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The Hydrogen Ductilisation Process (HyDP) for Shaping NdFeB Magnets.**O. Brooks, A. Walton, W. Zhou and I.R.Harris.****School of Metallurgy and Materials,****College of Science and Engineering.****University of Birmingham, UK.****Abstract:**

One of the major drawbacks of NdFeB-based, fully dense, sintered magnets is that they are hard and extremely brittle. Therefore, in order to produce the final shape and precise dimensions, they often have to be ground and this process is time consuming, energy intensive and produces a significant amount of waste material which is not readily recyclable. This paper reports a potentially new and exciting application of hydrogen as a promising processing tool in which the normally brittle Nd₂Fe₁₄B based intermetallic could be compressed at room temperature in a ductile, disproportionated condition and then restored to its original state by the removal of the hydrogen under partial vacuum at elevated temperatures. Under appropriate conditions, this stage can also produce a useful degree of anisotropy. This paper describes the salient feature of this process which has been called the Hydrogen Ductilisation Process (HyDP) and describes possible applications of the HyDP in the production of NdFeB-type permanent magnets.

Keywords: Hydrogen Disproportionation, Neodymium, Magnets, Compression, Ductility

1 Introduction

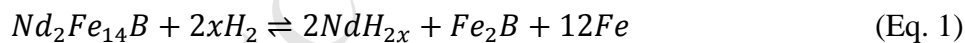
Since their introduction around 1984 [1, 2, 3], NdFeB-type magnets have been used increasingly in a range of components, from hard drive disks (HDDs) in computers, to large scale wind and tidal generators [4]. Typically, these magnets will be produced from a cast alloy containing $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains surrounded by a Nd-rich material, together with a minority phase with the approximate formula NdFe_4B_4 . Typically, alloys are processed using the Hydrogen Decrepitation process (HD) [5, 6] where the cast NdFeB alloys are exposed to hydrogen at room temperature causing them to react exothermically, and consequently, decrepitating into a highly friable powder which can then be jet-milled, aligned, compressed and liquid phase sintered to form a conventional, fully dense NdFeB-type magnets. To improve the degree of alignment of the milled powder in the case of subsequent and more recent, high $(\text{BH})_{\text{max}}$, near stoichiometric grade magnets, the hydrogen is degassed from the matrix, $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase, and this occurs at around 350°C [7].

Subsequently, it was found [8, 9] that, by re-introducing hydrogen to the sintered magnets they also go through the HD process and, as with the initial material, form a demagnetized friable powder which can then be blended, compressed, aligned and re-sintered in order to form recycled magnets. The HD technique is currently being exploited as a means of separating and recycling a range of NdFeB fully dense type magnets, such as, those employed in very large numbers in hard disc drives (HDDs) [10, 11, 12].

Since their discovery, the magnetic properties of these materials have improved remarkably due to changes in both the microstructure and composition [13, 14, 15]. One such example of

this was discovered through the exploitation of the Hydrogenation-Disproportionation-Desorption-Recombination (HDDR) process [16, 17]. Here it was discovered that it is possible to produce anisotropic powder with nanocrystalline (~300nm) grains by careful control of the hydrogen absorption and desorption conditions, of Nd₂Fe₁₄B [16, 18]. This has allowed the production of commercially exploitable, bonded, anisotropic magnets.

During conventional HDDR processing, the hydrogen is introduced at near atmospheric pressure at room temperature and then the material is heated to >650°C [17]. The room temperature hydrogenation causes decrepitation of the material, where the Nd-rich material forms NdH_{2.7} and the Nd₂Fe₁₄B matrix grains form an interstitial hydrogen solution. The material expands by ~5% and because of its brittle nature and differential expansion, undergoes decrepitation [16]. Upon subsequent heating in a hydrogen atmosphere, the matrix grains disproportionate into a nanocrystalline structure containing a mixture of NdH₂, α-Fe and Fe₂B (Eq. 1). Whilst still at an elevated temperature and by applying a reduced pressure, the hydrogen is desorbed and the Nd₂Fe₁₄B matrix phase reforms by a process of recombination. The newly formed grains are typically in the order of 300nm in diameter [16] and the coercive powder is used in resin bonded magnets.



Previous work in the authors' laboratory has shown that, by introducing the H₂ at elevated temperatures (>650°C), it is possible to avoid completely the decrepitation stage and hence form a solid HDDR structure [19, 20, 21]. Early resistivity studies [19, 20, 22] showed clearly, that solid NdFeB-type alloys (or finished sintered magnets) can be maintained in the solid form (without cracking) providing the hydrogen is introduced at high temperatures

(~650°C or higher). It was also shown that, when the Nd-rich eutectic phase at the grain boundaries is initially in the liquid state, then, when hydrogen is introduced there is a rapid onset of the disproportionation reaction starting at the, now solid, grain boundaries and other interfacial regions [23].

Normally, as the fully dense sintered magnets are not produced in the net shape form, they have to be machined (ground) to the final dimensions. This process can be very costly and produces a substantial amount of waste material, which because of extensive oxidation, can be very difficult to recycle.

In practice, one way to overcome these difficulties can be to employ particles of melt-spun ribbons consisting of nanocrystalline grains of $\text{Nd}_2\text{Fe}_{14}\text{B}$ which are mixed with a binder to produce a range of net shape bonded magnets [24]. However, these binders are non-ferromagnetic and together with the isotropic character of the ribbon, result in an overall dilution of the magnetic strength. This effect can be reduced appreciably by employing magnetically anisotropic HDDR-based powder, as developed by Aichi Steel [18]. However, as expected, the bonded magnets always have a lower remanence than those of the fully dense sintered form because of the non-ferromagnetic binder. An advantage of all the bonded magnets is their high electrical resistance and hence the corresponding reductions in eddy-current losses.

The main aim of the present investigation was to see if it is possible to overcome the brittle nature of $\text{Nd}_2\text{Fe}_{14}\text{B}$ and this has been achieved by disproportionating the alloys prior to shaping in order to create appreciable ductility.

In the present work, two compositions of NdFeB alloys were processed using the solid HDDR process discussed above. The mechanical properties of the disproportionated alloys were then investigated and interpreted in terms of the fine microstructure.

2 Experimental Work

In the present studies, book mould cast materials of composition $\text{Nd}_{12.2}\text{Fe}_{81.3}\text{B}_{6.5}$ (Aichi Alloy, designated Alloy 1) and $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ (Neomax composition, designated Alloy 2) have been employed. The former was provided by Aichi Steel Japan and the latter by Less Common Metals (LCM UK).

These particular alloys were selected as book-mould castings. The Alloy 1 composition was close to that of stoichiometry ($\text{Nd}_{11.8}\text{Fe}_{82.3}\text{B}_{5.9}$) and, in the cast condition, contained α -Fe dendrites whereas, in Alloy 2 ($\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$) composition, formation of α -Fe was avoided. Thus, in the as-cast condition Alloy 1 contains α -Fe, $\text{Nd}_2\text{Fe}_{14}\text{B}$, Nd-rich material and some NdFe_4B_4 (approximate formula) whereas, in Alloy 2, there is no α -Fe in the cast condition with Nd-rich material and NdFe_4B_4 confined to the grain boundaries [25]. These features can be seen in the SEM investigations shown later.

Initially, these materials were cut either into cylinders, of ~9.5mm diameter and ~5mm height, or cubes, of ~5x5x5mm, using spark erosion, as this technique limits the oxidation process which previous work [26] has shown, can have a marked influence on the disproportionation reaction.

To produce fully disproportionated material, as outlined by Harris et al [19, 20], the solid disproportionation reaction was employed. This involved heating the particular NdFeB alloy under vacuum, to 915°C, and then introducing hydrogen, to a pressure of 1200mbar, in order to achieve 100% disproportionation, without decrepitation.

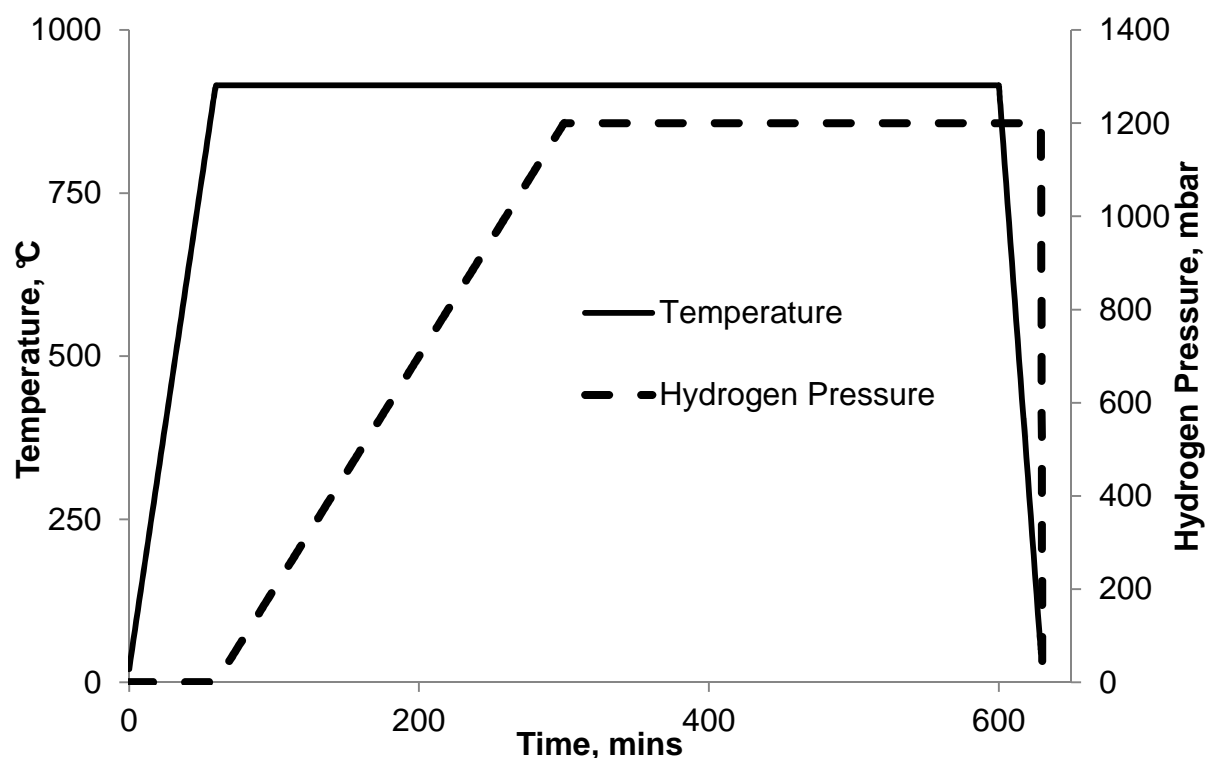


Figure 1 A schematic of the variation in Hydrogen Pressure and Temperature vs. Time during the disproportionation reaction

In a particular sample at 915°C, SEM and XRD studies revealed that a period of around 5 hrs was sufficient to achieve 100% disproportionation of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. In order to maintain the disproportionated state the material was then cooled rapidly in hydrogen. Figure 1 shows a schematic representation of the change of hydrogen pressure and temperature vs. time. The conditions were also adjusted to avoid the formation of the more reactive $\text{NdH}_{2.7}$ component by partially degassing the material (after quenching in hydrogen) by heating the samples to 350°C under vacuum.

2.1 Microscopy

In an attempt to relate the mechanical behaviour to possible changes in the microstructure and in order to examine the fine structure of the disproportionated material both before and after

compression, a Jeol 6060 and a Jeol 7000 scanning electron microscope (SEMs) were employed in the backscattered mode, using a 20kV accelerating voltage. Compositional analysis was also carried out using the EDX facilities on both microscopes.

2.2 XRD

Phase analysis was achieved with the use of a Bruker D8 Advanced Diffractometer with Cu-K α X-ray radiation, between 5°-100° 2 θ with a step size of 0.02° and varying step times.

