

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.


Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: <i>In-Situ</i> Synchrotron Diffraction of the Electrochemical Reduction Pathway of TiO ₂	Experiment number: MA478
Beamline: ID15A	Date of experiment: from: 28-02-08 to: 04-03-08	Date of report: Aug 2009 <i>Received at ESRF:</i>
Shifts: 15	Local contact(s): Thomas Buslaps	
Names and affiliations of applicants (* indicates experimentalists): R. Bhagat*, R. J. Dashwood* (Warwick University) D. Dye*, S. L Raghunathan*, R. J. Talling*, B. K. Jackson*, D. Inman (Imperial College) K. K. Rao* (Metalysis) M. Jackson* (University of Sheffield)		

Report:

Despite over ten years of research into the low-cost electrowinning of titanium direct from the oxide, the reduction sequence of TiO_2 pellets in molten CaCl_2 has been the subject of debate, particularly as the reduction pathway has been inferred from ex-situ studies. Here, for the first time white beam synchrotron X-ray diffraction is used to characterize the phases that form, in-situ during reduction and with $\sim 100 \mu\text{m}$ spatial resolution. It is found that TiO_2 becomes sub-stoichiometric very early in reduction facilitating the ionic conduction of oxygen ions, that CaTiO_3 persists to nearly the end of the process and that, finally, CaO forms just before completion of the process. The method is quite generally applicable to the in-situ study of industrial chemical processes. Implications for the industrial scale-up of this method for the low-cost production of titanium are drawn.

Performed experiments and current status:

R. Bhagat , D. Dye , S. L. Raghunathan, R. J. Talling, B. K. Jackson , K. K. Rao , and R. J. Dashwood; Analysis of the FFC reduction of

TiO_2 using white beam X-rays. Status: Analysis complete and paper submitted to journal. [1]

B. K. Jackson , D. Dye , S. L. Raghunathan, R. J. Talling, B. K. Jackson , R. Bhagat, M. Jackson, and R. J. Dashwood; Analysis of the FFC reduction of NiTiO_3 using white beam X-rays. Status: Analysis complete and paper submitted to journal. [2]

Highlight 1) Molar fractions of phases present during reduction of TiO_2 .

Measuring the evolution of phases during reduction is of critical importance for both fundamental studies and scale-up issues. Two key points are mentioned in regard to Figure 1:

- It is interesting to note that the phase Ti_3O_5 is not detected during reduction. The Ti-O phase diagram predicts that this phase should precede the formation of Ti_2O_3 . In addition, significant quantities were observed by researchers such as Schwandt *et al.* [3], Dring *et al.* [4] and by the authors during *ex-situ* analysis of thin films. Thus this experiment furthered the fundamental

understanding of the FFC process. In addition, there are implications for scale up and improvements in efficiency.

- CaO is detected throughout the pellet at the later stages of reduction. This phase forms when the electrolyte in the pores becomes saturated with oxide ions (22 mol. %). The onset of CaO formation appears to correlate with the reduction of calcium ternary phases. This results in a rapid evolution of oxide ions that have to be transported through the pellet pores to the bulk electrolyte. During reduction the porosity of the pellet, which is originally highly porous (60 % open porosity), is reduced through a combination of sintering of titanium and formation of titanate phases. This significantly reduces the permeability of the pellet allowing oxide ion saturation to occur. In addition, the removal of CaO appears to occur relatively easily once the flux of oxide leaving the cathode is reduced. Previously, it was previously believed that the formation of CaO resulted in the reduction of permeability of the cathode. The investigators believe this will have significant implications for further fundamental studies and scale up.

Highlight 2) Oxygen content of Ti during reduction

The interstitial oxygen content of alpha titanium can be calculated from the lattice parameter c . The thermal expansion data for lattice parameter of Berry and Raynor [5], based on a temperature range of room temperature to 700°C, was combined with the room temperature dependence of oxygen content on lattice parameter measured by David *et al.* [6]. It should be noted that the hexagonal a -axis length is largely independent of O content, so only the c -axis data was used in the analysis. It is further assumed that the titanium that first forms was saturated with oxygen (14 wt.% O at 900°C). The variation in c -axis lattice parameter and inferred interstitial oxygen content in the α -Ti phase are shown in Figure 2. It was found that the formation of the phase TiC is linked with the removal of interstitial oxygen from Ti. TiC is an undesired product of this process, leading to losses in efficiency and end product. Thus understanding the formation and establishing routes to minimise the formation is of critical importance.

