

INDUSTRIAL PRODUCTION OF SPONGY TITANIUM OF LOW HARDNESS AND
PREVENTION OF GAS-SATURATED INCLUSIONS.

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Abstract

The main factors that define the quality of spongy titanium and allow its production with low hardness and without gas-saturated inclusions are: high level of magnesium and titanium tetrachloride purification, optimization of technological conditions using automated processes control systems, high level of cleanliness in the apparatus, and establishment of strict control at all stages of titanium production.

Introduction

Consequence of interaction with the impurities is considerably more substantial for titanium, than for most structural metals. Contaminated titanium refining presents a complex scientific-technical problem, which has not yet been introduced into the industrial practice. That is why the quality of primary (spongy) titanium is in the centre of attention since the moment of organizing the industrial production.

Purity of Reactants

Purity of the finished products is, in many respects, defined by the purity of used reagents and the problem of spongy titanium quality is considered as a complex of problems of metal associated manufacturing operations. Influence of each manufacturing stage on the change of spongy titanium hardness is set forth in (1). The technology was developed on the basis of an extensive programme of investigations (2) and includes a matrix of all technical stages of titanium production. Thus, there have been developed apparatus and technology of preparing magnesium as a reducing agent of high purity and transporting it in the molten form to reduction apparatus (reactor) without the intermediate depressurization (3,4). Such technology is possible thanks to the fact that titanium production is an integrated technolo-

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Another problem is the O₂ content of the CaTiF₆ powder produced, which must be lowered from the present 1 wt pct in order to produce Ti ingot of acceptable purity. Use of excess Ca in the reduction step did not lower the O₂ content of the Ti product to acceptable purity.

Another improvement would be a directed heating source, such as a plasma arc torch, to melt the slag since the slag presently is heated only by conduction of heat from the Ti ingot.

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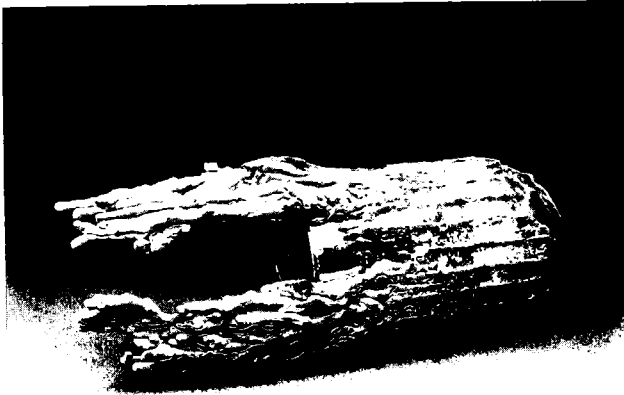


Figure 4 - Separation of CaF_2 slag from Ti ingot.

Using the furnace operation procedures described above, CaTiF_6 and Ca were fed onto the stub at low temperatures to cause reduction, and then power was increased to form a molten Ti pool and to consolidate the Ti to the ingot and to separate byproduct slag. Titanium recovery of 93 pct was obtained, including complete separation of Ti from slag in a test using 2305 g of reactants to produce 344 g of Ti. Titanium distribution, shown in Table III, was calculated from chemical analyses of the products for Ti. Nearly complete separation of Ti from the byproduct slag reporting to a removable container at the bottom of the furnace enclosure ("slag trap") is shown. Some slag that remained in the crucible was easily removed from the outside surface of the ingot and contained a small amount of Ti.

TABLE III Titanium Distribution and Analyses for CaTiF_6 Reduction Run

Product	Weight (g)	Ti distribution (pct) from CaTiF_6 feed ¹	X-ray diffraction
Ti ingot	Ingot gain of 344 g	92.85	NA
Slag in slag trap	1,979	0.09	P = CaF_2 , BDT = CaO
Slag in crucible	377	3.23	P = CaF_2 , BDT = CaO
Furnace dust	150	3.81	P = CaF_2 , T = CaTiF_6

NA Not analyzed.
 P Primary phase (40-100 pct).
 T Trace phase (1-10 pct).
 BDT Barely detectable trace phase (less than 1 pct).

¹Ti analysis of starting CaTiF_6 powder was 22.5 wt pct.

