Production of Fine Titanium Powder from Titanium Sponge by the Shuttle of the Disproportionation Reaction in Molten NaCl–KCl

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Titanium and its alloys are key materials for various fields. Low cost and high-quality titanium powder production methods are crucial for powder metallurgy (PM) and additive manufacturing (AM) of titanium to significantly decrease the manufacturing cost. In this study, the production of titanium powder from raw material titanium sponge was achieved through the shuttle of the disproportionation reaction and the backward reaction of Ti^{2+} to Ti^{3+} and Ti metal in molten NaCl–KCl at 750°C. With the addition of a very small amount of TiCl_2 , over 7~70 times of titanium powder in mass comparing to the added Ti^{2+} was obtained. The primary particle size of the powder formed based on the disproportionation reaction was approximately 1 μm , while the secondary agglomerated particle size was in the range of 25~50 μm . No significant difference of the particle size distribution was found for the experimental runs with different TiCl_2 concentrations and holding times. The proposed production method of titanium powder from titanium sponge is expected to significantly decrease the production cost of titanium powder. [doi:10.2320/matertrans.MA201811]

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1. Introduction

Titanium and its alloys have been extensively developed and are becoming the key advanced materials for various fields such as aerospace, marine, and automobile industries, owing to their excellent physical, chemical, and mechanical properties, particularly for their light weight (4.5 g·cm⁻³), high specific strength, extraordinary corrosion resistance, and excellent flexibility.¹⁾ Unfortunately, titanium and its alloys are classified as difficult-to-machine materials, which highly increases the manufacturing cost and limits their further use.²⁾ Given their attractive properties and current cost, reducing the cost of titanium production and manufacturing has been a continuing and primary motivation for titanium research. Among all the alternative technologies, powder metallurgy (PM) techniques, being a near-net-shape manufacturing technology, are attracting increasing attention in the most recent decades and are considered as potentially cost-effective alternative to conventional wrought titanium process.³⁾

The cost of fine titanium powder is cited as a main hurdle that prevents the further development of PM Ti materials and products.³⁾ Currently, the commercial titanium powder production methods mainly include gas atomization (GA), plasma atomization (PA), hydride de-hydride (HDH), rotation electrode process (REP), and plasma rotation electrode process (PREP).^{3–5)} The REP and PREP titanium powder have very high purity and near-perfect spherical shape; however, the particle size (e.g. 50~350 μm) is too coarse for general PM techniques of titanium.^{4,5)} The methods of GA and PA can produce finer titanium powder. However, typical GA and PA powder have a very wide particle size range (e.g. 10~300 μm), resulting in a much lower yield of fine powder and therefore increasing the powder cost used for PM of titanium.⁵⁾ Meanwhile, molten titanium is used in typical atomizing techniques wherein extremely high operation

temperatures up to 1800°C are required. Finer titanium powder can also be produced using HDH method, however, the powder shape control is difficult and contamination by oxygen is easy.⁴⁾ As of now, none of the inexpensive sources of titanium powder are available in the market,³⁾ and production of high-quality fine titanium powder at low cost therefore becomes crucial.

The disproportionation reaction of titanium ion in molten salt provides an optional opportunity to produce fine titanium powder. Oi and Okabe have attempted to produce titanium from TiCl_2 based on the disproportionation reaction of Ti^{2+} ($3\text{Ti}^{2+} \rightarrow 2\text{Ti}^{3+} + \text{Ti}$) in molten MgCl_2 .⁶⁾ The MgCl_2 – TiCl_2 salt, with a composition of approximately MgCl_2 –50 mass% TiCl_2 , was used as the starting material and titanium powder was finally obtained after holding for several hours at 1000°C. However, the amount of the obtained titanium powders was limited to less than 1/3 of the starting amount of TiCl_2 , based only on the disproportionation reaction of Ti^{2+} .

In molten chloride melt, Ti^{2+} , Ti^{3+} and metallic titanium are in equilibrium with each other according to the reversible reaction $3\text{Ti}^{2+} \rightleftharpoons 2\text{Ti}^{3+} + \text{Ti}$. The thermodynamic equilibrium of titanium ions and metallic titanium in various molten alkali chlorides and molten fluoride-chloride salt has been extensively studied for fundamental knowledge.^{7–12)} Because the solubility of metallic titanium in molten salt is extremely low, close to zero, in order to achieve equilibrium, the reaction $2\text{Ti}^{3+} + \text{Ti} \rightarrow 3\text{Ti}^{2+}$ occurs in the region where there is a sufficient amount of titanium metal, while its reverse reaction $3\text{Ti}^{2+} \rightarrow 2\text{Ti}^{3+} + \text{Ti}$ occurs in the region where metallic titanium is deficient resulting in the production of titanium powder. Thus, by the shuttle of titanium ions of the above reactions, titanium powder is proposed to be produced from titanium metal block, such as titanium sponge or titanium scrap, in molten salt without the consumption of the said titanium ions.

