Polar™ Titanium – Development of the BHP Billiton Titanium Metal Production Process

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Titanium 2005 – Emerging Technologies session
21st Annual ITA Conference
25-27 September 2005, Scottsdale, AZ, USA

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The Polar™ Titanium process is based on reduction of TiO_2 to Ti using molten salt electrochemistry

Cathodic reactions

$$CaO_{(in\ salt)} + 2e^- = Ca_{Met\ (in\ salt)} + O^{2-}$$

$$TiO_2 + 2Ca_{(in\ salt)} = Ti + 2CaO_{(in\ salt)}$$

Anodic reactions

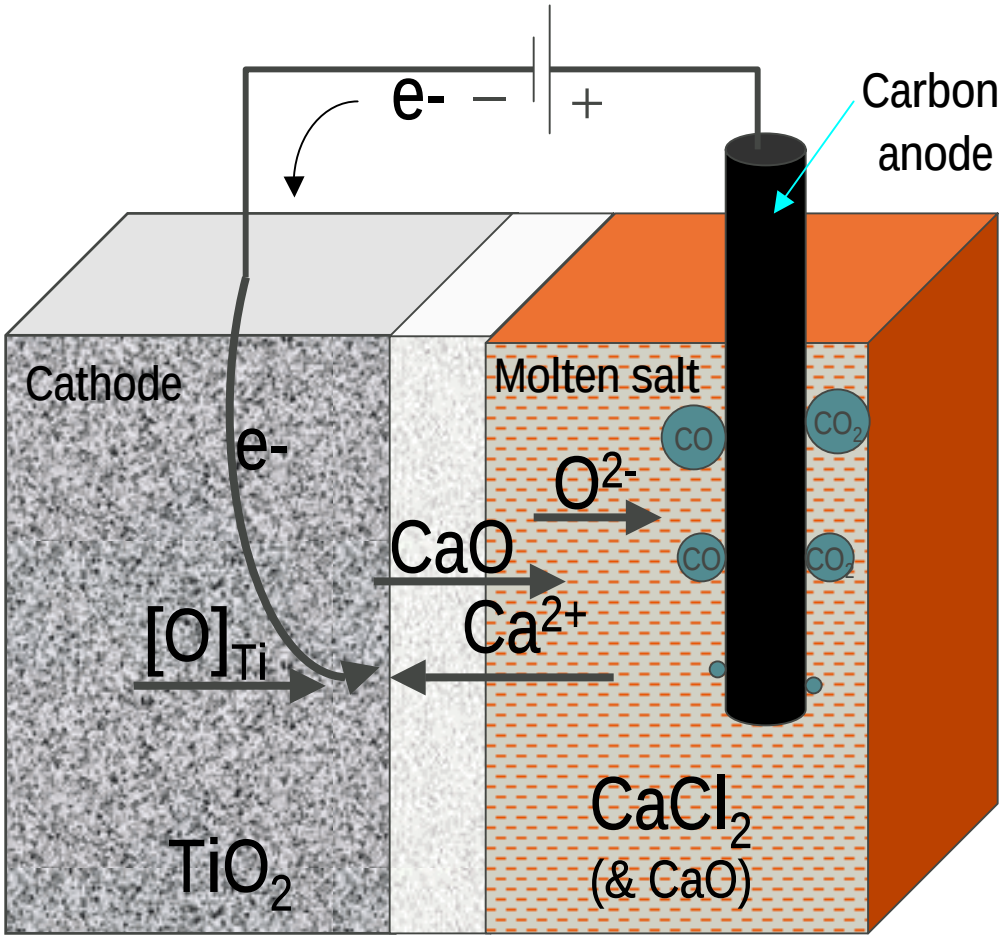
$$O^{2-} + C_{(anode)} = CO_{(gas)} + 2e^-$$

$$2O^{2-} + C_{(anode)} = CO_{2(gas)} + 4e^-$$

$$TiO_2 + C = Ti + \{CO_{(gas)} + CO_{2\ (gas)}\}^*$$

Kinetics of the reaction are important – key parameters for investigation include:

- Reactor temperature,
- Applied voltage,
- Electrolyte composition
- Feed properties



* *Stoichiometry not shown, CO/CO_2 ratio varies with process conditions*

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Polar™ Titanium - Project history

2001 - 2002
Gram-scale fundamentals

2003 - 2004
Design, construction, commissioning

2004 - 2005
kg-scale operation

2001 2002 2003 2004 2005 2006

Fundamental program

- Elucidated the key reaction mechanisms and provided an IP portfolio base.
- Provided key understanding of reduction kinetics as a function of electrode design, current densities, process voltage, temperature, salt composition, feed morphology & properties.

