

Titanium Powder Preparation by Mg Reduction of Titanium Chlorides in the Molten Salt

R. O. Suzuki, T. N. Deura, M. Wakino, T. Matsunaga,

T. N. Harada, R. Ishii and K. Ono

*Department of Energy Science and Technology,
Kyoto Univ., Kyoto 606-8501 Japan*

Abstract

Two processes are proposed to produce Ti powder directly from TiCl_4 gas using molten magnesium as reductant. Comparing with the conventional Kroll process, the heterogeneous nucleation and its growth to the aggregates were commonly minimized and the well-isolated fine particles were obtained.

TiCl_4 gas injection into molten chloride salts, on which a liquid Mg layer was floated, produced the Ti powder of 1 to 10 μm in diameter. Neither the operation temperature nor the salt composition affected the powder morphology.

However, it was changed when the reduction was separated into two steps: TiCl_4 dissolves once in the molten salt as Ti^{2+} , and this Ti^{2+} in the molten salt was successively but separately reduced by Mg. The Ti morphology varied from the needle-like to the round shape by rising the reduction temperature. The powder size depended on the initial Ti^{2+} concentration, temperature, holding time, stirring, and concentration of by-product MgCl_2 . The reaction to metallic state finished in a short time, and the successive holding in the salt grew the particles.

1. Introduction

Previous studies on continuous Ti reduction are classified roughly into two categories; those on electrolysis of Ti-containing molten salts and those on pyrometallurgical processes [1,2]. Serious problems in electrolysis include the morphology control of Ti deposits and the low current efficiency caused by multivalent Ti ions. Pyrometallurgical processes to produce Ti liquid also have difficulties for industrial application because of high chemical reactivity of molten Ti with the reactor materials. Therefore, only two processes have been applied industrially; the Kroll process and Hunter process. Both are batch-type operations.

In a modification of Hunter process (sodium reduction of TiCl_4), 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 as "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]. Currently in Japan, the industrial operation of Hunter process is interrupted, in spite of the strong demand of Ti fine powder with a reasonable price.

The Kroll process is based on the chemical reaction of TiCl_4 reduction by liquid metallic magnesium [5,6]. Liquid TiCl_4 is dropped onto the Mg molten surface in a sealed vessel, as illustrated in **Figure 1** (a). Metallic titanium is produced as,



at around 1173K in an Ar gas atmosphere. Porous aggregates known as "Sponge Titanium" form in a vessel of stainless steel or mild steel. Sponge titanium consists of tightly connected Ti particles about 10 μm in size, as shown in **Figure 2** (b). The by-product, MgCl_2 , and the residual reductant, Mg, are contained in the fine porosity inside this sponge titanium, and removed after reduction by evacuation at 1273K for a few days. During MgCl_2 separation, however, the particles are firmly sintered in 20 to 100 μm in size, as shown in **Figure 2** (a), and they could not be pulverized mechanically.

An explanation of reduction mechanism and particle growth in the Kroll process has been accepted as shown in **Figure 3** [7,8]. The residual Mg covers the Ti surface precipitated freshly. The supplied TiCl_4 gas successively reacts with the Mg layer attached on Ti surface, accompanying with the heterogeneous nucleation. "Sponge" titanium is thus hard-sintered and adhered to the vessel. Therefore, accompanying with the sintering problem during MgCl_2 separation, it is difficult for the Kroll process to produce Ti fine particles well separated from the others.

Another problem with the Kroll process is the costly and time-consuming batch operation for the reduction of TiCl_4 and the separation of MgCl_2 . An important advantage, however, is that the combination of chlorination of TiO_2 and the successive TiCl_4 distillation allow one to

remove many metallic impurities in addition to oxygen [9] prior to the reduction to metallic Ti. We hope to utilize this distilled TiCl_4 as the starting material for reduction, in the design of an alternative Ti production process.

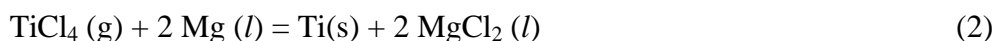
The purpose of this work is to propose an alternative continuous reduction process for the mass production of titanium, and to examine experimentally the fundamental behavior of the chemical reaction. We are interested in whether Ti is suitable for the continuous operation and for powder metallurgy.

Some new production processes such as Hydride-DeHydride (HDH), gas atomizing and Plasma Rotating Electrode Process (PREP) are applied for Ti powder suitable to powder metallurgy [10]. However, these processes do not satisfy the reasonable price, fundamentally because they need the pre-cast Ti ingot or compact as the starting material. To exclude the extra cost for ingot making, a specialized powder production directly from its chloride looks promising [11].

2. A new concept of Ti reduction by Mg layer on the molten salt

The concept behind the process we propose is presented in **Figure 4** [11]. In common with Kroll process, magnesium is utilized as the reductant and distilled TiCl_4 as the intermediate product. However, there are two characteristic differences between this and the Kroll process. The first is that the reductant, Mg, is spatially separated from the product, Ti, by molten MgCl_2 , and the second, that TiCl_4 gas reacts at the interface between Mg and MgCl_2 . Note that liquid TiCl_4 is injected on top of the Mg for the Kroll process (Figure 1).

Both Mg and MgCl_2 are initially melted in a vessel before reduction. Because these two have little mutual solubility at 1173K [12], they separate chemically into two melts. The lighter magnesium melt physically floats on the molten MgCl_2 , because of specific gravity difference. When we inject the gaseous TiCl_4 into MgCl_2 melt from the bottom of the vessel, TiCl_4 bubbles rise through the MgCl_2 melt to the Mg layer. At the interface between MgCl_2 and Mg melts, titanium is produced by the following chemical reaction,



The titanium product settles through the MgCl_2 melt also due to specific gravity difference, and piles up at the bottom of the vessel. These Ti precipitates can be taken out continuously from the vessel, because the strong reductant magnesium is well separated by the MgCl_2 melt and because Ti solid precipitates are not as chemically reactive as the molten titanium.

The merits of this proposal can be summarized as follows. Firstly, continuous reduction is possible. Secondly, the industrial cost of using this process to replace the Kroll method is expected to be less than for other proposals, because the starting materials are the same. Thirdly, the reaction mechanism can be limited to a gas-liquid reaction between $\text{TiCl}_4(\text{g})$ and $\text{Mg}(\text{l})$ at their interface. This leads to a homogeneous precipitation and morphology of the

product. It is well known that particle morphology with the Kroll process depends on the location of the chemical reaction, because the gas-liquid, gas-gas and liquid-liquid reactions between TiCl_4 and Mg occur simultaneously [13].

3. Experimental procedure for reduction by Mg layer

A schematic illustration of the experimental apparatus is shown in **Figure 5**. The reduction experiments were conducted in a columnar vessel purged by Ar gas. Pure MgO or Al_2O_3 served as the material for the crucible and the lance. The gas outlet was connected to a water trap for the capture of residual TiCl_4 gas.

