

Production of Metallic Titanium by Electrowinning in Molten Salts of Titanium Oxycarbide Anode †

Btissem Malek ¹, Jerome Serp ^{1,*}, Franck Doreau ¹ , Manuel Miguirditchian ¹, Marion Vandenhende ², Nicolas Pradeilles ² , Yann Lepetitcorps ³ and Alexandre Maitre ² 

¹ CEA, DES, ISEC, DMRC, University of Montpellier, Marcoule, 30207 Bagnols sur Ceze, France; btissem.malek@cea.fr (B.M.); franck.doreau@cea.fr (F.D.); manuel.miguirditchian@cea.fr (M.M.)

² IRCER, Institute of Research for Ceramics, University of Limoges, 87068 Limoges, France; marion.vandenhende@unilim.fr (M.V.); nicolas.pradeilles@unilim.fr (N.P.); alexandre.maitre@unilim.fr (A.M.)

³ LCTS, Laboratory of Thermo Structural Composites, University of Bordeaux, 33000 Bordeaux, France; LEPETITCORPS@lcts.u-bordeaux.fr

* Correspondence: Jerome.serp@cea.fr; Tel.: +33-4-66-33-94-72

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Abstract: The electrochemical behavior of Ti^{3+} in $LiCl-LiF-TiF_3$ salt was investigated by cyclic and square wave voltammetries at 853 K. Both methods confirm the presence of a single reduction wave of Ti^{3+} ions to metal, at a potential of -2.3 V vs. Cl_2/Cl^- . The closeness of the potentials of TiC_xO_y dissolution and Ti^{3+}/Ti^{4+} wave is an issue during the electrorefining of the anode. A low current density has to be applied to stay within the titanium oxycarbide dissolution and avoid the formation of Ti^{4+} . The titanium deposition was studied by electrorefining of a titanium metal plate in $LiCl-LiF-TiF_3$ (0.62 mol/kg). The cathodic deposit analysis by XRD and SEM confirms the formation of titanium metal with an average grain size of 150 μm . The faradic deposition yields are above 85% and constant between 60 and 160 mA/cm^2 .

Keywords: Chinuka process; titanium electrowinning; electrochemical deposition; fluoride chloride melt; titanium oxycarbide



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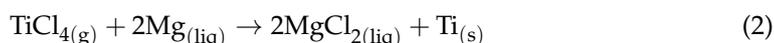


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1. Introduction

Titanium, the ninth most abundant element in the earth's crust, has many attractive properties such as lightweight, high specific strength, corrosion and oxidation resistance at elevated temperatures. It can be used as high-temperature structural material widely used in aerospace, petrochemical, automobile, and metallurgical industries [1].

This material is produced by the Kroll process since 1940s. The process allows the conversion of TiO_2 into Ti metal. TiO_2 is transformed into $TiCl_4$ by the action of chlorine gas at high temperature (carbochlorination). $TiCl_4$ is then converted to metal by reduction with metallic magnesium. This highly exothermic reaction leads to the formation of liquid $MgCl_2$ and a metallic titanium sponge [2], according to the following reactions:



Titanium sponge is finally obtained after a $MgCl_2$ distillation step.

This high-cost batch [3] process requires optimal operation and wastes minimization, a chlorine gas production unit, and a magnesium metal production workshop by electrolysis of $MgCl_2$ (resulting from the reduction reaction of $TiCl_4$).

As an alternative method of the Kroll process, molten salt electrolysis has been frequently proposed.

The first difficulty in the electrochemistry of titanium lies in controlling its oxidation state in the molten salt solution [4].

