THE POSSIBILITY OF ELECTRO-WINNING OF LIQUID TITANIUM USING ESR APPARATUS

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ABSTRACT

Solid electro-deposit from molten salts is likely to be dendritic, which restricts the application of molten salt electrolysis to smelting of refractory metals. If the electro-deposit can be obtained in liquid state, the above problem is solved. On the other hand, the metal pool in water-cooled mold is obtained in "Electro Slag Remelting (ESR)" operation which is one of steel refining processes. A small scale ESR unit of 110 mm inner diameter was operated in DC reverse polarity mode, where a graphite rod was used as anode and a steel plate was used as cathode. The used slag was $CaO-CaF_2-TiO_2$ mixture. The current was about 1,500 A. In a certain experimental condition, some amount of titanium was electro-deposited in the metal pool. But most of it was in the form of TiC. The current efficiency for the reduction was as low as 1.5 %. From the view point of heat balance, the sufficient heat was supplied by the Joule heating in molten slag phase. It can be seen from these that the present process is possible in principle. But, further study is necessary to obtain the optimum electrolysis condition.

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 electro-deposits from molten salt are likely to be dendritic, which necessitates such succeeding process as vacuum arc remelting. If the electro-deposit can be obtained in liquid state, the above problem is solved. In general, it is considered very difficult to hold liquid titanium because of high reactivity. One possibility is to use self-lining vessel. In the "Electro Slag Remelting (ESR)" operation which is used some times in steelmaking practice, the metal pool is maintained in a water cooled mold. In the process, a consumable electrode is melted by Joule heat which is generated by the high current in molten slag. The metal droplets are collect in the metal pool and then solidified unidirectionally. Although the process is by alternating current, direct current can be used. In the case, electrolytic effects can be expected. Namely, titanium can be electro-deposited in metal pool cathode, if a certain condition is satisfied. In the present work, the possibility of electro-winning of liquid titanium has been examined with the aid of small scale ESR unit.

2. PRINCIPLE

The principle of the process is schematically shown in Fig. 1. If the ESR apparatus is operated in DC reverse polarity mode, the cathodic reaction occurs at the metal pool. Since the process should proceed at as high temperature as over 1,600℃, the titanium source must be TiO_2, rather than chlorides. The cathodic reaction is expected to be

$$Ti^{4+} + 4e = Ti \qquad .....(1)$$

A graphite rod is used as an anode, just like as in aluminum electrolysis. The anodic reaction is expected to be