After confirming that about 150g MgCl_2 melted in the crucible, the lance was immersed into MgCl_2 . About 30g metallic Mg was then charged onto the upper surface of the MgCl_2 using the feeding Mg blocks. When all the Mg blocks charged were completely melted as a layer on the MgCl_2 melt, Ar carried the gaseous TiCl_4 into the vessel. When the molten salt is heavily stirred by gas injection, the magnesium melt is suspended in the MgCl_2 melt.

The extraction of the product from the crucible was not attempted here during TiCl_4 gas injection. After cooling, the residual magnesium and MgCl_2 were removed with water, acetic acid aqueous solution and dilute hydrochloric acid solution. In some cases, CaCl_2 or MgCl_2 -47.2mol% CaCl_2 was used for the molten salt as an alternative to pure MgCl_2 .

4. Results and discussion of Ti reduction by Mg layer

4.1 *Ti powder preparation*

The injected TiCl_4 gas was bubbled through the molten MgCl_2 with an accompanying flash in the Mg layer, indicating a rapid and exothermic reaction between TiCl_4 and Mg. A faint amount of TiCl_4 was detected at the gas outlet. This shows that a small portion of TiCl_4 gas remained even after passing through a Mg layer only tens of mm thick.

After cooling, the solidified salt was white. This shows that it contained no titanium chlorides. The solidified Mg adhered to the upper part of the crucible surface, when the Al_2O_3 crucible and the MgO lance were used. The surface of the ceramic crucible was slightly roughened by melting MgCl_2 . Metallic powder was taken out from the bottom of the crucible. The metallic powder was so brittle that the sinter was easily crushed by ultrasonic vibration for cleaning. EDX and XRD analysis showed all the powder obtained in the range of 1023K to 1273K was metallic α -titanium.

4.2 Powder morphology

SEM images of the powder are shown in **Figure 6**. The round particle size distributed in the range of 1 to 8 μm for all the experiments above 1123K, and no morphological change was recognized at these higher temperatures. The powder obtained at 1023K was, however, about 1 μm in size at most.

The morphology did not change at 1123K for 1.8ks when the TiCl_4 gas injection rate was varied from 2.5 to 8.3mg/s (0.15 to 0.5g/min.). No clear relationship was observed between the total amount of TiCl_4 gas and the particle size. Namely, the size and its distribution were almost constant. Considering the total volume of TiCl_4 gas injected and the recovery of Ti powder, the yield of Ti powder was calculated as about 80% when the Mg layer was a few ten mm thick, and as a few ten % when a few mm thick.

Note that all the Ti particles contained some cracks, as shown in Figure 6. These cracks were also found in the Ti commercial powder (-325mesh) when it was independently heated at 1123K in pure molten MgCl_2 , while no crack was found in the Ti powder heated in the Ar gas atmosphere. The oxygen content of the commercial powder was increased from 0.65 to 1.5 mass% after soaking in MgCl_2 [11] The mechanism of crack initiation would be closely related with the presence of oxygen in the molten salt. The oxygen contained in the salt is absorbed into Ti particles and makes them brittle. The oxygen concentration in the powder produced in this study was in the range 0.54 to 2.3 mass%. Oxygen contamination could be reduced by purifying the molten salt in advance or by scaling up the experimental apparatus.

The titanium prepared by injection of TiCl_4 into molten salt was mainly a fine powder of 1 to 10 μm in size, although these experiments were conducted using the same reductant and feed material as for the Kroll process. The applied temperature range was also the same. As shown in Figure 2, the particles produced by the Kroll process were similar in size, although firmly sintered. A fine particle formation may be essential in the chemical reaction with Mg and TiCl_4 .

4.3 Choice of molten salts

Sodium chloride (NaCl) is often used for molten salt chemistry [14]. Molten NaCl , however, floats on molten Mg due to the specific gravity change. This spatial separation of the two liquid phases is not desired for the purpose of this study. When pure CaCl_2 or the eutectic MgCl_2 -47.2mol% CaCl_2 was used as the molten salt, a separate reductant Mg liquid layer floating on the salt was observed. These salts are also thermodynamically more stable than MgCl_2 , and thus are not reduced by Mg.

When pure CaCl_2 or the eutectic MgCl_2 -47.2mol% CaCl_2 was used at 1123K, Ti powder or its aggregates were also obtained, about 1 to 8 μm in size, as shown in **Figure 7**. No morphological change among these two molten salts and pure MgCl_2 salt was noticed on SEM observation. It is clear that, even pure CaCl_2 applied as the initial salt becomes chloride

mixture during TiCl_4 reduction because MgCl_2 is the by-product. Note that, in surface tension and viscosity, the molten salts differ from MgCl_2 . The result that other chlorides such as CaCl_2 in MgCl_2 were not sensitive for homogeneous powder production may give us flexibility in selecting the composition of molten salt. The by-product MgCl_2 in the industrial reactor was recycled to reductant magnesium by MgCl_2 electrolysis. For better electrolysis, a mixture of MgCl_2 , NaCl , CaCl_2 , KCl , and/or some fluorides was used in the industrial process [15]. This complex salt mixture is expected not to influence the morphology of the Ti powder produced by the process proposed in this study.

4.4 Mechanism of powder formation

With the proposed process, we expected that the injected TiCl_4 is reduced in the Mg layer. Titanium precipitates at the interface between injected TiCl_4 bubble and liquid Mg as illustrated in **Figure 8**. When TiCl_4 gas in the bubble is reduced during the ascent of the bubble through the Mg layer, the Ti particles initiate and become coarse in size. When TiCl_4 is completely consumed, these Ti particles sink to the bottom of the vessel. The Ti particles piled up on the bottom are isolated from the region where the reduction of TiCl_4 takes place. Additional growth of individual particles does not occur at the bottom because there is no supply of TiCl_4 and Mg toward the particle surface. Namely, the molten MgCl_2 acts as "a separator" of Mg and the produced titanium. Titanium particles accumulated on the bottom may sinter slightly by self-weight at the reduction temperature, but not as much as the commercial Ti sponge. This mechanism well explains the morphology of our fine Ti powder and the steady homogeneous powder formation.

5. Possible reduction from lower chlorides dissolved in molten salt

Because the solubilities of TiCl_4 in the chloride salts are only a few mass% as listed in **Table 1**, we had considered that a large amount of the supplied TiCl_4 could not dissolve in the salt and should be reduced mostly in the molten Mg layer. The total chemical reaction can be indeed written as Eq. (2), but the elementary reactions contained in Eq. (1) may be more complex, because the lower chlorides such as TiCl_3 and TiCl_2 can contribute. In case of direct contact with TiCl_4 and Mg, these lower chlorides can be easily reduced to metallic state, and no detailed reports were found on their existence in Kroll process.