In this study, the production of fine titanium powder from raw material titanium sponge by the disproportionation reaction and its backward reaction (proportionation reaction) was studied. A very small amount of Ti^{2+} was added and

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Fig. 1 The principle of the titanium powder formation by shuttle of the disproportionation reaction and proportionation reaction of the titanium ions.

shuttled around the bath. Molten NaCl–KCl served as a medium to separate the region for consuming titanium sponge and the region for producing titanium powder. Fine titanium powders were successfully produced from titanium sponge, and the effect of varying TiCl_2 concentrations and holding times on the fine titanium powder production was discussed.

2. Principle and Experimental

2.1 Principle

Figure 1 schematically describes the principle of the titanium powder production from titanium sponge based on the shuttle of the disproportionation and proportionation reactions. In molten salt, metallic titanium, Ti^{3+} , and Ti^{2+} are in equilibrium according to eq. (1). The equilibrium constant of this reaction, K , is a function of the composition of molten salt and temperature.

$$K = a_{\text{Ti}^{3+}}^2 a_{\text{Ti}} / a_{\text{Ti}^{2+}}^3 \quad (2)$$

$$= (f_{\text{Ti}^{3+}} x_{\text{Ti}^{3+}})^2 a_{\text{Ti}} / (f_{\text{Ti}^{2+}} x_{\text{Ti}^{2+}})^3$$

$$= (f_{\text{Ti}^{3+}}^2 / f_{\text{Ti}^{2+}}^3) \cdot (x_{\text{Ti}^{3+}}^2 a_{\text{Ti}} / x_{\text{Ti}^{2+}}^3)$$

where, K is the equilibrium constant; $a_{\text{Ti}^{3+}}$, $a_{\text{Ti}^{2+}}$, and a_{Ti} are the activities of Ti^{3+} , Ti^{2+} , and titanium metal, respectively; $x_{\text{Ti}^{3+}}$ and $x_{\text{Ti}^{2+}}$ are the concentrations of Ti^{3+} and Ti^{2+} in molten salt; $f_{\text{Ti}^{3+}}$ and $f_{\text{Ti}^{2+}}$ are the activity coefficients of Ti^{3+} and Ti^{2+} in molten salt, respectively. $f_{\text{Ti}^{3+}}$ and $f_{\text{Ti}^{2+}}$ follow the Henry's law and are kept constant when Ti^{3+} and Ti^{2+} are in dilute concentrations. Thus, K_C can be used to describe the equilibrium of titanium ions and metal.⁷⁾

$$K_C = x_{\text{Ti}^{3+}}^2 a_{\text{Ti}} / x_{\text{Ti}^{2+}}^3 \quad (3)$$

In molten salt, a_{Ti} is unity and K_C only depends on the concentration ratio of Ti^{3+} and Ti^{2+} .⁷⁾ Wang *et al.* have experimentally investigated the K_C for eq. (1) in molten NaCl–KCl and showed that K_C is 1.55 at 750°C when molar ratio is taken as the concentration unit.⁷⁾ Thus, with the presence of metallic Ti, the concentration of Ti^{3+} and Ti^{2+}

will be kept at a fixed value. For example, in a melt containing metallic Ti and 1 mol% Ti^{2+} ($x_{\text{Ti}^{2+}} = 0.01$), the concentration of Ti^{3+} will be kept around 0.124 mol% ($x_{\text{Ti}^{3+}} = 0.00124$). In macro thermodynamic viewpoint, the equilibrium of eq. (1) exists for the whole system. However, since Ti metal has extremely low solubility in molten NaCl–KCl melt, in micron molten salt bulk, there always exists a region where Ti is not present. Thus, in such region, the disproportionation reaction expressed by eq. (4) will occur resulting in the production of fine titanium powders in the bulk. Additionally, the concentration of Ti^{3+} increases while Ti^{2+} concentration decreases. This shift of concentration will cause the backward (proportionation) reaction, as shown in eq. (5), at the region where there is a large surface of Ti block, such as the titanium sponge. Such forward and backward reactions will shift the system from nonuniform to uniform, resulting in the conversion of Ti block into fine Ti powders dispersed in molten salt.

