

## Electron microscopy studies of a TbNiAl compound processed by the HDDR route

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### Abstract

A TbNiAl compound processed by the hydrogenation disproportionation desorption recombination route has been studied using a combination of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM backscattered electron (BSE) images showed fine scale composition variations associated with the disproportionation stage while in the recombination stage no structure was visible. TEM examination showed nanocrystalline regions in the disproportionation stage. Selected area diffraction (SAD) showed the existence of two phases TbD<sub>2.2</sub> and NiAl in the disproportionation stage and single phase TbNiAl in the recombination stage and the measured *d*-spacings correlate well with the literature. The distribution of the phases in the disproportionation stage was studied by high-resolution TEM.

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### 1. Introduction

The intermetallic compound TbNiAl can absorb up to 1.4 deuterium atoms per formula unit at room temperature and 1 bar H<sub>2</sub>/D<sub>2</sub> pressure [1–3]. The hydrogenation–disproportionation–desorption–recombination (HDDR) process is an effective way to refine originally coarse grains into much finer grains [4]. In particular, the method is important for obtaining highly coercive isotropic and anisotropic magnets [5,6]. The TbNiAl compound in the disproportionation stage of the HDDR process is nanocrystalline and multiphase by design. Therefore, a better understanding of the nature of this compound, the distribution of the phases in each particle and the relationship between the phases is necessary.

Some work has been done examining physical-chemical characteristics (morphology, composition) of Nd<sub>2</sub>Fe<sub>14</sub>B-based alloys processed by the HDDR route using transmission electron microscopy (TEM) [7].

The purpose of this research was to study the microstructural transformations induced by the HDDR process. The work was carried out using a combination of scanning electron microscopy (SEM) and TEM investigations in conjunction with X-ray diffraction analysis.

### 2. Experimental

The TbNiAl alloy was prepared from Tb (purity 99.8%), Ni (99.9%) and Al (99.9%) by arc melting in an argon atmosphere. The ingots were remelted several times to increase their homogeneity and annealed at 800 °C. Unit cell dimensions (*a*=7.003 Å, *c*=3.877 Å) determined by powder X-ray diffraction (PXD) agreed well with literature data [8]. Samples of approximately 1 g for each temperature and heating rate condition were prepared. The samples were first activated in vacuum at temperatures between 400 and 600 °C. In the disproportionation case after the activation and absorption of D<sub>2</sub>, the sample was heated in a D<sub>2</sub> atmosphere with a heating rate of 0.5 K/min to 600 °C and kept for 20 h. Between 450 and 550 °C the pressure

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decreases equivalently to an increase of 1.1D/formula unit (Fig. 1a). The resulting  $\text{TbNiAl}_{1.4}$  decomposes into  $\text{TbD}_{2.2}$  and NiAl phases at  $p_{\text{D}_2}=3$  bar. In the recombination case the disproportionation starts at 470 °C at a heating rate of 5 K/min and is essentially completed in 20 min. The HDDR

procedure was completed by replacing the  $\text{D}_2$  atmosphere at 600 °C with vacuum (Fig. 1b).  $\text{D}_2$  is desorbed in 3 h and Tb and NiAl react to form  $\text{TbNiAl}$ . PXD data confirm the existence of both phases in the disproportionation stage and single phase in the recombination stage. After the

