INDUCTION SLAG PROCESS FOR PRODUCING TITANIUM BY REDUCTION OF CALCIUM FLUOROTITANATE

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Abstract

As part of a U.S. Bureau of Mines program to develop a more continuous Ti metal process that uses domestic resources, a study was made of the reduction of $CaTiF_6$ to Ti metal using Ca as reductant. Two-stage batch reduction tests carried out at 30-kW power in an induction slag batch furnace show reaction initiation and completion within 5 min. Techniques were devised to feed this reacted product into an induction slag ingot furnace to produce a Ti ingot with 94 pct Ti recovery and to separate the Ti from the byproduct CaF_2 slag. The latter technique also was applied to investigate a single-step reduction test in which $CaTiF_6$ and Ca reactants were fed to the ingot furnace to produce Ti ingot directly.

Introduction

A process to manufacture pure Ti that would use lower grade, less costly, and more available domestic raw materials, such as ilmenite ($FeTiO_3$), has long been sought. A process that is continuous, thus less costly, and uses fewer, simpler process steps would be of great advantage.[1] Early attempts to obtain such an ideal process usually involved a Ti oxide ore such as ilmenite, and fluoride salts as the Ti extraction agent to produce fluorotitanates and Ti fluorides.

In 1952, Kroll[2] discussed the advantages and problems of producing TiF_4 and alkali fluorotitanates such as Na_2TiF_6 as alternatives to the chloride route to Ti. The distinct advantage seen by Kroll[3] is that O_2 does not displace the fluoride from the Ti as it does from the chloride, making the fluorotitanates somewhat easier to handle. Hunter[4] found that reduction of Na_2TiF_6 with K produced a product with only 73 wt pct Ti. At about the same time, Weiss[5] attempted to produce Ti by pressing a mixture of K_2TiF_6 and Al or Na into a pencil-shaped electrode, which was reduced by melting in an arc furnace. The product contained 97.5 wt pct Ti and was quite brittle, indicating interstitial contamination.

Most subsequent research (post-1945) emphasized fluorotitanate salt electrolysis in a molten salt bath to form metallic Ti.[6-8] Methods other than electrolysis to obtain metallic Ti, using fluorotitanates as the raw feed material, also have been proposed. These methods include the AlTi-Oxy process[9, 10-12] using Al as a reductant in a Zn bath, as well as methods using Na,[5, 13] K,[14-15], Mg,[16] and Al[5, 16-18] as reductants. None of these methods have proved to be commercially successful, and none produce Ti ingot directly.

A simpler, more efficient route to Ti metal is by chemical reduction of the fluorotitanate salts to directly form Ti ingot. However, molten Ti and its alloys are reactive with materials commonly used for containment. An ideal reactor for the reduction of the fluorotitanate salts would provide (1) an enclosure that is nonreactive with the Ti and byproducts, (2) a volume with sufficient residence time for completion of

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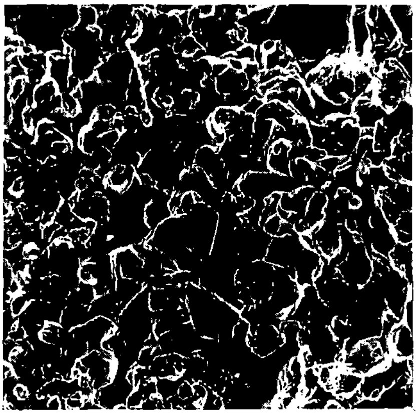
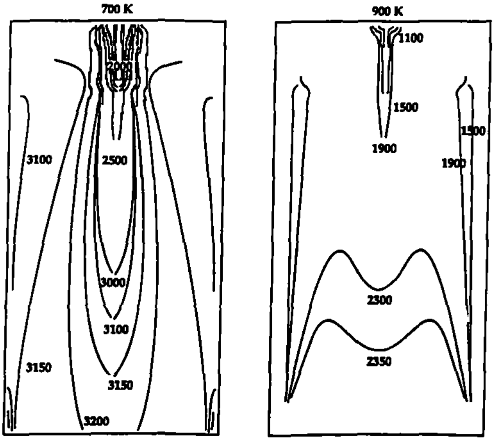


Microscopic cut in a spiral stalactite recovered in the burner (x 200)

fig. 9

fig. 10 Partly molten and agglomerated titanium particles recovered in the crucible (x3500)



(a) Adiabatic conditions

(b) Walls at 1400 K

fig. 11
Isotherms inside the burner according to mathematical modelling (SZEKELY)

