Titanium Powder Prepared by Magnesiothermic Reduction of Ti^{2+} in Molten Salt

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A process to produce titanium powder from Ti^{2+} in the molten salt was confirmed experimentally. It consists of two steps. In the first step, titanium (IV) chloride gas dissolves in the molten salt as the titanium (II) chloride by reacting chemically with the metallic titanium or magnesium. In the second step, this molten salt is exposed to the metallic reductant Mg for the final reduction to the metallic Ti powder. Experimentally, the feed of $TiCl_4$ gas and the subsequent reaction with Ti prepared the molten salt containing 5 to 10 mass pct Ti^{2+}. By Mg reduction of this salt, the well-isolated fine Ti particles were recovered. The powder morphology and particle size depended on the Ti^{2+} concentration, reduction temperature, time, and concentration of the by-product $MgCl_2$. The stirring by argon gas bubbling effectively grew the fine and round particles to a few tens of microns in size.

I. INTRODUCTION

SOME new production processes such as hydride-dehydride (HDH), gas atomizing, and plasma rotating electrode process (PREP) are applied for the preparation of titanium powder suitable to powder metallurgy.[1] However, these processes do not satisfy the reasonable price, fundamentally because they need the precast Ti ingot or compact as the starting material. To exclude the extra cost for ingot making, a specialized powder produced directly from its chloride looks promising.[2]

$TiCl_4$ is an indispensable intermediate compound for titanium metal production, and it has been used as common base material in the established titanium industries. In a modification of the conventional Hunter process (sodium reduction of $TiCl_4$), a method has been industrially applied, where $TiCl_4$ was dissolved as $TiCl_2$ in the molten salt (main constitution is NaCl) after the weak sodium reduction.[3,4] When subsequent reduction by sodium is applied to the molten salt, the slightly sintered titanium called "sponge fine" powder is produced after the mechanical crashing. This powder is commercially supplied to powder metallurgy. When sodium is used as the reductant, however, there are some technical and economical problems in the handling of metallic sodium, NaCl removal, and sodium recycling by electrolysis of NaCl.[3] In the magnesium reduction (Kroll process), the electrolysis of its by-product, $MgCl_2$, has been developed more efficiently and becomes economical by the improved operating techniques and modernized facilities. Considering the industrial backgrounds surrounding the Kroll process, we expect that the electrolysis of $MgCl_2$ will

be available, when we can reduce Ti^{2+} in the molten salt using not Na but Mg.

In the Kroll process, $TiCl_4$ is fed to the top surface of the molten Mg, as illustrated in Figure 1(a). However, it could not produce the Ti powder. Its product was heavily sintered as "sponge" titanium.

Recently, the authors proposed an alternative titanium production process, as shown in Figure 1(b), where the Mg melt floated on the heavier molten $MgCl_2$.[2] When the gaseous $TiCl_4$ was fed from the bottom of the molten Mg, metallic Ti powder could be successfully produced from $TiCl_4$ in the Mg layer. The particles settled through the molten $MgCl_2$ did not sinter as firmly as the Kroll sponge and were easily pulverized.[2] The obtained powder was well isolated and about 1 to 10 μm in size. Because the solubilities of $TiCl_4$ in the chloride salts are only a few mass pct, as listed in Table I, a large amount of the supplied $TiCl_4$ could not dissolve in the salt, and should be reduced in the molten Mg layer.

Table I shows that the solubilities of Ti^{3+} and Ti^{2+} are generally larger than that of Ti^{4+}. Using the lower chlorides such as $TiCl_3$ and $TiCl_2$, we can expect the higher total concentration of Ti ions in the salt.

The purpose of this article is to develop the method specialized for the isolated particle production of Ti using Mg, Ti^{2+}, and the molten salt as the solvent. Here, some basic experimental evidence in laboratory scale is shown under this concept to consider the technical aspects for industrial application.

II. CONCEPT OF TWO-STEP PRODUCTION

Our concept for Ti powder preparation using magnesium as the reductant is illustrated in Figure 1(c). It consists of the two steps.

In the first step, $TiCl_4$ is fed and dissolved into the molten salt. Both $TiCl_4$ molecules and Ti^{4+} react with Mg, where a half amount of Mg required for the complete reduction of Ti^{4+} to Ti is consumed for Ti^{2+} formation as follows.

$$TiCl_4 + Mg = TiCl_2 + MgCl_2 \qquad [1]$$
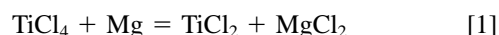
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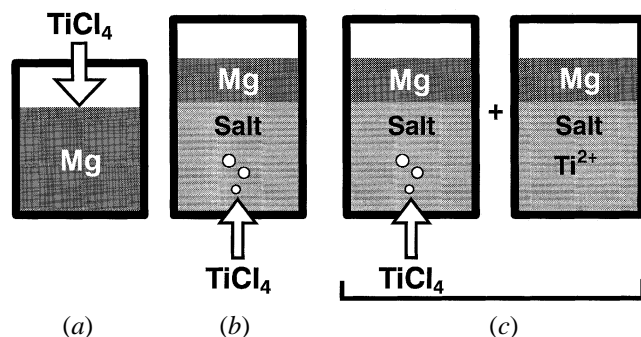Manuscript submitted August 6, 1998.

Fig. 1—Concepts of Ti production by Mg reduction: (a) TiCl$_4$ gas feed into molten Mg (Kroll process), (b) TiCl$_4$ gas feed to bottom of Mg layer through the molten salt,[2] and (c) combined process with TiCl$_4$ gas feed for Ti^{2+} formation and metallic Ti formation from its molten salt (this study).

