



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:**

n-Situ Characterisation of the Production of Ti-6Al-4V via the FFC Process

Experiment**number:**

MA1349

Beamline:

ID15A

Date of experiment:from: 22nd July 2010 to: 26th July 2010**Date of report:**25th May 2011**Shifts:**

12

Local contact(s):

Thomas Buslaps

*Received at ESRF:***Names and affiliations of applicants (* indicates experimentalists):**

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K. K. Rao, M. Conti (Metalysis)

Report:

Despite over ten years of research into the lowcost electrowinning of titanium direct from the oxide, the reduction sequence of TiO₂-V₂O₅-Al₂O₃ pellets in molten CaCl₂ 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 ~100 μm spatial resolution. It is found that TiO₂-V₂O₅-Al₂O₃ becomes substoichiometric very early in reduction facilitating the ionic conduction of oxygen ions, that CaTiO₃ 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.

Experimental

Precursors were formed using reagent-grade TiO₂, V₂O₅ and Al₂O₃ (99.5% Alfa Aesar), ball milled with ethanol and zirconia spheres for 24 h. The slurry was dried and the powder ground in a mortar and pestle with a small quantity of distilled water, which acted as a binding agent. 0.4 g of powder was uniaxially compacted at 100 MPa in a 13 mm diameter die. The precursors were then drilled to accept the commercial-purity (CP) Ti current collector and sintered in Ar (BOC pureshield – 150 mL min⁻¹ at 1373 K for 3 h at a rate of 3 K min⁻¹). The pellets were then ground to approximately 7mm and 0.2 g. The electrochemical cell was designed to minimize attenuation of the white X-ray beam and avoid additional sources of diffraction. Reductions were performed in a resistance furnace-

heated quartz glass vessel (Fig. 1), as in Ref. [11]. Openings were incorporated into the furnace for the synchrotron X-ray beam. A glassy C crucible was used to contain the salt and act as a consumable anode. CaCl₂ granules (Fluka) were dried and prepared [11] within the C crucibles, which were then vacuum sealed prior to use.

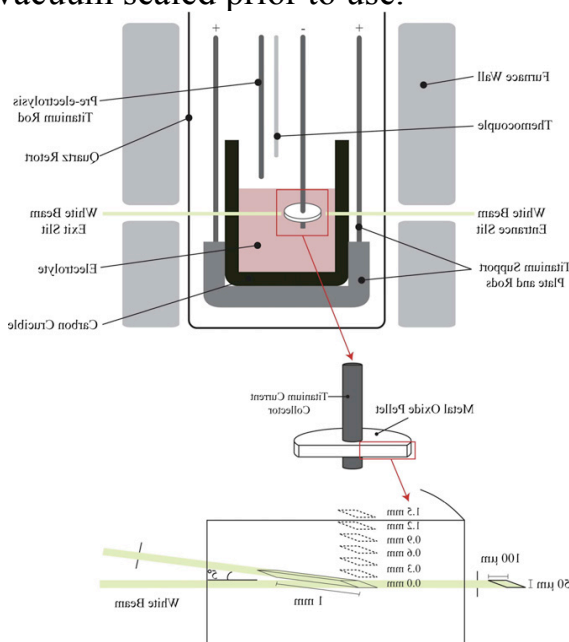


Figure 1 Apparatus

The sintered mixed oxide precursor precursor was attached to the Ti current collector and suspended above the salt prior to pre- electrolysis. The apparatus was heated at a rate of 1 K min⁻¹ under Ar (BOC pureshield – 50 mL min⁻¹) to the electrolysis temperature (1173 K). The electrolyte was then thermally equilibrated for 3 h. Prior to experiments the salt was pre-electrolysed for 1–3 h to remove electroac- tive impurities by polarizing a grade 2 CP-Ti rod (3 mm) vs. the graphite crucible. Following the pre-electrolysis, the precursor was lowered into the molten salt and polar- ized at a rate of 0.5 mV s⁻¹ from open circuit to ± 3100 mV vs. the C anode. The ID15A beamline at the ESRF was used to produce an unmonochromated (white) X-ray beam in energy dis- persive mode. A 50 μm \times 100 μm incident beam and 5 $^\circ$ scattering angle were defined by slits yielding a gauge length of 1000 μm (Fig. 2). The assembly was mounted on a translation stage, allowing nine locations at different heights in the pellet to be studied. Acquisition times were 60 s per pattern. The diffraction patterns were analysed by Rietveld refinement using GSAS [11], allowing phases to be identi- fied and atomic fractions obtained. The source spectrum was normalized using both an Al powder and the powder TiO₂ pattern obtained from the pellet prior to insertion into the cell. Beam hardening within the cell was accounted for by comparison with the initial patterns obtained from the pellet.

