

SINGLE STEP ELECTROLYTIC PRODUCTION OF TITANIUM

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ABSTRACT

Titanium tetrachloride usually obtained through high temperature chlorination of titanium dioxide is used as the raw material for the production of titanium sponge by the commercial processes of Kroll and Hunter. An alternate method for the production of titanium sponge has been tried. It is essentially an electrochemical dissolution of titanium dioxide-carbon composite anodes and deposition of titanium metal particles over a molten aluminium cathode. This electrolytic route is relatively inexpensive and reduces hazards due to metal chloride evolution and energy consumption. Present study involves preparation and characterization of titanium dioxide-carbon composite anodes and electrolyzing them in molten equimolar NaCl-KCl. Anodic current efficiency of the dissolution of the anodes around 90% and cathodic deposition efficiency, by chemical analysis, around 20% are reported.

1. INTRODUCTION

The metallothermic reduction process is the only commercially available process, presently, for the industrial production of titanium sponge from titanium tetrachloride. A widely published electrolytic route, namely the "Ginatta Process", is still not gone beyond the pilot plant status¹. This process also uses titanium tetrachloride for the production of titanium sponge. Attempts have been made for directly dissolving titanium dioxide, in appropriate melts and carrying out the electrolysis². Low dissolution (~ 0.2%) and pickup of oxygen from the oxide by the metal were the major difficulties encountered in those studies. Recently, Ratvik *et al* reported that a composite anode made up of the metal oxide and carbon could be leached out electrolytically into a melt resulting in successful winning of metals like aluminium and magnesium³. A similar study was also carried out at this laboratory using alumina and carbon composites in KCl-NaF melt⁴. The same technique has been tried for winning of titanium in this study. The unit operation and process involved for the production of titanium tetrachloride from titanium dioxide and thus venting of gaseous pollutants are avoided.

The other innovative idea introduced in this study is the utilization of a molten aluminium cathode. Patents are already registered for the production of titanium metal from titanium tetrachloride using molten zinc cathode and the zinc is removed by volatilization⁵. It is known that titanium is used as alloys for its better properties, and aluminium is one of the frequently used alloying elements. The phase diagram of Ti-Al system shows around 800°C (operating temperature in the present study) the liquid aluminium having very low concentration of titanium is in equilibrium with solid peritectic intermetallic compound

TiAl₃. This suggests that titanium crystallites nucleating and growing over the molten aluminium surface will have only a few molecular thickness of TiAl₃. If the condition of deposition and the physicochemical properties are favorable, then the titanium particles are expected to sink into the molten aluminium pool. Once they go deep into the melt the particles will be surrounded by the more active aluminium. Separation of the two phase system, *i.e.*, almost pure molten aluminium and the solid titanium particles can be effected by centrifuging or filtering, which consume less energy compared to the leaching or vacuum distillation processes. Hence this may be a modified electrolytic method for economic production of titanium.

This study involves the preparation and characterization of composite anodes, determination of their current-voltage characteristics, operations of experimental titanium electrolysis cells and the determination of amount of titanium metal in the aluminium cathode.

2. EXPERIMENTAL

2.1 Preparation of Composite Anodes

Composite anodes with different compositions were prepared by mixing powdered (100 mesh) carbon and metal oxide (TiO₂, 0.22µm). The pitch content of the mixture was adjusted to 10-15%. A weighed mass of the mixture was then pressed in a hydraulic press at 100 N/mm² for 120 seconds. Anode blocks of two different types were prepared, one for characterization and the other with a steel rod projection (3 mm diameter) as the current lead, for using as an electrode in electrolytic studies. Anode blocks thus prepared were baked around 900°C for 4 to 6 hours in a reducing atmosphere.

2.2 Characterization

The dimensions of the cylindrical composite anode blocks used for characterization studies were 33 mm diameter x 30 mm height. Properties like density, porosity and electrical resistivity, which influence the electrolytic dissolution characteristics of the composite anodes were studied.

Apparent densities of the baked blocks of different anode composition were calculated by measuring their mass and volume (using a slide caliper) accurately. The real density of the respective blocks were determined by crushing the blocks into powder and using a specific gravity bottle. Porosity (defined as the ratio of void space to apparent volume) of the electrode blocks were calculated using their real and apparent densities. The porosity of the electrode directly gives the measure of voids present in the electrode specimen⁶.

