



Titanium Molten Salt Electrolysis – Latest Developments

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Abstract

The importance and demand for titanium are increasing worldwide. A big market could be opened, but the development of new applications is constrained by the high costs for titanium. The Kroll process is the only available method to produce titanium in large-scale quantities.

The need for a cheaper and quicker process has encouraged the research in various alternative methods. A study performed in 2004 by the US Department of Energy [11] identified 16 different techniques that are actually being developed. Some promising new approaches could reduce the cost for titanium by as much as 30 to 50 %. The main objective is to develop alternative procedures reducing the number of steps of the Kroll-process either by combining some of them in only one step or by completely substituting them. The main targets are to obtain a product of high purity, especially with a low oxygen content, to receive a marketable form of the final product (powder, sponge,...) and to reach a continuous process. In the past many kind of researches have been conducted but all of them failed.

This article will give an overview over the actual state of art of the titanium molten salt electrolysis processes, their advantages and disadvantages as well as problems and expectations. The definition for an electrolytic process is used in a broader sense, i.e. containing an electrolysis even if it is not directly for titanium. These approaches can be structured in:

- electrolytic reduction of TiCl_4 in a molten salt bath
- direct calciothermic reduction of TiO_2 in a molten CaCl_2 -bath
- direct winning by electrolyzing a titanium raw material-carbon-anode
- electronically mediated reaction without direct contact between the titanium raw material and the reductant.

The raw materials can be Ti-chlorides, Ti-carbides, Ti-oxides or other Ti-compounds. The molten salt bath composition varies, often including NaCl, KCl, CaCl_2 or MgCl_2 . The results regarding purity of the metal are partially very promising. Most procedures are still in the very beginning of the research while others already have been scaled-up to pre-commercial pilot plants.



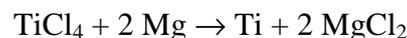
Actual Situation

The only large-scale process for titanium production is the Kroll process. It has been developed in 1946 by Mr. Kroll, himself foreseeing that because of the low effectivity of the process, its complicatedness and its high costs, it would be substituted by a better process within few years. This has not happened despite of many researches and trials. One direction that is being considered since then is the electrowinning of titanium from molten salts. This direction is considered to be the most promising since all the other light metals like aluminium and magnesium are won by electrolysis in molten salt.

In a first step the Kroll process will be described shortly and relevant alternative methods will be mentioned. In a second step the state of art of the actual research in the production of titanium from a molten salt bath will be shown. Finding a cost-reducing technology is an indispensable basis to increase significantly the actual production of 60 000 t/y [4], especially since there is no limit on the raw materials side.

The Kroll Process and Alternatives

The enriched titanium ore is chlorinated, TiCl_4 is obtained. This titanium chloride is reduced in the Kroll reactor with magnesium:



The reduction takes place under argon gas because of the high affinity of titanium to atmospheric gases. Subsequently the obtained titanium sponge is cleaned by vacuum distillation and molten into an ingot in a vacuum arc furnace. The whole process takes up to 6 days, it is only possible in batchwise operation and is very energy intensive. The process is illustrated in figure 1. [5]

Many alternative processes have been developed in the past decades, their goal was to completely substitute the Kroll process or at least group or improve some steps of it. The most promising alternative methods are: [5] [8] [11]

- electrolysis
- batchwise or continual metallothermic reduction with Ca or Al
- reduction of titanium-plasma
- reduction of gaseous TiCl_4 with gaseous Mg
- reduction with hydrogen
- reduction with aluminium iodine in a "shaking reactor"

These processes are in different stages of the development from laboratory scale to pilot plants. The resulting titanium is won as a powder, liquid, as granules, as sponge or as a block. [5] [6]

