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3-D Laser Confocal Microscopy Study of the Oxidation of NdFeB Magnets in Atmospheric Conditions

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Abstract

Neodymium iron boron (NdFeB) magnets are used in a number of important applications, such as generators in gearless wind turbines, motors in electric vehicles and electronic goods (eg - computer hard disk drives, HDD). Hydrogen can be used as a processing gas to separate and recycle scrap sintered Nd-Fe-B magnets from end-of-life products to form a powder suitable for recycling. However, the magnets are likely to have been exposed to atmospheric conditions prior to processing, and any oxidation could lead to activation problems for the hydrogen decrepitation reaction. Many previous studies on the oxidation of NdFeB magnets have been performed at elevated temperatures; however, few studies have been formed under atmospheric conditions.

In this paper a combination of 3-D laser confocal microscopy and Raman spectroscopy have been used to assess the composition, morphology and rate of oxidation/corrosion on scrap sintered NdFeB magnets. Confocal microscopy has been employed to measure the growth of surface reaction products at room temperature, immediately after exposure to air. The results showed that there was a significant height increase at the triple junctions of the Nd-rich grain boundaries. Using Raman spectroscopy, the product was shown to consist of Nd_2O_3 and formed only on the Nd-rich triple junctions. The diffusion coefficient of the triple junction reaction product growth at 20°C was determined to be approximately $4 \times 10^{-13} \text{ cm}^2/\text{sec}$. This value is several orders of magnitude larger than values derived from the diffusion controlled oxide growth observations at elevated temperatures in the literature. This indicates that the growth of the room temperature oxidation products are likely defect enhanced processes at the NdFeB triple junctions.

Keywords: NdFeB; Magnet; Oxidation; Confocal Microscopy; Raman Spectroscopy

Introduction

Rare earth permanent magnets based on neodymium-iron-boron (NdFeB) alloys have a wide range of commercial applications. These include renewable energy technologies such as generators in gearless wind turbines, electric/hybrid vehicles and also in everyday applications such as computer hard disk drives (HDDs).

Recent studies [Walton et al, 2012; Walton et al, 2015] have shown that, by hydrogen processing, it is possible to separate NdFeB sintered magnets from electronic waste such as HDDs. The hydrogen breaks down the magnets into a non-coercive, hydrogenated powder [Harris, 1987], which can then be re-processed directly by sintering to produce new NdFeB magnets [Zakotnik et al, 2010]. In service, or during storage, sintered NdFeB magnets are likely to have been exposed to atmospheric conditions and hence will be coated with a surface oxide, which forms readily under these conditions. The presence and degree of such a layer on the magnets is likely to vary and could, therefore, influence the onset of hydrogen decrepitation and/or further processing into new magnets [Walton et al, 2012].

Further processes during recycling of sintered NdFeB includes re-sintering, melt spinning and hydrogenation-disproportionation-desorption-recombination (HDDR). It has been shown by Sheridan et al [2016] that the disproportionation stage of the HDDR process initiates along grain boundaries and triple junctions for processing of sintered NdFeB-type magnets. It was found that oxidised triple junctions do not react with hydrogen to form NdH_2 , leading to poor redistribution of the non-liquid Nd-rich phase during subsequent recombination. Therefore characterisation of the oxidation mechanism and reaction products formed on NdFeB magnets under atmospheric conditions is of high importance for all stages of the recycling process.

The existing literature relates predominantly to the oxidation of powdered NdFeB samples [Osawa et al, 1992; Higgins & Osterreicher, 1987], gravimetric measurements of corrosion/oxidation phenomena at room temperature or low temperature (80°C) on solid NdFeB magnets [Tenaud et al, 1990; Jacobson & Kim, 1987] or high temperature (>250 °C) XRD/microscopy studies of the oxidation of solid NdFeB samples [Edgley et al, 1997; Skulj et al, 2005].

Sintered NdFeB magnets often have, predominantly, a three-component microstructure: the matrix phase, $\text{Nd}_2\text{Fe}_{14}\text{B}$ (Φ -phase), the Nd-rich grain boundary phase, and a very small amount of $\text{Nd}_{1.1}\text{Fe}_4\text{B}_4$ (η -phase). The Nd-rich grain boundary phase forms predominantly at triple junctions where the grain boundaries intersect. The phases present in the Nd-rich grain junctions have been described by Fidler [1987], Vial et al [2002], Sepehri-Amin et al [2012] and Woodcock et al [2012] to contain crystalline oxides such as NdO , Nd_2O_3 and NdO_2 , which tend to be in the centre of the triple junctions. If other rare-earth elements such as Pr and Dy are present in the material, then other phases such as $(\text{Nd,Pr,Dy})_2\text{O}_3$ are formed. Studies of the oxidation and corrosion of NdFeB have sought to relate the observed degradation mechanisms and observed corrosion and oxidation products to these salient microstructural features of NdFeB.

