Contactless Electrochemical Reduction of Titanium (II) Chloride by Aluminum

T. UDA, T.H. OKABE, Y. WASEDA, and K.T. JACOB

Because of the strong affinity between aluminum and titanium, it has not been possible to produce pure titanium by direct aluminothermic reduction of titanium chlorides. Described in this article is a new process for contactless reduction of titanium dichloride by aluminum in which titanium dichloride and the reductant (aluminum or aluminum alloy) were physically separated, but electrochemically connected through molten NaCl and an external circuit. Titanium dichloride was spontaneously reduced to metal by a cathodic reaction with the simultaneous discharge of chlorine ions into the melt. At the anode, metal aluminum was oxidized to form aluminum chloride dissolved in the molten salt. The electrons were transferred between the electrodes through the external circuit. The concentration of aluminum in titanium produced at 1223 and 1273 K varied from values below the detection limit of the X-ray fluorescence analysis (0.01 mass pct) to 4.5 mass pct. The average contamination was 0.76 mass pct Al. When an aluminum-nickel alloy was used as the reductant, nickel was not detected in the titanium obtained by reduction. This observation suggests that aluminum scrap may be used as a cheap reductant in this contactless electrochemical process.

I. INTRODUCTION

TITANIUM and its alloys have attractive mechanical properties such as strength-to-weight and rigidity-to-weight ratios and excellent corrosion resistance. Nevertheless, the application of titanium alloys in use is limited compared to other structural materials (*e.g.*, steels and aluminum alloys) because of the high cost of production. Titanium is produced by metallothermic reduction of $TiCl_4$ by magnesium (Kroll process).[1] The process is batch type and labor intensive and uses an expensive reductant, magnesium.

Recently, Sadoway and Okabe[2,3] have demonstrated the importance of electrochemical reactions in the sodiothermic reduction of K_2TaF_7. They demonstrated that the reduction can proceed without direct physical contact between reactants and euphemistically characterized it as electronically mediated reaction (EMR). Following this, studies of EMR in the metallothermic reduction of titanium chloride were carried out by our group.[4,5,6] The importance of electrochemical reactions during magnesiothermic reduction of titanium chlorides was experimentally demonstrated, and some applications were proposed. These studies indicate that the location of titanium deposition can be controlled using long-range EMR (LR-EMR).[7] Titanium powder can also be produced by magnesiothermic reduction using a reaction mediator (*e.g.*, Dy^{2+}/Dy^{3+}) in the molten salt.[8,9,10] In principle, short-range EMR (SR-EMR) can be used to design a continuous process for the production of titanium powder.

Reported in this article is an exploratory study of the use of aluminum, instead of magnesium, as a reductant for titanium chloride. Aluminum and aluminum scrap are lower priced reductants compared to magnesium. However, when attempts were made in the past to use aluminum as a reductant, only titanium alloys containing a large amount of aluminum were obtained because of the strong affinity between the two metals.[11] An attempt was made in this study to minimize aluminum contamination of titanium by avoiding physical contact between reactants; an electrical circuit links anodic and cathodic reactions at different locations and provides a path for rapid electron transfer.

II. BACKGROUND

A. *Thermodynamics of the System Ti-Al-Cl*

The results of earlier studies on the aluminothermic reduction of titanium compounds reported in the literature are summarized in Table I.[12–16] Pure titanium was not obtained during the conventional aluminothermic reduction; aluminum-titanium alloys and intermetallics containing a significant amount of aluminum were formed. Maeda and coworkers[12,17] and Kamlet[14] tried to remove aluminum from the alloys as gaseous aluminum suboxides (Al_2O) or aluminum subhalides (AlCl) at high temperatures.

Variation of the chlorine chemical potentials with the temperature are shown in Figure 1 for the systems Ti-Cl and Al-Cl. The thermodynamic data on the binary systems Ti-Cl and Al-Cl used for constructing the diagram are taken from Knacke *et al.*,[18] and representative values at 1273 K are listed in Table II. The presence of all species reported in the system Al-Cl have been taken into consideration in computing the chlorine chemical potential displayed in Figure 1. The aluminum chloride gas in equilibrium with aluminum metal is mainly a mixture of $AlCl_3$ and $(AlCl_3)_2$, with the dimer predominating at lower temperature. Similarly, the simultaneous presence of different species ($TiCl_2$, $TiCl_3$, $(TiCl_3)_2$, and $TiCl_4$) have been taken into account in determining the stability domain of titanium chloride gas phase. The lines for Ti (s)/$TiCl_2$ (s) and Al (s, l)/$AlCl_x$ (g) cross at 988 K when activities of the metals are unity, and

Table I. Summary of the Representative Results of Aluminothermic Reduction of Titanium Compounds Reported in the Literature