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Attributes of the experimental facilities – main reactor

REACTORS

- Containment of up to 1 t of molten salt ($CaCl_2$).
- $CaCl_2$ preheating and melting plant for reactor startup (patented).
- Molten $CaCl_2$ salt temperature up to 150°C of salt superheat (i.e. to 930°C in-salt temperature).
- Variable reduction power to 4800 A, or to a potential of 16 V.
- Off gas handling facilities and reactor shrouding to 28 m^3 min^{-1} (1000 cfm). Off gas scrubbing facilities for HCl, Cl_2, and $CaCl_2$ fume.
- Inert gas (Ar) shielding for mitigation of metal re-oxidation.

PROCESS CONTROL & MONITORING

- Cascaded, multi-zone, flux-limited control for near isothermal furnace heating.
- Individual current and voltage monitoring for every electrode.
- Real-time product gas analysis (CO, CO_2, and O_2).

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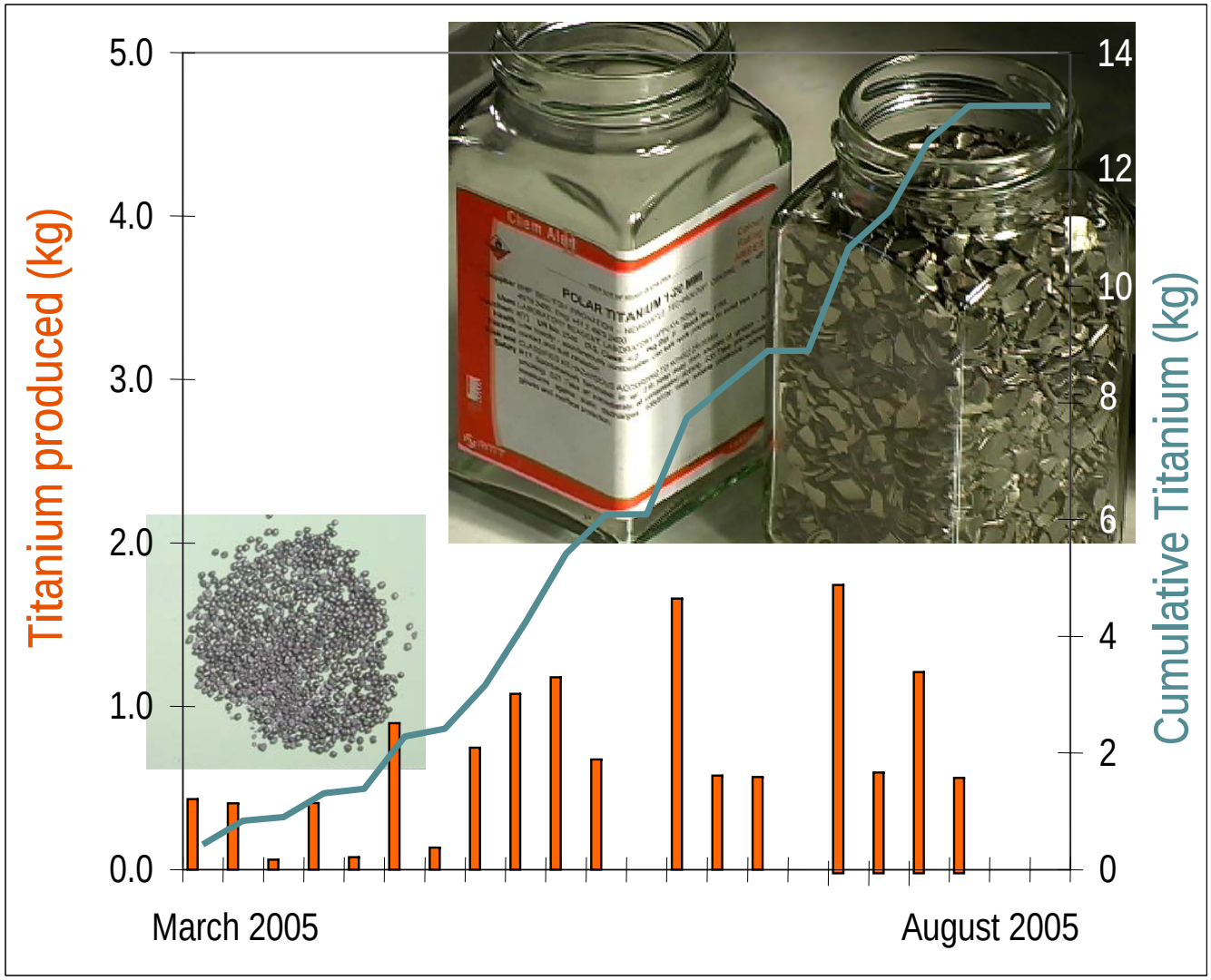
Titanium produced in recent reactor trials for a range of feed types



