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Further studies of hydrogenation, disproportionation, desorption and recombination processes in a $Nd_5Fe_2B_6$ boride

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Abstract

The hydrogen absorption and desorption characteristics of, $Nd_5Fe_2B_6$ were studied in this work, particularly at high temperatures where the hydrogenation, disproportionation, desorption and recombination (HDDR) process takes place. Two events of hydrogen absorption were observed for the ρ-$Nd_5Fe_2B_6$ compound when heated in hydrogen ($p(H_2)=1$ bar). In the lower temperature region (from 335 to 745°C) the formation of an insertion type rhombohedral hydride $Nd_5Fe_2B_6H_x$ was observed, leading to a rather small anisotropic lattice expansion (up to 2.63 vol%) in the [001] direction. At temperatures higher than 745°C, a disproportionation of this hydride occurs resulting in the formation of NdH_{3-x}, NdB_4 and η-$Nd_{1.1}Fe_4B_4$. The recombination of the three phase mixture proceeds readily on heating in vacuum, employing conditions similar to those applied in the HDDR route for Φ-$Nd_2Fe_{14}B$.

Keywords: HDDR process; Hydrides; Neodymium; Borides

1. Introduction

The hydrogenation, disproportionation desorption and recombination (HDDR) process is of major interest for the production of bonded and hot pressed Nd–Fe–B type magnets [1,2]. Three borides are formed in the Nd–Fe–B system, namely Φ-phase which is the major constituent of, for instance, the $Nd_{16}Fe_{76}B_8$ alloy used for permanent magnet materials. The disproportionation of the Φ-phase occurs at elevated temperatures ($T=650$°C for $p(H_2)=1$ bar) and this results in the formation of a very finely divided mixture of $NdH_{2\pm x}$, α-Fe and Fe_2B within the confines of the original grain structure [3]. On desorbing hydrogen the intimate mixture of iron, ferro-boron and neodymium becomes thermodynamically unstable and reverts to the more stable $Nd_2Fe_{14}B$ phase, now with a submicron grain size [1,2]. The η-boride is also formed in as cast $Nd_{16}Fe_{76}B_8$ alloys [4,5] and it is important to understand its HDDR characteristics under similar experimental conditions to those used for the Φ-compound. In contrast to the Φ-compound (5.9 at.% B), both the η- and ρ-borides are boron rich 44.0 and 46.1 at.% B respectively. However, these two borides are very different in terms of their rare earth content (12.1 and 38.5 at.% Nd respectively) and crystal structures, which results in significant differences in their hydrogenation behaviours. The η-boride does not react with hydrogen up to 500°C but at high temperatures above 700°C, it absorbed hydrogen and a disproportionation type reaction occurs. This reaction results in the formation of $NdH_{2\pm x}$ binary hydride, Fe_2B boride and a non identified boron-rich product [6]. An experimentally observed oxidation of boron near the grain boundaries in the decomposed material could explain the non-reversible character of the decomposition of the $Nd_{1.1}Fe_4B_4$ boride which is not recovered completely on vacuum heating [6].

A very fast, near room temperature hydrogenation of the ρ-boride was observed for as cast $Pr_5Fe_2B_6$ and $Nd_5Fe_2B_6$ ρ-borides [7]. A decomposition of the hydrided compounds occurred when heated in hydrogen pressures of up to 5 bars and temperatures above 700°C, resulting in the formation of rare earth hydrides $RH_{2\pm x}$ and two borides, namely $R_{1.1}Fe_4B_4$ and R_2B_5 (R=Nd,Pr). A reverse recombination reaction occurred in vacuum producing the initial ρ-borides [7].

In the present work, the aim was to provide more information on the HDDR processes in a single phase $Nd_5Fe_2B_6$ boride by application of hydrogen absorption

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and desorption measurements, X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. Experimental details

The arc-cast $Nd_5Fe_2B_6$ boride was annealed at $T=700°C$ for 4 weeks in order to obtain single phase material. Temperature pressure analysis (TPA) and hydrogen differential thermal analysis (DTA) (HDTA) techniques were used to characterise the hydrogen absorption and desorption properties of the $Nd_5Fe_2B_6$ boride. Experimental details of these methods have been published previously [7]. X-ray diffraction studies were performed using a Phillips PW 1012/10 diffractometer with Cu-K_α radiation. The microstructural evolution in the different stages of the HDDR processes has been studied by SEM on a JEOL 6300 and high resolution SEM (HRSEM-Hitachi S-4000 FE).