Conclusions

Reduction of CaTiF_6 with Ca was investigated in both batch and continuous processes using, respectively, the induction slag batch and ingot furnaces. Reduction and slag separation operations must be performed at different temperatures. Batch reduction tests and DTA results show that the reduction reaction ignition temperature is low (<873 K). In contrast, byproduct slag separation must be accomplished at temperatures above the melting point of CaF_2 (1696 K) using heat from a molten pool of Ti in the induction slag ingot furnace. Byproduct CaF_2 slag separation was obtained, with good Ti recovery to the ingot. However, combining the reduction and slag separation operations into a single-step process at slag separation temperature was unsuccessful due to volatilization of Ca metal reductant.

Slag melting was accomplished by conduction of heat from the induction heated Ti ingot. Once a molten pool was established, feeding of the reactants began.

Three methods were examined to react the feed material and separate the byproduct slag from the Ti ingot: (1) feed reactants directly onto molten pool, (2) feed prereduced product from the batch furnace onto a molten pool of Ti in a two-step process, and (3) feed reactants onto the hot, but solidified Ti ingot, with no power until a reduction occurred (to limit Ca volatilization), then turn power to 50 kW to obtain a molten pool of Ti. The third approach was found to be more satisfactory because it avoided Ca loss and was a single-step process.

A 9.53-cm-diameter Ti stub, weighing 5,768 g, was used in the reduction experiment, during which 773 g of reacted product was fed for the two-step reduction process. The majority of the slag remained in the crucible area, and chemical analysis for Ti in the slag was 1 wt pct. Weight gain of the Ti stub was 112 g, with a calculated Ti recovery of 85 pct. Brinell hardness of the top of the ingot increased from 188 HRB to 272 HRB, indicating O₂ contamination, as expected, from the pre-reacted feed. Oxygen content of 0.563 wt pct was measured at the top of the ingot, with a N₂ content of 0.004 wt pct.

One of the problems with this reaction is the excessive amount of CaF₂ slag produced as byproduct. The induction slag ingot furnace had no provision for continuous slag removal. In one run, reacted product was fed to the furnace and resulted in slag build-up in the crucible melting area. The run had to be prematurely terminated after 1.4 kg had been fed. Figure 3 shows the resulting ingot and slag. Therefore, a means of separating slag from the Ti ingot was necessary for continuous operation.

Slag was successfully separated from the ingot during a run (using 2.05 kg of reacted feed) in which a continuous slag layer formed around the stub. A machined Ti starting stub allowed for a 0.48-cm gap between the starting stub and the water-cooled Cu crucible, and approximately 1 kg of CaF₂ slag was added to the top of the ingot. Power was held low enough to melt the slag and form the desired slag layer, then raised to 70 kW to obtain a molten pool. Reacted product was fed to the pool for about 20 min with no build-up of slag. About 1.4 kg of slag fell to the bottom of the furnace, and the rest appeared as long drips below the Ti stub, as shown in Figure 4. The slag was removed, and the weight gain of the ingot was 325 g, for a Ti yield of 94 pct. The above procedure also was followed for ingot tests using CaTiF₆ and Ca powders for single-step reduction.

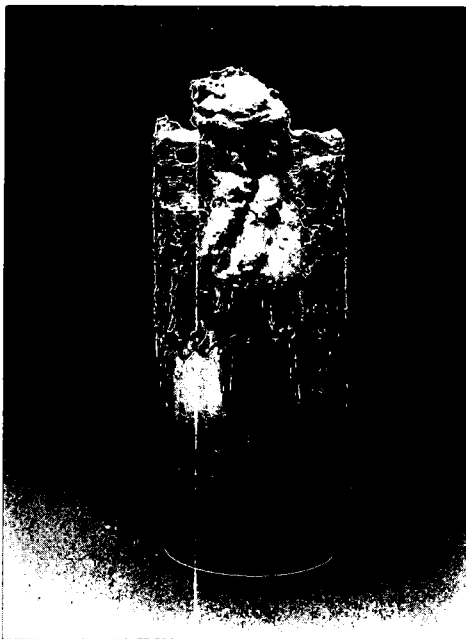


Figure 3 - Ti ingot and CaF₂ byproduct showing slag buildup.

