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High temperature oxidation of rare earth permanent magnets. Part 1 – Microstructure evolution and general mechanism

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ABSTRACT

The microstructure evolution and mechanism of oxidation of (Nd,Pr)FeB magnet in the range 700–1500 K have been investigated. Bulk ($10 \times 5 \times 5$ mm) and powder samples (~ 150 μ m) were oxidized under isothermal and non-isothermal conditions. DSC, XRD, high-temperature XRD, SEM and EPMA characterization techniques were utilized to investigate the general oxidation reactions, microstructure evolutions and phase transformations. Three different microstructure evolutions were observed in the temperature ranges 700–1000 K, 1000–1300 K and 1300–1500 K. The different product microstructures formed during the oxidation have implications for devising strategies for the recycling/recovery process of (Nd,Pr)FeB magnets.

1. Introduction

Rare earth elements (REE), particularly neodymium, praseodymium, and dysprosium are vital to the development of current green technologies. These elements are used to create small, but powerful magnets for wind turbines, electric motors for electric vehicle applications, hard drives and air conditioners. A number of processing techniques and strategies are being developed to recycle or recover the REE's from end-of-life (EoL) rare earth permanent magnets (REPM). Various processing routes – physical/mechanical separation, hydrometallurgical and pyrometallurgical extraction processes – can be applied depending on the stage at which the recycled product comes into the materials flow [1,2]. The conventional approaches are mainly based on hydrometallurgical routes where different combinations of leaching, precipitation and solvent extraction are used. For example, commercialised extractants used in the primary processing of REE's, such as D2EHPA-HDEHP, organophosphorous HEHEHP PC-88A, Cyanex 272-Ionquest 290 and Versatic acid, can also be used in the recycling process [3]. The processes often involve roasting the waste REPM at temperatures up to 1173 K prior to leaching to facilitate the formation of oxides/mixed-oxides, which are readily soluble in acids and also to improve the leaching kinetics [3]. These wet processes use large

amounts of water and chemicals, including industrial acids and alkalis and thus have significant environmental issues.

Pyrometallurgical routes can be alternatives to hydrometallurgical routes. The pyrometallurgical routes can be used to remelt the REE alloys and extract the different REE in different forms, i.e. as metal solutions or oxides [1]. Some disadvantages of pyrometallurgical routes include higher energy costs and a higher carbon footprint. In addition, most high temperature processes, such as direct melting, extraction using flux, liquid metal extraction, hydrogenation and electrolysis, are highly sensitive to the oxidation state of REE in the magnetic waste [1] and their optimisation requires understanding of the oxidation process of REPM at high temperatures.

Understanding the oxidation mechanism of REPM's at high temperature is important for the development of processing techniques and strategies to recover REE's such as Nd, Dy and Pr from end-of-life REPM's. There is however, currently little information on the mechanisms of formation of oxides from REPM's at high temperatures. Limited oxidation observations have been carried out to support the study of specific techniques but with little attempt to understand the mechanisms. In addition, most previous investigations have been carried out at low temperatures (< 773 K). The principal objective of the present study was to investigate the oxidation of a commercial REPM,

Abbreviations: CEMS, Conversion electron Mössbauer spectroscopy; DSC, Differential scanning calorimetry; EDS, Energy dispersive x-ray spectroscopy; EoL, End-of-Life; EOZ, External oxidation zone; EPMA, Electron probe micro analysis; IOZ, Internal oxidation zone; RE, Rare earth; REE, Rare earth elements; REO, Rare earth oxide; REPM, Rare earth permanent magnet; SEM, Scanning electron microscope; TGA, Thermogravimetric analysis; TEM, Transmission electron spectroscopy; WDS, Wavelength dispersive x-ray spectroscopy; XRD, X-ray diffraction

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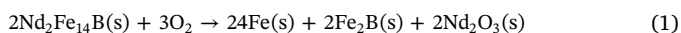
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particularly the (Nd,Pr,Dy)FeB type magnet, over the temperature range 700–1500 K (below the melting point). The oxidation of the Sm-Co REPM is not included in this study. For simplicity, the term of NdFeB magnet is used in this paper to represent the (Nd,Pr,Dy)FeB magnet. The mechanisms by which the reactants (in this case oxygen) may penetrate the oxide layer products are an important part of the overall mechanism of high temperature oxidation. Since all metal oxides are ionic in nature, it is clear that ions and electrons must migrate in order for the reaction to proceed. In this Part 1 paper, the detailed microstructure evolution during oxidation over a wide temperature range than previous studies was systematically tracked and analysed to understand the overall oxidation mechanism. In the Part 2 paper the detailed kinetics of magnet oxidation were investigated to understand the formation of oxides and determine the rate controlling mechanisms.