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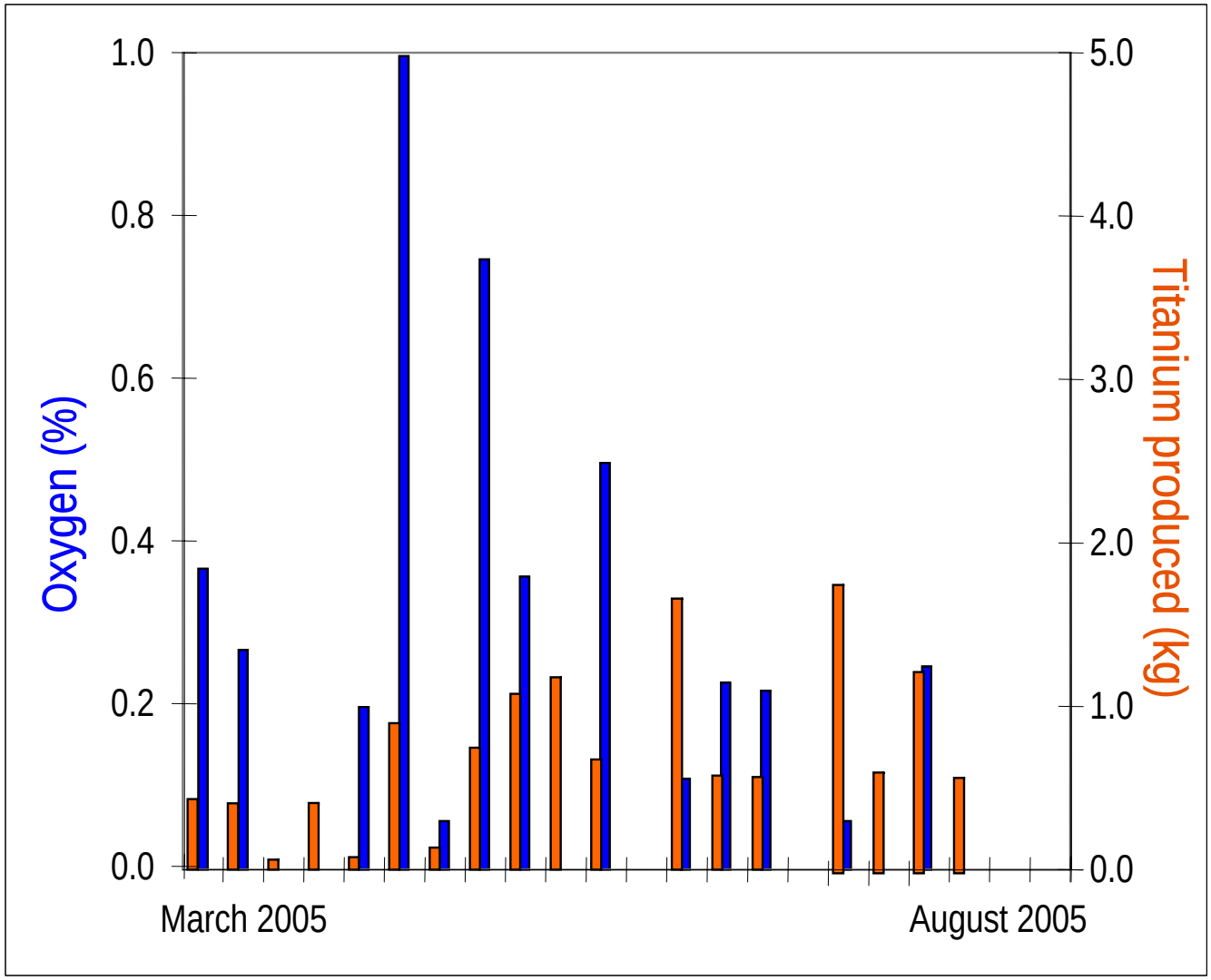
Oxygen content in reduced titanium during experimental program



