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Titanium Fabrication via $CaCl_2$ from $FeTiO_3$

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Abstract

Starting ore (ilmenite, $TiFeO_3$) was wet-chemically treated to remove Fe and the hydroxide of titanium was neutralized. The obtained precipitate was calcined to form $CaTiO_3$, which was electrochemically reduced to Ti in the molten $CaCl_2$-CaO. The wasted salt containing CaO could be recycled to form $CaTiO_3$. The operating conditions such as $(NH_4)_2S$ and tartaric acid concentrations for Fe removal, supplied charge, gas pressure and cooling atmosphere for molten salt reduction were optimized to obtain low-oxygen titanium.

Introduction

This work aims at the new process that the cheap ore, ilmenite ($TiFeO_3$), is selected as the starting material, and that a highly pure titanium metal can be produced in a low cost with mass productivity. Fig. 1 shows the concept of this work that $TiFeO_3$ is once converted to $CaTiO_3$ by acid leaching, and then it is reduced to metallic Ti using electrolysis of CaO in molten $CaCl_2$.

Conventionally Kroll process [1)] is taken for titanium metal production, where TiO_2 is starting material after Fe removal from $TiFeO_3$. TiO_2 is chlorinated to $TiCl_4$, and $TiCl_4$ is distilled for further complete removal of Fe. Finally $TiCl_4$ is reduced by liquid Mg to obtain Ti. Multi-step processes in the Kroll method requires a long operating time, and the molten salt electrolysis of $MgCl_2$ to recycle Mg consumes a lot of energy and electricity at an elevated temperature.

In contrast, this work will firstly skip the distillation of $TiCl_4$ for Fe removal by getting a highly purified starting material. We plan to decrease Fe contamination by introducing two wet chemical processes of $TiFeO_3$. Secondary, $CaTiO_3$ instead of TiO_2 is chosen as the raw material for

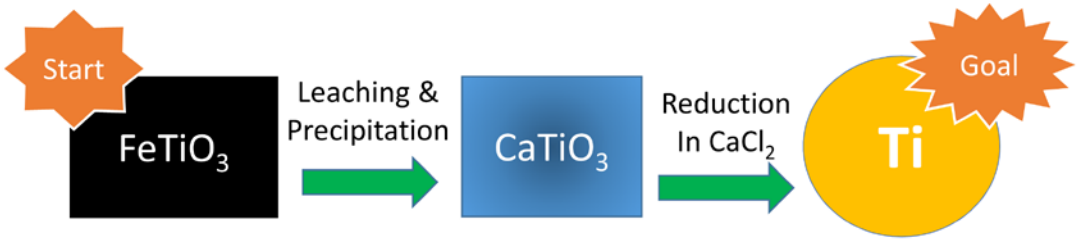


Fig. 1 Concept of titanium metal fabrication using wet chemical process and molten salt.

reduction. By taking CaO or $Ca(OH)_2$ and $CaCl_2$ as neutralizer in precipitation and as a source of Ca, $CaTiO_3$ (not TiO_2) can be prepared at room temperature. Thirdly, this work accepts the direct reduction and electrolysis of oxide in the molten salt, so-called OS process [2,3], by selecting $CaTiO_3$ as starting oxide. When we take $CaTiO_3$ [4-7], the larger amount of Ca can be used as the source of reductant Ca than the reduction of pure TiO_2 [8], and it may lead the larger current density (i.e., the higher productivity) and the faster reduction rate [4-6].

The purpose of this work is (1) to develop the techniques to remove Fe from $TiFeO_3$ to a sufficiently low level and to prepare $CaTiO_3$, and (2) to establish the direct oxide reduction technique to form a low oxygen and low Fe pure Ti from this $CaTiO_3$. Both (1) and (2) were examined here, but for convenience of the study of step (2), this work utilized the commercial powder of $CaTiO_3$ with a fine grain-size. Although the synthetic reaction between CaO and TiO_2 particles is slow [9,10], it is quickened in the molten salt [11-15]. Some previous works successfully reduced $CaTiO_3$ powder [5-7,16-18], although the reduction rate was discussed comparing to TiO_2 [5-7,10-18]. Most of them showed that $CaTiO_3$ is thermodynamically stable than TiO_2, and its reduction was not easy. In addition, there were no descriptions how to remove Fe in forming $CaTiO_3$.