Due to the volatilization of Ca, reactants cannot be fed onto a full pool of molten Ti. However, since the reaction temperature is low (<873 K), the power can be turned down (or off) momentarily when reactants are fed onto the stub. Due to the amount of CaF₂ slag produced by the reduction reaction (83 pct of the total mass), it was difficult to re-establish a fully molten pool after the reaction took place. Therefore, an auxiliary directed energy source, such as an Ar plasma torch, is recommended to assist in melting the CaF₂ slag in the reaction/separation zone.

product. To try to agglomerate these globules, a build-up run was made by consecutively reacting four batches of 400 g CaTiF_6 and 160 g of Ca to yield 2.24 kg of reacted product. This increased the amount of Ti in the crucible, but did not result in more agglomeration.

Ti globules were removed from a reacted mass and melted into a button for chemical analyses by non-consumable arc melting in a water-cooled Cu hearth in an inert atmosphere to determine the Ti product purity. In an initial test, O_2 content of the starting CaTiF_6 powder was 4.5 wt pct, which resulted in contamination of the Ti product (see test 1 in Table II). A second test using CaTiF_6 powder with O_2 content of 0.78 wt pct still resulted in high O_2 content (2.19 wt pct), and the button was extremely brittle. Thus, it is critical to have a CaTiF_6 powder with no O_2 contamination. Chemical analyses of these buttons are shown in Table II. Interstitial contents of Ti sponge (ASTM B299, GP) and unalloyed Ti (Grade 4) are given for comparison.

Table II Chemical Analyses of Ti Buttons (wt pct)

	Ca	F	N_2	O_2	C
Test 1 (4.5 wt pct O_2 in CaTiF_6)	0.032	0.032	0.08	2.27	0.12
Test 2 (0.78 wt pct O_2 in CaTiF_6)	NA	NA	0.05	1.95	NA
Test 3 (40 pct excess Ca)	.01	.12	0.08	1.64	0.05
Test 4 (60 pct excess Ca)	.02	.12	0.11	1.17	0.07
Ti sponge	NS	NS	.02	.15	.03
Unalloyed Ti (grade 4)	NS	NS	.05	.40	.10

NA Not analyzed. NS Not specified.

Thermodynamic information predicted that the Ca would remove O_2 from Ti. Therefore, tests were conducted with 20, 40, and 60 pct excess Ca. Brittle Ti buttons, which were high in O_2 , still resulted, as shown in Table II, although free Ca was present in the slag of the reaction product. Only the 40 and 60 pct excess Ca results are shown.

Reduction Tests in the Induction Slag Ingot Furnace

A schematic of the induction slag ingot furnace for the production of Ti ingot from the CaTiF_6 is shown in Figure 2. An initial starting stub of Ti was attached to the water-cooled Cu withdrawal stinger and positioned in the crucible about 7.62 cm from the top. Various diameters of the starting stub were investigated to achieve an adequate slag layer for separation of the byproduct CaF_2 slag from the Ti ingot. An initial amount of CaF_2 slag (about 700 g) was added on top of the stub. The furnace was evacuated to a pressure less than 50 μm Hg, then back-filled with Ar to 34 kPa. Power initially was turned up to 30 kW to melt the slag, then raised to 50 kW to obtain a molten pool of Ti.

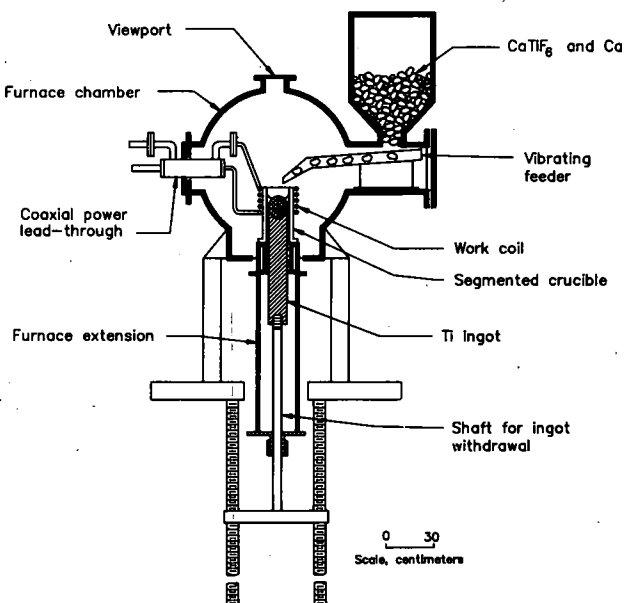
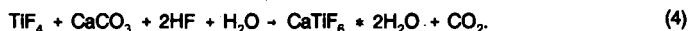


Figure 2 - Induction slag ingot furnace.