The formed TiCl$_2$ and MgCl$_2$ cannot completely mix in a homogenous liquid written as MgCl$_2$-50 mol pct TiCl$_2$, because the solubility of TiCl$_2$ in MgCl$_2$ is 35 mol pct at 1173 K.[6]

In the Hunter method, the formed TiCl$_2$ produces the salt mixture of NaCl-33 mol pct TiCl$_2$ by the following reaction:

$$TiCl_4 + 2Na = a\ salt\ (TiCl_2 + 2NaCl) \qquad [2]$$
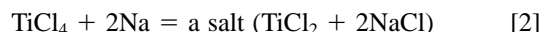
because the solubility of TiCl$_2$ in NaCl is 44 mol pct at 1123 K and 52 mol pct at 1173 K.[10]

In our case, the additional amount of molten salt is needed as the solvent of Ti^{2+}. This means that TiCl$_4$ is fed into the mixture consisting of the molten salt and the reductant Mg. This salt needs some requirements: a thermodynamic stability against both Mg and Ti, a large solubility of Mg and Ti ions, and a fast dissolution of TiCl$_4$.[2] The alkaline and alkaline-earth chlorides are studied here.

Because of the difference of specific gravity between Mg and the molten salt, the lighter Mg floats above the heavier salt.[2] When TiCl$_4$ is fed to the upper surface of the molten Mg layer, the spatial arrangement for the reduction becomes similar to the Kroll process (Figure 1(a)), and we cannot expect the continuos and homogenous reaction in Eq. [1]. Therefore TiCl$_4$ will be fed from the bottom of the molten Mg layer as in the arrangement shown in Figure 1(b).

The best method suitable to dissolve TiCl$_2$ into the molten salt is still not fixed when Mg is used. As another method, we can take the reaction as

$$TiCl_4 + Ti = TiCl_2\ (in\ the\ molten\ salt) \qquad [3]$$
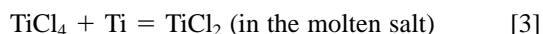
instead of the industrial reactions [1] and [2]. The Ti^{2+} is in a more stable oxidation state than Ti^{3+} when they coexist with metallic Ti in the molten chlorides.[16,17,18]

Figure 2 shows the conceptual view of Ti production using Eq. [3]. By feeding TiCl$_4$ gas into the prepared molten salt containing Ti powder, the titanium (IV) chloride dissolves as the lower oxidation state of Ti such as Ti^{2+}. Thus, obtained molten salt will be served for the next step.

The subsequent Mg reduction shown in Eq. [4] causes the nucleation in the salt:

$$TiCl_2\ (in\ salt) + Mg\ (liquid)$$
$$= Ti + MgCl_2\ (in\ salt) \qquad [4]$$
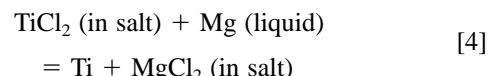
Because of density difference, the reductant Mg floats on the molten salt, as shown in Figure 1(c), and the precipitated Ti will settle on the bottom of the reaction vessel. In Figure 2, the Ti product will be extracted and the molten salt containing Ti can be partially returned as the salt for Reaction [3]. The other half of the Ti product will be separated from the molten salt as the final product. The distillation and electrolysis of MgCl$_2$ will be used for the close circulation of Mg when the process is industrially applied.

This work experimentally studies the feasibility of the second step in the laboratory bench to find the applicability of magnesiothermic reduction to the lower chlorides and to clarify the morphology of Ti precipitates. In spite of the concept of continuous production by connecting two steps (Figure 2), the individual steps are studied here in the separated experiments.

III. EXPERIMENTAL PROCEDURES

A. Preparation of Molten Salt

The molten salts dissolving Ti^{2+} were prepared using the experimental apparatus shown in Figure 3. Dehydrated LiCl (99.0 pct in purity), KCl (99.5 pct), NaCl (99.5 pct), and dehydrated MgCl$_2$ (98.8 pct, <3.0 pct water) were mixed in 150 to 200 g. About 8 g "sponge titanium" (99.5 pct) was set with the mixed chlorides in the Al$_2$O$_3$ (95.3 pct) crucible (40-mm i.d. and 150-mm high). The crucible was mounted in the reaction vessel, evacuated at 473 K for 7.2 ks to dry the molten salt, and heated to 1173 K in Ar gas flow. After melting the salt, 99 pct MgO lance (6 mm in

Table I. Solubility of Titanium Chlorides in the Molten Salts

Molten Salt	Melting Point (K)	Solubility at 1173 K (Mass Pct)		
		TiCl$_4$	TiCl$_3$	TiCl$_2$
MgCl$_2$	987	1.5[5]*	—	0[6]
NaCl	1073	1.2[7]* 4.1[8]**	>60[9]	69[10]
NaCl-50 mol pct KCl (eutectic composition)	930	5.8[7]*	>37[11]	35[12]†
LiCl-41 mol pct KCl (eutectic composition)	625	4.8[13]‡ 3.4[14]§	—	—
MgCl$_2$-34.7 mol pct LiCl-24.1 mol pct KCl	<943[15]	—	—	—