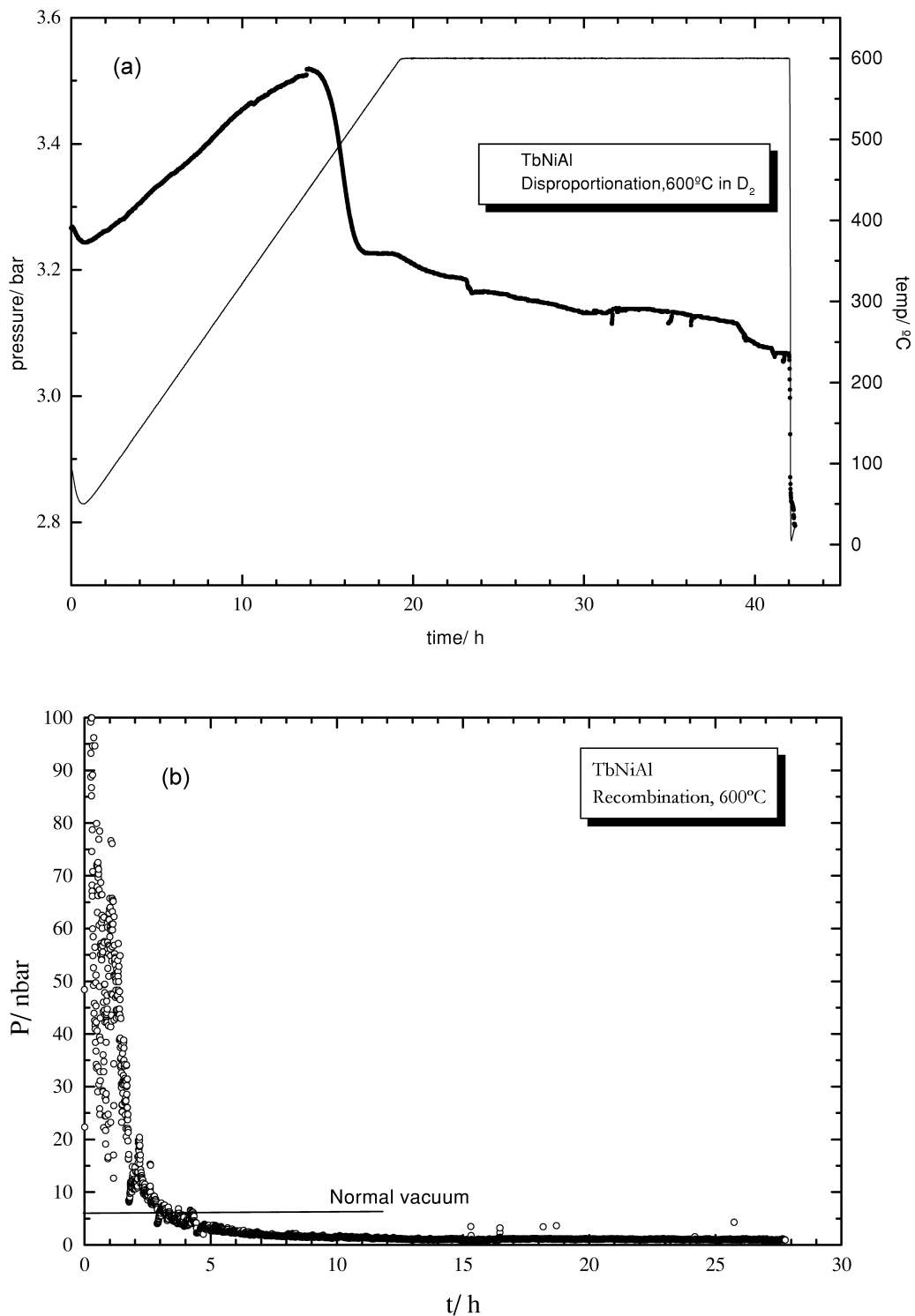


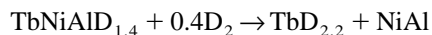
Fig. 1. Disproportionation process (a). Between 450 and 550 °C the pressure decreases and disproportionation occurs. Recombination process (b). The  $\text{D}_2$  atmosphere at 600 °C was replaced with vacuum and  $\text{D}_2$  is desorbed in 3 h.

HDDR process samples were stored in an argon atmosphere. PXD was performed with a Siemens D5000 diffractometer using Cu  $K\alpha_1$  radiation, Bragg–Bretano geometry, primary monochromator, and a position sensitive detector. Electron microscope samples were prepared by mechanical grinding in a silicate crucible and the dry powder was spread on a holey carbon film supported on a titanium grid. Electron microscopy studies were performed with a Philips CM 30 system operated at 300 kV (TEM) and a Hitachi S-4300SE system operated at 10 kV (SEM).

### 3. Results

A TEM bright field image of the TbNiAl compound before the hydrogenation process (mother alloy) is shown in Fig. 2a at a relatively low magnification. The  $d$ -spacings measured from selected area diffraction (Fig. 2b) closely match those of TbNiAl from the literature.