3. Results and discussion

SEM investigations of annealed ingot showed that single phase material was obtained after homogenisation. XRD patterns (Fig. 1a) were indexed on the basis of a rhombohedral cell characteristic of the ρ-type boride [8,9] with unit cell parameters of $a=5.4614(5)$ Å and $c=24.2472(3)$ Å. These parameters are in good agreement with the literature data ($a=5.469(1)$ Å; $c=24.02(2)$ Å [8] and $a=5.463$ Å; $c=24.281$ Å [9]). There was no evidence of additional phases. TPA investigations indicated a rather low hydrogenation activity of the boride. On heating in hydrogen (initial pressure 1 bar; heating 5°C min^{-1}) hydrogen absorption started only at a temperature of 335°C (see Fig. 2). On further heating, hydrogenation proceeded up to 470°C when it was followed by a desorption stage. The first absorption was associated with the formation of a saturated $Nd_5Fe_2B_6H_{8.6}$ hydride. XRD results (Fig. 1b) indicated that this hydride was an insertion type derivative of the initial boride. The unit cell parameters increased on hydrogenation to $a=5.455(8)$ Å and $c=24.97(8)$Å, with no changes in the initial rhombohedral symmetry of the ρ-boride. A rather small volume increase of 2.63% was the result of the lattice expansion in the [001] direction only ($\Delta c/c=3.96\%$) since the a-parameter does not change significantly on hydrogenation. ($\Delta a/a=-0.12\%$). At higher temperatures, a partial hydrogen desorption proceeded up to 745°C. At this point, the second absorption was observed, with the highest absorption rate at 825°C (the sample was heated to 850°C). On cooling, a slope change in the pressure–temperature curve at 800°C indicated a significant decrease in the rate of hydrogenation below that point. After cooling to room temperature, X-ray diffraction examination showed that this sample was a polyphase mixture (Fig. 1c). The main constituent was found to be a $Nd_5Fe_2B_6H_x$ hydride with a significantly decreased c-parameter and volume of the unit cell ($a=5.462(2)$ Å; $c=24.774(7)$ Å; $\Delta V/V=2.09\%$) compared with those of the saturated hydride. Such a decrease is the result of a partial hydrogen desorption from the sample on heating. At the same time, strong peaks of NdH_{3-x} were observed ($a=5.440(2)$ Å) showing that the decomposition of the boride which had started to occur above 745°C was not complete in the course of the experiment. The degree of disproportionation of the ρ-boride depends on temperature, hydrogen pressure and exposure time. For the sample heated in the HDTA rig up to 800°C (1 bar H_2) with a rate of 5°C min^{-1} and then furnace cooled to room temperature, a decrease in both temperature and time of a high temperature treatment in comparison with those applied in the TPA experiment, results in a much smaller degree of disproportionation. Only weak peaks of neodymium hydride are identified in addition to the main peaks of $Nd_5Fe_2B_6$ hydride (see Fig. 1d).

Hydrogen was then introduced into the reaction chamber at 825°C to a pressure of 1.5 bar. This treatment (Solid-HDDR) allowed disproportionation and subsequent recombination under vacuum to occur without decrepitation of the bulk material [10]. Such a procedure facilitates specimen preparation for electron microscopy and allows the HDDR reaction to be monitored by, for instance, electrical resistance and dilatometric measurements. The change in pressure was monitored and after reaching a steady value after 24 h, the sample was quenched to room temperature. XRD investigation confirmed that, after this treatment, the boride was completely disproportionated (Fig. 1e). Three components were identified in the reaction mixture, namely NdH_{3-x}, the binary compound NdB_4 and the ternary η-boride $Nd_{1.1}Fe_4B_4$. The lattice parameters of these compounds are in very good agreement with the reference data (see Table 1 for details). A possible disproportionation reaction scheme of the process is presented below:

$$Nd_5Fe_2B_6 + (5.175 - 1.725x)H_2 \rightarrow 3.45NdH_{3-x} + NdB_4 + 0.5Nd_{1.1}Fe_4B_4$$