The DITINGOT process

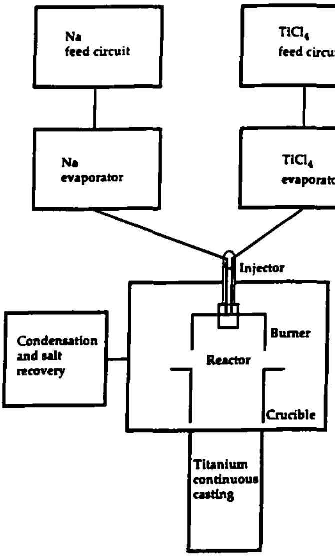


fig. 5 Idealized sketch of the process

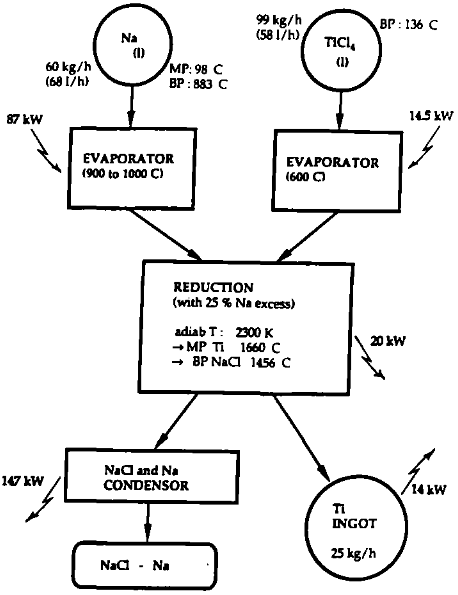
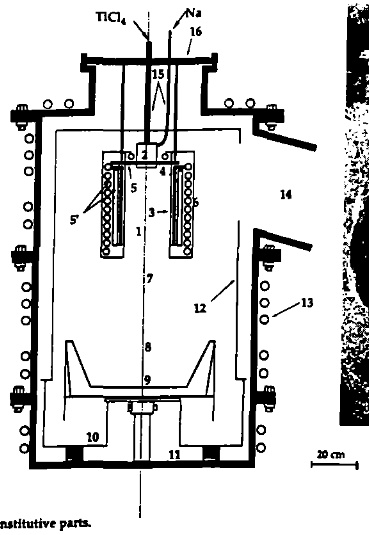


fig. 6 Approximate material balance and power consumption for a 25 kg Ti/h prototype.



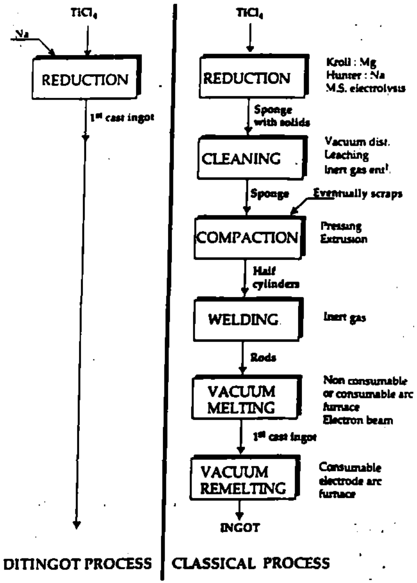
Reactor constitutive parts.

1. Inside part of the burner
2. Injector
3. Internal wall of the burner (SiC)
4. Dead angle of the burner
5. Upper wall of the burner
5' Insulation and sodium cooling circuit
6. Burner external coil
7. Burner to crucible free space
8, 9. Upper level and bottom of crucible
10. Salt container
11. Bottom of the reactor
12. Loose metal sheet
13. Reactor water cooling coil
14. Evacuation funnel to condensor
15. Reactants inlets
16. Reactor cover

fig. 7

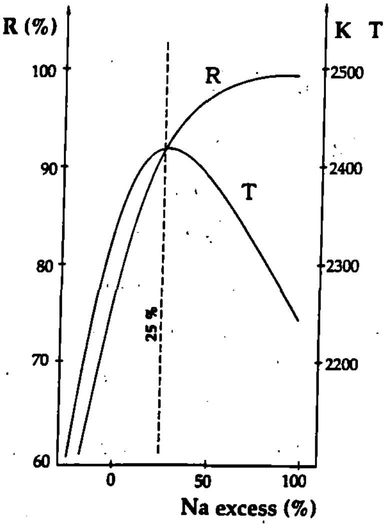
Macroscopic cut in a spiral stalactite recovered in the burner (x 40)

fig. 8



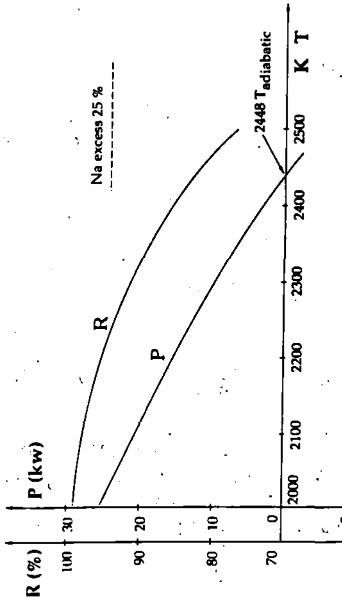
Bloc diagram comparing the DITINGOT process with conventional ones.

