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The oxidation morphology of SmCo alloys

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ABSTRACT

SmCo alloys form the basis of excellent permanent magnets with potential service applications up to 550 °C. It is suspected that their oxidation behaviour may limit their usefulness but this is a relatively unstudied subject. In this work, two grades of $Sm_2(Co,Fe,Cu,Zr)_{17}$-based alloys were oxidised in air at temperatures between 300 and 600 °C, and the oxidation morphology characterised by post-test SEM examination. Both alloys formed a thin external oxide scale composed of Cu and mixed Fe/Co oxides and an extensive internal oxidation layer consisting of Sm oxide within a (Co,Fe) solid solution. The depth of the internal oxidation zone (IOZ) was typically an order of magnitude thicker than the surface oxides and increased parabolically with time. The internal oxidation is an important degradation phenomenon because the transformation to (Co,Fe) causes a loss of magnetic properties proportional to the volume consumed. The morphologies of the oxidation zones, nature and mechanisms of various precipitated phases and the differences between the two alloys' oxidation behaviour is discussed.

1. Introduction

Rare-earth permanent magnets based on NdFeB or SmCo have relatively high energy densities and, therefore, have applications in efficient motors and generators with high power to weight ratios. While NdFeB-based magnets are cheaper to manufacture than SmCo-based magnets and have superior magnetic properties at room temperature, they suffer from a loss of magnetic properties at elevated temperatures. The highest temperatures at which NdFeB magnets can currently operate usefully is ∼200 °C. By contrast, recently developed SmCo-based magnetic alloys can retain useful magnetic behaviour at up to temperatures of ∼550 °C, making them candidates for aero-engine applications such as frictionless bearings or co-axial starter-motors/generators. However, at these high temperatures oxidation becomes a problem [1,2].

NdFeB magnets deteriorate primarily due to internal oxidation of the rare-earth element, creating an internal oxidation zone composed of a transition metal-based matrix with the rare-earth oxide finely dispersed throughout [3]. The inward growth of this oxidation zone causes a loss of alloy volume with the desired magnetic properties. It has been shown [1] that SmCo-based magnets will oxidise in a similar fashion, Sm oxidising internally to form a Sm-rich oxide embedded in a (Co, Fe) matrix. Similarities in morphology between NdFeB internal oxidation zones and published Sm_2Co_{17} reaction zones [4,5] appear to bolster this view, although Chen and co-workers attribute the phase transformation in these reaction zones to the outward migration and subsequent vapourisation of Sm from the outer surface [5].

The purpose of this present paper is to report the results of a detailed study into the microstructural morphology of the oxidised regions within two SmCo alloy variants and to determine compositional changes occurring as a result of oxidation.

2. Materials

This study examines the oxidation behaviour of two grades of $Sm_2(Co,Fe,Cu,Zr)_{17}$ alloy: a "standard" grade, $Sm(Co_{0.63}Fe_{0.27}Cu_{0.08}Zr_{0.02})_{8.35}$ and a "high-temperature" grade, $Sm(Co_{0.74}Fe_{0.1}Cu_{0.12}Zr_{0.04})_{8.5}$. These atomic proportions correspond to alloy compositions, in at.%, of 10.70 Sm, 56.26 Co, 24.06 Fe, 7.17 Cu and 1.82 Zr for the "standard" grade and 10.53 Sm, 66.21 Co, 8.95 Fe, 10.74 Cu and 3.58 Zr for the "high temperature" grade. Both alloys were manufactured by Precision Magnetics Ltd. The samples were supplied as rectangular coupons ∼10 mm × 10 mm × 2 mm in size of two types – firstly, with the *c*-axis alignment perpendicular to the major faces, and secondly, with the *c*-axis alignment in-plane with the major faces (see Fig. 1). This facilitated study of the oxidation zone penetration in the two different crystal directions. Throughout this work, the *c*-axis direction will be indicated on micrographs of alloy cross-sections by a small arrow.

The microstructure of Sm_2Co_{17}-type alloys has been characterised more fully elsewhere [6–8], but broadly consists of Sm_2Co_{17} cells ∼100 nm in size surrounded by $SmCo_5$ boundaries, both penetrated by Zr-rich lamellae with a thickness of several nm perpendicular to the *c*-axis. On a larger scale, this structure is divided into equiaxed grains approximately 40–50 μm across and interspersed with 2–5 μm particles of Sm oxide which form during alloy production. In the high-temperature grade examined here, Zr-rich particles are also found, similar in size but sparser in distribution than the Sm oxide particles. EDX point analyses of these particles yields concentrations of approximately 63Co–20Zr–9Fe (at%), a composition that is well within the $(Fe,Co)_2Zr–\alpha'–Zr_6Co_{23}$ mixed phase field on the Co–Fe–Zr ternary phase diagram [9]. The presence of Zr_6Co_{23} in SmCo-based alloys of this type has also been suggested by Derkaoui et al. [10].

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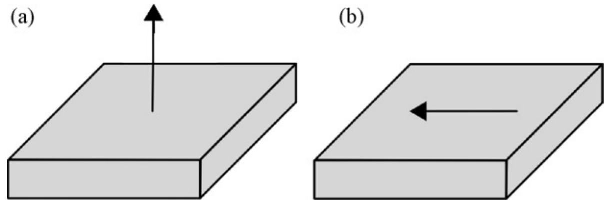

Fig. 1. Specimen coupons and the *c*-axis alignment directions (a) perpendicular and (b) in-plane.