Electrical resistance was measured by using Agronic 54C4 probe digital micro-ohm meter. Changes in electrical resistivity as functions of titanium dioxide in the composite anode and baking temperature were also evaluated.

2.3 Electrolytic Dissolution

A diagram of the experimental cell is shown in Fig.1. A graphite crucible (inner diameter 80 mm, depth 90 mm), kept in a steel container, served as container for electrolyte. A 75mm diameter alumina tube insert was used inside the graphite crucible to restrict the area of cathode. 50g of pure aluminium kept in the 12 mm diameter hole made in a 12 mm thick alumina disk which was kept at the bottom of the graphite crucible, acted as cathode. Another cathode used in the present study was a molybdenum wire of 1mm diameter. Electrolyte used in this study was equimolar mixture of NaCl and KCl. For conducting current-voltage characteristics studies titanium ions were introduced by electro dissolution of composite anodes or chemically pure titanium strip at appropriate current densities for required duration. Silver-silver chloride electrode, [0.1M AgCl/(NaCl+KCl)] was used as reference electrode⁷. Temperature of the cell was maintained at 780°C. Pre-electrolysis was carried out using a graphite anode and a mild steel cathode for about 2 hours by applying cell voltage of 2.5 volts. Electrolytic studies were performed using composite anodes having diameter 31 mm and height about 30 mm. Anode blocks with three different compositions, viz., 50:50, 60:40, 75:25 of titanium dioxide

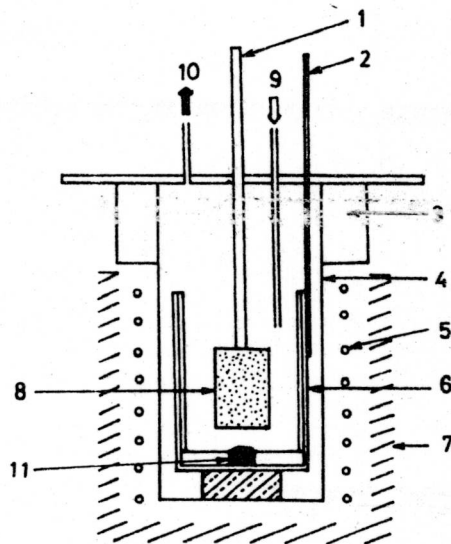


Fig. 1. Schematic diagram of the electrochemical cell;

(1) composite anode lead (2) cathode lead (3) water jacket (4) shell (5) electric heating coil (6) graphite crucible (7) furnace outer wall (8) TiO₂-C composite anode (9) argon in (10) gas out (11) molten aluminium

and carbon, respectively, were tried. However a detailed study was carried out only on the anode with 50:50 composition. The cathode connection was given via the steel rod welded to the steel jacket. The inter electrode distance was maintained at about 2 cm. For electrowinning studies, the applied voltage was kept about 4.5 volts, a current density of approximately 0.7 A/cm² was maintained over the anode surface and a current density of 3 A/cm² was maintained over the cathode.

Atomic absorption spectroscopic analysis and X-ray diffraction studies were carried out on the bath samples as well as on the aluminium used as cathode. Gases coming out from the cell was analyzed using infrared spectrophotometer.

3. RESULTS AND DISCUSSION

Table 1 shows the results of density and porosity measurements. It is apparent from the table that both apparent density and porosity of an anode block increase with increase of titanium dioxide content. The result of the electrical resistance measurements were presented in Tables 2 and 3. From the tables we see that the value of specific resistance of composite anodes increases as titanium dioxide content increases. But the resistance decreases with increasing baking temperature which may be due to the sintering or more specifically decrease of heterogeneous interface area between titanium dioxide and carbon particles.

Table 1. APPARENT DENSITY AND POROSITY OF COMPOSITE ANODES AT ROOM TEMPERATURE AFTER BAKING AT 900°C

Composition		Apparent density* (g/cc)	Powder density* (g/cc)	Porosity (p%)
TiO ₂ (w/o)	Coke (w/o)			
50	50	1.37	2.292	40.05
60	40	1.40	2.499	43.87
75	25	1.47	2.675	44.89

After determining the apparent density the anode block was crushed into powder and the density of the powder was determined using specific gravity bottle.

