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Environmental TEM investigation of the reduction of $\alpha$-Fe$_2$O$_3$ nanorods under H$_2$ atmosphere

Trevor P. Almeida$^1$, Michael W. Fay$^2$, Yanqiu Zhu$^3$, Thomas W. Hansen$^4$, Rafal Dunin-Borkowski$^{4,5}$ and Paul D. Brown$^1$

$^1$Division of Materials, Mechanics and Structures, Department of Mechanical, Materials and Manufacturing Engineering, Faculty of Engineering; &
$^2$Nottingham Nanotechnology and Nanoscience Centre; University of Nottingham, University Park, Nottingham, NG7 2RD, UK.
$^3$College of Engineering, Mathematics and Physical Sciences, University of Exeter, Streatham Campus, Exeter, EX4 4QF, UK.
$^4$Center for Electron Nanoscopy, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark.
$^5$Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons, Institute for Microstructure Research, Research Centre Jülich, D-52425 Jülich, Germany.

Abstract. The thermal reduction of hydrothermally synthesised $\alpha$-Fe$_2$O$_3$ nanorods (NRs) to Fe$_3$O$_4$ NRs under hydrogen is investigated. Complete reduction of $\alpha$-Fe$_2$O$_3$ NRs to Fe$_3$O$_4$ NRs was achieved during in situ XRD under 1 bar H$_2$ atmosphere at 360ºC. Complementary environmental transmission electron microscope investigation at high resolution, during in situ heating under an H$_2$ pressure of 5 mbar at 500ºC, provided evidence for the very first stages of transformation, supporting a model for the migration of oxygen along favoured $\alpha$-Fe$_2$O$_3$ lattice planes during the templated thermal reduction of $\alpha$-Fe$_2$O$_3$ NRs to Fe$_3$O$_4$ NRs.

1. Introduction

One-dimensional (1D) nanostructures have attracted considerable attention due to their novel magnetic properties which are greatly dependent on nanostructure size and shape [1]. Ferrimagnetic magnetite (Fe$_3$O$_4$) is of particular interest as a multifunctional nanostructured material with potential application in ferrofluids, magnetic recording and magnetic resonance imaging [2]. Acicular hematite ($\alpha$-Fe$_2$O$_3$) nanorods (NRs) may be used as a precursor for the synthesis of Fe$_3$O$_4$ NRs, through a process of partial reduction [3]. Hydrothermal synthesis (HS) constitutes an ideal method for the production of $\alpha$-Fe$_2$O$_3$ NRs from dilute iron (III) chloride (FeCl$_3$) precursor solution, via the formation of an intermediate $\beta$-FeOOH (akaganeite) phase. The addition of phosphate anions has been shown to play a decisive role in the anisotropic growth of $\alpha$-Fe$_2$O$_3$ NRs, defining their acicular shape by mediating the process of oriented attachment of primary $\alpha$-Fe$_2$O$_3$ nanoparticles (NPs) [4]. X-ray diffractometry (XRD) investigation of $\alpha$-Fe$_2$O$_3$ NRs heated in situ under a reducing atmosphere may be used to gain insight into the process of bulk phase transformation to Fe$_3$O$_4$. However, in order to elucidate the intricate details of this phase transformation process, it is necessary to visualise the reduction process at high resolution. Spherical aberration (Cs) correction combined with environmental TEM (ETEM) enables the detailed investigation of localised chemical reactions under gas atmospheres with interpretable spatial resolution at the sub-angstrom level [5, 6]. In this context, a high resolution ETEM investigation of the partial reduction of $\alpha$-Fe$_2$O$_3$ NRs to Fe$_3$O$_4$ under conditions of high temperature and reducing atmosphere is presented.

*Author to whom correspondence should be addressed: paul.brown@nottingham.ac.uk
2. Experimental

Acicular α-Fe₂O₃ NRs (Sample H) were prepared through the hydrothermal synthesis of 0.2 ml FeCl₃ aqueous solution (45% pure FeCl₃; Riedel-de Haen, Germany) in the presence of ammonium dihydrogen-phosphate (99.999% NH₄H₂PO₄; Sigma-Aldrich, UK) surfactant, further diluted in 40 ml distilled water and mechanically stirred in a 125 ml Teflon-lined steel autoclave. The autoclave was sealed and inserted into a temperature controlled furnace at a reaction temperature of 200˚C for 2 hours. The autoclave, once removed from the furnace, was allowed to cool down to room temperature naturally.