This problem is especially true in molten chloride, for which Ti^0 , Ti^{2+} , Ti^{3+} , Ti^{4+} can exist in the salt. This particularity is explained by the existence of several equilibria that lead to losses in faradic efficiency [4]:

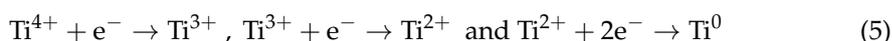


Since the 2000s, the FFC (Fray, Farthing, and Chen) [5] and OS (Ono and Suzuki) [6] processes have opened a new route through the electrolytic reduction of TiO_2 into Ti in molten chlorides. The metal production at the cathode involves a reducing agent formed in situ by reduction of the molten salt solvent (e.g., calcium). These processes overcome the difficulty of multiple oxidation states of titanium in solution since titanium is present in the processes as porous TiO_2 pellets reduced at the cathode. The TiO_2 electroreduction leads to the formation of oxide ions that can be converted at a graphite anode into CO/ CO_2 or O_2 with a non-consumable anode. However, the anodic reaction between graphite and oxides ions forms electro-reducible carbonates, which cause faradic yield losses and can contaminate the cathode deposit. Platinum, gold, SnO_2 anodes cannot be considered as non-consumable anodes as degradation products have been frequently reported [7]. These processes therefore still require further developments to find a suitable anode, and the titanium product is often contaminated with carbon and residual oxygen [8].

The process studied in this work is the Chinuka process (also studied in the literature under the names MER and USTB). In this route, titanium oxycarbide (TiC_xO_y) is used as the anode in molten chlorides. When the right potential is applied, CO is released at the anode together with Ti^{3+} and/or Ti^{2+} ions that are dissolved into the molten salt and transferred to the cathode for electrodeposition [9,10].

In this work, the melt composition has been optimized to minimize the Ti^{2+} concentration in the salt phase. The solution adopted to solve the problem of multiple oxidation states consists in adjusting the degree of complexation of titanium ions in solution, either by modifying the so-called chloroacidity of the medium or by adding fluoride ions.

Numerous studies dealt with the electrochemical behavior of titanium in chloride medium. They allowed highlighting the presence of Ti^{3+} and Ti^{2+} and identifying a multistep reduction mechanism [11] according to the reactions:



The existence of these multiple oxidation states in solution involves disproportionation reactions (3) and (4), which can decrease the faradic efficiencies [12,13] and generate sludge formation [14].

In chloro-fluoride salts, studies [15] have shown that increasing the concentration of fluoride ions in the molten salt leads removing the Ti^{2+}/Ti^{3+} electronic transition [16].

The overall idea of this work is to use a high concentration of fluoride ions (hence the use of a chloro-fluoride salt) in the Chinuka process.

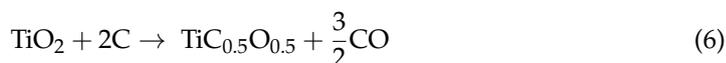
To study the reduction mechanism of titanium ions, the choice was made on a salt rich in fluoride: LiCl-LiF (70–30 mol%).

2. Experimental

2.1. Preparation of Titanium Oxycarbide Anode

The carboreduction route has been used to synthesize titanium oxycarbide anode from a mixture of titanium dioxide (Alfa Aesar, purity 99.6%) and black carbon (Alfa Aesar,

purity 99.9%). The raw powders were mixed in a mortar according to the stoichiometric proportion given by the following equation:



The mixtures obtained were then heat treated under flowing argon ($16 \text{ L}\cdot\text{h}^{-1}$) at 1773 K ($1500 \text{ }^\circ\text{C}$). This treatment lasted four hours followed by annealing at the same conditions as the first carboreduction in order to reach the desired stoichiometry of the titanium oxycarbide phase: Ti_2CO [17]. Finally, the titanium oxycarbide powder was sintered by SPS (Spark Plasma Sintering) [18] at 100 MPa for 5 min at 1923 K ($1650 \text{ }^\circ\text{C}$) (Figure 1).

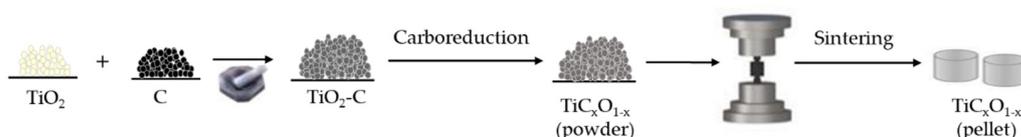


Figure 1. The diagram summarizes the process of synthesis and shaping of the titanium oxycarbide anode.