Preparation of $CaTiO_3$ from $FeTiO_3$

Two Approaches for Fe Removal

Two methods were tested for dissolution of $TiFeO_3$ into an aqueous solution. Fig. 2 shows the concept of the developed processes how to form $CaTiO_3$.

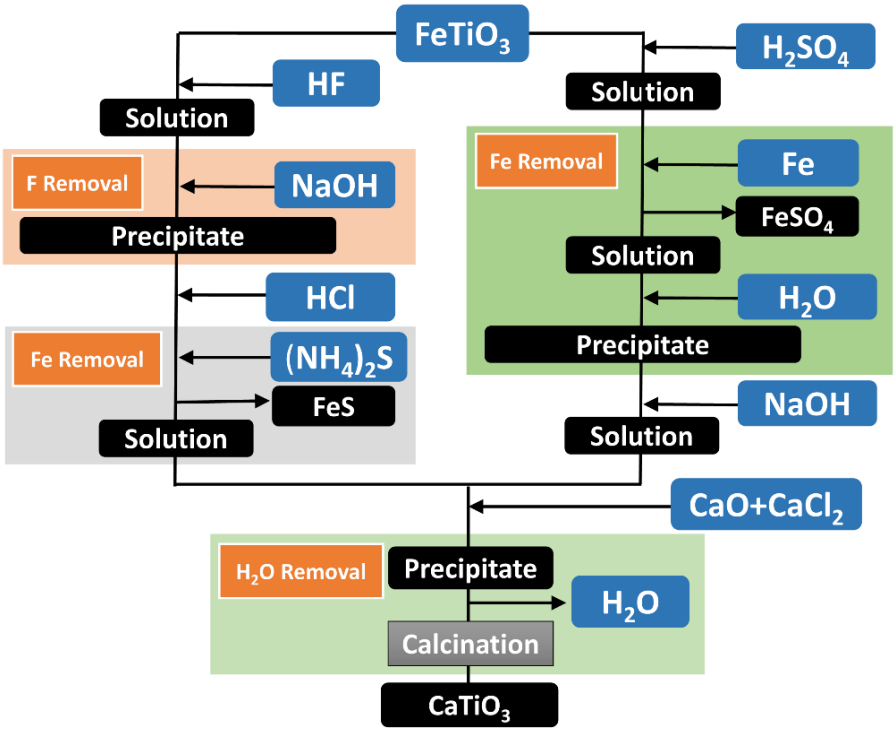


Fig.2 Two procedures for Fe removal and synthesis of $CaTiO_3$.

First approach uses an industrially applied process based on H_2SO_4 leaching as shown in eq.(1). The two products, $FeSO_4$ and $TiOSO_4$, can dissolve in hot and concentrated H_2SO_4.

$$FeTiO_3 + 2H_2SO_4 \rightarrow FeSO_4 + TiOSO_4 + 2H_2O \quad (1)$$

$TiOSO_4$ is hydrolyzed into the insoluble white precipitate, $TiO(OH)_2$, as shown in eq.(2).

$$TiOSO_4 + 2H_2O \rightarrow TiO(OH)_2\downarrow + H_2SO_4 \quad (2)$$

Second approach is to dissolve $TiFeO_3$ in HF acidic solution, where we can expect a rapid dissolution of $TiFeO_3$. As the existence of F in the final product is not desired, F^- is removed by rinsing. Then the solution containing both Fe and Ti is obtained as HCl acid based solution.

Dissolution in H_2SO_4

$TiFeO_3$ powder was dissolved in the concentrated H_2SO_4 by using the continuous stirring at 573 K for 1 hour. The complete solution after cooling was mixed with small amounts of distilled water and Fe powder, and again heated at 423 K for partial reduction of possible existence of Fe^{3+} ion. Black solution was heated at 363 K for hydrolysis, and a white precipitate A was separated by centrifugation. Fe-containing solution was removed from the precipitate A. Then, this precipitate A and $Ca(OH)_2$ solution were added to the NaOH solution at 373 K. After cooling and rinsing with distilled water, a white precipitate B is recovered by centrifugation.