*Extrapolated to 0.1 MPa TiCl$_4$ from reported data.
**At 1073 K under 88 kPa TiCl$_4$.[8]
†At 903 K.[12]
‡At 765 K.[13]
§At 763 K under 97 kPa TiCl$_4$.[14]

$$TiCl_4(g) + Ti = Ti^{2+}$$

$$Ti^{2+} + 2Mg(\ell) = Ti + MgCl_2(\ell)$$
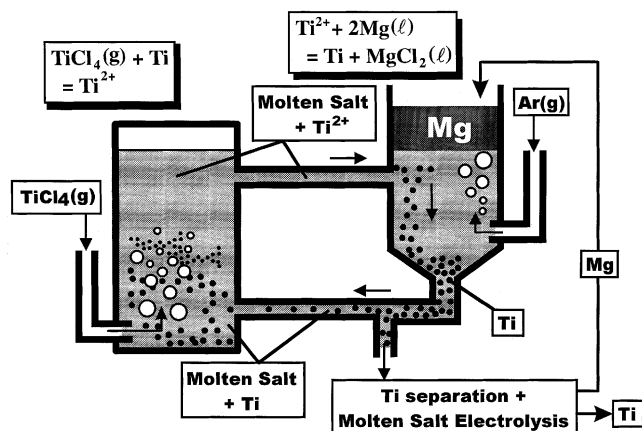
Fig. 2—Concept of continuous Ti powder production using the recycled Ti to produce the molten salt containing Ti^{2+}.
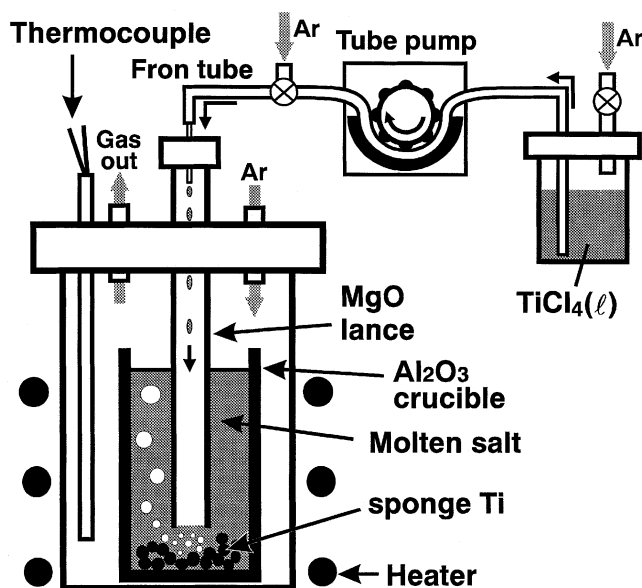

Fig. 3—Schematic illustration of experimental apparatus to prepare the molten salt containing Ti^{2+}.

Fig. 4—Schematic illustration of experimental apparatus to reduce Ti^{2+} in the molten salt.

i.d.) was immersed to contact titanium sponge and 25 or 50 g of $TiCl_4$ liquid (>99 pct) was fed at the constant rate of 3.3 mg/s from the $TiCl_4$ container by the tube pomp. After the feed at 1173 K, the reactor was once cooled in the furnace under Ar gas atmosphere. The solidified salt was taken off from the crucible and its bottom part was mechanically separated, because the residual Ti sponge was mixed.

A part of the solidified salt was dissolved in the dilute hydrochloric acid aqueous solution, and the titanium concentration in the salt was analyzed using the inductively coupled plasma–atomic emission spectrophotometer (ICP–AES).

B. *Mg Reduction of Molten Salt*

The molten salt thus produced was filled in the Al_2O_3 (>99.5 pct) crucible (34-mm i.d. and 150-mm high). In the same procedure as the salt preparation, the salt mixture was again melted under Ar gas flow using the experimental
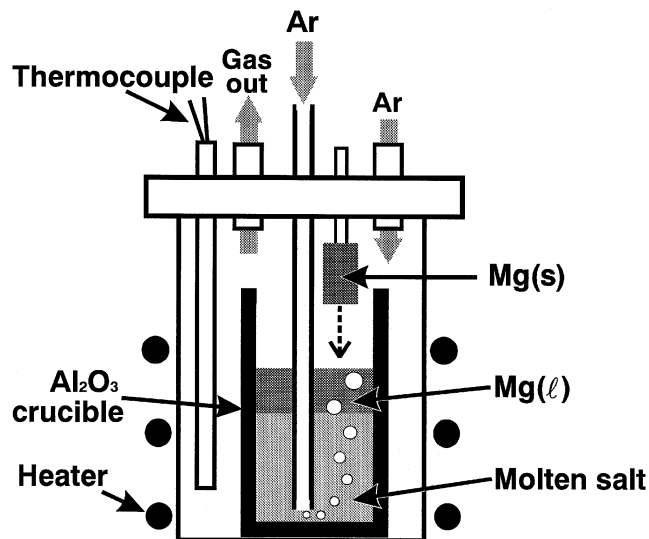
apparatus shown in Figure 4. In some experiments, the salts were diluted to be 1.43 mass pct Ti with the pure salt containing no titanium.

About 20 g Mg (99.9 pct) blocks were quietly charged using the Ti rod and melted on the molten salt. The Ar gas was bubbled in the salt at the rate of 8.3×10^{-6} m³/s through the MgO lance when stirring was needed. After cooling in the furnace, the crucible was crashed into pieces for macroscopic observation, and the solidified salt was leached by water and the dilute acetic acid solution. The powder that piled up on the crucible bottom and that which adhered to the crucible wall were separately recovered. The magnesium and salt residual in these powders were completely removed using ultrasonic cleaning equipment with the dilute hydrochloric acid solution. The powder was rinsed in water, alcohol, and acetone, in that order.

