

# Molten salt electrolysis of Titanium using a TiO<sub>2</sub>-C composite anode in halide electrolytes

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## ABSTRACT

At RWTH Aachen University, Germany investigations are ongoing in order to develop molten salt electrolysis of titanium using a TiO<sub>2</sub>/C composite powder anode. The main idea of the innovative process is based on the following principle. In a titanium halide (Hal) enriched and halide based electrolyte, TiHal<sub>x</sub> dissociates into Ti<sup>x+</sup> and xHal<sup>-</sup> at a defined potential (current density). Subsequently Ti<sup>x+</sup> is deposited at the cathode and Hal-atoms form at the anode. In “statu nascendi” these Hal-atoms react with the composite anode consisting of TiO<sub>2</sub> and C. TiHal<sub>x</sub> is formed again, which is dissolved in the electrolyte and a CO/CO<sub>2</sub>-mixture leaves the anode compartment.

The paper will show that only iodide based electrolytes are suitable for this process and that the anode composition is dependent on the working temperature.

## INTRODUCTION

For more than sixty years 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 no alternative has been successful introduced in industry. However the increasing demand for Titanium currently and in the future leads to a 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 - experimental research is ongoing based on the idea to support the international research on molten salt electrolysis of titanium by developing an in-situ validation step of TiO<sub>2</sub>. [1]. This reaction shall take place in the

same reactor and simultaneous to a TiHal<sub>x</sub>-reduction at temperatures below 600 °C. The project is part of the Helmholtz Young Investigators Group “Electrolytic Production Routes for Titanium Matrix Composites” in cooperation with the German Aerospace Centre DLR in Cologne. The main tasks within this project are:

- Design of a suitable electrolysis setup
- Development of a composite anode
- Selection and testing of electrolytes
- Evaluation of process parameters

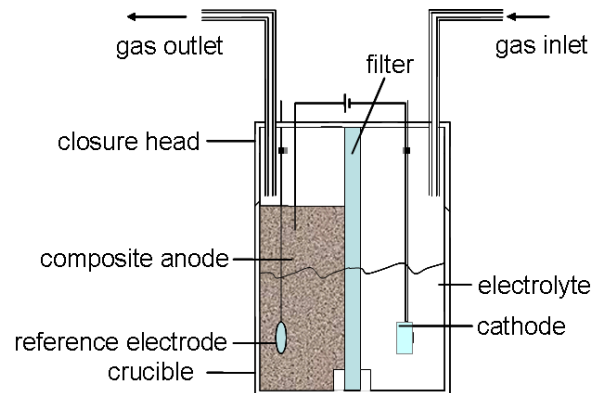
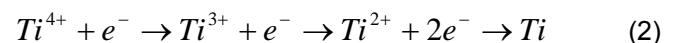


Figure 1: General cell design

Figure 1 shows the general cell design of the proposed process which is based on the following principle: In a titanium halide enriched and halide based electrolyte, TiHal<sub>x</sub> dissociates into Ti<sup>x+</sup> and xHal<sup>-</sup> at an adjusted potential (1). Ti<sup>x+</sup> is deposited at the cathode following the sequence described by (2) and Halide-atoms form at the anode. In “statu nascendi” the Halide-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<sub>2</sub> and carbon and forms CO/CO<sub>2</sub> as well as TiHal<sub>x</sub> (2) which is dissolved in the electrolyte.



The different valence states of Titanium likely being present in the electrolyte pose an enormous challenge due to the chemical reactions (4) and (5).



As can be seen, four valent titanium ions tend to dissolve metallic titanium and interfere with the aimed process. Therefore  $Ti^{4+}$  should be avoided within the electrolyte in order to maintain a sufficient current efficiency. But using a composite anode consisting of  $TiO_2$  and C the feed valence state of titanium is already four and at temperatures below  $600^\circ C$  no reduction with C takes place, so most probably all titanium dissolving from this anode is four valent. According to literature however [2], [3], a process window might be present to dissolve titanium with lower valence from this anodes.

## EXPERIMENTAL WORK

### Experimental Setup

The first challenge designing the experimental setup is to find a suitable crucible material, due to the fact that  $TiCl_2$  (which will be present in every electrolyte as titanium source) will react with all kinds of oxide based materials. Metallic or carbon crucibles also can not be used for this investigation because of the contact between the powder anode and the crucible. As a result, every electric conductive material might take part in the electrolysis causing uncontrolled reactions.