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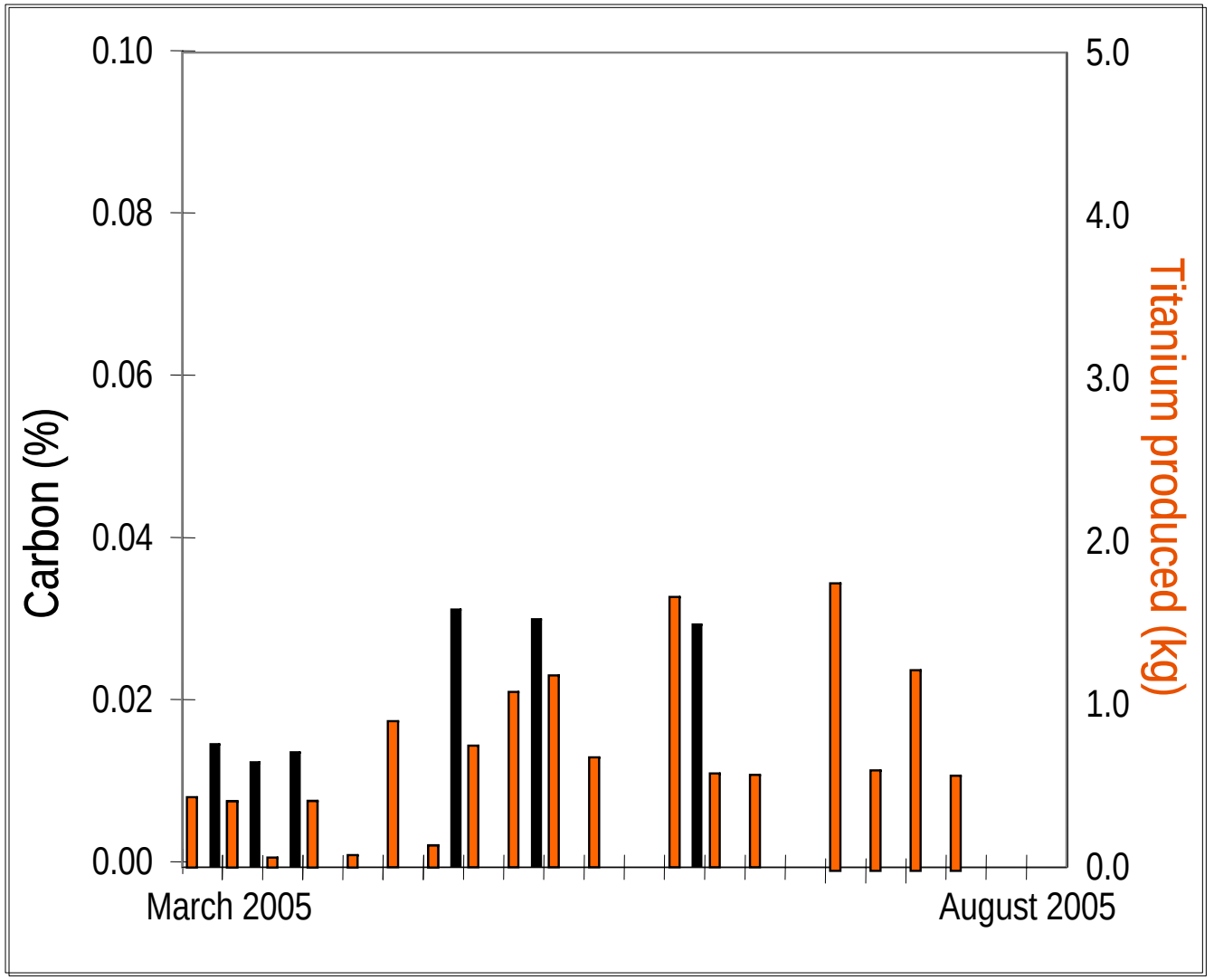
Carbon content in reduced titanium during experimental program