After drying, the powder was weighed and observed using a scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) analyzer. The phases were identified by X-ray diffraction (XRD) measurement. The impurity aluminum in the reduced powder was analyzed by ICP–AES, and the oxygen and nitrogen concentrations were analyzed by the inert gas fusion-infrared absorption method.

IV. RESULTS

A. *Molten Salt Containing Ti^{2+}*

The vibration of MgO lance indicated that the supplied liquid $TiCl_4$ was evaporated inside the lance (the boiling point of $TiCl_4$ is 409 K) and that its bubbles were fed into the molten salt. A fairly large amount of $TiCl_4$ gas was exhausted out of the vessel during the feed, although its quantity could not be measured because of strong reaction with the materials for exhaust circuit.

After solidification, the salts were usually dark green, as listed in Table II. A deep red salt was obtained when the feeding lance did not arrive at the Ti sponge. Because the $TiCl_3$ crystal is reddish violet,[16] such charge was excluded. After the experiments, a large amount of Ti sponge was

Table II.   Titanium Concentration in the Molten Salts after Feeding 25 Grams of TiCl$_4$

Molten Salt (Before Feed)	Color	Titanium Content, C_{Ti} (Mass Pct)	Yield R_{TiCl2}	R_{TiCl3}
MgCl$_2$	black green	3.48	0.405	0.627
MgCl$_2$	dark green	10.5*	0.912	1.528
NaCl	dark green	4.00	0.738	1.144
NaCl-50 mol pct KCl (eutectic composition)	emerald green	3.00	0.543	0.836
LiCl-41 mol pct KCl (eutectic composition)	dark green	5.70	0.572	0.903
LiCl-41 mol pct KCl (eutectic composition)	dark green	10.4*	0.827	1.384
MgCl$_2$-34.7 mol pct LiCl-24.1 mol pct KCl	black green	2.79	0.413	0.634

*50 g of TiCl$_4$ were supplied.

consumed. The residual Ti sponge was brittle and easily broken into small pieces. Its fine particles dispersed in the salt. Considering the wider reaction interface between the gaseous TiCl$_4$ and the solid Ti, the fine powder as Ti source seems better to ensure a good reactivity. However, this experimental result implies that the bulky Ti can be applied as the starting material.

The analyzed titanium concentrations, C_{Ti}, are listed in Table II. No systematic relation between the color of the salt and the titanium concentration was found. The C_{Ti} exceeded the equilibrium solubility of TiCl$_4$ at 1173 K, compared with the reported data listed in Table I.

Because the valancy analysis of titanium in the salt using H$_2$ gas evolution[18] did not show the reproducible values, the yields were deduced using the analytical values. Assuming that the dissolved TiCl$_4$ could be perfectly converted into TiCl$_2$, the amount of Ti^{2+} supplied from TiCl$_4$ in the salt, W_{Ti}, is equal to the amount of Ti^{2+} supplied from sponge Ti, and it can be calculated in Eq. [5].

$$C_{Ti} \text{ [mass pct]} = 100 \qquad [5]$$

$$\times \frac{2 \cdot W_{Ti}}{M_{salt} + W_{Ti} \cdot \left(2 + 4 \frac{M_{Cl}}{M_{Ti}} \right)}$$

where M_{salt}, M_{Ti}, and M_{Cl} are the mass of the initial salt and the atomic weight of Ti and Cl, respectively. The yield R_{TiCl_2} is defined as the molar ratio of the thus deduced W_{Ti} and the amount of the supplied TiCl$_4$, W_{TiCl_4}.

$$R_{TiCl_2} = \left(\frac{W_{Ti}}{M_{Ti}} \right) \Big/ \left(\frac{W_{TiCl_4}}{M_{TiCl_4}} \right) \qquad [6]$$

where M_{TiCl_4} is the molecular weight of TiCl$_4$. Similarly, the yield R_{TiCl_3} was defined.

Although a large amount of TiCl$_4$ gas was exhausted out, the calculated yield R_{TiCl_3} exceeded unity. Therefore, the chemical species dissolved in the salt was judged to be mostly at the oxidation state II, namely, Ti^{2+}. The exact ratio Ti^{3+}/Ti^{2+} under the coexistence with TiCl$_4$ and Ti should be determined in the further study, for example, from the electrochemical analysis.[19] Based on the previous studies,[17,18,19] we assume that Ti(II) is the main oxidation state when the metallic Ti coexists with its chlorides.[17,18]

The highest yield R_{TiCl_2} was recorded in the LiCl-KCl eutectic salt and the lowest in the MgCl$_2$ single salt. The yield might be improved by the technical methods, for example, by securing the wider reaction area with TiCl$_4$ bubbles. For this

work, the amount of charged Ti was limited so that C_{Ti} did not approach the saturation value, in order that the contamination of metallic Ti pulverized at the first step should be avoided for the morphology observation at the successive stage.

B. Mg Reduction of Molten Salt

After the Mg reduction of molten salts containing Ti^{2+}, a fine metallic powder was recovered and identified as α-Ti single phase by XRD. All salts after solidification were white. This indicates that there remained no Ti ions in the salt. The fine Ti particles dispersed in the salt disturbed the chemical analysis of Ti ions in the solidified salt.

Although the quantities of Ti powder were only 5 to 20 g, the yields were calculated to be roughly 85 to 90 pct, based on the amount of the used salt and C_{Ti}. Note that they contained an underestimation because of imperfect powder recovery from the crucible.