Feed	Product	Name	Year	Comments
K_2TiF_6	Ti-30 mass pct Al	Kamlet[14]	1958	Al removed as aluminum subhalide
TiO_2	$TiAl_3$	Fletcher[13]	1979	—
TiO_2	Al-5 mass pct Ti	Zhuxian et al.[16]	1988	using cryolite melt containing alumina
TiO_2	Ti-33 mass pct Al-1 mass pct O	Yahata et al.[12]	1990	Al and O removed as Al_2O by EB melting
$TiCl_4$	$TiAl_3$ in Al	Kumagai et al.[15]	1996	using molten chloride
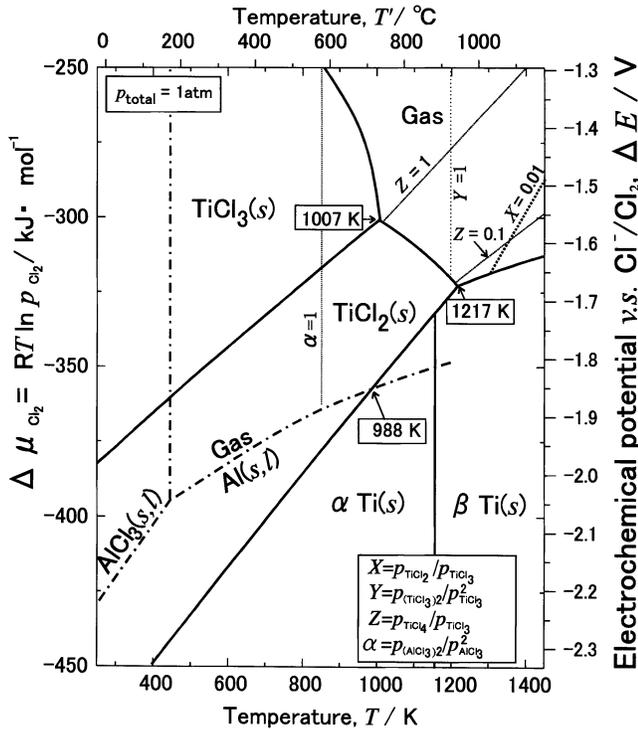
Fig. 1—Variation of the chlorine chemical potential of the systems Ti-Cl and Al-Cl with temperature. Solid and chain lines represent the phase boundary for the systems Ti-Cl and Al-Cl, respectively. The dotted lines represent constant ratio of the specified gaseous species. The gas species considered are $TiCl_4$, $TiCl_3$, $(TiCl_3)_2$, and $TiCl_2$ for the system Ti-Cl, and AlCl, $AlCl_2$, $AlCl_3$, and $(AlCl_3)_2$ for the system Al-Cl.

Table II. The Standard Gibbs Energy of Formation, $\Delta_f G°$, of Chlorides of Titanium and Aluminum at 1273 K[18]

Reactions	$\Delta_f G°/kJ \cdot mol \cdot Cl_2^{-1}$
$2Ti (s) + Cl_2 (g) = 2TiCl (g)$	44.6
$Ti (s) + Cl_2 (g) = TiCl_2 (s)$	−314.7
$Ti (s) + Cl_2 (g) = TiCl_2 (g)$	−265.2
$2/3Ti (s) + Cl_2 (g) = 2/3TiCl_3 (s)$	−300.9
$2/3Ti (s) + Cl_2 (g) = 1/3(TiCl_3)_2 (g)$	−314.3
$2/3Ti (s) + Cl_2 (g) = 2/3TiCl_3 (g)$	−317.8
$1/2Ti (s) + Cl_2 (g) = 1/2TiCl_4 (g)$	−305.1
$2Al (l) + Cl_2 (g) = 2AlCl (g)$	−318.5
$Al (l) + Cl_2 (g) = AlCl_2 (g)$	−327.7
$2/3Al (l) + Cl_2 (g) = 1/3(AlCl_3)_2 (g)$	−337.0
$2/3Al (l) + Cl_2 (g) = 2/3AlCl_3 (g)$	−353.2

this indicates that it is thermodynamically possible to reduce titanium(II) chloride to titanium by aluminum at high temperature as shown in Figure 1.
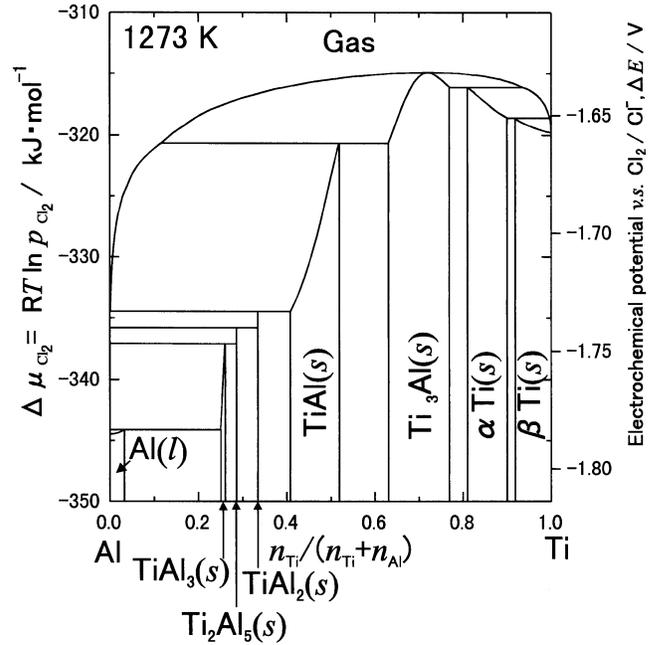
Fig. 2—Chlorine chemical potential diagram for the system Ti-Al-Cl at 1273 K.

Table III. The Standard Gibbs Energy of Formation, $\Delta_f G°$, of Intermetallic Compounds in the System Ti-Al at 1273 K[11]

Phases	Mole Fraction of Al, x_{Al}	$\Delta_f G°/kJ \cdot mol \cdot atoms^{-1}$
Ti_3Al (s)	0.25	−21.9
TiAl (s)	0.50	−28.0
$TiAl_2$ (s)	0.66	−24.6
Ti_2Al_5 (s)	0.71	−22.9
$TiAl_3$ (s)	0.75	−21.3

