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Author(s)	Suzuki, R. O.; Deura, T. N.; Ishii, R.; Matsunaga, T.; Harada, T. N.; Wakino, M.; Ono, K.
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TITANIUM POWDER PREPARATION FROM TiCl₄ IN THE MOLTEN SALT

R. O. Suzuki, T. N. Deura, R. Ishii, T. Matsunaga, T. N. Harada, M. Wakino and K. Ono
Department of Energy Science and Technology, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

Two processes are proposed to produce Ti powder directly from TiCl₄ gas using molten magnesium as reductant. TiCl₄ gas injection into a liquid Mg layer through the molten chloride salts could produce the Ti powder of 1 to 10 μm in diameter. Neither the operation temperature nor the salt composition affected the powder morphology. When TiCl₄ was dissolved once in the molten salt as Ti²⁺, and when Mg successively reduced this Ti²⁺, the Ti morphology varied from the needle-like to the round shape by raising the reduction temperature.

KEYWORDS: MOLTEN SALT, TITANIUM CHLORIDES, GROWTH MECHANISM, MORPHOLOGY

I. INTRODUCTION

A major method producing metallic titanium is so-called Kroll method (as illustrated in **Fig. 1** (a)), where liquid TiCl₄ is dropped onto the molten Mg surface in a sealed vessel and titanium is produced as,



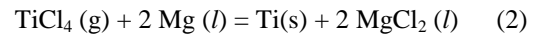
Porous aggregates known as "sponge" titanium consist of Ti primary particles about 10μm in size. After MgCl₂ separation, however, they have firmly sintered in 20μm to 50mm in size, and could be hardly pulverized in the mechanical ways. Because the surface of Ti fresh precipitate becomes the center for heterogeneous nucleation, new other particles created on the pre-existed Ti particles [1]. Therefore, the particles were connected each other and the sintered sponge were not served to powder metallurgy. Another problem with the Kroll process is the costly and time-consuming batch operation for TiCl₄ reduction and the separation of MgCl₂. An important advantage, however, is that the TiCl₄ distillation allow to remove many metallic impurities in addition to oxygen [2].

In Hunter process (sodium reduction of TiCl₄), TiCl₄ was dissolved as TiCl₂ in the molten salt (main constitution is NaCl) with the weak Na reduction [3]. After the subsequent reduction to the molten salt, the slightly sintered Ti powder called as "sponge fine" was served commercially to powder metallurgy. The reductant Na, however, holds some technical and economical problems, and the industrial operation of Hunter process is interrupted currently in Japan, in spite of the strong demand of Ti fine powder with a reasonable price.

We propose two continuous production processes of titanium powder, utilizing the distilled TiCl₄ and Mg as the starting materials, and taking the merits of molten salt [4-6]. The morphology of the produced Ti is checked considering the suitability for powder metallurgy.

II. A REDUCTION IN Mg LIQUID LAYER ON THE MOLTEN SALT

Mg and MgCl₂ separate chemically into two melts as illustrated in **Fig. 1**(b), because Mg and MgCl₂ have little mutual solubility. When we inject the gaseous TiCl₄ into MgCl₂ melt from the bottom of the vessel, TiCl₄ bubbles rise through the MgCl₂ melt to the Mg layer. At the interface between TiCl₄ and Mg melts, Ti is produced as,



As shown in **Fig. 2**, the solid Ti settles through the MgCl₂ liquid due to specific gravity difference, and piles up at the bottom of the vessel. The growth of Ti aggregates will be suppressed, because the heterogeneous nucleation center is removed toward the molten salt, because the volume of supplied TiCl₄ gas is limited in a bubble, and because the molten salt acts as "a separator" between Mg and the produced powder. These Ti precipitates can be taken out continuously from the vessel, because the strong reductant is well separated by the MgCl₂ liquid [4,5]. The usage of same starting materials as Kroll method becomes an advantage for the new investment to our proposal.

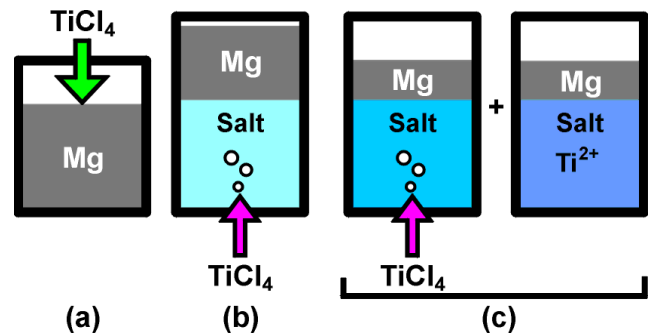


Fig. 1: Concepts of Ti production by Mg reduction. (a) Kroll process, (b) TiCl₄ gas feed through the molten salt, and (c) combined process with TiCl₄ gas feed for Ti²⁺ formation and metallic Ti formation from its molten salt.

