

Real Time Evolution of the Reduction of Ilmenite in H₂: A Correlative *In Situ* and *Ex Situ* Study

Arne Janssen, Eric Prestat and M. Grace Burke

Materials Performance Centre, School of Materials, The University of Manchester, Manchester, UK.

In situ TEM, particularly *in situ* high voltage electron microscopy (HVEM) has been utilised in the past to provide a unique perspective on the reduction of oxides. Since the early 1970's when Tighe and Swann [1] reported the first *in situ* observations of iron oxide reduction in a special differentially-pumped gas reaction cell in an AEI EM 7 HVEM, there have been significant advances in the ability to perform detailed nanostructural and chemical analysis of materials in a gaseous environment at elevated temperatures. In this study the reduction of ilmenite (FeTiO₃) in H₂ has been examined using a special environmental heating and gas cell TEM holder in the analytical electron microscope (AEM). In addition, a complementary approach exploring the production of high-grade TiO₂ via an *ex situ* heat treatment and acid leaching has been examined for comparison purposes.

Ilmenite is essential for the production of TiO₂, which is widely used in ceramics, paints, paper and plastics. The high stability of ilmenite means that a combination of extensive energy-consuming methods such as heat treatment (both oxidising and reducing), mechanical activation and acid leaching are required to produce high quality synthetic TiO₂. The pre-reduction treatment converts the mineral to TiO₂ and the contained Fe³⁺ and Fe²⁺ to Fe. The present investigation is directed at generating fundamental information about the reduction reaction mechanism as well as elucidating the structural and chemical relationships at the nanometre scale during the oxygen transfer.

The ilmenite used in this study was obtained from a bulk Norwegian hard-rock ilmenite mineral specimen, which was subsequently cut and ground with ethanol. To generate the appropriate TEM samples, droplets of this suspension were deposited on the surface of the heater E-chip. The real-time evaluation of ilmenite reduction was performed at 470 °C in 950 mbar H₂ using the Protochips Atmosphere *In Situ* Heating and Gas Reaction Cell (Protochips Inc.). Analytical TEM investigation has been carried out using a spherical aberration corrected FEI Titan G2 80-200 with Super X EDX and X-FEG operated at 200 kV and equipped with a GIF Quantum ER. Energy Electron Spectroscopy (EELS) in STEM mode have been used to map selected areas to observe chemical changes during the reduction process. Electron loss near-edge structure (ELNES) analyses have been used to extract O bonding information [2].

The obtained results revealed that the decomposition of ilmenite to Ti and Fe resulting in restructuring of the overall morphology of the initial grains (Fig1), with a non-uniform distribution of Fe particles on the surface due to volume diffusion of Fe towards the surface, as Ti is not mobile below 900 °C [3]. We have previously reported that the formation of porosity in the residual TiO₂ is due to the volume reduction of nearly 40% associated with the ilmenite reduction [4]. Our ELNES analyses of the oxygen K-pre-edge indicated that most of the iron is still covalent bonded with oxygen and not reduced to metallic iron (Fig2). However, a complete reduction of Fe oxides can be accomplished at this temperature by a disproportionation reaction of FeO to Fe₃O₄ to Fe [5]. Our *in situ* observations will be compared and discussed with respect to the analyses of the *ex situ* processed ilmenite [6].

References:

- [1] NJ Tighe and PR Swann, *Metall. Trans. B* **8** (1977), pp. 479-487.
 [2] PA van Aken *et al*, *Phys Chem Minerals* **25** (1998), pp. 494-498.
 [3] DB Rao and M Rigaud, *Oxidation of Metals* **9** (1975), pp. 99-116.
 [4] A Janssen *et al*, *Microscopy and Microanalysis* **21** (2015), pp. 565-566.
 [5] WK Jozwiak *et al*, *Applied Catalyst A: General*, **326** (2007), pp. 17-27.
 [6] We acknowledge BP for financial funding. The authors thank Matthew A. Kulzick and Nestor J. Zaluzec for helpful discussions.

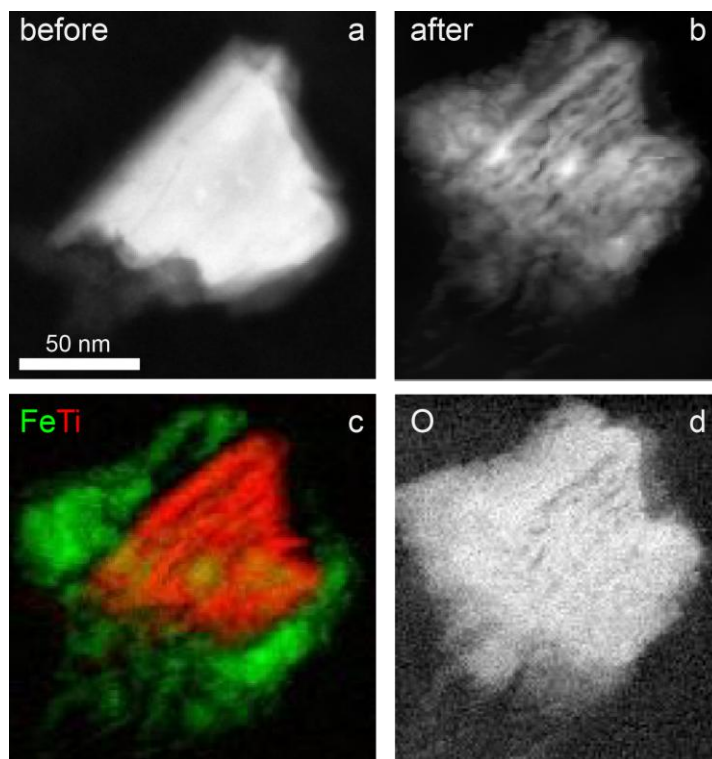


Figure 1. STEM-HAADF images before (a) and after (b) H₂ reduction, EELS elemental maps (c-d) of the decomposed ilmenite.

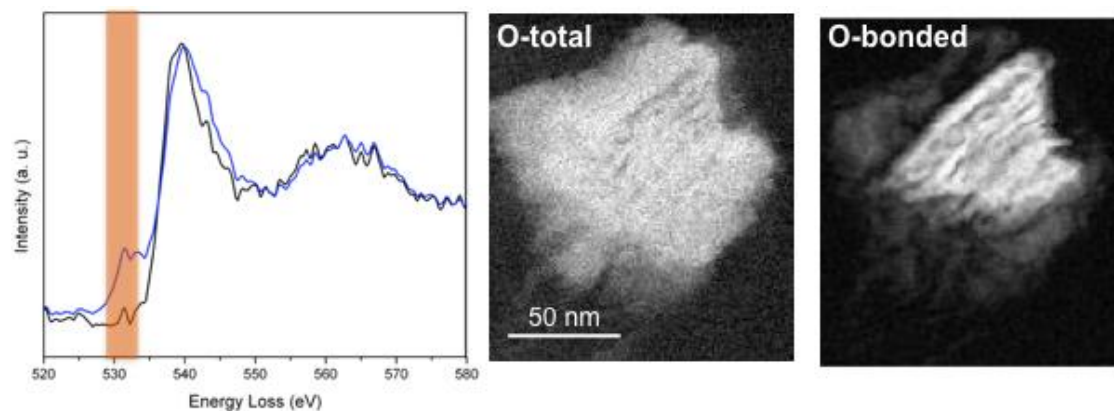


Figure 2. O K-pre-edge map at 530 eV indicating covalent bonding of O with Fe or Ti.