2. Previous studies on the oxidation of REPM

The corrosion [4–6] and oxidation [6–9] behaviour of REPM's in different atmospheric condition have been extensively studied particularly in the context of the degradation of magnetic properties at temperatures up to 873 K. Many attempts have been made to improve the corrosion and oxidation resistance of NdFeB magnets, including alloy additions [10,11] and surface coatings [12]. Blank and Adler [13] showed that oxidation between 673 and 873 K resulted in the formation of a grey layer of oxides on the surface of the bulk magnets and that its thickness increased parabolically with oxidation time. At lower temperatures (423–573 K), a general parabolic oxidation behaviour was also observed in studies using thermogravimetric analysis (TGA). [8] The results showed that rapid surface oxidation on powdered uncoated REPM's occurred within the first minute and that this became substantial as the average particle size decreased. [6,8,14] The surface oxide layer appeared not to inhibit further diffusion of oxygen. Later works on the oxide microstructure of bulk NdFeB magnets were carried out by Breton and Edgley et al. [7,9], mainly using Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), and Conversion Electron Mössbauer Spectroscopy (CEMS) to identify the oxidation products. They found that the main reaction was the dissociation of the Nd₂Fe₁₄B phase into α -Fe nanocrystals, Fe₂B and small Nd-oxide particles according to the following reaction:



Although the oxidation products were fine grained, it was established using SEM and Transmission Electron Microscopy (TEM) that the dominant grey zone represented a zone of internal oxidation (IOZ) consisting principally of an α -Fe matrix containing Nd-oxide particles [9]. Li et al. [13], Skulj et al. [10] and others [15,16] further studied the microstructures of the material under similar conditions of oxidation. Edgley et al. [14] reported there was no degradation of the Nd₂Fe₁₄B phase in the grains (found using CEMS), and additional analysis by TEM confirmed that dissociation of the grains was unlikely and happened only when it reacted with oxygen. They concluded there was no diffusion of Nd into the IOZ and proposed that oxygen transport occurred by short-circuit diffusion and that the most likely diffusion paths were via the high-angle α -Fe grain boundaries. The results showed that the α -Fe columnar grain structure coarsened as the oxidation front traversed the original alloy grains. This coarsening has been associated with the loss of relatively low-angle grain boundaries which carry less of the inward oxygen flux. These findings are typical of other studies at low temperatures ($T < 750$ K).

In the authors' previous study [16] on the oxidation of (Nd,Pr,Dy)FeB magnet carried out in air, the samples oxidized at 773 K and 1173 K showed evidence of a different microstructural evolution. The microstructure of the magnet oxidized at 773 K consisted of a dark external outer zone (EOZ) layer and a grey internal oxidation zone that progressed inwards with time. This indicates similarity with the mechanism of oxidation of NdFeB magnets below 700 K. In contrast,

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

	Nd	Pr/Dy	Fe	B
Commercial Typical Range	23–31	0–7	65–70	0.9–1.2
Samples used in the experiments ^a	22.4	8.5 (Pr)	68	1.0

^a Composition analysed using ICP-AES.

however, the oxidation process at temperatures above 973 K resulted in a more complex microstructure, with the EOZ growing outwards and an intermediate layer and IOZ growing inwards. Examination of the Fe depleted region showed that there was substantial Fe diffusion to the outer scale (EOZ) which was not seen in the magnet oxidized at $T < 773$ K. Based on these observations, the mechanism of oxidation may include both the diffusion of oxygen and iron into and out of the substrate. Further systematic investigations to clarify and establish the mechanism at different temperature ranges was the focus of the current work.

3. Experimental methodology

3.1. Materials, approach and parameters

In this study, new and clean magnet samples were used for the oxidation experiments. The sintered N45-NdFeB magnets were supplied by Alpha Magnetics Ltd, Melbourne and had a nominal composition within the range given in Table 1. The supplied magnet samples had a nickel coating to prevent oxidation. The clean magnet was thermally demagnetised at 573 K for 30 min in an oven furnace and bulk samples ($10 \times 5 \times 5$ mm) were cut from the magnets using a Struers Secotom-15/-50 high performance cutting machine. The nickel coating was removed manually after cutting by grinding the surface using SiC impregnated papers. The bulk composition of the prepared magnet sample, analysed using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), is also shown in Table 1. The typical NdFeB magnet system consists of two major phases: the ϕ phase which is a Nd₂Fe₁₄B matrix and a Nd-rich grain boundary phase typically rich in Nd, Pr, Dy, and also containing a minor amount of Fe. A small amount of η phase NdFe₄B₄ is also present to balance [1] However from Table 1 there was no Dy detected in the sample. The typical microstructure of the magnet sample used in the study is shown in Fig. 1.

The surfaces of the samples were ground using 1200-grade SiC

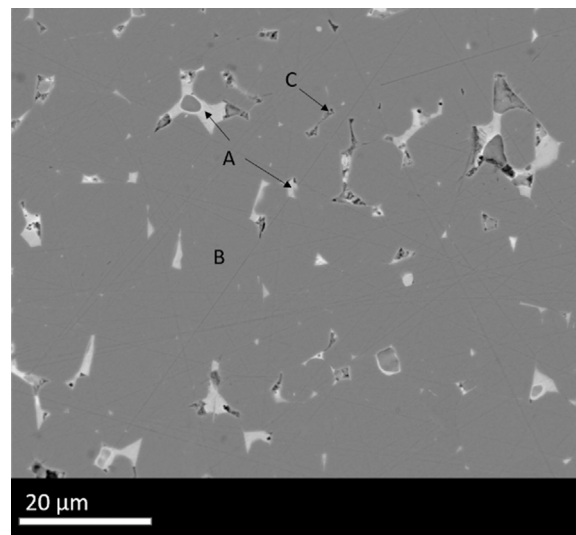


Fig. 1. A typical microstructure of the magnet sample used in the current study indicating (A) the intergranular Nd-rich phase, (B) the main ϕ -phase and (C) the small intergranular η phase.

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