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Magnetite/hematite core/shell fibres grown by laser floating zone method

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ABSTRACT

Magnetite (Fe_3O_4) is a very important material due to its unique physical and chemical properties. However, the low redox stability and tendency towards oxidation impose certain limitations on the conditions, where Fe_3O_4 can be successfully used. A possibility to control and prevent oxidation of Fe_3O_4 thus represents an important challenge for materials engineering. In the present work, the laser floating zone (LFZ) method was employed to produce Fe_3O_4 fibres using hematite (Fe_2O_3) as a precursor material. Different growth conditions, namely pulling rate in the range 10–400 mm/h, were studied. The prepared fibres showed a core/shell structure, where the core is isolated by a shell of Fe_2O_3. The pulling rate was found to be a crucial growth parameter to control the crystalline nature of the fibres, particularly, the thickness of the shell. Increasing the pulling rate favours the formation Fe_2O_3 phase and, thus, decreases the width of shell isolating phase. X-ray diffraction (XRD) analysis was performed to identify the presence of Fe_3O_4 and Fe_2O_3 phases. The morphology and phase distribution of the grown fibres were analyzed by optical microscopy. Electrical properties of the fibres were measured at various temperatures, to understand the influence of pulling rate on the fibres shell. Vibrating sample magnetometer (VSM) measurements were used to study the dc magnetic susceptibility and hysteresis curves behaviour of Fe_3O_4 phase in the temperature range 5–300 K.

1. Introduction

Iron oxides are important in many industrial applications, including pigments, magnetic materials, electrical materials, catalysts and sensors [1–3]. Potential applications of the most stable phase in air (Fe_2O_3) are mainly related to its semiconducting behaviour and/or its band gap in the visible range (e.g. Ref. [4]), and differ markedly from those of magnetite (Fe_3O_4), with superior magnetic properties and significant electronic conductivity. However, magnetite/hematite composites might also raise opportunities to seek novel applications or different combinations of relevant properties (e.g. Ref. [5]).

The phase transformation from hematite (Fe_2O_3) to magnetite (Fe_3O_4) and oxidation states of iron was, thus, widely studied by different methods and techniques [1–3,6,7].

The present work relies on the laser floating zone (LFZ) method to obtain core–shell magnetite–hematite fibres, and to adjust their characteristics and properties, based on the flexibility of the method to obtain materials with unique features such as high quality single crystals of a variety of oxides [8,9], eutectic structures [10], highly oriented polycrystalline materials [11], etc. Different approaches for the floating zone technique have been used to grow crystals of intermetallic systems, where heating and melting are achieved using conducting properties of the metal, e.g., an induction furnace or an electron-beam system [8,12,13]. Following the series of discoveries of interesting correlated electron phenomena in complex ceramic oxides such as cuprates, manganites, ruthenates, titanates and ferrites, there has been an increased interest among materials scientists within the condensed matter community in studying single crystals of these systems [8].

In this paper, we report the successful growth of magnetite/hematite – core/shell by the floating zone method, using Fe_2O_3 as a precursor. Fibres were grown using different pulling rates, examined by X-ray diffraction, optical microscopy, VSM and electrical measurements, to observe the effect of growth conditions on physical properties.

2. Experimental procedure

Fe_2O_3 powder (Aldrich +99%) with addition of a binder (PVA – Polyvinyl alcohol) was extruded as precursor rods [8], which were used as feed in the LFZ method, equipped with a continuous CO_2 Spectron SLC laser ($\lambda = 10.6\,\mu m$; 200 W) to grow dense fibres. The growth rate varied between 10 and 400 mm/h, and the seed and feed rod precursors rotated in opposite directions to provide better homogeneity of the target fibres.

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The phase composition and crystalline structure were investigated at room temperature by X-ray diffraction (XRD) analysis, using a PANalytical X'Pert PRO system; the obtained pattern were analyzed using the JCPDS database. Phase distribution in the samples was examined by Raman spectra (SPEX, Jobin Yvon T64000) at room temperature in backscattering configuration, using the 532 nm exciting line, from 100 to 2100 cm^{-1}. The sample's morphology at polished cross-section and transversal regions was characterized by optical microscopy (Olympus BH-2). The results were used for the determination of Fe_2O_3 shell thickness. Scanning electron microscopy (Hitachi SU 70) was unable to reveal relevant microstructural features of the magnetite-based core or its orientation.

The electrical response of core–shell fibres was monitored by dc and ac measurements in a suitable home-made cryogenic system, comprising a Keithley 617 Programmable Electrometer for dc measurements, an Agilent 4292A Precision Impedance Analyser (40 Hz – 2 MHz) for ac resistivity and capacity studies, and an Oxford ITC4-Inteligent Temperature Controller for variation of temperature from 80 to 360 K. One of the electrodes was applied with Ag paste onto one top of the fibre, to provide electrical contact to the magnetite-based core, and the second electrode was applied to the external cylindrical surface of the hematite shell. One attempted to confirm the core–shell microstructure by the prevailing effect of the conductivity hematite shell; this should be accounted by

X/(R × A), where (*X*) is the thickness of the hematite shell, *R* the resistance measured, *A* is the contact area calculated by $A = \pi DL$, with *D* diameter of the fibre and *L* the length of the external electrode.

The dc magnetic measurements were performed on fibre samples (50–100 mg) using a vibrating sample magnetometer-VSM, (Cryogenic–Cryofree). The dc magnetization was recorded on field-cooled (FC) under 0.1 T, between 5 and 300 K. Typical hysteresis curves were obtained at several temperatures (5–300 K), for all samples in magnetic field up to 10 T. The magnetic parameters such as saturation magnetization (Ms), coercivity (Hc) and magnetic moment are obtained from the VSM results.