Fig. 3 shows the X-ray diffraction (XRD) patterns of the precipitates A and B. A was identified as titanium hydroxide with anatase structure, although all diffraction peaks were broad. The crystallinity of this precipitate A was worse than the commercial anatase powder. It is well known that fairly large amount of Fe is included in the precipitate A in the industrial process.

The precipitate B was grown in hot NaOH solution before adding CaO and $CaCl_2$. A faint amount of $CaTiO_3$ in this precipitate B was detected, although strong and sharp diffractions due to $CaSO_4$ and broad diffractions due to anatase-type TiO_2 were found. Because the solubility of $CaSO_4$ in water is very small, $CaSO_4$ often appeared in the precipitate B when the solutions containing SO_4^{2-} and Ca^{2+} were mixed. The thermal decomposition of $CaSO_4$ occurs above 1473 K, and it is not easy to remove $CaSO_4$ from B by evaporation, once $CaSO_4$ coexists with B. Therefore, before

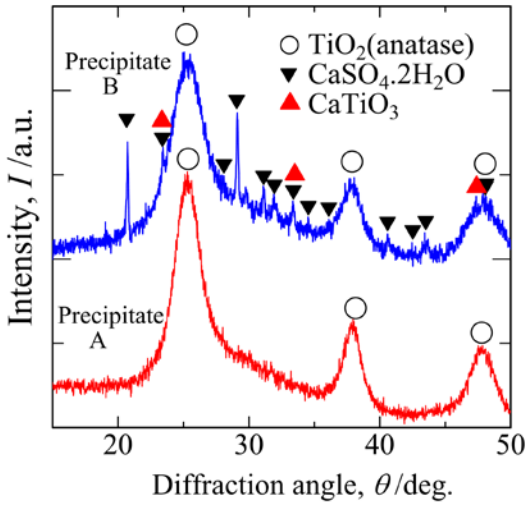


Fig. 3 X-ray diffraction patterns for Precipitate A and B.

mixing with Ca containing solution and the precipitate, the small amount of SO_4^{2-} should be separated completely. The anatase-type TiO_2 in Precipitate B may show that some portion of TiO_2 remains unreacted as shown in Fig. 3. Any crystalline phases containing Fe was not detected. We may conclude that Fe contamination was lower than the analytical limit by XRD, and the contamination by $CaSO_4$ should be excluded.

Dissolution in HF

Fig. 4 shows the summary of operation flow sheet starting from $TiFeO_3$ to prepare $CaTiO_3$. HF acid was used as handy reductant to dissolve $TiFeO_3$ at room temperature for a short time. However, the handling of F may cause an environmental pollution, and the post-treatment of F increases the cost of process. The minimal amount of 2 M HF to dissolve 1 g $TiFeO_3$ was 100 mL, and the complete conversion to HCl acidic solution was conducted by the repeated rinsing. In order to sustain Ti^{4+} in the solution, tartaric ammonium solution or citric acid was added as masking reagent, and $(NH_4)_2S$ was added to precipitate FeS. Once Ti^{4+} was masked, any sulfide such as H_2S gas might be used to remove Fe. Because the solubility of FeS in water is very low, a complete Fe separation can be expected comparing to the industrial H_2SO_4 process as above-mentioned. The clear solution containing Ti^{4+} was recovered by basic solution (pH>12) such as NaOH or $Ca(OH)_2$. Taking account into recycling of $CaCl_2$ and CaO after the molten salt electrolysis, $CaCl_2$ was also tested as Ca source of $CaTiO_3$ formation.

Fig. 5 shows the mass of Fe and Ti in the solutions, which were deduced from the concentration analysis by ICP. The sample 1 is the solution after dissolution of 1.00 g $TiFeO_3$, 2: after F removal, 3: after FeS precipitation, and 4: after $CaCl_2$ addition. During F treatment, about 30 % of constitutions were lost, although there are still margins for further improvements. Fe was successfully removed as FeS by $(NH_4)_2S$ addition with masking of Ti^{4+}. The amounts of Fe in the solutions 3 and 4 were 1/1000 times lower than that of solution 2.