However, as shown in Table 1, the solubilities of Ti^{3+} and Ti^{2+} in the molten salts 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. When the molten salt containing these lower chlorides contacts directly with the reductant Mg, we can not confirm their existence, because they are easily reduced to metallic titanium by Mg. The Mg solubilities in these molten salts are as small as 0.3 mol%, whereas the Na solubility in NaCl is about 3 mol% [12,16]. In addition to the small solubility, it is reported that the dissolution of Mg into

the salt was slow [17]. We assume, therefore, that TiCl_4 can be partially reduced to a lower chloride, but that it takes longer time to reduce it to the metallic state.

Here we will discuss such possible route of Ti reduction in the molten salt. To clarify the possibility that TiCl_4 is reduced to the lower titanium chlorides in the molten salt and that they are reduced to metallic titanium in the Mg layer, we separate the reduction in two steps, as shown in Figure 1 (c).

At 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.



The formed TiCl_2 and MgCl_2 can not completely mix in a homogenous liquid written as MgCl_2 - 50 mol% TiCl_2 , because the solubility of TiCl_2 in MgCl_2 is 35 mol% at 1173 K [18]. In the Hunter method, the formed TiCl_2 produces the salt mixture of NaCl - 33 mol% TiCl_2 by the following reaction,



because the solubility of TiCl_2 in NaCl is 44 mol% at 1123 K, and 52 mol% at 1173 K [19].

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 [11]. The alkaline and alkaline-earth chlorides are here studied.

Because of the difference of specific gravity between Mg and the molten salt, the lighter Mg floats above the heavier salt [11]. When TiCl_4 is fed to the upper surface of the molten Mg layer, the spatial arrangement for the reduction becomes similar with the Kroll process (Figure 1 (a)). Therefore TiCl_4 will be fed from the bottom of the molten Mg layer like 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,



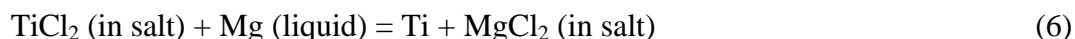
instead of the industrial reactions (3) and (4). Ti^{2+} is more stable oxidation state than Ti^{3+} when they coexist with metallic Ti in the molten chlorides [20-22].

6. A concept of continuous stepwise reduction

Figure 9 shows the conceptual view of Ti production using Eq. (5). 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. (6) causes the nucleation in the salt,



Because of density difference, the reductant Mg floats on the molten salt as shown in Figure 9, and the precipitated Ti will settle on the bottom of the reaction vessel. In Figure 9, the Ti product will be extracted and the molten salt containing Ti can be partially returned as the salt for the reaction (6). The another 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.

The latter half of 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 9), the individual steps are here studied in the separated experiments [23].

7. Experimental Procedure for two step reduction

7.1 Preparation of molten salt

The molten salts dissolving Ti^{2+} were prepared using the experimental apparatus shown in **Figure 10**. LiCl, KCl, NaCl and MgCl_2 were mixed in 150 - 200g. About 8g sponge Ti was set with the mixed chlorides in the Al_2O_3 crucible. After melting the salt, MgO lance was immersed to contact titanium sponge, and 25 or 50g of TiCl_4 liquid was fed at the constant rate of 3.3mg/s. After the feed at 1173 K, the salt was once solidified in the furnace, and taken off from the crucible. The Ti concentration of the solidified salt was analyzed using ICP-AES.

7.2 Mg reduction of molten salt

The molten salt thus produced was again filled in the Al_2O_3 crucible and melted using the experimental apparatus shown in **Figure 11**. About 20g Mg blocks were quietly charged and melted on the molten salt. Ar gas was bubbled in the salt through the MgO lance when the stirring was needed. The solidified salt was leached by water and the dilute acetic acid solution. The powder was rinsed in water, alcohol and acetone in that order, and served to chemical and metallographic analysis.

8. Results of two step reduction

8.1 Molten salt containing Ti^{2+}

The vibration of MgO lance indicated that the supplied liquid $TiCl_4$ was evaporated inside the lance (the boiling points 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. After solidification, the salts were usually dark green as listed in **Table 2**. A large amount of Ti sponge was consumed during $TiCl_4$ feed. The residual Ti sponge was brittle and easily broken into small pieces. Its fine particles dispersed in the salt. The analyzed Ti concentrations, C_{Ti} , were listed in **Table 2**. C_{Ti} exceeded the equilibrium solubility of $TiCl_4$ at 1173 K (**Table 1**).

Because the valence analysis of titanium in the salt using H_2 gas evolution [22] 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 was deduced [23]. Although a large amount of $TiCl_4$ gas was exhausted out, the chemical species dissolved in the salt was judged to be mostly at the oxidation state II, namely Ti^{2+} . Based on the previous studies [21,22,24], we assume that Ti(II) is the main oxidation state when the metallic Ti coexisted with its chlorides.

8.2 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. It 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 - 20 g, the yields were calculated to be roughly 85 - 90%, 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 3** summarizes the experimental conditions and the powder morphology.

(1) Effects of Stirring and Reduction Temperature

Using LiCl-KCl eutectic salt containing 5.7 mass%Ti, the effects of stirring and reduction temperature on morphology were shown in **Figure 12**. 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. When Ar gas was bubbled, no rods was found, and only the round particles with smooth surface was recovered. The diameter of their particles was larger at 1173 K. At 973 K the finer particles of 1 - 5 μm were aggregated.

(2) Effect of Titanium Concentration

Figure 12 (c) and **Figure 13** 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%Ti were smaller than the others. Even when the titanium content in the salt was diluted, the effect of stirring on powder shape was similar. The narrow rods were found when no stirring.

(3) Effect of Time

Using the salt containing 5.7 mass%Ti, the effect of holding time on morphology was studied at 1173 K with stirring as shown in Figure 12 (c) and **Figure 14**. Under these conditions, the rod-like powder was not formed. 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 10-30 μm after 21.6 ks, and of >50 μm after 86.4 ks.

(4) Effect of Salts

Other 4 molten salts were studied as listed in Table 3 and the morphology of Ti particles are shown in **Figure 15**. Powder morphology obtained in the NaCl-KCl eutectic salt (Figure 15 (c)) was similar with that in LiCl-KCl (Figure 12 (c)), although Ti^{2+} in the Li-containing salt is more stable than that in NaCl-KCl [24]. Those in the salts containing MgCl_2 were the mixtures of two types: One was the large round particle of tens μm with smooth surface similar as in LiCl-KCl, and the another was the finer round particle of 1-5 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 be soon contaminated in the progress of reduction. In this work, the final increase of MgCl_2 concentration was less than 20 mass% MgCl_2 even at the salt with the highest Ti^{2+} concentration.

9. Precipitation from Ti^{2+} in the molten salt

Because Ti^{3+} becomes more stable at low temperatures [24], the oxidation state of titanium may affect nucleation. However, once the metallic Ti is formed, the disproportionation reaction to form Ti^{2+} occur [22] and Ti^{2+} becomes the main oxidation state.