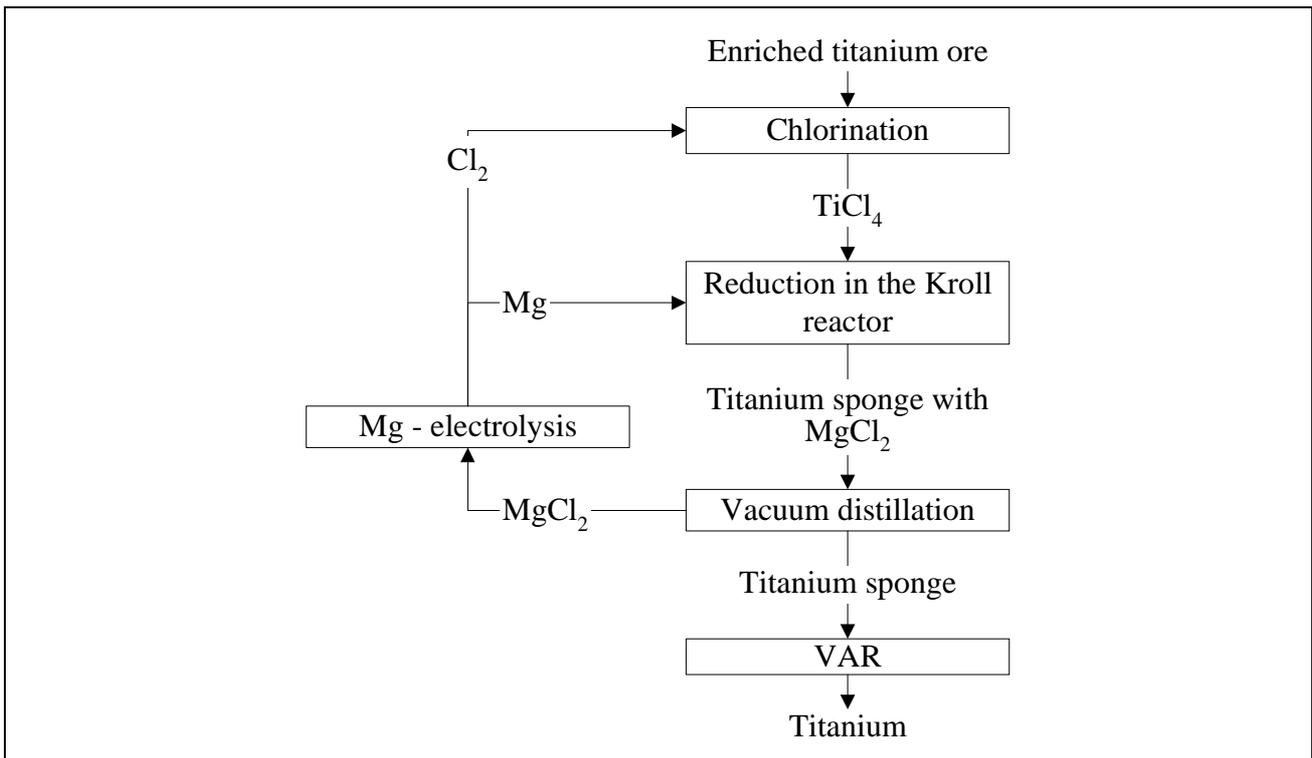


Figure 1: Flow chart of the actual titanium production route (Kroll process).

The electrolysis processes in molten salt will be described in the next chapter.

Molten Salt Processes

The electrolytic winning of titanium from molten salts is supposed to deliver a more homogeneously cleaner metal sponge than the Kroll process, where the metal in the centre of the reactor is much cleaner than the one on the outer sides. The energy consumption should also be much lower.

Many researches conducted to find less cost-intensive methods for producing titanium are based in the molten salt research. It is considered to be the most probable method to function since all other commercial light metals are produced by an electrolytic way. Specific reasons for choosing the molten salt electrolysis are: [4]

- all high temperature reduction processes for titanium need temperatures which can not be stood by the actual equipment materials
- because of its unnable electrochemical characteristics, titanium can not be produced in aqueous solutions.

Typically extraction of metals by electrowinning processes in molten salt, involves dissolution of the metal oxides in the electrolyte and subsequent decomposition of the dissolved metal oxides. Molten salt-based electrochemical processes, which aim on the refining of metals use an impure



metal ingot forming the anode of the cell, the pure metal is collected at the cathode. In the so called direct electrochemical reduction, the metal oxide is reduced at the cathode to the metallic form, oxygen evolves at the anode, a dissolution of the metal oxide is not necessary. Already Kroll was involved in these kind of researches 50 years ago. In the former Soviet Union, many researches have been conducted in the field of the molten salt electrolysis, varying parameters like temperature and current density. Table 1 shows some precursors, electrolytes and operation parameters.

Table 1: Charges, electrolytes, operation parameters for and titanium purity from the electrolytic synthesis of titanium. [5]

Ti-precursor	Electrolyte	T [°C]	Current density [A /cm ²]	Ti [%]	O [%]	N [%]	C [%]
Ti _x Cl _y	NaCl, KCl, NaCl-KCl, NaCl-LiCl, KCl-MgCl ₂ , NaCl-K ₂ TiF ₆ , NaCl-KCl-CaCl ₂ , KCl-MgCl ₂ -CaF ₂ , NaCl-KCl-BCl ₂	500-850	i _C = 0,1 - 0,5 i _A = 0,5 - 1,0	-	-	-	-
K ₂ TiF ₆	NaCl, NaCl-KCl, KCl-LiCl	740-800	i _C = 1,0 - 3,0	99,5 - 99,8	0,05 - 0,10	0,04 - 0,02	0,03 - 0,13
TiO ₂	NaCl, CaCl ₂ , NaCl-CaCl ₂ , NaCl-K ₂ TiF ₆ , NaCl-CaCl ₂ -KCl ₂ , CaCl ₂ -CaO	700-1100	i _C = 4,5 i _A = 0,3	99,9	-	-	-
Ti _x C _y	LiCl - KCl, NaCl, NaCl - K ₂ TiF ₆	675-1000	i _C = 2,0 - 2,5 i _A = 0,2 - 0,3	-	0,12 - 0,30	-	0,05 - 0,50
Ti _x N _y	NaCl - K ₂ TiF ₆	-	i _C = 1,3 - 1,5 i _A = 0,2 - 0,5	98,0 - 99,0	< 0,1	0,03	--