$$O^{2-} + C = CO + 2e \qquad .....(2)$$

Then, the overall reaction is expected to be

$$Ti^{4+} + 2O^{2-} + 2C = Ti + 2CO \qquad .....(3)$$

or

$$TiO_2 + 2C = Ti + 2CO \qquad .....(4)$$

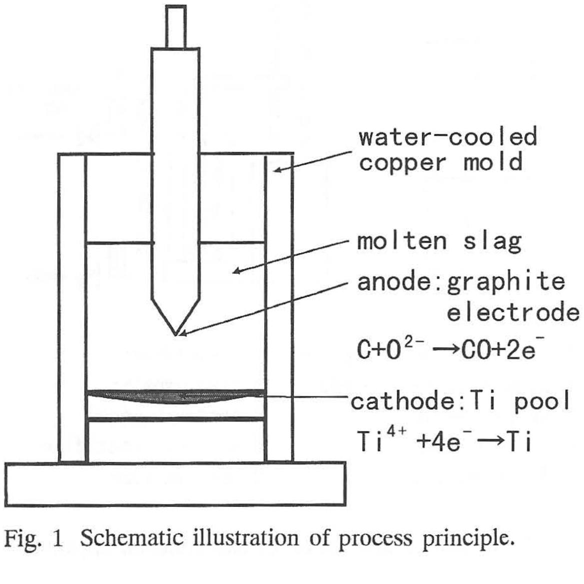


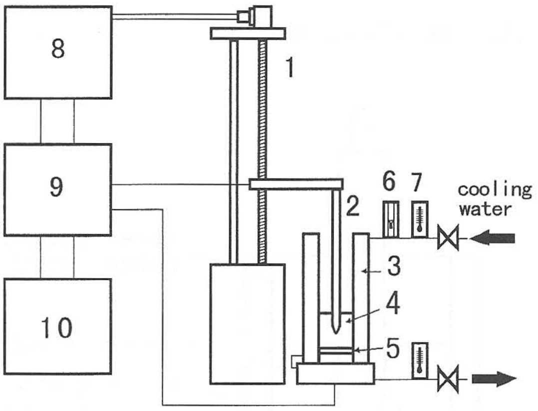
Fig. 1 Schematic illustration of process principle.

Therefore, the main component of slag should be more stable than TiO_2. In the present work, $CaO-CaF_2$ was selected as the supporting slag system.

3. EXPERIMENTS

The experimental apparatus is schematically shown in Fig. 2. The mold and base were made of copper and cooled by water stream. The inner diameter of mold was 110 mm ϕ and the height was 400 mm. The water cooling system was equipped with a flow meter and two thermo-meters at the inlet and outlet of mold. The heat loss from mold and base can be estimated from water flow rate and the temperature change. A graphite rod was used as anode. The diameter of rod was 40, 50 or 60 mm ϕ and the height was c.a. 1 m. The rod was driven up and down at a constant speed with the aid of electrode driving unit. The D.C. current was supplied through silicon rectifier. The maximum capacity of power source was 162 kVA. The maximum D.C. current and voltage were 2.5 kA and 50 V. The electric power unit was equipped with voltage and current recorders and current integrator which showed the total supplied electricity.

A thin iron plate of 110 mm ϕ and 20 mm thickness was put on the base. The graphite electrode with sharpened tip was driven down so that the tip should just touch the iron plate. About one kilogram of the pre-melted slag powder was supplied to the mold. Staring the process, the current of about 1 kA was supplied instantaneously. Then, the electric arc was generated between the electrode tip and base plate. By the arc heating, the surrounding slag powder melted down gradually. After melt down of the primary slag powder, the slag powder was supplemented. The total amount of slag was c.a. 3 kg. As the process proceeded, TiO_2 component should be consumed. In order to compensated the loss, small pellets of TiO_2 were supplied to the slag.



1:electrode driving unit	6:flow meter
2:graphite electrode	7:thermometer
3:copper mold	8:control panel
4:molten slag	9:silicon rectifier
5:Ti or Fe plate	10:pen recoder

Fig. 2 Schematic illustration of experimental apparatus.

After stopping the power supply, the electrode was pulled up. The weight change of base plate and electrode was measured. The hot spot of base plate was cut vertically. The cross section was polished with water proof abrasive papers down to # 1200, and then examined by SEM, EPMA and XRD.

4. RESULTS AND DISCUSSION

4.1 Process document

Figure 3 shows an example of change in current and voltage with time, where TiO_2 content in the slag was 5 mass %. At the beginning, the current did not vibrate so much. In this period of time, electric arc was generated exclusively between the base plate and graphite electrode. But it vibrated very much after 14 min in which the current flew through molten slag phase and CO bubbles were formed at the slag-graphite electrode interface. During the current vibration, the molten slag splashed very much. The current vibration was due to coverage and detachment of the bubbles. This CO bubble formation suggests that the electrochemical process occurred through molten slag phase and both electro-deposition of titanium according to equation (1) and CO formation according to equation (2) were expected to occur. The voltage vibrated all the time, even in the time period of arc generation. But the amplitude of vibration was larger in CO formation period. The voltage could be changed to some extent by adjusting the distance between base plate and graphite electrode. Figure 4 shows another example of change in current and voltage with time, where TiO_2 content in the slag was 20