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 16 (a)**, the Ti nodules, rods or dendrites grow from the bottom part of molten Mg layer, depending on the 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 16 (b)**), the strong stirring disperse mechanically the Mg droplets into the salt such as 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 to form the long 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 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 μ m/s for 50, 10 and 1 μ m particles, respectively, applying the Stokes law to Ti particles in MgCl₂ [25,26]. 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 Ti²⁺ concentration. The collision rate becomes lower, and the aggregation of particles is suppressed even in the stirred salt. In the Ti²⁺ 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, as illustrated in Figure 3, 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 [7,8]. The characteristic morphology in the Kroll process, i.e., the aggregated and strongly sintered Ti particles of few ten μ m, 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 usually said to be several tens μ m. The existence of the fine particles smaller than 10 μ m might be uncomfortable for this purpose. Therefore, the result in the salt containing 41.2 mass%MgCl₂ shows that the concentration control for the solvent salt is indispensable to produce the larger particles in a homogeneous quality.

Considering that the industrial MgCl₂ salt in the Kroll process contains a high content of LiCl, KCl, NaCl etc. for the better efficiency in the 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 completed in a short time shows the growth mechanism is a key to obtain the powder suitable for powder metallurgy.

10. Conclusion

TiCl_4 gas injection into molten chloride salts, on which a liquid Mg layer was floated, is proposed to recover Ti particles separated from Mg. The Ti powder thus obtained consisted of fine particles of 1 to 10 μm in diameter. Neither the operation temperature nor the composition of the salt affected the powder morphology [11].

As an modification of this process, and for the detailed analysis of the above proposal, two step reduction is also proposed. 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 [23].

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.

At present, titanium powder is produced industrially either by Hydride-DeHydride process (HDH), gas atomizing process or Plasma Rotating Electrode Process (PREP). All three methods utilize the titanium sponge as starting material and, therefore, their powders are expensive. Our two proposals are alternative processes for producing powder that can serve as the raw material for powder metallurgy at lower cost. A further approach will be needed to grow the fine powder to adjust to the demand of powder metallurgy.

11. Acknowledgments

The authors thank T. Unesaki, I. Nakagawa and M. Hamura for SEM-EDX and ICP-AES analysis, K. Hashimura and T. Yamaguchi for experimental assistance, Dr. T.H. Okabe at Tohoku Univ. and Dr. T. Irie formally at Toho Titanium Co., Ltd. for stimulating discussions. Financial support came partially from Grant-in-Aid for Scientific Research under Contract No. 10355031.

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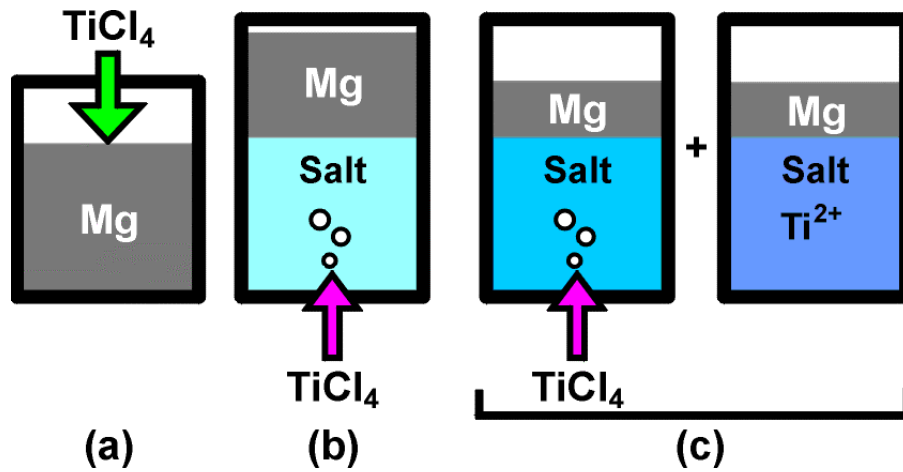
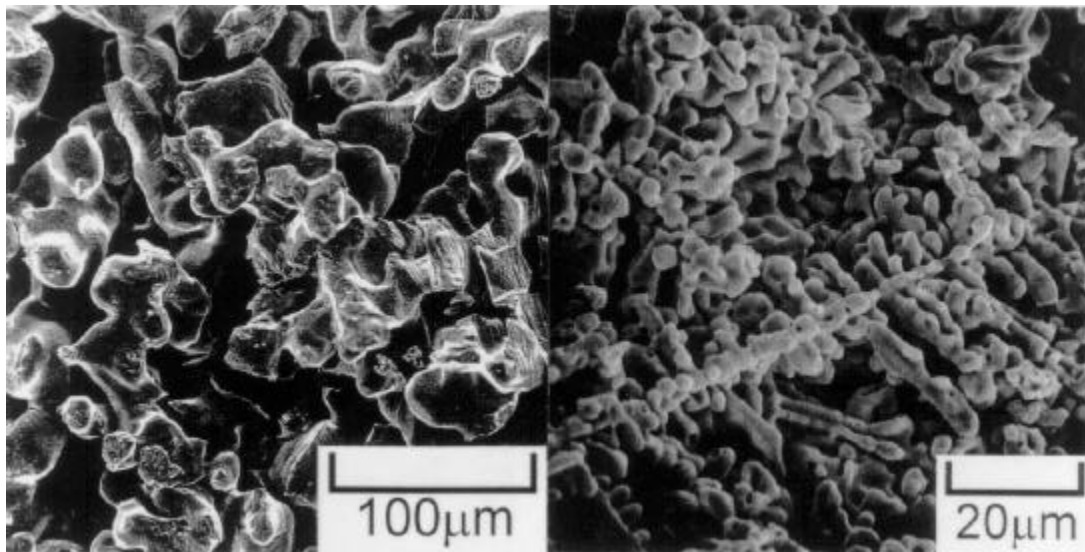


Figure 1: Concepts of Ti production by Mg reduction. (a) TiCl_4 gas feed into molten Mg (Kroll process), (b) TiCl_4 gas feed to bottom of Mg layer through the molten salt, and (c) combined process with TiCl_4 gas feed for Ti^{2+} formation and metallic Ti formation from its molten salt.



(a)

(b)

Figure 2: SEM images of the sponge titanium produced by the conventional Kroll process in (a) 8 ton and (b) 20 g batches.

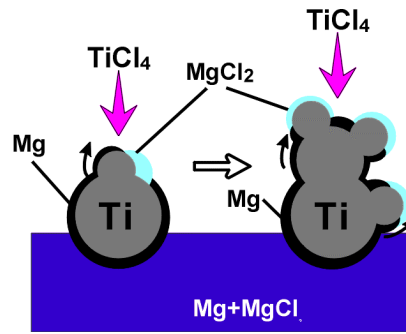


Figure 3: Heterogeneous growth of Ti particles when the reductant Mg surrounds the initial Ti nucleus [7].

