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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 $(\text{NH}_4)_2\text{S}$ 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 process¹⁾ 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

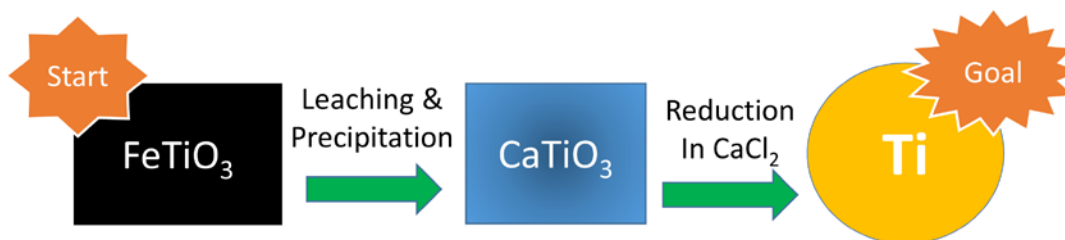


Fig. 1 Concept of titanium metal fabrication using wet chemical process and molten salt.

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 rate⁴⁻⁶⁾.

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 salt¹¹⁻¹⁵⁾. 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 .

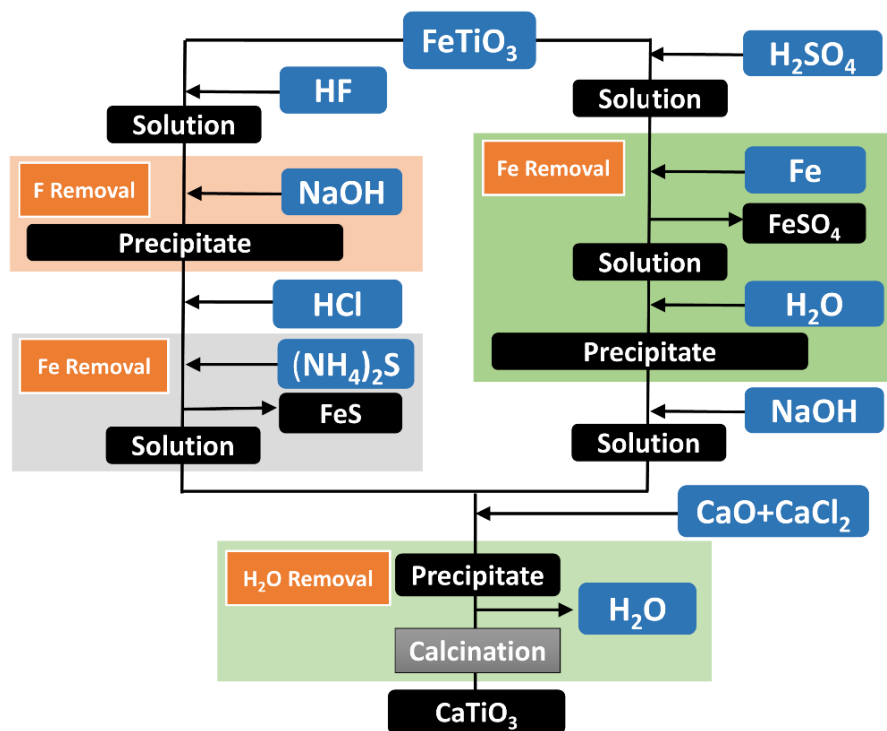
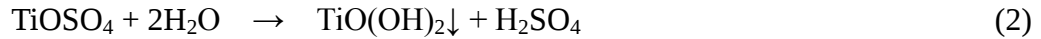


Fig.2 Two procedures for Fe removal and synthesis of CaTiO_3 .

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 .



TiOSO_4 is hydrolyzed into the insoluble white precipitate, $\text{TiO}(\text{OH})_2$, as shown in eq.(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 $\text{Ca}(\text{OH})_2$ 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

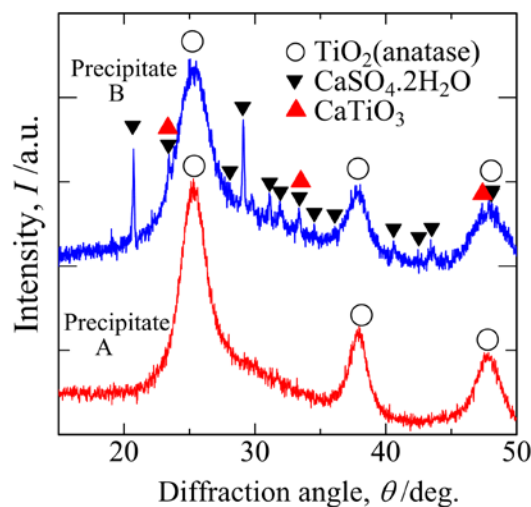


Fig. 3 X-ray diffraction patterns for Precipitate A and B.

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 $(\text{NH}_4)_2\text{S}$ 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 ($\text{pH} > 12$) such as NaOH or $\text{Ca}(\text{OH})_2$. 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 $(\text{NH}_4)_2\text{S}$ 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.