In the disproportionation stage of the HDDR process, TbNiAl<sub>1.4</sub> exposed to D<sub>2</sub> at temperatures above 450 °C decomposes into TbD<sub>2.2</sub> and NiAl according to the reaction:



The TEM dark field image of the TbNiAlD compound in the complete disproportionation stage (Fig. 3a) is made from reflections indicated in the SAD pattern (Fig. 3b). Due to high absorption and the shape of the particle the contrast in Fig. 2a is weak away from the edge of the particle. Indexing of the SAD pattern showed that only the NiAl phase (110) spacing could be detected. All the other reflections correspond to the TbD<sub>2.2</sub> phase (confirmed also by PXD data). Since Tb ( $Z=65$ ) is a much stronger scatterer than Al ( $Z=13$ ) or Ni ( $Z=28$ ), other reflections from the NiAl phase are probably too weak to be observed. The main  $d$ -spacings in the disproportionation sample are listed in Table 1. The diffraction pattern shows a high degree of crystalline imperfection, either due to strain or mosaicity. An orientation relationship between planes in the two phases can be seen (Fig. 3b).

One method for studying the distribution of the phases in the disproportionation stage is high-resolution TEM (HRTEM). Useful information is obtained from the thin areas at the edge of the particle (Fig. 4). Near the middle of the particle phases overlap and Moire fringes are visible.

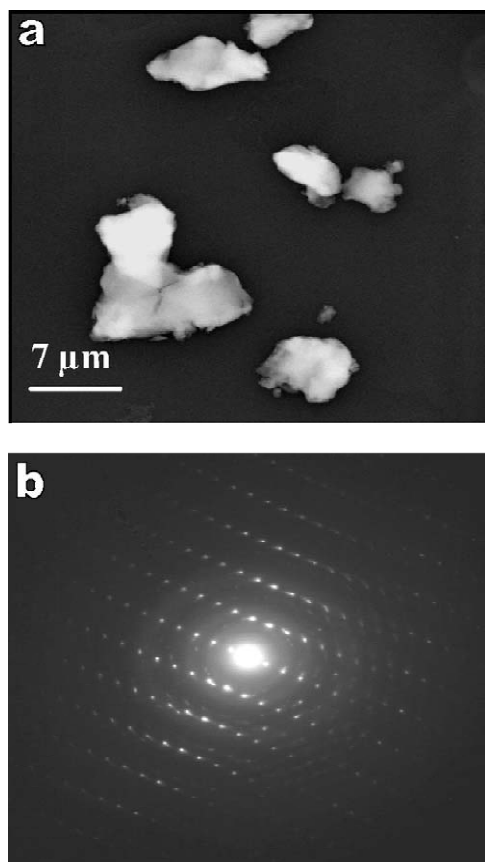


Fig. 2. TEM bright field image (a) and selected area diffraction pattern (b) of TbNiAl (mother alloy) before the hydrogenation process.

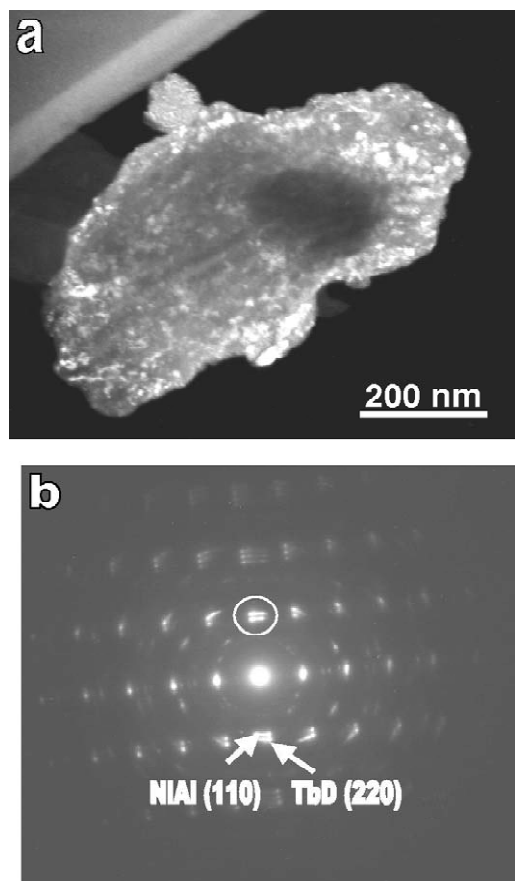


Fig. 3. TEM dark field image (a) and SAD pattern (b) of the TbNiAlD compounds in the complete disproportionation stage of the HDDR process showing two phases NiAl and TbD<sub>2.2</sub>.

