The New Concept for Electrowinning Process of Liquid Titanium Metal in Molten Salt

Toshihide TAKENAKA,* Takayuki SUZUKI, a Masahiro ISHIKAWA, Eiichi FUKASAWA, b and Masahiro KAWAKAMI

Faculty of Engineering, Toyohashi University of Technology (Hibarigaoka 1-1, Tempaku-cho, Toyohashi 441-8580, Japan)

*Graduated from Toyohashi University of Technology (Present application: Mitsubishi Motors Corporation, Nakashinkiri, Hashime-cho, Okazaki 444-8501, Japan)

bSponge Titanium Division, Toho Titanium Co. Ltd. (Chigasaki 3-5-3, Chigasaki 253-8510, Japan)

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Direct electrowinning of liquid titanium metal has been investigated by using a DC-ESR (Direct Current Electro Slag Remelting) apparatus. A small scale DC-ESR unit was operated in a DC reverse polarity mode, where a graphite rod was used as anode and a steel or a copper base-plate was used as cathode. The used salt was CaO-CaF₂-TiO₂ mixture. The distance between the cathode and the anode was essential to the electrolysis. A metal pool was formed on the base-plate and the current efficiency for the reduction was up to 18\% with the proper distance between the electrodes. Some amount of titanium was electrodeposited on the base-plate though its state changed with the electrolytic condition. Pure titanium metal pieces were obtained in the solidified salt after the run with the bigger distance. It is concluded that the electrowinning of liquid titanium metal by the present process is possible if sufficient heat to form a metal pool can be supplied at the bigger distance between the electrodes.

**Key Words**: Titanium, Electrowinning, Electro Slag Remelting, Metal Pool

1 Introduction

Titanium has such good properties as high specific strength and high corrosion resistance. The availability of titanium has been limited because of its high production cost. If the solid ingot of titanium can be obtained by direct electrolysis from molten salt, it might be of some help to reduce the production cost. However, solid electrodeposits from molten salt are likely to be dendritic, which necessitates such a succeeding process as vacuum arc remelting. If the electrodeposits can be obtained in liquid state, the above problem will be solved. However, in general, it is considered very difficult to hold liquid titanium because of high melting point and high reactivity.

The "Electro Slag Remelting (ESR)" operation is one of the steel refining processes. In the process, a consumable electrode is melted by Joule heat which is generated by the high current passing through bath, and the temperature around reaches more than 2000 K. The metal droplets from the consumable electrode are collected in a metal pool and then solidified unidirectionally on a base-plate. Because the vessel is water-cooled continuously, the inside surface is in self-lining condition. Although the process is usually by alternating current, direct current can be used. In the case, electrolytic effects can be expected. Namely, titanium can be electrodeposited in metal-pool cathode if a certain condition is satisfied.

Our group has already shown that the electrowinning of titanium was possible with the aid of a small scale ESR unit. In the present work, the effect of the electrolytic conditions on the purity of deposit and on the current efficiency have been investigated.

2 Principle

If an ESR apparatus is operated in a DC reverse polarity mode, a cathodic reaction occurs at the metal pool on the bottom of cell. Since the process should proceed at as high temperature as 2000 K, the titanium source must be TiO₂, rather than chlorides. The virtual cathodic reaction is expected to be

\[ \text{Ti}^{4+} + 4e^- = \text{Ti} \quad (1) \]

A graphite rod suspended in the middle of cell is used as an anode. The virtual anodic reaction is expected to be

\[ \text{O}^{2-} + \text{C} = \text{CO} + 2e^- \quad (2) \]

Then, the overall reaction is expected to be

\[ \text{Ti}^{4+} + 4e^- + \text{O}^{2-} + \text{C} = \text{Ti} + \text{CO} \]
Therefore, the bath should have enough solubility of TiO₂ at the concerned temperature and its main components should be more stable electrochemically than TiO₂. In the present work, CaO-CaF₂ was selected as an electrolytic bath.