2.3 Compression Trials

In order to assess initially, whether there had been any radical change in the brittle-ductile mechanical behaviour, the hydrogen treated and untreated samples were compressed in 10mm diameter “Specac” die sets with an Atlas T25 press, capable of a load of up to 25 tonne. Later, more detailed compression trials were carried out on an ESH 200kN servo hydraulic mechanical press which allowed readings of both the force applied and the displacement to be measured, so that details of the mechanical behaviour of the particular material could be determined. In this study, the change in cross sectional area during compression is not taken into consideration, therefore the well-established “engineering” stress/strain is employed.

2.4 Magnetic Measurements

To measure the magnetic properties of the material both before and after the compression trials at room temperature and after the subsequent recombination process, a Lakeshore vibrating sample magnetometer (VSM), capable of measurements up to a field of 2T, was employed. Self-demagnetisation factor has been taken into consideration with all measurements

3 Results and Discussion

3.1 SEM

3.1.1 Starting Alloys

The SEM images shown below are of the two starting materials used in the compression trials.

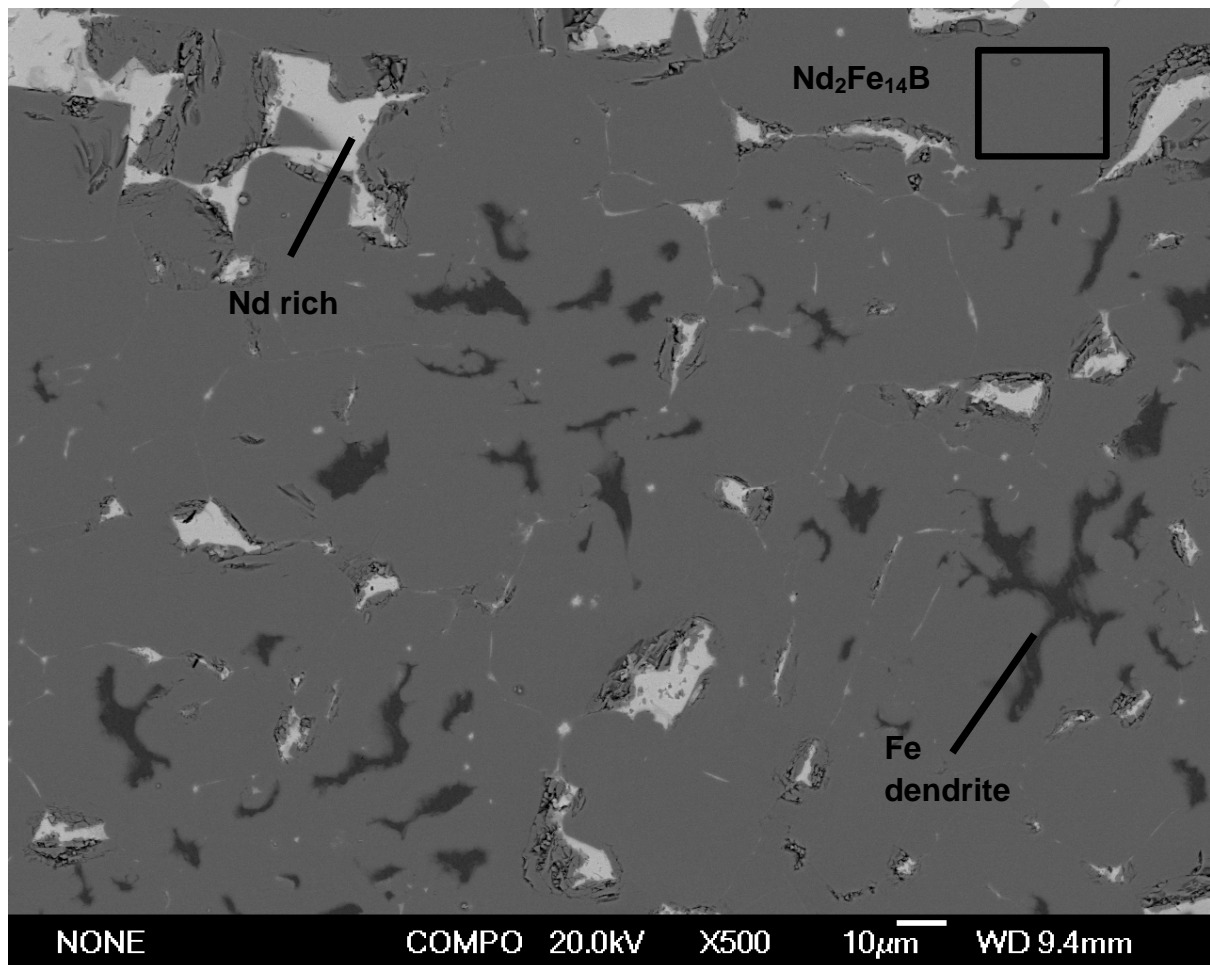


Figure 2 Backscattered SEM of Alloy 1 starting material

The SEM image of the as-received Alloy 1 shown in figure 2, reveals clearly the presence of three phases in the material; first several large dark regions (typically A), then several light areas (typically B) and finally a large grey area (typically C). There is some evidence of a light grey phase within the Nd-rich eutectic which can be identified as the phase NdFe₄B₄.

The overall composition of this alloy is near to that of stoichiometry ($\text{Nd}_{11.8}\text{Fe}_{82.3}\text{B}_{5.9}$) and the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phases (large grey areas) are formed by a peritectic reaction. Because of the expected incomplete peritectic reaction, some dendrites of $\alpha\text{-Fe}$ would also be expected (dark areas on SEM images). According to the phase diagram [25] an incomplete reaction could also result in the formation of NdFe_4B_4 which, from SEM backscattered imaging, is difficult to distinguish from the $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix phase. This NdFe_4B_4 phase is more readily observable in the disproportionated state of this alloy.

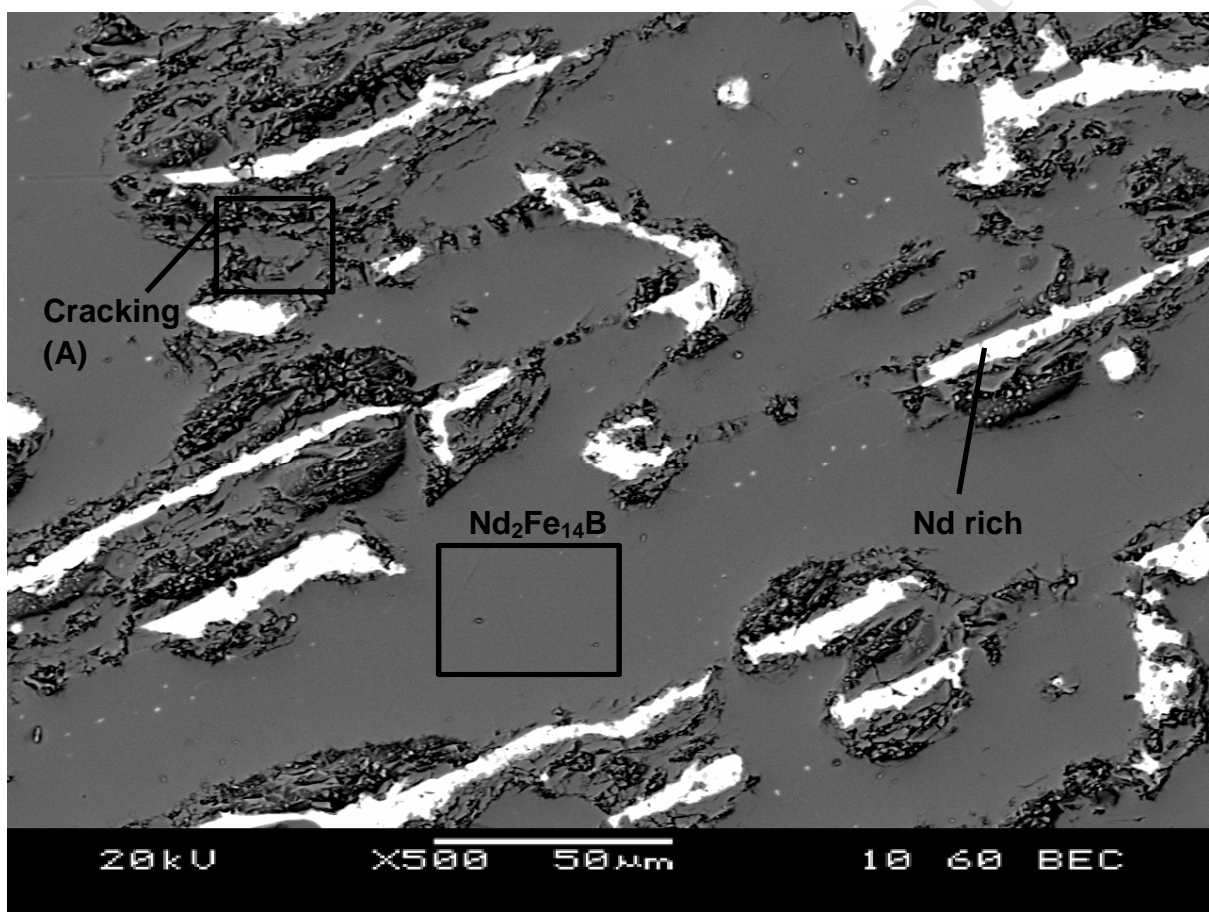


Figure 3 Backscattered SEM image of Alloy 2 starting material

The microstructure of Alloy 2 (figure 3) is unlike that of the Alloy 1 shown previously in figure 2; there are no dark regions of $\alpha\text{-Fe}$ dendrites, there are several larger isolated and

elongated, intergranular areas of light Nd rich material and the predominant grey areas of $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase [25].

The apparent additional phase shown in figure 3 (e.g. areas such as A) can be ascribed to polishing debris as a result of the cracking of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ and this has been confirmed by the EDX measurements.

In summary, in the as-cast condition Alloy 1 contained significant amounts of α -Fe. However, this is not the case for Alloy 2 where the α -Fe is absent and the NdFe_4B_4 phase always occurred in close association with grain boundary, Nd-rich material. This can, in places, just be distinguished by the SEM studies but becomes much more apparent in the disproportionated material shown below.