From the XRD spectra of as-prepared NdFeB surfaces, Edgley et al [1997] inferred that NdO_x was likely to be present in the Nd-rich grain boundaries. As the temperature of oxidation was increased it was noted that the NdO_x phase stabilised into Nd_2O_3 . Above 250 °C, the matrix phase (Φ - $\text{Nd}_2\text{Fe}_{14}\text{B}$) dissociated into a mixture of α -Fe and Nd oxides, observable as a grey uniform layer. At

temperatures higher than 250 °C, the dissociated layer grows transgranularly through the magnet. It was noted that the grain boundaries were not involved in the progression of oxide growth at higher temperatures. Li et al [2003] reported a similar dissociation phenomenon in the oxidation of NdFeB in air at 500 °C.

Tenaud et al [1990] reported that sintered NdFeB magnets degraded in conditions of 80°C/90% humidity by the rapid formation of Nd(OH)₃ in the grain boundary regions. Similar findings were reported by Tokuhara & Hirose [1991]. Jacobson & Kim [1987] measured the weight gain of a NdFeB magnet exposed to atmospheric conditions at 20-50 °C over 6 weeks and found that oxidation products formed randomly near the edge of the specimen. They noted that the product consisted mainly of iron oxides/hydroxides with small amounts of neodymium oxides. The authors summarised the effects of alloy oxygen content on the corrosion stability of NdFeB magnets by noting that the magnetic properties are gradually lost due to the oxidation of the Nd-rich phases at the grain boundaries. Fidler [1987] arrived at similar conclusions, again proposing the grain boundaries as the likely site of oxidation/degradation in sintered NdFeB magnets. In reviewing earlier work, Kobayashi et al [2002] concluded that the corrosion of NdFeB magnets proceeds mainly in the Nd-rich grain boundaries and also noted that, the humidity of ambient air at room temperature may encourage the formation of Nd(OH)₃ in the initial stages of degradation.

In summary, the low temperature studies of sintered NdFeB magnets exposed to atmospheric conditions indicate that:

- In humid conditions at low temperatures, the degradation of the magnetic properties is rapid and proceeds by the formation of Nd(OH)₃ and Fe/Nd oxides. The reaction rates are influenced strongly by the test conditions, the specific composition of the magnet and the trace amounts of environmental contamination.
- For dry air at low temperature, whilst the rates are lower than in the presence of humidity, the particular nature of the oxidation of the matrix phases remained unidentified.
- During several studies of the oxidation of NdFeB in dry air, the NdO_x-type oxide is assumed to be associated with the Nd-rich grain boundaries, but no direct observations have been made.

The purpose of the present work is to investigate the initiation and early stages of growth of oxidation/corrosion products on sintered NdFeB surfaces, in air at room temperature. None of the earlier work appeared to have examined the nucleation and growth of the reaction products on sintered NdFeB surfaces in this manner at room temperature. The nucleation and growth phenomena have been investigated using primarily, confocal microscopy. The oxide/corrosion product(s) have been established using Raman spectroscopy equipped with a confocal microscope. This is believed to be the first time these types of instrument have been employed in studies of this kind. The studies were carried out in an air conditioned laboratory atmosphere and no attempt was made to control or vary the degree of humidity.

Experimental

Sintered NdFeB magnets (Ugimag, China) with a composition of $\text{Nd}_{12.52}\text{Pr}_{0.17}\text{Dy}_{1.8}\text{Fe}_{72.49}\text{B}_{6.44}\text{Al}_{0.88}\text{Co}_{4.98}\text{Nb}_{0.61}$ (minor constituents not included) (at%) have been investigated. In order to minimise exposure to oxygen and water vapour before starting the experiment, all preparatory work on the magnets was carried out in an argon filled glove box. To remove any pre-existing oxide layer, the samples were ground, under cyclohexane in the glove box using P400, P800 and P1200 grit silicon carbide grinding paper. The samples were then polished using 6 μm , 1 μm and 0.25 μm diamond polishing paste again under cyclohexane. The samples were transferred under an argon atmosphere to the microscope using a Kilner jar. Images of the magnet surfaces were recorded, in air, using an Olympus LEXT OLS3100 Confocal Scanning Laser microscope at 100x magnification. The sample surface was imaged every 20 seconds for a total of 6 hours in order to characterise the reaction of the sample with the atmosphere and any associated change in height. The images were then analysed using step measurement readings. The microscope had a planar resolution of up to $\pm 0.12 \mu\text{m}$ and a height resolution of up to $\pm 0.01 \mu\text{m}$.

