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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Mechanism and Kinetics of Processes Occurring at TiO₂ Cathode in CaCl₂-CaO Melt

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Abstract—Preparation of titanium by the electrochemical reduction of titanium dioxide in a CaCl₂–CaO melt in a diaphragm electrolyzer using a graphite anode was studied.

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Data on the kinetics and mechanism of the cathodic processes in electrochemical production of titanium from oxide raw materials within the framework of the FFC process [1] are limited:

$$TiO_r + 2xe = Ti + xO^{2-}$$
. (1)

The process kinetics is limited by electrical conductivity of the oxide phase [2]. As TiO_2 is reduced, the electrical conductivity of the oxide phase increases, which gives rise to an extremum in the current vs. time dependence.

Chen et al. [3] studied the mechanism of the cathodic deoxidation of oxidized titanium in molten $CaCl_2$ by cyclic voltammetry, with *IR* compensated by an external power source, along with pulsed ac measurements.

The potentials of various cathodic peaks observed in the *I*–*E* curves are given in Table 1 relative to a current peak potential of the reduction of Ca^{2+} ions to metallic calcium (c₁) [3].

The c_5 and c_6 peaks are due to the reduction of titanium dioxide to Ti₂O₃ and TiO; the c_3 peak, due to removal of dissolved oxygen from metallic titanium; and the c_2 peak, due to reduction to metallic titanium.

We used these data for interpreting the results of this study.

EXPERIMENTAL

Pigment-grade titanium dioxide with a micrometer grain size was used as the starting material for the electrochemical reduction. To fabricate electrodes, titanium dioxide was wetted in distilled water to paste and 1-2 cm³ pellets were formed by pressing or modeling.

The pressing was performed with a mechanical screw press under a pressure of more than 1000 kg cm⁻². The pellets obtained were dried at 50-70°C in air and calcined at 800-850°C for 2-3 h, with the temperature raised at a rate of 300 deg h^{-1} . The mechanical strength of the calcined pellets was low. It was found that the strength of the pressed pellets is lower by an order of magnitude than that of the modeled pellets. After the calcination, the pressed pellets spontaneously separated into layers 2 mm and less thick in a direction transverse to application of the pressure, whereas the modeled pellets showed similar strength in all directions and therefore could be crushed mechanically to necessary pieces. The density of the titanium dioxide was $1.9-2.1 \text{ g cm}^{-3}$ for pressed pellets and $1.7-1.9 \text{ g cm}^{-3}$ for modeled pellets, and their porosity, evaluated from these values and the true density of TiO₂ (4.1–4.2 g cm⁻³), was 49-54 and 54-59%, respectively.

An attempt to increase the mechanical strength of the pellets by impregnation with a saturated calcium

Table 1. Current peak potentials (V) elative to c_1 peak potential in the *I*-*E* curves

<i>T</i> , °C	c ₃	c ₆	с ₅	c ₂	
800	0.15	0.53	0.90	1.6	
900	0.20	0.50	0.954	1.5	



Fig. 1. Electrolytic reduction cell: (1) rubber stopper, (2) steel container, (3) current lead to electrodes, (4) graphite anode, (5) reference electrode (lead or titanium), (6) TiO₂ cathode (6a, coil; 6b, perforated; 6c, grid), (7) lead–calcium anode, and (8) alundum crucible.

chloride solution, followed by modeling or pressing and calcination, did not give positive results. The strength of the pellets decreased considerably. Therefore, the modeled pellets disintegrated to 2–5-mm pieces to avoid spontaneous breakdown were used for electrochemical reduction after the calcination.

