A critical evaluation of processes to produce primary titanium

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Synopsis

Over the last 60 years many different processes were conceived to reduce the cost of titanium produced by the Kroll process. However, success eluded all previous efforts, which were consequently terminated in periods of economic downturn. Recently, the growth in demand for titanium and the high cost of producing the metal again sparked renewed attempts in various parts of the world to replace the antiquated Kroll process with a more efficient route.

The different options to produce titanium are reviewed, classified and evaluated in terms of the fundamentals underlying the technologies, and it is shown that the options considered to be the most likely to replace the Kroll process, are continuous processes to reduce $TiCl_4$ metallo-thermically to titanium powder. Of these, continuous magnesio-thermic reduction of $TiCl_4$ would conceptually result in the lowest-cost and highest-value product. However, when considering by-product salt removal from the titanium product and recycling of the salt as well, sodio-thermic reduction of $TiCl_4$ is better.

Introduction

Many different processes were conceived over the last 60 years to reduce the cost of titanium produced by the Kroll process. However, success eluded all previous efforts, which were consequently terminated in periods of economic downturn. Recently, the growth in demand for titanium and the high cost of producing the metal again sparked renewed attempts in various parts of the world to replace the antiquated Kroll process with a more efficient route.

Several excellent reviews or summaries on new, potentially low-cost titanium production technologies have been published[1–4] from time to time. In general these reviews give good descriptions of the work done in the field, but fail to indicate clear preference for any particular process or processes. The objective of this study was to develop a rational basis for selecting which route to pursue to develop more economic primary titanium metal production technology. This was done by comparing the underlying fundamentals that ultimately determine the costs and benefits of the various proposed processes.

Comparative framework

Figure 1 illustrates the framework used to compare different primary titanium production processes. In order to produce titanium, a feedstock is required. This feedstock is not a naturally mined mineral, but rather a precursor from which impurities in the mineral have been removed so that titanium, meeting strict impurity specifications, can be produced. Precursors used in various approaches include $TiCl_4$, TiO_2, fluotitanate salts, titanium suboxide/carbide mixtures and heavier titanium tetrahalides.

The various precursors can be reduced using any one of a number of different reducing agents to produce a product that is either in sponge, powder or in a fully consolidated form (ingot). The reducing agents used include electrons (as in electrowinning processes), Mg, Al, Na, Li, Ca and with limited success H_2.

Currently the preferred industrial process is the Kroll process that entails reduction of $TiCl_4$ with Mg in a batch manner. Processes such as the Kroll process that use batch operations are indicated in Figure 1 with dashed lines. In contrast, processes that use continuous process operations are indicated by solid lines. Thick dashed lines represent processes that have been operated on an industrial scale (i.e the Kroll[5], Hunter[5] and MHR[1] processes). All the lines shown in Figure 1 represent actual attempts somewhere in the world to produce primary titanium more cost-effectively.

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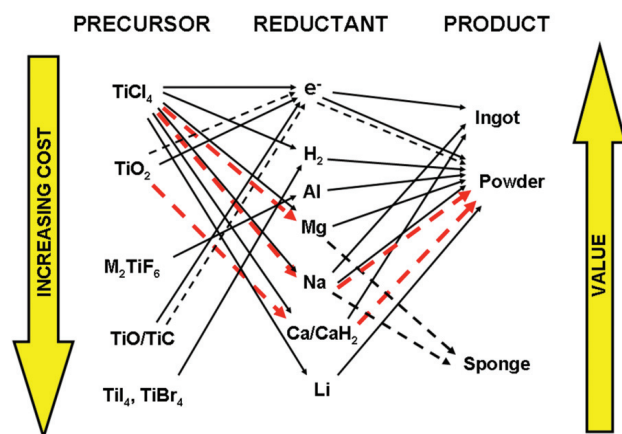# A critical evaluation of processes to produce primary titanium

Figure 1—Comparative framework

Following the reaction step to produce primary titanium, the product has to be separate from by-products, excess reagents or from the medium in which the reaction took place. This is not indicated in Figure 1, but is addressed later to complete the analysis.

Precursors

Attempts have been made to use ilmenite or slag directly[6] and Dr. Hill[7] of the CSIRO has stated that it is the Holy Grail of titanium to use the mineral directly. However, all attempts to date have apparently failed.