Table 2. ELECTRICAL RESISTIVITY AND CONDUCTIVITY OF COMPOSITE ANODE AT ROOM TEMPERATURE (Baked at 750°C)

Composition		Resistivity (ohm. cm)	Conductivity (mho cm ⁻¹)
TiO ₂ (w/o)	Coke (w/o)		
50	50	0.745	1.342
60	40	0.936	1.068
75	25	1.371	0.729

Table 3. ELECTRICAL RESISTIVITY AND CONDUCTIVITY OF COMPOSITE ANODE (50:50, TiO₂:C) BAKED AT DIFFERENT TEMPERATURES (HOLDING TIME 4 HOURS)

Temperature (°C)	Resistivity (ohm cm)	Conductivity (mho cm ⁻¹)
Green	3828.8	0.00026
750	0.7450	1.3420
800	0.3163	3.1615
850	0.1043	9.5870
900	0.0216	46.5116
950	0.0159	68.8900

Fig. 2 shows the current-voltage characteristics of solvent melt (KCl: NaCl, 1:1 mol ratio) on molybdenum wire cathode and graphite anode. Sodium and potassium discharged at the molybdenum cathode while chlorine gas evolved at the anode. Extrapolation of the smooth active region of the curve showed a decomposition potential of 3.3 volts. The decomposition potential of NaCl and KCl previously reported were 3.34 volts and 3.4 volts, respectively⁸. The value obtained by this study almost agree with reported values. The merging of the decomposition potentials of NaCl and KCl to a single value may be due their closeness and the study was conducted on the molten equimolar mixture of the salts⁹. When the potential of the molybdenum cathode was measured against Ag/AgCl reference electrode, (Fig. 3) instead of the graphite anode, the study resulted in a cathodic potential of 1.9 volts for sodium and potassium discharge, which can be considered

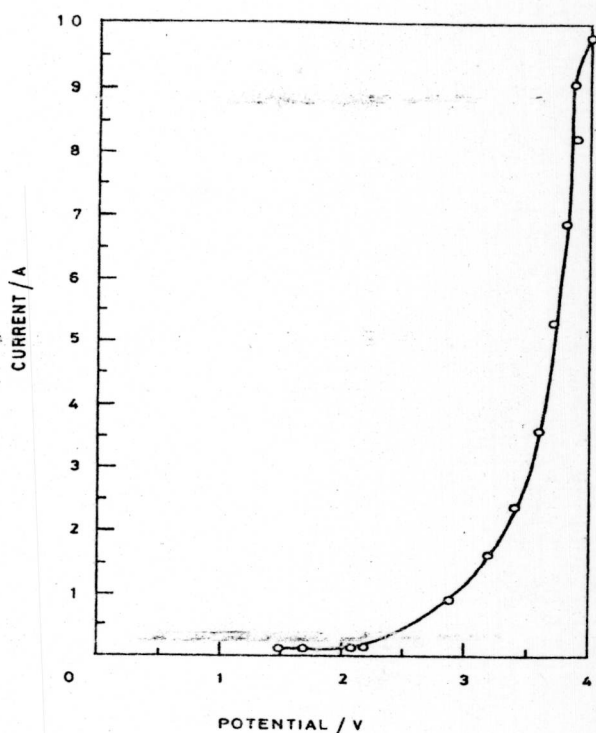


Fig. 2. Current-voltage characteristic of KCl:NaCl (1:1 mol ratio)

as an internal reference system to test the reliability of the Ag/AgCl reference electrode¹⁰

The V-I characteristics of the composite anode with respect to Ag/AgCl reference electrode is shown in Fig.3. Two prominent waves can be considered. The first one results in 1 volt on extrapolation to zero current and the second wave