- (b) Calcium carbonate (CaCO_3) then is added to the solution in a water bath at 338 K, after which CaTiF_6 precipitates by reactions (3) and/or (4).



The CaTiF_6 slurry is dried overnight at 338 K, and then dried for 3 days at 468 K. The dry powder is crushed and stored in a glovebox or in an oven (373 K) to prevent absorption of moisture. Typical CaTiF_6 chemical analyses, shown in Table I, indicate that the CaTiF_6 produced to date has not been free from water of hydration. In addition, an O_2 -containing species, TlOF_2 , also can be present.

Table I. Typical CaTiF_6 Chemical Analyses, weight percent^{1,2}

C	0.0001-0.001	N ₂	0.02
Ca	18.5-20.7	O ₂	0.78-2
F	45.8-50.5	Si	0.07-0.22
Fe	0.09	Ti	21.1-22.5
Mg	0.15-0.22		

¹Impurity phases detected by X-ray diffraction included CaF_2 , TlOF_2 , and $\text{CaTiF}_6 \cdot 2\text{H}_2\text{O}$.

²Theoretical stoichiometric wt pct for CaTiF_6 : 19.85 Ca, 56.44 F, 23.71 Ti.

Differential Thermal Analyses (DTA)

Differential thermal analyses conducted in an atmosphere of flowing argon (Ar) were performed to obtain information on the reaction temperature for the reduction reaction 1. An exothermic reaction was observed at 833 K. Results of X-ray diffraction indicate complete reduction, with a primary phase of CaF_2 and a trace phase of Ti detected. Therefore, with induction heating, a moderate ignition temperature is required by the Ca metal to cause a reaction to occur in induction slag furnace batch reduction tests. In practice, heat from a hot ingot in the ingot furnace would be sufficient to cause complete reduction of the feed material. Therefore, power could be decreased during reactant feeding to avoid volatilization of Ca and then raised to melt the Ti and separate it from the byproduct CaF_2 slag.

Batch Reduction Tests Using Induction Slag Batch Furnace

The induction slag batch furnace was used for batch reduction tests with and without graphite containment crucibles. The furnace contained a 12.7-cm-diameter, 24-segment water-cooled Cu crucible, and power was supplied by a 100-kW, 10,000-Hz motor generator. To minimize the amount of reactants needed, a graphite containment crucible was used for initial tests. The crucible acted as a heat source, being rapidly heated by the induction field. Tests were conducted by placing 100 g CaTiF_6 and 40 g Ca (stoichiometric amount) in a graphite crucible inside of the water-cooled Cu crucible. The system was evacuated to below 50 μm Hg and backfilled to 69 kPa Ar prior to the run. The reduction of CaTiF_6 took place according to Equation 1. The reduced product contained approximately 17 wt pct Ti and 83 wt pct CaF_2 slag. Power levels investigated ranged from 10 to 75 kW. Power levels as low as 15 kW were sufficient to initiate a complete reaction. After completion of a test, the charge was allowed to cool for 2 h prior to removal. The reacted product was easily removed from the graphite container and was then ground using a shatter box to prepare a sample for X-ray diffraction and chemical analyses. Typical X-ray diffraction analyses indicated a primary phase of CaF_2 and trace phases (1-10 pct) of Ti, TiC (at higher power levels), CaO, and Ca(OH)_2 .

