Impedance spectroscopy analysis of TiₙO₂ₙ₋₁ Magnéli phases

D. Regonini a,⁎, A.C.E. Dent a, C.R. Bowen a, S.R. Pennock b, J. Taylor b

a Materials Research Centre, Department of Mechanical Engineering, University of Bath, UK
b Department of Electronic & Electrical Engineering, University of Bath, UK

1. Introduction

It is well known that the electrical conductivity of titanium dioxide can be enhanced by heat-treating the oxide at high temperature in a reducing atmosphere, usually in the presence of hydrogen or carbon. This process leads to the formation of sub-stoichiometric oxides with the general formula TiₙO₂ₙ₋₁ (with 3 ≤ n ≤ 10), known as Magnéli phases [1]. In non-stoichiometric titanium dioxide, TiO₂-x, with low x (0 < x < 0.10), the dominant point defects in the structure consist of Ti³⁺ and Ti⁴⁺ interstitials and oxygen vacancies [2]. However, the Magnéli phases (x = 0.10–0.34) are characterised by extended planar defects and crystallographic shear planes which vary according to the oxygen deficiency [3,4]. Magnéli phases are of interest in cathodic protection, batteries, catalytic support for fuel cells, treatment of aqueous waste and contaminated water due to their high electrical conductivity and chemical resistance [5–7].

A comprehensive understanding of the electrical properties of Magnéli phases is crucial to the progress of the aforementioned fields. The dc electrical conductivity of TiₙO₂ₙ₋₁, with 3 ≤ n ≤ 6 has been studied by Bartholomew and Frankl from 78 to 298 K [8]. Inglis et al. [9] performed a similar study for 4 ≤ n ≤ 9 at 4–320 K. In both studies, a transition in the conductive mechanism from semiconductor to metallic was observed at ~150 K. The ac electrical properties of TiₙO₂ₙ₋₁ have not been extensively investigated and in this letter we discuss the manufacture and microstructure of Magnéli phases along with impedance spectroscopy (IS) of the frequency and temperature dependence of ac conductivity and relative permittivity (εr).

2. Experimental methods

The TiO₂ powder (3 μm, Pikem, 99.5%) was processed by adding 3 wt.% of Polyethylene Glycol (PEG) 8000 MW to distilled water to create a slurry which was ball-milled for 24 h. The slurry was dried and the resulting powder sieved through a 45 μm mesh. Pellets were formed by uniaxial pressing at 200 MPa. The green bodies were then fired at 1300 °C (4 h) and reduction of TiO₂ was achieved by carbothermal reduction at 1300 °C (6 h). Typical sample dimensions were 10.6 mm diameter (d), and 1.4 mm thickness (t). For electrical measurements samples were polished to a mirror finish and electroded with Au using an Edward E306 Evaporator. The ac conductivity and permittivity were measured from 25 to 375 °C using a Solartron 1260 Impedance Analyser with a Solartron 1296 Dielectric Interface. The range of frequency investigated was from 0.1 Hz to 1 MHz and the applied voltage was 0.1 Vrms. Microstructural characterisation was undertaken by using optical microscopy and a Scanning Electron Microscope (SEM) and X-ray diffraction (XRD). The density of the tablets was obtained using the hydrostatic method (BS Standard No. EN 623-2:1993).

3. Discussion and results

The microstructure of a typical TiₙO₂ₙ₋₁ specimen thermally etched in argon, Fig. 1a, reveals a dense structure, calculated to be 95 to 95.5% of theoretical density (4.3 g/cm³) [6]. The presence of large grains, over 30 μm, is clearly observed in Fig. 1a, suggesting that a degree of grain growth has occurred during the reduction treatment of TiO₂. For comparison, the grain size of non-reduced TiO₂ was typically in the order of 10 μm (not shown). The residual porosity (5%) measured is similar to the low porosity observed in the SEM image, Fig. 1b.
higher than 1 MHz. The only observable arc in Fig. 3 appearing in the relaxation time (\(\tau\)) at room temperature (RT) or higher temperature because the (RGB) [12] and corresponds to a resistance of approximately 1400 \(\Omega\). TinO\(_2\) and a resistivity of 10\(^2\)–10\(^{3}\) \(\Omega\) m. The intercept, RB, is not significantly affected by the temperature and, as expected considering the residual TiO\(_2\), the resistivity is 2 to 4 orders of magnitude higher than values reported for pure Magnéli Phases [5-7]. The impedance plot for TinO\(_2\) samples. As a result, the electrical conductivity of our specimens is expected to be few orders of magnitude lower than for pure Ti4O7, Ti5O9 and Ti6O11, reported to be in the order of 10\(^5\)–10\(^6\) S/m [5-7].

The impedance plot for TinO\(_2\)–1, Fig. 3, can be interpreted as the result of two RC elements in series, where the non-zero intercept at high frequency (inset of Fig. 3) provides an estimation of the resistance of the bulk of the grains (RB) [11], which is approximately 12 \(\Omega\) and taking into account the size of the specimens corresponds to a resistivity of 10\(^{-1}\) \(\Omega\) m. The intercept, RB, is not significantly affected by the temperature and, as expected considering the residual TiO\(_2\), the resistivity is 2 to 4 orders of magnitude higher than values reported for pure Magnéli Phases [5-7]. The semicircle for the grain bulk is not observed at room temperature (RT) or higher temperature because the relaxation time (\(\tau = RC\)) of the grain bulk regions is at a frequency higher than 1 MHz. The only observable arc in Fig. 3 appearing in the region 100 kHz–0.1 Hz is assigned to the grain boundary response (R\(_{GB}\)) [12] and corresponds to a resistance of approximately 1400 \(\Omega\) and a resistivity of 10\(^2\) \(\Omega\) m at room temperature. At room temperature R\(_{GB}\) is therefore approximately three orders of magnitude higher than R\(_B\), however since R\(_{GB}\) decreases systematically with increasing temperature it eventually approaches R\(_B\) (10\(^{-1}\) \(\Omega\) m) at 375 °C.