Table III summarizes the experimental conditions and the powder morphology. No difference was found between the powder at the bottom of the alumina crucible and that at the crucible wall, although some morphological change was reported when an Fe crucible was used.[2,20–22]

1. Effects of stirring and reduction temperature

Using LiCl-KCl eutectic salt containing 5.7 mass pct Ti, the effects of stirring and reduction temperature on morphology were shown in Figure 5. When Ar gas was not bubbled, the narrow rods were obtained at 1173 K for 21.6 ks in addition to the granular Ti. At 973 K, only the thin rods were found, and the round grains were rare. In removing the salt, some flakes floated in the acid solution. Their morphology was dendritic but their volume fraction was very small.

When Ar gas was bubbled, neither rods nor dendrites were found, and only the round particles with smooth surface were recovered. The diameter of these particles was larger at 1173 K. At 973 K, the finer particles of 1 to 5 μm were aggregated.

2. Effect of titanium concentration

Figures 5(c) and 6 show the powder morphology precipitated from the salts at 1173 K with stirring. The round particles were commonly found in the molten salts with different Ti concentrations. The particles precipitated from the salt containing 1.43 mass pct Ti were smaller than the others.

Even when the titanium content in the salt was diluted,

Table III. Impurity Concentration and Morphology of Titanium Powder

| | | Experimental Conditions | | | | Impurity in the Ti Powder | | | |
Number	UsedSalt	Temperature (K)	Time (ks)	Titanium Concentration (mass pct)	Ar Gas Bubbling	Oxygen (Mass Pct)	Nitrogen (Mass Pct)	Aluminum (Mass Pct)	Morphology of the Ti Powder
1-(1)	LiCl-KCl	1173	21.6	5.70	none	2.47	—	0.92	granular (10 to 30 μm) and rod (20- to 60-μm long, 5 to 10 μmϕ)
1-(2)	LiCl-KCl	973	21.6	5.70	none	1.60	0.39	0.27	rod (5- to 10-μm long, 3 to 5 μmϕ) and dendrites
1-(3)	LiCl-KCl	1173	21.6	5.70	bubbling	1.94	0.68	2.40	granular (10 to 30 μm)
1-(4)	LiCl-KCl	973	21.6	5.70	bubbling	1.86	0.61	0.55	granular (1 to 5 μm)
2-(1)	LiCl-KCl	1173	21.6	1.43	none	2.17	0.32	3.75	rod (20- to 40-μmϕ long, 5 to 10 μm)
2-(2)	LiCl-KCl	1173	21.6	1.43	bubbling	3.16	0.79	5.11	granular (1 to 5 μm)
2-(3)	LiCl-KCl	1173	21.6	10.4	bubbling	1.83	0.41	—	granular (5 to 30 μm)
3-(1)	LiCl-KCl	1173	0.30	5.70	bubbling	3.40	—	1.46	granular (<1 μm)
3-(2)	LiCl-KCl	1173	86.4	5.70	bubbling	3.35	—	2.86	granular (50 to 100 μm)
4-(1)	NaCl-KCl	1173	21.6	3.00	bubbling	2.21	0.49	1.34	granular (5 to 30 μm)
4-(2)	NaCl	1173	21.6	4.00	bubbling	2.23	0.43	1.55	granular (5 to 30μm)
4-(3)	MgCl$_2$	1173	21.6	3.48	bubbling	—	—	5.87	granular (1 to 5 μm)
4-(31)	MgCl$_2$	1173	21.6	10.5	bubbling	2.06	0.36	—	granular (5 to 30 μm)
4-(4)	MgCl$_2$-LiCl-KCl	1173	21.6	2.79	bubbling	—	—	1.02	granular (5 to 20 μm)
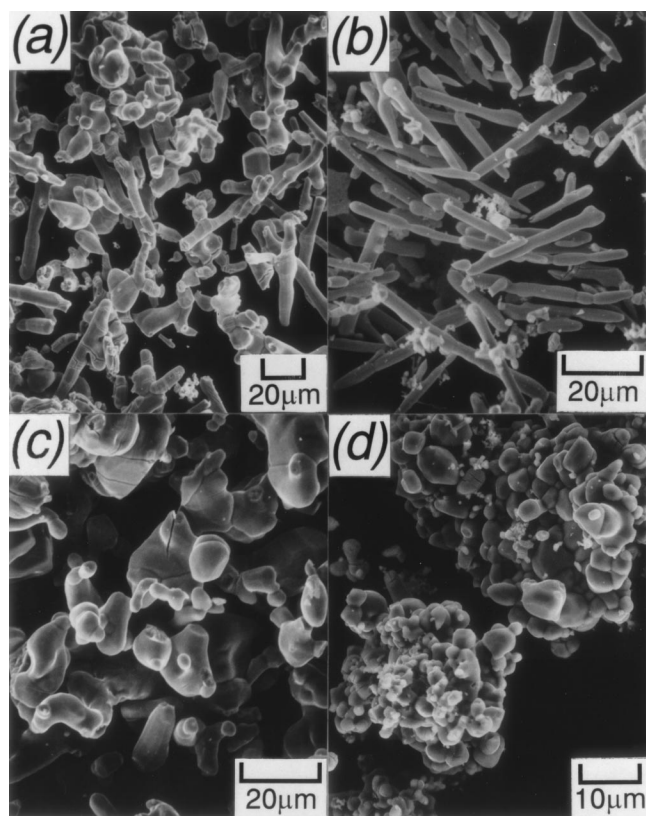
Fig. 5—SEM images of Ti powder obtained from the LiCl-KCl eutectic salts containing 5 mass pct Ti after treating for 21.6 ks. The Ar gas was not introduced (*a*) at 1173 K and (*b*) at 973 K, and it was bubbled (*c*) at 1173 K and (*d*) at 973 K.
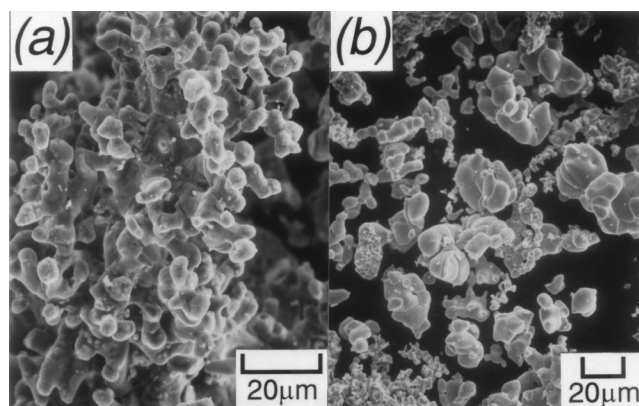