Reduction of TiCl₄ in a Molten Salt Bath

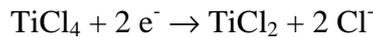
In the seventies the Italian company GTT (Ginatta Titanium Turin) developed a process based on the reduction of TiCl₄ in a molten salt bath and scaled it up until a pilot plant with a capacity for 70 t/y that worked for several years. The operating temperature was 950°C, the current 50 kA. The obtained titanium contained 0,059% oxygen and 0,0566% chlorine. Dow-Howmet/Freeport and New-Jersey Company/Palmerton in the USA developed similar processes. The electrolyte used at New-Jersey Company/Palmerton was a KCl-LiCl-NaCl-mixture with a eutectic melting point at 362°C. As a diaphragm material nickel was chosen. The remaining impurities in the titanium sponge are shown in Table 2. [5][6]



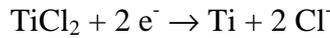
Table 2: Composition of the titanium sponge after reduction [%]. [5]

O	H	N	C	Fe	Cl
0,06	0,003	0,01	0,005	0,005	0,03

This process was developed further with the aim to obtain directly alloyed titanium powder. The electrolysis operated in a LiCl-KCl-salt at 520-600°C. The anode was separated by a diaphragm from the molten salt bath. Between the diaphragm and the anode, TiCl₄-gas was introduced and reduced to TiCl₂ at the diaphragm which acted as an auxiliary-cathode:



The electrolyte is able to dissolve about 2% of TiCl₂. At the cathode it was completely reduced, titanium deposited as dendrites.



At the anode chlorine evolved:



The obtained titanium had low impurity contents, depending on the purity of the obtained TiCl₄. The objective of having a diaphragm was, to avoid a back reaction between TiCl₂ and chlorine to TiCl₄. In practice this back reaction could not be avoided, even worse, the diaphragm acted as a cathode and metallic titanium deposited on its surface, hindering its action. Other problems that appeared and led to the abandonment of the process, where difficulties to change the cathodes and a high corrosion caused by the hot chlorine gas. The uncontrollable back reaction led D-H Titanium Co. and Timet to abandon this process. At Ginatta the programme was stopped because of the impossibility to solve engineering problems. [5] [6]

Some general concerns with the chlorine system are: [4]

- below 900°C the plant engineering and the materials question is easier to resolve but the chemistry is much more complicated, as the next points will explain. Above 900°C it is the opposite
- a very precise process control is necessary otherwise titanium sludge forms at the bottom of the cell, lowering the current efficiency and making it necessary, to remove it. This formation of solid titanium sludge from titanium chloride is illustrated by the lower line on the left side in figure 2 (formation of metallic titanium)
- the left side of figure 2 also shows that titanium can have different valences, having negative impacts on the efficiency of the process.