The chlorine chemical potential diagram of the system of Ti-Al-Cl at 1273 K computed from thermodynamic data is shown in Figure 2. For the binary system of Ti-Al, the data suggested by Zhang et al.[11] were used. Representative values are summarized in Table III. Figure 2 indicates that titanium produced by the reduction of titanium chloride will react with aluminum. Even if an excess of reductant (aluminum) is used, it is thermodynamically difficult to obtain a product containing more titanium than Ti_3Al at 1273 K. A similar situation is encountered at other temperatures. Therefore, it is quite difficult to obtain pure titanium by the conventional metallothermic reduction based on direct physical contact between the feed and the reductant.
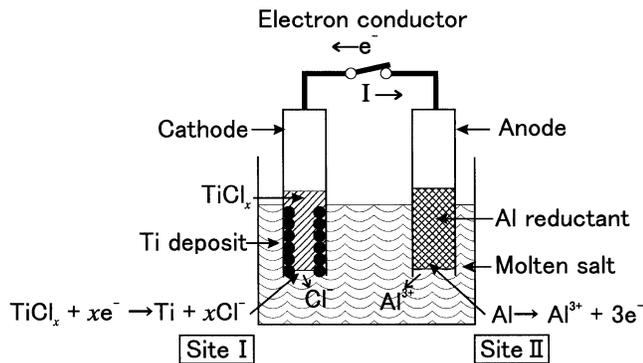
Fig. 3—Concept of the reduction of titanium chloride by aluminum utilizing LR-EMR. Titanium chloride and the reductant aluminum are physically separated by the molten salt. An external circuit permits the flow of electrons from the anode to the cathode.

B. *Long-Range EMR*

The concept of LR-EMR of titanium reduction has been fully discussed earlier.[6] Only the essential details regarding its application to contactless aluminothermic reduction of $TiCl_4$ are discussed here. The overall metallothermic reduction reaction is split into two electrochemical steps, which can occur at separate locations. In LR-EMR, the electrons are transported from the anodic to the cathodic site through an external metallic conductor. In SR-EMR, the electrons are transported through an electronically conducting molten salt.[3,6] The concept of the LR-EMR is schematically illustrated in Figure 3. Titanium chloride and the reductant aluminum are fed into isolated locations. The following reactions can occur at each site, without physical contact between the reactants.

$$\text{Site I: } TiCl_4 + e^- \rightarrow TiCl_3 + Cl^- \qquad [1]$$

$$\text{Site I: } TiCl_3 + e^- \rightarrow TiCl_2 + Cl^- \qquad [2]$$

$$\text{Site I: } TiCl_2 + 2e^- \rightarrow Ti\ (s) + 2Cl^- \qquad [3]$$

$$\text{Site II: } Al + 3Cl^- \rightarrow AlCl_3 + 3e^- \qquad [4]$$

where titanium reduction site and reductant aluminum site are defined as sites I and II, respectively. In this study, experiments were mainly conducted with titanium dichloride as the feed material. In principle, the scheme outlined previously allows production of titanium without serious aluminum contamination at site I. Since the lines for the chemical potential of chlorine for Ti (s)/$TiCl_2$ (s) and Al (l)/$AlCl_x$ (g) equilibria cross at 988 K in Figure 1, reduction experiments using LR-EMR were conducted at 1223 and 1273 K. The driving force for the reduction reactions increases with temperature from 988 to 1217 K and, thereafter, remains approximately constant. However, the partial pressure of $TiCl_3$ gas, which is the dominant gas species in equilibrium with Ti (s) and $TiCl_2$ (s), increases with temperature and attains a pressure of 0.101 MPa (1 atm) at 1217 K. Considering uncertainties in thermodynamic data, the optimum temperature for reduction of $TiCl_2$ by aluminum is estimated to fall in the range 1100 to 1300 K. The dominant gas species equilibrated with metal titanium is $TiCl_3$ (g) at 1273 K. The activity of $TiCl_2$ (s) corresponding to the equilibrium between $TiCl_3$ (g) and metal titanium is 0.61 at 1273 K. In the molten salt, the dominant titanium ion in equilibrium with metal titanium is expected to be Ti^{2+}.
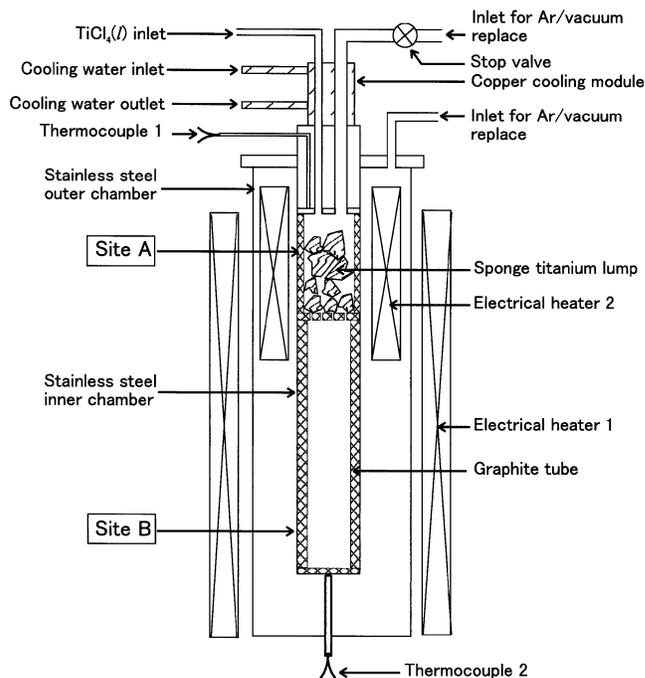
Fig. 4—Schematic diagram of the apparatus for the synthesis of $TiCl_2$. Sites A and B were maintained at about 1300 K and at about 1050 K.