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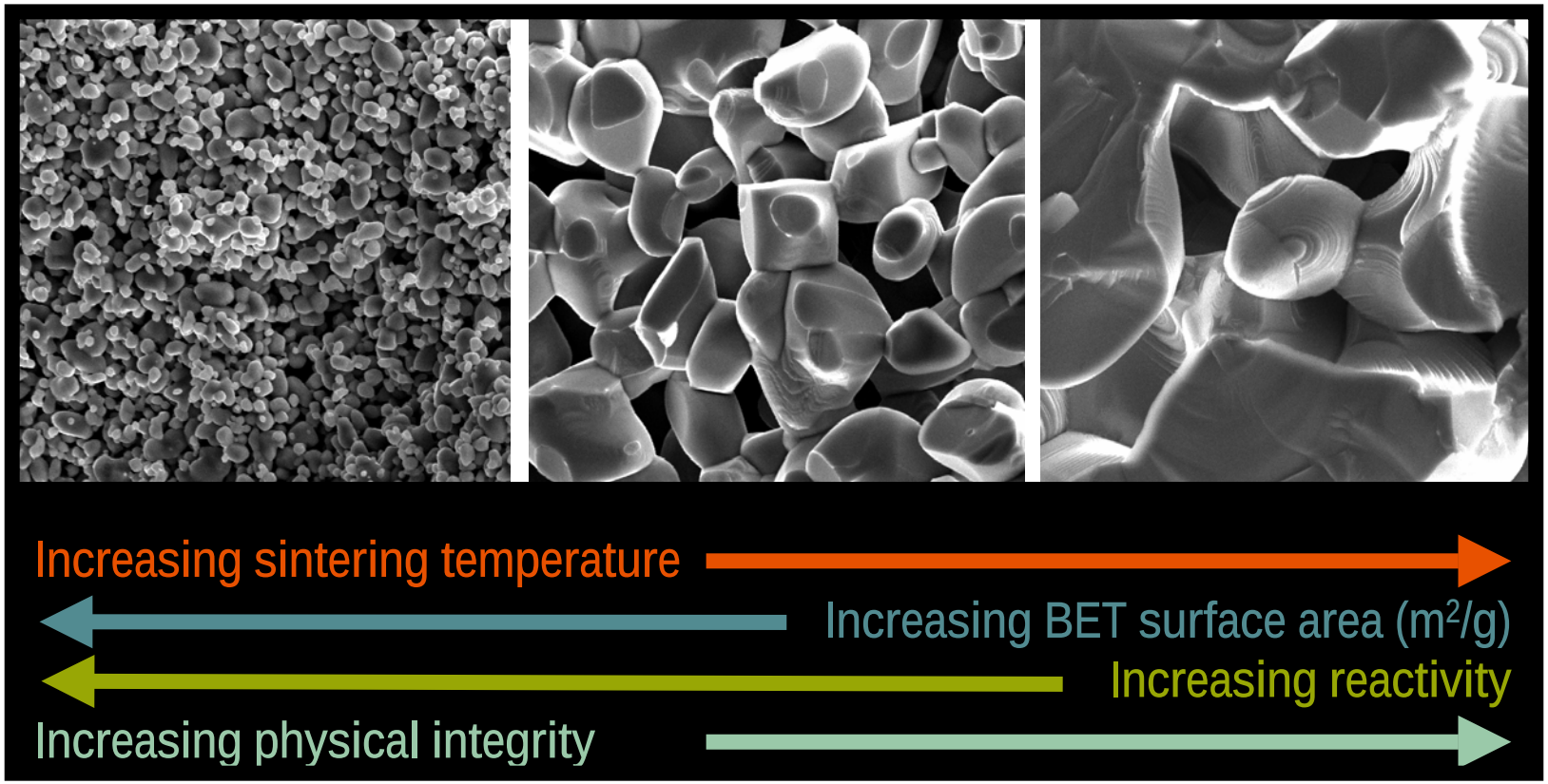
A range of TiO_2 feed morphologies have been tested

Micrographs show fracture surfaces of TiO_2 feed forms.