3. Experimental

Interrupted oxidation testing was carried out in laboratory air at temperatures between 300 and 600 °C for up to 1000 h at the lower temperatures and 350 h for the higher temperatures. For each unique combination of temperature, alloy grade and crystal orientation, six specimens were polished to an 800 grit finish, cleaned ultrasonically in ethanol and weighed. The specimens were placed within alumina tubes approximately 15 mm in diameter and then loaded into the furnace, which was brought to temperature within 5 min. At intervals during the test, single specimens were removed from the furnace within their tubes and allowed to cool to room temperature before being weighed again. When the test was complete, the furnace

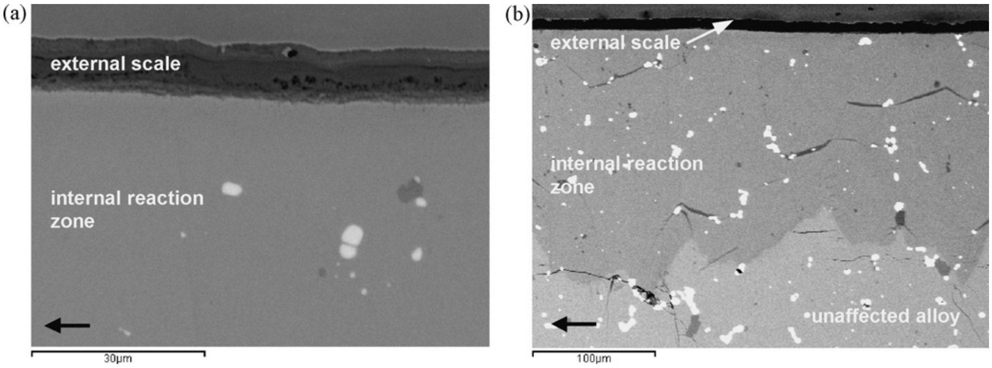

Fig. 2. BSE images of the high-temperature grade alloy after exposure at 600 °C for 24 h, showing (a) the external oxide scale, and (b) a typical internal reaction zone. The external oxide is visible in (b) as the near-black layer just above the internal reaction zone.

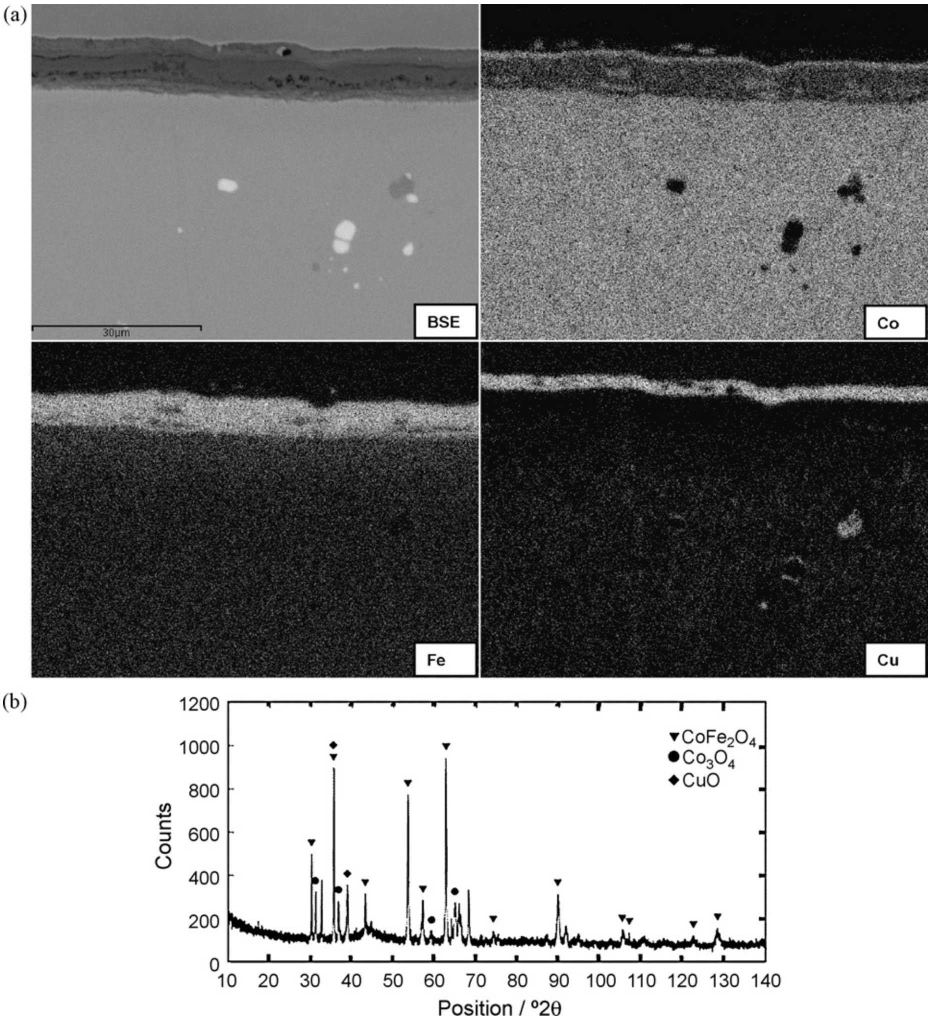

Fig. 3. Analysis of the high-temperature alloy exposed at 600 °C for 24 h. (a) EDX maps of the surface oxide scale, and (b) XRD peaks for the surface oxide scale.