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AN EVALUATION OF U. S. PATENT LITERATURE PERTAINING
TO THE PRODUCTION OF TITANIUM

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AN EVALUATION OF U.S. PATENT LITERATURE PERTAINING
TO THE PRODUCTION OF TITANIUM

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SUMMARY

During the last seven years titanium metal has found increasing use as a constructional material, mainly because of its high strength to weight ratio and because of its excellent corrosion resistance properties.

The high cost of the metal, which is mostly produced at the present time by a development of the 'Kroll Process" (a process patented by W. J. Kroll), has prevented the metal from being used in many potential applications. As a consequence, considerable importance is attached to the discovery of a more economical production process.

This investigation has been aimed at surveying the U.S. Patent literature with a view to choosing the most economical process.

After giving a sketch of the growth of the titanium industry, a description of present technological practice in the titanium industry is presented. This has enabled a direct comparison to be made between patented processes and the process on which they must be an improvement to be of any significance.

Some factors which are essential to the determination of the economic and physical feasibilities of the patented processes appear next. It is established in this section that the presence of such impurities as oxygen, nitrogen, and hydrogen have an embrittling effect on titanium which must be avoided by conducting all operations under inert gas atmospheres at temperatures much in excess of room temperature and by using reactants of high purity. It is also pointed out that sodium, magnesium, and titanium tetrachloride are the least costly starting materials.

Comments have been made on thirty-five patents which have been summarized and classified. Many useful comments made by W. J. Kroll on some of the patents have been included. General conclusions have been reached with regard to the most promising process in each class, after having first decided upon the significance of each class. The most important conclusion is the one indicating that the direct reduction of titanium tetrachloride by sodium or magnesium is the most economical type of process. This conclusion is not in contradiction to present industrial practice.

Up to May 7th 1946, patent information was obtained from the U.S. Official Patent Gazette. After this date, and up to the end of January, 1956, recourse was had to actual patents.

CHAPTER I

INTRODUCTION

Titanium metal has been produced in the U.S.A. and the U.K. on a commercial scale during the last seven years. Production has increased rapidly over this period mainly because of the huge demand for the metal for aircraft construction. The high strength to weight ratio and the superior corrosion resistance properties of pure titanium seem not to have been generally recognized until the period from 1937 to 1942 when the U.S. Bureau of Mines was instrumental in developing a suitable process and in evaluating the properties of the metal. All the firms producing titanium in the U.S.A. up to the end of 1955 have been using a development of the 'Kroll Process,' the patent for which was applied for on September 1st, 1937. In the U.K. a different process is in operation, sodium instead of magnesium being used as a reducing metal. The indication is that neither process has any significant advantage over the other. A recent News Release by Union Carbide and Carbon Corporation has made it known that the first heat of sponge titanium produced by a division, the Electro Metallurgical Co., was completed on April 26th, 1956 using sodium as a reducing metal. Many proposed alternative methods of production have been patented. The vast majority of these patents were applied for in the last seven years.

As the 'Kroll Process' has certain drawbacks, the chief one being its batchwise nature, attempts have been directed recently toward developing

a continuous or partly continuous process. A second major disadvantage of the Kroll Process is that it produces a sponge which must be remelted. More recent attempts have been aimed at an electrolytic process.

Patent appraisal and evaluation is an important aid in seeking a process possessing economic advantages over conventional processes. This thesis comprises descriptions of conventional technological practice and of 35 U.S. patents. A historical sketch provides background reading while some restrictions and difficulties relating to titanium production are presented as being essential to patent consideration.

Only those patents that specify sponge or massive ductile titanium as an end product and which include a reduction step have been taken into account.

Up to May 7th. 1946 the U.S. Patent Office Official Gazette provided patent information. After this date, recourse was had to U.S. patents up to the end of January 1956.

Patents in many cases are wider in scope than as described. In particular many reducing agents as well as titanium compounds are usually enumerated as possible reactants. Comments (if any) on patents have been placed both after individual patent descriptions and after patent classes.

Note on Nomenclature.---Arabic numerals have been used to number both patents and references. Whenever a patent is referred to, the word 'patent' is always present. The patents are listed in the order in which they were applied for in the appendix.