As a consequence different nitride based materials were tested showing that BN and AlN were stable for at least a couple of days. However it turned out, that crucibles made from hexagonal BN were not mechanically stable during the solidification process causing problems to remove the electrolyte. Hence an AlN crucible was designed and built as shown in Figure 2. This crucible is used within a closed cell made from steel. The water cooled lid has airtight fittings allowing for electrical connection, temperature measurement, insertion of reference electrodes and sampling. (Figure 2)

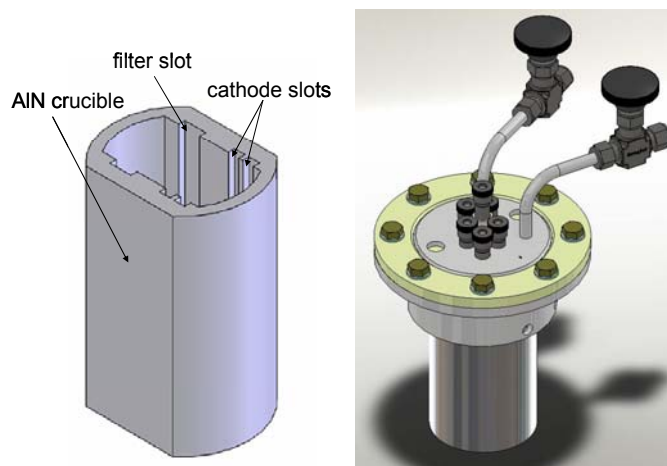


Figure 2: Designed AlN-crucible (left) and cell (right)

The cell itself is prepared in an argon filled glove box preventing contamination of water and/or oxygen. During the hole trial the cell is constantly flushed with argon and the off gas was passed into a washing bottle, collecting the salt components within the off gas. All electrolysis trials are controlled by a potentiostat (Iviumstat) using a silver reference electrode.

### Electrolyte Selection

Four electrolyte systems were tested using an equimolar mixture of  $TiO_2/C$  as anode, analyzing the dissolution of Ti-ions from this anode. The base electrolytes investigated are shown in table 1. An amount of 1.25 Mol%  $TiCl_2$  was added to each of these electrolytes.

Table 1: Electrolytes tested (all containing additional 1.25 Mol%  $TiCl_2$ )

Base electrolyte	Melting point [ $^\circ C$ ]	Process Temperature [ $^\circ C$ ]
$(KCl-LiCl)_{eut.}$	353	387
$(KBr-LiBr)_{eut.}$	329	383
$(LiBr-CsBr)_{eut.}$	289	382
$(LiJ-CsJ)_{eut.}$	217	297

All electrolytes were based on alkali halides due to the fact that these chlorides have the lowest solubility for  $TiO_2$  and it is assumed that the same accounts for the bromide and iodide systems.

The dissolution mechanism of the anodes was analyzed in a first step by linear sweep voltametry. All sweeps were done at scan rates of 1 mV/s resp. 0.5 mV/s up to the evolution of the corresponding halide ( $Cl_2$ ,  $Br_2$ ,  $I_2$ ). An example displaying the result of the linear sweep plot in the KCl-LiCl- $TiCl_2$  system is shown in Figure 3.

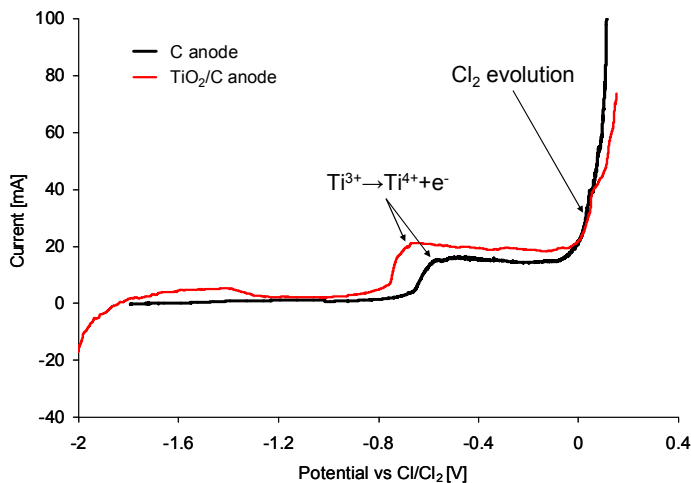


Figure 3: Linear sweep of a C and a TiO<sub>2</sub>/C composite anode in the KCL-LiCl-TiCl<sub>2</sub> electrolyte

