COMBINED TIO_2-CHLORINATION AND ELECTROLYTIC $TICL_X$-REDUCTION

-Progress report-

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Introduction

Today titanium is industrially produced by the Kroll process, which has a couple of disadvantages like low efficiency, high cost, batch wise operation, high energy consumption, complicated process control and a batch period of up to six days. Even Kroll thought his process would be substituted within a few years but until now there is no successful alternative. However the increasing demand for Titanium currently and in the future leads to an market pressure for a cheaper and high productive process. Since all commercial light metals are produced by molten salt electrolysis due to their ignoble character this seems to be a promising way for the production of titanium as well. Hence there are different electrochemical approaches being tested in the past and at the moment, but none of them has reached full production state until now.

Invention of the IME Process

At IME Process Metallurgy and Metal Recycling - Department and Chair of RWTH Aachen University - investigations have started recently based on the idea to support the international research on molten salt electrolysis of titanium by developing an in-situ chlorination step of TiO_2. [1]. This reaction shall take place in the same reactor and simultaneous to the $TiCl_x$-reduction at temperatures below 600 °C. The project is funded partly by DFG in the frame of the Helmholtz Young Investigators Group “Electrolytic Production Routes for Titanium Matrix Composites” in cooperation with the German Aerospace Centre DLR in Cologne.

The suggested process is based on the following principle. In a $TiCl_2$ enriched and chloride based electrolyte, $TiCl_2$ is split into Ti^{2+} and $2Cl^-$ at a adjusted potential (1). Ti^{2+} is deposited at the cathode and Cl-atoms form at the anode. In “statu nascendi” the Cl-atoms react chemically with the components of a composite anode, which is the main invention of the process presented here. The anode consists of TiO_2 and carbon and forms CO/CO_2 as well as $TiCl_x$ (2) which is dissolved in the electrolyte.

$$TiCl_x \rightarrow Ti^{x+} + 2Cl^- \qquad (1)$$

$$TiO_2 + 2C + xCl \rightarrow TiCl_x + 2CO/CO_2 \qquad (2)$$

To proof the principle of this process, first tests were carried out in a lab scale molten salt electrolysis cell using a $NaCl\text{-}CaCl_2$ electrolyte and a composite anode with a C/TiO_2 ratio of 1,85 Mol %. It was possible to deposit Titanium on the cathode proved by ICP analysis of the deposit and the results have shown that the process suggested is generally applicable for the synthesis of titanium. Expected problems however occurred at the cathode where the dissolved TiO_2 caused the following disproportion reaction dissolving the already deposited Titanium.

$$Ti + Ti^{4+} \rightarrow 2Ti^{2+} \qquad (3)$$

Challenges for the following work as learned from these first trials are:

- Identification of a suitable electrolyte
- Improvement of the composite anode
- Design of a chemically and mechanically stable electrolysis cell
- Definition of major process parameters (temperature, current density, $TiCl_2$-concentration)
- Testing of different cathode materials

Identification of a Suitable Electrolyte

For finding a suitable electrolyte first the most important requirements were defined:

- High electric conductivity
- High decomposition potentials (> 3,0 V)
- Low solubility for TiO_2
- High solubility for $TiCl_2$
- Melting point below 550 °C

The first two requirements are valid both for alkali chlorides and alkaline earth chlorides, whereas only the alkali chlorides have a low solubility for TiO_2 as can be seen from table 1.

Table1: Solubility of TiO_2 in alkali and alkaline earth chlorides [2]

KCl	LiCl	NaCl	$CaCl_2$	$MgCl_2$
i	i	i	ss	ss

i: insoluble, ss: slightly soluble

Considering the binary phase diagrams of the alkali chlorides and $TiCl_2$ it was obvious, that LiCl would be the ideal base electrolyte because it is the only system not forming intermediate compounds. The maximum $TiCl_2$ solubility (without forming stable components) decreases with increasing ion radius of the alkali metal. Unfortunately the melting point of the system LiCl-$TiCl_2$ is never below 550°C. The latter accounts for all other binary systems. Therefore a ternary system of two alkali chlorides and $TiCl_2$ is needed, but none of the corresponding phase diagrams is known so far. On one hand the LiCl-NaCl system should be preferred due to a higher solubility, but unfortunately even its eutectic melting point is above 550 °C. Considering the binary phase diagrams of LiCl in combination with the other alkali chlorides it was obvious that the most promising system was KCl-LiCl due to its eutectic melting point of 353 °C.