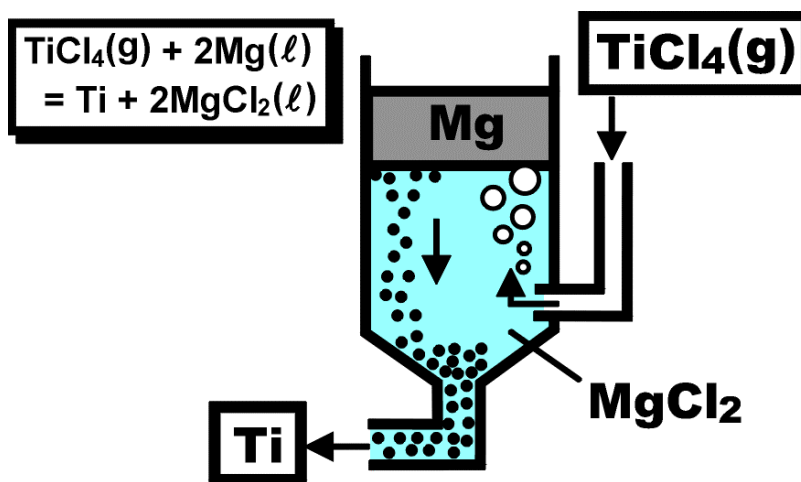


Figure 4: A conceptual process of continuous titanium production.

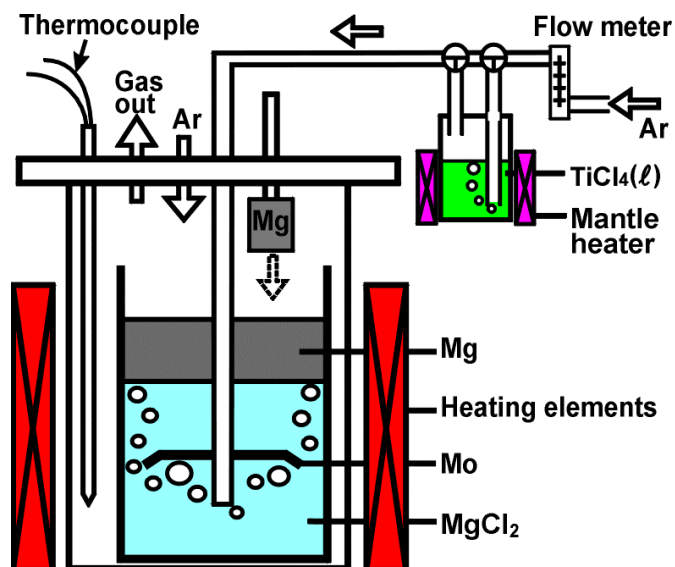


Figure 5: Experimental apparatus for TiCl₄ injection.

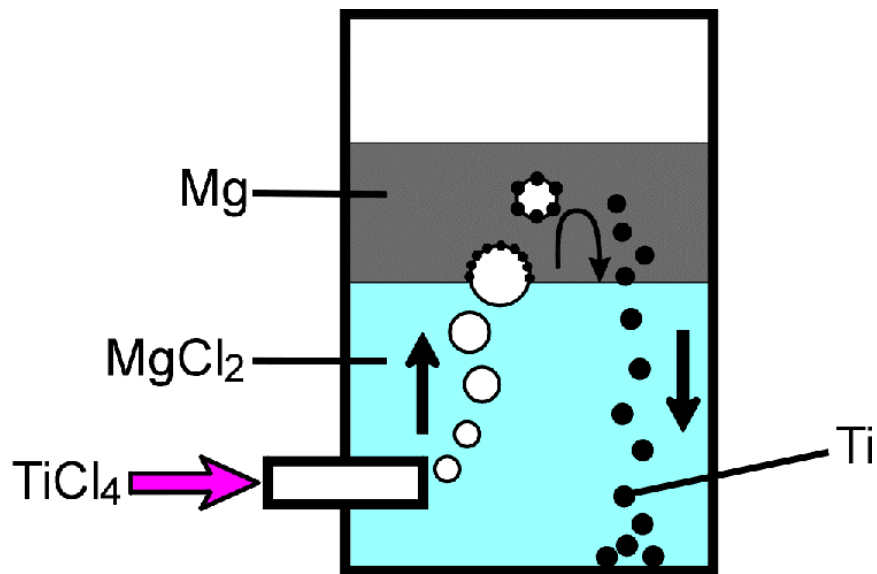
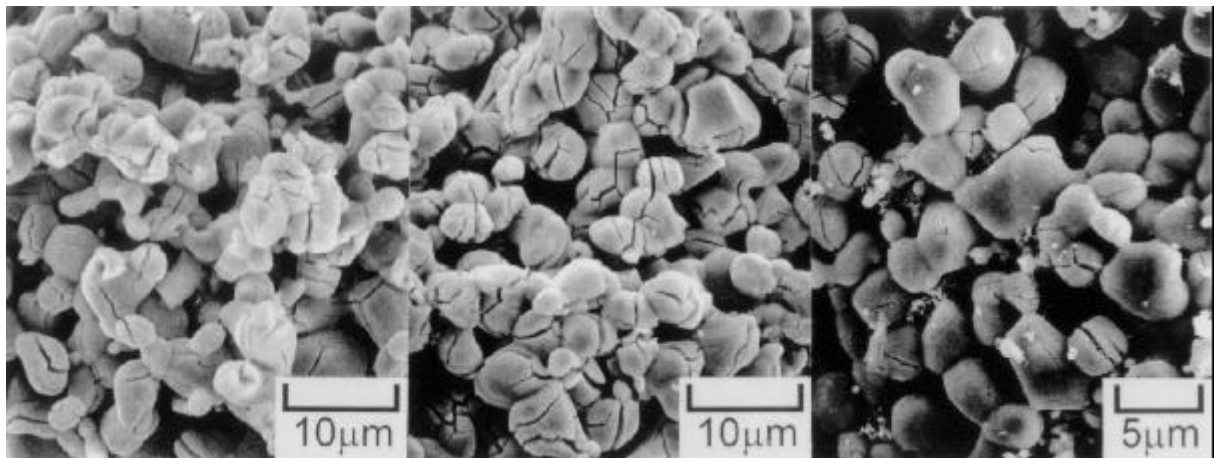


Figure 6: SEM image of Ti powder produced by TiCl_4 injection into a Mg-MgCl₂ bath.



(a)

(b)

(c)

Figure 7: SEM images of Ti powders produced at 1123 K by TiCl_4 injection into the salts. (a) MgCl_2 , (b) MgCl_2 -47.2 mol% CaCl_2 (eutectic composition), and (c) CaCl_2 .