2.2. Electrolysis Process

The electrolyte consisted of a eutectic LiCl-LiF melt (70–30 mol%, 99–99.98%). It was dried at 423 K for a minimum of 24 h. Experiments were carried out in an argon glovebox. The salt was introduced in a glassy carbon crucible. Temperature was progressively risen to the working temperature (853–953 K) under argon atmosphere.

A concentration of 0.62 mol/kg of potassium hexafluorotitanate solute (K_2^+ , Ti^{4+} , F_6^-) was added to the electrolyte and reduced to Ti^{3+} with a pure titanium plate. The working temperature was measured by a thermocouple protected by a glassy carbon tube and inserted into the melt.

2.3. Electrodes

To investigate the electrochemical behavior of titanium ions, a three-electrode setup was used. A tungsten wire with a diameter of 0.5 mm served as the working electrode, a molybdenum spiral was used as the counter electrode, and a molybdenum wire with a diameter of 1 mm was utilized as the quasi-reference electrode. All RE potentials were referred to Cl_2/Cl^- redox couple. The conversion was obtained by graphical estimation of the potential at zero current in the linear variation region during the positive scan of voltammograms, as shown in reference [19].

For the electrorefining experiments, a titanium plate is used as an anode to study titanium electrodeposition. The cathode is a 5 mm diameter molybdenum rod.

2.4. Electrochemical Techniques Used

Electrochemical techniques, including cyclic voltammetry and square wave voltammetry, were used to study the mechanism of titanium ions reduction.

2.5. Materials Characterization

After electrolysis, the cathode was removed from the bath and washed in an ultrasonic tank containing a water solution to remove all residual salt. Titanium deposits were characterized using X-ray diffraction (XRD). The scanning electron microscopy (SEM) was carried out to observe the microstructure of titanium deposits.

3. Results and Discussion

3.1. Electrochemical Behavior of Titanium Ions

In order to be representative of an electrolyzer (reducing conditions), a titanium plate was dipped permanently into the molten salt.

3.1.1. Cyclic Voltammetry (CV)

The chloro-fluoride salt LiCl-LiF (70–30 mol%) has an F/Cl ratio of 0.43. After adding K_2TiF_6 , the F/Cl ratio becomes 0.58 and the F/Ti ratio is 23.

The cyclic voltammograms obtained in LiCl-LiF containing dissolved titanium as well as the anodic polarization curve of titanium oxycarbide in LiCl-LiF at 853 K (580 °C) are shown in Figure 2. The scan rate was 100 mV/s.

After the addition of K_2TiF_6 and titanium plate in pure LiCl-LiF molten salt, two oxidation peaks associated with two reduction peaks appeared. The first one at around -0.5 V vs. Cl_2/Cl^- corresponds to the Ti^{3+}/Ti^{4+} soluble-soluble redox couple. The second one at about -2.3 V vs. Cl_2/Cl^- is attributed to the reduction of Ti^{3+} in Ti metal in a single step associated to its sharp stripping peak:

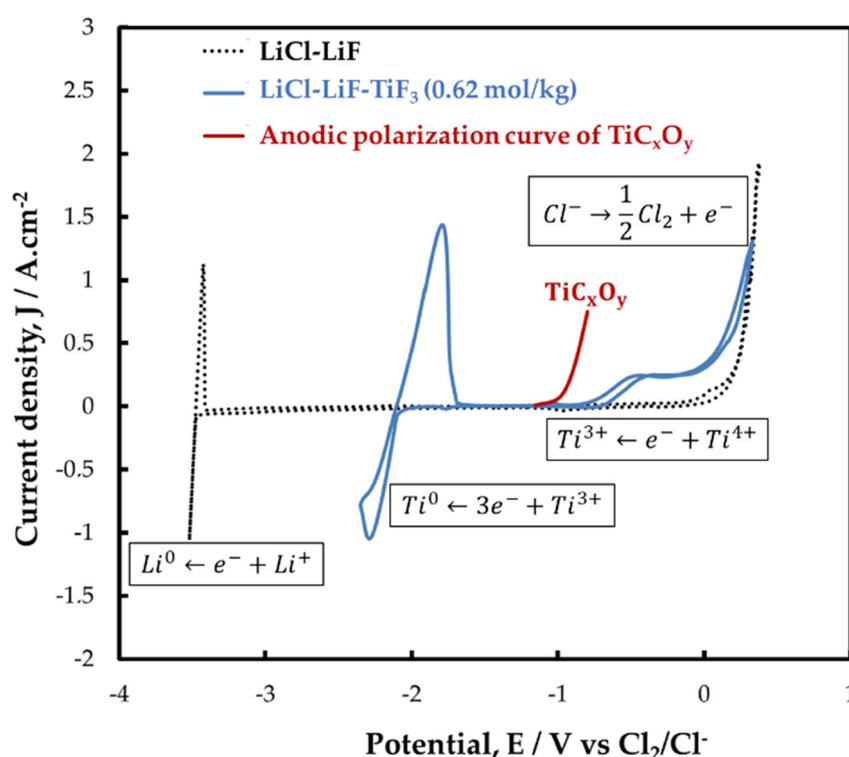


Figure 2. Cyclic voltammograms on a tungsten electrode ($S = 0.2 \text{ cm}^2$) in LiCl-LiF (black) and LiCl-LiF-TiF₃ (0.62 mol/kg) (blue) and anodic polarization curve of TiC_xO_y (Red), at 853 K with the scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$.

3.1.2. Square Wave Voltammetry (SWV)

SWV was used to estimate the number of electrons exchanged on the -2.3 V vs. Cl_2/Cl^- system. Figure 3 shows that the peak current density is increasing with the increase of frequency.

As shown in the inserted figure (in Figure 3), the differential current density (δJ) ($\text{A}\cdot\text{cm}^{-2}$) is proportional to the square root of the frequency (f (Hz)). Square wave voltammetry allows thus, by measuring the width at half-height of the peak ($W_{1/2}$), to calculate the number of electrons exchanged, using the following equation [20]:

$$W_{\frac{1}{2}} = 3.52 \frac{RT}{nF} \quad (8)$$

where, R is the ideal gas constant ($8.314 \text{ J K}^{-1} \cdot \text{mol}^{-1}$), T is the temperature (K), n is the exchanging electron number, and F is the Faraday constant ($96,500 \text{ C} \cdot \text{mol}^{-1}$).

To overcome the disturbance caused by nucleation phenomenon, the measurement of the half-width at half-height $0.5 W_{1/2}$ was performed on the second half of the metal reduction signal, as shown in Figure 3.

Using Equation (8), the average number of electrons in the frequency range of 9 to 49 Hz varies between 3.07 and 3.17. This confirms that the reduction peak at -2.3 V vs. Cl_2/Cl^- can be attributed to the reduction of Ti^{3+} into metallic titanium.