Rutile was reduced in a cell (Fig. 1) at 840– 960°C in argon. Melted calcium chloride was heated in a vacuum to 500°C to remove water. Current was fed to titanium oxide through a steel wire or perforated steel plate. In the first case, the wire was twisted in the form of a coil, with 0.5–1-mm separation between the turns (Fig. 1, section A–A). The upper part of the wire was enclosed in a ceramic straw to prevent deposition of calcium on it. The coil was placed in an alundum tube 1–1.5 cm in diameter. Onto the coil, a 1.5–2-cm layer of TiO₂ (2–3 g) was poured. In the second case, a layer of the wet paste 3–4 mm thick was deposited onto a perforated iron plate (area 2 cm²) with the subsequent drying and calcination. A graphite rod served as anode. In some experiments, the same rod served as reference electrode for measuring the cathode potential after switching off the current. The current was set within 0.2–4.7 A with a stabilized power source. The voltage and potential were recorded with a RECORDER two-coordinate potentiometer. The amount of the passed electricity was varied within 60–300% of the theoretical value necessary for TiO₂ reduction.

First, the polarization measurements were performed with a polarizing current switched on for a short time (0.5-5 min), with raising its value from 0.2 to 4.7 A. The current density counting on the geometric surface area of the pellets was from 50 mA cm⁻² to 2–3 A cm⁻². In the course of the main electrolysis, the cathode potential was recorded at the moments when the current was switched off for a short time and at the end of the experiment. After the experiment was complete, the electrodes were withdrawn from the electrolyte, transferred into the cold zone of the cell, and cooled to room temperature in argon. A visual examination of the crucible, electrolyte, and electrodes in the experiments with a carbon electrode revealed the formation of a finely divided carbon foam in an amount increasing with the amount of passed electricity, The amount of carbon foam in the electrolyte containing calcium oxide is the largest.

Presumably, calcium that has not reacted with TiO_2 dissolves in the electrolyte and reacts with gaseous carbon dioxide evolved on the anode to reduce it to amorphous carbon by the reaction

$$2Ca + CO_2 = 2CaO + C.$$
 (2)

After the experiment was complete, the cathode was thoroughly washed to remove residual salts, dried, and classified with respect to the extent of darkening. It was noted that the parts of the cathode located directly on the iron current lead became dark from the surface and from the inside. The extent of darkening decreases with increasing distance from the current lead. When the excess amount of passed electricity is small, most of the cathode surface remains light, whereas when the excess is considerable (300–500%), virtually the whole bulk of the cathode becomes dark, which shows that the degree of TiO₂ reduction increases.

Run no.	Electrolyte	T, °C	TiO ₂ weight, g	<i>Q</i> , A h (excess, %)	Fraction yield	
					dark	light
1 2	$\begin{array}{c} \text{CaCl}_2\\ \text{CaCl}_2 + 10 \text{ wt }\% \text{ CaO} \end{array}$	860 880	3.2 3.06	7.1 (60) 10.6 (160)	30 80	70 20

Table 2. Conditions and results of electrochemical reduction of TiO_2 with graphite anode

The obtained fractions of the reduced product were ground in an agate mortar, their photographs at a magnification of 120 were taken, and X-ray phase analysis was done.¹ The results of the TiO₂ reduction with a graphite electrode are presented in Table 2.

All samples of the ground and reduced product had typical metallic luster and the structure of a titanium sponge (Fig. 2). The size of titanium grains was, however, small (several micrometers and less). In both experiments, the samples had light areas of unreduced rutile and formed perovskite; their amount was larger in the light fractions. An X-ray phase analysis (Table 3) revealed no titanium peaks but revealed peaks of unreduced phases (perovskite and rutile) in a ratio depending on the electrolysis conditions.

The perovskite content is higher at a large excess of the amount of passed electricity (run no. 2 compared to run no. 1). More complete conversion of unreduced rutile into perovskite is associated with the presence of the CaO additive in the electrolyte and with a larger amount of calcium oxide formed inside the cathode.

Finely dispersed metallic titanium was X-ray amorphous: only an increase in the total background intensity was observed in the X-ray diffraction patterns.