3.1.2 Disproportionation

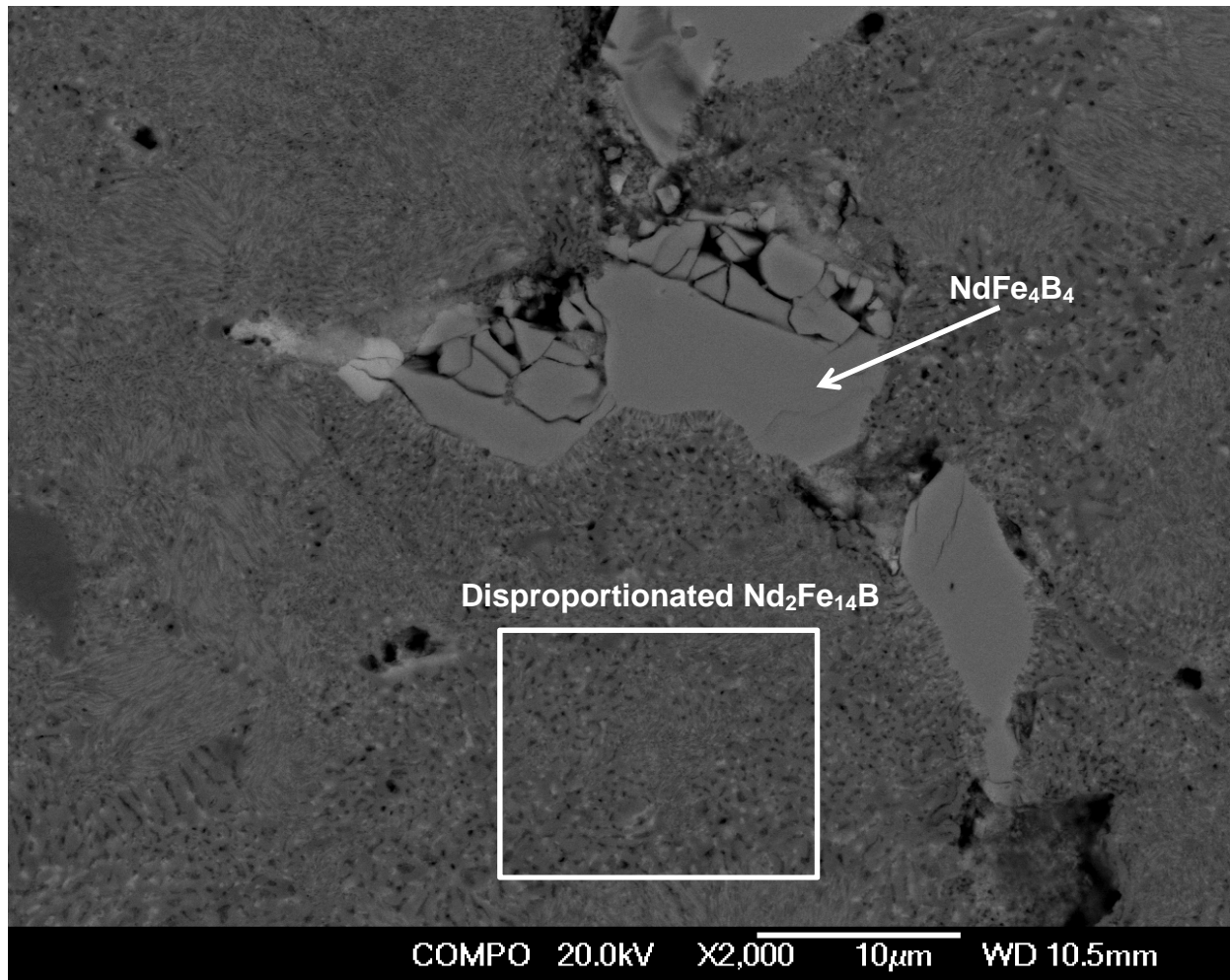


Figure 4a Backscattered SEM image of Alloy 1 after disproportionation

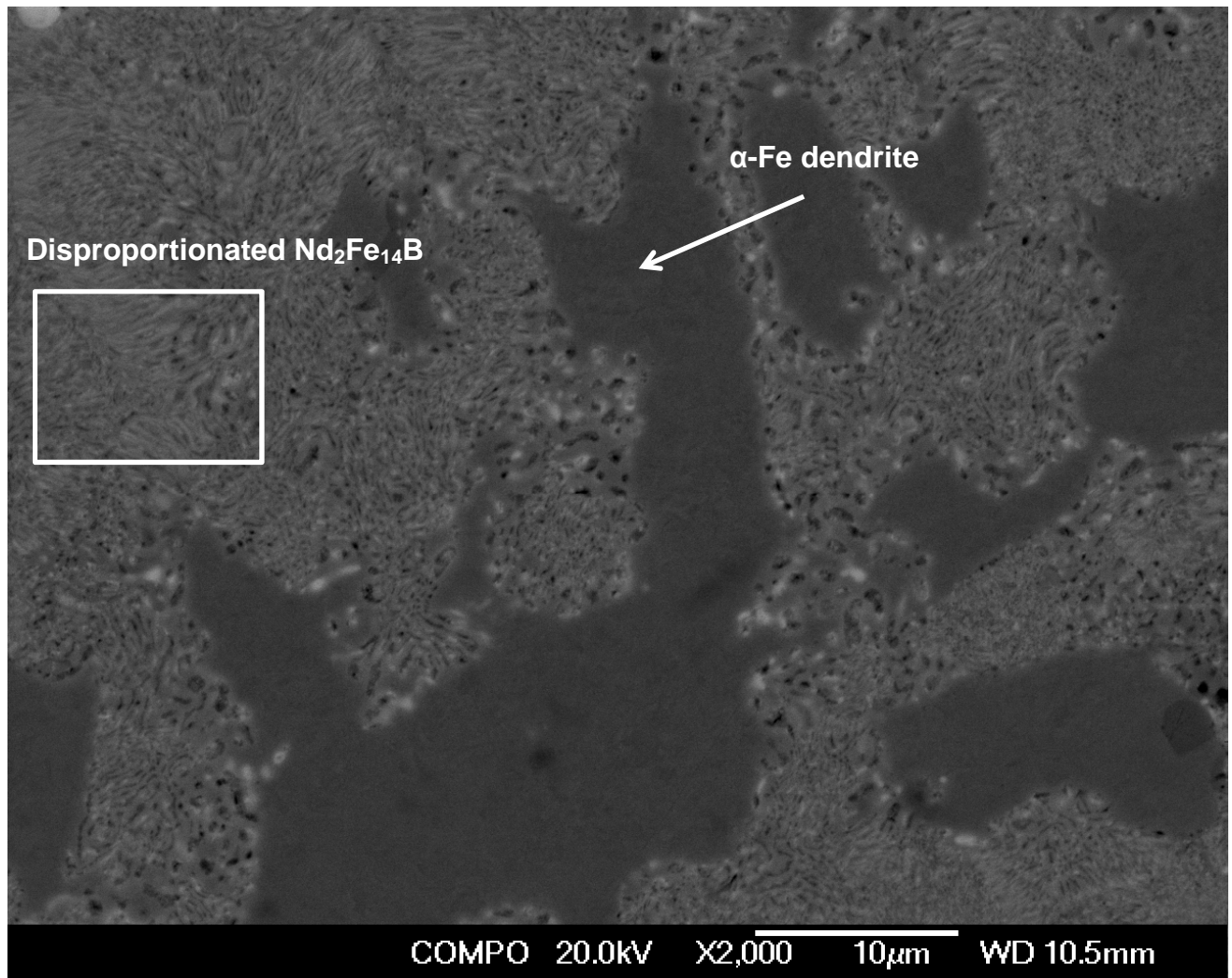


Figure 4b Backscattered SEM image of Alloy 1, after disproportionation

Figure 4a and 4b show the microstructure of Alloy 1 after the hydrogen treatment described earlier (disproportionation). The Nd₂Fe₁₄B matrix phase has transformed into a much finer disproportionated mixture; the dark regions of the α-Fe dendrites remain as they do not react with hydrogen but are clearly distinguished by the coarser disproportionated mixture surrounding them. This observation is in agreement with previous studies [23] which showed that the disproportionation reaction initiates at interfaces such as the grain boundaries and the interface between the Fe dendrites and the matrix. The irregular appearance of the previously smooth α-Fe dendrites was also apparent in previous studies which showed that there was

enhanced homogenisation in the disproportionated state [27] after the above treatment; the small bright areas of the Nd rich material remain. In addition, because of the disproportionation the NdFe_4B_4 phase has become more visible and its composition has been confirmed by complimentary EDX measurements (table 1). Under the conditions employed in these experiments, there was little evidence of any reaction of this phase with hydrogen, unlike earlier studies [28]. This can be ascribed to the higher pressure range of hydrogen (1-5bar) and longer hold time employed in the earlier investigations. It will be seen later that the areas of NdFe_4B_4 observed above become fractured in the compressed samples (see for example figure 11). The boron content could not be determined in these measurements so the significant data in Table 1 are the ratios of the elements. In the disproportionated material the Fe/Nd ratio is 6.8 and the value obtained from equation 1, assuming x is one, is 7.0. The value for the NdFe_4B_4 phase is 3.9.

Table 1 EDX data for the disproportionated Alloy 1

Alloy 1			
Disproportionated		Unreacted (NdFe_4B_4)	
Fe at%	Nd at%	Fe at%	Nd at%
87.23±1.1	12.77±1.1	79.74±3.0	20.26±3.0