The current reality is therefore that it is essential to first produce a high-purity, intermediate titanium precursor that can subsequently be reduced to give commercially pure (CP) grade titanium. Different precursors have been used in the past by different researchers to produce titanium. These include $TiCl_4$, TiO_2, fluotitanates, TiC/TiO and TiN. In addition there have been attempts to use other titanium halides, but none of these has been commercially successful for large-scale titanium production.

Compared to $TiCl_4$, it can be expected that high purity TiO_2 would be more expensive. The reason is that, in the pigment industry, $TiCl_4$ is used as precursor to produce TiO_2. TiO_2 produced via the sulphate route cannot be cheaper than $TiCl_4$ because the TiO_2 pigment produced via the sulphate route is priced in the market at similar prices to that of chloride route pigment, and in the last two decades, the chloride route has actually been the preferred route by pigment producers across the world.

A process using a fluotitanate as precursor is currently being developed by Anglo American through Peruke (Pty) Ltd[8]. Albany Titanium[9] also used fluotitanate as precursor in their attempt to develop the technology patented by Occidental Research Corporation[10] and more recently the University of Melbourne filed a patent on the production of titanium through the reduction of a fluotitanate salt by aluminium[11]. The key chemical property of the fluotitanate salts is that they can be precipitated from aqueous solutions as oxygen free salts.

From a process point of view, producing pure fluotitanate as described in the patent of the Peruke process[8] occurs at similar process conditions (aqueous media at atmospheric pressure and relatively low temperatures) as the process to produce pure TiO_2 via the sulphate route. However, upfront production of HF is required and additional reagents are required to precipitate the fluotitanate, whereas hydrolysis is used when producing TiO_2. In both cases the mineral feedstock is first digested in acid and then purified by selective precipitation and washing of the precipitate. The chemical steps to produce fluotitanate vs. the production of TiO_2 via the sulphate route are as illustrated in Figure 2.

Six moles of HF (equivalent to the use of three moles of sulphuric acid) are used to digest one mole of $FeO.TiO_2$ in the Peruke process compared to the consumption of only 2 moles of sulphuric acid when making TiO_2. Furthermore, no fluorspar is required when making TiO_2 and no extra chemical is required to precipitate the TiO_2, whereas in the case of fluotitanate 2 moles of MX (NaCl, KCl or NH_4Cl) are required to precipitate the fluotitanate.

It is therefore concluded that it would be more expensive to produce one mole of fluotitanate using HF digestion than producing one mole of TiO_2 via the sulphate route, which would be more expensive than producing one mole of $TiCl_4$. However, it must be mentioned that with the Peruke process, AlF_3 might ultimately be recovered in the form of a valuable by-product, which would reduce the cost of using fluorides significantly.

The use of TiC, that may contain minor quantities of titanium suboxides, as both precursor and anode was patented and tried already in 1954 by the Norton Wheel Company[12]. The aim was to electrowin molten titanium directly. Currently the MER Corporation is developing a similar process aimed at recovering titanium powder[13].

In order to produce a TiC/TiO anode containing few impurities apart from carbon and oxygen, high grade TiO_2 has to be reduced with high-purity carbon at temperatures in the order of 1500°C or above. This is an additional, expensive

Peruke	"Sulphate TiO_2"	
HF PRODUCTION		
$CaF_2 + H_2SO_4 \leftrightarrow CaSO_4 + 2HF$	n.a.	
DIGESTION		
$FeO.TiO_2 + 6HF \leftrightarrow FeTiF_6(aq)$	$FeO.TiO_2 + 2H_2SO_4 \leftrightarrow FeSO_4(aq) + TiOSO_4(aq)$	
PRECIPITATION		
$FeTiF_6(aq) + 2MCl \leftrightarrow M_2TiF_6\downarrow + FeCl_2(aq)$	$TiOSO_4(aq) + H_2O \leftrightarrow TiO_2\downarrow + H_2SO_4(dil)$	

Figure 2—The Peruke and the sulphate TiO_2 processes

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process step and adds to the cost of TiO_2. It is also likely to be more expensive than fluotitanate because of the more extreme process conditions required.

A last class of precursors that have been considered are TiI_4 as in the Van Arkel and De Boer process[5] and $TiBr_4$ as considered by the author[14]. These precursors are even more expensive and have consequently not received much attention as feedstock to produce titanium for the metallurgical industry.