For the purpose of in situ XRD investigation, the HS product suspensions were centrifuged for 6 minutes at 6000 rpm, cleaned with acetone, deposited onto single crystal silicon substrates and analysed using a Bruker D8 Advance X-ray diffractometer (Cu Kα radiation; θ/2θ diffraction geometry). Sample H was examined at room temperature and then heated to 360˚C in a sealed XRD sample chamber under an H₂ atmosphere of 1 bar for 30 min (Sample M). For the purpose of TEM investigation, the centrifuged HS and XRD reaction product samples were cleaned with acetone and dispersed using an ultrasonic bath before deposition onto carbon film / gold mesh support grids (Agar Scientific Ltd, UK). Conventional diffraction contrast bright field (BF) imaging of the reaction products was performed using a JEOL 2000FX electron microscope. Further, ETEM investigation of the reduction of Sample H as a function of temperature (room temperature to 500 ˚C at 20 ˚C / min) was performed using a Gatan double tilt heating holder within a FEI Titan E-Cell TEM with a C corrector on the condenser system, operated at 300 kV (Centre for Electron Nanoscopy (CEN), Technical University of Denmark). High angle annular dark field (HAADF) imaging was performed using a FEI Titan (S)TEM with a C corrector on the condenser system, operated at 300 kV (CEN).

3. Results

The BF diffraction contrast TEM images of Figures 1a-c illustrate the morphology of the initial HS reaction products (Sample H) and the products formed following annealing at 360˚C under ~ 1 bar H₂ atmosphere for 30 min, with indexed SAED (inset). The associated XRD patterns of Samples H and M, indexed to α-Fe₂O₃ (JCPDS 72-469) and Fe₂O₃ (JCPDS 88-315), respectively. TEM investigation of Sample H (Figure 1a) confirmed the initial HS suspension to comprise acicular α-Fe₂O₃ NRs (~ 420 nm long, ~ 60 wide nm), whilst Sample M (Figures 1b,c) consisted of similar sized acicular α-Fe₂O₃ NRs (~ 420 nm long, ~ 60 wide nm), as evidenced by the {220} (d₁₀₀ = 2.70Å) and {111} (d₁₁₁ = 4.83Å) lattice fringes (Figures 2e & f). Figure 2j shows the newly

Figure 1 (a-c) BF diffraction contrast TEM images of: (a) α-Fe₂O₃ NRs (Sample H) formed from the HS of 0.2 ml FeCl₃ at 200˚C for 2 hours in the presence of 3 mg NH₄H₂PO₄, with indexed SAED (inset); (b,c) Fe₂O₃ NRs (Sample M) formed following the annealing of Sample H at 360˚C under ~ 1 bar H₂ atmosphere for 30 min, with indexed SAED (inset). (d) Associated XRD patterns of Samples H and M, indexed to α-Fe₂O₃ (JCPDS 72-469) and Fe₂O₃ (JCPDS 88-315), respectively.
developed Fe₃O₄ NP (outlined) and reveals the presence of additional Fe₃O₄ NPs (arrowed) developed on the α-Fe₂O₃ NR surface during heat treatment.

Figure 3 similarly presents phase contrast ETEM images from Sample H acquired at 500°C under an H₂ atmosphere of 5 mbar. Figure 3a presents a close examination of the tip of an α-Fe₂O₃ NR, as identified by {104} lattice fringes (d₁₀₄ = 2.70Å) (inset). The defects in the α-Fe₂O₃ NR are an effect of the coalescence of α-Fe₂O₃ particles during growth [4]. Figures 3b,c show the localised development of an Fe₃O₄ NP (arrowed), as identified by {220} lattice fringes (d₂₂₀ = 2.96Å, Figure 3c, inset).

Figure 4 presents BF diffraction contrast and HAADF images of Sample H acquired after 5 hours of heating under a reducing atmosphere within the ETEM. The BF TEM of Figure 4a shows a single crystalline α-Fe₂O₃ NR (~ 420 nm long, ~ 70 nm wide), as identified by SAED (inset). Figures 4b & 4c present HAADF images of α-Fe₂O₃ NRs before and after heating in the ETEM, respectively, with a porous structure of the annealed α-Fe₂O₃ NR revealed in Figure 4c.