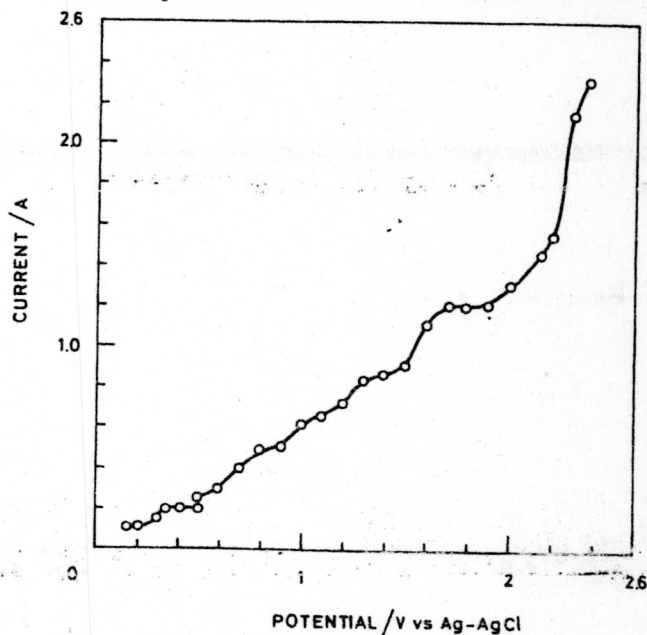


Fig. 3. Current-voltage characteristic of TiO₂-C composite anode.

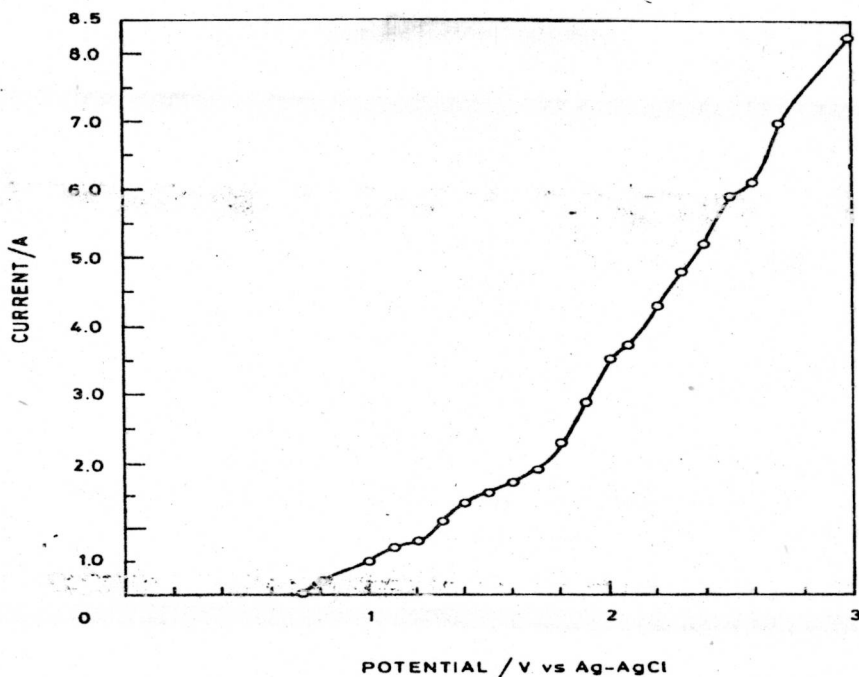


Fig. 4. Current-voltage characteristic of molybdenum cathode in NaCl-KCl melt containing titanium ions.

at higher current density resulted about 1.35 volts. The possible reactions on the anode blocks are the simultaneous formation of titanium tetrachloride and carbon dioxide and liberation of chlorine gas. For chlorine evolution in molten salt system 1.39 volt was reported, with respect to Ag/AgCl. This suggest that at higher current densities chlorine is discharged at the anode. At lower current densities, at about 1.0 volt with respect to Ag/AgCl, oxygen ions from the titanium dioxide lattice combines with carbon present in the anode to form carbon dioxide and the active titanium ions combine with chloride ions available at the anode surface to form titanium tetrachloride. During the prolonged electrolysis uniform dissolution of the anode blocks was noticed. Dissolution of the anode was smooth and the concentration of titanium ions in the melt was found to be increasing. When the current density was high the decomposition of the melt was faster and the exhaust from the cell contains titanium dioxide particles along with hydrogen chloride smell.

Fig. 4 shows voltage-current characteristics of the molybdenum cathode with respect to Ag/AgCl reference electrode in the chloride melt containing titanium ions (Anode = $\text{TiO}_2\text{-C}$). The curve includes two clear reduction waves and the third one is not very significant. The wave which appear just before alkali metal ion discharge corresponds to the reduction of Ti(II) to Ti(0) ¹¹. Extrapolation of voltage values to zero current gives the value 1.1 volts.