CHAPTER II

HISTORICAL

In order to provide a background as an aid to patent appraisal, a brief sketch of the train of events leading from the discovery of titanium to the present day large scale extraction of the metal is presented. The commercial history has been confined to the U.S.A. and the U.K.

Development of Extraction Processes.—The element titanium was discovered by Gregor in England in 1790 in iron bearing sands today known as ilmenite. Later, in 1795, it was found by Klaproth in Hungary in rutile sands. Klaproth gave the element its name. Both, however, only isolated the oxide, TiO_2 (1).

In 1825, Berzelius and his followers (2) reduced potassium fluo-titanate with potassium and obtained a blue metal powder that was heavily oxidised and nitrided (3). Nilson and Petterson (4) reduced titanium tetrachloride with sodium in a bomb in 1887 but obtained only a nitrided powder metal (3). Hunter (5), in 1910, copied this method and obtained titanium granules which were malleable when hot but brittle when cold. Scubert and Schmidt (6), in 1892, reduced titanium tetrachloride with magnesium filings in a carbon dioxide atmosphere and obtained a black oxide powder (3).

In 1925, Van Arkel and De Boer (7; patent 3) found an effective way of preparing pure ductile titanium by thermally decomposing the

tetraiodide. It consisted of: (a) packing the periphery of a glass tube with crude titanium, (b) evacuating and introducing a small amount of iodine into the system, (c) electrically heating to about 1300° C a tungsten filament that had been sealed into the centre of the tube, and (d) warming the entire tube to about 150° C.

Kroll (8; patent 6) experimented in 1937 with the reduction of titanium tetrachloride under a noble gas at substantially atmospheric pressure with calcium and magnesium. At about the same time, Freudenberg (patent 5) reduced titanium tetrachloride with sodium in a salt bath under hydrogen. The hydrogen contaminated the metal obtained (3). Kroll's results, which included descriptions of a vacuum separation process for the separation of zirconium from the salts formed during its preparation and a vacuum arc melting furnace to make ingots from sponge titanium, were published in 1940 (8; patent 6). The melting furnace was a modification of a previous development by Von Bolton (9).

Sponge titanium has been so called because the resulting metal produced using present day reduction methods inside reduction vessels is in the form of a solid porous mass.

The U.S. Bureau of Mines initiated an investigation into the technology of titanium in 1938 and a critical survey and small scale test of virtually all known methods of producing the metal were made (10). Kroll's method (patent 6) appeared to be the best for immediate commercial production and development was undertaken in 1942 at their Salt Lake City Station. The size of the batch produced was increased from a few grams to 15# (11) and the project was transferred to the Boulder City Station in 1944. Titanium was then produced in 100# batches (12) and by 1951 in

200# batches (13). Allocation of metal produced in these pilot plants to Bureau of Mines and other government laboratories resulted in widespread dissemination of knowledge regarding the properties of titanium.

Kroll and others (14), while at the U.S. Bureau of Mines, in 1946 described an arrangement (a sequel to work done in 1939 (8; patent 6)) for the industrial high temperature separation of the salts from the reaction product formed in the production of zirconium. This method was adopted by the U.S. Bureau of Mines and other commercial producers of titanium for the separation of magnesium and magnesium chloride from sponge titanium.

The original process, as devised by Kroll, was started by melting magnesium in an argon atmosphere in an oxide and moisture free molybdenum iron reaction chamber. Before the magnesium was melted, any moisture film was removed by chemical gettering with calcium vapour and a small amount of titanium tetrachloride. Titanium tetrachloride was then introduced, the temperature being carefully controlled and allowed to rise to 1,180° C towards the end of the addition. After cooling in an argon atmosphere, the reaction mass was milled out and leached with water and hydrochloric acid, leaving clean titanium metal which was washed and dried. Any particles of iron present were separated magnetically.

It has been found by the Bureau of Mines that no advantage is to be gained in increasing the size of the batch, in their development of the Kroll Process, to more than 200# of titanium. The principal reason is that an increase in the rate of addition of titanium tetrachloride would result in overheating of the sponge.