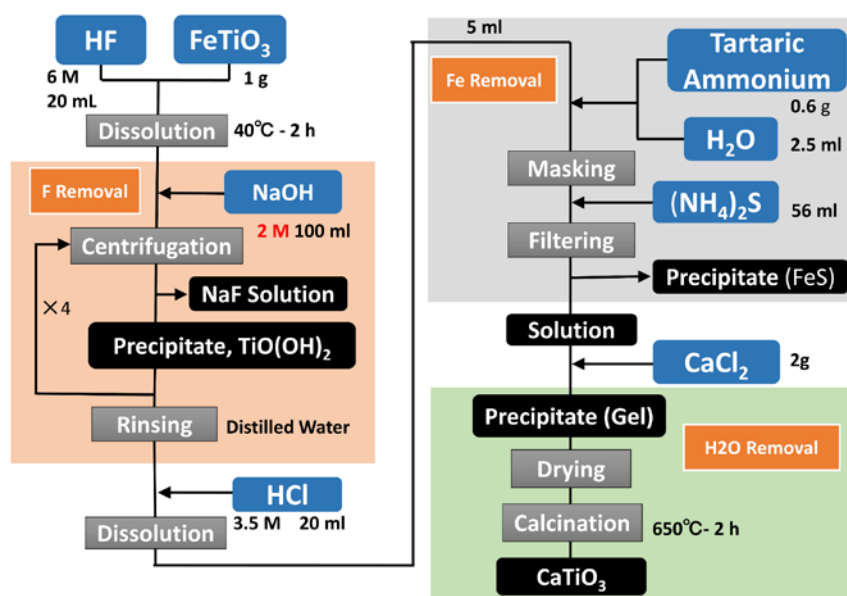


Fig. 4 Flowsheet of CaTiO_3 preparation from FeTiO_3 using HF acid.

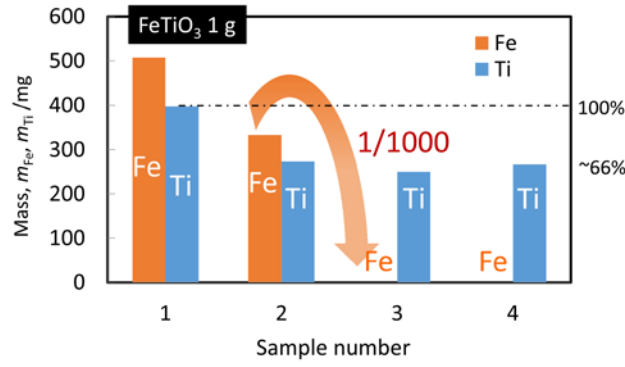


Fig. 5 Iron removal starting from 1g TiFeO₃.

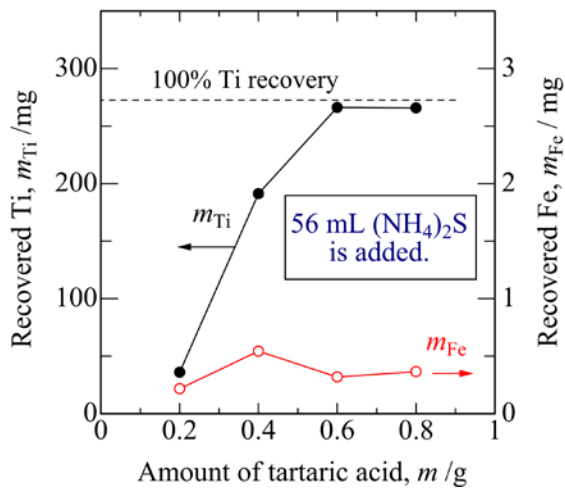


Fig. 6 Effect of Fe removal by the added amount of tartaric acid, where 56 mL of (NH₄)₂S was added.

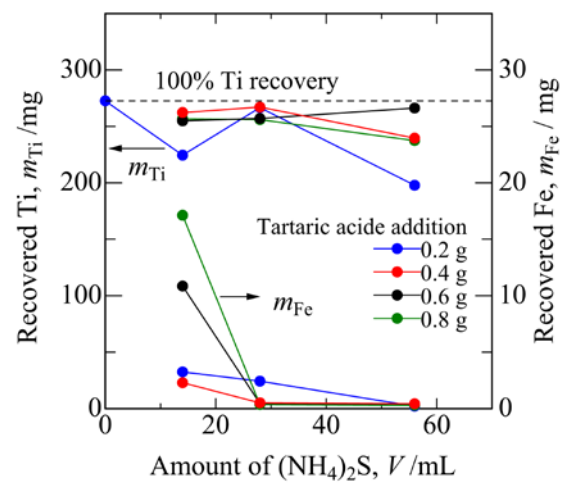


Fig.7 Effect of Fe removal by (NH₄)₂S addition.

Fig. 6 shows the amount of recovered Ti content in the solution 3 (after FeS precipitation). For 1 g FeTiO₃, 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 (NH₄)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 CaCl₂ addition did not change the yield of Ti and the Fe contamination, such as 266 mgTi and 0.37 mgFe.