It is interesting to observe how the real ac conductivity, \(\sigma(\omega)\), of TinO\(_2\)-1 varies with frequency, as shown in Fig. 4. There is no frequency dependence of the conductivity at low (0.1 Hz) and medium (1 kHz) frequencies, whereas for higher (1–10 kHz) frequencies the conductivity begins to rise with frequency and the same trend is observable over the all range of temperatures investigated. The lower the magnitude of the conductivity (i.e. at lower temperature), the earlier it becomes frequency dependent, following the “universal” power law behaviour [13] of the type \(\sigma(\omega) = \sigma(0) + B\omega^p\), where \(\omega\) is the angular frequency (2\(\pi\)f\(_p\)) and p a constant between 0 and 1, and \(\sigma(0)\) the conductivity at low frequency (also identified as \(\sigma_d\), dc conductivity). It has been previously shown that power law dispersions in conductivity and permittivity can be explained at a microscopical level by a resistor–capacitor (RC) network without the need to introduce novel many-body relaxation phenomena [14].

In the particular case of Magnéli phases the resistors in the RC network are represented by sites in which the oxygen has been stripped out during the carbothermal treatment to generate TinO\(_2\)-1, whereas the stoichiometric and more resistive TiO\(_2\) areas correspond to the capacitative sites. This is supported by the XRD analysis, that indicated the ceramic is such a mixture. Based on this assumption we would also expect a similar, but opposite, power law dispersion of the relative permittivity (\(\varepsilon_r\)) of the Magnéli phases, with a decrease of the permittivity with frequency (\(\varepsilon_r\) approaching a constant value at higher frequency (>10 kHz). However, it is observed in Fig. 5, especially at low temperatures (<300 °C), that there is only a slight decrease of the relative permittivity with frequency in the range 1 Hz to 100 kHz, followed by an abrupt decrease at frequencies higher than 100 kHz. Interestingly, the impedance plot in Fig. 3, suggests that the grain boundary response for TinO\(_2\)-1 occurs in the region 0.1 Hz to 100 kHz. The abnormally high relative permittivity (10\(^5\)–10\(^6\)) and its

![Fig. 1. Optical (a) and SEM (b) images of the microstructure of thermally etched Magnéli Phases.](image1)

![Fig. 2. XRD spectra of TinO\(_2\)-1 obtained from carbothermal reduction (a) and TiO\(_2\) before the reduction step (b).](image2)

![Fig. 3. Impedance plot for TinO\(_2\)-1 (1 MHz to 0.1 Hz, RT to 375 °C). The inset shows the non-zero intercept on the Z’ axes, from which the resistance (R\(_B\)) of the grain bulk can be obtained. The only observable arc is attributed to the grain boundaries (R\(_{GB}\)) response.](image3)
lack of frequency dependence over the 1 Hz to 100 kHz range, particularly at low temperature (<300 °C), can be explained by the presence of insulating grain boundaries, with a $R_{cb}$ resistivity two to three orders of magnitude higher than $R_\infty$, creating an Internal Barrier Layer Capacitor (IBLC) effect [15]. A possible reason for the presence of more resistive grain boundaries is that the reduction of TiO$_2$ occurs preferably in the bulk of the grains rather than at the interface between grains, although further analysis are required to confirm this hypothesis. The significant drop of the permittivity at higher frequencies (100 kHz–1 MHz) is thought to occur when the more resistive intergranular regions also begin to contribute to the network conductivity. The drop of the permittivity is more dramatic at lower temperature (<300 °C) because at higher temperatures (>300 °C) the resistivity of the grain boundaries decreases and $R_{cb}$ approaches $R_\infty$. As a consequence the IBLC becomes less significant and a power law behaviour of the type $\varepsilon(\omega) = D \omega^{-\gamma} + \varepsilon_\infty$, where $D$ is a constant and $\varepsilon_\infty$ is the limit of permittivity at high frequency, is instead observed.

4. Conclusions

The microstructure, X-ray analysis and impedance spectroscopy (IS) characterisation of Ti$_n$O$_{2n−1}$, have been presented, with the objective to enhance the understanding of ac electrical properties of these materials. The reduced specimens contain a mixture of Ti$_n$O$_{2n−1}$ phases and some unreduced TiO$_2$ with a dc conductivity 7–8 orders of magnitude higher than pure TiO$_2$ at room temperature. The ac conductivity increases with frequency (and temperature) following a power law dispersion, as expected for a material which can be modelled by a RC network. However the relative permittivity, especially at low temperatures (<300 °C), is less frequency dependent due to the presence of grain boundaries three orders of magnitudes more resistive than the grain bulk. This suggests that intra-grain reduction is favoured over inter-grain reduction and as a result an Internal Barrier Layer Capacitor (IBLC) effect is produced. Further work in evaluating activation energies for conduction for stoichiometric and non-stoichiometric titania based materials is currently in progress [16].

Acknowledgements

The research leading to these results was funded by the European Union Seventh Framework Programme (FP7/2007–2013) under grant agreement no CP-TP 229099–2 as part of the ‘MesMesh’ project.

References