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Magnetic Co_2Y ferrite, $Ba_2Co_2Fe_{12}O_{22}$ fibres produced by a blow spun process

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Gel fibres of Co_2Y, $Ba_2Co_2Fe_{12}O_{22}$, were blow spun from an aqueous inorganic sol and calcined at temperatures of up to 1200°C. The ceramic fibres were shown by X-ray diffraction to form crystalline Co_2Y at 1000°C, and surface area and porosity measurements indicated an unusually high degree of sintering at this temperature. The fibres also demonstrated a small grain size of 1–3 μm across the hexagonal plane and 0.1–0.3 μm thickness at 1000 °C. This only increased to 3 μm in diameter and 1 μm thickness even at temperature up to 1200 °C. The fibrous nature combined with the improved microstructures could be an important factor in improving the magnetic properties of this material.

1. Introduction

A new class of planar hexagonal ferromagnetic mixed oxides, related to $BaFe_{12}O_{19}$ (M ferrite), were discovered in 1956 at the Philips Research Laboratory [1], and they were named the ferroxplanar compounds. The complex chemical formulae and crystal structures reported [2] included $Ba_2Co_2Fe_{12}O_{22}$, or Co_2Y, which unlike M ferrite has the direction of magnetism perpendicular to the *c*-axis. This results in an even larger crystalline anisotropy of 2222.8 Am^{-1} (M ferrite = 1352.8 Am^{-1}) and a high magnetic permeability [3], and led to the development of a group of new soft ferromagnetic materials with low losses at high frequencies coupled with a very low conductivity [1]. These properties, combined with the rather low saturation magnetization meant that Co_2Y was ideally suited to a variety of uses in microwave devices rather than as a permanent magnet [4].

General methods for producing ferroxplanar compounds are very similar to those used for M ferrites [5], but processes also exist to produce crystal-oriented Co_2Y from sintering [6] and topotactic reactions [7], and near-perfect single crystals useful for some microwave devices can be grown by the flux method [8]. However, even greater care must be taken to get the stoichiometry [9], sintering conditions [10] and homogeneity and particle size [11] of the precursor correct due to the more complex nature of the chemical compositions.

This work on Co_2Y ferrite fibres is part of a programme to demonstrate how a number of refractory and effect fibres can be made by an aqueous sol–gel route. The fibrous form of a ceramic material can be made stronger and often stiffer than the bulk ceramic [12], and this would be advantageous if the Co_2Y were used in resin composites. Hale [13] has reviewed the effects of composite phase geometry on material properties and it is apparent that the incorporation of a magnetic material in fibrous form would have a much greater impact. The practical consequences have been demonstrated by Goldberg [14] who showed that in special cases, short fibres of 50:1 aspect ratio give a 50 fold advantage in magnetic permeability over the same volume of material in non-fibrous form.

Sol–gel routes to inorganic fibre forms bring advantages in processing. Sol–gel provides a means for the fine scale mixing of multiple components at low temperatures, resulting in a more homogenous precursor. Consequently improved sintering rates at lower temperatures can be expected, leading to improved microstructure, and the inconvenient increased shrinkage between gel and ceramic product is more acceptable in an inorganic fibre due to its virtually one-dimensional nature. Therefore, given the potential advantages of a sol–gel based route for spinning Co_2Y ferrite fibres, such a process has been investigated.

2. Experimental procedure

2.1. Sample preparation

An acid-peptized halogen-stabilized iron(III)hydroxide sol (Fe:anion = 3:2) was doped with stoichiometric amounts of cobalt(II) and barium salts, which had been previously dissolved into a solution with an organic chelating agent. Spinnability was conferred by the addition of a small amount of polyethylene oxide as a spinning aid, and the fibres were produced using a proprietary blow spinning process [15]. The resulting gel fibres were collected as random staple and stored in a circulating air oven at 110 °C. The gel fibres were heat treated in a muffle furnace, firstly being pre-fired to 400 °C at 200 °C per h to remove water and any residual organic compounds. The samples were then further heat treated at 200 °C per h to 600, 800, 1000, 1100 and 1200°C in a re-crystallized alumina vessel for 3 h.

2.2. Characterization

2.2.1. Photon correlation spectroscopy (PCS)

Particle size measurement of the sol above the 3 nm diameter range was measured on a Malvern Instruments Lo-C autosizer and series 7032 multi-8 correlator, using a 4 mW diode laser, at a wavelength of 670 nm.