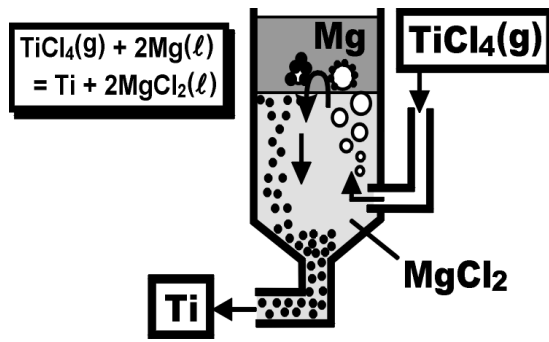


Fig. 2: A conceptual process of continuous Ti production. The Ti particles precipitate at the surface of TiCl_4 bubbles, grow in the Mg layer, and sink downward through the molten salt.

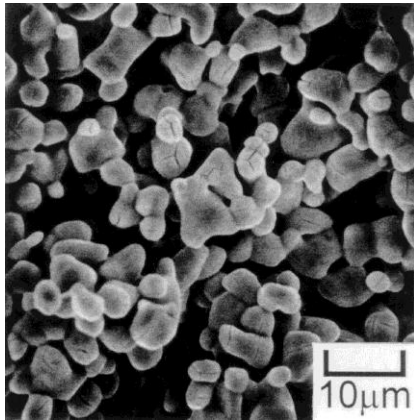


Fig. 3: SEM image of Ti powder produced at 1123K by TiCl_4 injection into a Mg- MgCl_2 bath.

Experimentally about 150g MgCl_2 and about 30g Mg melted in MgO crucible. The injected TiCl_4 gas through MgO lance was bubbled with an accompanying flash in the Mg layer, indicating a rapid and exothermic reaction. A faint amount of TiCl_4 was detected at the gas outlet. The extraction of the product from the melt was not attempted here. After cooling, the residual Mg and MgCl_2 were dissolved in water and the acid solutions.

All the powders obtained in the range of 1023K to 1273K were metallic α -Ti by EDX and XRD analysis. They were so brittle that the sinter was easily crushed. The solidified salt was white, showing that it contained no titanium chlorides. SEM images of the powder are shown in **Fig. 3**. The round particle size was distributed in the range of 1 to 8 μm for all the experiments. The morphology of particles, size and its distribution were almost same against the total amount of TiCl_4 gas (5-50g), the injection rate (0.15 to 0.5g/min.), temperature (>1123K), and the molten salts (MgCl_2 , CaCl_2 or MgCl_2 -47.2 mol% CaCl_2) [4,5]. The primary particles were also similar in size with those produced by the Kroll process. This fine particle formation may be essential in the chemical reaction with Mg and TiCl_4 .

All the Ti particles contained some cracks, which is common feature for high oxygen-Ti powder. The oxygen content in the obtained powder was in the range of 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.

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.

The usage of the other chlorides such as CaCl_2 in MgCl_2 may give us flexibility in selecting the composition of molten salt. The by-product MgCl_2 in the industrial reactor was recycled to Mg by electrolysis. For better electrolysis, a mixture of MgCl_2 , NaCl, CaCl_2 , KCl, and/or some fluorides was used in the industrial process [7]. This complex salt mixture is expected not to influence the morphology of the Ti powder.

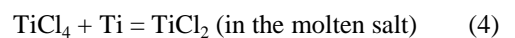
III. REDUCTION OF LOWER CHLORIDES IN MOLTEN SALT

Although the solubility of TiCl_4 in the chloride salts is at most a few mass%, the solubilities of TiCl_3 and TiCl_2 are generally larger than that of Ti^{4+} [6,8]. Using these lower chlorides, we can expect the higher total concentration of Ti ions in the salt. When this molten salt contacts with the reductant Mg, metallic titanium will be formed. The Mg solubilities in these molten salts are as small as 0.3 mol%, whereas the Na solubility in NaCl is about 3 mol% [4,6,8]. The dissolution of Mg into the salt was slow [4]. 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.

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 into two steps, as **Fig. 1(c)**. At the first step, TiCl_4 is fed and dissolved into the molten salt, where a half amount of Mg required for the complete reduction of Ti^{4+} to Ti is consumed for Ti^{2+} formation as,

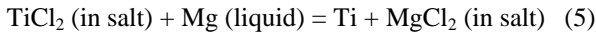


The formed TiCl_2 and MgCl_2 cannot completely mix in a homogenous liquid written as MgCl_2 - 50 mol% TiCl_2 , because the solubility of TiCl_2 in MgCl_2 is 35 mol% at 1173 K [4,6,8]. The additional amount of molten salt is needed as the solvent of Ti^{2+} . The best method suitable to dissolve TiCl_2 into the molten salt is still not fixed. As another method, we can take the reaction as,



instead of the industrial reactions (3). Ti^{2+} is more stable oxidation state than Ti^{3+} when they coexist with metallic Ti in the molten chlorides [4,6,9].