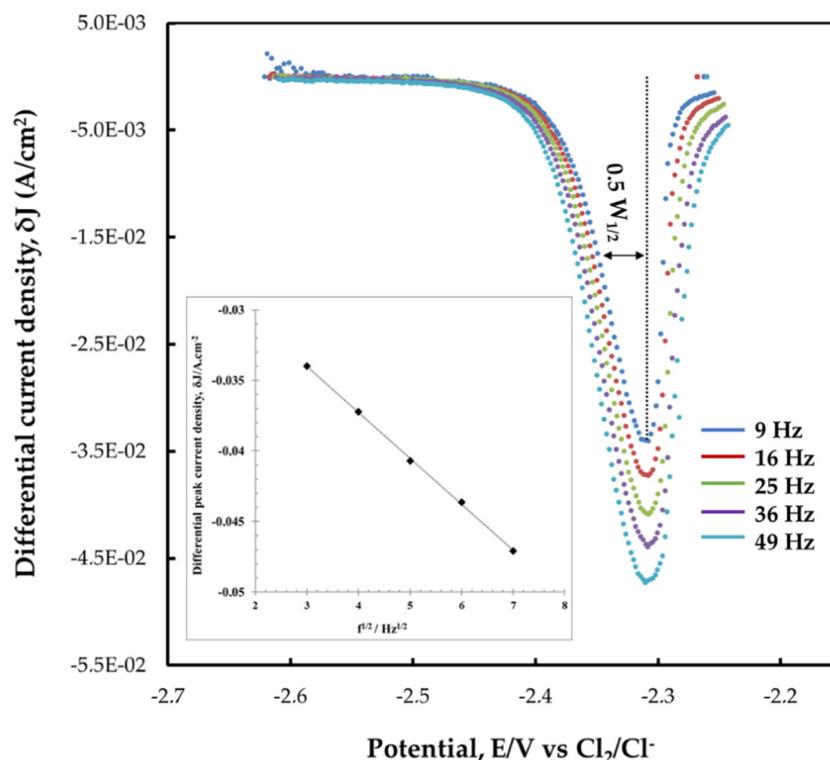


Figure 3. Square wave voltammograms on a tungsten electrode (0.12 cm^2) in LiCl-LiF-TiF_3 ($7.25 \times 10^{-2} \text{ mol} \cdot \text{kg}^{-1}$) at 853 K under various frequencies. Insert linear relationship of Ti^{3+} peak current density versus square root of frequency.

3.1.3. Titanium Oxycarbide Anodic Dissolution

The red curve in Figure 2 shows the anodic polarization curve of TiC_xO_y . As the potential was raised beyond -1 V vs. Cl_2/Cl^- , the current density increased rapidly, attributed to the occurrence of electrochemical dissolution of TiC_xO_y solid solution.

The dissolution potential of titanium oxycarbide is close to the potential of $\text{Ti}^{3+}/\text{Ti}^{4+}$ couple, i.e., -0.5 V . During the electrorefining of $\text{TiC}_{0.5}\text{O}_{0.5}$ low current densities will have to be applied in order to avoid the formation of Ti^{4+} and the problem of disproportionation reaction between Ti^0 and Ti^{4+} that would decrease the faradic yield.

3.2. Electrodeposition of Titanium

Electrorefining of titanium was performed at high Ti^{3+} (0.62 mol/kg) concentration in LiCl-LiF at different temperatures. The elaboration of metallic titanium deposits by electrorefining in a molten LiCl-LiF salt is realized in the first step by anodic dissolution of a titanium plate in order to optimize the electrochemical parameters.

Electrolysis was performed at a current density of $60 \text{ mA} \cdot \text{cm}^{-2}$ for 2 h and 30 min. After electrorefining tests, the cathode was coated with a mixture of titanium deposit and salt (see picture in Figure 4). The deposit was washed, dried, and weighed. The metal after cleaning is easier to obtain in a powder form than a dendritic one. Figure 4 shows

XRD pattern of cathode deposit. It confirms that the obtained cathodic deposit is metallic titanium.