Reductants

There are only a limited number of practical means to reduce any one of the titanium precursors. These are via electrolysis (or reduction with electrons), metallothermic reduction using an alkali metal, an alkali earth metal or aluminum; and reduction with hydrogen. The various alkali and alkali earth metals considered by various researchers are sodium, lithium, magnesium and calcium.

Direct electrowinning of titanium is conceptually the most economical way to produce the metal since all the other metals that can be used to reduce any of the titanium precursors are produced electrolytically. Many attempts have therefore been directed at the development of titanium electrowinning from either the chloride[15,16], the oxide[6,17] or the carbide[12,13].

If hydrogen were produced electrolytically, it would be more expensive than the direct used of electricity. However, if hydrogen is produced from natural gas or coal, it might be cheaper than the use of electricity. SRI International[18], Idaho Titanium Technologies[3] and the CSIR[14] worked on processes to reduce titanium tetrahalides with hydrogen. To date no practical process was developed. The CSIR terminated its work on the use of hydrogen because it became clear that its approach was not going to be economical.

The use of magnesium in the Kroll process is currently the industrially preferred metal to produce titanium. Aluminium, on the other hand, has been considered only in a small number of attempts. However, a fundamental problem when using aluminium, is that it is thermodynamically more favourable to produce titanium aluminide instead of titanium. In order to overcome this problem Occidental Research[10], developed an elaborate countercurrent, molten salt/molten zinc extraction system to separate the aluminium from the titanium. In the patent on the Peruke process[8], it is claimed that pure titanium is produced when reducing TiF_3 with aluminium and removing the AlF_3 by sublimation at 1250°C.

Following aluminium and magnesium, sodium is the next in terms of cost. Sodium is used in the Hunter process[5] and is also the basis of the Armstrong process that is being developed by International Titanium Powders (ITP) in the USA[3,4].

Calcium has been used on a large scale in Russia to reduce TiO_2 via the MHR process[1] and calcium dissolved in $CaCl_2$ is being considered in recent developments of the Japanese Titanium Society[19].

Lithium is much more expensive than the other metals, which is probably the reason why very few of organizations have considered it as a reductant for producing titanium. One of the more serious attempts is that of Seon and Nataf[20] that worked on a process to reduce $TiCl_4$ with lithium dispersed in a molten salt.

The market prices for electricity, aluminium and magnesium are readily available, but not for hydrogen, sodium, calcium and lithium. Except for electricity, listed market prices are also not accurate reflections of the costs that will be incurred to produce titanium via the different routes because such prices are not the same as what in-house production costs would be, or what long-term contractual prices between suppliers and buyers are. Nevertheless, market prices do give an indication of the relative costs of the different reductants. Table I is a summary of indicative market prices of the different reductants in absolute terms as well as in terms of equivalent cost per kilogram of titanium.

For electricity, the average industrial electricity price in 2007 in the United States is given[21]. Alumium and magnesium prices are as listed on the London Metal Exchange on 26 September 2008[22]. For sodium, the US customs value for sodium imported from France in January 2004 of $1/lb is given, which is perhaps more realistic than the $0.83/lb in 2007 that allegedly depressed DuPont's prices for sodium metal, siphoned off its market share, and snuffed out the profits of DuPont's sodium metal business[23]. The price for calcium crowns apparently remained unchanged from 1987 to 2001 at $3.85/lb ($8.50/kg)[24].

Market prices for lithium are not readily available. However, Ober[25] gave prices up to 1997 and Jaskula[26] prices for lithium carbonate and lithium hydroxide up to 2007. In 1997, lithium average metal prices were $95/kg ($43/lb) and in 2007 the price for lithium carbonate increased to $6000/t in the US (or $46/kg Li) while it was already $7000/ton in Japan (or $75/kg Li). It can be seen that the high price of lithium raw materials contributes significantly to the cost of lithium metal.

As mentioned, listed market prices are not accurate reflections of the cost that would be incurred to produce titanium if the reductant is produced inhouse. Such prices would be more misleading for large-scale plants where the bulk of the by-product salt is recovered and recycled to in-house electrolysis cells for regeneration of the reducing metal. In such cases, the electricity consumption required to regenerate the various reductants is a better indicator of the relative costs that would be incurred. Table II is a summary of the theoretical and industrial cell potentials, current efficiencies and electricity consumptions for producing the various reducing metals.