fig. 1



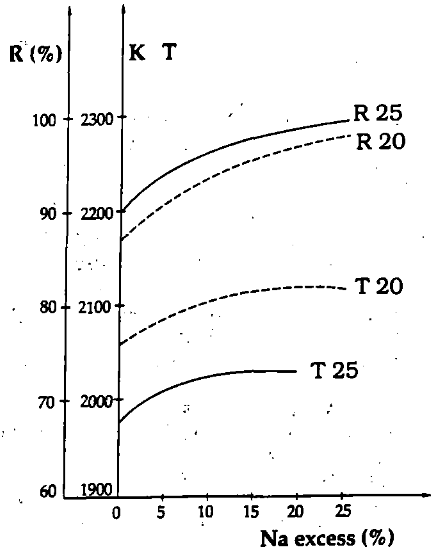
Metallurgical efficiency R and reaction temperature T in function of the percentage of excess sodium - Adiabatic conditions - Sodium and titanium tetrachloride introduced as gases at their boiling point at atmospheric pressure (Na : 1156 K, TiCl4 : 400 K) - No dilution by inert gas

fig. 2



Metallurgical efficiency R versus reaction temperature T for various values of the heat losses P in a reactor capable of 25 kg titanium per hour. Other conditions : 25 percent excess sodium, Na introduced at 1273 K and TiCl4 introuduced at 573 K - (EQUILIB FACT).

fig. 3



Metallurgical efficiency R and final temperature T for two values of the heat losses P (20 and 25 kW) in a reactor capable of 25 kg titanium per hour, in function of the sodium excess percentage. Other conditions : Na introduced at 1273 K and TiCl4 introduced at 573 K. - (EQUILIB FACT).

fig. 4

CONCLUSIONS

The 25 kg Ti/h experimental set up was used for 24 runs lasting up to 2 hours. Some of them rated 35 kg Ti/h for 1 1/2 hour.

It proved satisfactory from the following stand points :

- storage and purification of reactants
- measure and control of reactant flows
- evaporators and injection in the burner
- geometric stability of the burner
- condensation of molten sodium chloride out of the reaction zone

Problems that are still to be solved :

- a satisfactory preheating system to overcome the transient period at the beginning of the reaction to avoid the burner clogging. A temperature higher than the titanium melting point must be reached in the burner. Induction heating seems the most promising, but a plasma torch should also be considered.
- increase the diameter of titanium particles to keep them in the crucible. This point can not be studied if the previous one is not solved.
- realize the continuous casting of titanium.

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The burner internal shape was fixed after experiments making use intentionally of too long burners : it was shown that the maximum temperature was reached at a 30 cm distance from the injector nozzle. A narrowed section had to be introduced in the sodium vapor tube to increase the pressure drop and avoiding flow oscillations. The main achievements of these experiments were that sodium and titanium tetrachloride could be securely fed as vapors to the injector in a constant, controllable and reproducible way; that temperatures as high as 2 000 Celcius were effectively obtained in the burner; that large amounts of titanium were recovered in the crucible and in the burner; that no lower valency titanium chlorides were observed and that sodium chloride was mainly condensed on the loose cylinder in the reactor itself.

However, titanium in the crucible was mainly recovered as fine particles with diameters in the range of 2 to 10 micrometers. The inside of the burner itself proved to be clogged in a very short time (ten to fifteen minutes) by sodium chloride and titanium metal conglomerates who changed the burner internal shape and finally the whole reactor zone.

The same results were observed with swirling coaxial and with toroïdal burners.

Experiments with preheating

The first preheating was done by means of an electrical resistance placed like a candle inside the reactor zone and by introducing an electric resistance in the alumina refractory material in the crucible. The maximal temperatures achieved by this method were 800° C in the burner and 1 100° C in the crucible. This proved to be ineffective, so a Kanthal electrical resistance mantel was placed inside the burner walls , behind the silicon carbide.