III. EXPERIMENTAL

A. *Materials*

In this study, $TiCl_2$ (s) and $TiCl_4$ (l) were used as feed materials. $TiCl_2$ (s) was synthesized by the reaction between $TiCl_4$ (g) and Ti (s) at 1300 K, using the apparatus shown in Figure 4. Liquid $TiCl_4$ at room temperature was fed into a graphite tube containing sponge titanium at about 1300 K (site A). $TiCl_2$ was obtained from the gas phase as a condensate about 1050 K (site B) inside the graphite reaction tube. $TiCl_2$ contained 59.0 mass pct Cl, 40.9 mass pct Ti, 0.12 mass pct Fe, and 0.02 mass pct Cr. The mole ratio of chlorine to titanium was 1.95. When $TiCl_2$ was dissolved in ethanol, no insoluble residue was observed. Thus, the contamination of $TiCl_2$ (s) by metallic titanium and iron was not significant. NaCl of 99 pct purity obtained from Wako Pure Chemical Industries, Osaka was vacuum dried at 473 K for 2 weeks before use.

B. *Reduction of $TiCl_2$*

The apparatus used for the reduction of $TiCl_2$ by aluminum is shown in Figure 5. A stainless steel crucible (i.d. approximately 75 mm) filled with molten NaCl was placed in a gas-tight stainless steel container. An iron feed tube (i.d. 14 mm) with a closed end, containing $TiCl_2$ (s), was suspended in the center of the crucible above the molten salt. A slit (width 13 mm, length 50 mm) was provided on the iron feed tube to facilitate the formation of a molten salt bridge to $TiCl_2$ (s) when the feed tube is lowered. The $TiCl_2$ in the feed tube was covered with NaCl (thickness 10 mm). The feed tube was held above the molten salt in the crucible until the temperature reached 1223 or 1273 K. A stainless steel current lead, 9 mm in diameter, was welded to the crucible. The current in the external circuit was measured
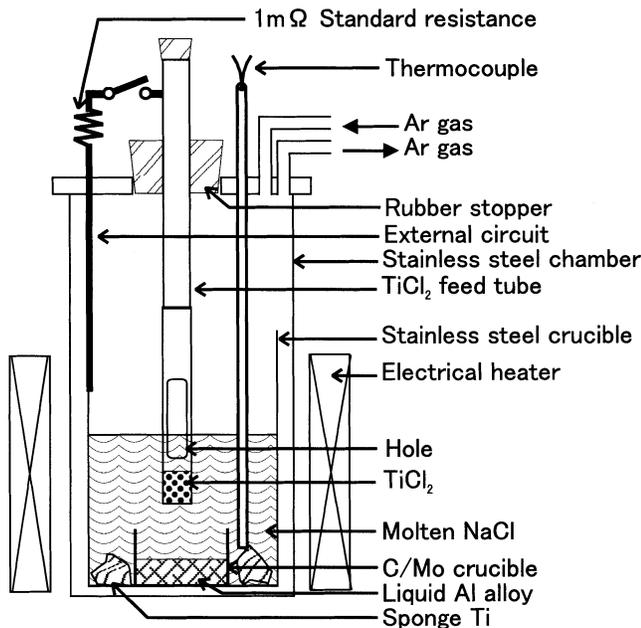
Fig. 5—Experimental setup for the aluminothermic reduction of $TiCl_2$.

Labels in figure:
1 mΩ Standard resistance
Thermocouple
Ar gas
Ar gas
Rubber stopper
External circuit
Stainless steel chamber
$TiCl_2$ feed tube
Stainless steel crucible
Electrical heater
Hole
$TiCl_2$
Molten NaCl
C/Mo crucible
Liquid Al alloy
Sponge Ti

as an equivalent potential drop across a standard resistance (1 mΩ). For the measurement of the open circuit potential between the feed tube and the aluminum holder, the external current was interrupted periodically. The temperature of the molten salt, the argon flow rate, and potential difference across the standard resistance were continuously measured by using a high-resolution digital multimeter equipped with ten channel scanning inputs.

The reductant aluminum or aluminum alloy, held in containers made of graphite, molybdenum, or copper, was placed at the bottom of the crucible containing molten salt. Because of the strong affinity between aluminum and iron, a steel container for the reductant could not be used. Even when a separate graphite or molybdenum container was used for aluminum, there was significant attack of the stainless steel crucible by aluminum that diffused through the molten salt on prolonged exposure. Al-Ni alloy was employed as the reductant in some experiments. Nickel in the alloy acted as a marker for the physical movement of the reductant. For example, if there was direct contact between the reductant and the titanium chloride, the titanium metal would have been contaminated by nickel. The amount of aluminum used was more than the stoichiometric requirement for the reduction of $TiCl_2$. The removal of dissolved oxygen from the molten salt is a necessary prerequisite for obtaining pure titanium metal. Since the equilibrium concentration of oxygen in titanium at the oxygen potential established by Al/Al_2O_3 equilibrium is about 13 mass pct[18–21] at 1273 K, sponge titanium was placed at the bottom of the crucible containing the molten salt for sacrificial gettering of oxygen. However, aluminum from the container diffused through the molten salt and reacted with the titanium sponge during experiment. The sponge titanium, therefore, served as a local getter both for dissolved oxygen and aluminum in the molten salt. In experiment A4, sponge titanium was placed in the aluminum holder.

Sodium chloride was used as molten salt because of its relatively low vapor pressure (0.001 MPa (0.01 atm)[18]),

good electrical conductivity (4 S/cm[22]), and relatively high melting point (1074 K[18]). The high melting point is useful for preventing the reversal of Reactions [3] and [4] during cooling. The experimental conditions are summarized in Table IV.

A feed tube containing $TiCl_2$ (s) was immersed into molten salt when the temperature reached the set value of either 1223 or 1273 K. At the end of each experiment, the feed tube was pulled up above the molten salt, and the stainless steel container was cooled to below 350 K. The deposit in the feed tube and the molten salt in the crucible were mechanically recovered. The deposit was repeatedly rinsed with cold or hot water. Quantitative analysis of the deposit was conducted by X-ray fluorescence analysis (XRF) or electron probe microanalysis (EPMA) for all elements in the periodic table heavier than oxygen. The phases present in the deposit were identified by X-ray powder diffraction analysis (XRD), and its morphology was observed by a scanning electron microscope (SEM). Analysis for titanium and aluminum in the molten salt was done by inductively coupled plasma–atomic emission spectrometry (ICP–AES).