Table 1

Index of the  $d$ -spacings of disproportionation sample

$d$ -spacing (Å)	ASTM index	Identification	$hkl$	Intensity (%)
2.987	3.014	TbD <sub>2.2</sub>	112	100
2.003	2.04	NiAl	110	100
1.81	1.84	TbD <sub>2.2</sub>	220	25
1.80	1.84	TbD <sub>2.2</sub>	204	20
1.54	1.57	TbD <sub>2.2</sub>	312	25

The detailed structure is shown in Fig. 5 with both the TbD<sub>2.2</sub> and NiAl phases present. A lattice spacing of  $d_{112} = 3.14$  Å corresponds to the dominant TbD<sub>2.2</sub> phase. Using the TbD<sub>2.2</sub> as internal reference, a particle region of several nanometers with a lattice spacing of 2.03 Å is identified in the image. This corresponds well with the NiAl phase (110) spacing.

An SEM image taken with backscattered electrons (BSEs) of the TbNiAlD compound in the disproportionation stage (Fig. 6a) also indicates variations in the composition on a scale of tens of nanometers. By comparison in the corresponding secondary electron (SE) image (Fig. 6b), which is more sensitive to the surface topography, the fine scale contrast seen in the BSE image is absent.

Fig. 7 shows a TEM bright field image (a) and a selected area diffraction pattern (b) of the recombined TbNiAl. The crystallites are smaller compared to the sample in the disproportionation stage. The measured  $d$ -spacings from

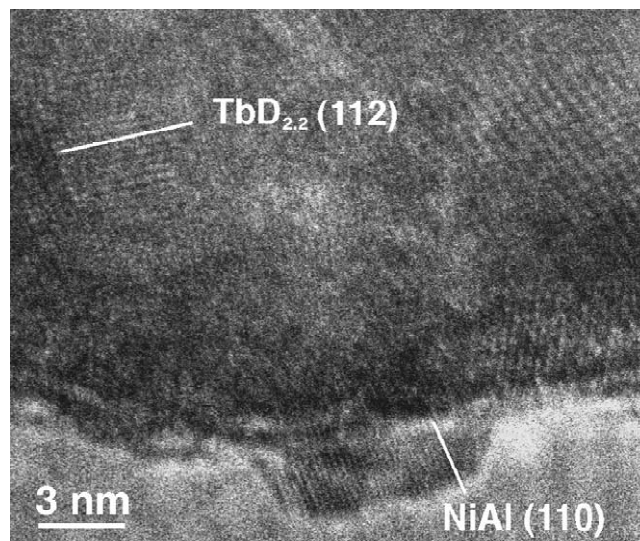


Fig. 5. HRTEM image from small area in Fig. 3 showing lattice fringes from the two phases.

SAD closely match with literature data for single phase TbNiAl.

The SEM BSE images of recombined TbNiAl (Fig. 8a) show no evidence of the fine scale composition contrast that is seen in the disproportionation stage.

Samples from the different temperature and heating rate conditions in the disproportionation stage were studied and