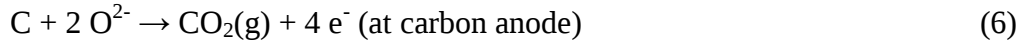
Calcination

After drying the precipitate, CaTiO₃ was successfully synthesized at 923 K for 2 hours in air, although the mixture of TiO₂ and CaO reagents did not form CaTiO₃ 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 CaTiO₃ in Molten CaCl₂

Residual Oxygen in Cathodic Basket

As shown in Fig. 8, α -Ti particles were successfully electrolyzed by starting from CaTiO₃ 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 form Ti and of the electrolysis to form Ca from a faint amount of CaO in the melt ^{2,3)}.



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 CO₂ 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 CO₂ gas emitted on the anodic surface can be removed by continuous evacuation, it is expected from the thermodynamics that evacuation can enhance the

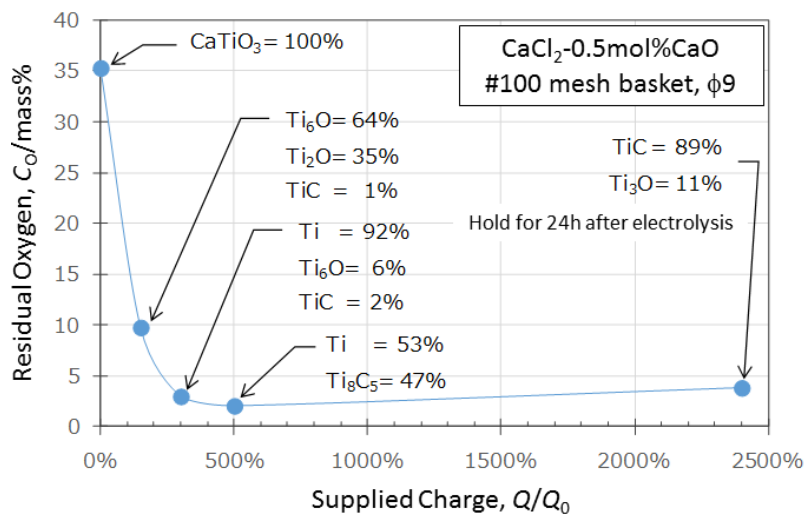
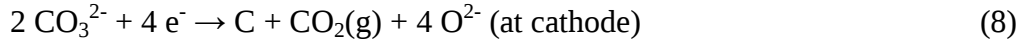


Fig. 8 Residual oxygen and phases identified by XRD in the powder obtained from molten CaCl₂-0.5mol%CaO at 1173 K. The volume fraction was evaluated based on the reference patterns.

reduction according to eq.(6). Continuous evacuation during the reduction of TiO₂ using electrolysis in CaCl₂ was patented by Hayashi and Uda¹⁹⁾, 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 CO₂ dissolves in the molten CaCl₂ and forms CO₃²⁻. This CO₃²⁻ precipitates carbon at the cathode and reacts with Ti to form carbides.



Apparently these parasite reactions due to CO₃²⁻ reduce the current efficiency for Ti forming by removing oxygen. Large electric charge such as $Q/Q_0=600\%$ was given to CaTiO₃, 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 CO₂ 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 CaTiO₃ 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.

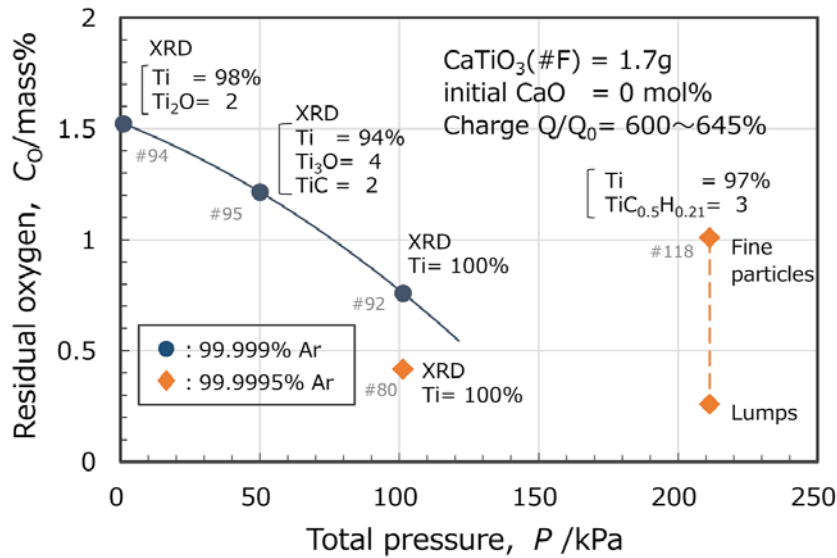


Fig.9 Residual oxygen and phases identified by XRD in the obtained Ti powder.

Conclusions

This work proposed a new procedure consisting of two steps; CaTiO₃ formation with Fe removal from TiFeO₃, and electrochemical reduction of CaTiO₃ in CaCl₂-CaO melt. Using dissolution of TiFeO₃ into HF solution and the successive F removal, Ti and Fe were ionized in aqueous solution. The addition of (NH₄)₂S with a masking agent such as tartaric acid could separate Fe²⁺ 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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