Current Status

The analysis of the data is currently being academically reviewed, by the authors, with intention to submit the completed paper to *Electrochimica Acta* in the upcoming weeks.

Highlights

Molar fractions of phases present during reduction of TiO₂. 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:

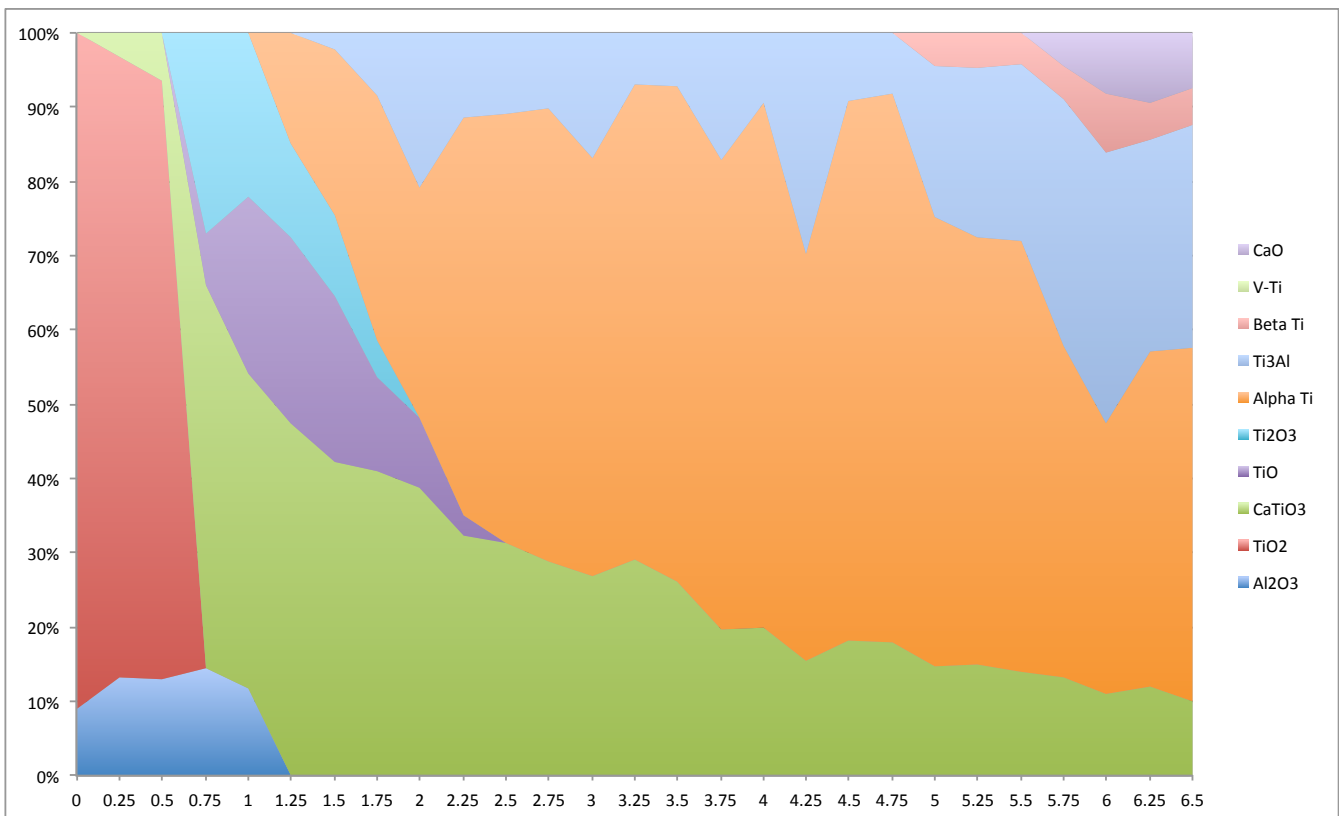
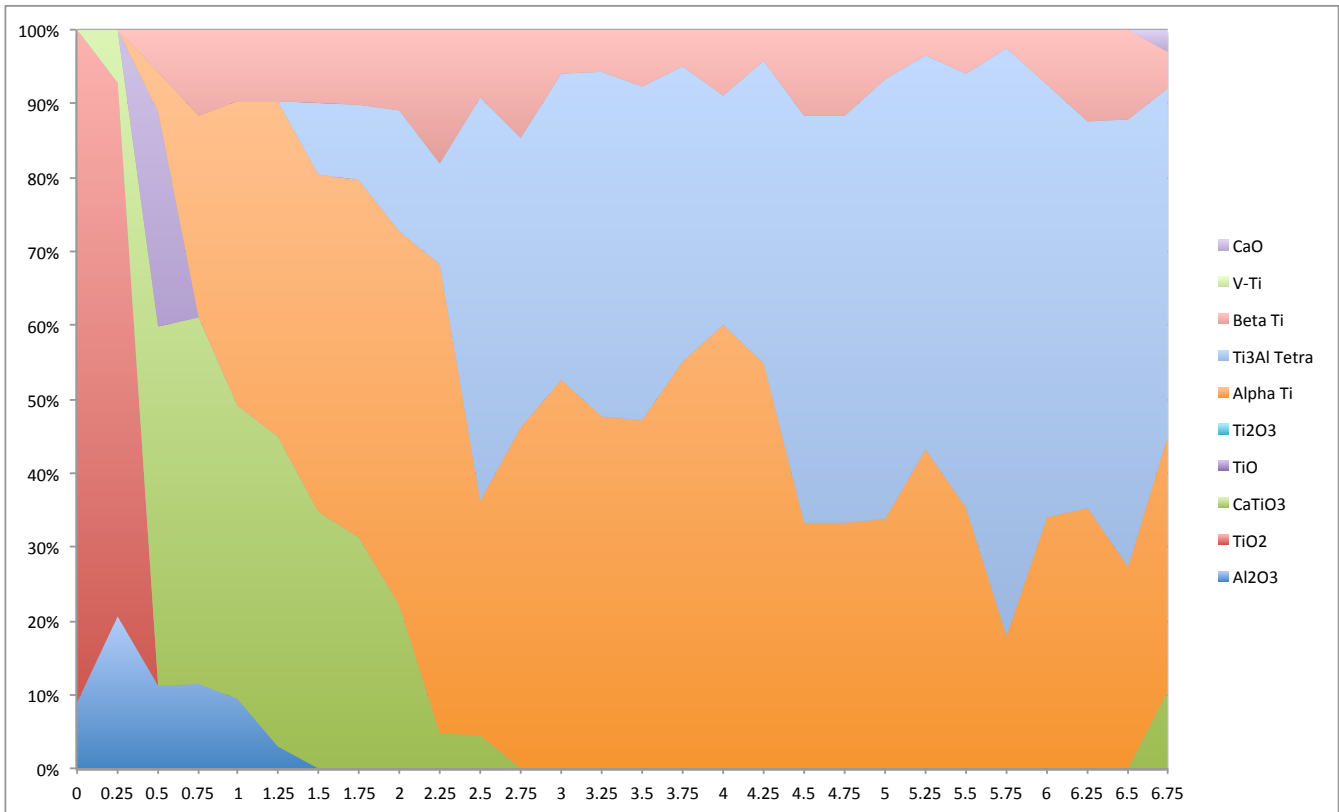


Figure 2 Molar fraction of phases present at the edge volume (top) and core volume (bottom)

Early beta Ti formation.

The formation of beta Ti was expected to occur at the end of reduction as predicted by the Ti-O phase diagram. However the molar fraction charts shown in Figure 1, clearly show that this phase forms much earlier on. This is due to the reduction of V₂O₅ early on which stabilise the cubic form of Ti.

Formation of Ti₃Al

This is the first study where this phase has been identified in the reduction of TiO₂-V₂O₅-Al₂O₃ mixed oxides. More so it appears to be one of the more dominant phases during reduction. This clearly has bearing on the reduction behaviour of the mixed oxide and the size and chemical composition of the alloy grains post reduction. The presence of this phase also has context in the homogenisation of the alloy with respect to vanadium and aluminium content.

Al₂O₃ stability.

Alumina was found to be much more stable than TiO₂ and in fact only reduced once all TiO₂ has been converted. In addition the reduction of this phase gives rise to the Ti₃Al phase mentioned earlier. More homogeneous distribution of Al₂O₃ in the mixed oxide preforms may improve the reduction kinetics and final homogeneity of the alloy by minimising the formation of Ti₃Al.