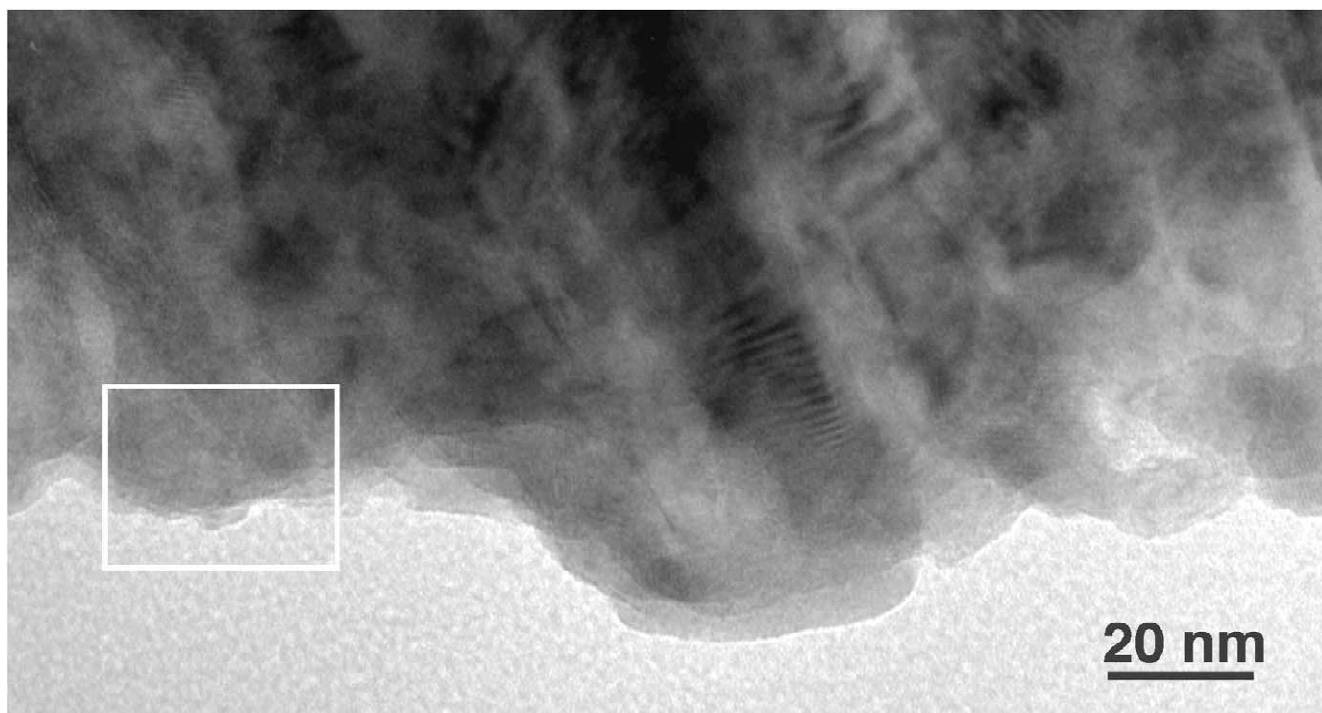


Fig. 4. HRTEM image from the edge of a particle in the disproportionation stage. The rectangle marked is enlarged in Fig. 5.

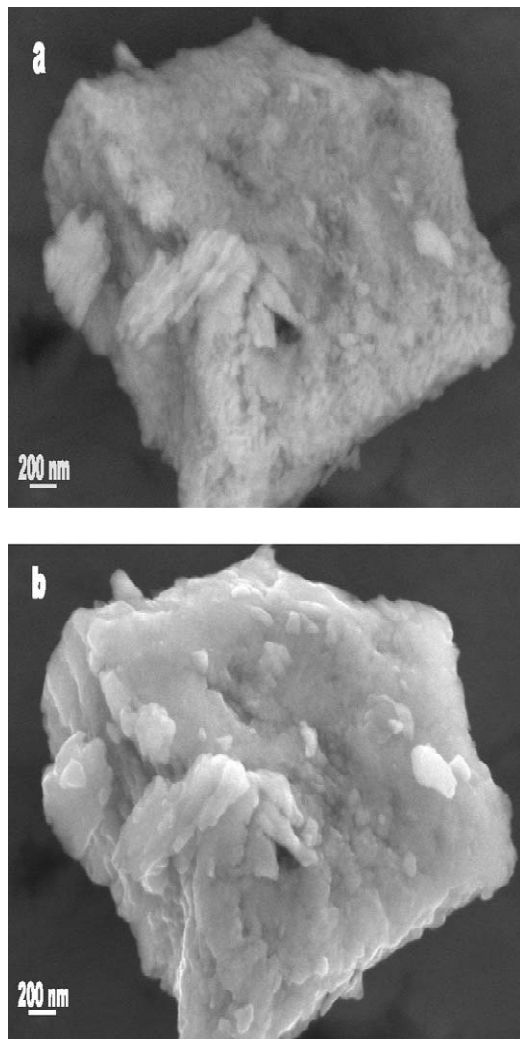


Fig. 6. Backscattered electron (BSE) image (a) and secondary electron (SE) image (b) of the TbNiAlD compound in the disproportionation stage.

no differences could be distinguished with these microscopy methods.