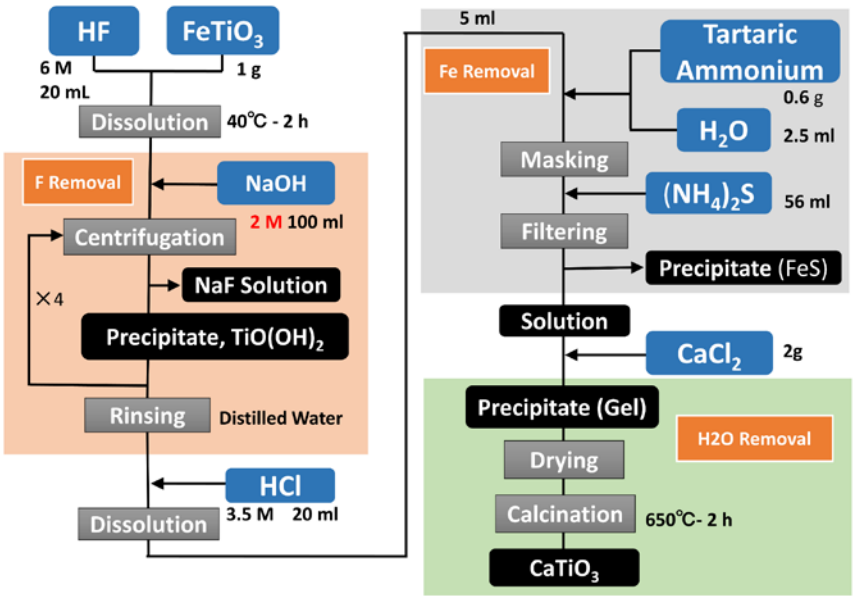


Fig. 4 Flowsheet of $CaTiO_3$ preparation from $FeTiO_3$ using HF acid.

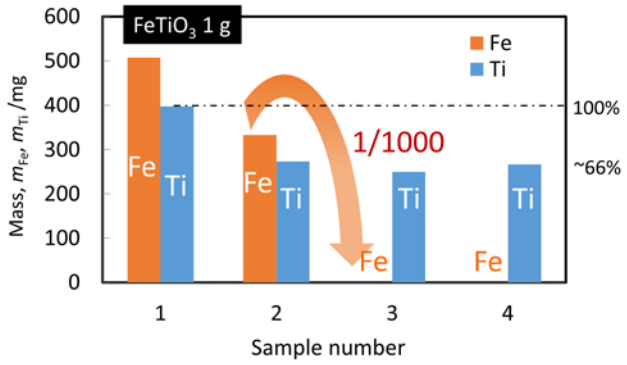


Fig. 5 Iron removal starting from 1g $TiFeO_3$.

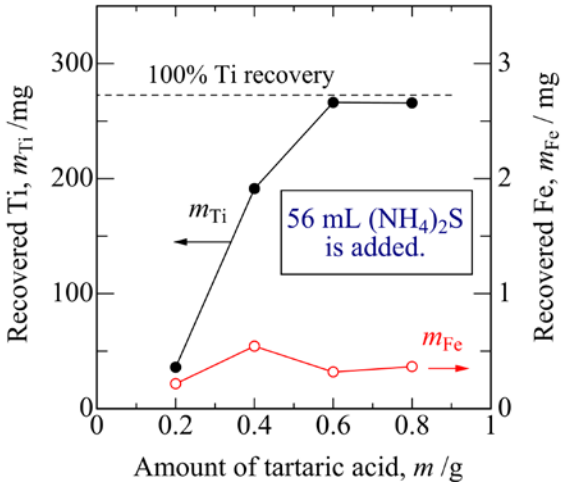


Fig. 6 Effect of Fe removal by the added amount of tartaric acid, where 56 mL of $(NH_4)_2S$ was added.

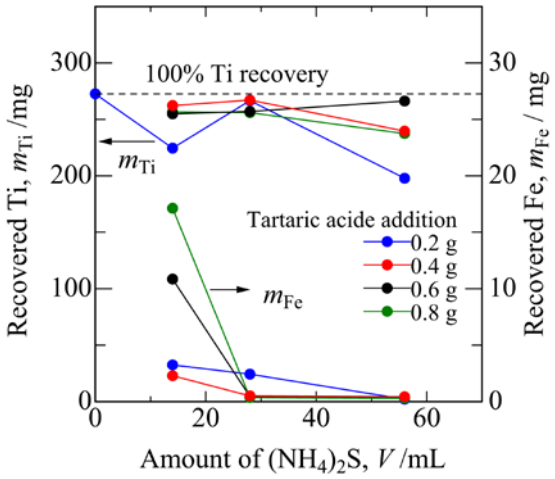


Fig.7 Effect of Fe removal by $(NH_4)_2S$ addition.