C. Reduction of $TiCl_4$

A few experiments were conducted to test the reduction of $TiCl_4$ (l) as the charge instead of $TiCl_2$ (s), using the apparatus shown in Figure 5, but with minor alteration in the method of charging titanium chloride into the reduction location. The feed tube for $TiCl_4$ gas made of iron (i.d. 14 mm) was provided with two holes (diameter 10 mm), which were immersed in the molten salt. As $TiCl_4$ is liquid at room temperature, it was pumped into the iron feed tube through a TEFLON* tube (i.d. 1 mm) by a microperistaltic pump at

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*TEFLON is a trademark of E.I. DuPont de Nemours & Co., Inc., Wilmington, DE.

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a rate of 2 to 4 mg/s. Argon gas (5 to 10 cm^3/min) was also flowed into the iron feed tube. The gas mixture of Ar and $TiCl_4$ bubbled through holes at the bottom of the iron feed tube immersed in the molten salt. There was more effective contact between gaseous $TiCl_4$ and molten salt than that shown in Figure 5. In some experiments, a molybdenum tube was used to feed $TiCl_4$ into the molten salt instead of the iron tube.

IV. RESULTS

A. Reduction of $TiCl_2$

The feed tube shown in Figure 5 containing $TiCl_2$ was immersed in the molten salt, and the current flowing through the external circuit was measured. Representative results are shown in Figure 6. The feed tube was immersed at time zero in Figure 6. The positive current indicates a cathodic reaction at the feed tube. The periodic current spikes are associated with the interruption of the current for the measurement of the open circuit potential. External current over 1 A was measured in all experiments on the reduction of $TiCl_2$. Since monovalent titanium ion is not stable in the molten salt, the current in the external circuit corresponds to the reduction of $TiCl_2$ to metal titanium at the cathode. The amount of charge (Q_m) that passed through the circuit, the theoretically equivalent mass of deposit (w_{cal}), and the

Table IV. Summary of Experimental Conditions for the Contactless Electrochemical Reduction of Titanium Chlorides by Aluminum at 1273 K

| | Weight, w_i/g | | | | Reductant | Container | Feed | Temperature, | Amount of Getter |
Experiment	$TiCl_2$	$TiCl_4$	Al*	NaCl	(Mol Pct)	for Al	Tube	T/K	Sponge Ti (g)
A1	6.6	—	51	1560	pure Al	Cu	Fe	1273	no sponge Ti
A2	5.7	—	41	1523	Al-3Ni	Mo	Fe	1273	100
A3	5.2	—	41	1514	Al-3Ni	C	Fe	1273	47
A4	4.2	—	45	773	Al-34Ti	C	Fe	1223	45**
B1	—	10.2	41	1516	Al-3Ni	C	Fe	1273	no sponge Ti
B2	—	15.2	45	716	Al-33Ti	C	Fe/Mo†	1273	45**
B3	—	15.0	45	716	Al-33Ti	C	Mo	1273	45**
B4	—	20.0	35	716	Al-54Ti	C	Mo	1223	76**

*Aluminum contained in reductant alloy.
**Sponge Ti was placed in Al container.
†Iron tube was lined with Mo foil.
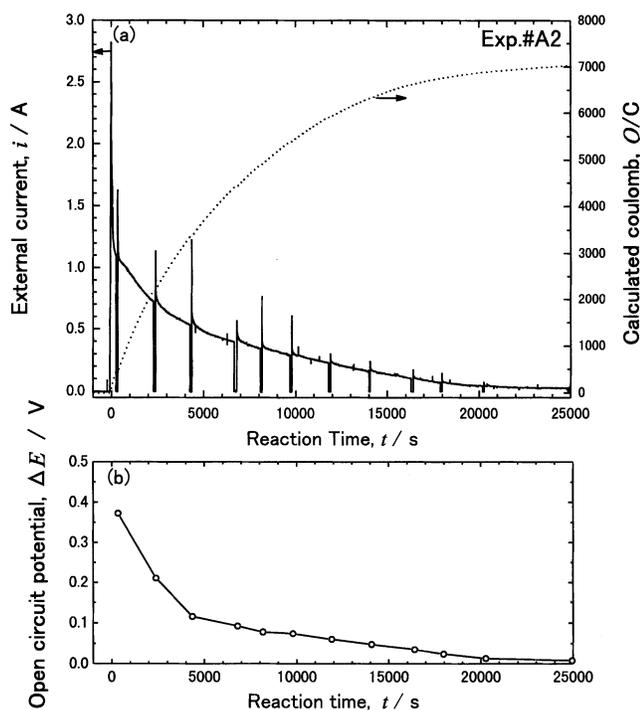
Fig. 6—(a) and (b) Variation of the external current, the total quantity of charge transfered through the external circuit, and open circuit potential vs reductant aluminum alloy with time during reduction of $TiCl_2$ (experiment A2).

actual mass of deposit recovered (w_{depo}) from the feed tube after each experiment are summarized in Table V. The current of 0.2 to 0.5 A was observed even after a long reaction time (10 ks) in all experiments related to the reduction of $TiCl_2$. It was difficult to judge the terminal point of the reduction. Therefore, the experiments were terminated after arbitrarily chosen time intervals shown in Table V by pulling up the feed tube above the surface of the molten salt.