#### 4. Conclusions

A TbNiAl compound was examined at different stages of the HDDR process. Electron microscopy imaging and diffraction techniques were used to characterize the microstructural changes. The following conclusions can be drawn:

1. TEM dark and bright field images through the HDDR process reveal the structure of the TbNiAlD mixture down to the nanometers scale. The microstructure was found to be quite complicated. The three dimensional morphology of the particles and the high absorption of

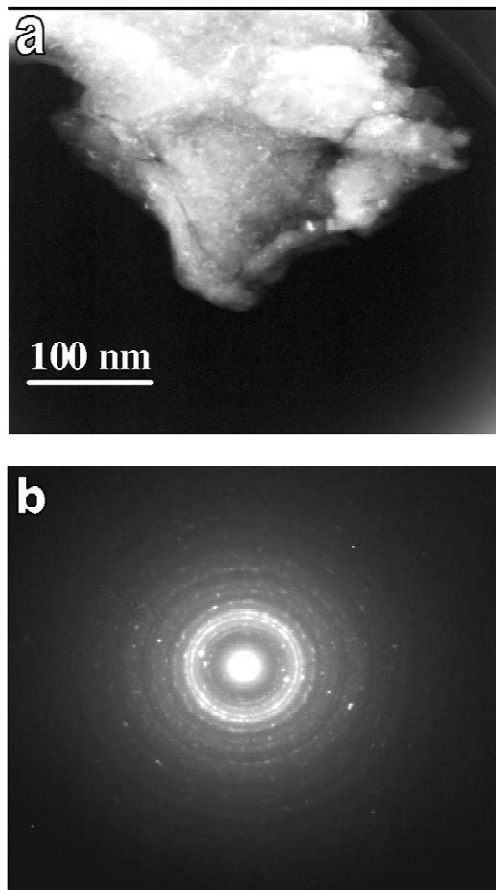


Fig. 7. TEM bright field image (a) and selected area diffraction pattern (b) of TbNiAl in the recombination stage of HDDR process.

the electron beam by the material makes them difficult to study.

2. Selected area diffraction patterns confirm that the TbNiAlD compound in the disproportionation stage consist of both the TbD<sub>2.2</sub> and NiAl phases. The measurement of the *d*-spacings closely matches those of TbD<sub>2.2</sub> and NiAl phases.
3. In the disproportionation stage each particle shows a complicated nanoscale distribution of the two phases. Some parallel orientation of textured crystal planes in the two phases is observed.
4. SEM BSE images show evidence of fine scale composition variations associated with the disproportionation process. This contrast is absent in secondary electron images which are most sensitive to surface topography.
5. The crystallites that have undergone the recombination process are smaller in size.
6. BSE images of TbNiAl in the recombination stage shows no visible indication of compositional inhomogeneity.
7. PXD data confirm the existence of both phases in the

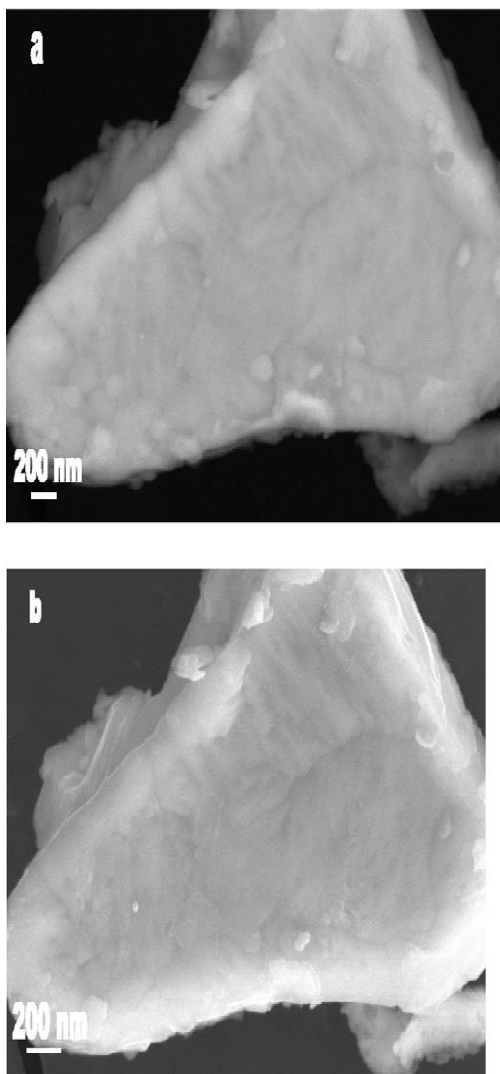


Fig. 8. Backscattered electron (BSE) image (a) and secondary electron (SE) image (b) of TbNiAl in the recombination stage of the HDDR process.

disproportionation stage and single phase in the recombination stage. Peaks get broad with the HDDR process which means we have small particle size and therefore chemical analysis of the formula was impossible.

Fine scale composition and crystallography in the disproportionation stage will be further investigated using field emission gun (FEG) TEM.

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