Fig. 6 shows the amount of recovered Ti content in the solution 3 (after FeS precipitation). For 1 g $FeTiO_3$, 0.6 g tartaric acid was needed for >95% recovery of Ti, and the Fe contamination level was low so that it could pass over the industrial purity level in the reduced Ti metal.

Fig. 7 shows that 56 mL $(NH_4)_2S$ addition, which was three times larger than the stoichiometric amount for FeS precipitation, was also needed to pass its level. The further optimization is planned. The obtained level of Fe contamination was less than industrial criteria, 1000 ppm in Ti, even if it is assumed that all the impurities remain in the final product, Ti metal. It is natural that $CaCl_2$ addition did not change the yield of Ti and the Fe contamination, such as 266 mgTi and 0.37 mgFe.

Calcination

After drying the precipitate, $CaTiO_3$ was successfully synthesized at 923 K for 2 hours in air, although the mixture of TiO_2 and CaO regents did not form $CaTiO_3$ even at 1073 K [9,10]. This indicates that our deposit from the aqueous solution consists of fine mixture having the stoichiometric composition.

Reduction of $CaTiO_3$ in Molten $CaCl_2$

Residual Oxygen in Cathodic Basket

As shown in Fig. 8, α-Ti particles were successfully electrolyzed by starting from $CaTiO_3$ regent at 1173 K. The oxygen content in the obtained Ti powder gradually decreased as the supplied charge increased. Here we define that Q_0 and Q are the stoichiometric electric charge and the supplied charge, respectively. The reduction mechanism can be interpreted by so-called "OS process" that it consists of the calciothermic reduction to from Ti and of the electrolysis to form Ca from a faint amount of CaO in the melt [2,3].

$$CaTiO_3 + 2\,\underline{Ca} \rightarrow Ti + 3\,\underline{CaO} \quad (3)$$

$$\underline{CaO} \rightarrow Ca^{2+} + O^{2-} \quad (4)$$

$$Ca^{2+} + 2\,e^- \rightarrow \underline{Ca}\ \text{(near cathode)} \quad (5)$$

$$C + 2\,O^{2-} \rightarrow CO_2(g) + 4\,e^-\ \text{(at carbon anode)} \quad (6)$$

where the underline shows the dissolved substance. As shown in Fig. 8, the residual oxygen was the lowest at Q/Q_0 = 500%. When the basket diameter was larger than 9 mm [6], the oxygen concentration was higher at the same Q/Q_0. Inhomogeneous distribution of oxygen concentration in the cathodic basket was due to the flow of Ca-rich liquid from the bottom of cathode to the upper part, and from the outside of the basket to the inner part [5-7].

Electrolysis in Vacuum

The oxide electrolysis shown in Fig. 8 was conducted in pure Ar gas flow. The exhaust gas at the anode was expected to flow out, but it was not completely extracted from the reaction vessel. Under an atmosphere containing CO or CO_2 gas, the obtained Ti powder is significantly oxidized even in cooling. Therefore, a rapid cooling after the electrolysis was needed to avoid the gas oxidation. Because the CO and CO_2 gas emitted on the anodic surface can be removed by continuous evacuation, it is expected from the thermodynamics that evacuation can enhance the