Scanning electron microscopy (SEM) equipped with energy dispersive x-ray spectroscopy (EDS) and wavelength dispersive x-ray spectroscopy (WDS) of the as-prepared and reacted samples was also undertaken using a Jeol 7000 microscope. The magnets were cross-sectioned and ground in the glove box and were then polished according to the procedure described above.

A Renishaw inVia Raman spectrometer equipped with a confocal microscope was used to identify the nature of the corrosion products developed on the surface of the magnets. The magnets were first ground and polished using an identical procedure to that described above. They were then exposed to air at room temperature for 2 hours in order to allow sufficient time for reaction.

Results and Discussion

Confocal microscope observations of reactant growth, morphology and kinetics

Once polished in the glove box, the NdFeB samples were exposed to air at room temperature and the surface imaged at 20 second intervals for a total period of 6 hours. The 3D images over the first 60 minutes of air exposure are shown in figure 1. It is evident from figure 1 that the detectable reaction products nucleate exclusively at grain boundary triple junctions. In agreement with earlier work by Fidler [1987], SEM with EDX studies have confirmed these sites to be much more Nd-rich compared to the Nd content of the matrix phase.

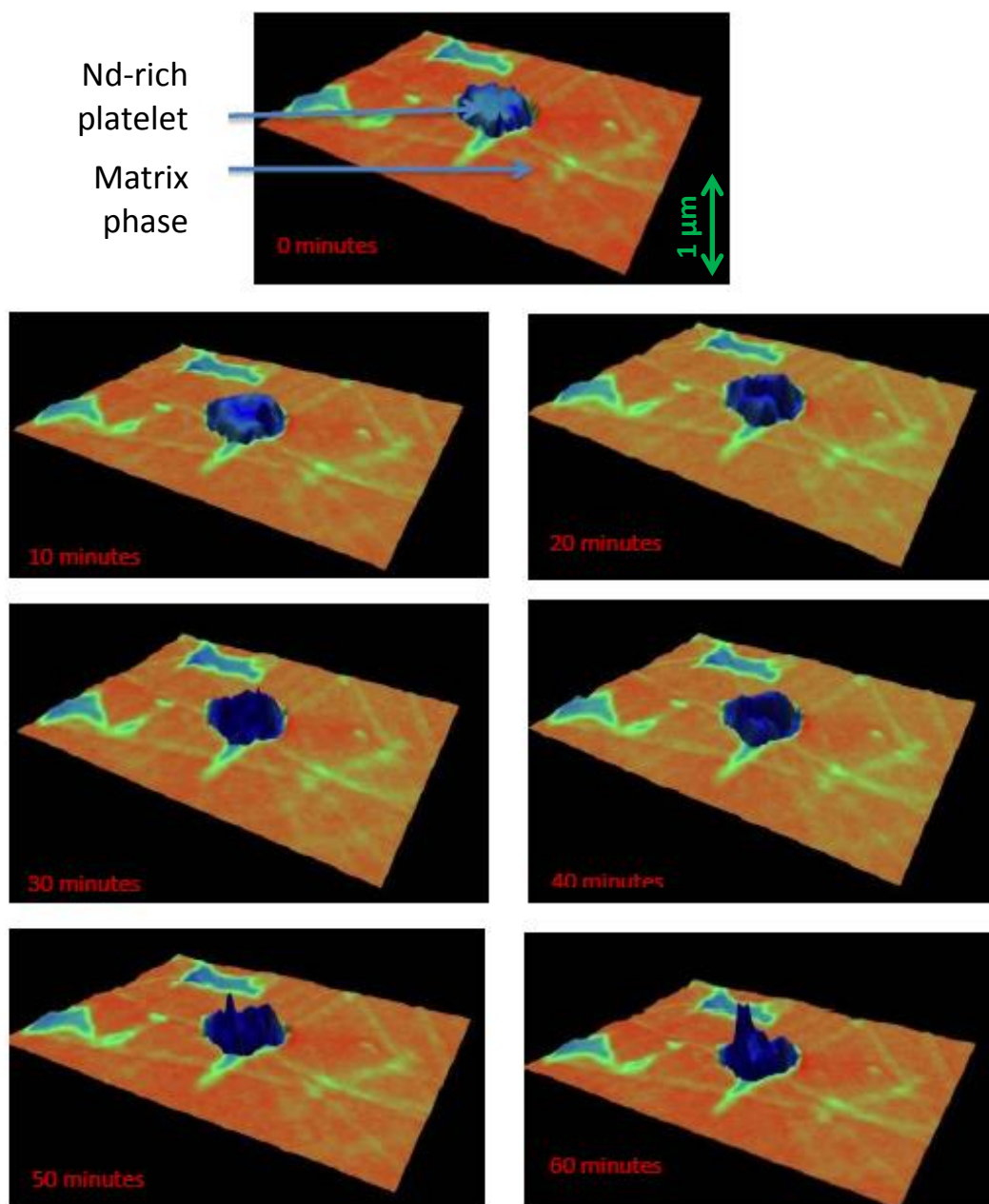


Figure 1 - 3D confocal image of a Nd-rich triple junction imaged at 100x magnification after exposure to air at room temperature for a total of 1 hour.

The reaction at the triple junction appears to take place in two stages:

Stage 1: During the first few seconds of exposure to the atmosphere there is very rapid formation of reaction product platelets, approximately 1 μm diameter and 0.2 μm height. This can be observed at the 0 minutes mark as the sample was loaded onto the confocal microscope.

Stage 2: Subsequent growth of the reaction product occurs within the initially formed platelet perimeter, however, different areas within the perimeter grow at significantly different rates. The differential growth rates could be due to the variation of composition within the Nd-rich triple junction. After 6 hours there was an average height increase of 0.7 μm of the highest features of the reaction products, but no apparent change in the appearance of the matrix phase.

During this period there was also little increase in the lateral dimensions of the platelet footprint beyond that observed in Stage 1. Within the 6 hour period of this experiment, there was no apparent change in the composition or morphology of the matrix phase, which SEM with EDS studies confirmed to be $\text{Nd}_2\text{Fe}_{14}\text{B}$ (Φ -phase). It is possible, however, that the matrix phase could have increased uniformly in height upon exposure to air. The surface of the matrix phase has been used as a reference for the step height measurements of the grain boundary triple junctions shown in figure 3 and this could lead to inaccuracies in the absolute step height measurement. EDS and WDS line scan analysis confirmed much higher oxygen content in the Nd-rich triple junction at the edge of a sample than in the matrix phase, as shown in Figure 2.

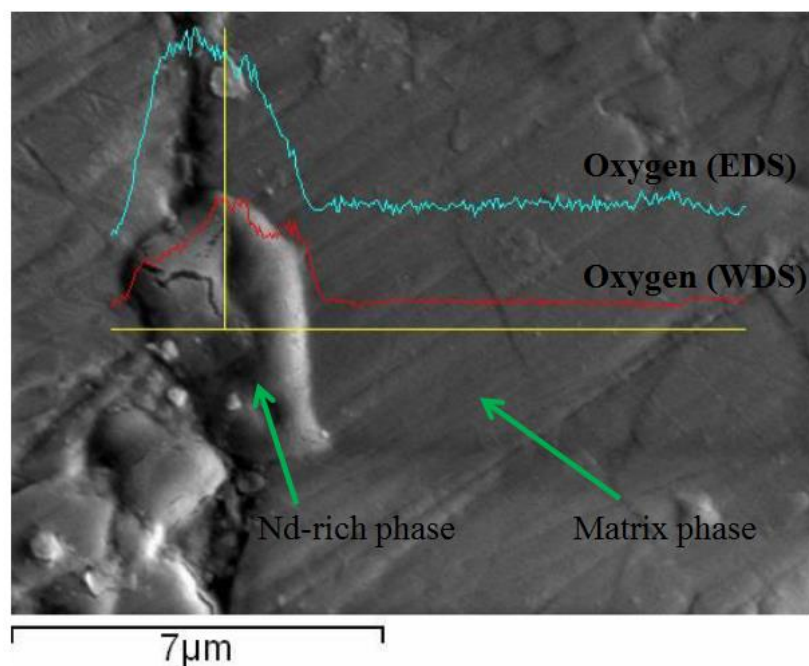


Figure 2 – EDS and WDS traces of oxygen content through Nd-rich and matrix phases at the edge of a sintered NdFeB magnet.