Table I

Indicative prices and costs

| Reductant | Price | Units | Use* | | Cost |
			Unit/kg Ti		$/kg Ti
Electricity	6.7	c/kWh	9	kWh	0.60
Al	2.5	$/kg	0.8	kg	2.00
Mg	3.1	$/kg	1.0	kg	3.10
Na	2.2	$/kg	1.9	kg	4.20
Ca	8.5	$/kg	1.7	kg	14.50
Li	95	$/kg	0.6	kg	57.00

*For electricity an energy efficiency of 40% was assumed to electrowin Ti from $TiCl_4$ and for the metals the stoichiometric amounts of metal to reduce tetravalent titanium were used

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Table II					
Electricity consumption to produce metals electrolytically[27–29]					
Metal	Cell temperature (°C)	Theoretical cell potential (V)	Cell potential used (V)	Current efficiency (%)	Energy (kWh/kg Ti)
Al	950	1.1	4.5	85–90	10–13
Mg	700	2.5	6–7	85–90	17–19
Na	580	3.4	6.5–7	85	19–22
Li	450	3.6	6–7	80–85	16–23
Ca	800	3.3	20		75

Aluminium production requires the least electricity, but in contrast to the other metals that are produced from their respective chloride salts, electrowinning of aluminium from Al_2O_3 requires a consumable carbon anode. The cost of such electrodes would offset a large part of the electricity cost saving.

It is interesting that for Mg, Na and Li the respective electricity consumptions are similar. A cost difference of 2 kWh/kg Ti is equivalent to a saving in titanium production cost of about $0.13/kg. This is less than 2% of listed titanium sponge market prices.

Products

Primary titanium can conceptually be made either in the form of sponge, powder or ingot. Sponge is the form in which it is made industrially, but since significant downstream processing costs would be saved if ingot or powder were made directly[3], many attempts have been made to either produce ingot or powder.

The value of ingot is clearly much higher than that of sponge. Mean year-end prices for titanium sponge varied between $7.93/kg and $20.60 (constant 2006 prices) between 2000 and 2006[30] and average prices of melted product from Timet between $10.05/kg and $39.95/kg.

It is not clear how much more titanium powder would be worth than sponge if it became available at acceptable prices. Currently titanium powder is either produced by the hydride-dehydride route or by spray atomization of molten titanium using argon. Indicated prices vary greatly between $8/lb ($17.62/kg) and $100/lb ($220/kg)[31]. These high prices suppress the growth of the titanium powder market, which is currently estimated at only about 2000 tpa. In order to grow the titanium powder market substantially, its price would have to be reduced to about the same price as that of ingot.

Mode of operation

The Kroll process is a batch process. The cycle time for loading, reaction, stripping and unloading is typically in the order of one week to produce a single batch of about 7 tons. Not much can be gained by increasing the batch size since the cycle time simply increases.

Following the batch-wise production of a sintered mass of titanium sponge, the sponge is removed from the reactors, crushed and sorted manually in order to control the quality of the product.

If it were possible to operate the titanium process in a continuous manner, significant savings in both capital and labour costs would be achieved. It would conceptually also be possible to have a higher yield of high quality product.

Consequently many attempts to improve on the Kroll process are aimed at streamlining the operation to a continuous mode of production.

By-product removal

In most processes, including even electrolytic processes operating below the melting point of titanium, the titanium product has to be separated from by-product salt, excess reactant, or the salt medium in which the reaction occurs. Physical separation techniques such as decanting, settling or filtration are cheaper than separation processes involving a phase transition such as vacuum distillation or leaching. Unfortunately physical separation processes are normally not sufficient to achieve the desired titanium product specification and therefore either a leaching or a vacuum distillation step is typically used subsequently.

Physical separation techniques are difficult to do continuously because of the high temperatures required to melt the respective salts, the corrosiveness of the chemicals involved and the stringent specifications that the titanium product must meet.

The melting points of various salts and solubilities in water at room temperature are given in Table III. Typical solid liquid separation processes such as filtration and centrifuging are difficult and standard equipment is not readily available for operating with these salts above their melting points. Thickeners can probably work, but operating thickeners at high temperatures with a molten salt is also complex, especially if a clear liquid phase and a high concentration slurry are desired.

