High temperature oxidation of rare earth permanent magnets. Part 2–Kinetics

Muhamad Firdaus[a,b], M. Akbar Rhamdhani[a,*], Yvonne Durandet[a], W. John Rankin[a,b], Kathie McGregor[b]

[a] Department of Mechanical and Product Design Engineering, Swinburne University of Technology, Melbourne, VIC 3122, Australia
[b] CSIRO Mineral Resources, Clayton, VIC 3169, Australia

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ABSTRACT

Oxidation is an integral part of some high temperature recycling routes for rare earth permanent magnets. This paper deals with a study of oxidation kinetics of commercial permanent (Nd,Pr)FeB magnet samples, re-sized to $5 \times 5 \times 10$ mm, in the temperature range 700–1500 K. The results show that the oxidation behaviour follows a parabolic rate law and that the kinetics can be described using the Ginstling–Brounshtein diffusion model. In line with the microstructure study that shows three different oxidation mechanisms, the kinetics study also reveals that there are probably three different rate-controlling mechanisms in the temperature range studied.

1. Introduction

Understanding the oxidation of Rare Earth Permanent Magnet (REPM) at high temperature is important for the development of processing techniques and strategies to recover rare earth elements (REE) such as Nd, Dy and Pr from end-of-life (EoL) REPM. Many existing techniques and process routes (through pyrometallurgy, hydrometallurgy, and their combination) for recovery of REE require information on the oxidation including the kinetic behaviour [1–4]. There is currently little information on the kinetic behaviour and formation mechanisms of the oxides from new and waste REPM, particularly at high temperatures (T > 700 K). Simple oxidation observations, mostly at low temperatures, have been carried out to support the study of specific techniques but there has been little attempt to date to understand the mechanisms.

The corrosion and oxidation kinetics of REPM in air have been extensively studied in the context of the degradation of magnetic properties at temperatures up to 873 K. Blank and Adler [5] demonstrated that oxidation at temperatures between 673 and 873 K results in the formation of a grey layer on the surface of the bulk magnets which was attributed to iron oxide phases. Later work on the oxide microstructure of bulk NdFeB magnets was carried out by Breton and Edgley et al. [6,7] mainly using conversion electron mössbauer spectroscopy (CEMS) to identify the oxidation products. Based on the fitting of Mössbauer spectra of each oxidised powder, Steyaert et al. [8] determined the

mössbauer relative intensity of the $Nd_2Fe_{14}B$ phase to investigate the oxidation kinetics. The experimental kinetic conversion R was defined by

$$R = \frac{V(t)}{V(t=0)} x100 \qquad (1)$$

where V(t) is the volume of the $Nd_2Fe_{14}B$ phase at time t based on the relative intensity of the $Nd_2Fe_{14}B$ phase contribution to the Mossbauer spectrum after t days at a given temperature. They found that the R curve fitted the Jander diffusion model and the activation energy E_a and the diffusivity D_o of the intragranular diffusion process were determined to be $110 \, kJ \, mol^{-1}$ and $2.4 \, mm^2 \, s^{-1}$, respectively.

Li et al. [5], Skulj et al. [9] and others [10–14] further studied the microstructures of the oxidised material. It has been established using SEM and TEM that the dominant grey zone is a zone of internal oxidation (IOZ) consisting principally of an α-Fe matrix containing Nd-oxide particles [5,15–17]. The external surface oxide layer (EOZ) appeared not to inhibit further diffusion of oxygen. They found that the thickness of the IOZ increased parabolically with oxidation time. At lower temperatures (423–573 K), a general parabolic oxidation behaviour was also observed in studies using thermogravimetric analysis [18]. The results showed that rapid surface oxidation on powdered, uncoated REPM occurred within the first minute and that this became substantial as the average particle size decreased [18–20]. The internal-oxidation kinetics has been described in terms of Wagner's model as

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modified by Maak to account for the presence of an external oxide layer [5]. Over the temperature range 423–873 K, the IOZ thickness χ can be calculated using Eq. (2),

$$\chi = (k(T)t)^{1/2} \qquad (2)$$

where t is the reaction time, and k(T) is the parabolic rate constant, which is a function of temperature. The value of k(T) also depends on microstructural features. Changes to the basic $Nd_{16}Fe_{76}B_8$ composition might also change the microstructure of the IOZ and have a corresponding effect on the oxidation kinetics. Steyaert et al. [8] concluded, based on their microstructural study, that both particle size and temperature range play an important part in the determination of the kinetic parameters of Nd-Fe-B powders oxidation.

In Part 1 of this paper [21], it was shown that the oxidation of (Nd,Pr)FeB magnet at high temperatures (700–1500 K) exhibits three different microstructure evolutions for three different temperature ranges: (I) 700–1000 K; (II) 1000–1300 K; and (III) 1300–1500 K. Temperature range (I) produces two layer of scale, the EOZ which contain mostly Fe and O and IOZ. Temperature range (II) shows more complex mechanism, which results in a formation of three layers of scale and the remaining un-oxidised zone. The scales contain mixtures of fine grain of oxides ($NdBO_3$, $NdFeO_3$, FeO, Fe_2O_3 and Fe_3O_4) and γ-Fe matrix. Temperature range (III) has a similar mechanism. In this case, however, the products consist of separated layers of $NdBO_3$, $NdFeO_3$ and Fe_2O_3. The overall process for the three temperature ranges is shown schematically in Fig. 1. To simplify the problem in this study the overall process can be treated as a single reaction as follow:

$$Nd_2Fe_{14}B(s) + \tfrac{51}{4}O_2 \rightarrow \tfrac{13}{2}Fe_2O_3(s) + NdFeO_3(s) + NdBO_3(s) \qquad (3)$$
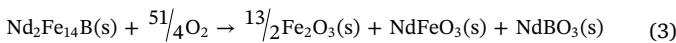
The aim of the present study was to investigate the oxidation mechanism of a commercial rare earth permanent magnet (REPM), particularly the (Nd,Pr)FeB type, over the temperature range 700–1500 K (below the melting point). The oxidation of the Sm-Co REPM is not included in this study. The microstructural evolution and oxidation mechanism was discussed in detail in Part 1. The present paper describes a detailed kinetic study of (Nd,Pr)FeB magnet oxidation.