To determine the exact melting point of the elctrolyte and the maximum $TiCl_2$ concentration the pseudo binary phase diagram $(KCl\text{-}LiCl)_{eut.}\text{-}TiCl_2$ was accurately measured by DTA/TG.

Before starting the measurements pre-tests were conducted in order to identify a suitable crucible material. Investigated were Al_2O_3, BN, Pt and AlN. Al_2O_3, was the least suitable material since it was reacting with the $TiCl_2$ converting it to a Titaniumoxide. BN on the contrary was chemically stable and even after a couple of days there was no BN dissolution into the electrolyte. Unfortunately it became clear that the mechanical stability of DTA crucibles made from BN is not sufficient. AlN and Pt both were mechanical and chemical stable wheras Pt DTA crucibles were easily available and therefore selected for this investigation. The use of these crucibles however was limited to the phase diagram measurements (no chlorine formation).

The chemicals used were ultra dry, ultra pure salts with a purity of 99,995% for LiCl, KCl and 99.98% for $TiCl_2$. To ensure the same chemical composition of the base electrolyte for each DTA test an eutectic mixture of KCl-LiCl was premolten under Argon and grinded. The necessary amounts of $TiCl_2$ and base electrolyte were calculated and each sample (mixture) was prepared directly inside the DTA crucible. Preparation and storing of the salts was done inside a Jacomex Glovebox. All samples were molten before measuring the cooling curve. Parameters for the measurement were a maximum temperature of 600°C, a cooling rate of 5K/min and a minimum temperature of 250 °C. The parameters have been established in a couple of preliminary test trials. After the measurements the TG curves were checked to ensure that no evaporation of electrolyte has taken place and the hole sample was chemically analysed. The generated phase diagram is shown in Fig. 1.

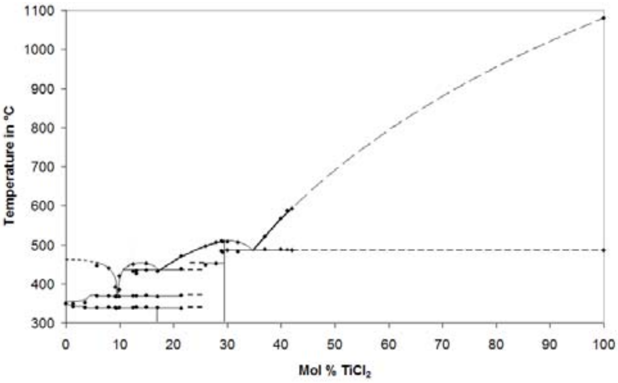

Figure 1: Pseudo binary Phase Diagram $(KCl\text{-}LiCl)_{eut.}\text{-}TiCl_2$

In contrast to the binary Phase Diagrams of KCl-$TiCl_2$ and LiCl-$TiCl_2$ the measured quasi-binary phase diagram contains three eutectic points. The first one is at 9,4 mol % $TiCl_2$ with an eutectic temperature of 368 °C, the second one with 17 mol % $TiCl_2$ melts at 432 °C. Here the stable phase K_2TiCl_4 is forming. The third eutectic point is found at a composition of 34,8% $TiCl_2$ and T_{eut} of 486 °C. At 28,97 mol %

$TiCl_2$ the stable component $KTiCl_3$ is forming with a melting point of 509 °C. However there seems to be a third stable phase in this system at a $TiCl_2$ concentration between 21,5 and 26 mol %, but this still has to be investigated.

As a result of these measurement the maximum $TiCl_2$ content of the electrolyte was set to 9 Mol % to avoid complex ion formation.