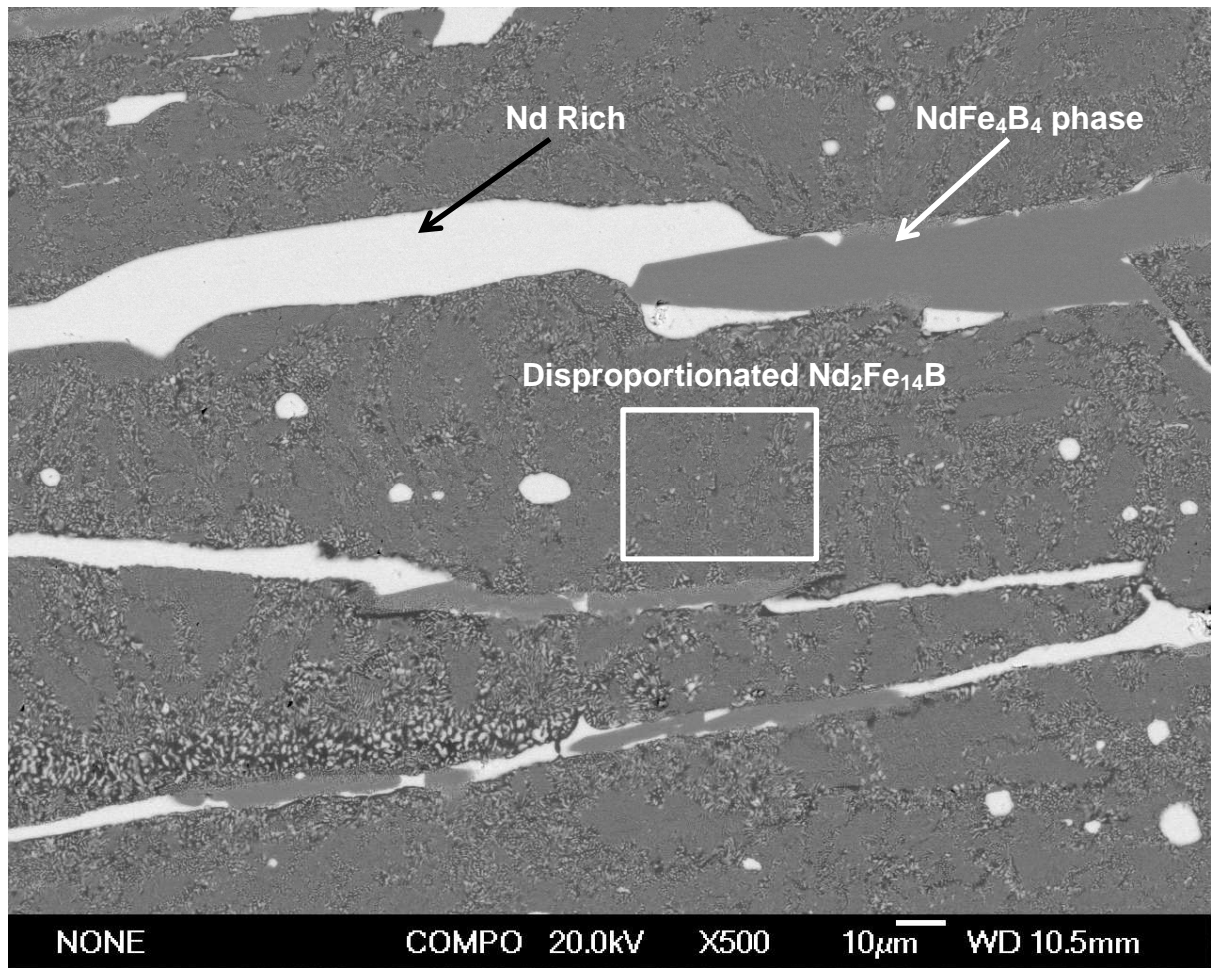


Figure 5a Backscattered SEM image of Alloy 2 after hydrogen heat treatment

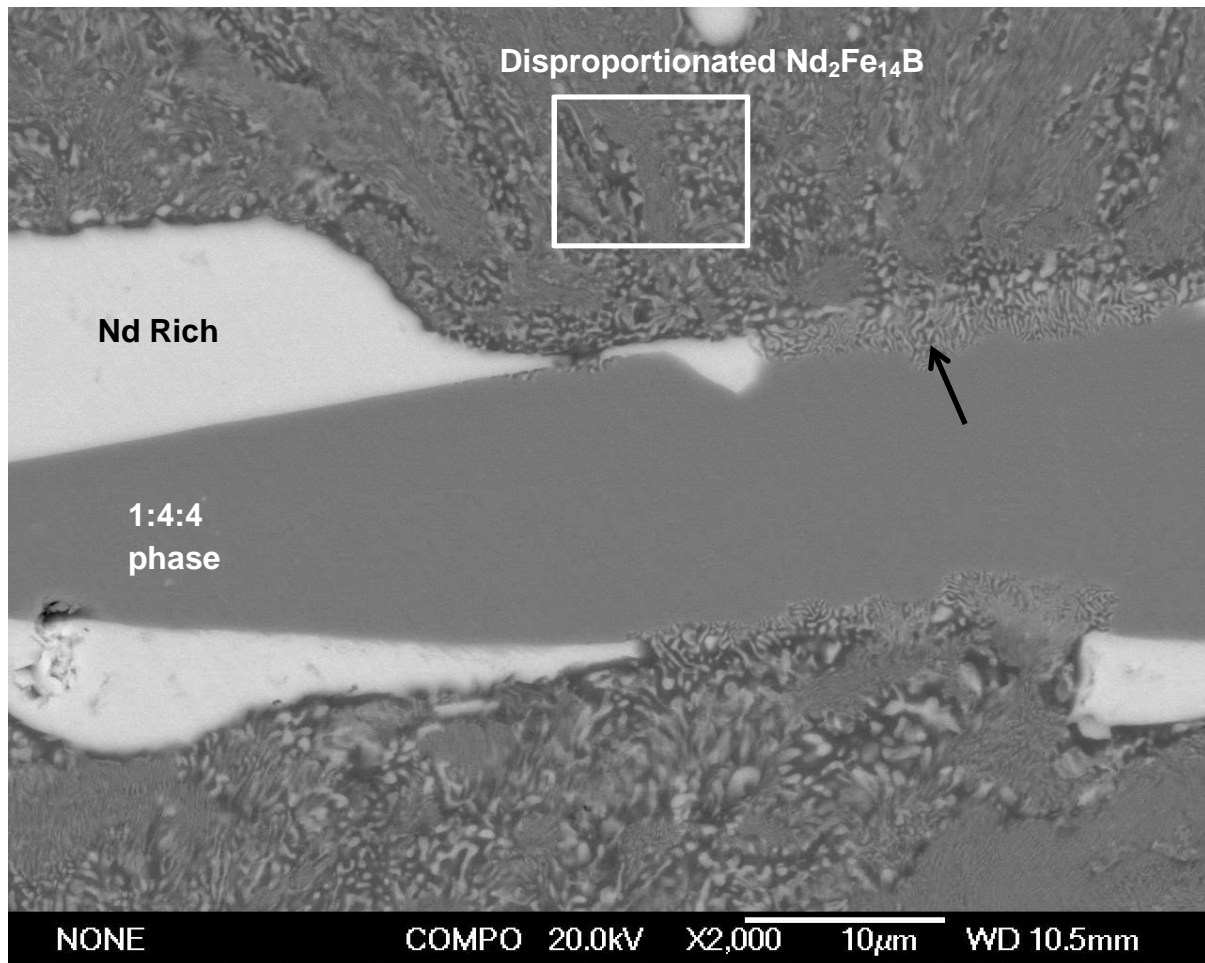


Figure 5b Backscattered SEM image of Alloy 2 after hydrogen heat treatment

An identical hydrogen treatment to that used for was also applied to Alloy 2 material and the effect of this is shown in figure 5a and 5b. The $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix material has been transformed into the intricate disproportionated mixture, the lighter areas of intergranular, Nd rich material are still present and there is also clear evidence of the NdFe_4B_4 phase, which has been confirmed through EDX measurements (table 2), present exclusively at the Nd rich grain boundary and this has been highlighted by the formation of the disproportionated matrix. This microstructure is consistent with the phases present in the phase diagram [25]. There is evidence of a limited disproportionation of the NdFe_4B_4 phase (arrow shown in figure 5b) and this is in agreement with the earlier work reported by Yartys et al [28] where much more extensive disproportionation of the NdFe_4B_4 phase has been observed.

Table 2 EDX data for the disproportionated Alloy 2

Alloy 2			
Disproportionated		Unreacted (NdFe₄B₄)	
Fe at%	Nd at%	Fe at%	Nd at%
87.11±1.5	12.89±1.5	80.05±2.9	19.95±2.9

The boron content could not be determined in these measurements and the ratios of Fe to Nd are 6.8 and 4.0, respectively.

3.2 XRD and Quantification of phases

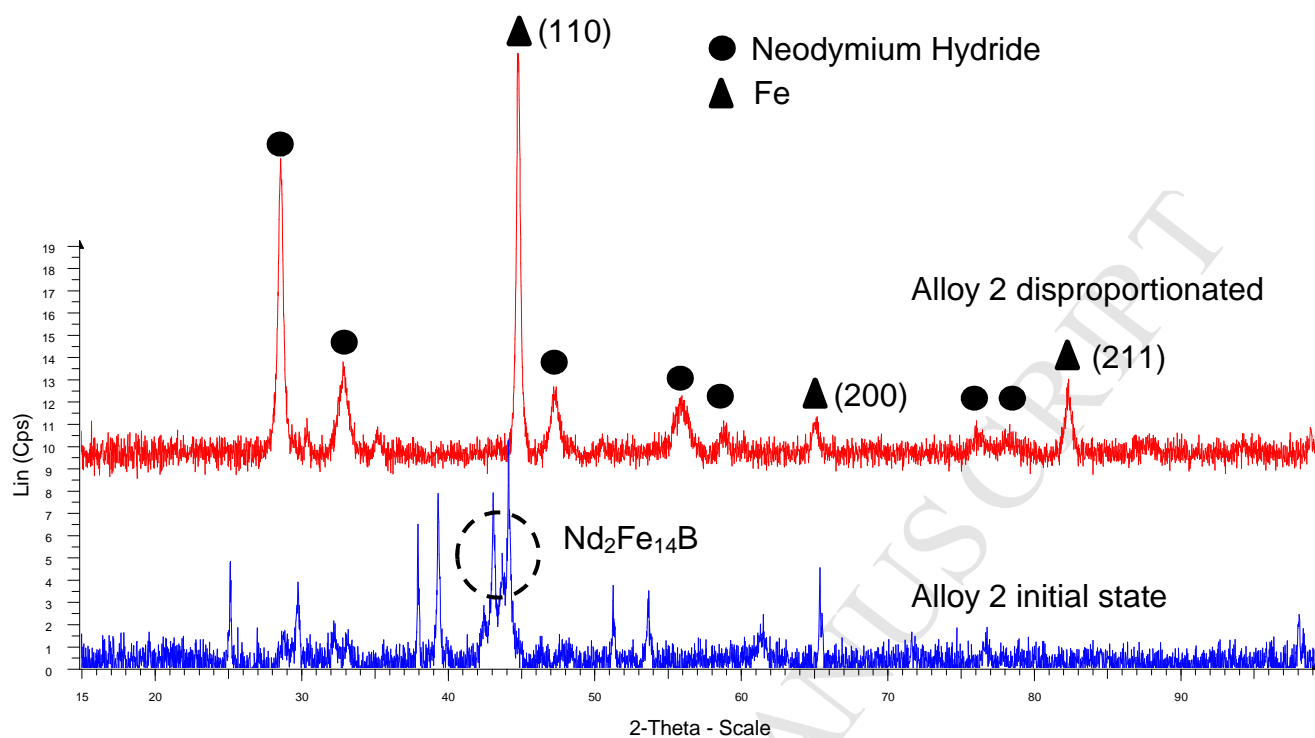


Figure 6 XRD trace of Alloy 2 before and after hydrogen disproportionation

Figure 6 shows a comparison of a 40 minute XRD scan of Alloy 2 before and after disproportionation. The key feature here is the complete removal of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ peaks and the addition of Fe and Neodymium hydride peaks after disproportionation. Another noticeable feature in the disproportionated trace is the peak broadening, which is found in materials with nanoscale microstructures, this is therefore consistent with the SEM images shown earlier.

Table 3 Quantification of phases via image analysis of SEM images

Alloy 1			Alloy 2		
Starting mixture			Starting mixture		
Phase	Weight%	Error	Phase	Weight%	Error
Grey Phase	85.62%	1.5%	Grey Phase	90.02%	1.1%
Nd rich	6.06%	1.2%	Nd rich	9.98%	1.1%
Fe	8.32%	1.2%			

Table 3 shows results a simple area mapping of several SEM images (x500 magnification) of the two compositions before hydrogen disproportionation, using ImageJ. In Alloy 1 the weight% of the grey phase is 85.62% where as in Alloy 2 it is 90.02%, this can be ascribed to the removal of the Fe dendrites in Alloy 2.

From this technique it is almost impossible to estimate the NdFe_4B_4 phase as the contrast is so similar to that of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase and thus hard to distinguish.

Identifying the weight% through XRD is also problematic as the amount of NdFe_4B_4 phase is so low.

3.3 Initial Compression Trials

The initial trials were carried out on Alloy 1 ($\text{Nd}_{12.2}\text{Fe}_{81.3}\text{B}_{6.5}$). Specimens of this alloy were subject to a rapid compression test, both in the as-received condition and after the solid hydrogen disproportionation treatment, by the method described earlier. Thus, samples were compressed in a die with a maximum load of approximately 20 tonne. This provided a rapid means of assessing any effect of the hydrogen treatment on the mechanical behaviour, as a useful precursor to the more detailed stress/strain measurements.

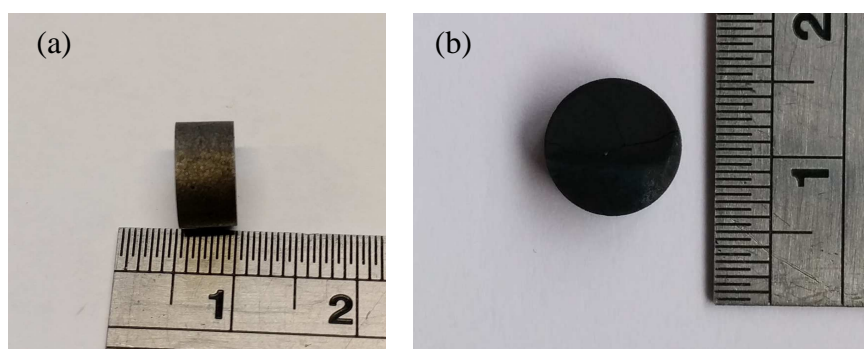


Figure 7 Disproportionated Alloy 1 cylinder before compression; side (a) and face (b) view

The cylindrical samples of NdFeB alloy, shown in figure 7, were produced by a spark erosion technique to produce sizes of ~9mm diameter and varying heights from 4.1-5.4mm. These samples were then compressed in a 20mm diameter die set, in air, up to a load of 7 tonne (~1095MPa), producing extensive cracking and disintegration of the untreated sample and, in the treated sample, only a minor, permanent reduction in height of ~1.5% and no noticeable change in diameter.

The load on the samples was then increased to the maximum setting of 20 tonne (~3130MPa) and, in the case of the hydrogen treated samples, this procedure changed dramatically the shape of the material, which experienced a height reduction of up to 70% and the material remained mostly as one piece. Figure 8 shows an image of such a sample after a die set compression of 20 tonnes. In marked contrast when the non-treated sample was pressed, the alloy broke apart into a powder, as is seen in figure 9.