Based on the shuttle of titanium ions shown in eq. (4) and eq. (5), fine titanium powder is proposed to be produced from titanium sponge in molten NaCl–KCl containing very small amount of Ti^{2+} . On the surface of titanium sponge found at the bottom of the salt, eq. (1) proceeds towards the reverse direction (eq. (5)) due to the existence of metallic titanium sponge, and the concentration of Ti^{2+} will slightly increase, as shown in Fig. 1. The generated Ti^{2+} will be shuttled around the salt bulk by stirring. In the bulk of molten salt far from titanium sponge, the amount of metallic titanium is negligible and so a_{Ti} is zero. Equation (1) will proceed towards the forward direction (disproportionation reaction, eq. (4)) to keep the system at equilibrium. Thus, fine titanium powder will be produced. Some Ti^{2+} will be consumed and Ti^{3+} concentration will increase. With the help of stirring, the reactions expressed by eq. (4) and eq. (5) will continue to proceed in a cyclic manner, as shown in Fig. 1, and titanium sponge will be converted into fine titanium powder continuously.

Fig. 2 Schematic apparatus of the preparation of TiCl_2 -containing salt (a), and NaCl–KCl eutectic salt before (b) and after (c) TiCl_2 production using HCl gas.

2.2 Experimental

Titanium sponge (> 99.0% purity, 1.2~2.4 mm, Fujifilm Wako Pure Chemical Corporation), NaCl (> 99.5% purity, Fujifilm Wako Pure Chemical Corporation), and KCl (> 99.5% purity, Fujifilm Wako Pure Chemical Corporation) were used as the starting materials. NaCl and KCl were dried at 200°C in the oven for 24 hrs to remove the moisture, and then were mixed at eutectic composition.¹³⁾ The mixtures were then melted at 750°C under argon atmosphere in an alumina crucible ($\phi 60 \times 180$ mm, Nikkato corporation, Japan), and then pure HCl gas was fed using alumina tube for 2 hours to remove the residual moisture. The well dehydrated eutectic salt was collected for further usage.

The TiCl_2 -containing salt was first prepared by the reaction between metallic titanium sponge and pure HCl gas ($\text{Ti} + 2\text{HCl} = \text{TiCl}_2 + \text{H}_2$) at 750°C. A quartz reaction tube with a quartz filter was used for the TiCl_2 -containing salt preparation, and the schematic apparatus was shown in Fig. 2(a). The prepared NaCl–KCl eutectic salt containing 10 mass% of titanium sponge was filled in the quartz reaction tube above the quartz filter. The atmosphere in the reaction tube was switched to argon after vacuum. The gas was switched to HCl gas to react with titanium sponge when the salt was heated up to 750°C. After the bubbling of HCl gas from the bottom of reactor for 100 minutes, gas was switched to argon gas to remove the residual HCl gas in the molten salt. Finally, the formed TiCl_2 -containing salt was filtered to remove the residual titanium sponge. The NaCl–KCl eutectic salt containing TiCl_2 (Fig. 2(c)) was compared to that before the reaction (Fig. 2(b)). The color of the salt changed from white to deep green.

The TiCl_2 concentration in the prepared salt was determined by H_2 volumetric analysis as expressed by eq. (6):

The TiCl_2 concentration was calculated by measuring the hydrogen volume. For details of the TiCl_2 concentration measurement, please refer to previous work.⁷⁾ The TiCl_2 concentration in the prepared TiCl_2 -containing salt shown in Fig. 2(c) was measured as 8 mass%.

Fig. 3 The schematic reaction apparatus for the titanium powder production based on the disproportionation reaction.

A 50 g mixture of the prepared NaCl–KCl eutectic salt, TiCl_2 -containing salt, and titanium sponge was put into a graphite crucible ($\phi 50 \times 50$ mm, ISEM-3, Toyo Tanso Co., Ltd.) for the titanium powder production. The amount of the TiCl_2 -containing salt was controlled to make the TiCl_2 concentration in the mixed salt to be 0.1 mass% or 0.5 mass%. The crucible with the mixed salt and titanium sponge was put into a stainless-steel reaction tube. The stainless-steel reaction tube, with a designed lid assembling a rubber O-ring, was vacuumed firstly, and then was filled in by high purity argon gas before heating. Figure 3 shows the schematic experimental apparatus.