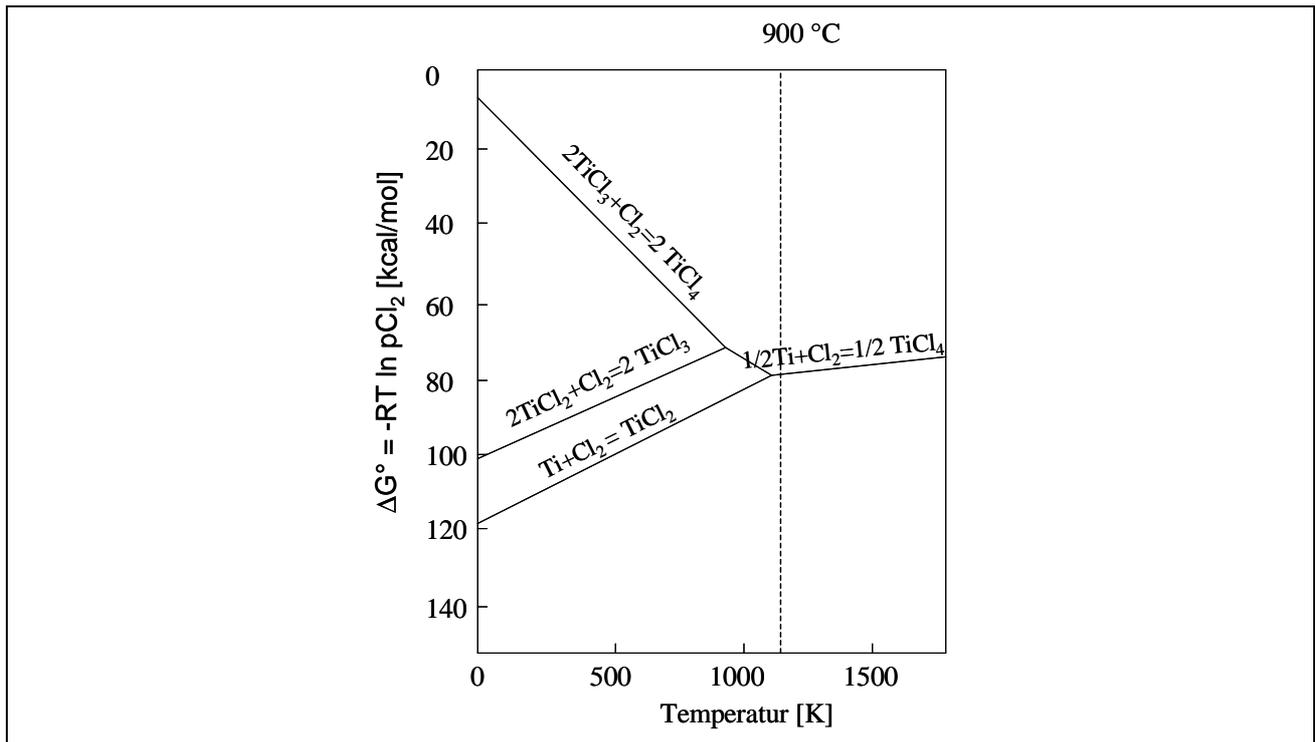


Figure 2: Standard free energies of formation of titanium chlorides. [4]

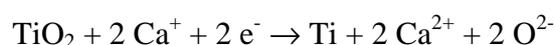
Direct Calciothermic Reduction of TiO_2 in a Molten CaCl_2 -Bath

One big advantage in titanium metallurgy is that TiO_2 is available easily from many sources worldwide and in sufficient quantities. A direct calciothermic reduction of TiO_2 occurs mostly in molten CaCl_2 , which has the advantages of being non-toxic, cheap and dissoluble in water.

A molten CaCl_2 -bath consists stoichiometrically of Ca^{2+} and Cl^- ions. An addition of a few % calcium metal leads to a situation where the bath contains Ca^+ and Ca^{2+} ions and free electrons. This mixture has a strong reducing power and presents a quite large solubility for CaO , which is formed during the process. Figure 3 shows the region where the reactions occur in the three-phase-diagram CaCl_2 - CaO - Ca . [12] Two process variants (FCC and OS) will be described in more detail.

FCC Process

This semi-continuous process was developed by Fray, Farthing and Chen. A sintered TiO_2 -cathode is introduced into a molten CaCl_2 -bath. By polarizing it cathodically, oxygen is removed from the feed TiO_2 . The titanium oxide reacts with the liquid calcium droplets or the free calcium ions:



The oxygen ions dissolve in the melt and migrate to the anode where they react with the carbon to CO_2 -gas, the titanium is left over as a spongy cathode.

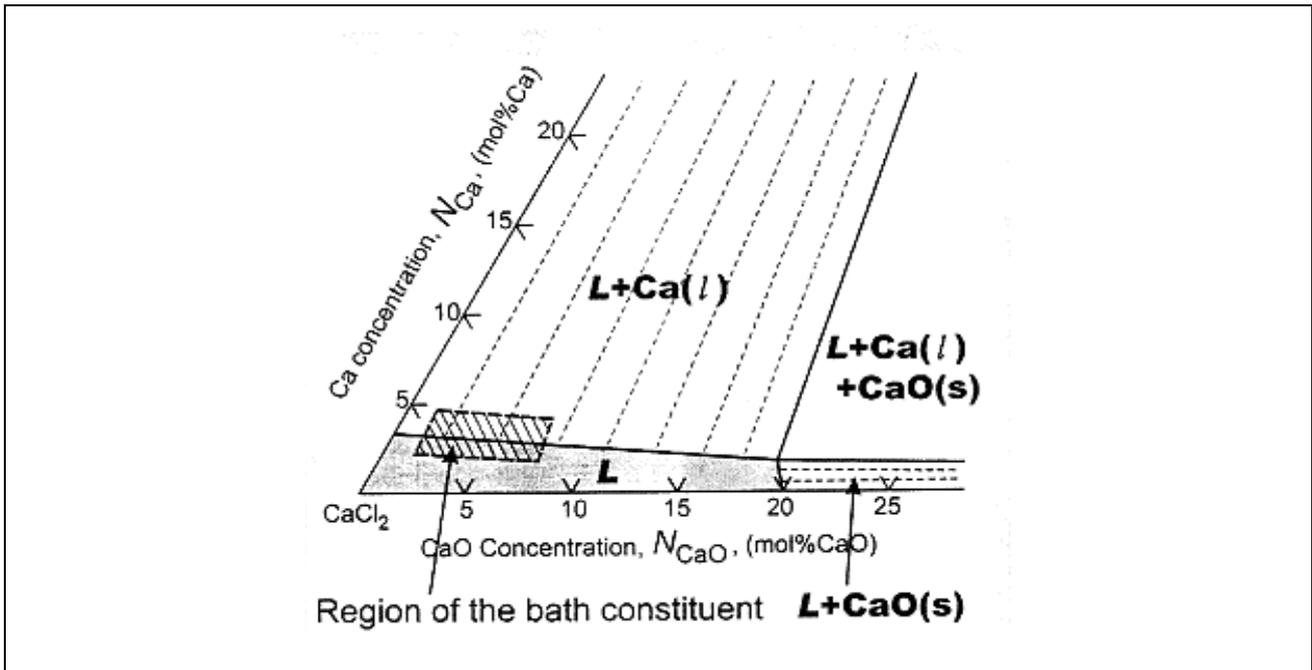


Figure 3: Isothermal cross-section of the CaCl₂-CaO-Ca-system at 1200 K. [12]

The reactions that occur are:



The operating temperature is between 850 and 950 °C, the voltage between 3,0 and 3,2 V. The obtained metallic titanium is a solid sponge, contaminated by the salt. A schematic diagram of the cell is shown in figure 4.