3. Results and discussion

XRD patterns of crushed fibres showed the presence of magnetite (Fe_3O_4) and hematite (Fe_2O_3) phases for all powder samples (Fig. 1). However, the intensity of hematite peaks is rather residual

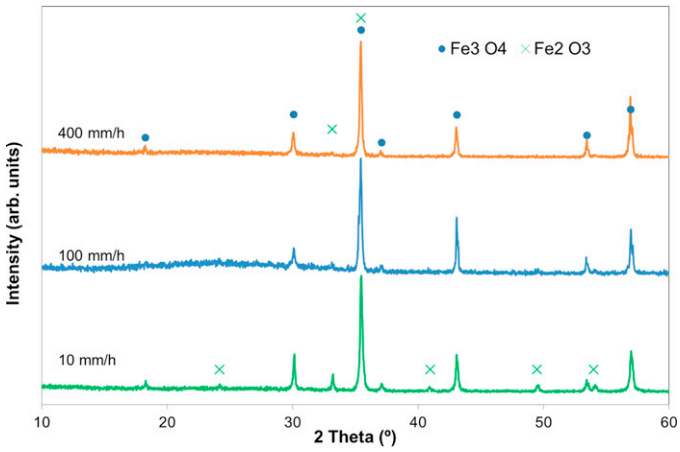

Fig. 1. XRD pattern of powdered samples for different pulling rate.

for fibres grown at the highest pulling rates, and are most obvious for <100 mm/h.

Optical observations (Fig. 2a) revealed the presence of two different contrast regions in samples, and Raman spectra confirm the presence of two distinct phases, as indicated by the shell signed to Fe_2O_3 phase (612 cm^{-1}), whilst the middle/bulk component can be signed to Fe_3O_4 phase (668 cm^{-1}), in accordance with literature data [14,15].

The presence of a core/shell structure can be due to thermal gradients in the radial and longitudinal directions, and possibly also by transient redox changes [9]. Note that hematite may be transformed into magnetite: $3Fe_2O_3 \rightarrow 2Fe_3O_4 + \frac{1}{2}O_2$ at sufficiently high temperatures, probably before melting. Thus, one expects transformation to magnetite before melting, at the front of the hot zone, and magnetite should also be the primary solidified phase at the rear of the molten zone. Onset of the outer hematite shell may, thus, be due to reoxidation of previously solidified magnetite, or delayed solidification occurring under significant undercooling. The melting temperatures of magnetite (≈1597 °C) and hematite (≈1565 °C) are similar. Note also that microcracks were observed for the lowest pulling rates (<100 mm/h), possibly due to thermal stresses and slightly expansive transformation of magnetite to hematite. The thickness of shell layer (Fig. 2) shows a decrease with an increase in growth rate up to ~100 mm/h.

High pulling rates (>100 mm/h) may yield porosity instead, possibly because heat transfer limitations in the radial direction may

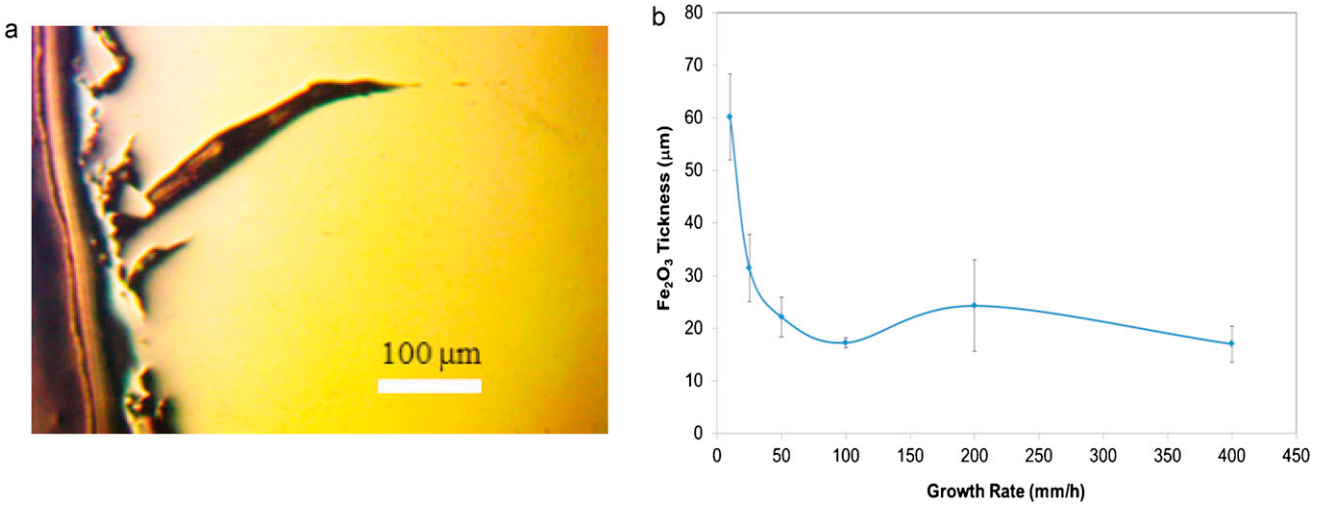

Fig. 2. (a) Optical microscopy of longitudinal section for sample grown at 50 mm/h, (b) evolution of Fe_2O_3 thickness layer with pulling rate.