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The main constituent of the disproportionated mixture was neodymium hydride (57.8 vol%). The two other constituents were present in nearly equal proportions, namely, 21.7 vol% for NdB_4 and 20.5 vol% for $Nd_{1.1}Fe_4B_4$. This process was not accompanied by decrepitation of the material. SEM (Fig. 3a) and HRSEM studies (Fig. 3b) of the disproportionated material showed that the appearance of the multiphase mixture differs from those reported for the disproportionated η- [6] and Φ-borides [3]. More detailed studies need to be carried out in order to identify the phases seen in the backscattered electron micrographs. However, the amount of NdH_{3-x} was significantly higher than that observed in the dis-

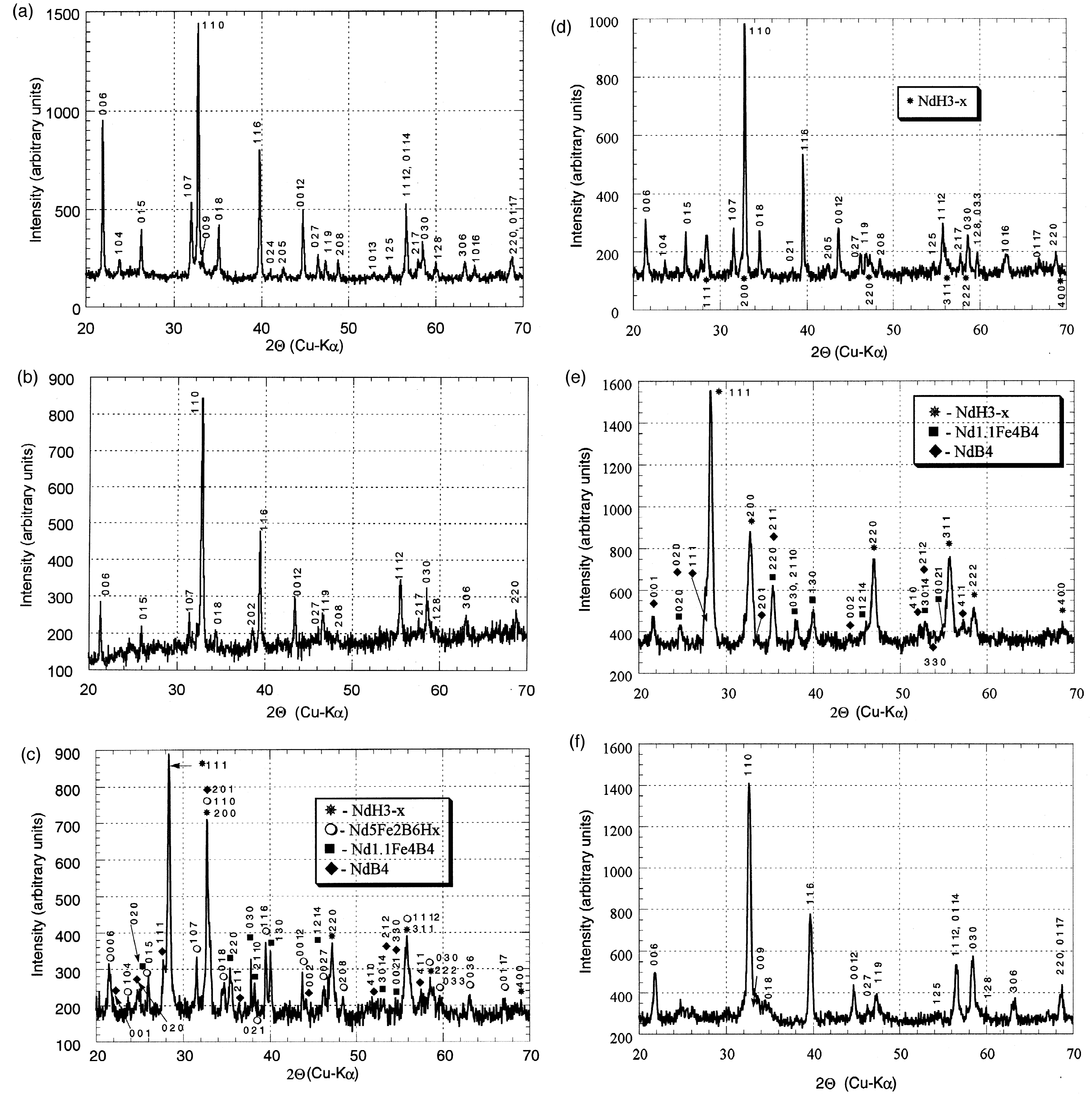

Fig. 1. X-ray diffraction patterns of $Nd_5Fe_2B_6$ ρ-boride based materials: (a) initial $Nd_5Fe_2B_6$ (annealed at 700°C for 4 weeks); (b) saturated (1 bar H_2) $Nd_5Fe_2B_6H_{8.6}$ hydride; (c) partially decomposed (TPA rig, 1 bar H_2, heating to 850°C at a rate of 5 C° min^{-1}); (d) partially decomposed (HDTA rig, 1 bar H_2, heating to 800°C with a rate of 5 C° min^{-1}); (e) completely decomposed (HDTA rig, 1.5 bar H_2, decomposition proceeded at 825°C for 24 h); (f) recombined in vacuum after HDDR process.

proportionated $Nd_2Fe_{14}B$ or $Nd_{1.1}Fe_4B_4$, in good agreement with the above description of the disproportionation reaction.