Charges of up to 800 g of CaTiF_6 with stoichiometric amounts of Ca also were reacted without use of a graphite container in the water-cooled Cu crucible. In this case, low-temperature induction heating of the Ca metal was sufficient to initiate the highly exothermic reaction. Power typically was held between 30 and 60 kW. The charge also was allowed to cool for about 2 h prior to removal. As was found in the graphite container tests, X-ray diffraction analyses indicated a primary phase of CaF_2 and trace phases of Ti, CaO, and Ca(OH)_2 . The Ti had formed small globules distributed in the CaF_2 slag by-

the reaction, (3) input of heat to maintain reaction and maintain the Ti and byproducts in the molten state, (4) mixing of the reactants and products to ensure both reactant availability for reaction and product homogeneity, and (5) a method to add more feed and to remove and separate product Ti ingot and byproduct slag to make the process continuous. The induction slag process developed by the Bureau of Mines¹⁹ provides mixing, continuity, and containment, and thus is the ideal reactor. The process was designed specifically for melting Ti scrap and sponge in a water-cooled, segmented crucible by induction heating. In the melting technique, the bottom of the crucible is formed by the cooled Ti ingot, which is continuously withdrawn. The Ti metal route proposed by the Bureau of Mines²⁰⁻²² uniquely applies the induction slag furnace to the reduction of fluorotitanate directly to Ti metal ingot by using a low-cost, domestically available ilmenite as raw feed material.

A system involving calcium fluorotitanate (CaTiF₆) feed and Ca reductant was chosen for simplicity of chemical species, and in consideration of the volatility of reductant and slag. Calcium has the highest boiling point among the alkali and alkaline-earth elements commonly used for reduction (i.e., Na, K, Mg, and Ca). An additional advantage for the use of Ca in this route was indicated by the thermodynamic work of Mah,²³ Kelley,²⁴ and Kubaschewski,²⁵ and the experimental processing work of Suzuki,²⁶ which showed that Ca has the greatest potential to deoxidize the Ti metal product. A process to deoxidize Ti scrap and powders with Ca in a Na carrier was patented recently by Fisher.²⁷

This paper discusses the reduction of CaTiF₆ to Ti metal using Ca metal reductant, with calcium fluoride (CaF₂) as byproduct. Batch-type studies were conducted in an induction slag batch furnace with and without graphite containment crucibles. Continuous production of Ti was tested in an induction slag ingot furnace employing either a two-step process (with reacted feed) or the preferred single-step reduction with Ca metal reductant and CaTiF₆ feed.

Experimental Procedures and Results

Process Flowsheet and Chemistry

A process flowsheet for the proposed route to Ti metal²⁰⁻²² is shown in Figure 1. Details of the process unit operations to produce the CaTiF₆ from ilmenite used in the reduction step are presented elsewhere.²¹⁻²² The reduction step is given by--



CaTiF₆ Preparation

To expedite the research effort, a synthetic CaTiF₆ was prepared using pure TiO₂ (anatase) instead of ilmenite ore for the reduction process studies. The synthesis of the fluorotitanate compound is a two-step process.

- (a) TiO₂, leached with 48 to 52 pct HF at 338 K, produces an aqueous solution of TiF₄ and is represented by the reaction--



The HF solution first is heated in a water bath to 338 K, then placed in an ice bath to control reaction temperature. TiO₂ is added and the leach solution temperature is maintained at 343 to 353 K by the exothermic reaction and rate of feed of the TiO₂. Unreacted solids are filtered prior to the crystallization step.

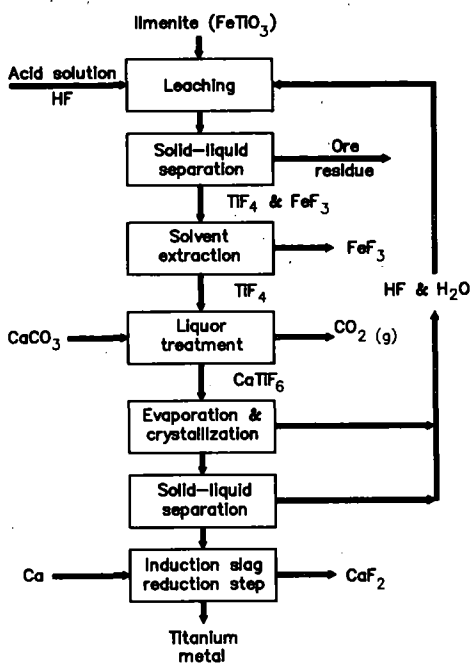


Figure 1 - Process flowsheet of CaTiF₆ route to Ti.