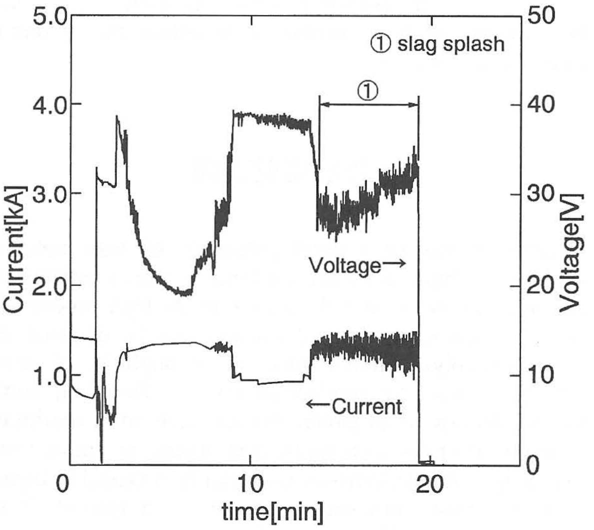


Fig. 3 An example of change in current and voltage with time: 5 mass % TiO_2.

mass %. In this run, CO formation was violent and lasted longer. The average current and amplitude of its vibration were larger with higher TiO_2 content. The voltage vibration was also more violent with higher TiO_2 content.

The morphology of base plate after the process is shown in Photo. 1. Only central part of the plate was melted. The reaction product seemed to pile up at the center. The weight gain of plate was so small as a few grams. The solidified slag was black, although the color was white initially.

4.2 Examination of electrodeposit

The SEM image and Ti mapping of EPMA of the cross sections are shown in Photo. 2, where the TiO_2 content in the slag was 5 and 10 mass %. Small rectangular particles were distributed throughout the melted part. The particles contained Ti and C. When the TiO_2 content in the slag was 20 mass %, larger particles (A) were observed as

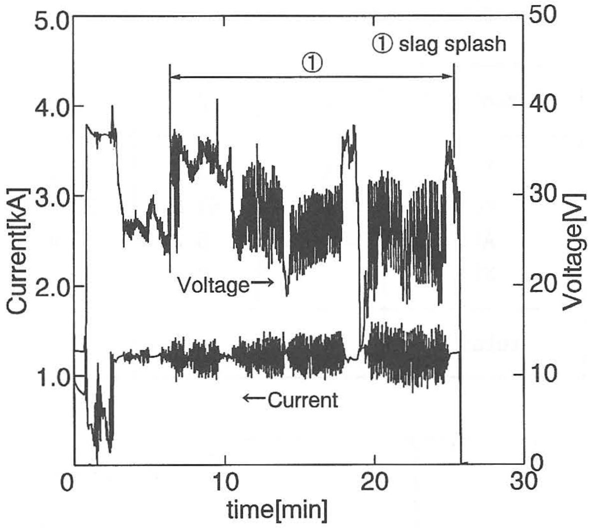


Fig. 4 An example of change in current and voltage with time: 20 mass % TiO_2.

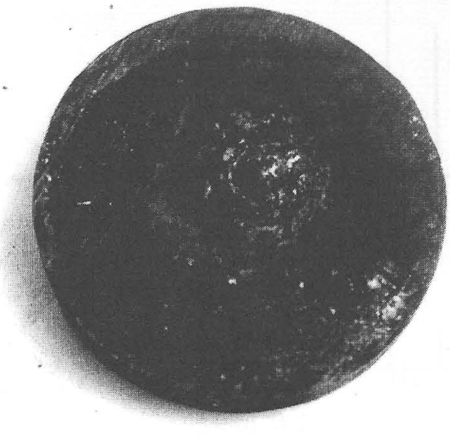


Photo. 1 Feature of the electrodepot on base plate.