On heating the decomposed material in vacuum, hydrogen desorption began at 210°C and was completed at around 840°C (Fig. 4). Two events of hydrogen evolution can be seen in the pressure–temperature curve with peaks at 330°C and 730°C. As expected, the hydrogen desorption behaviour of the disproportionated $Nd_5Fe_2B_6$ boride is similar to that of neodymium hydride (see [11] for reference data). This similarity is a result of essentially the same hydride constituents in both cases. The main, high temperature, desorption effect, is observed at 720°C and slight differences are observed for the low temperature desorption events [11]. In the case of the Nd binary hydride, two desorption events are separated by a tempera-

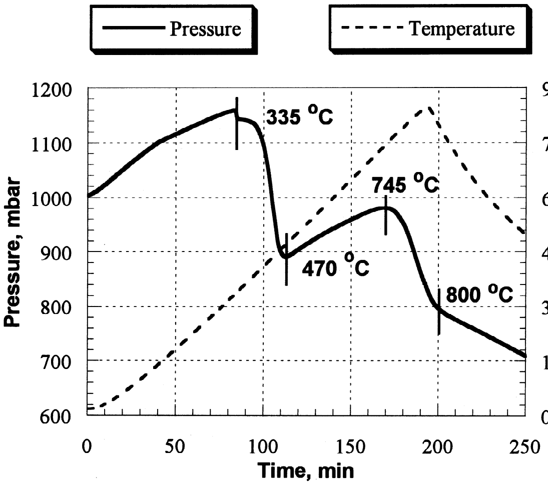

Fig. 2. TPA traces of hydrogen absorption by $Nd_5Fe_2B_6$ boride.

ture range where there is no significant hydrogen desorption [11]. In contrast, a continuous rise of hydrogen desorption pressure on heating was found for the disproportionated $Nd_5Fe_2B_6H_x$ material. A similar behaviour was observed previously for the $Pr_5Fe_2B_6H_x$ decomposed hydride [7] where it was suggested that such a behaviour is the result of gradual recombination starting below the onset of the high temperature desorption event. XRD studies showed (Fig. 1f) that, within experimental error, cell parameters for the recombined $Nd_5Fe_2B_6$ boride ($a=5.460(2)$ Å; $c=24.30(2)$ Å) are close to those of the initial ρ-compound ($a=5.4614(5)$ Å; $c=24.272(3)$ Å). The