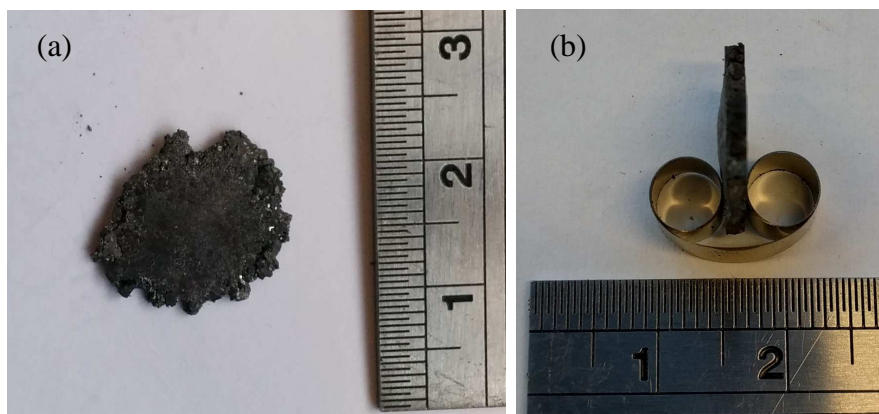


Figure 8 Hydrogen treated Alloy 1 material after 20 tonne compression. (a) Front, (b) side.



Figure 9 Untreated Alloy 1 after only 7 tonne compression

These simple trials serve to emphasise the dramatic change from brittle to ductile behaviour after the hydrogen treatment with the untreated material exhibiting virtually no ductility. This dramatic change has been confirmed by the subsequent, more carefully controlled, compression trials.

The thin compacts, produced from the disproportionated material, could be handled without disintegrating into a powder, with little to no powder being left behind after the compression test. Some small, but solid pieces of the compact appeared to have broken off at the unconfined edge of the samples, thus giving the flower-like appearance, as shown in figure 8(a).

3.4 Mechanical Testing

Cylinders (~9mm diameter and ~5mm height) of the disproportionated cast materials were compressed in order to ascertain the detailed stress-strain behaviour of the various samples.

Figure 10 shows the curves for the hydrogen treated Alloy 1 cast material.

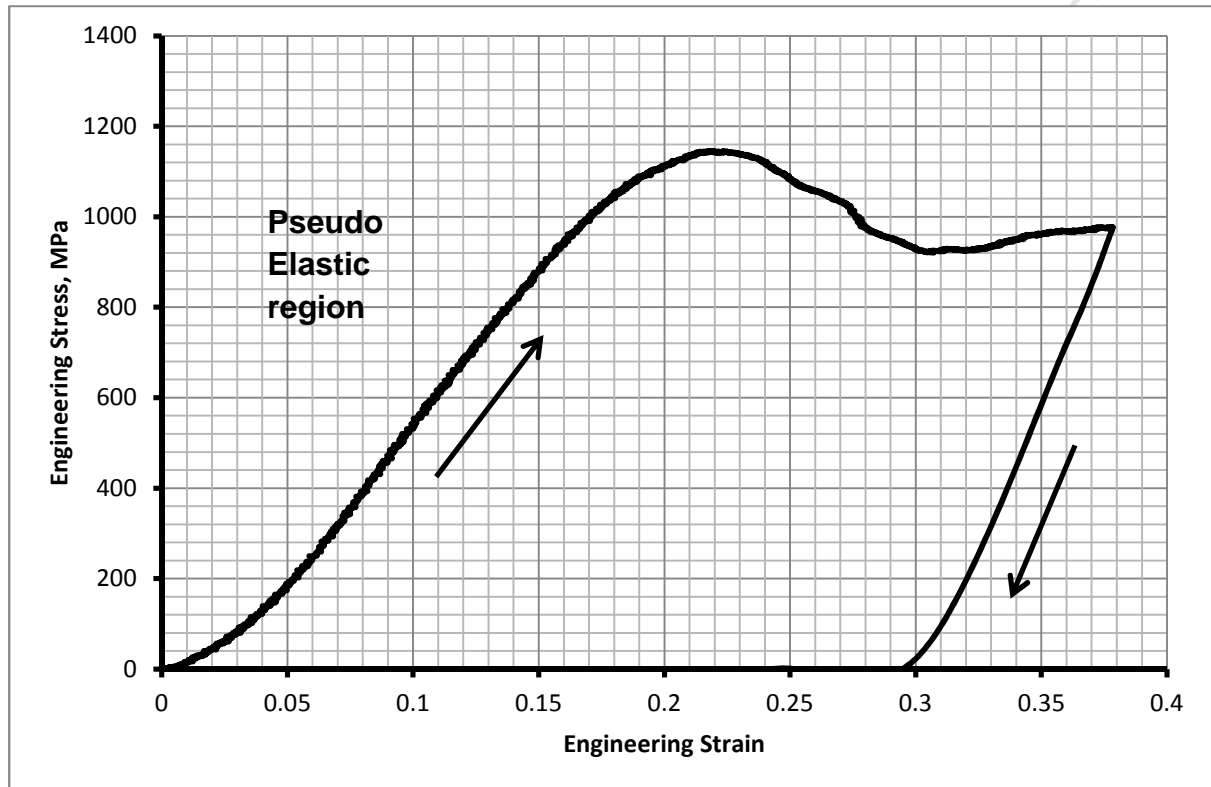


Figure 10 Stress-strain curve of hydrogen treated Alloy 1 material compressed at a rate of 0.5mm/min

The very extensive pseudo-elastic range and the decrease in stress after the apparent yield point shown in figure 10 are likely to be due a brittle component in the material, resulting in some local fracturing of the sample which would decrease momentarily the stress level in the sample.

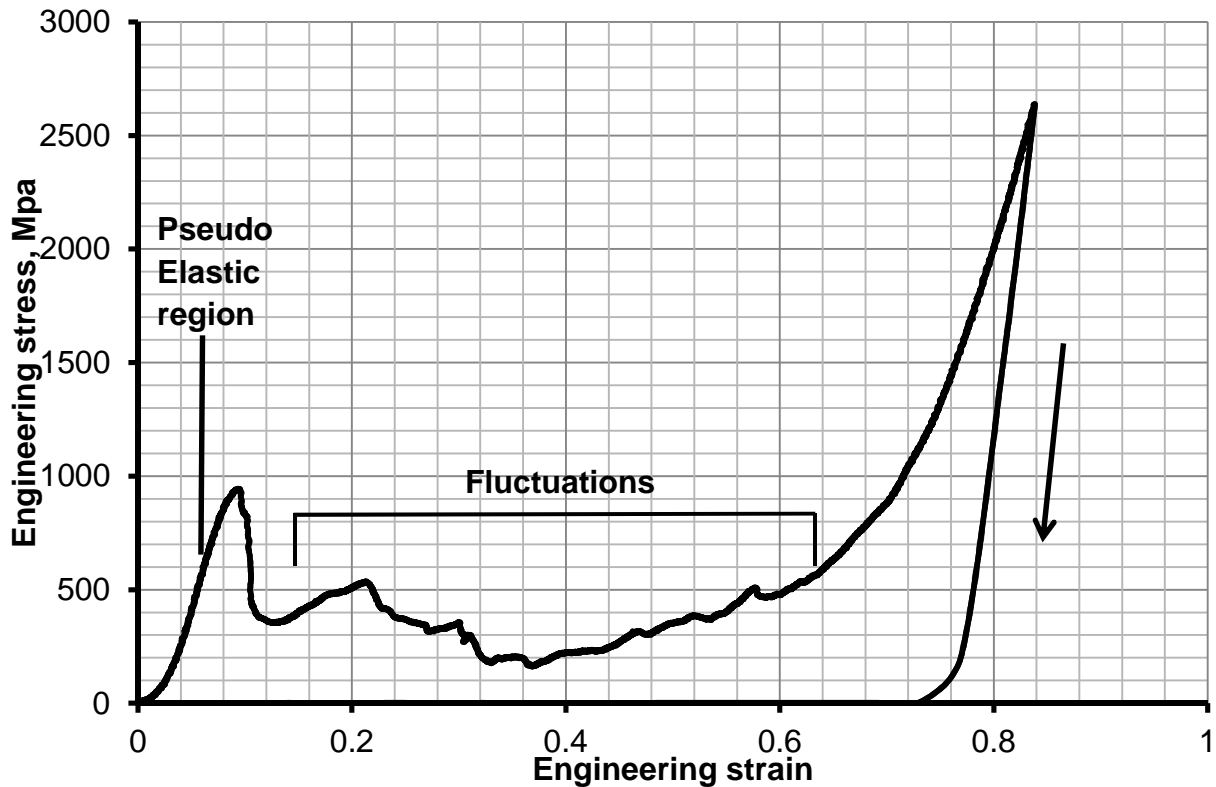


Figure 11 Stress-strain curve for a hydrogen treated Alloy 2 compressed at a rate of 0.5mm/min

Figure 11 shows the stress-strain curve for an Alloy 2 sample which has significant differences to the behaviour shown in figure 10. The apparent yield point for the hydrogen treated material is much more pronounced than in the previous alloy with an almost 50% reduction of the peak stress. There is also a marked reduction in what has been referred to as the pseudo-elastic region. There is further stress relief after this point and this ends with a rapid increase in stress at around 67% reduction in the thickness of the sample. The remarkable feature of figure 11 is the overall reduction in thickness of some 75% and, of this reduction, up to 65% can be achieved at a very low and almost constant stress level. The significant fluctuations in stress shown in figure 11 once again point to a brittle component in the material.

