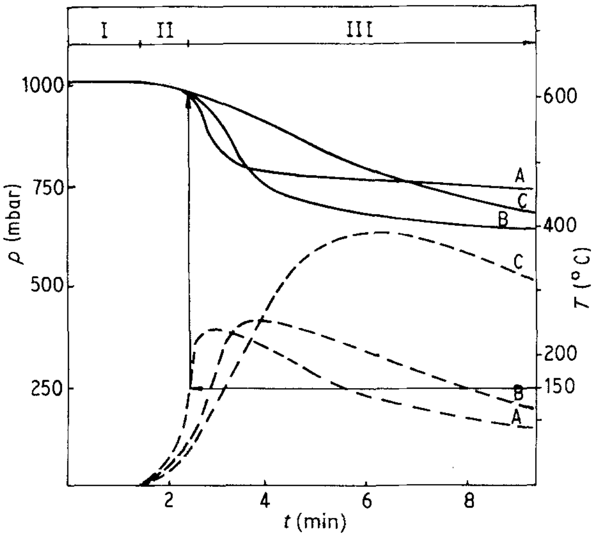

Figure 3 (——) H_2 pressure and (– – –) temperature of Fe–Nd–B alloy versus hydrogenation period.

grains of hard magnetic $Nd_2Fe_{14}B$ matrix phase with Nd-rich grain boundary phase are formed. Due to the unstable solidification conditions, dendrites of α-Fe also occur.

A two-phase structure, as observed in the hydrogenated sample (Fig. 4) was not distinguished in SEM micrographs of non-hydrogenated alloy (Fig. 2). From the irregular shapes with sharp features and a smooth surface we can deduce the brittle nature of the fracture, without preferential orientation, mainly through the brittle matrix phase.

Hydrogen pressure changes during the reaction with the alloy, as well as the specimen temperature. These changes as a function of the alloy granulation are shown in Fig. 3. Temperature changes were measured directly during the reaction. The weight of the samples was about 30 g in the case of A and B granulation and about 100 g in the case of C granulation. All samples used in the experiment were prepared in a very pure atmosphere (Ar 5.9) so that the oxygen pick-up of the alloy was negligible. From the pressure and temperature changes during the hydrogenation process, one can conclude that the granulation of the alloy has no influence on the incubation period, t_i (Fig. 3, part I). On the other hand, the granulation of the alloy influences the rate of hydrogen absorption which was defined by the pressure changes with time during the experiment. This rate increases with increased surface of the alloy granulate. The reaction rate of the alloy with hydrogen does not depend on the amount of Dy in the $Nd_{16-x}Dy_xFe_{76}B_8$ ($x = 0$–3) alloy, and we used $Nd_{14}Dy_2Fe_{76}B_8$ alloy for further work.

The hydrogenation process of Nd–Fe–B alloy is an exothermic process [2] which takes place in two stages due to the alloy composition. At room temperature, the Nd-rich phase is hydrogenated first [3] (Fig. 3, part II), and after the heating of alloy to about 150 °C, the T_1 phase also starts to react (Fig. 3, part III) because of the exothermic reaction of Nd-rich phase with hydrogen [4]. After the incubation period the hydrogenation of sample A is faster than the hydrogenation of samples B and C, due to its higher surface/volume ratio. Heat transfer from the surface of large pieces is faster and the hydrogenation reaction is retarded.

Figs 4 and 5 show the fractures of partially hydrogenated alloy (30 s after the incubation period). Hydrogenation was interrupted by evacuation of the hydrogen from the reactor in 5 s. The morphological changes in the intermatrix Nd-rich phase, resulting

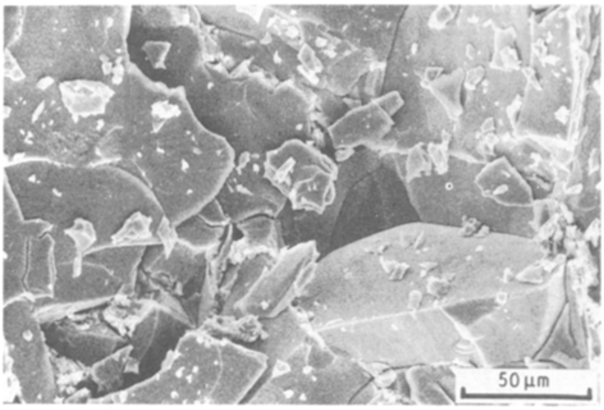

Figure 2 SEM image of fractured melted Fe–Nd–B alloy.