Fig. 6—SEM images of Ti powder obtained from the LiCl-KCl eutectic salts at 1173 K for 21.6 ks. The Ti concentration in the salt was (*a*) 1.43 mass pct and (*b*) 10.4 mass pct Ti.

the effect of stirring on powder shape was similar. The narrow rods were found when there was no stirring.

3. *Effect of time*

Using the salt containing 5.7 mass pct Ti, the effect of holding time on morphology was studied at 1173 K with stirring, as shown in Figures 5(c) and 7. Under these conditions, the rodlike powder was not formed. The white color of the solidified salt indicated that, surprisingly, the Mg reduction had been over for 0.3 ks after Mg melting. Note that it took a relatively longer time to cool in the furnace. The round particles were finer than 1 μm when they formed for 0.3 ks. In the prolonged holding time, they were aggregated and sintered to the larger single particles of 10 to 30 μm after 21.6 ks and of >50 μm after 86.4 ks.

4. *Effect of salts*

Another four molten salts were studied, as listed in Table III, and the morphology of Ti particles is shown in Figure 8. Powder morphology obtained in the NaCl-KCl eutectic salt (Figure 8(c)) was similar to that in LiCl-KCl (Figure 5(c)), although Ti^{2+} in the Li-containing salt was more stable than that in NaCl-KCl.[9] Those in the salts containing MgCl$_2$ were mixtures of two types: one was the large round particle of tens of microns with a smooth surface similar to that in
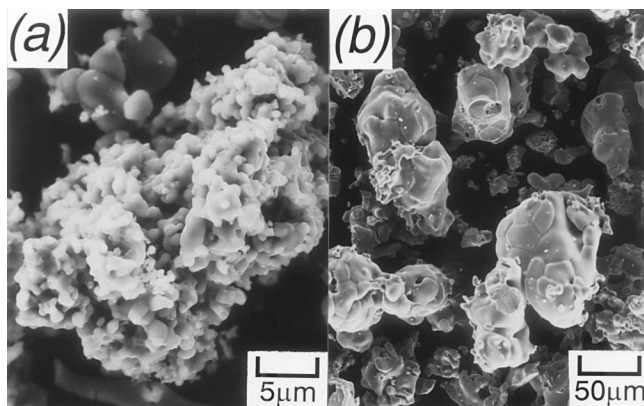
Fig. 7—SEM images of Ti powder obtained from the LiCl-KCl eutectic salts containing 5 mass pct Ti at 1173 K. The reaction time was (*a*) 0.3 ks and (*b*) 86.4 ks.
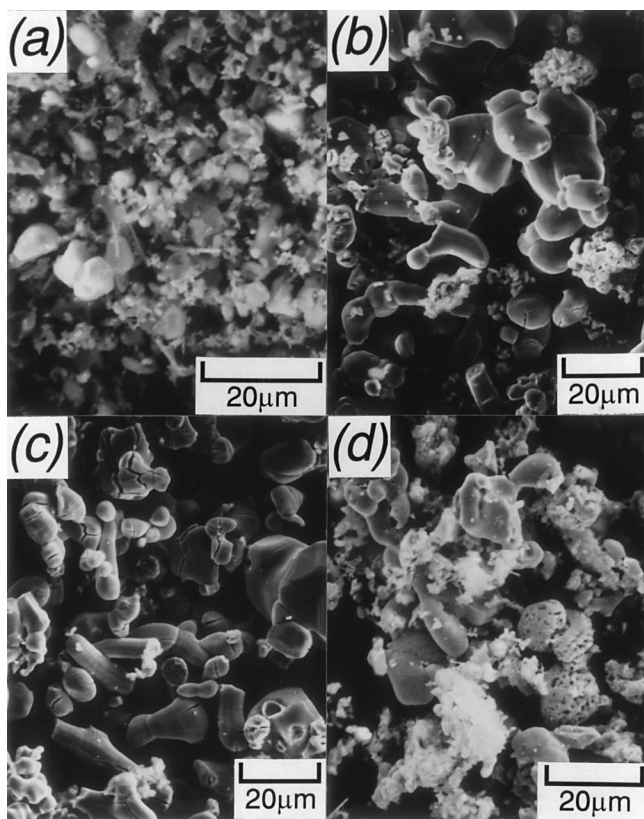

Fig. 8—SEM images of Ti powder obtained from the molten salts containing 5 mass pct Ti at 1173 K for 21.6 ks: (*a*) $MgCl_2$, (*b*) NaCl, (*c*) NaCl-KCl, and (*d*) $MgCl_2$-LiCl-KCl.