In Figure 3, the average peak height of 6 triple junction reaction products is plotted versus square root of time for 6 hours of air exposure. The straight line dependence of height versus \sqrt{t} suggests that the underlying growth mechanism is diffusion controlled. Using the formula $x = \sqrt{Dt}$ where x is the diffusion distance, i.e. height of feature (cm), D the diffusion coefficient (cm^2/s) and t is time (s) yields a value of $4 \times 10^{-13} \text{ cm}^2/\text{s}$ for the diffusion coefficient of growth of the reaction products in Stage 2.

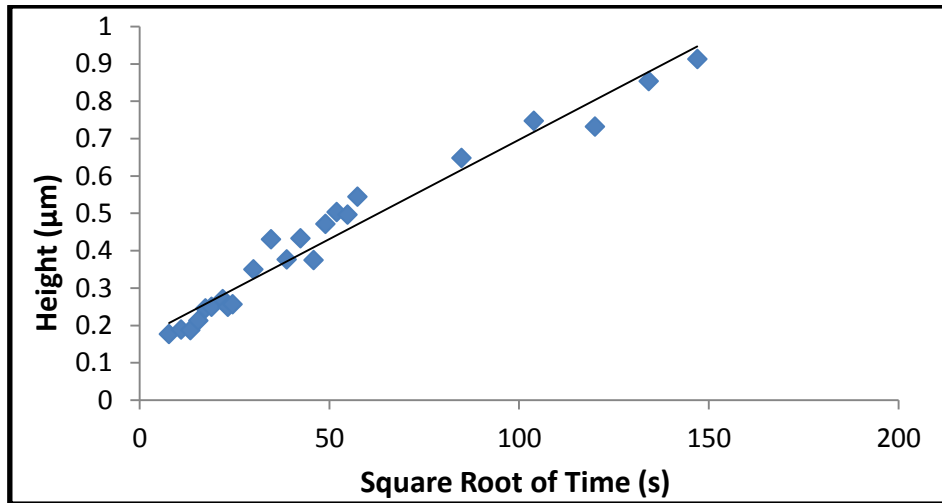


Figure 3 – Average height of 6 Nd-rich triple points versus the square root of time when exposed to air for 6 hours.

Raman spectroscopy

Raman spectroscopy was used to identify the corrosion products observed on the surface of the NdFeB magnets. An in-situ confocal microscope was used to focus on the grain boundary triple points of the magnets. Strong resonances were observed (as shown in figure 4). There is an excellent match with the spectra obtained from a Nd_2O_3 reference specimen. No peaks corresponding to $\text{Nd}(\text{OH})_3$ or $\text{Fe}(\text{OH})_2$ were observed.

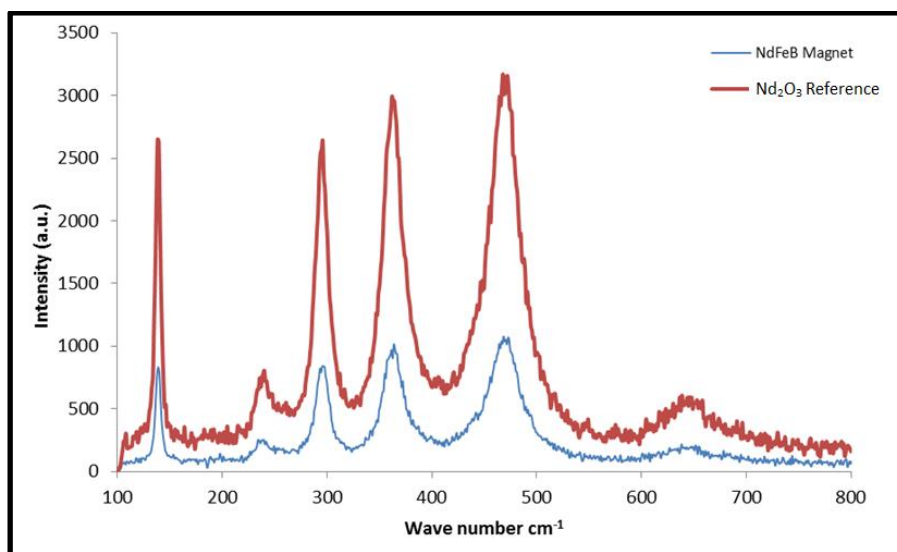


Figure 4 - Raman results for the corroded triple point area of a NdFeB magnet compared with the spectrum for Nd_2O_3 .