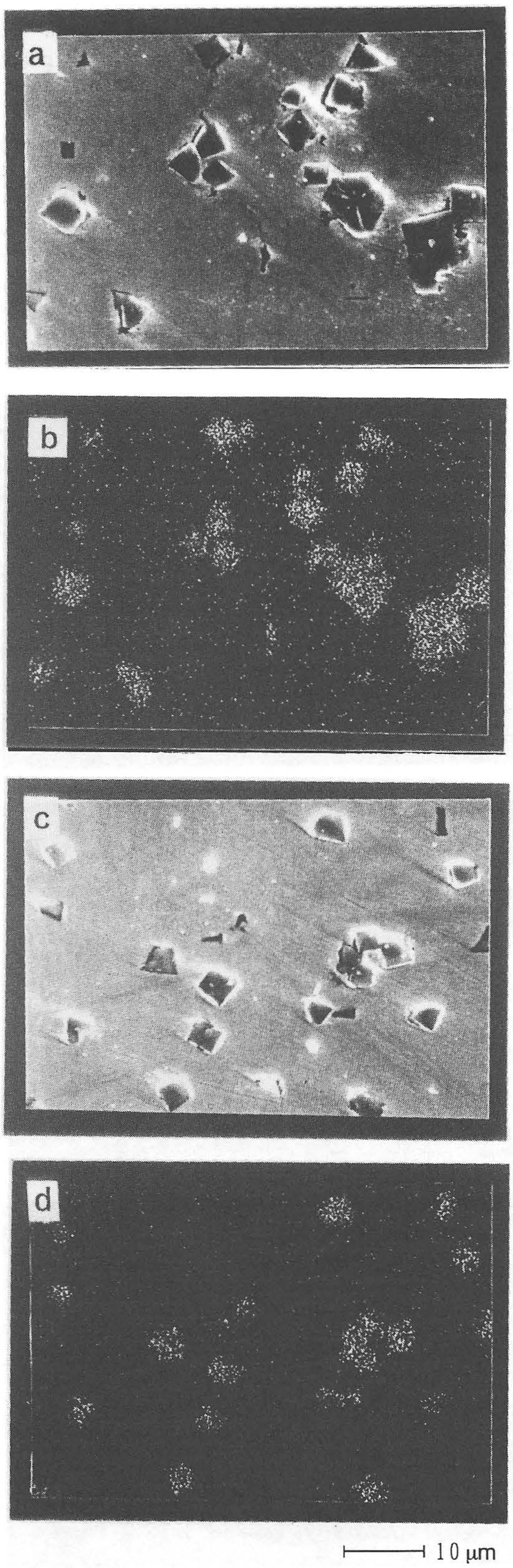


Photo. 2 Microstructure of the cross section of base plate: a; SEM image (5 mass % TiO_2), b; Ti mapping (5 mass % TiO_2), c; SEM image (10 mass % TiO_2), d; Ti mapping (10 mass % TiO_2).

shown in Photo. 3. They were round shaped. They contained much Ti but not Fe. The surrounding phase (B) contained both Ti and Fe, while the phase (C) did not contain so much Ti.

The quantitative analysis of phase (A), (B) and (C) are shown in Table 1. By this EPMA equipment, carbon could not be analyzed. Assuming mass % of carbon as the residual, the carbon content in phase (A), (B) and (C) are 24.2, 3.4 and 2.5 mass %, respectively. The atomic ratio of Ti/C in phase (A) was estimated as 1/1.3. Thus, the phase (A) can be seen as TiC. From this conclusion, particles in Photo. 2 can be considered as TiC. The atomic ratio of Ti/Fe in phase (B) was estimated as 0.83/2. Thus, the phase (B) can be seen as $TiFe_2$ intermetallic compound[1]. The phase (C) can be seen as the Fe phase containing small amount of Ti.