LiCl-KCl, and the other was the finer round particle of 1 to 5 μm in diameter.

Because $MgCl_2$ is the main by-product in Mg reduction, even if the initial salt does not contain $MgCl_2$, it will soon be contaminated in the process of reduction. In this work, the final increase of $MgCl_2$ concentration was less than 20 mass pct $MgCl_2$ even in the salt with the highest Ti^{2+} concentration.

C. *Impurity Contamination*

Impurity concentrations in the recovered Ti powder were analyzed by ICP–AES and they are listed in Table III. The

powder contained 1 to 4 mass pct oxygen, 0.3 to 0.8 mass pct nitrogen, and 0.2 to 6 mass pct aluminum. The higher aluminum and oxygen contents were recorded in the powder when it was treated at higher temperatures or when the amounts of produced titanium were smaller. The nitrogen concentration did not depend on the reaction conditions. Therefore, the sources must be the atmospheric nitrogen and impurity nitrogen in Mg.

In the same charge of the reduction, the same Al concentrations were analyzed by EDX over all the particles with different morphologies. The impurity source of Al is therefore judged to be the Al_2O_3 crucible, because the strong reductant Mg can reduce alumina thermodynamically.

Water in the salt and the atmospheric oxygen may be the oxygen sources in addition to Al_2O_3. This oxygen can react with Mg to form MgO. MgO was also used as the lance. Under the coexistence of Mg (reductant) and MgO, the oxygen concentration in Ti can rise thermodynamically to 2.0 to 3.0 mass pct at 1173 K.[23,24] The analytical values of oxygen may reflect such a thermodynamic saturation value. For the commercial application as pure Ti, oxygen should be kept at a thousand mass parts per million level. The effect of hydrogen and oxygen may be suppressed, by using the metallic vessel, by reducing water contamination in the initial $MgCl_2$ or by improving the handling of the continual operation.

If we can suppress the undesired dendritic precipitation at the iron wall,[2,20–22] the steel is applicable for the reactor's material, because iron does not contaminate titanium as heavily as Al_2O_3, as confirmed in the industrial Kroll process.

V. DISCUSSION

When the molten salts based on alkaline and alkali-earth chlorides are used, the reductant Mg floats on them. The Mg solubilities in these molten salts are as small as 0.3 mol pct, whereas the Na solubility in NaCl is about 3 mol pct.[25,26] In addition to the small solubility, it is reported that the dissolution of Mg into the salt was slow.[27]

When $TiCl_4$ gas fed in the molten LiCl-KCl or NaCl-KCl eutectic salt was reduced in one step by Mg, the isolated particles larger than 10 μm were often the angular polyhedra with good crystalline form.[27] Its morphology suggested that titanium could nucleate homogeneously in the molten salt. However, such morphology was never observed in this study.

Because Ti^{3+} becomes more stable at low temperatures,[19] the oxidation state of titanium may affect nucleation. However, once the metallic Ti is formed, the disproportionation reaction to form Ti^{2+} occurs[18] and Ti^{2+} becomes the main oxidation state.

Therefore, we assume here that Ti^{2+} in the salt would react inhomogeneously only near the interface between molten Mg and the molten salt. The product Ti is assumed to precipitate gradually as a nodule, as illustrated in Figure 9, although the local precipitation mechanism is not clear in atomic scale. Under these assumptions, the experimental observation of powder morphology will be explained as follows.

When the quiet interface can be kept as illustrated in Figure 9(a), the Ti nodules, rods, or dendrites grow from the bottom part of the molten Mg layer, depending on the
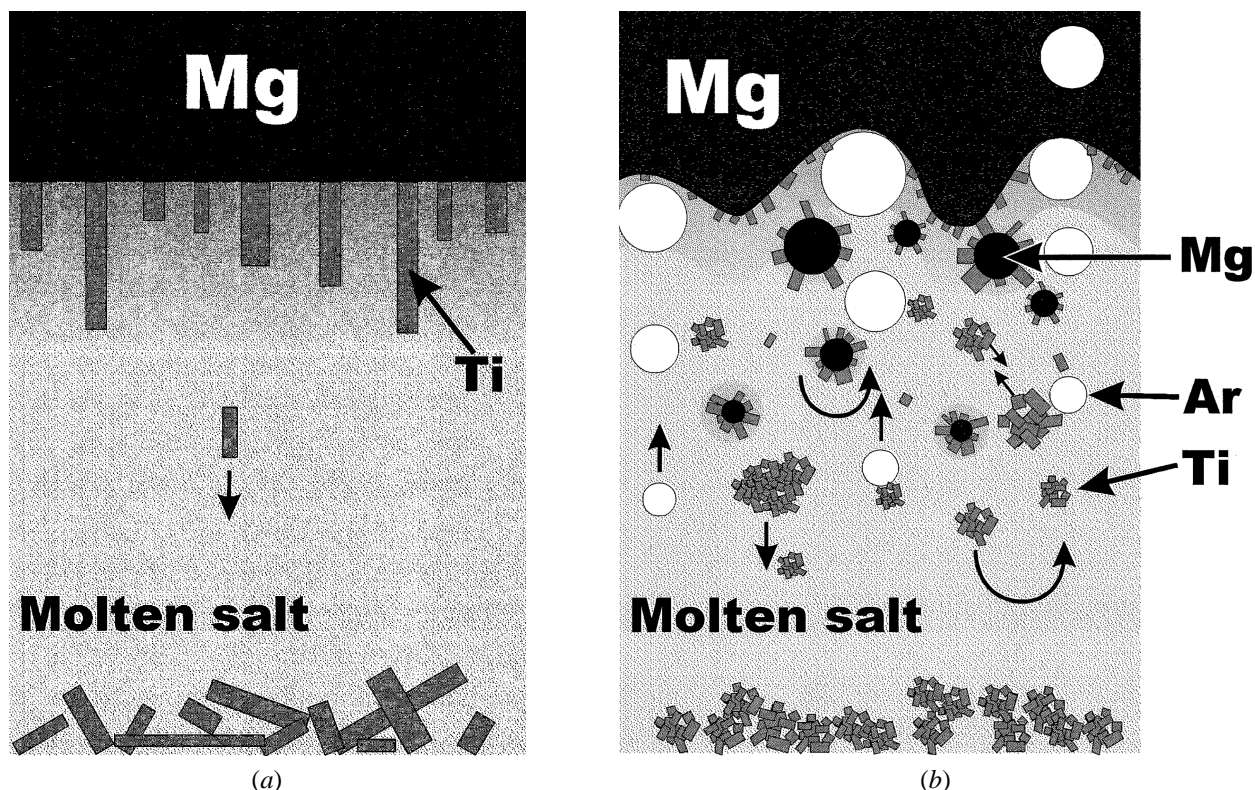
Fig. 9—Growth of Ti particles in the molten salt containing Ti^{2+}: (a) no stirring and (b) with stirring.