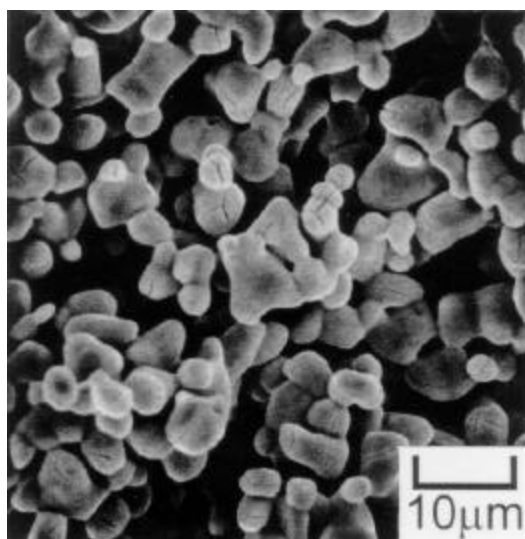


Figure 8: Schematic illustration for Ti growth with the proposed process. The injected TiCl_4 gas arrives at the interface of Mg layer, where the reduction starts. The precipitated Ti particles grow in the Mg layer, and sink downward through the MgCl_2 molten salt.

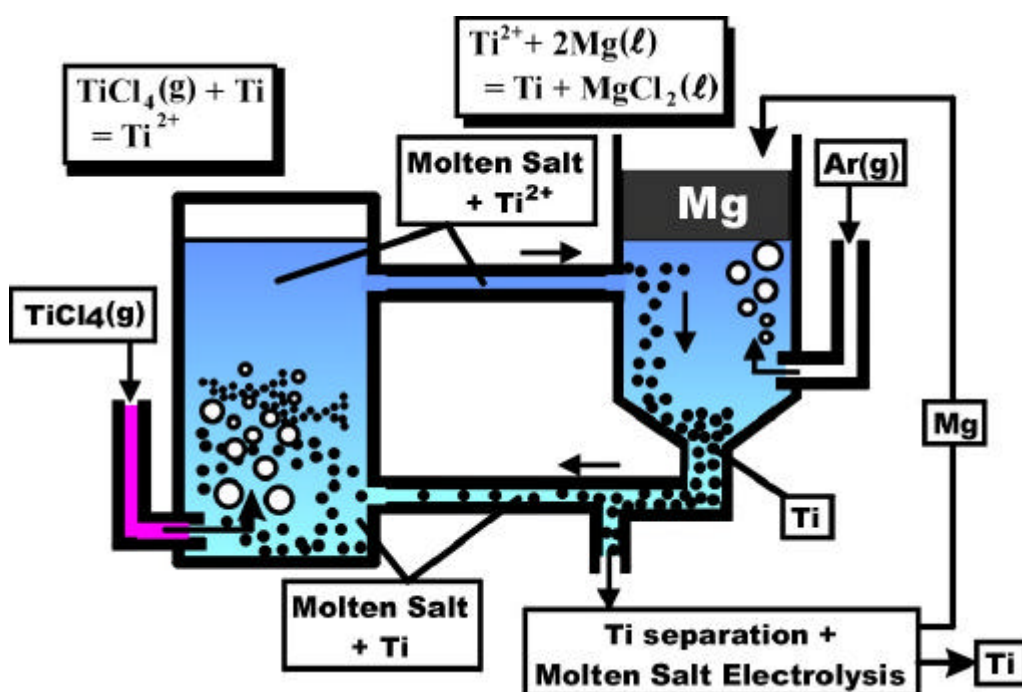


Figure 9: Concept of continuous Ti powder production using the recycled Ti to produce the molten salt containing Ti^{2+} .

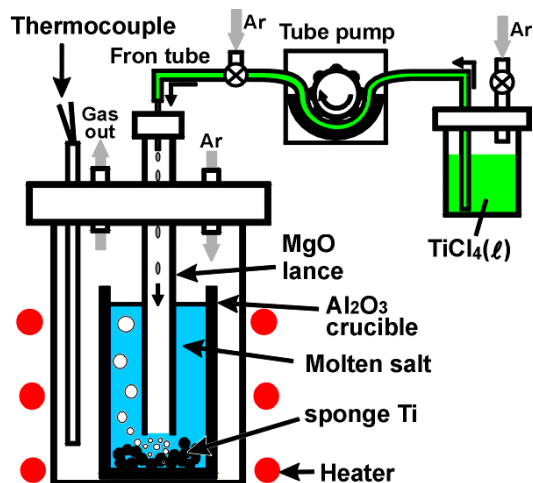


Figure 10: Schematic illustration of experimental apparatus to prepare the molten salt containing Ti^{2+} .

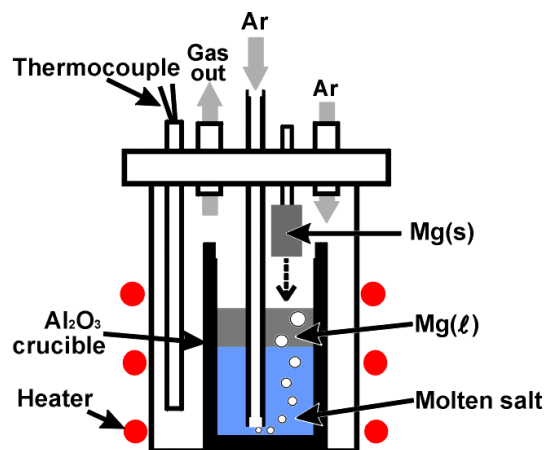


Figure 11: Schematic illustration of experimental apparatus to reduce Ti^{2+} in the molten salt.