The temperature of the salt was controlled by a Kanthal furnace connected to a proportional-integral-differential (PID) controller with a K-type thermocouple. Under argon atmosphere, the salt was heated up to 750°C, and argon gas was bubbled into the salt using an alumina tube (SSA-S $\phi 5$ mm, Nikkato, Japan) after melting. The flow rate of the argon gas for bubbling was controlled at $20 \text{ ml} \cdot \text{min}^{-1}$ (CCM). After the designed holding time (40~180 min), the alumina tube was pulled out of the salt, and the furnace was cooled by air. In one of the series of the experiments, a quartz tube ($\phi 10$ mm) with a pipette attached on top was used for the sampling of the molten salt containing titanium powder after the designed holding time.

The titanium powder in the molten salt after the experiments was recovered by dissolving the salt into deionized water, and then filtered. The collected titanium powder was well dried at 50°C in a drying oven, and then was weighed. The crystallography of the collected titanium powder was investigated by X-ray diffractometer (D8 Advance, Bruker). The morphology and the shape of the collected titanium powders were investigated by scanning electron microscope (SEM, FEI-XL30FEG, Philips). The distribution of the particle size of the collected titanium powder was analysed by laser diffraction particle size analyser (LMS-2000e, Seishin, Japan).

Fig. 4 The images of (a) the titanium sponge used for titanium powder production, (b) the side and bottom of the salt after the experiment, and (c) the collected titanium powder by dissolving the salt.

Fig. 5 The XRD result of the collected metallic powder.

3. Results and Discussion

Fine titanium powder was successfully produced from titanium sponge based on the shuttle of disproportionation reaction of titanium ion and its backward reaction in molten NaCl–KCl. The raw material titanium, titanium sponge with an average diameter of approximately 2 mm, was used as shown in Fig. 4(a). As a typical example, the salt after the experiment with 0.1 mass% TiCl_2 addition and a holding time of 60 min is shown in Fig. 4(b). It was found that white NaCl–KCl eutectic salt changed to black after the experiment, which indicates that fine metallic powder was dispersed in the salt. By dissolving the black salt into deionized water, metallic fine powder was collected after filtration, and its photo is shown in Fig. 4(c). It was confirmed that titanium sponge was converted into very fine metallic powder with a uniform size.

Figure 5 shows the XRD pattern of the collected powder. The XRD peaks are well fitted to the standard pattern of hexagonal α -Ti (JCPDS file # 44-1294), confirming that the collected powders are pure titanium.

The effect of TiCl_2 concentration and holding time were investigated, and the results are shown in Table 1. The temperature employed was 750°C and 50 g of NaCl–KCl containing 5 g of titanium sponge was used in each

experimental run. The TiCl_2 concentration in experiment No. 3 (0.5 mass%) was 5 times higher than that of experiment No. 2 (0.1 mass%), while the holding time used was 60 minutes for both. With the same starting mass of 5.0 g of titanium sponge, 1.4 g and 0.7 g of titanium powder were obtained in experiments No. 2 and No. 3, respectively. This result indicated that the increase of TiCl_2 concentration did not promote the titanium powder production. Thus, the effect of TiCl_2 concentration is not significant.

On the other hand, the effect of the increase in holding time between experiments No. 1 and No. 2, as well as between No. 3 and No. 4, were investigated, while TiCl_2 concentrations were held constant. It was found that the weight of the collected titanium powder increased with increasing holding time, from 0.4 g (No. 1, 40 min) to 1.4 g (No. 2, 60 min), and 0.7 g (No. 3, 60 min) to 3.6 g (No. 4, 180 min). With the increase in holding time, the production of titanium powder is continued according to the proceeding of both the disproportionation reaction of Ti^{2+} and the proportional reaction of Ti^{3+} and the metallic titanium sponge.

The ratio of the obtained titanium powder ($M_{\text{Ti(sponge)}}$) to the weight of Ti^{2+} added in the salt previously ($M_{\text{Ti(II)}}$) was used to further show the proceeding of the shuttle of titanium ions of the disproportionation reaction (eq. (4)) and the proportionation reaction (eq. (5)). The ratio of the generated titanium powder and the initial Ti^{2+} in the melt is 1/3 if the powder is only produced by the disproportionation reaction of Ti^{2+} (eq. (4)) without the backward reaction eq. (5) with the titanium feed. This is the case when the starting material is only TiCl_2 without titanium metal feed.⁶⁾ It was found that the ratios calculated from the experimental results, as shown in Table 1, are generally several hundred times of 0.33 (1/3) in all the experimental series, which indicates that the produced Ti powder is through the shuttle of titanium ions between eq. (4) and eq. (5). Owing to the shuttle reactions of metallic titanium and titanium ions, titanium sponge is converted to fine titanium powder continuously.