As can be seen only one anodic reaction is proceeding before chlorine evolution. According to literature [4] this reaction should correspond to the Ti<sup>3+</sup> → Ti<sup>4+</sup> oxidation. If this is true it will be not possible to dissolve titanium ions with lower valences than Ti<sup>4+</sup>. To proof this, electrolysis trials were conducted at two different potentials. The first experiment was conducted at a potential slightly lower than the reaction potential (about -0.81 V) and the second one at a slightly higher potential (about -0.51 V). After each experiment the electrolyte and the off gas washing water were chemically analyzed.

### Experimental Results

After exposing the composite anode to the electrolytes, the same chemical reaction (6) proceeds in all electrolytes, leading to increased amounts of titanium in the electrolyte. This reaction transfers all two valent titanium to the valence of three and relocates the reaction potential and increases the current (Figure 3).



All electrolytes investigated showed the same characteristics in their linear sweeps. One reaction always occurs at the same potential difference to Cl<sub>2</sub> and then Cl<sub>2</sub>, Br<sub>2</sub> or I<sub>2</sub> evolution. The chemical analysis revealed that the appearing peak can be attributed to the oxidation of Ti<sup>3+</sup>. Therefore it is not possible to dissolve TiO<sub>2</sub> with a lower valence than 4<sup>+</sup>. As a consequence, chloride and bromide based electrolytes can not be used, as the evaporation point of TiCl<sub>4</sub> is 136°C and that of TiBr<sub>4</sub> is 230 °C, both significant below the lowest possible process temperature. Consequently the solubility of Ti<sup>4+</sup> in the tested chloride and bromide based electrolytes is extremely low, which was also proofed by the electrolysis trials and the high amounts of titanium in the off gas scrubbing water when using chloride and bromide based systems. The only possible electrolyte system seem to be a iodide based one, and the only possible mechanism is a iodination of the anode followed by a dissolution and reduction of TiI<sub>4</sub> according

to (1) - (3). But for this process an intermediate (auxiliary) electrode will be necessary for prereduction in order to prevent unwanted reactions between Ti<sup>4+</sup>-ions and the deposited metallic titanium.

### ANODE MODELLING

The anode is a mixture of carbon and TiO<sub>2</sub> powder. To ensure the aimed semicontinuous process it is not feasible to use block anodes which would be better, as one of the requirements for a reliable electrode is its electrical conductivity. But the electrical conductivity of a powderized anode mix is lower than that of pressed anode due to its smaller contact area and is strongly dependent on the carbon content of the anode as can be seen from figure 4. Main reason for that is the low electrical conductivity of TiO<sub>2</sub>. Figure 4 shows that the best compositions are reached at C/TiO<sub>2</sub> ratios above 2.

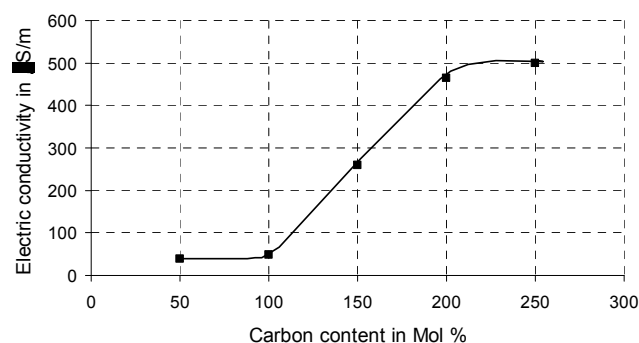
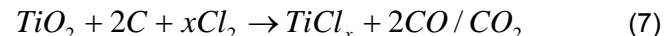


Figure 4: Electrical conductivity of a pressed TiO<sub>2</sub>+C mixture at room temperature [3]

The optimal C/TiO<sub>2</sub> ratio according to the chlorination reaction, which is assumed to be similar to the iodation process, is investigated in the next step. The gross reaction of the proposed process (7) shows a simultaneous reaction between two solids and a gaseous compound at the same time.