3 Experimental

3.1 Apparatus

The experimental apparatus is schematically shown in Fig. 1. Two types of vessel as shown in Fig. 2, which consisted of side-molds and base-mold of copper, were used. The inner diameter of the vessel was 110 mm φ and the height was 400 mm. The side-molds and base-molds were cooled by stream water. The water cooling system was equipped with a flow meter and two thermometers at the inlet and outlet of the molds. The heat loss from the molds can be estimated from water flow rate and the temperature change.

A graphite rod with a sharpened tip was used as anode. The diameter of the rod was 40, 50 or 60 mm φ and the length was c.a. 1 m. The rod was driven up and down at a constant speed with the aid of an electrode driving unit. A thin metal base-plate of 110 mm φ and 20 mm thickness was put on the base-mold. Although the base-plate should be titanium in practical use, an iron plate was used in this work to analyze the electrodeposited elements accurately. A copper plate, filled up in an iron cup to prevent it from reacting with the copper molds, was also used instead of the iron plate.

The CaO-CaF₂ mixture was melted in the vessel. The weight ratio of CaO to CaF₂ was fixed in the present work; 20 : 80. This mixture was pre-melted beforehand and TiO₂ of 3-20 mass % was added to the mixture in electrolysis.

A DC current was supplied through a silicon rectifier. The maximum capacity of power source was 182 kVA. The maximum DC current and voltage were 2.5 kA and 50 V. The electric power unit was equipped with voltage and current recorders and a current integrator which showed the total supplied electricity. The positive terminal of the power supply was connected with the graphite anode, and the negative terminal was with the base-mold. The side-molds were electrically insulated from the base-mold in the insulated-mold type vessel, while un-insulated in the live-mold type vessel. A hundred percent of current flows from the graphite rod to the base-plate in the insulated-mold type, whereas some portion of current would bypass through the side-mold in the live-mold.

3.2 Experimental process

The graphite electrode was driven down so that the tip should just touch the base-plate. About 1 kg of the CaO-CaF₂-TiO₂ mixture was supplied to the vessel. Starting the process, the primary salt powder melted down gradually. After it melted down com-
pletely, the salt powder was supplemented. The total amount of salt was c.a. 3 kg. Since TiO₂ component should be consumed as the process proceeded, small pellets of TiO₂ were supplied to the salt to compensate the loss. The distance between the cathode and the anode could not be measured continuously. The distance, discussed in this paper, was estimated by the thickness of the base-plate, the length of cathode and the position of cathode after each experimental run.

After stopping the power supply, the electrode was pulled up. The weight changes of the base-plate and the graphite electrode were measured. The base-plate was cut vertically. The cross section was polished with water proof abrasive papers down to #1200, and then examined by SEM, EPMA. The solidified salt was crashed up to collect the metallic pieces which were sometimes found in it. The crushed salt powder was analyzed by XRD.

3.3 Current efficiency
Expecting the reaction (1), the current efficiency for cathodic reaction is given by

$$\eta_{\text{CATH}} = \left\{4FW_{T1} / (M_{T1}Q)\right\} \times 100 \, (\%) \quad (4)$$

where, \(F\) is Faraday constant, \(W_{T1}\) is the weight gain of base plate, \(M_{T1}\) is the atomic weight of Ti and \(Q\) is the total electricity supplied. The weight of the metal pieces collected from the solidified salt was added to \(W_{T1}\) if obtained.

The current efficiency for anodic reaction is given by

$$\eta_{\text{ANO}} = \left\{2FW_{C} / (M_{C}Q)\right\} \times 100 \, (\%) \quad (5)$$

where, \(W_{C}\) and \(M_{C}\) are weight losses of the graphite electrode and the atomic weight of carbon, respectively.

4. Results

4.1 Process document

Figure 3 shows an example of changes in current and voltage with time. At the beginning, the current did not vibrate so much. In this period, electric arcs were generated exclusively between the base-plate and graphite electrode. The current vibrated very much and the molten salt started splashing frequently over the vessel after a few minutes. The voltage could be changed to some extent by adjusting the distance between the base-plate and the graphite electrode.