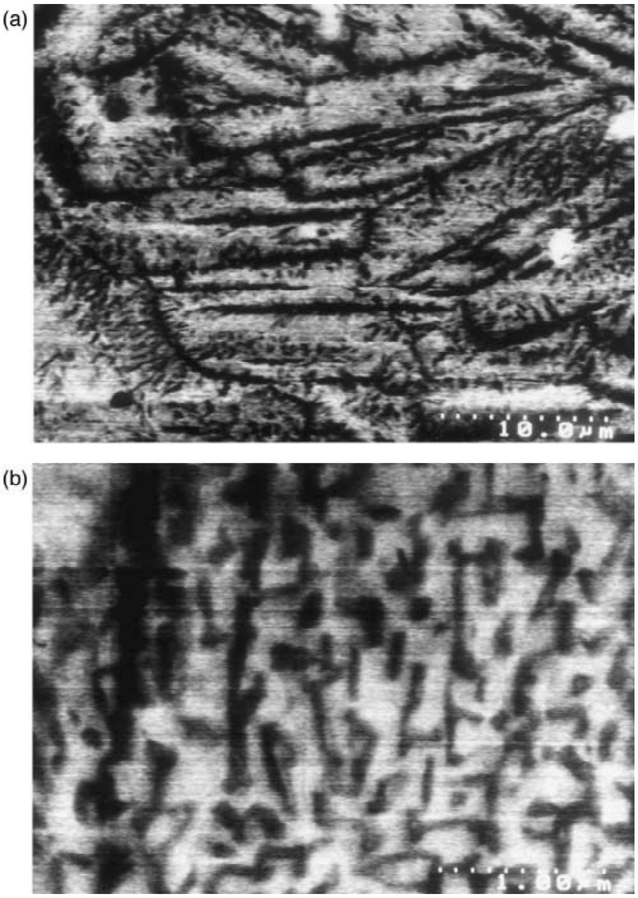

Fig. 3. Partially disproportionated in hydrogen $Nd_5Fe_2B_6$ ρ-boride (backscattered mode): (a) SEM image; (b) HRSEM image.

Table 1

Material under investigation	Phase constituents	Cell constants(Å)
Annealed alloy	$Nd_5Fe_2B_6$ boride	$a=5.4614(5)$ $c=24.272(3)$
Saturated (1 bar H_2) hydride	$Nd_5Fe_2B_6H_{8.6}$ saturated hydride	$a=5.455(8)$ $c=24.97(8)$
Recombined after completing HDDR process material	$Nd_5Fe_2B_6$ boride	$a=5.460(2)$ $c=24.30(2)$
Decomposed (HDTA rig; 1 bar H_2; heating to 800°C with a rate 5°C min^{-1})	$Nd_5Fe_2B_6H_{8.6-x}$ hydride,	$a=5.451(2)$ $c=24.87(1)$
	NdH_{3-x} hydride	$a=5.431(1)$
Decomposed (TPA rig; 1 bar H_2; heating up to 850 °C with a rate 5 °C min^{-1})	$Nd_5Fe_2B_6H_{8.6-x}$ hydride,	$a=5.462(2)$ $c=24.774(7)$
	NdH_{3-x} hydride	$a=5.440(2)$
	$Nd_{1.1}Fe_4B_4$ boride	$a=7.118(4)$ $c=34.97(7)$ (indexed as pseudotetragonal 2x)
	NdB_4 boride	$a=7.20(2)$ $c=4.095(4)$
Decomposed (1.5 bar H_2; kept at 825°C for 24 h)	NdH_{3-x} hydride	$a=5.457(2)$
	$Nd_{1.1}Fe_4B_4$ boride	$a=7.140(10)$ $c=35.18(8)$ (indexed as pseudotetragonal 2x)
	NdB_4 boride	$a=7.181(8)$ $c=4.086(4)$

For comparison below are presented reference data for the compounds found in the disproportionated hydrogenated material: NdB_4: tetragonal, $a=7.220$, $c=4.102$ Å [12]; $Nd_{1.1}Fe_4B_4$: tetragonal, $a=7.117$, $b=7.117$, $c=35.07$ Å [13]; NdH_3: cubic, $a=5.419$ Å [14]; NdH_2: cubic, $a=5.470$ Å [14].