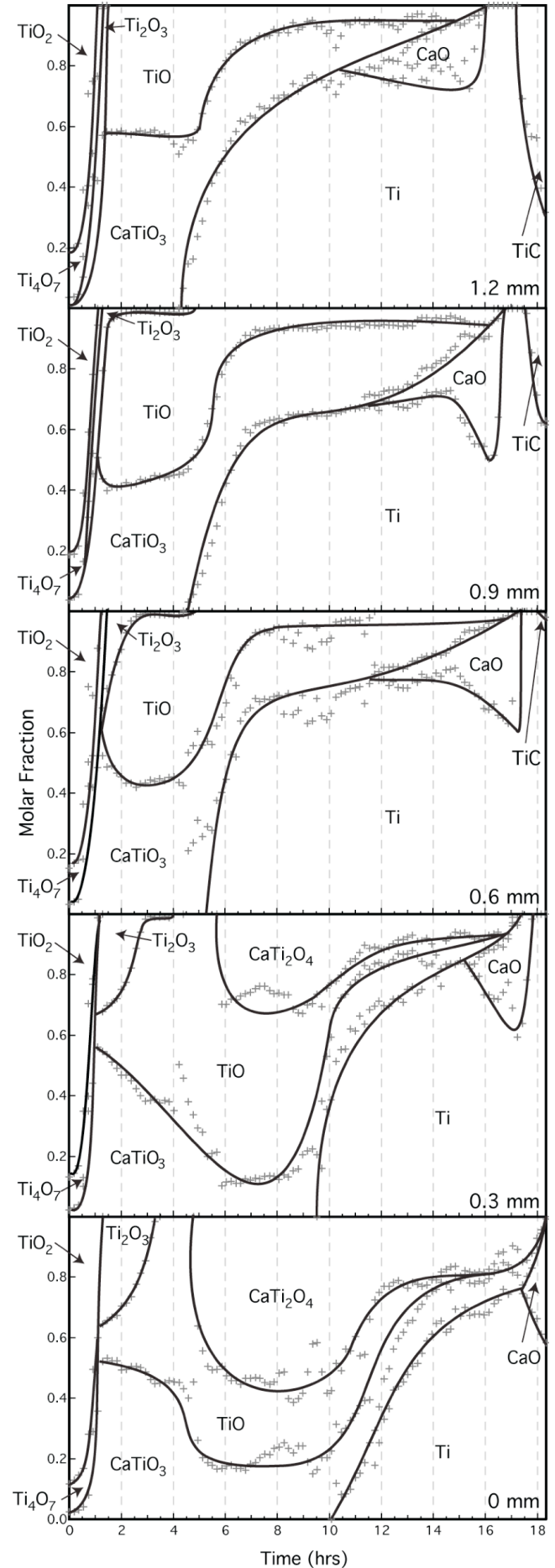


Figure 1 Molar fraction Charts for Several Sampling Sites in the Cathode

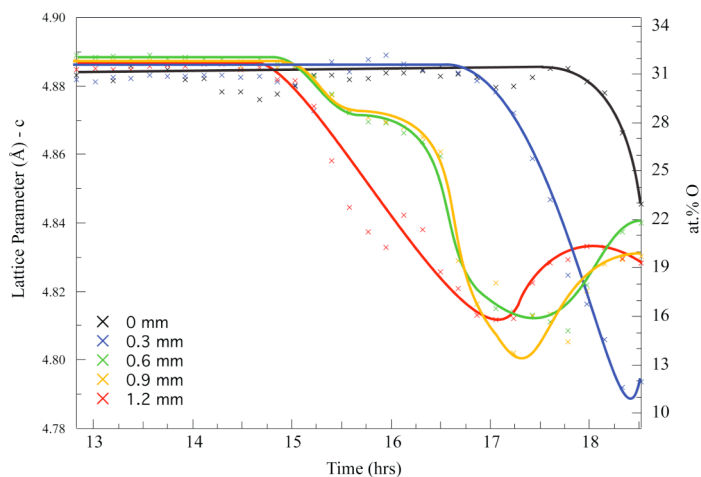


Figure 2 Variation in the c - lattice parameter of α -Ti and inferred interstitial oxygen content during reduction.

References

[1] R. Bhagat, D. Dye, S. L. Raghunathan, R. J. Talling, D. Inman, B. K. Jackson, K. K. Rao, and R. J. Dashwood *In-Situ* Synchrotron Diffraction of the Electrochemical Reduction Pathway of TiO_2

[2] Jackson, B. K. Dye D., Inman D., Bhagat R. Talling R. J., Raghunathan S. L., Jackson M., Dashwood R. J. Characterising of the FFC Cambridge Process for NiTi Production Using *in-situ* X-ray Synchrotron Diffraction.

[3] Schwandt C. and Fray D.J., Determination of the kinetic path-way in the electrochemical reduction of titanium dioxide in molten calcium chloride. *Electrochimica Acta*, 2005. 51(1): p. 66-76. 152(10): D184-D190.

[4] Dring K., Dashwood R.J. and Inman D., Voltammetry of Titanium Dioxide in Molten Calcium Chloride at 900°C . *Journal of The Electrochemical Society*, 2005. 152(3): p. E104-E113.

[5] Berry R.L.P. and Raynor G.V., *Research*, 1953. 6(21S)

[6] David D., Garcia E.A., Lucas X. and Beranger G., Etude de la Diffusion de l'Oxygene Dans le Titane a Oxyde Entre 700°C et 950°C *Journal of the Less-Common Metals*, 1979. 65: p. 51-69.