This kind of reaction is quite unlikely and therefore the reaction mechanism has been investigated more in detail by W. E. Dunn [4]. He discovered that 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<sub>2</sub> ratios were calculated and plotted versus the temperature (Figure 5).

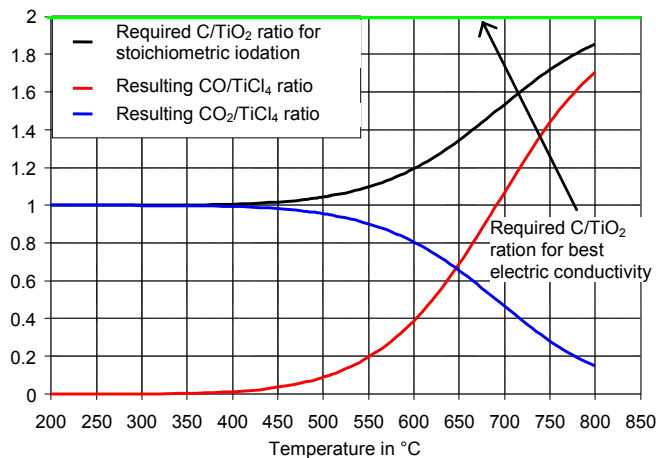


Figure 5: Stoichiometric Anode composition in correlation with the temperature

Figure 5 shows that the stoichiometric composition is strongly dependent on the temperature. The required C/TiO<sub>2</sub> 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 significant higher temperatures than 800 °C. The evaporation point of all Titanium-halides including TiI<sub>4</sub> (377 °C) is lower than 400 °C, so the maximum process temperature must be far below 800 °C most probably below 350 °C. The consequence is that the anodes in the suggested process will not have the optimal electric 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 this critical parameter might be the use of different carbon sources like tar and coal. An advantage of tar for example is the improved contact between TiO<sub>2</sub> and C, but on the other hand, the C content of the anode is not predictable due to evaporation of volatile arenes

## CONCLUSION

A modified anode concept for molten salt titanium electrolysis is suggested and investigated. This process is based on an in-situ halidation of TiO<sub>2</sub> in the electrochemical process. The reaction shall take place in the same reactor and simultaneous to the TiHal<sub>x</sub>-reduction at temperatures below 600 °C.

First investigations, analyzing different electrolyte systems by linear sweep voltametry showed that the dissolution of Ti-ions from the anode will be as Ti<sup>4+</sup>. This

results in the fact that TiCl<sub>4</sub> and TiBr<sub>4</sub> are volatile even at the lowest possible process temperature for chloride/bromide systems. Therefore the only suitable electrolyte system seems to be iodide based. The second challenge is the investigation of the anode electrical conductivity and the influence of carbon content, grain size and carbon source on this property. This will be done by impedance analysis using a two electron setup. Finally a third project task is the necessity to work with an intermediate electrode to prevent reactions between Ti<sup>4+</sup> and the deposited metallic titanium. The development of this intermediate anode will be done in future parallel to the verification of the proposed and explained anode process and the optimization of the anode electric conductivity.

## REFERENCES

- [1] K. Sommer, B. Friedrich  
Titanium Molten Salt Electrolysis – Latest Developments, Proceedings of EMC 2005, Dresden, p. 1495-1508
- [2] M. V. Smirnov, S. V. Pal'guev  
Behaviour of anodes of an intimate mixture of titanium dioxide with carbon during electrolysis of fused salts, in: Trudy. Inst. Elektrokhim., No 1, 1960, p. 29-33
- [3] F. Gusin, A.I. Belayev  
Elektrochemisches Verhalten von Kohlenoxidanoden aus TiO<sub>2</sub>+C in chloridischen Schmelzen, Nichteisenmetallurgie, No. 5, 1963, p. 83-88
- [4] A. M Martinez et al.  
A chemical and electrochemical study of titanium ions in the molten equimolar CaCl<sub>2</sub>+NaCl mixture at 550°C, Journal of Electroanalytical Chemistry, Vol 449, 1998, p. 67-80

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