Mg distribution in the salt near the interface. These morphologies are dominant especially at the lower temperatures at which Mg diffusion into the salt is slow.

When Ar gas is injected (Figure 9(b)), the strong stirring disperses mechanically the Mg droplets into the salt. Two liquid phases mix like the emulsion. The reduction rate is enhanced because the interface between Mg and the salt increases and because the dissolving rate of Mg is accelerated. The unsteady interface by Ar gas bubbling disturbs a continuous growth of the nodules. Thus, nucleated fine particles frequently collide by themselves, aggregate, and sinter to the coarser particles. The union of particles in the stirred salt generates the coarsening for the long holding time. It is supported by the fact that the morphology of the recovered large particles was round but uneven.

The settling rate of the precipitate Ti particle in the molten salt depends mainly on the particle size. The terminal velocity in the quiet salt at 1173 K is evaluated as 2.78, 0.111 mm/ s, and 1.11 μm/s for 50, 10, and 1 μm particles, respectively, applying the Stokes law to Ti particles in $MgCl_2$.[28,29] The realistic settling rate of Ti particles is much slower, considering a heavy stirring by gas bubbling. The particles do not settle until they grow up to a certain size in the salt.

Due to the inevitable use of the molten salt, the number density of the precipitated Ti particles is low, particularly in the molten salt of the low Ti^{2+} concentration. The collision rate becomes lower, and the aggregation of particles is suppressed even in the stirred salt. In the Ti^{2+} rich molten salt, the Ti particles have precipitated at the initial stage of reduction (for example, for 0.3 ks at 1173 K), and they may absorb the fine particles that were formed at the final stage.

It was reported in the Kroll process that the residual magnesium physically attaches to the precipitated Ti particles

and that the attached Mg layer enhances the coarsening and agglomeration to Ti sponge.[30,31] The characteristic morphology in the Kroll process, *i.e.*, the aggregated and strongly sintered Ti particles of a few tens of microns, however, was hardly observed in this work. It is suggested that the generated Ti particles sank in our molten salt without the further contact with Mg. This may be one of the reasons why the obtained particles were well isolated.

For use in powder metallurgy, fine powder with a weak size distribution is required. The suitable size is dependent on the final product and is usually said to be several tens of microns. The existence of the fine particles smaller than 10 μm might be uncomfortable for this purpose. Therefore, the result in the salt containing 41.2 mass pct $MgCl_2$ shows that the concentration control for the solvent salt is indispensable to produce the larger particles in a homogeneous quality.

Considering that the industrial $MgCl_2$ salt in the Kroll process contains a high content of LiCl, KCl, NaCl, *etc.* for better efficiency in electrolysis, we may find the nice molten salt suitable both for the large Ti powder production and for the good $MgCl_2$ electrolysis.

The fact that the reduction from Ti^{2+} in the salt was completed in a short time shows that the growth mechanism is a key to obtaining powder suitable for powder metallurgy. A further approach will be needed to grow the fine powder to adjust to the demand of powder metallurgy.

VI. CONCLUSIONS

A process was proposed to produce titanium powder in two steps using $TiCl_4$ and magnesium. In the first step, $TiCl_4$ dissolves once in the molten salt as Ti^{2+}, where either a half amount of the reductant Mg or a part of the final product

Ti is used to convert $TICl_4$ into Ti^{2+}. In the second step, Mg reduction of Ti^{2+} in the molten salt precipitates the fine Ti powder.

The powder morphology was experimentally studied under this concept. The reduction finished within 0.3 ks at 1173 K, and the successive holding in the salt grew the particles. The powder size depended on the initial Ti^{2+} concentration, temperature, holding time, and concentration of by-product $MgCl_2$. Stirring of the molten salt was enhanced to produce the round and well-isolated particles of a few tens of microns, which is suitable for powder metallurgy.

This process can produce the titanium powder in the shorter steps compared with the other methods, such as HDH and PREP. The industrial application of this proposal seems technically possible, when the additional method to separate Ti powder from the molten salt is developed.

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