The electrolysis using calcium chloride occurred at a stable voltage at each polarizing current. After switching off the current, fast variation of the cathode potential relative to graphite anode was observed, without any phase transitions recorded. This is due to fast removal of chlorine on the anode in the reaction with dissolved calcium, making the anode potential unstable.

With 10 wt % CaO added, the mechanism of the anode process changed. The evolution of oxygen with the subsequent formation of CO and CO_2 were observed on the anode. At the moment of switching off the current, we recorded the reverse emf of the electrochemical cell relative to a graphite electrode, which regularly increased from 0.5 to 3.5 V as the current

strength was increased from 1 to 4.7 A. The value of the reverse emf (3.5 V) confirms deposition of metallic calcium at the anode. Then, the cathode potential rapidly changed and stabilized at 1.4 V. The potential difference was 1.5-2.1 V and, according to the data of Table 1, the stabilization potential corresponded to metallic titanium. However, in this case also the anode as reference electrode is insufficiently reliable because of variations of its potential with time in the course of desorption of CO and CO₂ and their reaction with dissolved Ca and CaO.

The cell voltage in an electrolyte containing CaO was very unstable. This may be due to intense deposition of finely divided carbon, which was found after completing the experiment on the electrolyte surface under the anode and over the cathode.

Thus, the electrolysis in a diaphragmless cell using a graphite electrode involves a number of undesirable side processes: formation of $CaCO_3$ by reaction of CO and calcium oxide (Table 3, run no. 2); deposition of finely dispersed carbon leading to carbonization of the melt and formation of titanium carbide; oxidation of calcium dissolved in an electrolyte on the anode and by anode gases (Cl₂, CO₂), which considerably decreases the current efficiency.



Fig. 2. Structure of the surface of finely divided reduction product (run no. 1). Magnification 120.

¹ X-ray phase analysis was performed at the Institute of Solid State Chemistry, Ural Division, Russian Academy of Sciences.

Run no.	Dark fraction, %		Light fraction, %		
(sample no.)	CaTiO ₃	TiO ₂	CaTiO ₃	TiO ₂	CaCO ₃
1(1.4) 2(2.3)	85 100	15	36.1 79.2	63.9	20.8

Table 3. Results of X-ray phase analysis of the TiO_2 reduction product

Therefore, it was of interest to use a Pb–Ca melt containing 15–25 wt % Ca as anode and pure calcium chloride without calcium oxide additive as electrolyte. The study showed that the mechanism of the anode process principally changed. The dissolution of calcium from a lead alloy, instead of evolution of anode gases, occurred at the anode.

To make the TiO_2 reduction more complete, a smaller portion of TiO₂ (250-300 mg) was applied as paste to a perforated or grid cathode. As reference electrode (Table 4, run no. 3) we used a Pb-Ca alloy prepared directly in an electrochemical cell. To do this, calcium was deposited onto lead to 20 wt % content. In this case, the amount of calcium in lead was higher by an order of magnitude than that necessary for reduction of the TiO₂ portion and affected only slightly the composition of the Pb-Ca alloy in the course of the electrolysis. After the Pb-Ca alloy was formed, a graphite anode was withdrawn from the electrolyte, and evolved chlorine was evacuated. However, these precautions led only to a decreased amount of amorphous carbon. Therefore, in the further experiments a separate cell was used to form the Pb-Ca alloy, which made it possible to eliminate virtually completely the presence of carbon in the electrolyte upon electrochemical reduction of titanium dioxide. The conditions of the experiments are presented in Table 4.

The deposition potential of calcium (1.7 V) and two plateaus of the potential stabilization, at 0.8 and 0.34 V, were revealed by measuring the cathode potential relative to lead reference electrode after completing the electrolysis (run no. 4). The potential difference between the calcium deposition and the second plateau was 1.4 V, which, according to the data of Table 1, corresponds to metallic titanium. The first plateau with a potential difference of 0.9 V corresponds to formation of Ti_2O_3 . One more plateau of the potential stabilization at 0.18 V, which corresponds to removal of dissolved oxygen from titanium, was found at short-time polarization of the cathode.