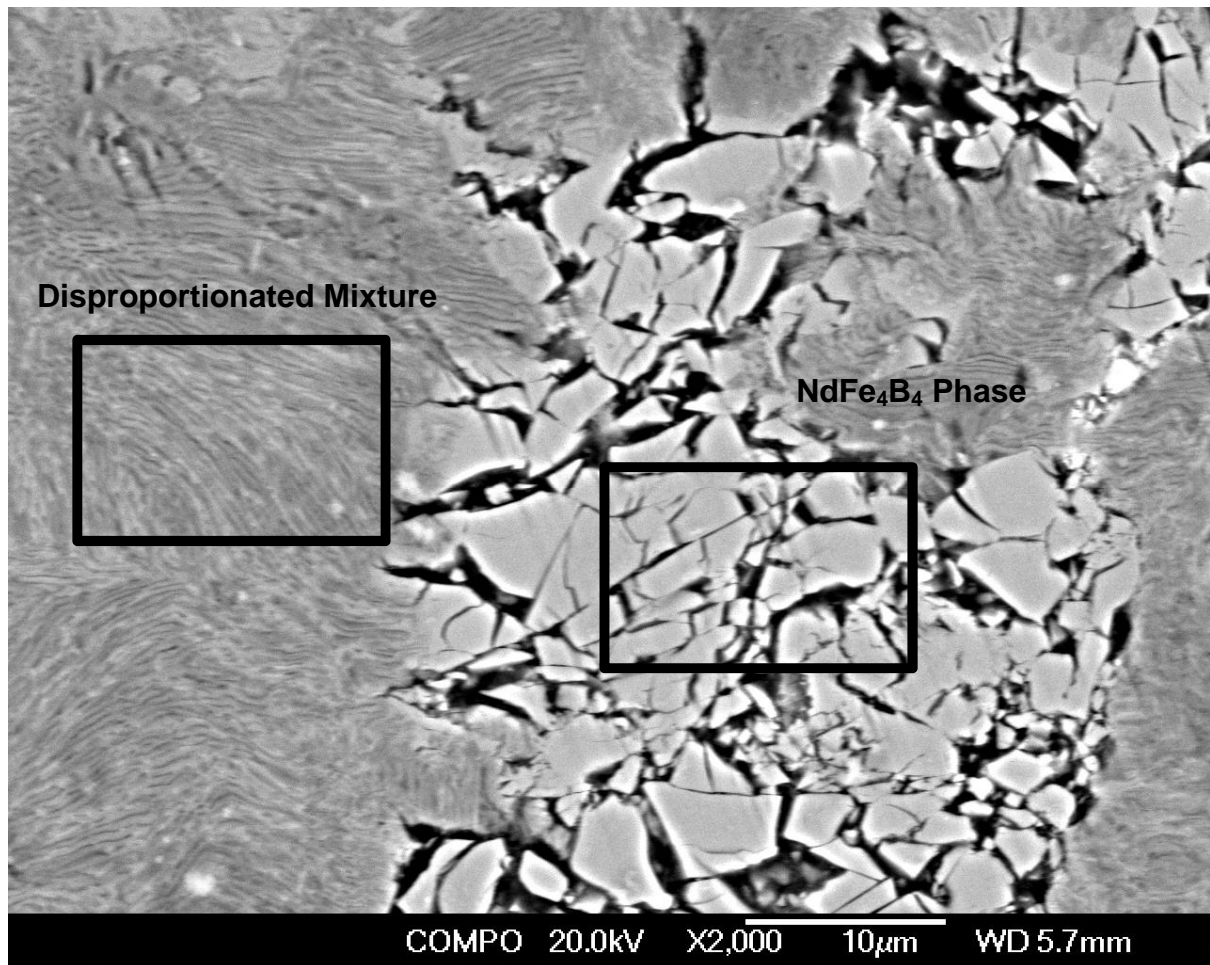


Figure 12 Backscattered SEM image of hydrogen treated and compressed Alloy 1

Figure 12 shows a backscattered SEM picture of a region of a disproportionated Alloy 1 after compression. A critical feature of this microstructure is that all the cracking is confined exclusively to the white phase which has been identified by EDX as the NdFe₄B₄ phase (table 1). The overall extensive ductility of this sample can therefore be ascribed completely to the behaviour of the disproportionated mixture. The behaviour of the NdFe₄B₄ as revealed in this and other micrographs, also explains the behaviour exhibited in the detailed compression trials shown in figure 10 and 11, in terms of the early, apparent yield point and subsequent fluctuations in stress.

Figure 13 shows the backscattered image of the cross section of a compressed sample with the compression axis indicated by the arrows. Where the disproportionated mixture has coarsened at the interface with the iron dendrites, it is possible to discern the elongated nature of the dark (iron) components such that the major axis appears to be perpendicular to the direction of compression. This strengthened further the proposed ductile nature of this mixture.

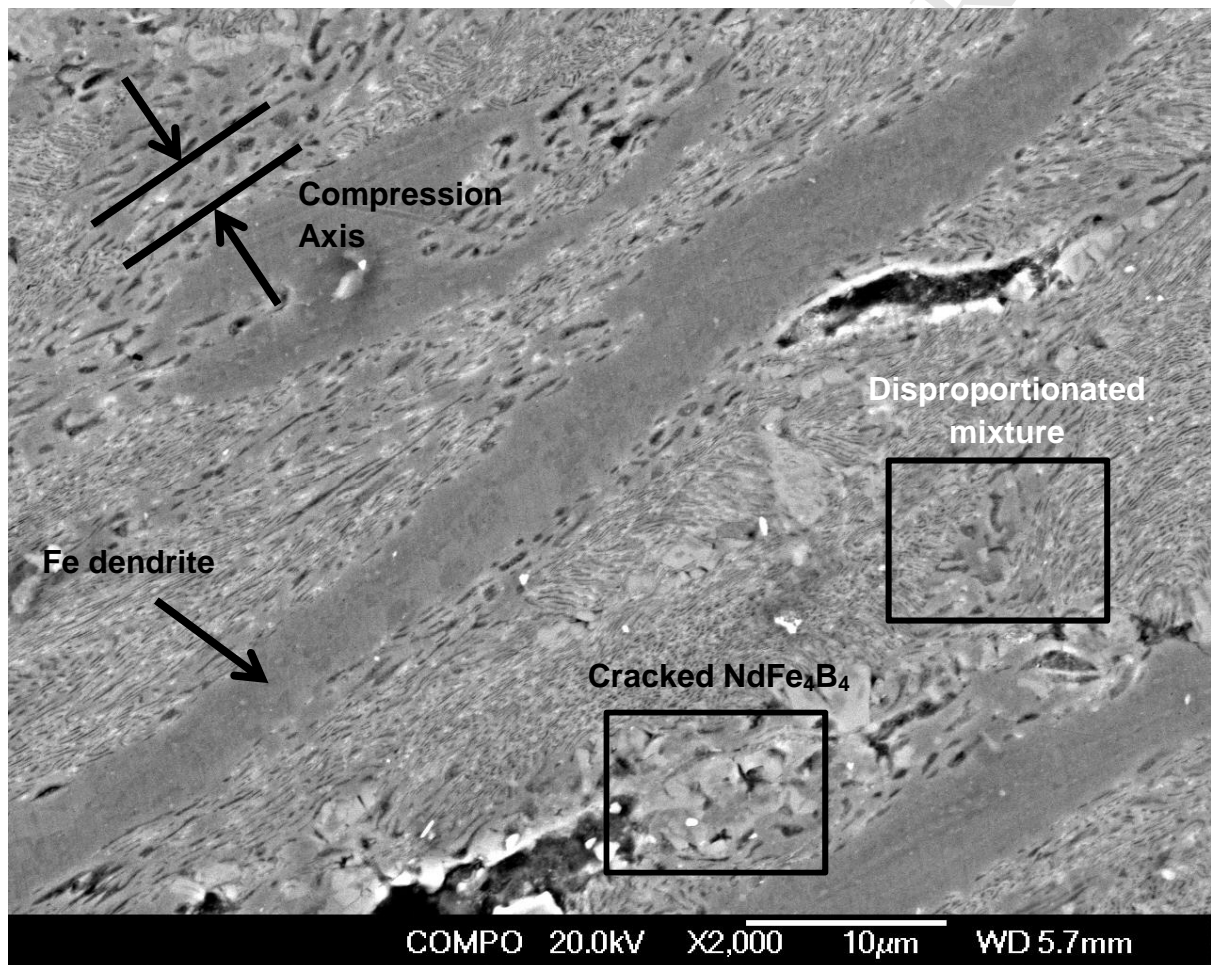


Figure 13 Backscattered SEM image of a cross section of Alloy 1 hydrogen treated material after compression, where the axis of compression is shown in the top left hand corner

As well as the finer, elongated rods of Fe, which is visible adjacent to the dendrite interfacial region in this micrograph, the Fe dendrites also appear to have elongated with respect the applied load.

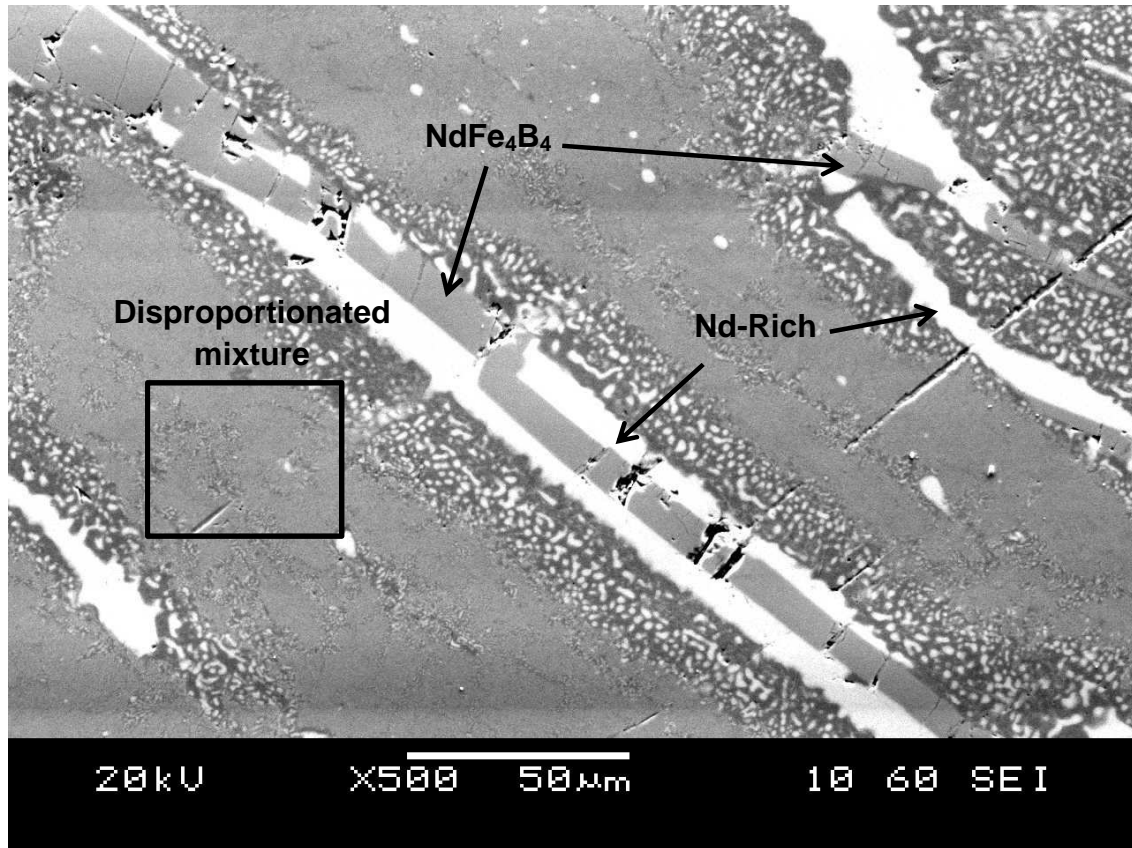


Figure 14 Secondary electron SEM image of hydrogen treated Alloy 2 after compression.

Figure 14 shows the hydrogen treated Alloy 2 after compression. As in the case of the Alloy 1, the NdFe₄B₄ material has begun to fracture whilst the disproportionated matrix remains completely intact.

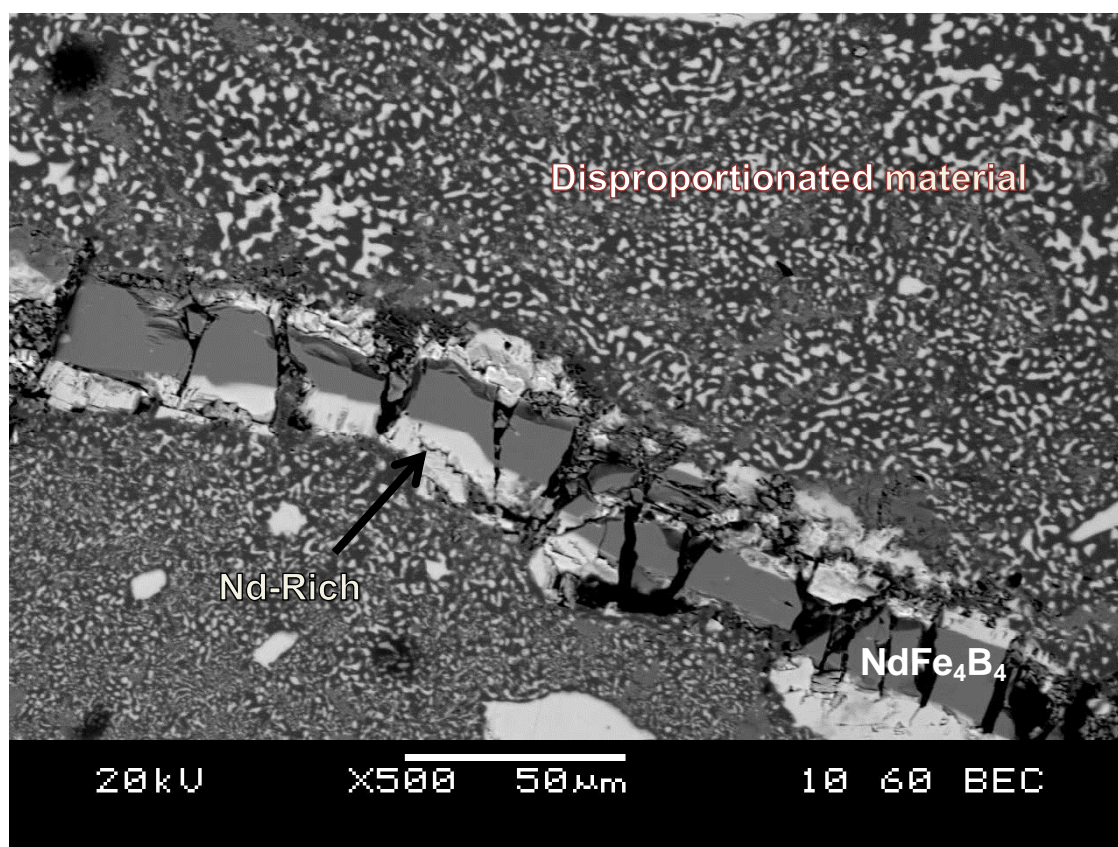


Figure 15 Backscattered SEM image of hydrogen treated Alloy 2 showing extensive fracturing of the NdFe_4B_4 phase after compression

In other areas of the sample the fracturing of the NdFe_4B_4 is far more severe, as can be seen in figure 15. In this image the fracturing has begun to pull the Nd rich material apart, thus causing further fracturing in the material.