After cooling, the gray metallic deposit was recovered from the feed tube. The results of composition analysis of titanium metal by XRF are shown in Table VI. As seen in the table, iron from the feed tube was found to contaminate titanium. Use of an alternative material for the feed tube is necessary for producing high purity titanium. The concentration of aluminum in the titanium metal produced by the

spontaneous electrochemical reaction varied from values below the detection limit of XRF (~0.01 mass pct) to 4.5 mass pct. In each experiment, a higher level of contamination was encountered in samples from the top of the deposit in the feed tube. Nevertheless, we emphasize that the average value for aluminum in the titanium produced was 0.76 mass pct. Furthermore, the composition of nickel was below the detection limit of XRF (~0.01 mass pct), although Al-Ni alloy was used as the reductant in experiments A2 and A3. These facts clearly indicate that titanium deposition at the cathode proceeded by LR-EMR, without direct physical contact between $TiCl_2$ and aluminum alloy. Because of the strong adhesion between the titanium deposit and the iron tube, it was difficult to collect all the titanium deposited. Only partial recovery was possible by mechanical methods. The partially recovered titanium amounted to 11 to 48 pct of the charge. Part of the $TiCl_2$ charged into the system escaped as $TiCl_3$ gas and a small part was dissolved in the molten salt.

The morphology of deposit is shown in Figure 7. Two types of deposit were observed in this study. Figures 7(a) and (b) show deposits that are similar to sponge titanium obtained by the magnesiothermic reduction.[4] Figure 7(c) shows angular titanium particles collected from the bottom of the feed tube. Angular titanium particles have not been obtained by magnesiothermic reduction. It is possible that the two distinct types of particles were formed by different mechanisms. In addition to the electrochemical reduction, titanium can also result from the disproportionation of $TiCl_2$:

$$3TiCl_2 \text{ (s)} \rightarrow Ti \text{ (s)} + 2 TiCl_3 \text{ (g)} \qquad [5]$$
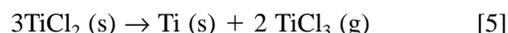
The X-ray diffraction patterns of the deposits, shown in Figure 8, indicate that deposits were primarily αTi (hcp-Ti). However, there is evidence of lattice expansion, probably caused by the impurities such as oxygen. Except iron, other metallic impurities were not observed by XRF analysis. The solubility of iron in titanium is too small (under 0.04 mass pct[23]) to cause a noticeable increase in lattice parameter. In experiment A3, minor amounts of the intermetallics TiFe2 and TiFe were found in the deposit. A small amount of TiFe2 was also detected in the deposit obtained from experiment A4. Except in experiment A4 (1223 K), the amount of titanium recovered from the iron feed tube was small in comparison with the quantity of electricity that flowed through the external circuit. The ratio of the deposit obtained to that calculated from the quantity of charge was 20 to 30 pct in

Table V. Summary of the Results of Contactless Electrochemical Reduction of TiCl₂

Experiment	Maximum Current, i_{max}/A	Reaction Time, t/ks	Quantity of Charge, Q_m/C	Calculated Deposit,* w_{cal}/g	Deposit Obtained, w_{depo}/g
A1	3.1	10.9	3721	0.92	0.30
A2	2.8	24.9	7024	1.70	0.47
A3	1.5	31.9	8815	2.20	0.52
A4	1.8	10.9	3366	0.84	0.81

*The mass of titanium deposit calculated from the quantity of charge through the external circuit (Q_m).

Table VI. Results of XRF Analysis of Deposits Obtained during Contactless Electrochemical Reduction of TiCl₂ by Aluminum

Experiment	Position	Analytical Results (Mass Pct*)							
		Ti	Fe	Al	Cl	Na	Si	Mn	Ni
A1	top	96	3.2	0.66	0.16	nd	0.15	nd	nd
	bottom	97	2.8	nd	0.14	nd	nd	nd	nd
A2	top	93	5.6	0.73	nd	nd	0.16	nd	nd
	bottom	99	0.8	nd	nd	nd	0.13	nd	nd
A3	top	91	4.2	4.50	nd	nd	0.11	nd	nd
	bottom	87	13.0	nd	0.11	nd	nd	0.26	nd
A4	top	94	5.4	0.17	0.15	nd	0.17	nd	nd
	bottom	93	6.3	nd	0.09	nd	0.36	nd	nd

*Excluding all gaseous components except halogens.
The term "nd" represents below detection limit of XRF analysis (about 0.01 mass pct).

experiments A1 to A3 and 97 pct in experiment A4. Since experiments A1 to A3 were conducted at 1273 K and experiment A4 at 1223 K, the lower temperature appears to be more favorable for the process.

When a copper container was used to hold liquid aluminum in experiment A1, there was a strong reaction between the two metals. However, metal-container interaction was negligible when containers made of molybdenum and graphite were used (experiments A2 to A4). There was no metallic aluminum left in the container after experiments. A large amount of aluminum was found to have reacted with the sponge titanium placed at the bottom of crucible for deoxidation. The transport of aluminum from the container to titanium sponge probably occurs by an electrochemical mechanism involving the dissolution of aluminum in the molten salt, its diffusion through the salt, and deposition on titanium. Use of a container made of an insulator material to hold either aluminum reductant or the titanium sponge may reduce the loss of reductant to the titanium getter and decrease the corrosion of the crucible by aluminum. In experiment A2, the molten salt in the feed tube after cooling was found to contain 0.14 mass pct Ti and 0.004 mass pct Al. The salt that condensed in the gas exit tube contained 0.03 mass pct Ti and 0.2 mass pct Al.

B. Reduction of TiCl₄

The variation of the external current with time during the reduction of TiCl₄ is shown in Figure 9. Experimental results are summarized in Table VII. Positive current was observed when molybdenum and iron were used as the TiCl₄ feed tube. The open circuit voltage at the beginning of the experiment was approximately 0.32 V, only slightly lower than that (approximately 0.38 V) obtained during reduction of TiCl₂.