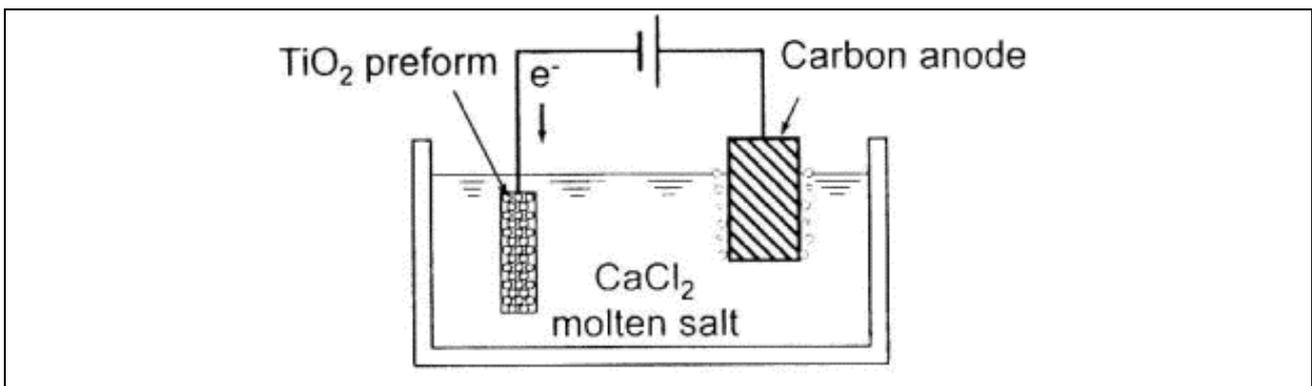


Figure 4: Schematic illustration of the FFC-Process. [1]

The advantages of this process are: [1] [2] [15]

- semi-continuous
- simple technique



- Low oxygen content.

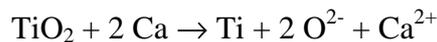
The disadvantages are: [1] [2] [15]

- difficult metal/salt separation
- reduction and electrolysis operation have to be carried out simultaneously
- sensitive to carbon and iron contamination, they accumulate in the titanium
- low current efficiency.

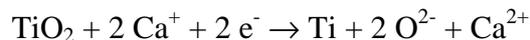
OS Process

The process was developed by K. Ono and R. Suzuki. TiO₂-powder is introduced into a molten CaCl₂-bath with additional calcium. A calciothermic reduction reduces the titanium oxide to pure titanium powder or sponge and calcium is continually regenerated by electrolysis at the cathode.

Calciothermic reaction if the titanium oxide meets liquid calcium droplets:



Calciothermic reaction if the titanium oxide meets liquid dissolved calcium ions and free electrons:

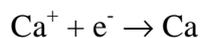


The formed CaO dissolves in both cases in the bath and can be converted into Ca, Ca⁺ and CO₂ by electrolysis. The applied current of 3,0 V is higher than the decomposition voltage of CaO but below that of CaCl₂ as can be seen in figure 5.

The occurring reactions are:



The Ca⁺ ions leave the cathode and migrate in the molten CaCl₂ bath. When the bath is saturated, liquid calcium forms at the cathode by the following reactions:



The theoretical oxygen levels in metallic titanium that can be attained by this method are 300-700 ppm. The theoretical solubility of calcium is 50-200 ppm. In practice they are higher because a CaO-level sticks to the surface of the titanium and hinders the further deoxidation. Figure 6 illustrates a possible cell design, the titanium dioxide is introduced in a basket, so after the reaction the metallic titanium can be removed easily. The heat to maintain the bath liquid is, like in an aluminium cell, provided by the resistance of the bath itself and through the consumption of the



carbon anode. Additionally there is the exothermic reduction of TiO_2 . The current efficiency can be lowered until 25% because of carbon precipitation and back reactions.