With titanium used as reference electrode (run no. 5), three plateaus of the potential stabilization were recorded after switching off polarization: 1.25 V is the potential of calcium deposition, and potentials pf 1.92 and 0.77 V correspond to c_3 and c_6 current peaks (Table 1). The potential of the TiO formation was not revealed.

The obtained products of the electrochemical reduction contained no light fraction and corresponded in the structure to dark fractions (run nos. 1, 2) with finely dispersed X-ray amorphous metallic titanium. Thus, the fineness of pigment-grade titanium dioxide predetermines the fineness of metallic titanium. Another factor is the formation of the intermediate oxide Ti_2O_3 , which was revealed in the X-ray diffraction pattern.

When two-side metallic grid was used as current lead, a plate of precalcined titanium dioxide was placed inside the grid. The TiO₂ pellet was prepared by dry pressing with addition of 5% MgO to enhance its strength. The pressed pellet was dried at $50-80^{\circ}$ C for 24 h and calcined for 5 h at 1050° C by raising the temperature at a rate of 300 deg h⁻¹ to obtain coarser TiO₂ grains. The strength of the calcined pellet prepared by dry pressing was higher than that of the pellets modeled from a wet paste.

Calcium was deposited on the cathode at $920-930^{\circ}$ C by raising the current density stepwise from 0.1 to 2.3 A cm⁻², using the Ca–Pb alloy as anode. The electricity was passed in 400% excess. A part of the electrochemical reduction product washed inside the metallic grid was in the form of grains whose size

Table 4. Conditions and results of electrochemical reduction of TiO₂ in CaCl₂ melt with Pb-Ca anode

Run no.	<i>T</i> , °C	TiO ₂ weight, g	Current excess, %	Reference electrode	Graphite	Current lead to cathode	<i>E</i> ,* V
3	880	300	200	Pb–Ca	Present	Perforated	2.0; 0.7; 0.4
4	910	250	200	Pb	Absent	Perforated	1.7; 0.8; 0.34
5	960	250	300	Ti	Absent	Grid	1.25; 1.02; 0.77

* Potential of the stabilization plateaus.

exceeded the size of the ground particles obtained in the previous experiments, and the remaining part was in the form of small metal-coated plates about 0.5 mm thick.

As seen from Fig. 3, the reduction product has a pronounced metal structure; grains are partially sintered and their size is substantially increased. By visual observation, most of the product is metallic titanium. However, despite large current excess, inclusions of incompletely reduced forms remained in the metal bulk.

The separation of the anode and cathode spaces with a ceramic diaphragm was necessary not only to make purity of the product higher but also to increase the current efficiency of the electrolysis. In a diaphragmless electrolyzer, most of the current is spent to compensate losses due to back reaction of the electrolysis products. The calcium evolving at the cathode can interact with the chloride and dissolve in it. The calcium solubility at 900°C is about 4 mol %. The dissolved calcium reacts with the anode products (gaseous chlorine or carbon dioxide) and transforms back into calcium chloride and oxide, or is anodically oxidized with the formation of bivalent ions. The occurrence of the side processes of calcium oxidation, first, results in the considerable overexpenditure of the electrical power for the electrochemical reduction of titanium from titanium oxide and, second, leads to a decrease in the efficiency or in the degree of titanium reduction owing to cathode depolarization. In the majority of the experiments performed, the cathode potential at the moment of switching off the current was lower than the deposition potential of metallic calcium, which, according to the results of X-ray phase analysis, mainly resulted in the reduction of titanium to intermediate products.