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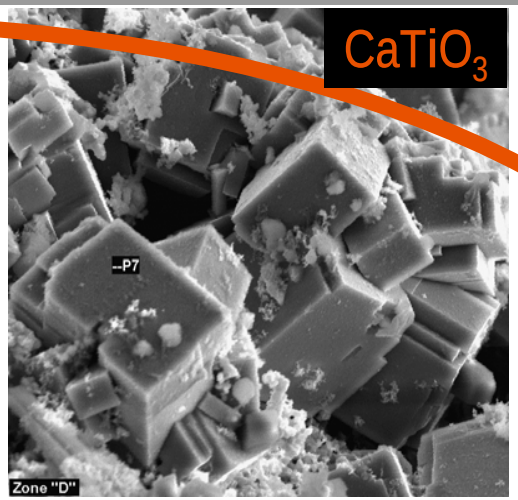
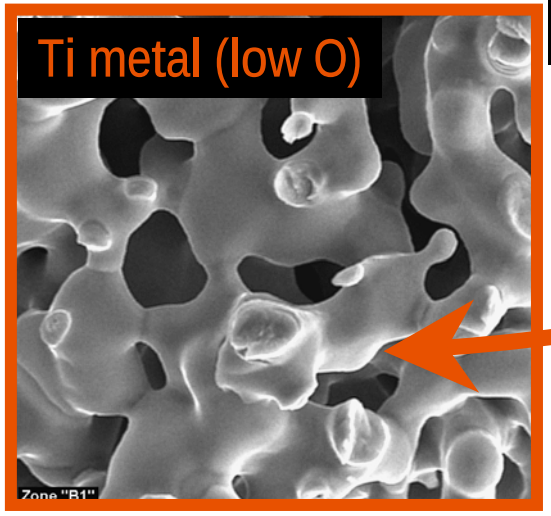
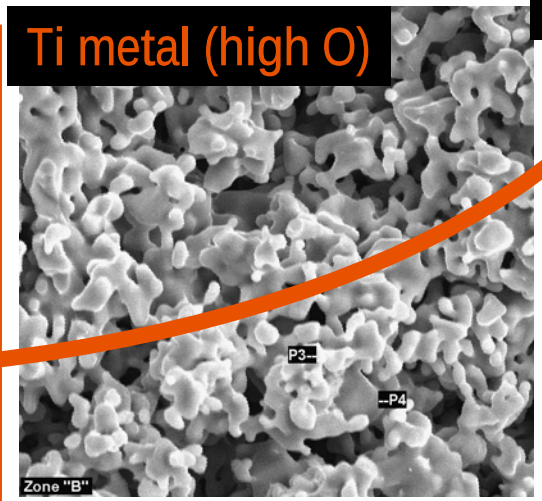
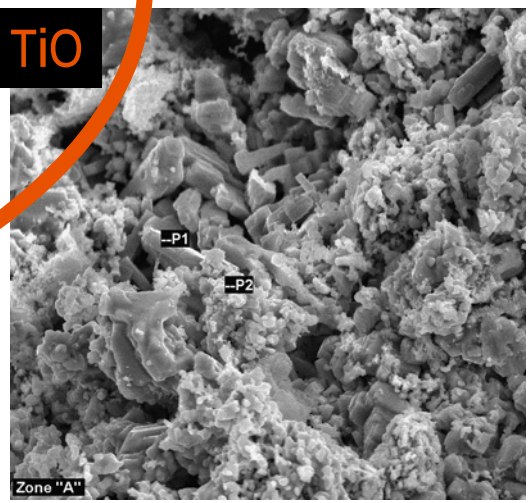
Final titanium metal product - morphology changes throughout the reduction process



- The morphology of the final titanium develops to the final form as the oxygen content is progressively reduced.







Scale
10 μm

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Typical product chemistry

Product analysis comments

- As reduction reactions proceed, the feed form progressively attains final product specifications, moving through a series of transitions to produce Ti:
  $TiO_2 \Rightarrow Ti_4O_7 \Rightarrow Ti_3O_5 \Rightarrow Ti_2O_3 \Rightarrow Ca_xTi_yO_z \Rightarrow TiO \Rightarrow$ Ti metal (0 to 15% O)

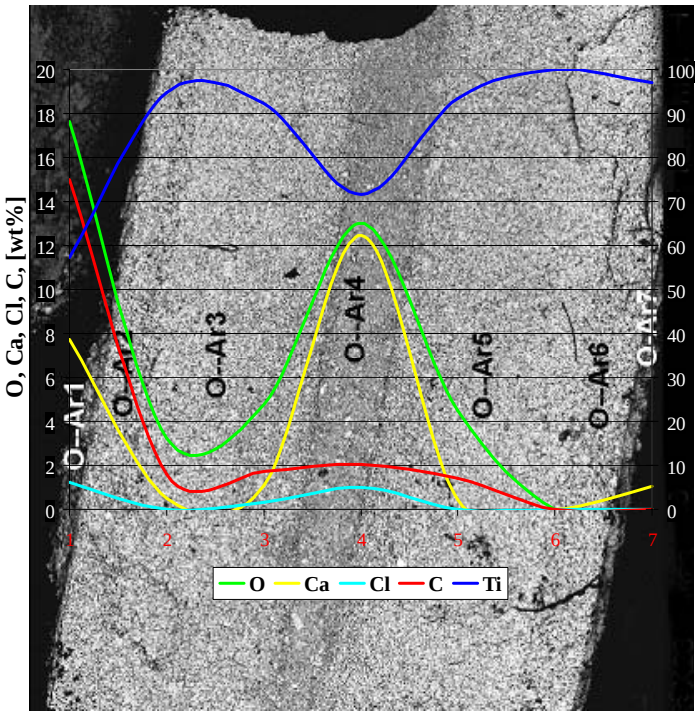
- Potential for a range of products:
  ingot, sheet, or powder.
- Product quality from the reactor can be varied to suit market requirements.
- Quality achieved to date

  Oxygen < 0.05%;

  Carbon < 0.02%;