In a usual ESR operation such as steel remelting, current is usually stable and salt does not splash so much. The current vibration and the salt splash in this system were considered due to the formation of gas bubbles. Because gas which could be generated in this system was limited and blue flame was observed sometimes, the CO gas generation according to equation (2) was expected to occur. The voltage vibrated all the time, even in the period of arc generation, but the amplitude of vibration was larger in CO formation period.

The current vibration got smaller and the salt splash got less-frequent after dozens of minutes. Because the current efficiency was low after the vibration and splash ended, the salt splash was a good indicator for efficient electrolysis. The operation was terminated when the salt splash ended. On the other hand, the splashed salt deposited on the upper part of the graphite anode and the inside of side-mold, and the drive of the graphite anode was sometimes obstructed by a visor-like deposit. The operation was also broken off in this situation.

The difference between the operation with the live-mold type vessel and that with the insulated-mold type vessel was not clear. However, the operation time tended to be longer with the insulated-mold type vessel.

4.2 Change of base-plate

Figure 4 shows the typical appearance of the iron base-plates after electrolysis. The reaction product piled up at the center and a metal pool seemed not to be formed. The copper base-plate was melted completely when the distance between the electrodes was small. After the operation with the copper base-plate, metallic pieces of 1-15 mm with silver color, as shown in Fig. 5, were obtained near the bottom of the solidified salt.

Figure 6 shows the relation between the weight gain of base-plate and the length of salt splashing time. The weight gain increased with salt splashing time so that the current efficiency did not depend strongly on the splashing time. The weight gain and
the current efficiency did not depend remarkably on TiO₂ content in the bath, either. Metallic deposit was obtained even in the bath with 3 mass % TiO₂. In the bath of 3 mass % TiO₂, the length of salt splashing time was usually longer and the obstruction in drive of the graphite anode by solidified splashed salt occurred hardly. The optimum concentration of TiO₂ should not be so high in this process.

4. 3 Analysis of solidified salt

The upper part of the solidified salt was light gray and the lower part was dark gray, although the color was white initially. The fine particles of bright color were found in the solidified salt after some runs. Metallic pieces were sometimes obtained from the solidified salt, which were collected before XRD analysis. The components of CaF₂, CaO, Ca(OH)₂ and CaTiO₃ were detected by XRD analysis. Calcium hydroxide is considered as hydrated CaO. Titanium carbide was also detected occasionally, but Calcium carbide was not found. The main reason why the salt was blackened seemed to be suspension of graphite fine particles.

4. 4 Formation of metal pool

Figure 7 shows the dependence of the cathodic current efficiency on the material of base-plate. The current efficiency was better with the copper base-plate than with the iron base-plate. A metal pool was not formed entirely with the iron base-plate, while it was formed with the copper base-plate when the distance between the electrodes was small. The cross sections of the copper base-plate after the electrolysis with different distance between the electrodes were shown in Fig. 8. The copper base-plate was melted completely at the distance of 5 mm, and could not be taken off from the iron cup. It was melted partially at 11 mm in distance, but its surface was uneven. At this distance, the formation of metal pool was limited on the surface, and it seemed to be agitated by electric arcs or by a strong salt flow with the pinch effect. The plate looked not to melt at 35 mm in distance. Considering the melting points of iron and copper, the surface temperature of the base-plate should be 1300-1400 K even when the distance between the electrodes was small. Metal pieces of
1.5 mm were obtained at the distance between the electrodes more than 10 mm.