To decrease the influence of the side processes impeding deposition of metallic calcium on the cathode, the experiments were performed in an electrolyzer with its cathode and anode spaces separated by a diaphragm. As diaphragm we used porous magnesium oxide ceramics containing yttrium and cerium oxides as binders (60% porosity). The ceramics was produced at the Siberian Chemical Combine. The design of the cathode and anode compartments of the electrolyzer is shown in Fig. 4. Wet titanium dioxide for fabricating the cathode was modeled in a pellet 7-10 mm diameter and 1.5-2 cm high (mass 2.5-3 g) inside an alundum tube and was calcined at 950-1000°C to obtain coarser grains. After the calcination, a 1.5–2-mm hole was drilled in the center of the tube, into which a current lead made of iron wire and



Fig. 3. Structure of the surface of finely divided reduction product (run no. 5). Magnification 300.



Fig. 4. Design of a diaphragm electrolyzer: (1, 2) rubber stoppers; (3) steel retort, (4, 6) current leads, (5) outlet of anode gases, (7) graphite anode, (8) alundum crucible, (9) electrolyte, (10) alundum tube, (11) rutile pellet, (12) diaphragm, and (13) titanium reference electrode.

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 80 No. 9 2007

covered with an alundum jacket to avoid contact with a salt melt was inserted.

A graphite rod inside a quartz tube was the anode. A ceramic diaphragm glued into the lower part of the tube impeded passage of dissolved anode gases into the catholyte and of dissolved calcium into the anolyte. A hole in the rubber stopper closing the cell allowed the upper part of the tube to be in contact with the atmosphere, which ensured outlet of the anode gases from the anode space and made their interaction with the catholyte minimal.

The electrolysis was performed in argon over the catholyte at 910–930°C in a calcium chloride melt with and without calcium oxide added. In this case, chlorine or carbon oxides were the anode products. The electrolyzer voltage, current, and the cathode potential relative to titanium reference electrode were recorded in the course of the experiments.

When the electrolysis was performed at low current densities $(0.2-0.3 \text{ A cm}^{-2})$, the cathode potential did not reach the deposition potential of calcium, and TiO₂ was reduced with the formation of CaTi₂O₄ as major product. In contrast to the diaphragmless electrolysis, the reduction product contained no initial rutile phase. The pressed product showed small electrical conductivity, confirming the occurrence of reduction.

With the current density increased to 1.2 A cm^{-2} , the cathode potential increased to approximately 3.7–3.8 V in the chlorine scale, which corresponds to the deposition potential of metallic calcium. The amount of passed electricity was 450% of theoretical value to ensure higher degree of reduction of complex titanium oxides.

As previously, the washed powdered product was dark gray. As compared to the previous experiment, the amount of metallic fraction increased considerably. The powder did not conduct electrical current in the loose state but exhibited high electrical conductivity in the pressed state. The powder had pronounced pyrophoric properties. It was highly inflammable, which also confirms the presence of a finely divided metallic phase in it. The reduction of rutile in a diaphragm electrolyzer made it possible to considerably increase the degree of reduction, with the same energy expenditure, and to shift the composition of the product toward formation of metallic titanium.

CONCLUSIONS

(1) The preparation of titanium by the electrochemical reduction of titanium dioxide in a $CaCl_2$ -CaO melt using graphite anode is complicated by formation of CO₂ on the anode. CO₂ and CaO, present or formed by the electrolysis, react in the salt melt to give CaCO₃, and then the CO₃²⁻ ions are reduced to amorphous carbon with calcium dissolved in the electrolyte. This inevitably results in carbonization of the electrolyte and leads to the formation of titanium carbide. It seems impossible to produce quality metal under these conditions.

(2) Titanium dioxide pellets should be precalcined at 1050–1100°C, which allows considerable coarsening of the grains of the cathodic titanium deposit obtained.

(3) The possibility of the electrochemical reduction of titanium dioxide in a diaphragm electrolyzer was demonstrated. The obtained metallized product has a low concentration of oxygen and a high electrical conductivity and is pyrophoric. The electrolysis efficiency can be increased further by using the bulk reduction of finely divided titanium dioxide and further improving the reductive characteristics of the cathode process by raising its electronegative potential.

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