2. Experimental methodology

2.1. Materials

New and clean magnet samples supplied by Alpha Magnetics Ltd, Melbourne were used in this study. The magnets had a nickel coating. The magnets were thermally demagnetised by heating in air at 573 K for 30 min then were cut to produce samples of size 10 mm x 5 mm x 5 mm. The nickel coating was removed manually from each sample by grinding the surface. The bulk composition of the prepared magnet samples, determined using ICP-AES is given in Table 1. A typical Nd-Fe-B magnet consists of two main phases: the φ phase ($Nd_2Fe_{14}B$) matrix and a Nd-rich grain boundary phase. A small amount of η phase ($Nd_1Fe_4B_4$) is also present. Dy and Pr are used to enhance coercivity of commercial Nd-Fe-B magnets. The substitution of Nd for Pr or Dy in the φ matrix leads to a reduction in the remanent magnetization and, consequently, in the maximum energy product [10,22,23].

2.2. Approach and parameters

Isothermal oxidation experiments were carried out in air in order to develop understanding of the kinetics and mechanism of oxidation of the samples. The surfaces of the samples were ground using SiC papers to 1200-grade and cleaned using ultrasonic agitation in acetone medium prior to an experiment. For each experiment, a sample of known mass was placed in a shallow 40 mm diameter alumina crucible then placed in a muffle furnace at a pre-set temperature. The experimental conditions used in the current study are listed in Table 2.
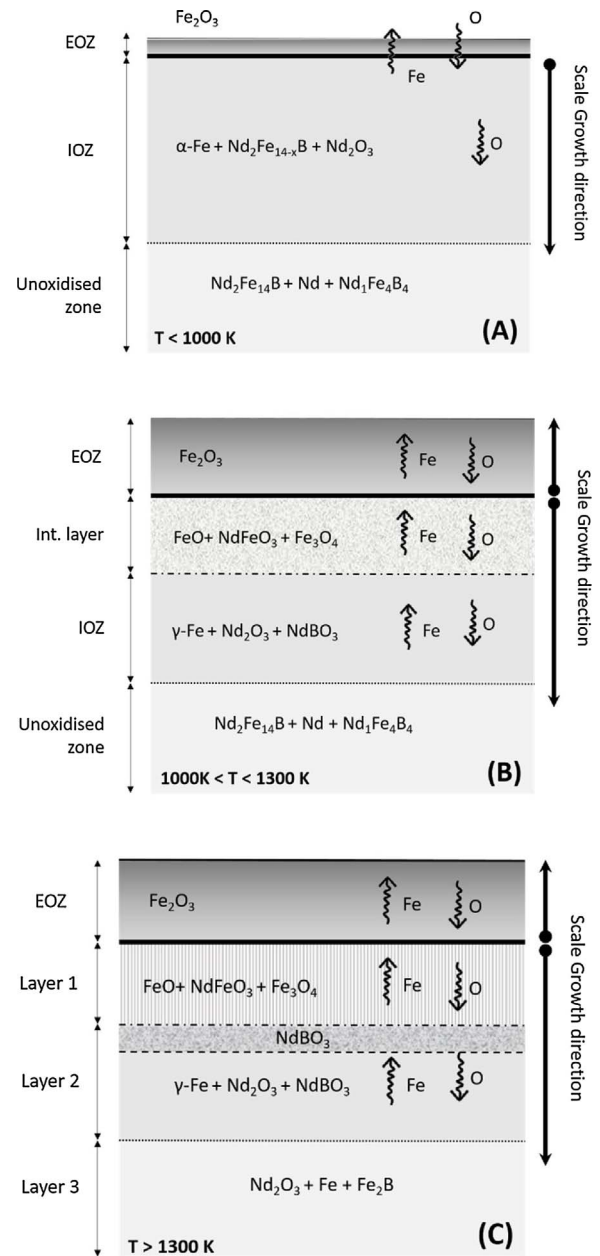

Fig. 1. Schematic of the observed layered scale (solid line is the original surface, the thickness ratio of layers is not to scale) and transport of different species in the scale (cationic transport and anionic transport) and corresponding oxide products and interface motion (bold arrow show the growth direction of the layer).

Table 1
Chemical composition of REPM sample (mass%).

	Nd	Pr/Dy	Fe	B
Typical commercial range	23–31	0–7	65–70	0.9–1.2
Samples used in the present study (analysed by ICP-AES)	22.4	8.5 (Pr)	68	1

Calculations indicated that the samples would reach the target temperature in less than one minute due to their small size. After the required oxidation time the sample was removed from the furnace then weighed to determine the change in mass. The time between removing the sample and weighing was kept to under one minute. The samples were then cooled in ambient air then placed inside 10 mL vials for further analysis.