Surprisingly, in all experiments related to the reduction of TiCl₄, very little deposit could be recovered from the feed tube. The very small amount that was obtained in some experiments was found to be an iron alloy containing titanium and aluminum, as shown in Table VII. Similar to the case of TiCl₂ reduction, aluminum was found to react with sponge titanium placed at the bottom of the crucible containing molten salt.

V. DISCUSSION

Utilizing LR-EMR, metal titanium could be produced by the contactless electrochemical reduction of TiCl₂ by aluminum. Although titanium produced was contaminated with aluminum to some extent (approximately 4.5 mass pct) in some experiments, this is a new achievement. The best result that was obtained earlier was the production of Ti containing 30 mass pct Al by aluminothermic reduction.[14] When TiCl₄ was used as titanium feed, there was no significant titanium deposit. The factors responsible for these observations are discussed subsequently.

A. Thermodynamics of Titanium Formation

The reduction of TiCl₂ occurs electrochemically. Combining the cathodic and anodic reactions represented by Eqs. [3] and [4], respectively, the overall reaction can be written as

$$\text{TiCl}_2 \text{ (s) (site I)} + 2/3\text{Al (l)(site II)} \rightarrow \text{Ti (s)(site I)}$$
$$+ 2/3\text{AlCl}_3 \text{ (g)(site II)} \quad [6]$$
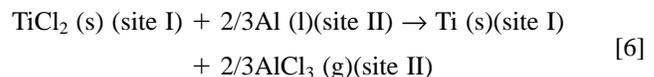
$$\Delta G_{(6)} = \Delta G_{(6)}^\circ + RT \ln \frac{a_{Ti}^I \, p_{AlCl_3}^{II 2/3}}{a_{TiCl_2}^I \, a_{Al}^{II 2/3}} \quad [7]$$
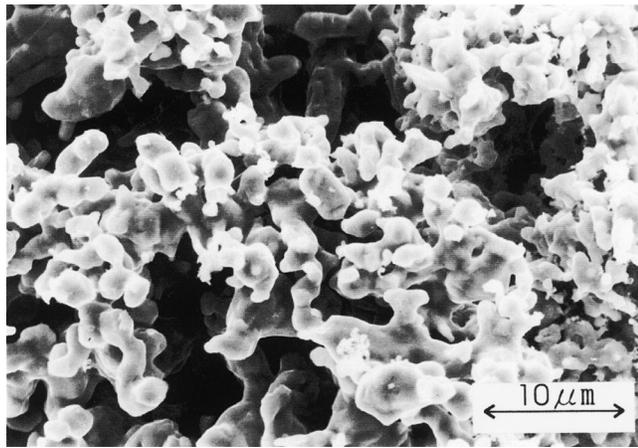
(a)
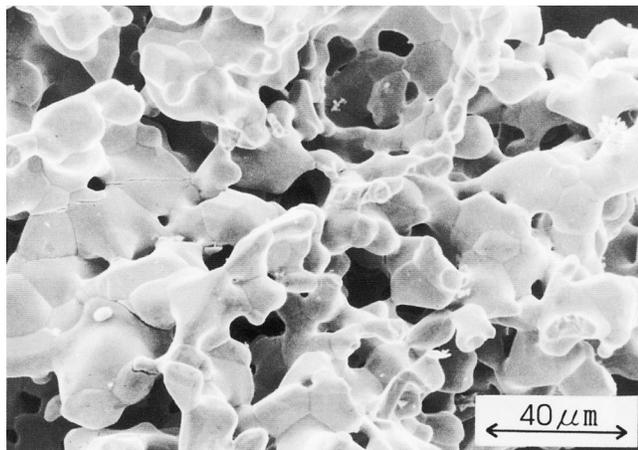
(b)
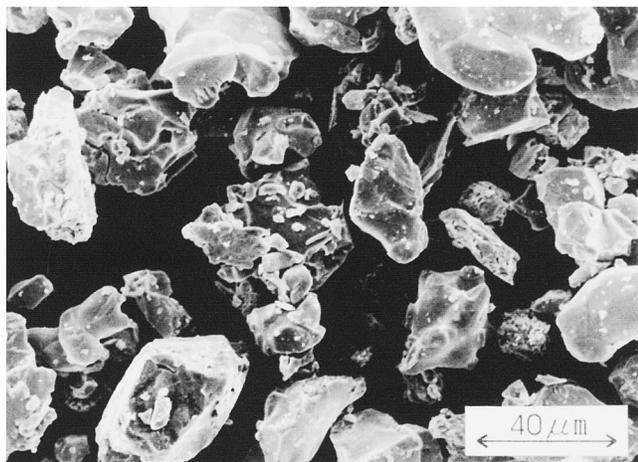
(c)

Fig. 7—Scanning electron micrographs of titanium deposits obtained from various locations in the feed tube (experiment A2): (a) very fine sponge titanium found at the top of the feed tube, (b) sponge titanium obtained at the top of the feed tube, and (c) angular titanium particles present at the bottom of the feed tube.