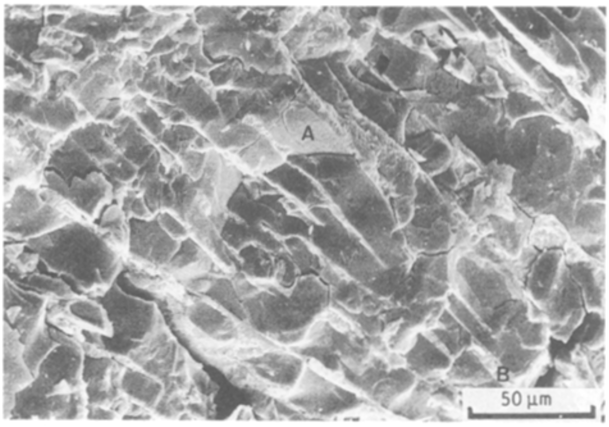

Figure 4 SEM image of partially hydrogenated Fe–Nd–B alloy (A = matrix, B = grain boundary phase).

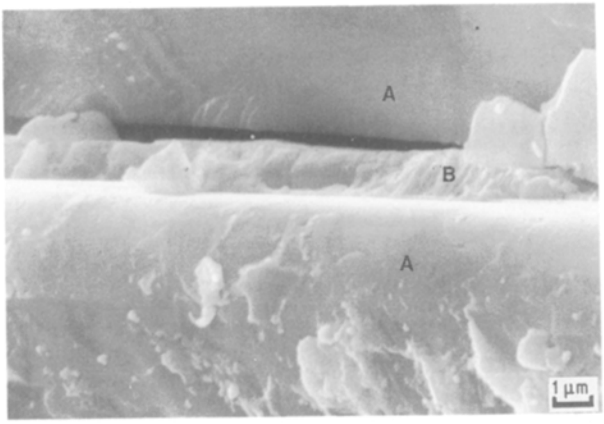

Figure 5 SEM image of partially hydrogenated Fe–Nd–B alloy: detail from grain boundary (A = matrix, B = grain boundary phase).

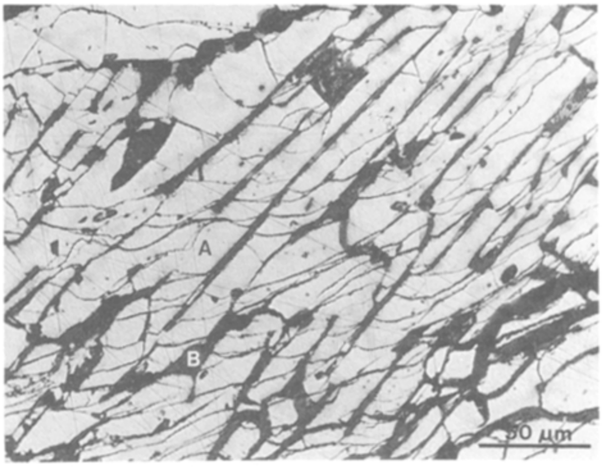

Figure 7 Microstructure of hydrogenated alloy (A = matrix, B = intermatrix space).

from the positive volume changes, are evident. The hydrogenated Nd-rich phase becomes brittle, but still remains in the intermatrix spaces, so that the columnar grains of $Nd_2Fe_{14}B$ are not separated yet. Cracks in the matrix phase were also not observed at this stage.

In Fig. 5, a detail from the grain boundary of a partially hydrogenated sample is shown. EDX analysis showed the presence of both matrix $Nd_2Fe_{14}B$ phase (A) and the grain-boundary Nd-rich phase (B). At this stage of hydrogenation, intergranular fracture started. A crack between the matrix phase and the grain boundary phase results from the volume changes of Nd hydride. Preferential hydrogenation of the Nd-rich phase causes shear stresses and as a consequence intercrystal fracture. Through the brittle Nd hydride, which falls out from the intermatrix spaces, hydrogen can easily penetrate into the matrix phase. Matrix hydrogenation is induced by the heating process due to the exothermic reaction of Nd-rich phase hydrogenation.

Fig. 6 shows a fully hydrogenated alloy. The grain boundary phase fell out and the matrix grains have cracked and spalled off at their edges. This effect is supposed to be the consequence of local overheating and preferential hydrogenation of the matrix phase in those spots. Scaling off of the T_1 phase (the "onion skin effect") [8] is the consequence of internal stresses between the hydrogenated and non-hydrogenated regions. Fig. 7 shows the microstructure of a completely hydrogenated alloy. The microstructure morphology is similar to that presented in Fig. 1. However, the matrix grains are separated and transgranularly fractured. Cracks from one grain to another show that transgranular fracture is caused also by the bilateral strain of Nd hydride, due to the positive volume change.