Anode Concept

The anode is a mixture of carbon and TiO_2 powder. To ensure the aimed semi continous process it is not easy feasible to use pressed compacts, but one of the requirements for a suitable elctrode is its electric conductivity. The electric conductivity of a powderized anode mix is certainly quite low due to its small contact area and is strongly dependent on the carbon content of the anode as can be seen from figure 2.

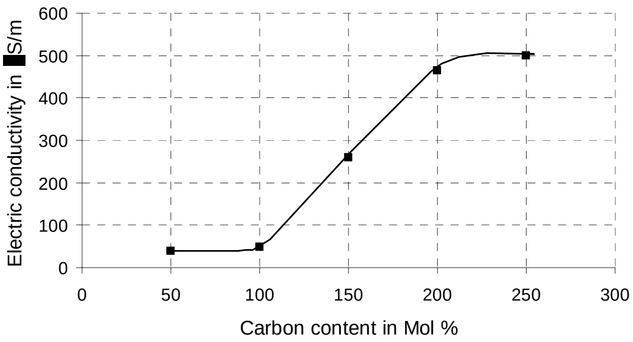

Figure 2: Electric conductivity of a pressed mixture TiO_2+C at room temperature [3]

The figure shows that a suitable composition is based on a C/TiO_2 ratio of 2. The optimal C/TiO_2 ratio according to the chlorination reaction is investigated in the next step. The gross reaction of the proposed process (4) shows a simultaneous reaction between two solids and a gaseous compound at the same time.

$$TiO_2 + 2C + xCl_2 \rightarrow TiCl_x + 2CO/CO_2 \tag{4}$$

This kind of reaction is quite unlikly and therefore the reaction mechanism needs to be investigated more in detail. At the moment only the chlorination of $TiCl_4$ has been analysed by W.E. Dunn [4] and for the calculation of the anode composition we will hold on to this mechanism. The reaction gets started by production of a small amount of $TiCl_4$ via direct chlorination (5):

$$TiO_{2(s)} + 2Cl_{2(g)} \rightarrow TiCl_{4(g)} + O_{2(g)} \tag{5}$$

The produced $TiCl_4$ is forming an equilibrium at the TiO_2 surface forming a gaseous $TiOCl_2$•$TiCl_4$ complex (6), which is diffusing to the carbon particles and reacting according to equation (7).

$$3TiCl_{4(g)} + TiO_{2(s)} \rightarrow 2(TiOCl_2 \cdot TiCl_4)_{(g)} \tag{6}$$

$$\begin{aligned}&(TiOCl_2 \cdot TiCl_4)_{(g)} + Cl_{2(g)} + C_{(s)}\\ &\rightarrow 2TiCl_{4(g)} + 2CO/CO_{2(g)}\end{aligned} \tag{7}$$

The overall reaction is proceeding via the shrinking particle model, so the optimal composition is the stoichiometric composition. Excess carbon results in carbon layer formation, decreasing the reaction rate. Therefore the chemical composition of the anodes is fixed according to the process temperature. The stoichiometric C/TiO_2 ratios were calculated plottet versus the temperature (Figure 3).

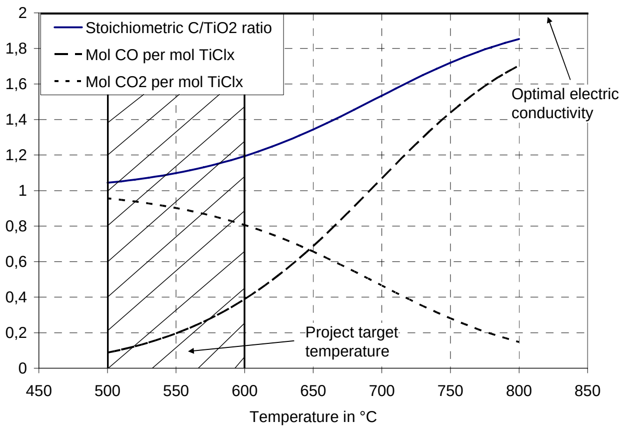

Figure 3: Stoichiometric Anode composition in correlation with the temperature

Figure 3 shows that the stoichiometric composition is strongly dependent on the temperature. A C/TiO_2 ratio of 2 can just be achieved if only CO is formed during the process. According to the Boudouard equilibrium this is only possible at a significant higher temperatures than 800 °C and therefore far from the project target temperature. The consequence is that the anodes in the suggested process will not have the optimal eletric conductivity.

