Electrolytic Production Route for Affordable Titanium Matrix Composites

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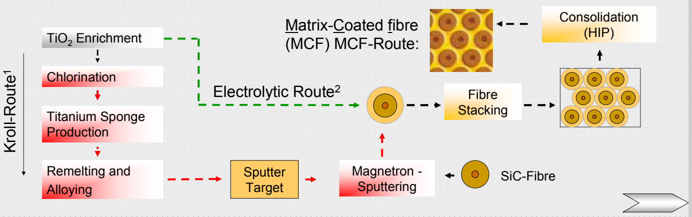
Motivation

In spite of outstanding properties and an increasing demand for high performance light weight materials the application of Titanium Matrix Composites (TMC) is limited by the price. An electrolytic production route is proposed to reduce the costs based on the idea that several economically and ecologically disadvantageous production steps can be avoided if raw materials like TiO_2 are used as the titanium source in an electrochemical fibre coating process.

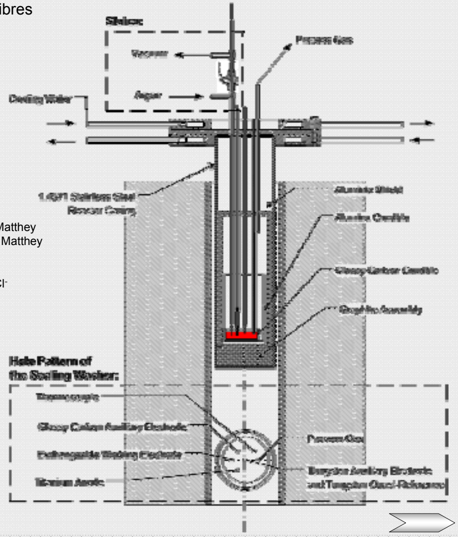
Conventional vs. Electrochemical Production Route



Investigation of Titanium Deposition (Methodology)

1) Development of reproducible salt drying procedures
2) Detection of residual water and other impurities by electroanalytical methods
3) Examination of the anodic dissolution using a titanium anode
4) Examination of the cathodic deposition
5) Enrichment of the electrolyte with $TiCl_2$ / K_2TiF_6
6) Coating experiments on SiC-fibres

Experimentals:



Electrolyte:
LiCl/KCl: eutectic mixture
Temperatur: 500°C

LiCl, KCl:	Fluka puriss. p.a., ACS reagent >99.0%, anhydrous

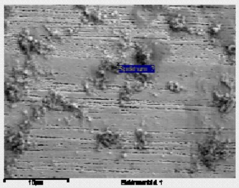
Electrodes:

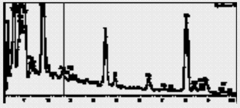
Tungsten:	1mm, 99,95%, Johnson Matthey
Titanium:	3,2mm, 99,99% Johnson Matthey
Glassy Carbon:	Sigradur G, 4mm, HTW

Quasi-Reference corrected vs. Li/Li^+ or Cl/Cl^- used as Internal Reference System [2]

Vacuum Drying Procedure:
Drying I: approx. 20h / 260°C / 1mbar
Drying II (following [5]): 0,1-0,2 mbar
1. step: approx. 36h, 25°C
2. step: approx. 24h, 150°C
3. step: approx. 48h, 260°C

Anodic Dissolution and Electrodeposition





In first experiments it could be demonstrated, that titanium had been dissolved in the electrolyte and deposited on the tungsten cathode. After titanium electrolysis additional peaks could be observed during cyclovoltammetry which might be attributed to titanium ions. The deposited material contained silver, zinc, iron and especially copper besides titanium.

Summary and Outlook:

The water/hydroxide content of the electrolyte estimated from the voltammograms is still too high in spite of improved drying procedures (approx. 10 times higher than those values reported in [1]). The detected elements (Cu, Fe, Ag, Zn) are mentioned as trace impurities in the specification of the manufacturer. Therefore, further efforts are necessary to improve the electrolyte quality by vacuum drying and preelectrolysis.

Acknowledgement:

The work is carried out within a Helmholtz-University Young Investigators Group that is partly funded by the Helmholtz Association of Research Centres.