Figure 9 shows the changes in current and voltage pattern with the distance between the electrodes. The vibrations in current and voltage diminished with the distance between the electrodes. The salt splash also got calmer with the distance between the electrodes though small splashes were seen occurring on the surface of the bath. The average current decreased with the distance between the electrodes. The average voltage increased with the distance between the electrodes, but was limited by the capacity of the used power supply. Figure 10 shows the relationship between the cathodic current efficiency and the distance between the electrodes with the copper base-plate. The efficiency showed the maximum value up to 18% at the distance of 5-10 mm, and then decreased with increase of the distance. These results indicate that the formation of larger metal pool is essential to the higher cathodic current efficiency.

4.5 Examination of electrodeposits

Titanium was detected in the melted part of the base-plate and the metal pieces collected from the solidified salt. However, the state of titanium was different with the electrolytic condition.

Figure 11 was the typical SEM image of the cross sections of the piled-up deposit on the iron base-plate with the small distance between the electrodes. Three phases were observed. The results by EPMA are shown in Table 1, where the assigned characters correspond to those in Fig. 11. The phase (A) consisted of Ti and C. The atomic ratio of C to Ti was about one so that the structure seemed TiC. The
between the electrodes was, the more often titanium carbide tended to be detected.

Titanium and Si were detected in the copper base-plate which was melted completely. Their accurate amount could not be measured because the amount of deposit was much less than the amount of the copper plate. Calcium was also detected in the plate. From the presence of Ca in the plate, Ti could be deposited not only by the electrochemical process as reaction (1) but also by the chemical reduction with the electrodeposited Ca.

Metallic pieces obtained from the salt were not dendritic but looked like droplets as shown in Fig. 5. Table 2 shows the typical composition of the pieces by EPMA and chemical analysis. Although there were some discrepancies by the methods, the pieces were almost pure Ti metal. The C content was very low. Oxygen seemed to be included considerably though it was not detected by EPMA. It was reported that a considerable amount of O was contained in the electrodeposited from the bath with TiO₂.⁴ Because the removal of O from Ti metal was very difficult, the reduction of O content must be an important subject.

It was shown that pure Ti metal was obtained by this process. In the case that the Ti metal pieces were obtained, the base-plate was not melted completely. The mechanism of the formation of taitanium droplets was not clear. However, the appearance of the pieces suggested that the deposited metal melted partially and gathered to form the droplets on the surface of the base-plate.

5 Discussion

5.1 Current efficiency

In the present work, the cathodic current efficiency was no more than 20 % even under the suitable condition. The anodic current efficiency appeared to be 50-80 %. However, the real anodic efficiency was much lower since the weight loss of graphite electrode included the loss by air oxidation.

It was well-known that dissolution and/or suspension of cathodic product makes cathodic current efficiency lower. This reason should be applied in the present work; Namely, if the deposited metal

<table>
<thead>
<tr>
<th>Method</th>
<th>Elements (at %)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Ti</td>
</tr>
<tr>
<td>EPMA</td>
<td>95.0</td>
</tr>
<tr>
<td>Chemical analysis</td>
<td>BAL</td>
</tr>
</tbody>
</table>

ND : not detected, BAL : balance.

Table 2 Quantitative analysis of metallic pieces in Fig. 5(b) by EPMA and chemical analysis (copper base-plate).
came apart from the base-plate, the apparent cathodic current efficiency should deteriorate. Fine metallic particles were found in the solidified salt in fact. Moreover, although the base-plate should be negative enough to reduce Ti ion to metal, the deposits apart from the base-plate might react with ion in the bath and the apparent efficiency might become worse. The following reaction was considered to occur:

\[
\text{Ti} + n / (4-n)\text{Ti}^{n+} = 4 / (4-n)\text{Ti}^{2+} \quad (n=2 \text{ or } 3)
\]

Because Ca was detected in the copper base-plate, some amount of Ca should be electrodeposited. Under the condition of Ca metal deposition, metal fog of Ca was likely to occur. The metal fog should make the cathodic current efficiency worse directly. The foggy Ca metal should be oxidized on the anode, and CO gas generation might be hindered. The effective way to prevent the cathodic product from dissolving and suspending should be the formation of metal pool on the base-plate. This deduction agrees well with the experimental results that the formation of large metal pool was essential to higher current efficiency.