  Nitrogen < 0.009%

  Hydrogen < 0.01%



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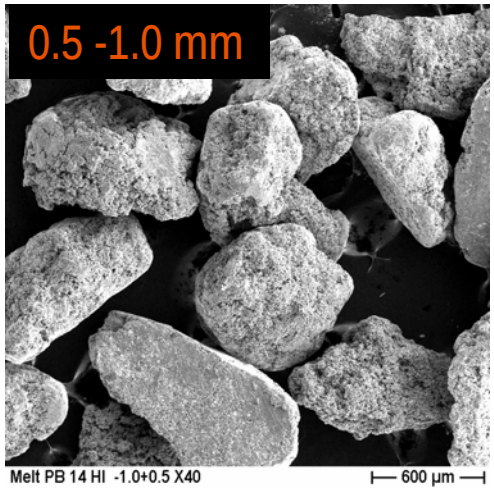
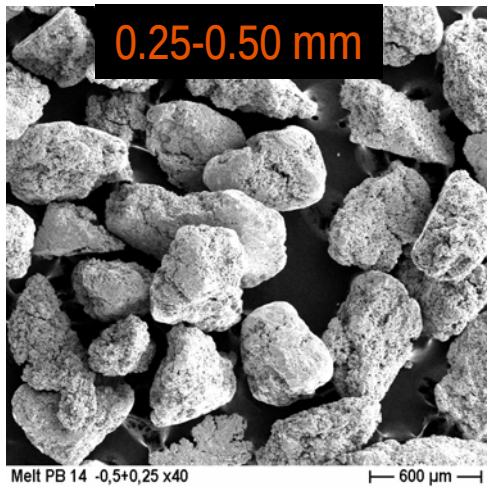
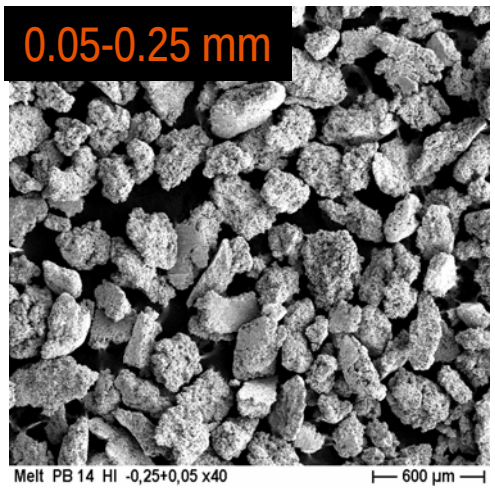
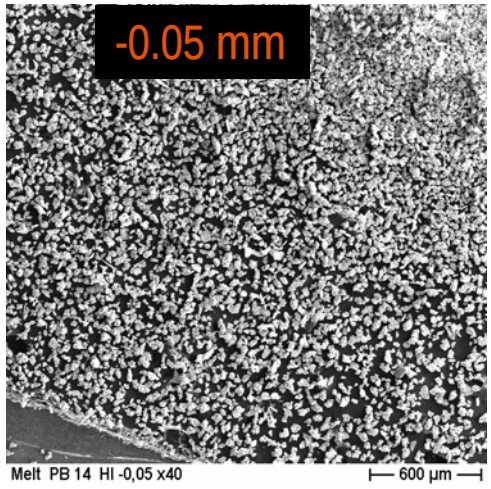
Titanium metal produced in the Polar™ reactor has been amenable to milling to powder

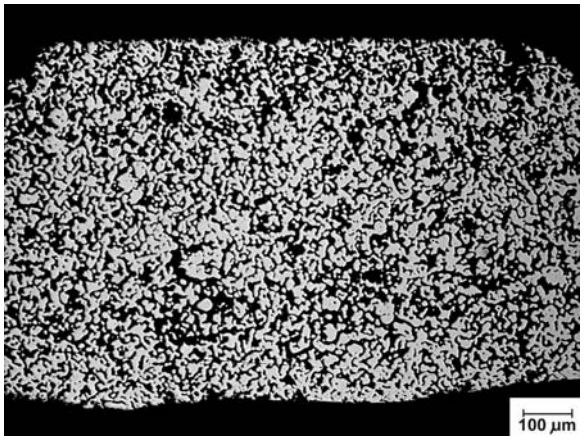








- Milling of Ti product accomplished using standard hammer and disc mill equipment with inert gas shroud.
- Milled shape is encouraging for all size distributions.
- Pre-milling morphology of uniformly-distributed microscale pores is preserved within individual particles.