The second step, i.e., subsequent Mg reduction causes the nucleation in the salt,



Because of density difference, the reductant Mg floats on the molten salt, and the precipitated Ti will settle on the bottom of the reaction vessel. In Fig. 4, the Ti product will be extracted and the molten salt containing Ti can be partially returned as the salt for the reaction (5). Another half of the Ti product will be separated from the molten salt as the final product. In spite of the concept of continuous production by connecting two steps (Fig.4), the individual steps are here studied in the separated experiments.

MgO lance was immersed to contact titanium sponge, and 25 or 50g of TiCl_4 liquid was fed to the molten salt at the constant rate of 3.3mg/s. After the feed at 1173 K, the salt was once solidified. Its Ti concentration was analyzed using ICP-AES. The salt thus produced was again melted. About 20g Mg blocks were quietly charged and melted on the molten salt. Ar gas was bubbled through the lance when the stirring was needed.

After TiCl_4 gas injection, the salts were usually dark green. A large amount of Ti sponge was consumed during TiCl_4 feed, although a large amount of TiCl_4 gas was exhausted out. The analyzed Ti concentrations, C_{Ti} , (Table 1 [6,9]) exceeded 0.3 mol%, the equilibrium solubility of TiCl_4 at 1173 K.

After the Mg reduction of molten salts containing Ti^{2+} , a fine metallic powder was recovered and identified as α -Ti by XRD. Although the quantities of Ti powder were only 5 - 20g, the yields were calculated to be roughly 85 - 90%, based on the amount of the used salt and C_{Ti} .

The effects of stirring and reduction temperature on morphology were shown in Fig. 5. When Ar gas was not bubbled, the narrow rods were obtained at 1173 K 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

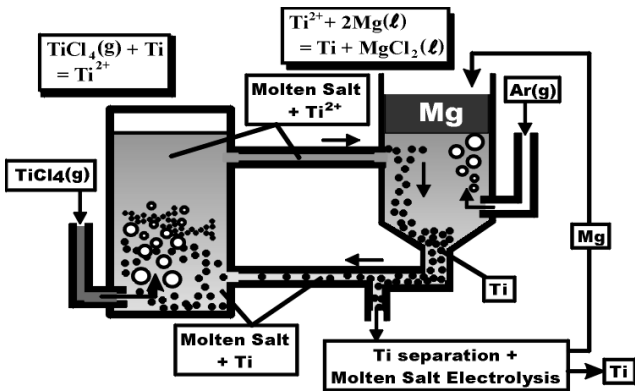


Fig. 4: Concept of continuous operation using the recycled Ti to produce the molten salt containing Ti^{2+} .

Table 1: Ti concentration, C_{Ti} (mass%), in the molten salts after feeding 25 g of TiCl_4 .

Molten salt (Before feed)	C_{Ti}	Yield (%)	
		As TiCl_2	As TiCl_3
MgCl_2	3.48	40.5	62.7
MgCl_2	10.5 *	91.2	152.8
NaCl	4.00	73.8	114.4
NaCl-50 mol\% KCl (eutectic composition)	3.00	54.3	83.6
LiCl-41 mol\% KCl (eutectic composition)	5.70	57.2	90.3
LiCl-41 mol\% KCl (eutectic composition)	10.4 *	82.7	138.4
$\text{MgCl}_2\text{-34.7 mol\% LiCl}$ -24.1 mol\% KCl	2.79	41.3	63.4

* 50g of TiCl_4 were supplied.

particles with smooth surface was recovered. The diameter of their particles was larger at 1173 K. Even when the titanium content in the salt was diluted, the effect of stirring on powder morphology was similar. The narrow rods were found when no stirring.

As shown in Fig.5(c) and Fig. 6, the round particles were finer than 1 μm when they formed for 0.3 ks. In the