The other reason for the low current efficiency should be caused by electric arcs. Although the salt splash seemed to correspond to the generation of gas bubble, the violent splash which sprang over the vessel might be explained by normal gas generation. Since the violent salt splash was often observed with the smaller distance between the electrodes but seldom with the bigger distance between the electrodes, it might occur with the combination of gas generation and arc discharge as shown in Fig. 12. By the formation of electric arcs, the volume of gas bubble should expand explosively, and the salt around should be flicked out. Electric arc current did not contribute electrodeposition so that the cathodic current efficiency should get worse. Moreover, the explosion by electric arcs might flick out the electrodeposits from the base-plate, and the deposit pulled apart should cause the decrease in current efficiency as mentioned above.

It can be seen from these discussions that the formation of lager metal pool and the bigger distance between the electrodes were keys in this process. However, these were hardly compatible and the suitable condition could not be found in this work because the capacity of power supply was limited.

5.2 Heat balance of the process

The heat balance of the process must be considered carefully to form a large metal pool. The enthalpy change of reaction (3) was calculated at 1973 K as \( \Delta H = +710.6 \text{ kJ/mol} \). If the current induces the reaction perfectly, the necessary heat to induce reaction (3) is given by

\[
Q_{30} = \Delta H \cdot I / 4F
\]

where, \( I \) is current and \( F \) is Faraday constant. When, \( I = 1.5 \text{ kA} \), then, \( Q_{30} = 2.76 \text{ kJ/s} \).

The Joule heat generation in the salt can be roughly estimated in the alternative way.

\[
Q_{\text{salt}} = L_v E_{av}
\]

where, \( L_v \) and \( E_{av} \) are average current and average voltage. Using equation (8), \( Q_{\text{salt}} \) was estimated as c.a. 35 kJ/s.

The heat loss from molds was estimated by

\[
Q_{\text{loss}} = R_w C_p (T_o - T_i)
\]

where, \( R_w \) is the flow rate of cooling water, \( C_p \) is the heat capacity of water, \( T_o \) and \( T_i \) are temperature of water at the outlet and inlet, respectively. The heat loss was different run by run. On average, it was estimated as c.a. 20 kJ/s. Thus, c.a. 60 % of the Joule heat was lost through the molds by cooling water. Radiation heat loss from a bath surface was estimated as 10 % by Mitchell and Joshi. The total heat loss can be estimated as c.a. 25 k. The net heat which is \( Q_{\text{salt}} \) minus total heat loss was estimated as 10 kJ/s. Comparing this value with \( Q_{30} = 2.76 \text{ kJ/s} \), it can be seen that the present process is possible from the view point of heat balance.

The temperature distribution in the vessel should be a main factor of the formation of a metal pool, because it was shown that the sufficient heat is supplied overall. It was reported that the highest temperature in ordinary ESR operation was at the tip of

![Image of violent salt splash.](image-url)
consumable electrode. In the present work, since the base-plate was cooled by the water-cooled base-molds, its temperature should be lower than the graphite anode and the bath. The Peltier's heat for the reaction (1) should be investigated, too. Further study is necessary on the temperature distribution.

6 Conclusion

The direct electrowinning of liquid titanium from molten CaO-CaF₂-TiO₂ has been investigated with the aid of a small DC-ESR unit. The results were summarized as follow:

1) It was confirmed that Ti was electrodeposited by this process. Titanium was in the form of TiC at the operation when the distance between the electrodes was small. Pure Ti metal pieces were obtained at the operation when the distance between the electrodes was bigger.

2) The current efficiency for the reduction reached 18%. The formation of larger metal pool on the base-plate was essential to efficient electrolysis.

3) From the view point of heat balance, the sufficient heat was supplied by the Joule heating in the bath.

It was concluded from these that the present process is possible in principle. But it should be necessary for better operation to form a larger metal pool and to keep a bigger distance between the electrodes simultaneously.

References