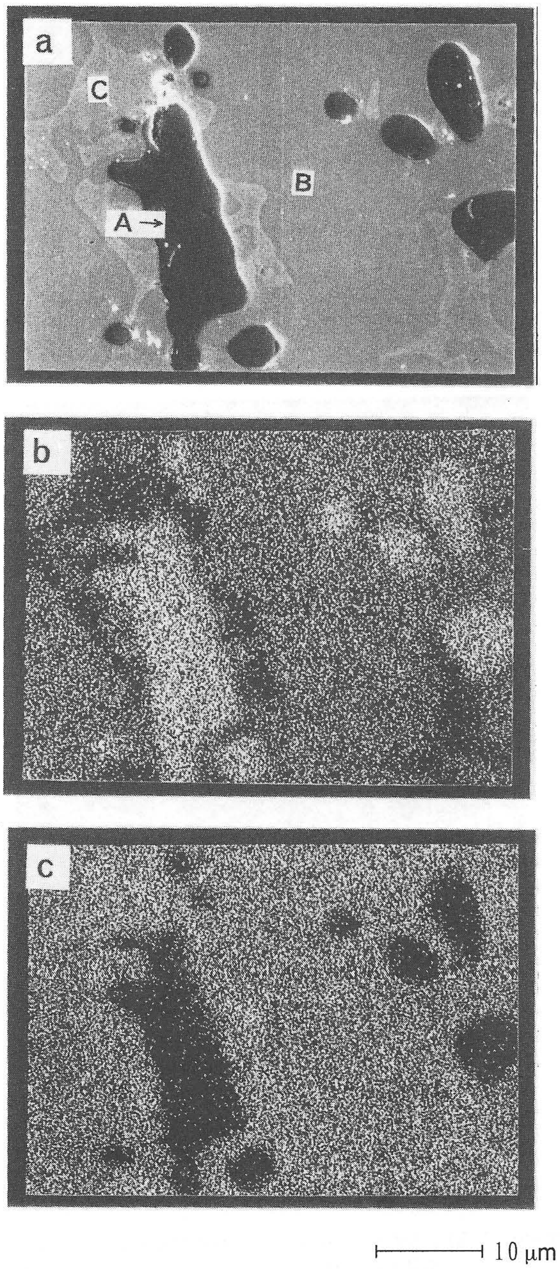


Photo. 3 Microstructure of the cross section of base plate: a; SEM image, b; Ti mapping, c; Fe mapping.

Figure 5 shows the result of XRD analysis of the deposit. The diffraction peaks corresponding to TiC and Fe were detected. Thus, the existence of TiC in the deposit was confirmed.

4.3 Examination of Solidified Slag

The solidified slag was black, which might suggest that the slag contained suspended fine particles of graphite. The fine particles of bright color were also found in the solidified slag. Figure 6 shows the result of XRD analysis of the slag. The added TiO_2 was detected in the form of $CaTiO_3$. $Ca(OH)_2$ is considered as hydrated CaO. TiC was also detected. Thus, the bright fine particles are seen to be TiC.

Table I Quantitative analysis of microstructure in Photo. 3 by EPMA.

element(wt%)	A	B	C
Ti	70.7	25.0	9.6
Fe	5.1	69.8	87.0
Al		0.2	0.4
Si		0.4	1.7
total	75.8	96.6	97.5