Table III		
Melting points and water solubilities of various salts		
Salt	M.P. (°C)	Solubility (g/100 cm³)
AlF_3	1291 subl.	0.559
NaF	988	4.22
$CaCl_2$	772	74.5
$Ca(OH)_2$		0.185
LiCl	614	63.7
LiOH		12.8
$MgCl_2$	708	54.25
$Mg(OH)_2$		0.0009
NaCl	801	35.7
NaOH		42

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Batch or semi-batch operation could considerably simplify gravity separation of molten salt and titanium powder, but at the expense of increased capital and operating costs.

The solubility of AlF_3 in water is very low. It is therefore not a practical option to leach it with water from the product. Leaching of fluorides with a molten salt as proposed by Occidental Research[10], or distillation as proposed by Pretorius[8] seem to be the only viable ways to separate TiF_3 from the product.

Aqueous leaching is well suited to separate alkali metal chlorides, calcium chloride and alkali metal hydroxides from titanium because the solubilities of these salts in water are high and recovery of the respective anhydrous metal chlorides from aqueous solutions are straightforward.

The solubility of magnesium chloride in water is high, but recovery of anhydrous magnesium chloride is difficult since MgO is formed when dehydrating the $MgCl_2.H_2O$. In order to prevent this, $MgCl_2.H_2O$ has to be dehydrated in an HCl atmosphere, which is expensive. $MgCl_2$ is therefore separated from the titanium product by firstly separating as much as possible by a physical separation step before removing the residual amount by vacuum distillation.

The vapour pressures of the various salts formed by the various reducing metals considered are given in Figure 3. As can be seen, the vapour pressures of $MgCl_2$ and LiCl are similar and the highest at temperatures below ca 1150°C. At 900°C the vapour pressure of NaCl is about five times lower and that of AlF_3 about 15 times lower than that of $MgCl_2$. In practical terms this implies that the vacuum that has to be drawn to evaporate these salts have to be so much higher and in a continuous system, the volumes of gas that has to be used to sweep these salts out of the evaporation kiln also have to be much higher. Another complication with distilling AlF_3 is that it does not form a liquid phase at atmospheric pressure. On cooling of gaseous AlF_3, it deposits on the cooling surfaces and would therefore have to be removed by some mechanical means.

It would not be practical to evaporate $CaCl_2$. Since its boiling point (1936°C) is higher than the melting point of titanium (1668°C), it is in principle possible to decant molten $CaCl_2$ from molten titanium. This property is used in the technique being developed by the Japanese Titanium Society[19] who is developing a process to directly produce titanium ingot by calciothermic reduction of $TiCl_4$.

Summary of process routes

The main process routes that have been considered in various approaches to produce titanium are summarized in Table IV.

Conclusions

➤ Of the various precursors that can be used to produce titanium, $TiCl_4$ is currently still the cheapest and most practical.

➤ None of the attempts to develop an economic process to produce titanium electrolytically have been commercially successful in spite of significant efforts across the world over a period of more than sixty years to do so. It is unlikely that success in this regard will be achieved soon

➤ Hydrogen from fossil fuels is the cheapest alternative reagent to reduce a titanium precursor, but it is impractical because the achievable conversions are too low.

➤ Metallo-thermic reduction of $TiCl_4$ is still the most economical way to produce titanium.

➤ Direct production of powder is more attractive than sponge or ingot production because of potential downstream cost savings and because the operating conditions required are not as sever as required for direct ingot production.

➤ In order to significantly reduce the cost of producing final titanium products, a continuous metallothermic $TiCl_4$ reduction process producing titanium powder seems to be the best route.

➤ Aluminium and magnesium are cheaper than other metals that can be used to produce titanium metallo-thermically; however, continuous separation of AlF_3 (in the case of using Al) or $MgCl_2$ (in the case of using Mg) is difficult.

➤ Aluminium reduction of TiF_3 might be economically competitive if saleable AlF_3 can be recovered from the process. If not, the use of fluotitanates and aluminium for titanium production would be uneconomical.

➤ The use of an alkali metal, such as Na, has the advantage that the by-product salt can be recovered relatively easily in a suitable form so that it can be recycled to an upfront electrolysis step.

➤ Continuous titanium powder production via metallo-thermic reduction of $TiCl_4$ using an alkali metal such as sodium (as for example in the case of the Armstrong process) seems to be the best route to produce primary titanium for mass production.