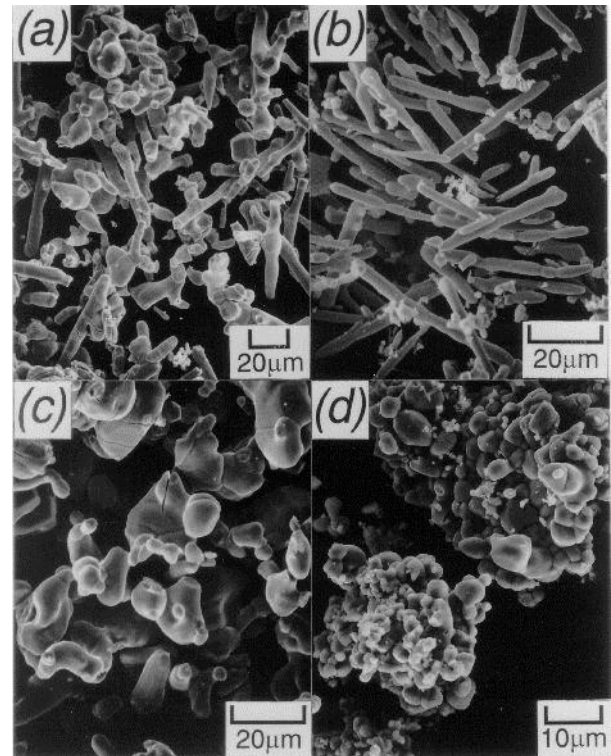


Fig. 5: SEM images of Ti powder obtained from the LiCl-KCl eutectic salts containing 5.7 mass%Ti after treating for 21.6 ks. The Ar gas was not introduced (a) at 1173 K and (b) at 973 K, and it was bubbled (c) at 1173 K and (d) at 973 K [6,9].

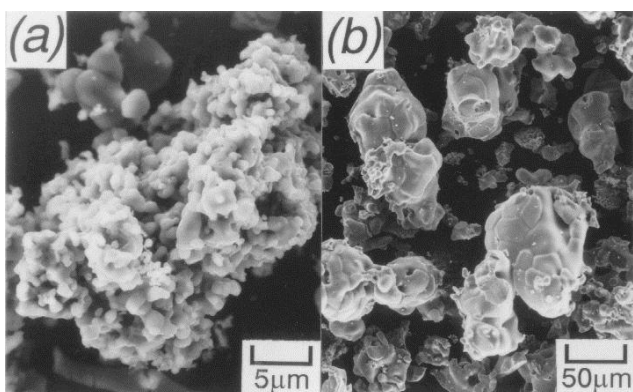


Fig. 6: SEM images of Ti powder obtained from the LiCl-KCl eutectic salts containing 5.7 mass% Ti at 1173 K. The reaction time was (a) 0.3 ks and (b) 86.4 ks.

prolonged holding time they were aggregated and sintered to the larger single particles of 10-30 μm after 21.6 ks, and of $>50 \mu\text{m}$ after 86.4 ks. White color of the solidified salt indicated that, surprisingly, the Mg reduction had been over for 0.3 ks after Mg melting.

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 **Fig.7(a)**, although the local precipitation mechanism is not clear in atomic scale. When the quiet interface can be kept, the Ti nodules grow from the bottom part of 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 may be slow.

When Ar gas is injected (**Fig. 7(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 [6,9].

For use in powder metallurgy, fine powder with a weak size distribution is required. The suitable size is usually said to be several tens μm . The existence of the fine particles smaller than 10 μm might be uncomfortable for this purpose. The concentration control for the solvent salt is indispensable to produce the larger particles in a homogeneous quality.

IV. CONCLUSION

TiCl_4 gas injection into the liquid Mg layer through the molten chloride salts formed the Ti fine particles of 1 to 8

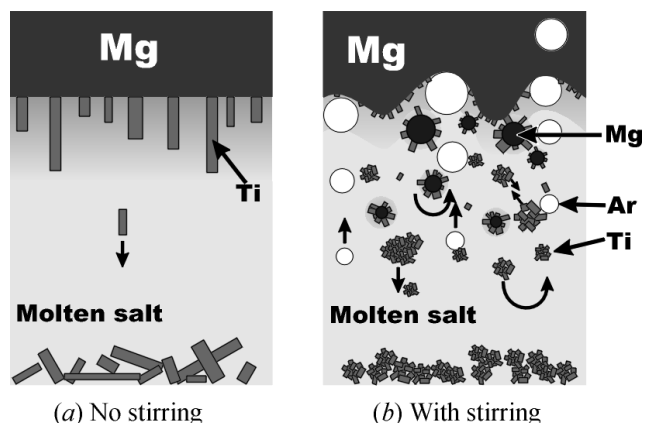


Fig. 7: Growth of Ti particles in the molten salt containing Ti^{2+} : (a) no stirring and (b) with stirring.

μm in diameter. Neither the operation temperature nor the composition of the salt affected the powder morphology [4,5]. In the two-step reduction, TiCl_4 dissolves firstly in the molten salt as Ti^{2+} , and secondly Mg reduction of Ti^{2+} precipitates the fine Ti powder. The reduction finished within 0.3 ks at 1173 K, and the successive holding in the salt grew the particles. Stirring of the molten salt was enhanced to produce the round and well-isolated particles of a few tens of microns [4,6,9].

All the current methods for Ti powder use the Ti sponge as starting material. Our two proposals are alternative processes that can serve Ti powder from TiCl_4 . A further approach will be needed to grow the fine powder to adjust to the demand of powder metallurgy.

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