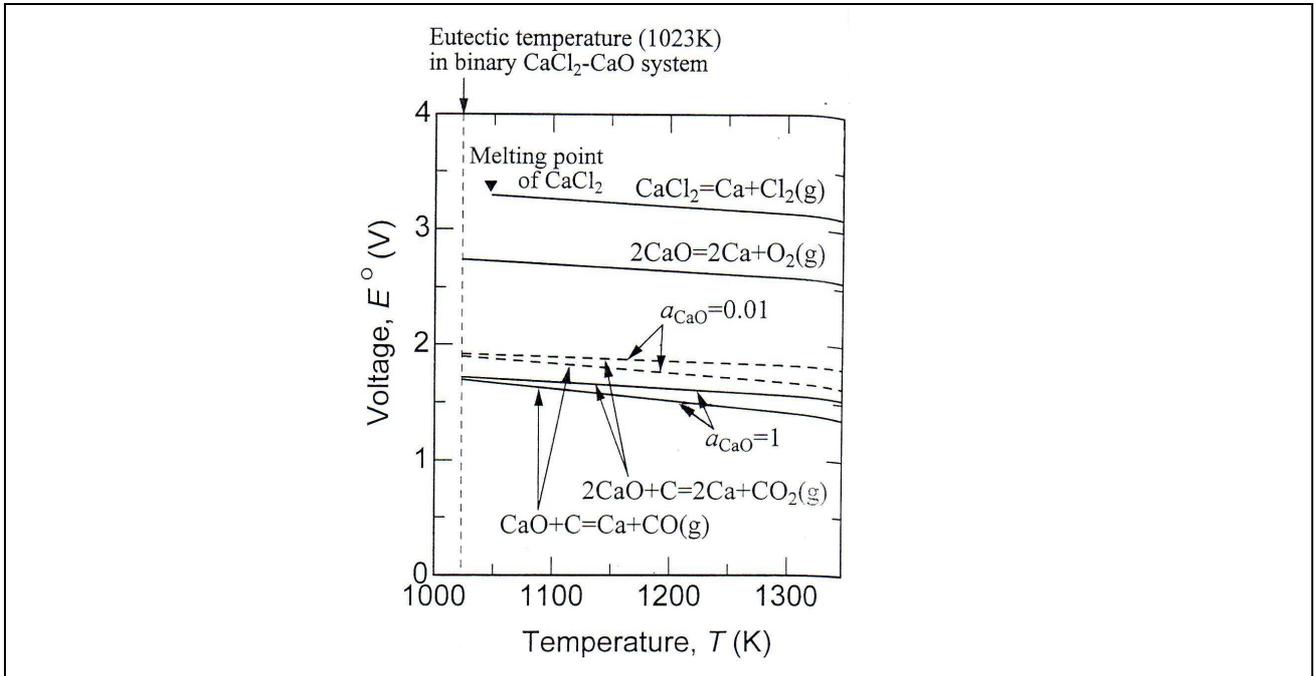


Figure 5: Electrochemical potentials for the decomposition of CaCl_2 and that of CaO in CaCl_2 . [15]

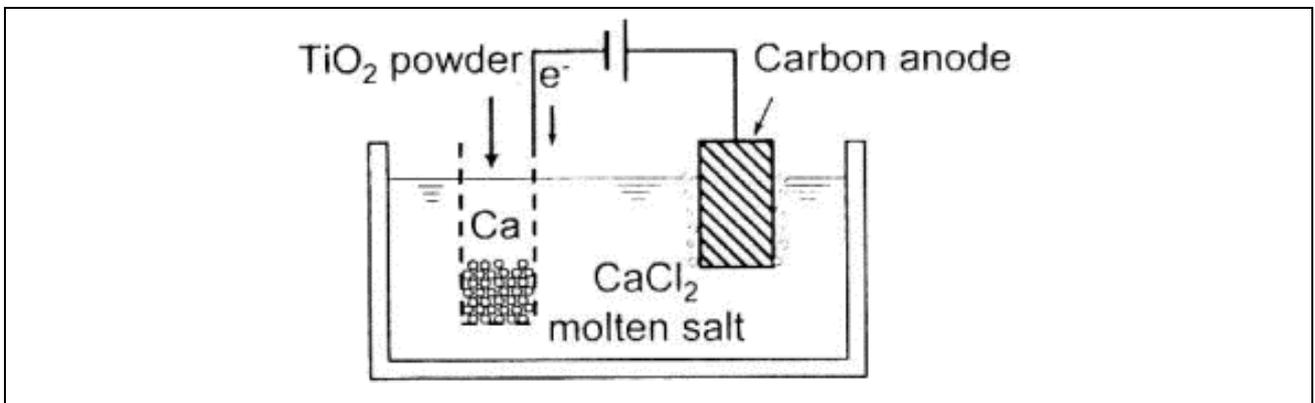


Figure 6: Schematic illustration of the OS-Process. [1]

The advantages of this process are:

- simple
- low oxygen content
- semi-continuous.

The disadvantages are:

- difficult metal/salt separation



- sensitive to carbon and iron contamination, they accumulate in the titanium
- low current efficiency
- large amount of salt required.

In comparison to the FFC process, the bath composition, the applied voltage and the carbon anode are similar but the operation mechanisms are different. The FFC process uses sintered TiO₂ pellets, for the reduction, oxygen diffusion in the titanium cathode is necessary. The OS process does not need a direct electric contact between the cathode and the TiO₂, also the titanium oxide can be fed as a powder, which is better for oxygen removal since there are no long diffusion ways.

[1] [5] [12] [13] [14] [15]

IME-Process: Direct Winning by Electrolysing a TiO₂-C-Anode

This process is actually being investigated at the IME in cooperation with Keio University in Japan [7] [9]. It is based on a process developed for magnesium in the former Soviet Union [10].