On the basis of the SEM images of the compressed material (see figure 12) it has already been speculated that the ductility of the disproportionated materials could be due, partially at least, to the re-alignment of the Fe rods (and probably associated minority phases, NdH_2 and Fe_2B) such that the long axis becomes perpendicular to the compression axis. This process is probably diffusion assisted, aided by the very fine scale of the disproportionated structure. This would be consistent with the extensive range of more or less constant stress shown in

figure 10 and the rapid rise in stress loads can be ascribed to the approaching saturation of the re-orientation process.

This proposition could be tested by a number of measurements such as a determination of the orientation distribution of the Fe rods as revealed by x-ray diffraction and high resolution SEM/EBSD and further work is being carried out in these areas. Such a preferred orientation would be expected to have a strong effect on the subsequent recombination process and could represent an important precursor to the development of magnetic anisotropy.

3.5 Density measurements

The density of the hydrogen treated Alloy 1 material, the results of which are shown in table 4, was determined by weighing the sample in air and then in diethyl phthalate. The untreated cast Alloy 1 exhibited a density 7.548 g/cc. Once disproportionated the density of the disproportionated material was measured to be 7.154 g/cc and once compressed by applying a load of 20 tonne, this value decreased further to 7.067 g/cc. The maximum possible density of stoichiometric disproportionated $\text{Nd}_2\text{Fe}_{14}\text{B}$ is reported to be 7.18 g/cc [21], the differences between this value and the value measured in the present work might be due to the presence of the combination of the Fe dendrites and NdFe_4B_4 phases present in the book mould material. The fall in density after compression can be attributed to localised cracking of the NdFe_4B_4 phase, as observed in the SEM studies.

Table 4 Densities of hydrogen treated samples before and after compression

Sample state	Density g/cc
Untreated	7.548±0.004
Hydrogen treated Alloy 1	7.154±0.004
Hydrogen treated Alloy 1 + compression of 20 tonne	7.067±0.010
Recombined compressed Alloy 1	7.278±0.007

Maximum theoretical density of hydrogen treated material	7.18 [21]
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3.6 Recombination Process

After the compression trials, samples of Alloy 1 were recombined by heating under vacuum to 900°C at a rate of 10°C/min followed by cooling rapidly to room temperature. This treatment produced a solid sample with no powder break off and this resulted in a slight rise in density to 7.278 ± 0.007 g/cc (table 4), this increase can be attributed to the recombination to $\text{Nd}_2\text{Fe}_{14}\text{B}$. The formation of some limited cavitation (A) is shown in figure 16 and this lowers the overall density [21], as will the extensive cracking of the NdFe_4B_4 phase (C). Another distinctive feature of the microstructure is the irregular interface with the Fe dendrites (D), indicative of the partial homogenisation process [27] and this can be observed more clearly in figure 17 where there is evidence of the previous Fe-rich regions.

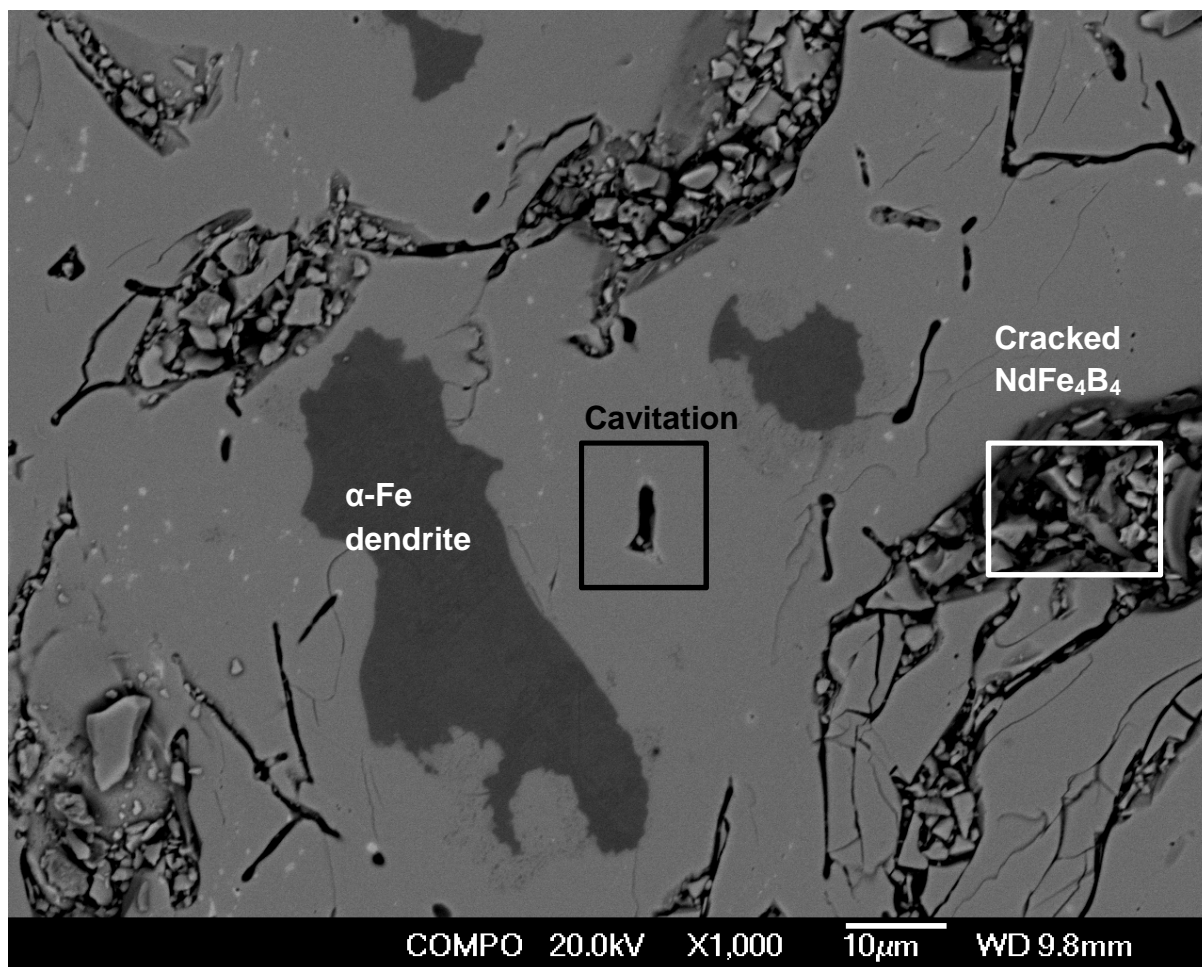


Figure 16 Backscattered SEM image of a compressed and recombined Alloy 1.

It should be noted that, by increasing the degree of homogeneity and employing a stoichiometric composition, it should be possible to eliminate both the cavitation and the NdFe_4B_4 phase, increase the density of the final sample and improve the final magnetic properties shown below.

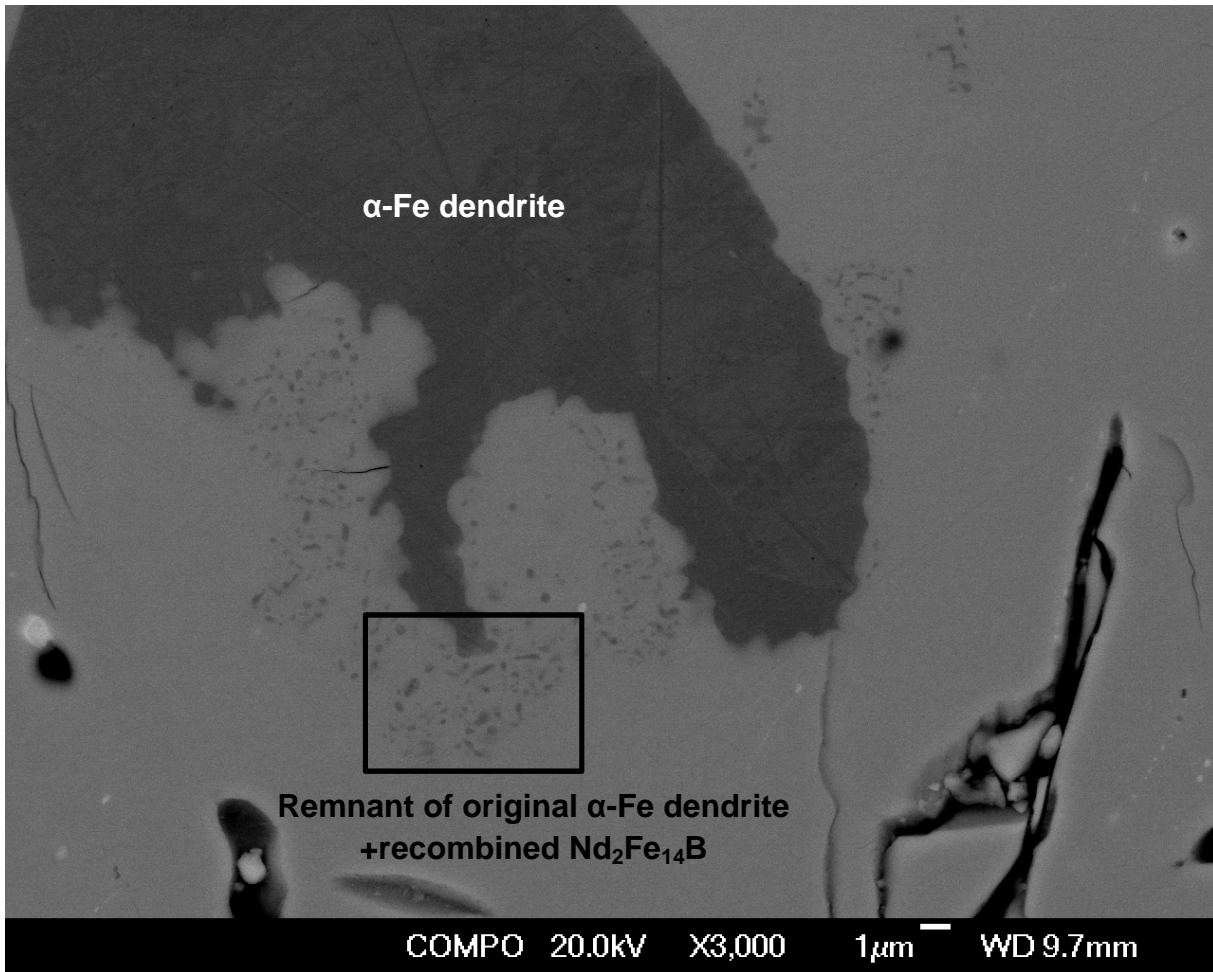


Figure 17 Backscattered SEM image of recombined compressed Alloy 1 material.