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Process and commercial development

- BHP Billiton have committed significant resources to the experimental program for Polar™ Titanium development.
- There has been promising experimental process development, from gram to kilogram scale at BHP Billiton's Newcastle Technology Centre.
- A program of product characterisation work is underway for all product forms.
- Operation at 10kg/day scale is planned by end of calendar year 2005, with a 0.25 t/day scale demonstration plant under design, dependent upon success of the 10kg/day pilot.
- BHP Billiton interest is ultimately aimed at commodity level production of titanium, and work is continuing to prove the commercial viability of the process.
- A collaboration strategy is being considered, but will be based on all collaborating parties adding value to the business.

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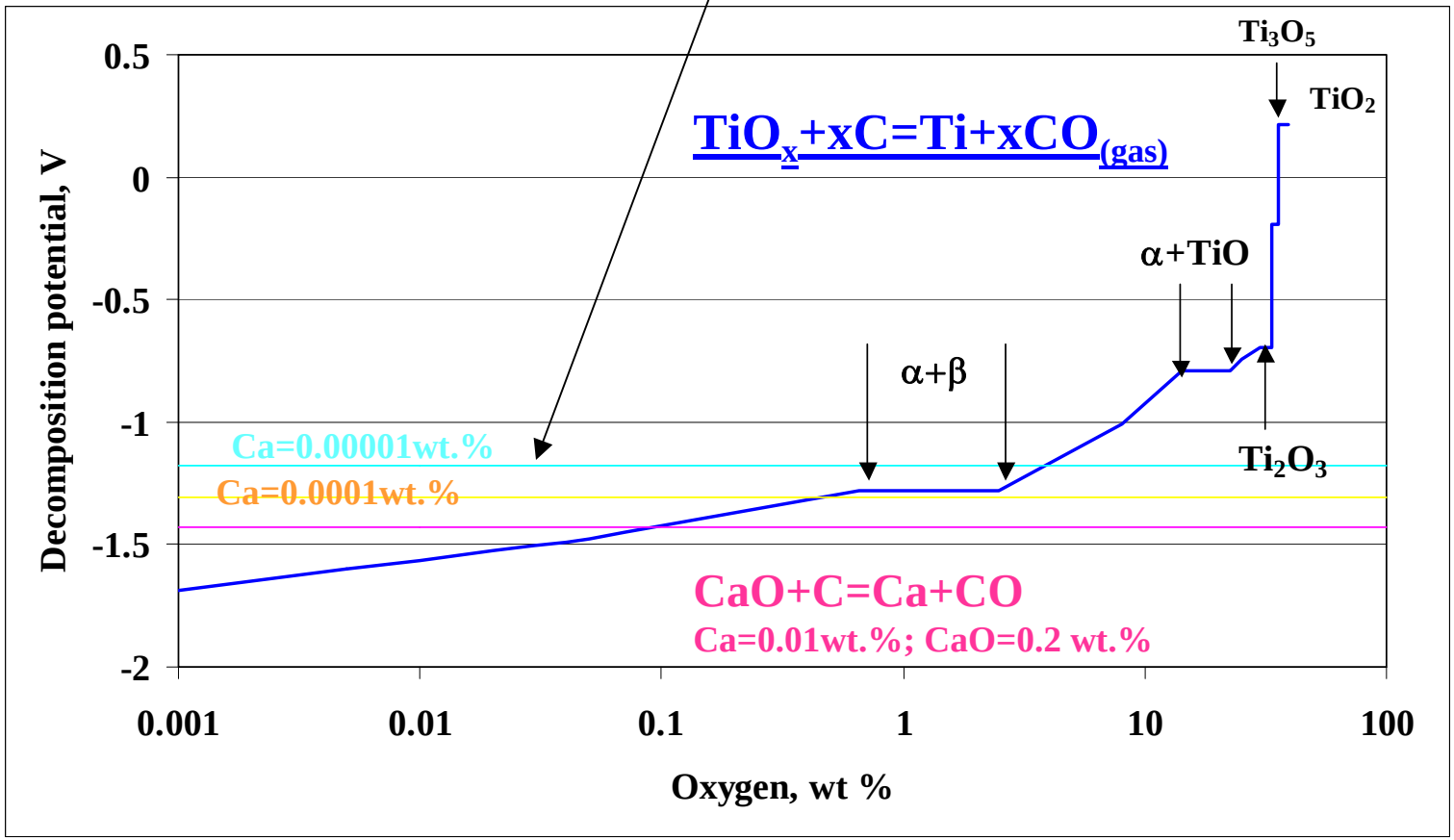
(Spare slide) Decomposition potentials of titanium oxides in the presence of solid carbon

- If the reduction process takes place via calcium, only negligible rates of reduction will be observed under voltages below ~1.2V.



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