The chlorination from the titanium oxides and the winning of the metallic titanium happens simultaneously in an electrolytic cell. The cell is divided by a diaphragm in the anode space and the cathode space. A mixture of TiO₂ and C is fed into the anode-space, the electrolyte is a mixture of NaCl, KCl and CaCl₂. As an inert gas, argon is used. The electric current splits CaCl₂ into Ca²⁺ and Cl⁻, the calcium is deposited at the cathode and dissolves in the molten salt, the chlorine-ions migrate towards the anode where they react with the titanium dioxide, forming titanium chlorides and CO/CO₂-gas. This reaction is illustrated by the following equation:



The current density has to be adjusted in a way that mainly TiCl₂ is formed, so the reaction is less energy intensive. The titanium chlorides dissolve in the molten salt and react with the dissolved Ca, forming Ti and CaCl₂:



The titanium is deposited on the cathode. This process is in an early laboratory-scale step. Figure 7 illustrates the investigated cell-design.

Expected advantages of this process are:

- low oxygen content since the titanium is first chlorinated, then only transformed into metallic aluminium. This avoids the existence of dissolved TiO or TiO₂ in the metal compared to the OS- and the FFC-process
- the whole process takes place in one apparatus
- the reacting agent is atomic chlorine, i.e. it ensures a quick reaction



- there is no diffusion controlled reaction since all the phases are liquid
- there is no preparation of the feed like pressing the TiO₂ into tablets,... also avoiding possible contaminations by the binder.
- the energy consumption will be relatively low

The main challenge will be to find an appropriate material for the diaphragm.

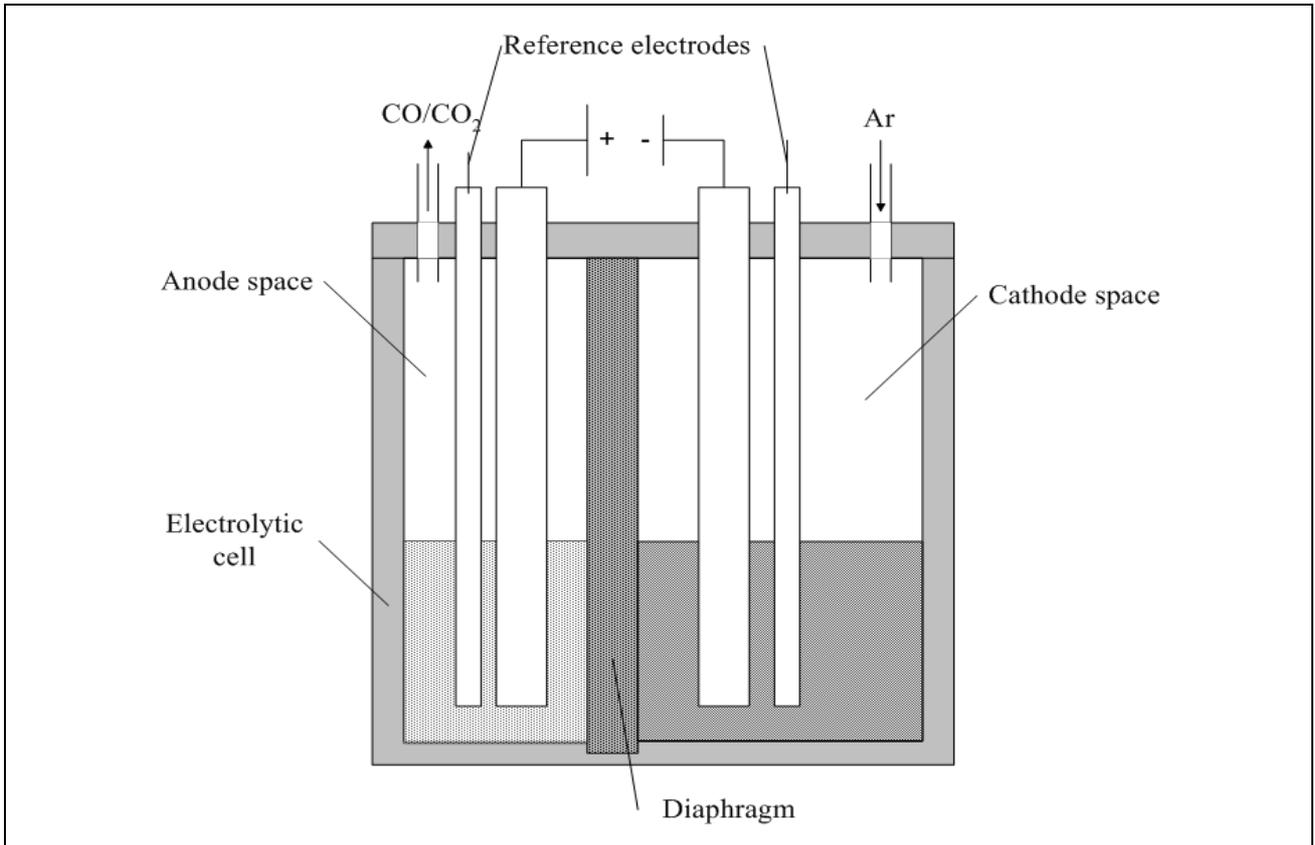


Figure 7: Electrolytic cell of the IME-Process for the production of titanium by electrolyzing a TiO₂-C-anode in a molten salt electrolyte.