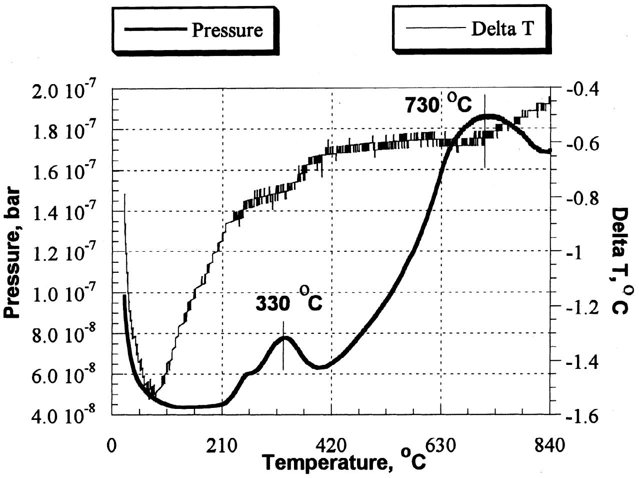

Fig. 4. HDTA traces of hydrogen desorption from the disproportionated $Nd_5Fe_2B_6$.

HRSEM micrograph of Fig. 5 shows a fracture surface of the recombined material indicating that the HDDR process resulted in a significant grain refinement of the initial material. This conversion into a submicron grain sized material is well established for the Φ-boride [1,2].

Significantly different hydrogenation behaviour has been observed in the case of a $Nd_5Fe_2B_6$ boride when studied in the as cast state [7]. A very fast, near room temperature, hydrogenation of the as cast ρ-boride, in contrast to rather small hydrogenation activity of the annealed, single phase alloy is, presumably, a result of the influence of the Nd-rich phase which exists only in the as cast material. However, similar hydrogen absorption properties were observed for both types of materials in the high temperature region. A stronger disproportionation reaction was observed for the annealed ρ-boride when NdB_4 was formed instead of Nd_2B_5 in the case of the as cast alloy. The two other decomposition products, neodymium hydride and η-$Nd_{1.1}Fe_4B_4$ were observed in both cases. A recombination process resulted in the recovery of the initial crystal lattice, independent of the type of material used, thus suggesting a possible use of the HDDR route for the homogenisation of cast $Nd_5Fe_2B_6$.

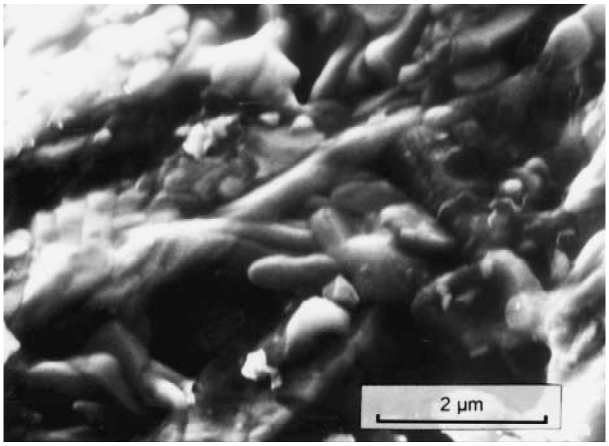

Fig. 5. Fracture surface of the recombined material.

4. Conclusions

The $Nd_5Fe_2B_6$ boride disproportionated in hydrogen at temperatures above 745°C forming a three phase mixture of NdH_{3-x}, NdB_4 and $Nd_{1.1}Fe_4B_4$. The rate of disproportionation was rather low compared with that of the Φ-phase, and a complete decomposition of the initial ρ-boride was achieved only after exposing the material to hydrogen at 825°C for 24 h. A full recombination of the $Nd_5Fe_2B_6$ boride occurred on heating the disproportionated mixture in vacuum together with a significant refinement in the grain size. These studies demonstrate a new example of the HDDR cycle for rare-earth containing compounds.

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