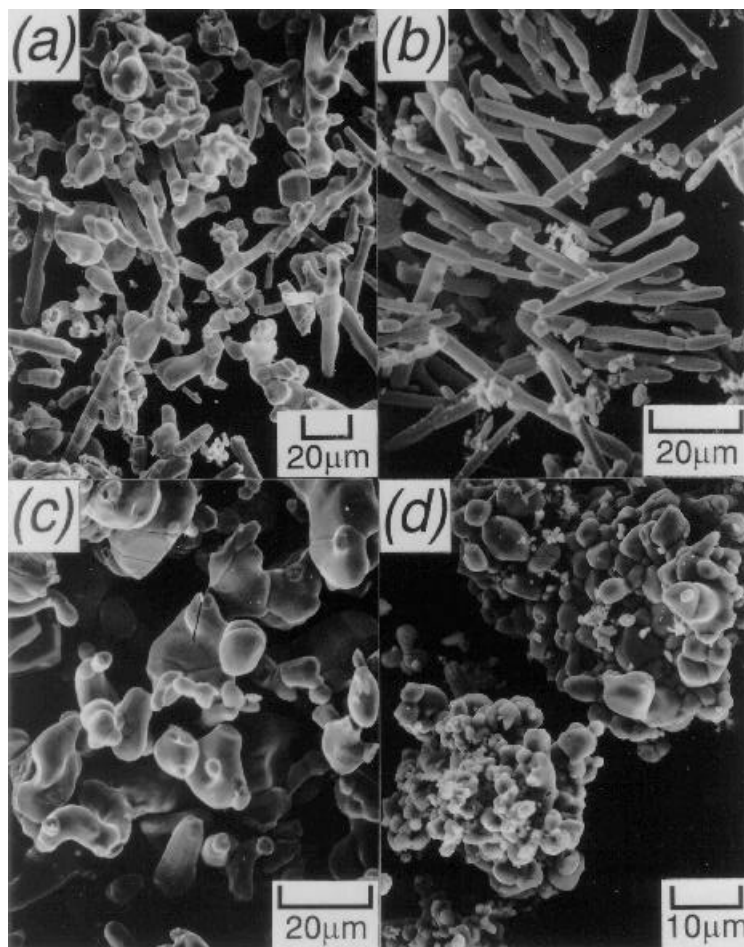


Figure 12: SEM images of Ti powder obtained from the LiCl-KCl eutectic salts containing 5 mass% Ti after treating for 21.6 ks. The Ar gas was not introduced (a) at 1173 K and (b) at 973 K, and it was bubbled (c) at 1173 K and (d) at 973 K.

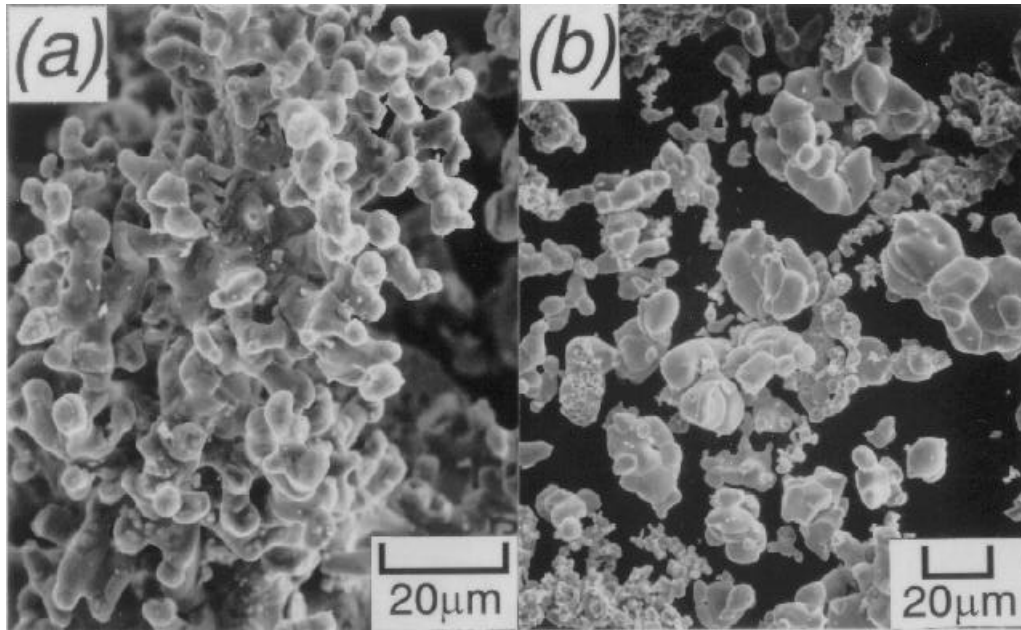


Figure 13: SEM images of Ti powder obtained from the LiCl-KCl eutectic salts containing at 1173 K for 21.6 ks. The concentration in the salt was (a) 1.43 mass% and (b) 10.4 mass%Ti.

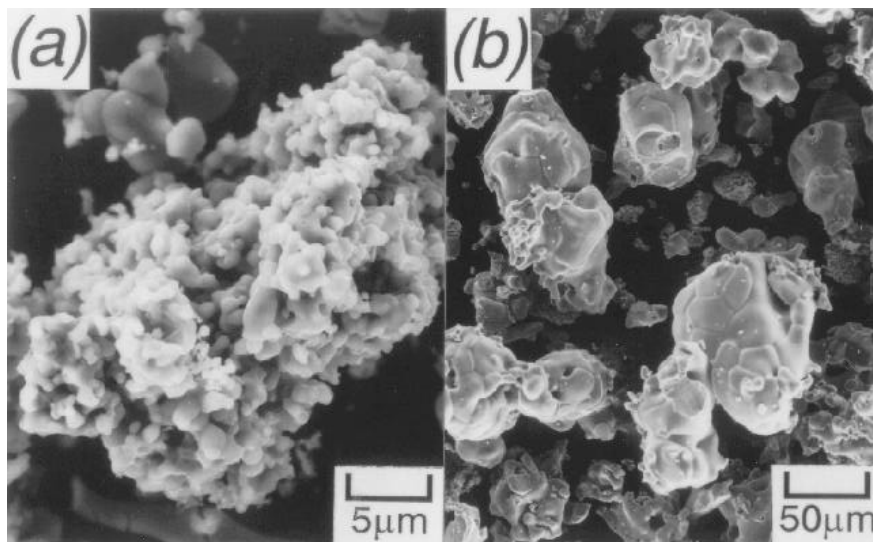


Figure 14: SEM images of Ti powder obtained from the LiCl-KCl eutectic salts containing 5 mass% Ti at 1173 K. The reaction time was (a) 0.3 ks and (b) 86.4 ks.

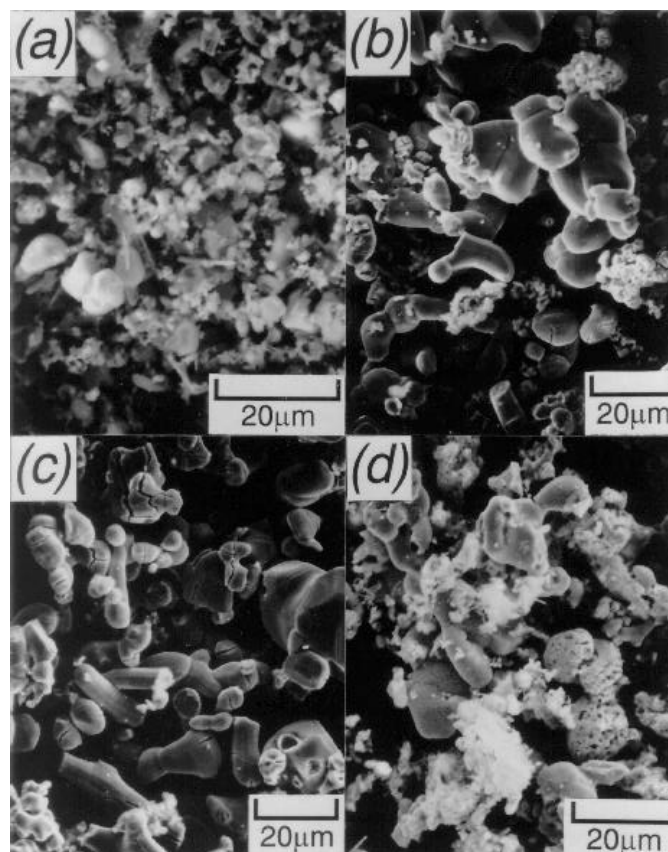


Figure 15: SEM images of Ti powder obtained from the molten salts containing 5 mass% Ti at 1173 K for 21.6 ks. (a) MgCl_2 , (b) NaCl , (c) NaCl-KCl and (d) $\text{MgCl}_2\text{-LiCl-KCl}$.