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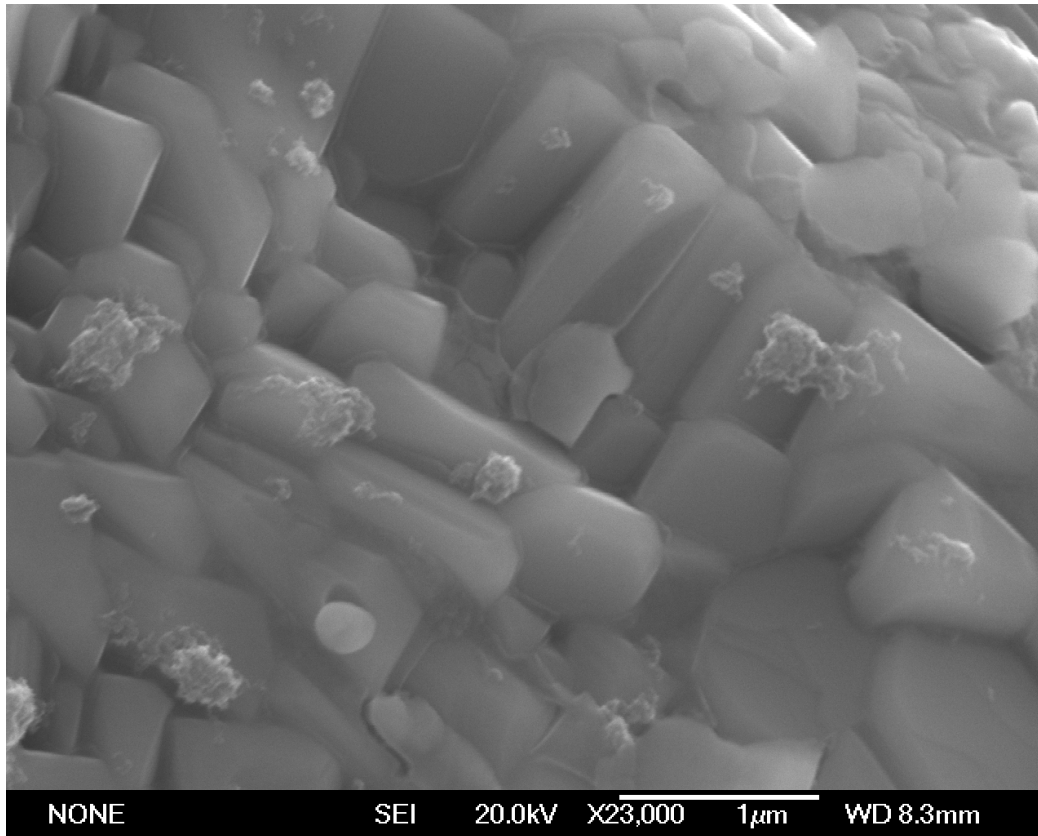


Figure 18 Secondary electron SEM image of fractured surface of recombined compressed Alloy 2

Figure 18 shows a fractured surface from a compressed and recombined Alloy 2 sample. As expected, the majority of the grains appear to be around 500nm. It is also clear from this image that the grains show indications of anisotropy as evident from their columnar shape.

3.7 Magnetic Measurements

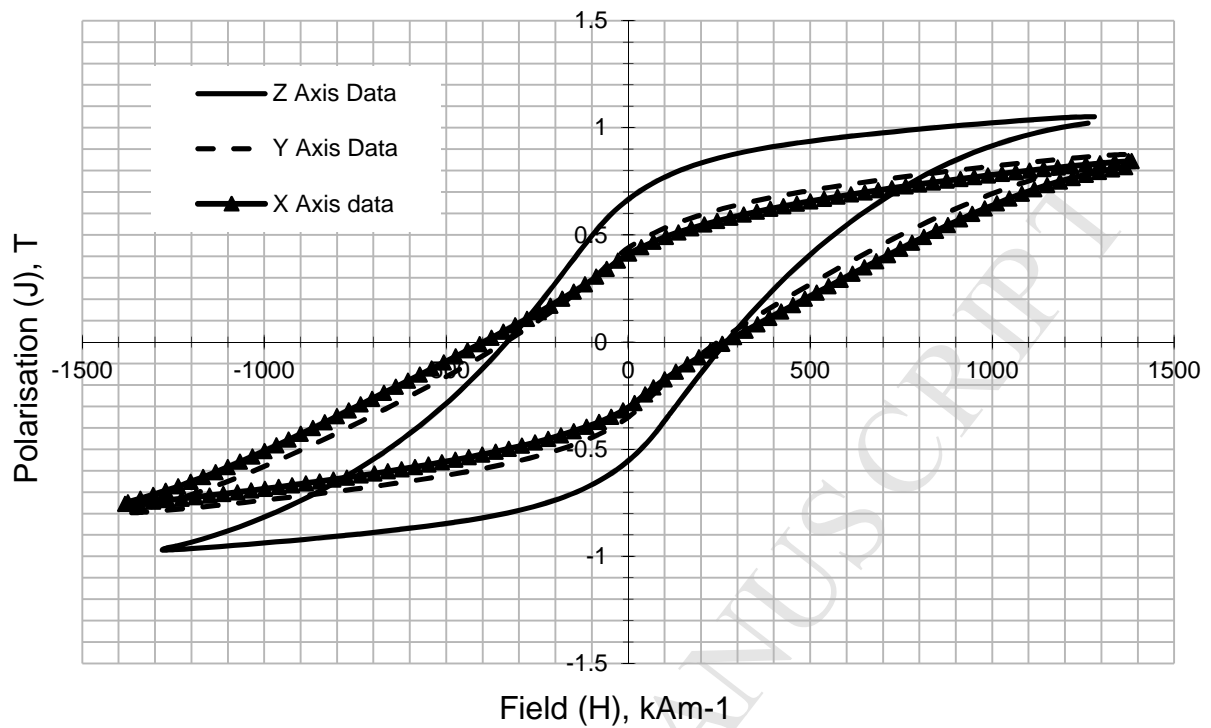


Figure 19 Magnetic hysteresis loop for compressed and recombined Alloy 2

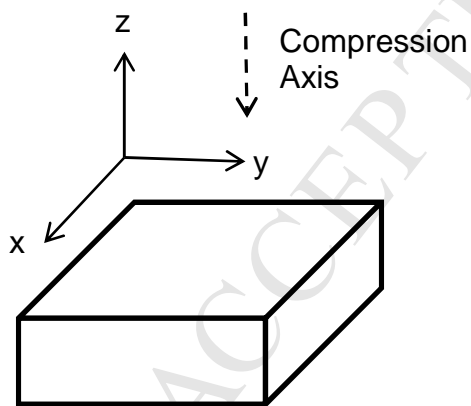


Figure 20 schematic showing axis of compression of the hydrogen treated Alloy 2 sample

Figure 19 and 20 show the magnetic hysteresis loops, with respect to the axis of compression, for a hydrogen treated, compressed Alloy 2 sample which has been recombined. The z

direction is the direction of compression and these results indicate that the compression has had a significant effect on the overall alignment of the material, thus producing an easy axis. As a comparison, figure 21 shows the magnetic hysteresis loop for recombined Alloy 2 which has not been compressed. This sample did not exhibit any signs of any preferred magnetic alignment and a much reduced coercivity. It should be noted that the microstructure of these samples has not been optimised and the results only indicate a preferred axis of magnetisation in the deformed sample.

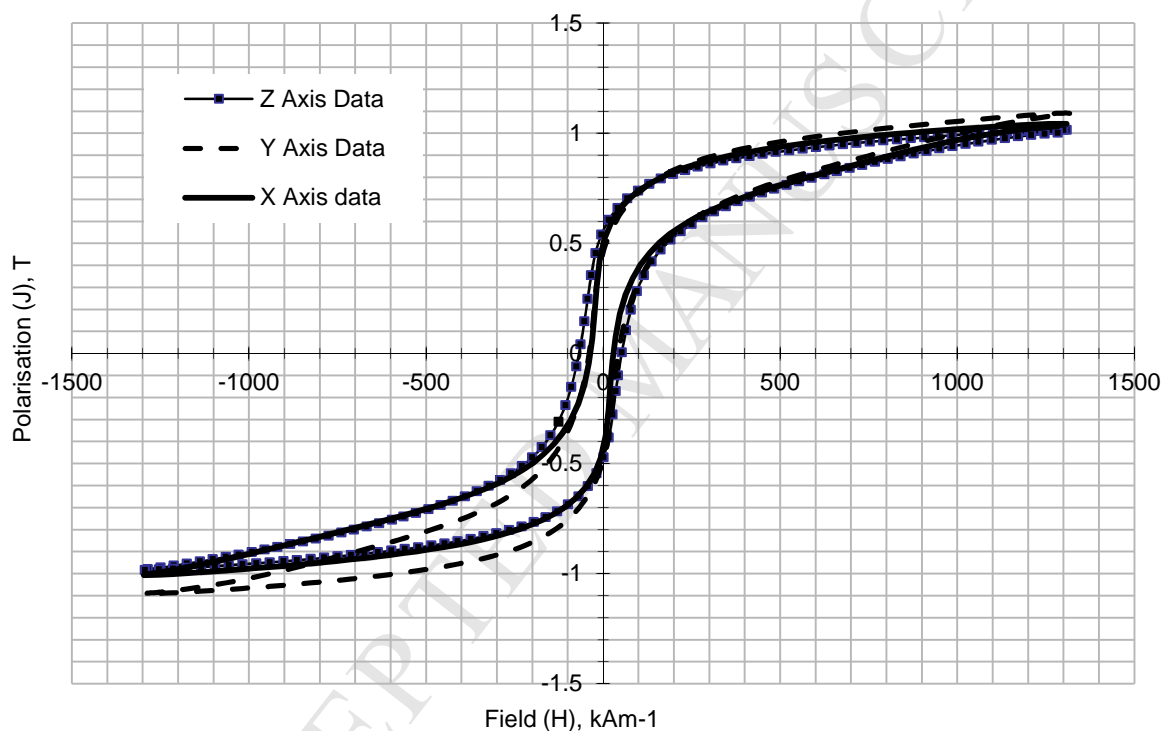


Figure 21 Magnetic hysteresis loop for Alloy 2 after recombination, without compression

4 Conclusion

The present investigations have demonstrated very clearly that the normally, extremely brittle NdFeB-based alloys can be converted to a ductile form by the application of the solid disproportionation process (HyDP) and, where appropriate, this process should have more general applicability. The present studies have also shown that the intimate mixture of

predominantly Fe and NdH₂ exhibits substantial ductility and any brittleness and cracking originates solely from the presence of the NdFe₄B₄ phase which is shown to have fractured extensively after the compression treatment. Preliminary magnetic data has been obtained on the recombined material and, under the present conditions; it has been shown that, by means of the compression treatment, it is possible to introduce a degree of magnetic anisotropy in the material.

By careful control of the composition and homogenisation treatment, it should be possible to produce a material with no or only limited NdFe₄B₄ content and hence reduce the localised cracking in the pressed samples. When this is combined with an optimised set of disproportionation and recombination conditions, together with suitable blending, acceptable values of the coercivity and remanence are likely to be achieved.

The present results could have an important bearing on the production of NdFeB magnets. The ductile disproportionated material could be cold rolled, extruded or forged and the process could also be applied to the hydrogen recycled material, if sufficient ductility can be induced in this material. All these will be the subject of further investigations.

One of the exciting features of hydrogen in all these applications is that the processes are all completely reversible and hence the hydrogen (now in an extremely pure form), can still be reused or consumed as a source of renewable energy via a fuel cell, catalytic burner or gas turbine.

The work outlined in this paper forms part of a pending patent application (GB1511553.8)
[29]

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- Solid hydrogen disproportionation is utilised to increase ductility of Nd₂Fe₁₄B
- Compression trials show an increase in ductility in the disproportionated state
- SEM studies reveal alignment of α -Fe in the compressed, disproportionated state
- Magnetic data shows a degree of anisotropy by means of the compression treatment

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