2.2.2. Scanning electron microscopy (SEM)

Scanning electron micrographs and an analysis of the morphology of the samples were produced using a Cambridge Instruments Stereoscan 90 SEM operating at 15 kV. Conducting samples were prepared by gold sputtering the fibre specimens.

2.2.3. Surface area and porosity measurements

Surface areas and pore size distributions of the fibres were performed on a Micrometrics ASAP 2000 using N_2 as the adsorption gas. Samples were degassed at 300 °C for 6 h prior to analysis.

2.2.4. X-ray photoelectron spectroscopy (XPS)

The XPS analysis was performed using a Kratos XSAM 800 spectrometer fitted with a dual anode (Mg/Al) X-ray source and a multichannel detector. The spectrometer was calibrated using the $Ag3d^{5/2}$ line at 397.9 eV and the AgMVV line at 901.5 eV. Al$K\alpha$ radiation (1486.6 eV) was the exciting source (120W) and spectra were collected in the high resolution mode (1.2 eV) and fixed analyser transmission (FAT). The Kratos DS800 software, running on a DEC PDP11/23 computer, was used for data acquisition and analysis.

2.2.5. X-ray fluorescence spectrometry (XRF)

The elemental composition of the samples was measured on a Philips PW2400 sequential X-ray spectrometer fitted with a rhodium target end window X-ray tube and Philips X-40 analytical software. The samples were analysed in the form of a fused bead, where 1g of sample was fused with 10g of lithium tetraborate flux at 1250 °C for 12 min and then cast to form a glass bead.

2.2.6. X-ray powder diffraction (XRD) measurement

X-ray powder diffraction patterns of the samples treated at various temperatures were recorded in the region of $2\theta = 10–80°$ with a scanning speed of 0.25 ° per min on a Philips PW1710 diffractometer using CuK_α radiation with a nickel filter. The refined cell parameters were obtained using linear regression procedures applied to the measured peak positions of all major reflections up to $2\theta = 90°$ with the Philips APD 1700 software. This software was also used to calculate the average size of the crystallites in a sample using the Scherrer equation:

$$D = K\lambda / h_{1/2} \cos\theta \qquad (1)$$

where D = average size of the crystallites, K = Scherrer constant (0.9 × 57.3), λ = wavelength of radiation (0.15405 nm), $h_{1/2}$ = peak width at half height and θ corresponds to the peak position.

3. Results and discussion

The stoichiometric mixture required to produce Co_2Y contains a high proportion of simple metal salts as dopants, which do not contribute to the gel formation and actually destabalize the sol itself. Therefore the preparation of a stable doped sol was achieved with difficulty, after experimentation with many combinations of various metal salts, acids and organic stabilizers. Sol stability and the resulting size of the sol particles is sensitive to the preparative techniques and conditions, and PCS enabled us to measure and control the properties of the sol to a certain extent. The PCS data indicates that the average particle size in the doped iron(III) sol was 8.4 nm, with a polydispersity of 0.524. By volume distribution, the mean size was found to be 7.5 nm, with an upper limit of 35 nm and an average molecular weight of 7.4×10^4 amu. It must be considered that the technique is unable to detect particles below the 3 nm threshold, and therefore these measurements may be higher than the actual true figures.

The dried fibre was strong and very handleable, becoming slightly less so above 1000 °C and becoming brittle at 1200 °C. At 800 °C the fibres were very smooth and still fibrous with a diameter of 4–8 μm, and some microstructure was apparent with a grain size of the order of 0.1 μm. After firing to 1000 °C the fibres appeared to consist of a densely packed mass of randomly oriented thin hexagonal plates (Fig. 1), which were between 1–3 μm in diameter but only a tenth of that size in thickness, and which did not compromise the fibrous nature of the material. Upon heating further to 1100 °C individual grains could be seen to be increasing in size at the expense of their

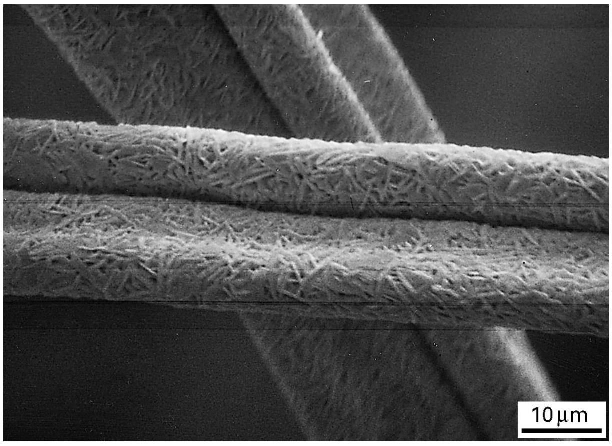

Figure 1 SEM micrographs of fibres fired to 1000 °C.