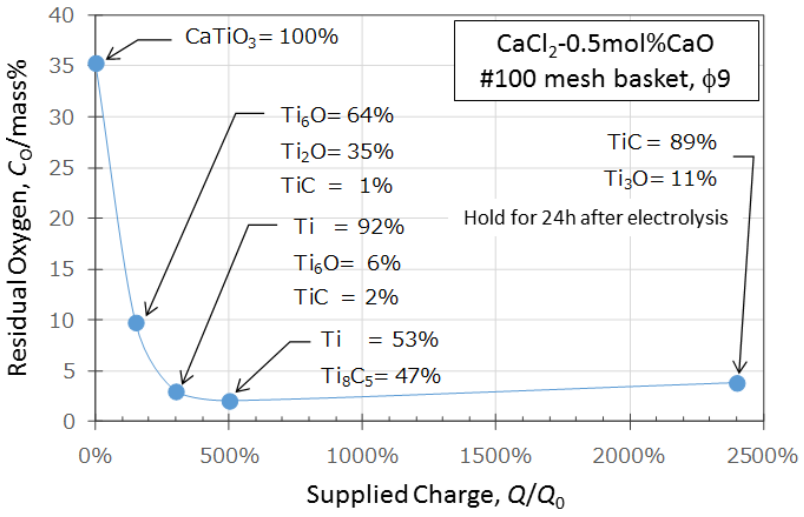


Fig. 8 Residual oxygen and phases identified by XRD in the powder obtained from molten $CaCl_2$-0.5mol%CaO at 1173 K. The volume fraction was evaluated based on the reference patterns.

reduction according to eq.(6). Continuous evacuation during the reduction of TiO_2 using electrolysis in $CaCl_2$ was patented by Hayashi and Uda [19], but the detailed mechanism was not clarified.

Resultantly the electrolysis at low pressure did not give a low oxygen concentration in the obtained Ti particles, as shown in Fig. 9. A large amount of CO_2 dissolves in the molten $CaCl_2$ and forms CO_3^{2-}. This CO_3^{2-} precipitates carbon at the cathode and reacts with Ti to form carbides.

$$CO_2(g) + O^{2-} \rightarrow CO_3^{2-} \text{ (near anode)} \quad (7)$$

$$2\ CO_3^{2-} + 4\ e^- \rightarrow C + CO_2(g) + 4\ O^{2-} \text{ (at cathode)} \quad (8)$$

$$CO_3^{2-} + 2\ e^- \rightarrow CO(g) + 2\ O^{2-} \text{ (at cathode)} \quad (9)$$

$$C + Ti \rightarrow Ti_xC \text{ (at cathode)} \quad (10)$$

Apparently these parasite reactions due to CO_3^{2-} reduce the current efficiency for Ti forming by removing oxygen. Large electric charge such as Q/Q_0=600% was given to $CaTiO_3$, but most of charge was spent for these parasite reactions. This was experimentally confirmed by analyzing the exhaust gas during the electrolysis, and about 80% of supplied electricity was used for CO_2 and CO gas formations. Some amount of oxygen remained in Ti and it transformed the lower oxides during cooling. Because the emitted gas bubbles at cathode caused significant stirring near the cathode, the dissolved Ca departed from the cathodic basket in which $CaTiO_3$ powder was filled. The environmental pressure in the vessel suppressed the gas formations (eq.(8) and (9)), although the impurity oxygen in Ar gas slightly contaminated the obtained Ti during cooling.

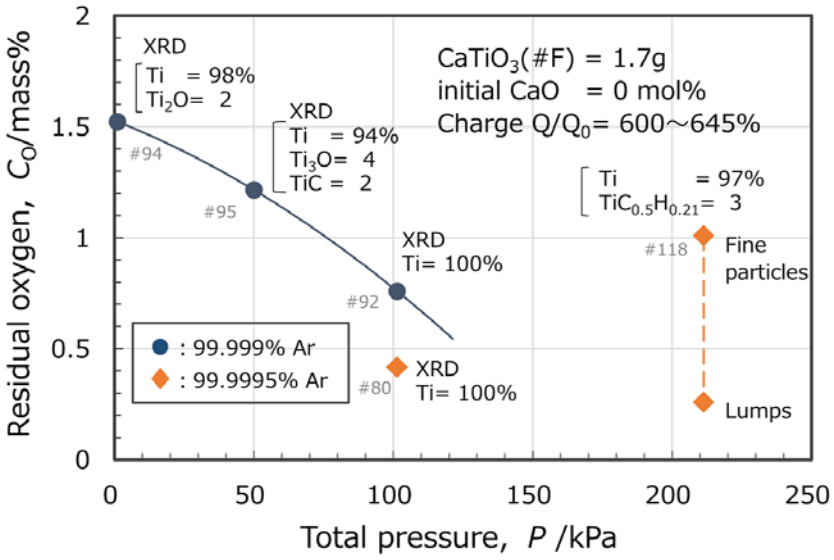


Fig.9 Residual oxygen and phases identified by XRD in the obtained Ti powder.