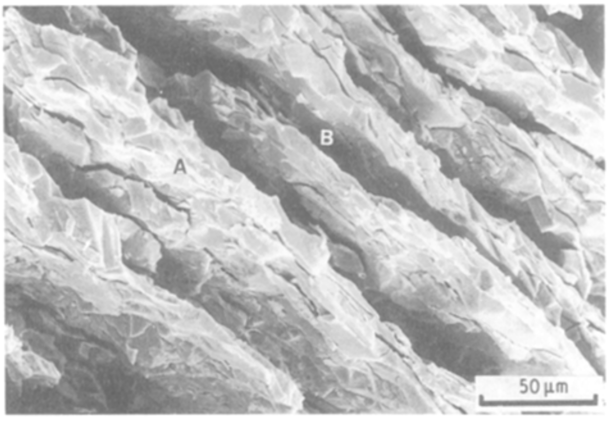

Figure 6 SEM image of hydrogenated Fe–Nd–B alloy (A = matrix, B = intermatrix space).

When lumps of Nd–Dy–Fe–B alloy were heated to a given temperature, the incubation time decreased and the maximum rate of hydrogen usage for the reaction increased. The results are presented in Table I.

The influence of alloy oxidation on the hydrogenation process was studied as well. Alloy lumps were exposed to atmospheric conditions for a certain period of time. Afterwards, the lumps were hydrogenated under the same conditions as the samples in our previous work. The results obtained showed the same course of the hydrogenation process as in the previous experiments, only the incubation time was longer. The incubation time as a function of the time of exposure, t_e, is shown in Fig. 8.

According to the diagram in Fig. 8, the incubation time increases as a function of the exposure of the alloy lumps to oxidation conditions. At the beginning a thin layer of Nd_2O_3 is formed [9]. The results of the analysis of oxygen content in the basic alloy and in alloy exposed to the air atmosphere did not differ significantly. The amount of oxygen was 0.03 ± 0.005 wt %.

TABLE I Incubation time and maximum reaction rate of hydrogen used for the hydrogenation of $Nd_{14}Dy_2Fe_{76}B_8$ alloy with granulation 5 mm as a function of the temperature

Temperature (°C)	Incubation time (s)	Maximum reaction rate (mbar s^{-1})
20	54	15
50	32	17
110	8	25
200	4	35

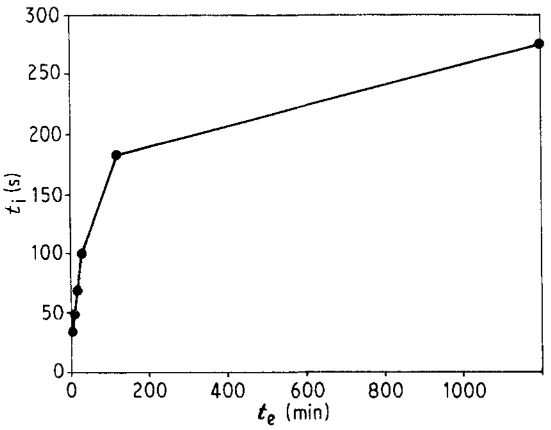

Figure 8 Incubation time, t_i, as a function of the exposure time, t_e.

On the basis of the results obtained, we can conclude that the oxide layer on the alloy surface, which was formed during exposure to atmospheric conditions, has a significant influence on the hydrogenation rate. It is known that the surface oxidation of Nd–Fe–B alloy under an atmospheric environment is very rapid and that a thin layer of Nd oxide and α-Fe precipitates is formed in the process [10]. Our observations show that the oxide layer acts as a barrier for hydrogen diffusion to the Nd–Fe–B alloy, as has already been noticed [9]. We can presume that the incubation period is the time necessary for hydrogen diffusion through the oxide layer to the interface of non-oxidized alloy after the hydrogenation reaction is started.

The formation of the oxide layer and the diffusion of hydrogen through this layer, according to the literature [11], follows the parabolic law. On the basis of the results obtained, we presume that the dependence between exposure and incubation time is linear only in the first part of the diagram. By increasing the exposure time Nd_2O_3 most probably reacts with the air humidity, and this hydrated oxide $Nd(OH)_3$ [12] retards further corrosion.

Preheating of the oxidized alloy promotes the hydrogen diffusion process. An Arrhenius plot of incubation time versus temperature is shown in Fig. 9. Assuming that the incubation period is the time required for hydrogen diffusion and that the layer thickness is constant, we calculated from the slope of the curve the activation energy for hydrogen diffusion through the oxide layer, which is (16.6 ± 1.5) kJ mol^{-1}.