neighbours, and by 1200 °C many larger and more equiaxed hexagonal crystals had formed, still no more than 3 μm in diameter, but now up to 1 μm thick (Fig. 2). The fibres had become mechanically very weak and virtually unhandleable by this stage. Bulk powdered Co_2Y specimens are usually prepared at temperatures over 1100 °C to obtain Co_2Y as the major phase, and show a uniform distribution of close packed grains between 3–10 μm in size across the hexagonal plane, and between 0.75–2 μm in thickness between 1200–1300 °C [16]. Therefore the fibrous Co_2Y ferrite appears to have a much reduced grain size than standard powder mixes at equivalent temperatures, and the magnetic properties may be enhanced accordingly. Surface area and porosity data on the fibre fired to 1000 °C supports the above results, giving a low surface area ($0.9\ m^2\ g^{-1}$) and little porosity ($0.004\ cm^3\ g^{-1}$), with an average pore diameter of 44 nm.

A deviation in either the stoichiometry or oxidation state of the material can have an adverse affect on its magnetic properties [17], thus it is important to measure these properties. The XPS analysis of the fibres fired to 1000 °C showed the oxidation state of the iron to be Fe(III) with a binding energy of 710.3 eV for the main Fe2p peak. The XRF elemental analysis for the oxides BaO, Fe_2O_3 and Co_3O_4 confirmed the composition to be $Ba_2Co_2Fe_{12}O_{22}$ at 1000 °C, and that all the halides were absent at this temperature.

The XRD patterns taken between 400–1200 °C are shown in Figs 3 and 4. Hematite has started to form by 400°C (Fig. 3a), and at 600°C it is still the major phase, the background remaining amorphous (Fig. 3b). At 800 °C the hematite peaks have disappeared and M ferrite has stared to form, along with the spinel ferrites $CoFe_2O_4$ and α-$BaFe_2O_4$ (Fig. 4).

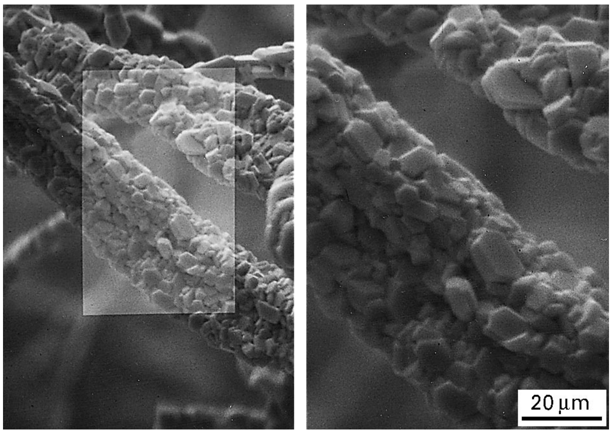

Figure 2 SEM micrographs of fibres fired to 1200 °C.

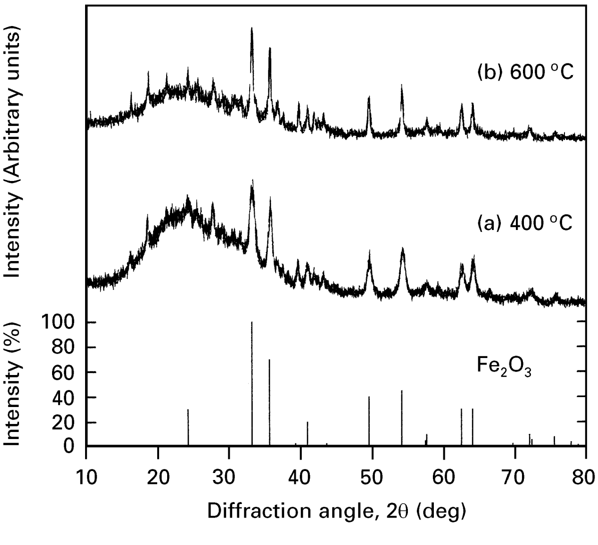

Figure 3 XRD patterns of the fibres fired to (a) 400 °C and (b) 600 °C. For comparison purposes the JCPDS file for Fe_2O_3 no. 33–664 is also shown.