This allowed preheating of the burner up to 1 100° C. The injector itself was preheated up to 750° C. The experiments performed with this preheating system showed that a maximum temperature of 1 350 to 1 400° C was reached on the external (opposite to the reactor zone) surface of the silicon carbide wall (after 15 to 30 minutes). A tantalum heating mantel was tried, in order to increase the preheating temperature, but it proved unpredictable : it broke usually before the experiment started. In all experiments, the inside of the burner was clogged like in experiments made without preheating, with, however, less sodium chloride in the titanium shapes recovered (see figures 8 to 10).

Concerning titanium recovery, the best results obtained were in the burner, with layers of pure and partially molten titanium and in the crucible, with partly molten titanium particles of about 10 micrometers diameter. The salt condensed on the loose metal sheet in the reactor was mainly sodium chloride and excess sodium but contained approximately half the titanium metal produced as fine powder (2 to 10 micrometers). The metal efficiency in the reaction zone was in the range of 40 to 45 % but not gathered in a satisfactory molten pool.

Supplementary experiments were carried out. One of them was made without sodium cooling the burner. The experiment was shortened in order to avoid destroying the burner. However, a maximum temperature of 1 350 Celcius was again observed after 15 minutes. After the experiment, a central egg of pure titanium and layers of titanium were found in the burner. Another experiment was carried out without burner walls, with only the injector and the crucible inside the reactor vessel. Making use of an infrared camera and of an ignition wire, it could be shown that the flame went back from the wire to the injector nozzle, showing the reaction rapidness.

MATHEMATICAL AND PHYSICAL MODELLING

A computer thermal model of the burner was made by BELSIM. On the basis of the measured temperature initial increase, the model showed that a transient time of two hours would be necessary to reach the titanium melting point on burner walls, even if these walls are preheated to 1 100° C. This was due to the sodium cooling, considered as necessary to keep the geometry of the reaction zone. A physical model of the burner and of various injectors was tested at the Von Karman Institute. The vapor mixing proved to be very satisfactory, and can not be considered as a limiting factor. Further mathematical modelling of the reaction was made by Professor J. SZEKELY at MIT. It allowed to determine velocities, temperatures and concentrations in the burner of various injector types. It was shown that the reaction is almost finished when the gases leave the burner, but that the temperature profile is very sensitive to the walls temperature (figure 11).

Therefore, it was decided to build a bigger installation able to produce 25 kg Ti/h in the hall for testing prototype of the Centre de Recherches Industrielles (CRI) de l'Université Libre de Bruxelles, at Nivelles, situated at approximately 25 km from Brussels. The experiments started in February 1987, in the form of a research contract between Cockerill Sambre S.A. - ULB and Région Wallonne, the Southern part of Belgium. This last equipment only and some of its experimental results will be described.

The equipment

Feed circuits

Except for sodium special purification problems, sodium and titanium tetrachloride feed circuits were identical. A first part was devoted to loading the reactants to the circuit by either pumping liquid $TiCl_4$ under argon or by manual transfer of sodium ingots. Sodium was melted under argon and transferred through a stainless steel filter to a second vessel. The second part of the feed circuits was a waiting loop where the liquid reactant was kept moving at the approximate flow rate necessary for the reaction. The third part of the feed circuits was made of Inconel 600 evaporator coils included in electric resistance furnaces and of heated transfer lines to the reactor. The third one was fed by opening the waiting loops to start the reaction. $TiCl_4$ was heated up to 400° C and sodium up to 950° C.

Reactor

The reactor was a watercooled vessel with a large lateral opening leading to the salt recovery circuit. The reaction zone included the burner on which the injector was fitted, and a fix-crucible placed to recover titanium. The internal wall of the burner was made of silicon carbide, eventually preheated by electric resistance. After a layer of heat insulator, a sodium cooled coil was inserted in order to maintain the overall shape of the burner during the reaction. The external walls of the burner were made of three titanium sheets placed at three different diameters. Seven different injectors were tried. Each of them provided $TiCl_4$ injection in the center and sodium at the exterior in order to prevent any unreacted $TiCl_4$ from escaping the reaction zone. The fix crucible was made of alumina eventually preheated by electric resistance. It was likely to be replaced by a continuous casting system. A loose cyclindrical metal sheet, which acted as molten salt condensor, was placed inside the vessel, surrounding the burner and the crucible. Molten salt was recovered at its bottom in a large metal crucible.

Salt circuit

At the reactor outlet, a special salt condensor, fitted with metal plates was foreseen. It was followed by three cyclones in series leading finally to a scrubber. This salt circuit proved to be useless because all the salts and the excess sodium were condensed on the loose cylinder inside the reactor during the two hours experiments.