4. Discussion

In situ heating of α-Fe₂O₃ NRs in the XRD at 360°C under an H₂ atmosphere of 1 bar for 30 minutes promoted their complete transition to Fe₃O₄. This is consistent with the reduction of precursor α-Fe₂O₃, being a recognised method for the production of Fe₃O₄, as summarised by the equation: 3Fe₂O₃ + H₂ → 2Fe₃O₄ + H₂O. The H₂ atmosphere interacts with the oxygen of the α-Fe₂O₃ NR surfaces to form water, whilst heating to 360°C provides sufficient thermal energy to promote oxygen diffusion from inside the α-Fe₂O₃ NRs to restore the equilibrium oxygen concentration at the surface, resulting in partial reduction to Fe₃O₄. SAED combined with TEM imaging of individual NRs showed that the major axes of the α-Fe₂O₃ (Figure 4a) and Fe₃O₄ NRs (Figure 1c) were <006>₃ and <111>₄, respectively. This orientation relationship between α-Fe₂O₃ and Fe₃O₄ is consistent with previous reduction studies, with oxygen considered to migrate along {006} planes [7]. Here, the restacking to Fe₃O₄ is not so severe as to affect the NR acicular morphology (Figure 1c), hence, the α-Fe₂O₃ NRs act as templates for the topotactic transformation to Fe₃O₄ NRs.

BF TEM imaging and SAED (Figure 4a) during ETEM investigation demonstrated that α-Fe₂O₃ NRs were only reduced to Fe₃O₄ at the NR surfaces, under an H₂ atmosphere of 5 mbar at 500°C for 5 hours, with the caveat that the achievable H₂ pressure of 5 mbar in ETEM was significantly lower than the 1 bar used during in situ XRD investigation. This low H₂ pressure was found to be insufficient to promote the thermal reduction of complete α-Fe₂O₃ NRs during in situ heating in the ETEM. Thermal effects, however, did lead to the development of porosity in the α-Fe₂O₃ NRs through the release of trapped water and phosphate [8], as revealed by HAADF imaging (Figure 4c). Nevertheless, it is recognised that the time-lapse imaging at 500°C during ETEM provided for direct observation of the very first stages of
After heating at 500ºC under an H₂ atmosphere of 5 mbar for 5 hours, as identified by SAED (inset, indexed). (b,c) HAADF images of the localised development of Fe₃O₄ NPs on the side and tip of α-Fe₂O₃ NRs (Figures 2 and 3, respectively). It is likely that focusing the 300keV electron beam, during imaging (Figures 2 & 3) contributed to the development of the Fe₃O₄ NPs in this low pressure H₂ environment. In Figures 2b-i, the electron beam was converged on an area slightly larger than the field of view, which included the location of the newly formed NPs (Figure 2j, arrowed). Likewise, formation of the Fe₃O₄ NP on the tip of the α-Fe₂O₃ NR (Figure 3c) occurred during high resolution imaging. Further, the surface of the α-Fe₂O₃ NR shown in Figure 2j became noticeably eroded. Hence, the high current density of the electron beam acted to destabilise the α-Fe₂O₃ NPs, leaving an oxygen deficiency in the α-Fe₂O₃ NR surface, whilst remaining unstable iron and oxygen supplied the growth of Fe₃O₄ NPs.

Considering the relationship between the orientation of the α-Fe₂O₃ NRs and the growth of the initial Fe₃O₄ NPs, Figures 2 and 3 illustrate the formation of Fe₃O₄ NPs on the side and tip of α-Fe₂O₃ NRs, respectively. Closer examination reveals the growth interface of the tip Fe₃O₄ NP to be parallel to the major axis of the α-Fe₂O₃ NR (Figure 3c, inset), and hence, in both cases, the Fe₃O₄ NPs grow on surfaces parallel to the α-Fe₂O₃ <006> direction. Elemental supply to developing Fe₃O₄ NPs through an interface parallel to the α-Fe₂O₃ c-axis reinforces the notion that α-Fe₂O₃ {006} planes are favourable for oxygen diffusion during the thermal reduction of α-Fe₂O₃ NRs to Fe₃O₄ NRs. The α-Fe₂O₃ {006} or Fe₃O₄ {111} planes may become unstable and collapse during oxygen diffusion, resulting in defects.

In summary, fine details of the reduction of α-Fe₂O₃ NRs to Fe₃O₄ NRs during in situ XRD were examined. ETEM experiment provided evidence to support a model for oxygen migration along favoured α-Fe₂O₃ lattice planes during templated thermal reduction of α-Fe₂O₃ NRs to Fe₃O₄ NRs.

References