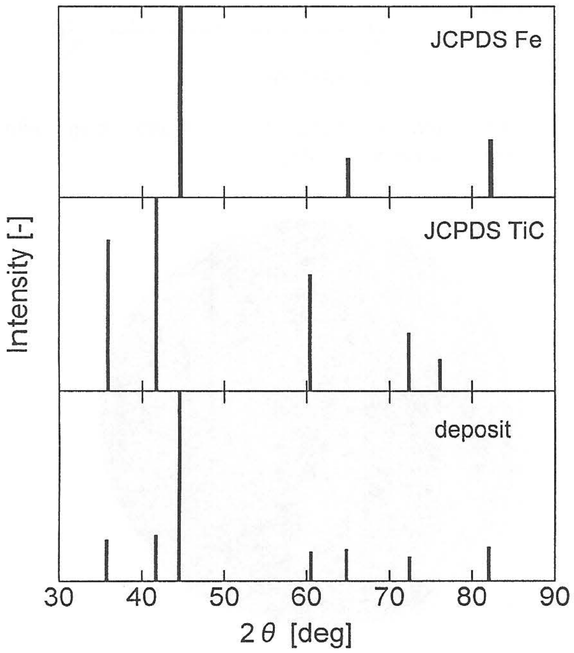


Fig. 5 Result of XRD analysis of the electrodeposit.

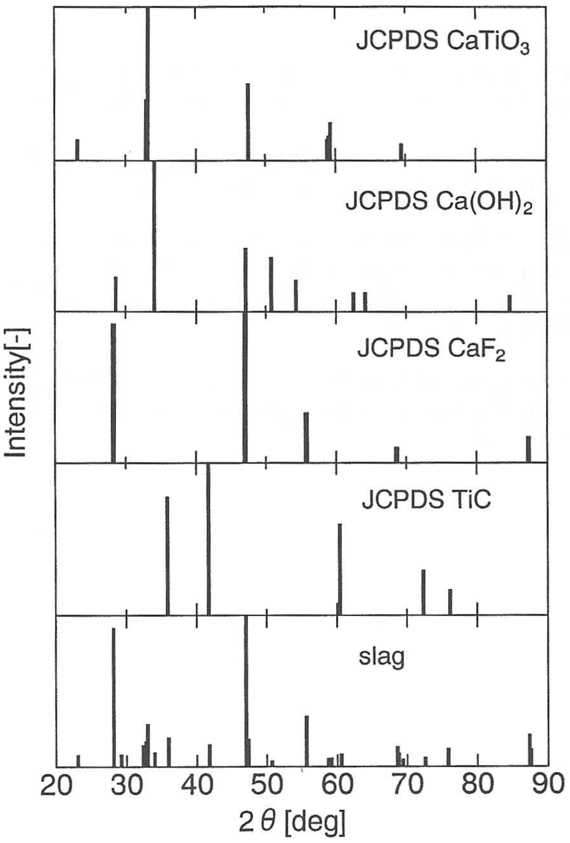


Fig. 6 Result of XRD analysis of the solidified slag.

4.4 Current efficiency

The current efficiency for cathodic reaction is given by

$$\eta_{CATH} = \{4FW_{Ti}/(M_{Ti}Q)\} \times 100\ (\%) \qquad .....(5)$$

where, F is Faraday constant, W_{Ti} is the weight gain of base plate, M_{Ti} is the atomic weight of Ti and Q is the total electricity supplied which was given by current integrator. Table 2 shows the current efficiency for cathodic reaction. The efficiency was very low. The maximum efficiency was 1.57 %.

The current efficiency for anodic reaction is given by

$$\eta_{ANO} = \{2FW_C/(M_CQ)\} \times 100\ (\%) \qquad .....(6)$$

where, W_C and M_C are weight loss of the graphite electrode and the atomic weight of carbon. The accuracy of weight change measurement was not so good, because the relative change was small. On average, the efficiency was 47 %. The efficiency for anodic reaction was apparently higher than that for cathodic reaction. But, the weight loss of graphite electrode included the loss by air oxidation. Thus, the efficiency for both reactions was considered very small. The possibility of reasons for the low efficiency is as follows.

Table II Current efficiency for cathodic reaction.