In order to improve the anode conductivity technically an increase of the contact area by variation of the particle sizes might be possible. Another way of influencing might be the use of different carbon sources like tar and coal. An advantage of tar for example is the improved contact between TiO_2 and C, but on the other hand, the C content of the anode is not predictable due to evaporation of volatile carbon components. To investigate the influence of this parameters on the electrical conductivity of the anode electrochemical impedance analyses with a two electrode system are planned.

Investigation of Chlorination Mechanism and Major Process Parameter

The actual chlorination mechanism and the required process window (set of influencing parameters) to establish the proposed electrolysis process will be investigated by electrochemical measurement techniques. Trials planned are current density versus potential measurements and cyclic voltametry with varying temperatures, $TiCl_2$ starting concentrations and different anode compositions/mixes. All trials will be carried out under argon using Ag/AgCl reference electrodes. For conducting these experiments a special BN insert was constructed for the electrolysis cell ensuring the reproducibility of electrode positions and cathode surface.

To compare the results of the different trials it is neceesary to determine the effective anode surface area first. This will be done by chronoamperometric measurements analysing them with the Cotrell equation (8). First trials were successfully conducted resulted in plots as shown in Figure 4, but for systematic analysis it is necessary to know the diffusion coefficient of Cl in the electrolyte which is not known yet.

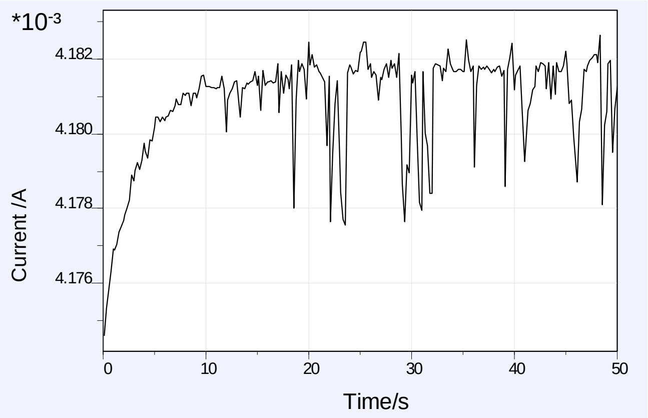

Figure 4: Chronoamerometric curve for a TiO_2-coal anode at 550 °C

$$i(t) = \frac{nFAD_0^{1/2} \cdot C_0}{\pi^{1/2} \cdot t^{1/2}} \qquad (8)$$

i: current, n: stoichiometric number of electrons involved in an electrode reaction, F: Faraday constant, A: area, D_0: diffusion coefficient, C_0: concentration, t: time

With the most promising process parameters electrolysis tests will be run in a new designed AlN cell. Observing process conditions and confirming the discovered process parameters will be maintained by chemical analysis of elctrolytes and electrodes.

Summary

A modified anode concept for molten salt titanium electrolysis is suggested and investigated by IME in Aachen. This process is based on an in-situ chlorination of TiO_2 in the electrochemical process. This reaction shall take place in the same reactor and simultaneous to the $TiCl_x$-reduction at temperatures below 600 °C. The challenges occuring after the first trials were named and the needed course of actions ere explained.

The determinition of a suitable elctrolyte was described resulting in a $(KCl\text{-}LiCl)_{eut.}\text{-}TiCl_2$ composition with less than 10 Mol% $TiCl_2$. The anode composition was calculated according to the temperature and possibilities to influence the electric conductivity were described.

The future course of action was also explained.

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