EMR/MSE Process: Electronically Mediated Reaction in Molten Salt Electrolysis without Direct Contact Between the Ti-Feed and the Reductant

In this concept there is no transport of reactants through the product phase, a transport which is often diffusion controlled and therefore slow. In the EMR/MSE process the reduction of the titanium dioxide is divided into two steps, which do not necessarily have to take place at the same location within the cell. There is no contact between the titanium oxide and the reductant alloy. Titanium is reduced by the electrons discharged from the reductant. The occurring reactions are:





The metallothermic reaction can be split into two parts:



To obtain the pure titanium metal, it is necessary to leach the product with acetic and hypochloric acid, rinse it with distilled water, alcohol, acetone and dry it under vacuum. Figure 8 illustrates schematically the cell design.

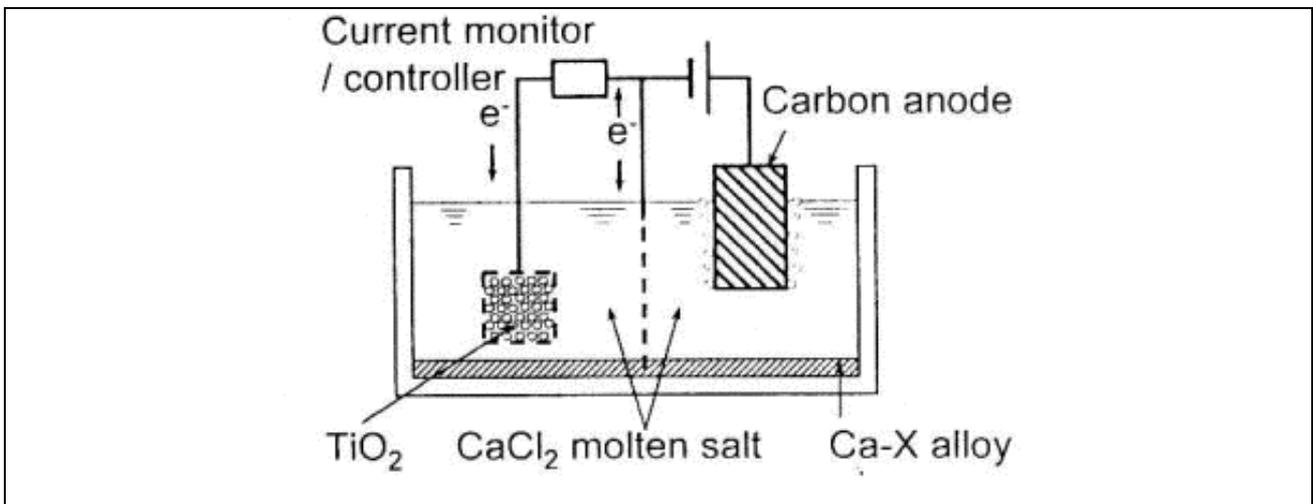


Figure 8: Schematic illustration of the EMR/MSE-Process. [1]

The advantages of this process are: [1]

- resistant to carbon and iron contamination
- semi-continuous
- reduction and electrolysis operation can be carried out independently.

The disadvantages are: [1]

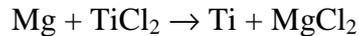
- difficult metal/salt separation
- complicated cell structure
- complicated process.

Other Electrochemical Methods

Other approaches are:



- use fluorides instead of chlorides. The problem is that this electrolyte system is much less known than the chloride system wherefore much data exists [4]
- the TiLAC process, which is based on the reduction of titanium chloride with magnesium: [3]



The by-product MgCl_2 is recycled to Mg by an electrolytic process.

Conclusions

The objectives are to increase the productivity and reduce the specific energy consumption of the titanium production. It is aimed to replace the Kroll process which involves several steps, has to be operated batchwise and takes up to 6 days to produce the titanium by a simpler, compact, preferably one step process. The electrolysis in molten salt is considered to have the biggest potential for a breakthrough because all the other non-ferrous metals are produced by this way.

Advantages of electrolytically produced titanium are the reduced energy need and the higher metal purity. The processes that are being inquired at the moment have been cited here above. In a laboratory scale they produce good results but most of them have not been scaled up yet and the ones that were scaled up, presented problems that could not be resolved up to know.

A problem that is common to all these processes is that, because they all take place below the melting point of titanium which is 1668°C , the final product is solid, frequently a sponge with low density, often deposited on a big surface whereof it has to be removed frequently. This operation inevitably entrains some electrolyte, which lowers the purity of the metal and makes subsequent operations for the removal of the residues necessary. Another problem is that the electrochemical characteristics of titanium limit the maximum current density and therefore lower the plant productivity.

Much work has been done in the last years, but much still will have to be done in the future to get to an efficient and cheap titanium production by electrochemical techniques.

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