The morphology of the obtained fine titanium powder was analysed by SEM, and the typical results are shown in Fig. 6. It was found that the obtained titanium powders are in different sizes and shapes. The particle size of the obtained titanium powders scatters, while most of them are approximately several tens of micrometres in size, such as that shown in Fig. 6(b) and (c). Meanwhile, the shapes of the

Table 1 Effect of TiCl_2 concentration and holding time on the titanium powder production.

No.	TiCl_2 concentration, (mass %)	Mass of the Ti^{2+} added, $M_{\text{Ti(II)}}$ /g	Holding time, t/min	Obtained titanium powder, $M_{\text{Ti(powder)}}$ /g	$M_{\text{Ti(powder)}} / M_{\text{Ti(II)}}$
1	0.1	0.02	40	0.4	20.3
2	0.1	0.02	60	1.4	69.8
3	0.5	0.10	60	0.7	7.0
4	0.5	0.10	180	3.6	35.9

Fig. 6 The morphology of the obtained fine titanium powders.

obtained titanium powders also vary. For example, the powder in Fig. 6(b) is irregular polygon, while powders in Fig. 6(c) are almost round. The surface of most of the obtained powders are found to be porous. It is noted that the powders obtained are the agglomeration of large amount of much finer powders. As a typical example, it can be found that the powder in Fig. 6(d) consists of a large amount of fine

powders. It was considered that the much finer powder is the primary titanium powder that was formed directly based on the disproportionation reaction of titanium ion. These primary fine powders agglomerate when the disproportionation reaction and its backward reaction proceed. Finally, larger titanium powder of about several tens of micrometres, is formed.

The particle size distribution of the obtained titanium powder was investigated, and the results are shown in Fig. 7. No significant difference of the particle size distribution was found for the experimental runs with different TiCl_2 concentrations and holding times, as shown in Fig. 7(a). Most of the obtained titanium powder is in the size range of approximately 25~50 μm . As also mentioned above, it is considered that the primary titanium powders formed directly based on the disproportionation reaction of titanium ion are very fine and found to agglomerate to form larger particles as the reactions proceed and the molten salt cools down. Another series of experiments were carried out by sampling the molten salt containing the titanium powder after the designed holding time using a quartz tube to rapidly cool the salt, and the results are shown in Fig. 7(b). Comparing with the titanium powder collected in the naturally cooled salt, the particle size of the titanium powder collected was found smaller, approximately 10~20 μm , which might be a result from the shorter agglomeration time. Another peak for

Fig. 7 The particle size distribution of the titanium powder collected from the naturally cooled salt (a), and that from the rapidly cooled salt by sampling the molten salt at 750°C (b).

the very fine titanium powder in size less than 1 μm was also found in Fig. 7(b), which might be the result of the fine powder formed based on the disproportionation reaction directly.

The above experimental results confirmed that titanium powder can be efficiently produced from titanium sponge by the shuttle of titanium ions of the disproportionation reaction in molten salt and approved the proposed principle introduced in Section 2. It was noted that Ti^{2+} served as the shuttle media to convert titanium sponge to fine titanium powder, and thus several ten times of titanium powder than the added Ti^{2+} in weight was produced. The proposed method, using titanium sponge as the raw material, can be achieved using very simple apparatus at relatively low temperature, and the produced fine titanium powders have a particle size range suitable for typical titanium PM technologies.⁵⁾ These advantages of the proposed method could lead to a significantly lower production cost of titanium powder.

4. Conclusions

The conclusions are shown as follows:

- (1) Fine titanium powder was produced from titanium sponge by the shuttle the disproportionation reaction and its backward reaction (proportionation reaction) of the titanium ions in molten NaCl–KCl at 750°C.
- (2) With the addition of a very small amount of TiCl_2 , over 7~70 times of titanium powder in mass comparing to the added Ti^{2+} was obtained after 1 hour of holding time at 750°C. The effect of TiCl_2 concentration on the conversion rate of titanium sponge to titanium powder is not significant.
- (3) No significant difference of the particle size distribution was found for the experimental runs with different TiCl_2 concentrations and holding times. Most of the obtained

titanium powder is in the particle size range of approximately 25~50 μm , which is considered as a result of agglomeration of large amount of much finer powders.

- (4) The proposed method has great advantages in significantly lowering the production cost of titanium powder.

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