General Discussion

In the present study, direct optical imaging has shown that rapid oxidation reactions occur at the Nd-rich triple junctions of the NdFeB surfaces on exposure to the laboratory atmosphere. Once removed from the inert argon atmosphere, the initial reaction (Stage1) at specific triple junctions on the surface is very rapid, giving a reaction product step height of $\sim 0.15 \mu\text{m}$ in 60 seconds.

In the present work no direct evidence of reaction products forming on the surface of the matrix phase has been found. However, it can be assumed realistically that the matrix $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase has formed an oxide layer coating with thicknesses of $\sim 100 \text{ \AA}$ after just a few seconds of growth, as previously described by Blank & Adler [1987]. For instance, Hongling et al [1993] reported the formation of oxides films of $\sim 10 \text{ nm}$ thickness on $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ surfaces at room temperature and noted it is likely that similar thin oxide layers would be present on NdFeB magnet surfaces. Skulj et al [2005] used X-ray diffraction (XRD) and Mössbauer spectroscopy to analyse the oxidation products of powdered NdFeB samples which were oxidised at 400°C for 96 h. It was observed that, in NdFeB powders, the main products were $\alpha\text{-Fe}_2\text{O}_3$, Nd oxides, Dy oxides (if Dy was present in the starting composition) and $\text{Nd}(\text{BO}_2)_3$.

As noted earlier, the diffusion coefficient estimated (from Figure 3) for the growth of the reaction products in Stage 2 is $4 \times 10^{-13} \text{ cm}^2/\text{s}$. There are no previously reported values of diffusion coefficients for the growth of oxidation reaction products on NdFeB surfaces at room temperature. In contrast there have been studies of the oxidation of bulk NdFeB in air at elevated temperatures; these are listed in Table 1.

Table 1 Oxidation of NdFeB Bulk samples.

Temperature range ($^\circ\text{C}$)	Atmosphere	Activation Energy (eV)	Reference
400-600	Air	1.27	Blank & Alder, 1987
365-611	Air	1.18	Edgley et al, 1997

Using data from the references in Table 1 to calculate values for the oxide growth on bulk NdFeB at room temperature yields diffusion coefficients in the range $10^{-21} - 10^{-17} \text{ cm}^2/\text{s}$. These values were calculated using the formula: $D = D_0 e^{-E_a/kT}$, where D is the diffusivity (cm^2/s), D_0 is the diffusivity pre-exponential factor, E_a is the activation energy (eV), k is the Boltzmann constant and T is the temperature (K). This range of values is several orders of magnitude smaller than the observed value derived from the room temperature oxide growth observations of the present work. This indicates that the growth of the observed room temperature oxidation products cannot be controlled by bulk diffusion processes operating at higher temperatures, hence, defect enhanced processes at the NdFeB triple junctions are the likely mechanisms. Since the activation energy for defect/grain boundary diffusion is generally much smaller than for bulk diffusion its effects tend to dominate at lower temperatures [Kirkaldy & Young, 1985] and arise from mechanisms other than those operative at higher temperatures. Similar behaviour has been reported elsewhere. The room temperature

diffusion coefficient derived here is in the range reported for defect/grain boundary diffusion processes.

Grain boundary and triple junction diffusion processes depend on the dimensions, the amount of, and composition of the boundary constituents. The precise structure and compositional distribution within sintered NdFeB triple junctions continues to be a subject of study. For example, recent work by Sepehri-Amin et al [2012] has shown that, within NdFeB triple junctions, there may be Nd-rich phases such as Nd, NdO_x and Nd₂O₃ present, with the metallic Nd predominantly at the sharp edges of the triple junction. The observed irregularity of the reaction product growth morphology observed in the present work could reflect the underlying compositional variations underlying the triple point areas.

The present work shows that, at room temperature and in laboratory conditions, some, but not all, triple junctions become decorated with reaction products with growth rates commensurate with defect/enhanced/electrochemical processes. Still under investigation are the compositional details of the reaction products, the associated kinetics of formation and role of ambient conditions.

This work could have implications with regard to the mechanism of hydrogen decrepitation of sintered NdFeB magnets during the well-established recycling process described by Walton et al [2012] and Walton et al [2015]. During this process, scrap sintered NdFeB magnets are damaged in air to expose a clean surface suitable for hydrogen decrepitation. Formation of oxides at triple junctions could act as a barrier to surface activation of the hydrogen absorption, which could inhibit the onset of the decrepitation process. Further work is ongoing to determine the effect of oxygen exposure on the onset of hydrogen decrepitation and subsequent recycling processes such as re-sintering and the HDDR process (as outlined by Sheridan et al [2016] will be included in future publications.

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