Control room

This room was containing a centralized command pulpit with a synoptic table showing the state of all the valves, pumps and levels of the reactants in their vessels. A centralized data logging system was able to handle more than two hundred measures on a P.C. Twenty measurements were carried out simultaneously and independently of the P.C. allowing permanent visual control.

Safety

The sodium and the titanium tetrachloride vapor feeding circuits were placed in separate small buildings inside the prototype testing hall. The bottom of the sodium building was provided with Graphex Ck 23, while the $TiCl_4$ building was closed and connected to a vertical scrubber placed outside the hall.

EXPERIMENTS

Only the experiments (in total 24) performed with the 25 kg Ti/h equipment will be shortly described.

Experiments without preheating

It was thought initially that preheating of the reaction zone was not necessary, because of the reaction's very high exothermicity . Moreover, as the reactants were introduced as vapors, ignition occured from itself.

This paper is describing the present status of a research aimed at developing a new continuous process [4] for making titanium ingots in one step.

BASIC IDEAS

The general principle of the process is to react, in one step and at atmospheric pressure, gaseous sodium with gaseous titanium tetrachloride. Adiabatic reaction temperature is easily in the range of 2 200-2 400 K, so that the products of the reaction are gaseous sodium chloride and liquid titanium. As titanium is the only condensed constituant, the pure metal should be recovered directly as an ingot (the DITINGOT Process).

Such a process, if successful, has many advantages versus those in use today, mainly because it is continuous and avoids making sponge or powder contaminated with salts as an intermediate. Figure 1 makes this very clear in a synthetic bloc diagram. A Cockerill Sambre industrial evaluation team came to the conclusion that advantages of this new process could be described as follows : The process is continuous, avoids the sponge and the associated operations, and is susceptible of full automation.

Accordingly, the plant can be very compact, reducing investment by a factor of at least two. Energy consumption can also be reduced by at least one third. The processing time and the metal inventory can be drastically reduced by at least 20. The manpower can also be reduced by at least 3. More best quality metal can be produced because no iron contamination can occur in the reactor, and no nitrogen or hydrogen contamination can occur before the ingot solidification due to suppression of any operation on high specific area intermediates, no carbon contamination can occur coming from any vacuum pumping system. Working conditions and environmental protection are also improved because very small amount of reactants are present in the reaction circuit at any time, manual operations during the process are drastically reduced and no handling nor physical treatment of sponge is necessary. All these advantages were due to reduce operating costs by at least twenty percent against conventional processes in use today. The process theoretical feasability was determined on the basis of thermodynamic calculations. Figure 2 shows the results for adiabatic conditions when sodium and $TiCl_4$ are introduced in the reactor at their boiling temperature, as gases. The metallurgical efficiency increases when the percentage of excess sodium increases. Temperature passes however through a maximum, at about 2 400 K, and 25 percent excess sodium. At that point, the metallurgical efficiency is of approximately 91 percent. In practice, some heat loss should be considered in the reaction zone. Further calculations were made for a reactor capable of 25 kg titanium per hour, supposing various heat loss levels in the reactor. Figures 3 and 4 show the favourable influence of such losses (expressed in kW) on the metallurgical efficiency, the reaction temperature remaining well above the titanium melting point. Theoretical optimum conditions could be operating with 10 to 15 percent excess sodium and a reactor heat loss of 20 to 25 kW (for 25 kg Ti/h), resulting in a metallurgical efficiency better than 95 % in the reactor, the rest of titanium being recovered outside, at a lower temperature, as a powder by product. Figure 5 gives an idealized sketch of the process, while figure 6 gives some important figures concerning material balance and power consumption for a 25 kg Ti/h prototype.

EXPERIMENTAL

Small scale laboratory experiments started in 1975 in the Université Libre de Bruxelles (ULB) by Winand, Fontana and Segers, without external funding. Initially, extra heat was provided to the reaction by a d.c. plasma torch but was found deleterious to the metallurgical efficiency in the reactor : argon was diluting the reaction gases, favouring the backward reaction. Further experiments made only use of some external resistance heating. At the end of 1979, a large belgian steel company - Cockerill S.A. - became interested in the project. The initial patent property was transferred to this company and the research went on in the frame of a contract between Université Libre de Bruxelles, Cockerill and IRSIA, a Belgian governmental sponsoring organization. In mid-1980, a new laboratory scale experimental set up was started, capable of 1.5 kg Ti/h. It was possible to feed a reactor with sodium and titanium tetrachloride in gaseous state, to reach the reaction temperature in a very short time, and to produce titanium metal, but it was impossible to achieve thermal autonomy at that scale.