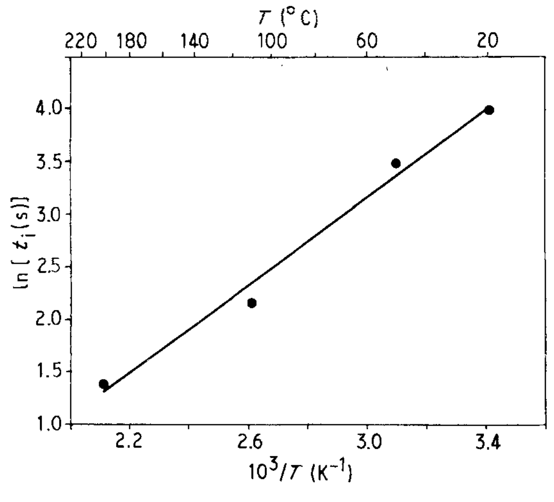

Figure 9 Arrhenius plot of $\ln t_i$ versus $1/T$.

A tentative model for the hydrogenation of Nd–Fe–B alloy is presented in Fig. 10. The incubation time t_i is needed for hydrogen diffusion through the oxide layer. When the hydrogen reaches the interface, the hydrogenation process of the Nd–Fe–B alloy starts (Fig. 10b). Positive volume changes of hydrogenated Nd-rich phase cause cracks between the grains of T_1 matrix phase. Hydrogen easily penetrates through those cracks into the alloy itself. Due to the exothermic reaction of Nd-rich phase with hydrogen, the T_1 phase is heated to 150 °C and the hydrogenation of the matrix phase starts as well (Fig. 10c). The reaction is promoted from the outside to the inside of the alloy lump, which accounts for the "onion skin" appearance.

4. Conclusions

The hydrogenation of $Nd_{16-x}Dy_xFe_{76}B_8$ alloy with different granulation was studied under the experi-

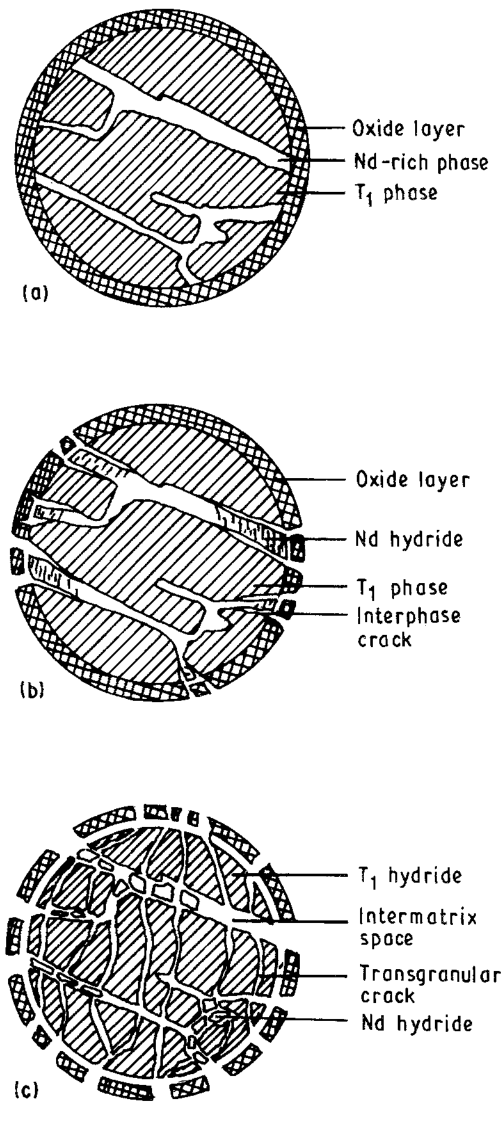

Figure 10 Hydrogenation of Nd–Fe–B alloy (schematically): (a) oxidation, (b) hydrogenation of Nd-rich phase, (c) hydrogenation of the matrix T_1 phase.

mental conditions of 1 bar pressure, initial temperature between 20 and 200 °C and different times of surface oxidation. On the basis of the results obtained we concluded that the course of the hydrogenation reaction is divided into the following two processes:

1. Hydrogen diffusion through the diffusion barrier, which is a thin oxide layer on the alloy surface. The time necessary for this process is the incubation time, which increases with the alloy's exposure to the atmospheric conditions.
2. Reaction of the hydrogen with the alloy itself. At room temperature, this is a two-stage process: hydrogenation of the Nd-rich phase in the first step and the hydrogenation of T_1 phase in the second. Above 150 °C, the hydrogenation of those two phases is simultaneous.

The surface oxidation process under atmospheric conditions is very rapid, but in the case of large pieces (ingots), the oxide layer does not influence the reaction course.

Acknowledgement

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