Conclusions

This work proposed a new procedure consisting of two steps; $CaTiO_3$ formation with Fe removal from $TiFeO_3$, and electrochemical reduction of $CaTiO_3$ in $CaCl_2$-CaO melt. Using dissolution of $TiFeO_3$ into HF solution and the successive F removal, Ti and Fe were ionized in aqueous solution. The addition of $(NH_4)_2S$ with a masking agent such as tartaric acid could separate Fe^{2+} to a level matching with the industrial purity standard of metal Ti.

Combination of calciothermic reduction of $CaTiO_3$ and electrolysis of CaO dissolved in $CaCl_2$-CaO melt could fabricate metallic Ti powder. Large supply of electric charge could form Ti particles with a low concentration of oxygen. Evacuation to remove the anodic CO_2 gas did not work well to produce a good quality of Ti. This was because a strong stirring diffuses Ca from the cathode due to CO_2 evolution at the both electrodes.

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References

1) W. Kroll: *J. Electrochem. Soc.*, **78** (1940), 35-47.
2) R.O. Suzuki, K. Teranuma, K. Ono: *Metall. Mater. Trans. B*, **34B** (2003), 287-295.
3) R.O. Suzuki: *J. Phys. Chem. Solids*, **66** (2005), 461-465.
4) R.O. Suzuki: *Proc. 1st Intern. Round Table on Titanium Production in Molten Salts*, (March 2008, Cologne, Germany), 20-26.
5) K. Kobayashi, Y. Oka, R.O. Suzuki: *Mater. Trans.*, **50** (2009), 2704-2708.
6) R.O. Suzuki: *Proc. 10th Intern. Conf on Molten Salt Chem. Techn. (MS10) and 5th Asian Conf. on Molten Salt Chem. Techn.(AMS5)*, (June, 2015, Shenyang, China) 1-4.
7) R.O. Suzuki, H. Noguchi, H Hada, S. Natsui, T. Kikuchi: *Mater. Trans.*, **58** (2017), 341-349.
8) G.Z. Chen, D.J. Fray, T.W. Farthing: *Nature*, **407**, 21 Sept., (2000), 361-364.
9) P. Dulian: *Perovskite Materials - Synthesis, Characterisation, Properties, and Applications*, L. Pan and G. Zhu (Ed.), (2016, InTech, Rijeka, Croatia) Chap. 1
10) J.-H. Du, Z.-P. Xi, Q.-U. Li, Q. Xu, Y. Tang, Z.-X. Li: *Trans. Nonferrous Met. Soc. China*, **17** (2007), 514-521.
11) K. Dring, R. Dashwood, D. Inman: *J. Electrochem. Soc.*, **152** (2005), D184-D190.
12) M. Liu, Z. Guo, W. Lu: *Trans. Inst. Min. Met. Sec. C*, **114** (2005), 87-94.
13) D.T.L. Alexander, C. Schwandt, D.J. Fray: *Acta Mater.*, **54** (2006), 2933-44.
14) D.T.L. Alexander, C. Schwandt, D.J. Fray: *Electrochim. Acta*, **56** (2011), 3286-95.
15) J. Mohanty, K.G. Mishra, R.K. Paramguru, B.K. Mishra: *Met.Mater.Trans.B*, **43**(2012),513-518.
16) L. Ru, Z. Li, C. Bai, N. Zhang, H. Wang: *Asian J. Chem.*, **25** (2013), 1814-1818.
17) J. Jia, B. Xu, B. Yang, D. Wang, H. Xiong, D. Liu: *Key Engg. Mater.*, **551** (2013), 25-31.
18) K. Jiang, X.H. Hu, M. Ma, D.H. Wang, G.H. Qiu, X.H. Jin, Z.Chen: *Angew. Chem. Int. Ed.*, **45** (2006), 428-432.
19) S. Hayashi, T. Uda: *Japanese Patent*, P2012-136766A, (P2010-291739) (2010).