Fig. 8—X-ray diffraction pattern of the reduction products in the feed tube and the reference pattern for αTi from JCPDS.[24]
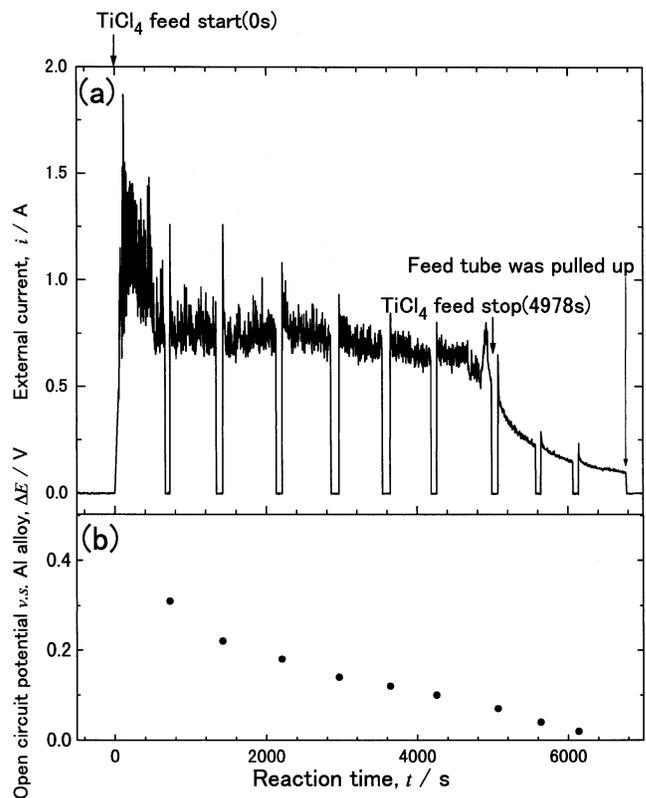
Fig. 9—(a) and (b) Variation of the external current and open circuit potential vs reductant aluminum with time during reduction of $TiCl_4$ (experiment B4). Positive current indicates a reduction process at the feed tube.

where a_i and p_i are the activity and partial pressure, respectively, of species i. The total pressure in the system is held constant at 0.101 MPa (1 atm). The standard Gibbs energy change for Reaction [6] at 1273 K is -30 kJ/mol. The equilibrium constant, $K_{[6]}$, is 17. The driving force of the reaction can be enhanced by having a low activity of $AlCl_3$ at site II or high activity of $TiCl_2$ at site I. The concentration

Table VII.   Summary of the Results Obtained during the Reduction of TiCl$_4$ by Aluminum

Experiment (Feed Tube)	Maximum Current, i_{max}/A	Quantity of Charge, Q_m/C	Reaction Time, t/ks	Deposit Obtained	
				Mass, w_{depo}/g	Composition* (Mass Pct)
B1(Fe)	3.0	25260	30.7	0.070	Fe-23Al-7Ti
B2(Fe/Mo)	2.1	4040	5.8	0.005	Fe-31Ti-11Al
B3(Mo)	1.9	3950	5.5	no deposit	
B4(Mo)	1.9	3610	5.8	0.002	FeTi,FeTi$_2$,Ti$_2$Si**

*Determined by XRF analysis.
**By EPMA analysis.

of AlCl$_3$ in the molten salt toward the end of the experiment can be estimated by assuming that the entire charge of titanium chloride is reduced according to Reaction [6]. For example, in experiment B1, the maximum calculated concentration of AlCl$_3$ in molten NaCl is 4.3 mass pct. The actual concentration would have been lower because of the anticipated vaporization of NaAlCl$_4$ (g) and AlCl$_3$ (g) from the melt. Vapor pressure measurements have been reported in the system NaCl-AlCl$_3$ in the temperature range 1048 to 1148 K.[25] Extrapolating these results to 1273 K, the partial pressure of AlCl$_3$ is 0.005 MPa (0.05 atm) when the concentration of AlCl$_3$ in NaCl-AlCl$_3$ melt is 4.3 mass pct. Electrochemical reduction of TiCl$_4$ dissolved in molten salt is faster than that of gaseous TiCl$_4$, because a three-phase interface (gas/molten salt/metal) is required for reduction of the latter. It has been reported that the rate of dissolution of TiCl$_4$ gas in molten salts is very low.[15,26,27] Therefore, the concentration of TiCl$_4$ in the salt is probably well below the equilibrium value. Consequently, the activity of TiCl$_2$ in the molten salt produced by the partial reduction of TiCl$_4$ at the feed tube was probably lower than when TiCl$_2$ was used as the feed material. The lower activity of TiCl$_2$ at site II may be one of the reasons for the absence of significant titanium deposition when TiCl$_4$ was used as the feed. A more important reason, perhaps, is the reaction of titanium deposit with TiCl$_4$ to form TiCl$_3$. The small amount of iron alloy containing titanium that was obtained in some experiments on the reduction of TiCl$_4$ is consistent with this explanation. For obtaining metal titanium during the reduction of TiCl$_4$, methods for effective removal of AlCl$_3$ from the molten salt and increasing the activity of TiCl$_2$ at the feed site have to be developed.

B. *Transport of Aluminum*

The presence of up to 4.5 mass pct Al in the titanium deposit obtained at a specific location in one experiment (Experiment A3) on the reduction of TiCl$_2$ and the presence of larger amounts of aluminum in trace deposits obtained during the reduction of TiCl$_4$ suggest some transport of aluminum ions from the anode to the cathode through molten NaCl and their discharge at the cathode. Therefore, effective methods for minimizing the accumulation of AlCl$_3$ in the melt will be required for improving the potential of the process. However, since a large amount of titanium is used in the form of Ti-6V-4Al alloy, the present authors maintain the view that small contamination of the titanium metal by aluminum may not cause significant problems for alloy production.

VI. CONCLUSIONS

The possibility of reducing titanium dichloride by aluminum to metallic titanium of purity sufficient for use in commercial alloys has been demonstrated using a new contactless electrochemical process. The average contamination of titanium metal by aluminum was 0.76 mass pct. The optimum temperature is probably close to 1200 K. Preliminary results clearly indicate that more electropositive elements present in the reductant at the anode are not transferred to the titanium formed at the cathode. Therefore, it may be possible to use scrap aluminum as the reductant in this process. More extensive research is needed for a more complete mechanistic understanding of the process. No attempt has been made to optimize materials and process parameters. This article provides proof of concept of the new process.

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