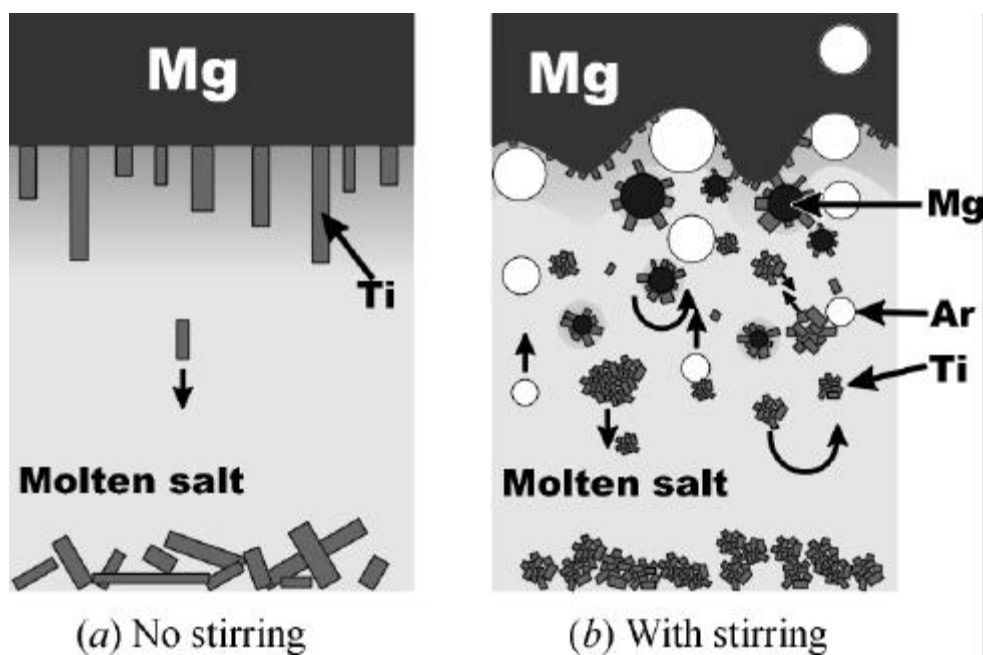


Figure 16: Growth of Ti particles in the molten salt containing Ti^{2+} :
(a) no stirring and (b) with stirring.

Table 1: Solubility of titanium chlorides in the molten salts summarized in [23].

Molten salt	Melting point (K)	Solubility at 1173 K (mass%)		
		TiCl ₄	TiCl ₃	TiCl ₂
MgCl ₂	987	1.5 ^a		40
NaCl	1073	1.2 ^a 4.1 ^b	>60	69
NaCl-50 mol% KCl (eutectic composition)	930	5.8 ^a	>37	35
LiCl-41 mol% KCl (eutectic composition)	625	4.8 ^d 3.4 ^e		
MgCl ₂ -34.7 mol% LiCl -24.1 mol% KCl	<943			

a : Extrapolated to 0.1 MPa TiCl₄ from reported data. b : At 1073 K under 88 kPa TiCl₄.

c : At 903 K. d : At 765 K. e : At 763 K under 97 kPa TiCl₄.

Table 2: Titanium concentration in the molten salts after feeding 25 g of TiCl₄.

Molten salt (Before feed)	Color after feed	Titanium content, C _{Ti} (mass%)	Yield (%)	
			As TiCl ₂	As TiCl ₃
MgCl ₂	Black Green	3.48	40.5	62.7
MgCl ₂	Dark Green	10.5 *	91.2	152.8
NaCl	Dark Green	4.00	73.8	114.4
NaCl-50 mol% KCl (eutectic composition)	Emerald Green	3.00	54.3	83.6
LiCl-41 mol% KCl (eutectic composition)	Dark Green	5.70	57.2	90.3
LiCl-41 mol% KCl (eutectic composition)	Dark Green	10.4 *	82.7	138.4
MgCl ₂ -34.7 mol% LiCl -24.1 mol% KCl	Black Green	2.79	41.3	63.4

* 50g of TiCl₄ were supplied.

Table 3: Impurity concentration and morphology of titanium Powder

No.	Experimental conditions					Impurity in the Ti powder			
	Used salt	Temperature (K)	Time (ks)	Titanium Concentration (mass%)	Ar gas bubbling	Oxygen (mass%)	Nitrogen (mass%)	Al (mass%)	Morphology of the Ti powder
1-(1)	LiCl-KCl	1173	21.6	5.70	none	2.47	-	0.92	granular (10-30mm) and rod (20-60mm long, 5-10mm ϕ)
1-(2)	LiCl-KCl	973	21.6	5.70	none	1.60	0.39	0.27	rod (5-10mmf long, 3-5mm ϕ) and dendrites
1-(3)	LiCl-KCl	1173	21.6	5.70	bubbling	1.94	0.68	2.40	granular (10-30mm)
1-(4)	LiCl-KCl	973	21.6	5.70	bubbling	1.86	0.61	0.55	granular (1-5mm)
2-(1)	LiCl-KCl	1173	21.6	1.43	none	2.17	0.32	3.75	rod (20-40mmf long, 5-10mm ϕ)
2-(2)	LiCl-KCl	1173	21.6	1.43	bubbling	3.16	0.79	5.11	granular (1-5mm)
2-(3)	LiCl-KCl	1173	21.6	10.4	bubbling	1.83	0.41	-	granular (5-30mm)
3-(1)	LiCl-KCl	1173	0.30	5.70	bubbling	3.40	-	1.46	granular (<1mm)
3-(2)	LiCl-KCl	1173	86.4	5.70	bubbling	3.35	-	2.86	granular (50-100mm)
4-(1)	NaCl-KCl	1173	21.6	3.00	bubbling	2.21	0.49	1.34	granular (5-30mm)
4-(2)	NaCl	1173	21.6	4.00	bubbling	2.23	0.43	1.55	granular (5-30mm)
4-(3)	MgCl ₂	1173	21.6	3.48	bubbling	-	-	5.87	granular (1-5mm)
4-(31)	MgCl ₂	1173	21.6	10.5	bubbling	2.06	0.36	-	granular (5-30mm)
4-(4)	MgCl ₂ -LiCl-KCl	1173	21.6	2.79	bubbling	-	-	1.02	granular (5-20mm)