References:

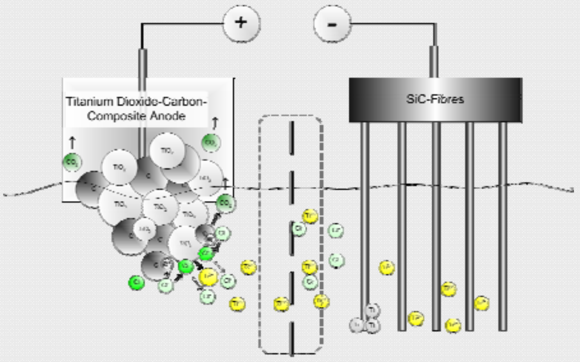
[1] Inman, D. and Lovering, D.G., eds. *Ionic Liquids*. 1981, Plenum Press: New York
[2] Berghoute, Y., Salmi, A.and Lantelme, F., *Internal reference systems for fused electrolytes.* Journal of Electroanalytical Chemistry, 1994. 365(1-2): p. 171-177.
[3] Kanzaki, Y. and Takahashi, M., *The hydrogen electrode in fused lithium chloride-potassium chloride eutectic containing hydrogen ion.* Journal of Electroanalytical Chemistry, 1975. 58(2): p. 349-356.
[4] Hamer, W.J., Malmberg, M.S.and Rubin, B., *Theoretical Electromotive Forces for Cells Containing a Single Solid or Molten Chloride Electrolyte.* J. Electrochem. Soc., 1956. 103(1): p. 8-16.
[5] Laitinen, H.A., Ferguson, W.S.and Osteryoung, R.A., *Preparation of Pure Fused Lithium Chloride-Potassium Chloride Eutectic Solvent.* J. Electrochem. Soc., 1957. 104(8): p. 516-520.
[6] Chassaing, E., Basile, F.and Lorthioir, G., *Study of Ti(III) solutions in various molten alkali chlorides. I. Chemical and electrochemical investigation* Journal of Applied Electrochemistry, 1981. 11(2): p. 187-191.
[7] Kommer, C., *Möglichkeiten der Kombination von TiO2-Chlorierung und elektrolytischer TiClx-Reduktion*. 2006, Lehrstuhl und Institut für Metallurgische Prozesstechnik und Metallrecycling, RWTH Aachen University, Diplomarbeit

Helmholtz-University Young Investigators Group

The aim of the project described here is the development of the proposed process up to an semi-industrial level. Because of the complexity subprocesses are examined which could come to operation either independently or in combination. The main topics are:
- Electrolysis of titanium dioxide-carbon-composite anode (anodic subprocess)
- Deposition of titanium on reinforcement fibres (cathodic subprocess)
- Combination of the subprocesses to a fibre coating process

Anodic Subprocess (IME - In Situ Chlorination Process)

Cathodic Subprocess:

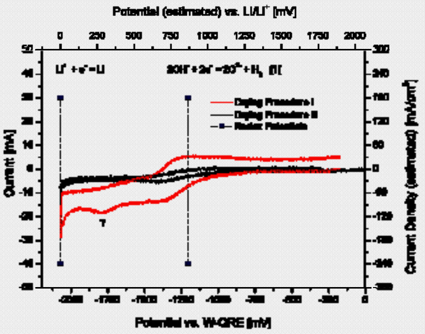


While titanium is deposited, chloride ions are reduced to chlorine, which react at the composite anode with titanium dioxide and carbon:
$Cl^- \rightarrow Cl + e^-$
$TiO_2 + C + 2Cl \rightarrow TiCl_2 + CO_2$
First experiments performed at IME demonstrated that it is possible to dissolve titanium from TiO_2/C [7]

Titanium is deposited on the substrate according to the cathodic reaction:
$Ti^{2+} + 2e- \rightarrow Ti$
The depletion of titanium ions is compensated by anodically dissolved titanium:
$Ti + 2Cl^- \rightarrow TiCl_2 + 2e^-$

Detection of Electroactive Species by Cyclovoltammetry:

Examination of the cathodic part of the electrochemical window:

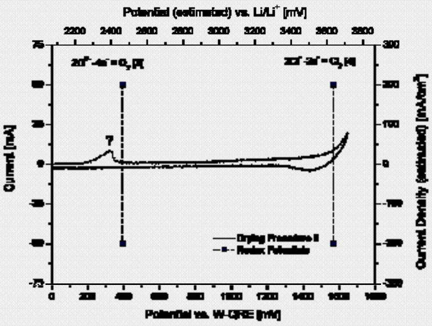


Electrodes:

WE:	Tungsten 1x5mm
CE:	Glassy Carbon 4x5mm
QRE:	Tungsten 1x5mm

Temperatur: 500°C
Scan-Rate: 1V/s

Examination of the anodic part of the electrochemical window:



Electrodes:

WE:	Glassy Carbon 4x1mm
CE:	Tungsten 1x5mm
QRE:	Tungsten 1x5mm

Temperatur: 500°C
Scan-Rate: 1V/s