Disclaimer

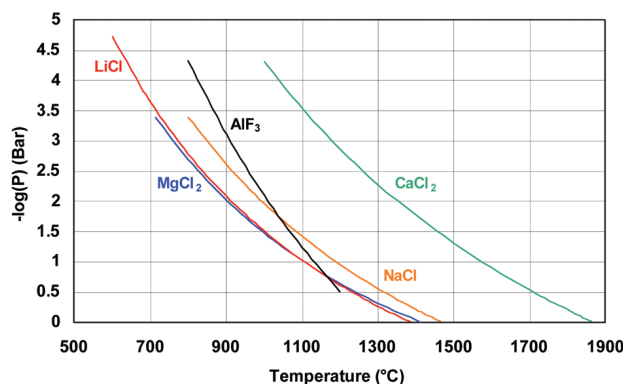The opinions expressed are that of the author and not of the CSIR.

Acknowledgement

Figure 3—Vapour pressures of various salts

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Table IV

Main process routes considered

Process	Precursor	Reductant	Prim. metal	Purification	Mode	Remarks/concerns
Ginatta[16]	$TiCl_4$	e-	Ingot	L-L Settling	Cont.	Long process times at extreme conditions Status uncertain
$TiCl_4$ electrolysis[17]	$TiCl_4$	e-	Powder	Draining then leaching	Cont.	Low current efficiencies Projects terminated
Kroll[5]	$TiCl_4$	Mg	Sponge	Draining then leaching or distillation	Batch	Slow and labour intensive Industry standard
Hunter[5]	$TiCl_4$	Na	Sponge	Leaching	Batch	Labour intensive Extensive leaching Most plants closed down
Armstrong[3,4]	$TiCl_4$	Na	Powder	Filtration then leaching	Cont.	Complex purification Pilot-scale demonstration
CSIRO[32]	$TiCl_4$	Mg	Powder	Distillation	Cont.	Complex reactor Complex purification Ongoing development
Du Pont[33,34]	$TiCl_4$	Na	Powder	Leaching	Batch	Slow and labour intensive
Vapour phase reduction[1]	$TiCl_4$	Mg	Powder	Leaching	Cont.	Particles too fine Complex purification
Aerosol reduction[1,35]	$TiCl_4$	Na	Ingot	Distillation	Cont.	Harsh operating conditions Product removal difficult
Combined Kroll-HDH[36]	$TiCl_4$	Mg	TiH_2 Powder	Draining then leaching	Batch	Reduction of process steps to produce powder Slow and labour intensive
Japanese Consortium[37]	$TiCl_4$	Mg	Powder	S-L settling then distillation	Cont.	Complex reactor Complex separation Project terminated
JTS[19]	$TiCl_4$	Ca	Ingot	L-L settling	Cont.	Harsh separation conditions Ongoing development
Rhone Poulenc[20]	$TiCl_4$	Li	Powder	Leaching	Cont.	Lithium cost Extensive leaching Project terminated
MHR process[1]	TiO_2	CaH	Powder	Leaching	Batch	High cost of CaH Extensive leaching Plant closed down
FFC Family[18]	TiO_2	e-	Powder	Draining and leaching	Batch	Inefficient Ongoing development
Ono+Suzuki[38]	TiO_2	Ca/e-	Powder	S-L settling then leaching	Cont.	Inefficient Continuation uncertain
Cardarelli[6] and CSIR[39]	TiO_2	e-	Ingot	L-L settling	Cont.	Does not work Projects terminated
SRI International[18]	$TiCl_4$	H_2	Powder	G-S filtration	Cont.	Large gas recycle loop H_2/HCl separation Continuation uncertain
Idaho Titanium Tech.[3]	$TiCl_4$	H_2	Hydride powder		Cont	Harsh plasma process Low thermal efficiency HCl recycle Continuation uncertain
AlTi[10]	Na_2TiF_6	Al	Powder	L-L extraction then distillation	Cont.	Product purity Complex purification Project terminated
Peruke[8]	M_2TiF_6	Al	Powder	Distillation	Cont.	Product purity Extensive distillation Bound to AlF_3 market Ongoing development
MER[13]	TiC/TiO	e-	Powder	Draining then leaching	Semi-Batch	Product quality Continuation uncertain
Norton Wheel[12]	TiC	e-	Ingot	L-L settling	Cont.	Does not work Project terminated

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