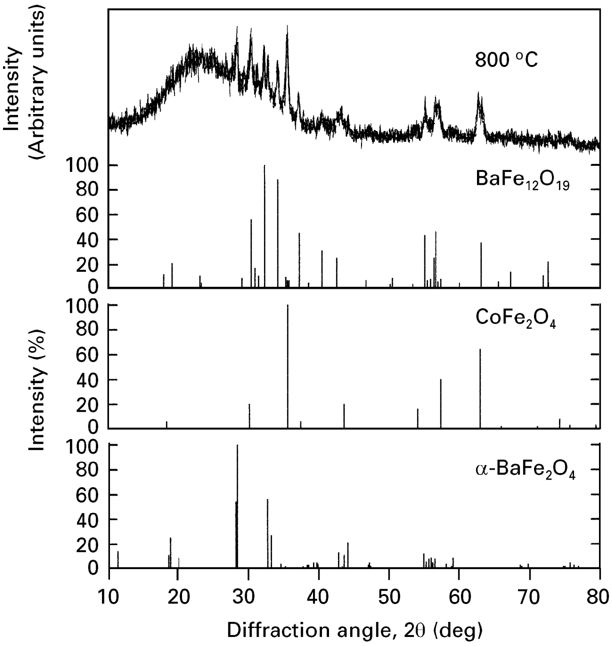

Figure 4 XRD pattern of the fibres fired to 800 °C. For comparison purposes the JCPDS files for α-$BaFe_2O_4$ (no. 25–1191), $CaFe_2O_4$ (no. 3–864) and $BaFe_{12}O_{19}$ (no. 27–1029) are also shown.

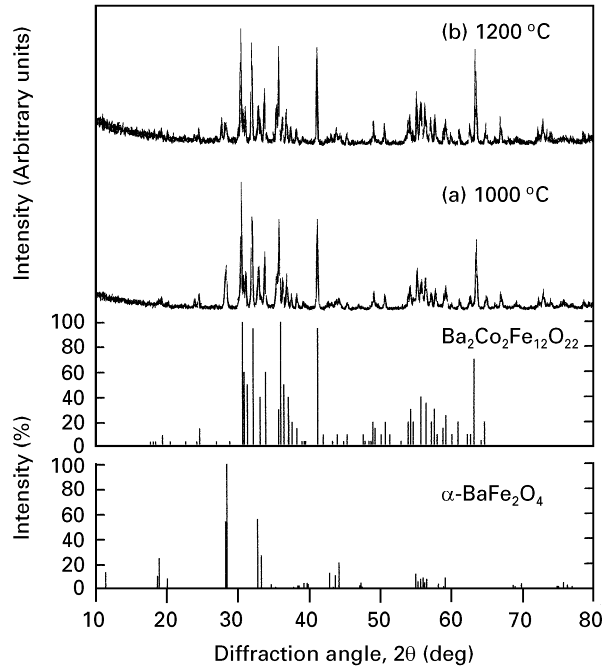

Figure 5 XRD patterns of the fibres fired to (a) 1000 °C and (b) 1200 °C. For comparison purposes the JCPDS files for α-$BaFe_2O_4$ (no. 25–1191) and $Ba_2CO_2Fe_{12}O_{22}$ (no. 19-100) are also shown.

This is supported by the findings of Vinik [9] and Castelliz *et al* [16], who reported that the M phase can persist to 1100 °C and that α-$BaFe_2O_4$ may co-exist with Co_2Y once it has formed as the major phase above 1100 °C. Indeed, by 1000 °C Co_2Y has crystallized as the major phase with α-$BaFe_2O_4$ persisting as a minor phase (Fig. 5a) and no further change occurs up to 1200 °C (Fig. 5b). The average crystallite size was estimated to be 70 nm at 1000 °C, using the Scherrer equation on the 100% peak at $2\theta = 30.52°$.

4. Conclusions

A gel fibre was successfully spun from a doped iron(III) sol, which on subsequent heat treatment produced fully crystalline Co_2Y at 1000 °C. This is a low temperature for the ferrite to form as the major phase, however it appeared to be more fully sintered and with a much improved microstructure at equivalent temperatures than in conventionally manufactured specimens. As the magnetic properties may be enhanced accordingly, a further investigation into the magnetic and structural properties of these fibres is currently in progress.

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