Fig. 5 shows the current-voltage characteristics of molten aluminium cathode with respect to Ag/AgCl electrode. The open circuit potential of aluminium cathode with respect to Ag/AgCl is given in Table 5. Extrapolation of waves to zero current value gives the discharge potentials of Ti(II) to Ti(0) (-0.95V) and Na/K ions to metal (-1.9V). Clearly the values obtained are less than the corresponding values obtained for the molybdenum cathode. This indicates the formation of aluminium alloys of titanium and alkali metals.

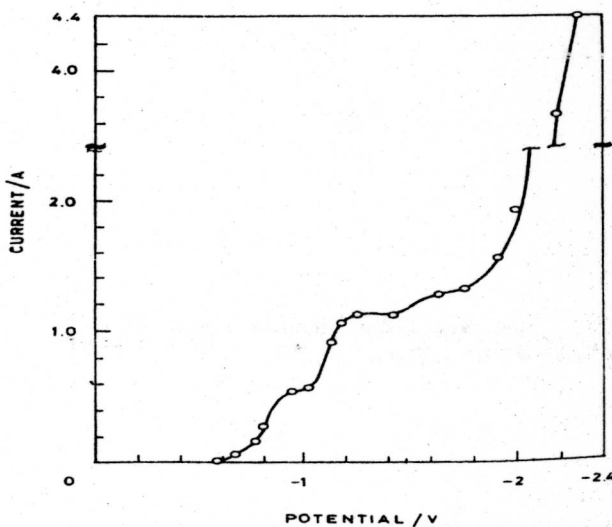


Fig. 5. Current-voltage characteristic of aluminium cathode in NaCl-KCl melt containing titanium ions.

Table 4. DETAILS OF CHEMICAL ANALYSIS : (in kg)

Run no	TiO ₂ consumed	Ti expected Theoretical	Ti Deposited/ 10 ⁻³	Ti as Ti ²⁺ /Ti ³⁺ /10 ⁻³	Ti as TiO ₂ / 10 ⁻³	Ti as TiCl ₄ /10 ⁻³
1.	0.03	0.015	*—	9.45	4.20	1.35
2.	0.02	0.010	@0.6	4.5	3.90	1.0
3.	0.03	0.015	@3.0	6.0	5.25	0.75
4.	0.08	0.020	@8.4	16.0	13.6	2.00

Cathode : * - Graphite crucible, @ - molten Al, c.d anode : 0.7A/cm²C.d cathode : 3.0A/cm²

Electrolysis experiments were conducted using composite anodes and molten aluminium cathode. During the electrolysis the current readings were decreasing and cell resistance was increasing steadily as dissolution of composite anode blocks was in progress. The continuous consumption of the anode blocks preferably from the bottom in an uniform manner causes increase in the inter electrode distance. Table 4 present the material balance of such experiments. The chemical analysis shows that concentrations of titanium in aluminium was increasing as electrolysis continues. Optical micrographic study using diammonium difluoride as colour etchant identified the titanium particles by its bluish spots embedded into aluminium matrix.

Table 5. OPEN CIRCUIT POTENTIAL OF METAL ELECTRODES WITH RESPECT TO Ag/AgCl REFERENCE ELECTRODE IN NaCl-KCl (1:1 mol) ELECTROLYTE

Electrode	Without Ti ions	With Ti ions
Aluminium	- 0.825	- 0.891
Nichrome	- 0.336	-
Iron	- 0.304	-

4. CONCLUSION

A mechanically stable and electrically conducting composite anode could be fabricated by pressing titanium dioxide and carbon powder and baking at 900C. Its electrical conductivity decreased with increase of titanium dioxide content. Density as well as porosity increased with increase of titanium dioxide content. The composite anode was leached electrolytically. Carbon is used by the oxygen liberated from titanium dioxide, and titanium goes in to solution as ions. Discharge potential of Ti²⁺ to Ti metal on molten aluminium of -0.95V, potentials of liberation of carbon dioxide about 1.6V and discharge potential of chlorine gas about 1.35V over the composite anode block

with respect to silver-silver chloride reference electrode were obtained. Titanium metal in the liquid aluminium after solidification was identified as particles.

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