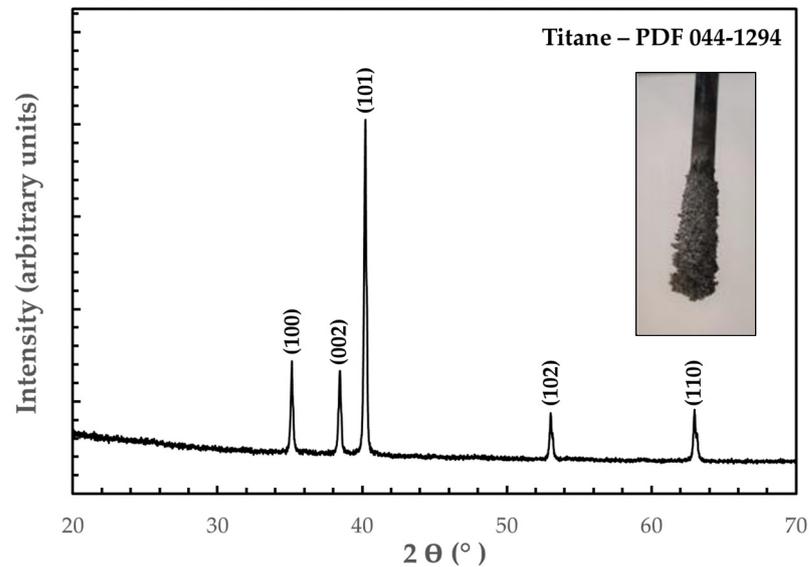


Figure 4. X-ray diffraction of titanium metal deposited on the cathode under the current density of $60 \text{ mA}\cdot\text{cm}^{-2}$ in LiCl-LiF-TiF_3 (0.62 mol/kg) at 853 K ($580 \text{ }^\circ\text{C}$). Insert image of titanium deposit.

Figure 5 shows an SEM micrograph of a titanium deposit obtained through electrolysis, which exhibits a crystalline microstructure. The crystallites are approximately $150 \mu\text{m}$, well above the limit where titanium is considered as pyrophoric (less than $5 \mu\text{m}$ [21]).

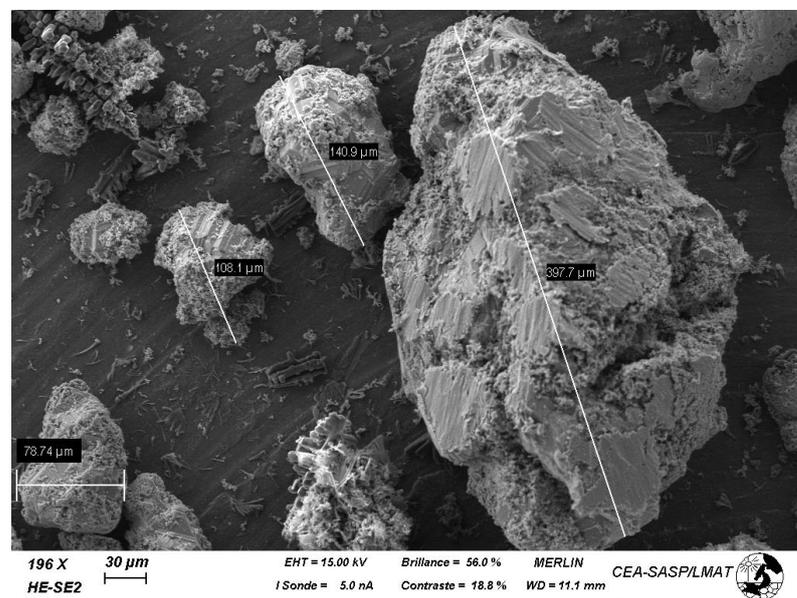


Figure 5. SEM micro-morphology of titanium metal deposit on the cathode under the current deposit of $60 \text{ mA}\cdot\text{cm}^{-2}$ in LiCl-LiF-TiF_3 (0.62 mol/kg) at 853 K ($580 \text{ }^\circ\text{C}$).

The faradic yields obtained from the calculated theoretical mass and the experimental mass obtained by weighing the deposits are about 85%.

The experiment was repeated at different current density over a range from 60 to $160 \text{ mA}\cdot\text{cm}^{-2}$, and temperature from 853 K ($580 \text{ }^\circ\text{C}$) to 953 K ($700 \text{ }^\circ\text{C}$). Faradic efficiencies were stable within this current range and slightly higher at 953 K .

4. Conclusions

The study of the reduction mechanism of titanium ions in LiCl-LiF chloro-fluoride salt showed that Ti^{3+} is reduced to Ti metal in a single step involving three electrons.

The dissolution potential of TiC_xO_y is close to the Ti^{3+}/Ti^{4+} wave. In electrorefining of titanium oxycarbide, it is important to apply low current density to avoid the formation of Ti^{4+} .

The faradic current efficiencies obtained after electrorefining a titanium plate between 60 and 160 $mA \cdot cm^{-2}$ are high, around 85% at 853 K and 90% at 953 K.

XRD and SEM characterization of the metal deposit shows the formation of metallic titanium with a grain size of around 150 μm .

Future work will be dedicated to the electrorefining of titanium oxycarbide in the experimental conditions optimized in this work.

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