Run No.	integral current (Ah)	weight gain (g)	current efficiency (%)
5	710	3.5	1.53
15	640	2.5	1.40
16	680	1.7	0.54
18	690	0.6	0.20
19	690	0.4	0.12
22	300	2.0	1.50
25	80	0.2	0.50
28	380	2.0	1.16
29	570	4.0	1.57

(1) current by arc
(2) current leak to mold
(3) metal fog formation
(4) change in electric property of molten slag

If there was vacant space between base plate and graphite electrode, the current flew by arc. In the case, no electrochemical process can be expected. Such phenomenon occurred at the beginning. But it did not last for so long time. The reduction of efficiency by arc can be estimated as less than 20 %. In the normal operation, solid skin of a few millimeter thickness is formed on mold surface. The solid skin is considered as electric insulator. Thus, current leak to mold is hard to occur. Occasionally, it happens that arc spots are observed on mold surface. Then, the current should leak to the mold. But no arc spot was observed in the present experiment. The metal fog formation was likely to occur. If it occurred, the titanium obtained by cathodic reaction of equation (1) did not come into the electro-deposit. Since TiC was observed in solidified slag, this possibility cannot be denied. The metal fog might migrate to the graphite electrode at which the reverse reaction of equation (1) might occur. In the case, the overall reaction of equation (3) or (4) does not occur, although the current flows. But the quantitative estimation of the loss for metal fog formation was impossible. The color of the slag was black because of fine graphite suspension. But this suspension does not change electrical property of the slag in general. The electronic conduction of molten $CaO-CaF_2$ slag by the addition of TiO_2 has not been reported. The electrical conductivity of this slag system should be measured in future.

4.5 Heat balance of the process

The enthalpy change of equation (4) was calculated at 1973 K as $\Delta H = +710.6$ kJ/mol[2]. If the current induces the reaction perfectly, the reaction rate is expressed by the current as

$$v = I/4F \qquad .....(7)$$

where, I is current and F is Faraday constant. Thus, the necessary heat to induce reaction (4) is given by

$$Q_{(4)} = \varDelta Hv \quad .....(8)$$

When, I = 1.5 kA, then, $Q_{(4)}$ = 2.76 kJ/s.

The Joule heat generation in the slag is approximately given by

$$Q_{SLAG} = I^2(1/\sigma)(L/S) \quad .....(9)$$

where, σ is the specific electrical conductivity, L is the distance between base plate and graphite electrode and S is the cross section of molten slag phase. The value of σ is taken from literature as 6.2 Ω/cm^3. Taking I = 1.5 kA, L = 4 cm and S = 23.8 cm^2, Q_{SLAG} was estimated as 35 kJ/s. Q_{SLAG} can be roughly estimated in the alternative way.

$$Q_{SLAG} = I_{av}E_{av} \quad ....(10)$$

where, I_{av} and E_{av} are average current ant average voltage. Using equation (10), Q_{SLAG} was also estimated as c.a. 35 kJ/s.

The heat loss from mold and base was estimated by

$$Q_{LOSSW} = R_W Cp(T_O - T_I) \quad ....(11)$$

where, R_W is the flow rate of cooling water, Cp is the heat capacity of water, T_O and T_I are temperature of water at the outlet and inlet. 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 mold and base by cooling water. Radiation heat loss from ESR slag surface was estimated as 10 % by Mitchell and Joshi[4]. The total heat loss can be estimated as c.a. 25 kJ/s. The net heat which is Q_{SLAG} minus total heat loss was estimated as 10 kJ/s. Comparing this value with $Q_{(4)}$ = 2.76 kJ/s, it can be seen that the present process is possible from the view point of heat balance.

5. CONCLUSION

The direct electro-winning of titanium from molten $CaO-CaF_2-TiO_2$ has been tried with the aid of small ESR unit. The current was supplied in D.C. reverse polarity mode, where the cathodic reduction of titanium was expected in the metal pool on the base plate. Some amount of titanium was found in iron base plate. But most of it was in the form of TiC. The current efficiency for the reduction was as low as 1.5 %. From the view point of heat balance, the sufficient heat was supplied by the Joule heating in molten slag phase. It can be seen from these that the present process is possible in principle. But, further study is necessary to obtain the optimum electrolysis condition.

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