Commercial History.--The commercial production of titanium in the U.S. and the U.K., since E. I. du Pont de Nemours announced the first commercial operation to extract titanium from its ores on September 14th, 1948, has been closely tied up with government contracts. This has been largely because of its usefulness in the construction of military aircraft and because of its many other defense applications. The high strength to weight ratio and the superior corrosion resistance properties of titanium are responsible for its many uses. Much space has been devoted in the literature to pointing out uses and potential uses of titanium. An article by Ralston and Cservenyak (15) is especially comprehensive. Apart from its contracts with titanium producers, the U.S. Government has given tax concessions to producers in order to promote the industry. Not until 1955 were firms disallowed from writing off their investments in titanium production, melting, or fabricating plant in less than the normal 20-25 years (16). In 1954 the U.S. Government gave permission for up to 10% of titanium mill products to be channeled into non-defense uses (17). In the U.K. the British Government has guaranteed to buy 75% of the output of Imperial Chemical Industries, with an option on it all, in the first four years of production at the prevailing world price (18).

It is not surprising that the firms that have entered the titanium industry are ones that have large financial and technical resources as well as much experience in similar operations. This in some measure is because of the advanced and complex nature of the technological practice required.

Titanium Metals Corporation of America, formed in 1950, is jointly owned by the National Lead Co. and Allegheny Ludlum Steel Corporation. It has the only fully integrated plant in the U.S.A., going from ore to mill products (19).

Rem-Cru Titanium Inc. was formed in 1950 as well. It is jointly owned by Remington Arms Co. Inc. (in which E. I. du Pont de Nemours and Co. Inc. have a controlling interest) and the Crucible Steel Co. of America. Mallory-Sharon Titanium Corporation, which was founded in 1951, is jointly owned by P. R. Mallory and Co. Inc. and Sharon Steel Corporation. Together with the latter two concerns, Republic Steel Corporation, starting with sponge titanium, turns out titanium and titanium mill products.

In the U.K., Imperial Chemical Industries Ltd. is the only producer, and largest fabricator of titanium metal. An extraction unit, capable of producing 1,500 tons of sponge titanium a year, came into operation in August 1955 and is the only large scale unit producing titanium by the sodium reduction of titanium tetrachloride in both the U.S.A. and the U.K. William Jessop and Sons were expected to begin melting metal early in 1956 with an initial output of about 350 tons of ingots a year (20).

All the titanium concerns mentioned above, with the possible exception of the latter, issue booklets periodically which give details regarding their commercial titanium products. These details comprise physical, mechanical, and corrosion properties, composition, uses, and other specifications (17; 21; 22; 23; 24; 25).

The Army Ordnance of the U.S.A. put large means at the disposal of the U.S. Bureau of Mines to industrialize the Kroll Process in 1942 (3). A contract was made with the Defense Materials Procurement Agency in 1953 for the production by the Bureau of Mines of between 360,000 and 500,000# of usable titanium within an 18 month period which ended in 1954.

In 1952, a contract between the D.M.P.A. and E. I. du Pont de Nemours and Co. Inc. asked for the additional production of 13,500 short tons of sponge titanium over a five year period with the D.M.P.A. advancing up to \$14.7 million (26).

Cramet Inc., a Crane Co. subsidiary, have contracted with the D.M.P.A. to construct and operate a plant to produce 30,000 short tons of titanium sponge over a five year period with the D.M.P.A. advancing \$24.95 million for construction and equipment costs (27). The plant was under construction in 1955 (19). Another government contract for 18,000 short tons over a five year period was made with Titanium Metals Corporation of America in 1953 (27). Dow Chemical Co. have a contract with the General Services Administration for 1,800 short tons annually (19). They are expected to approach capacity operation late in 1956. The Electro Metallurgical Co., a division of Union Carbide and Carbon Corporation, completed negotiations in 1954 concerning a plant with a capacity of 7,000 short tons a year with late 1957 the target for full production (19).

In addition, in 1955, the General Services Administration had under active consideration a second contract with Titanium Metals Corporation of America for the production of an additional 5,400 short tons a year and with E. I. du Pont de Nemours for an additional 7,200 short tons a year (19).

Imperial Chemical Industries Ltd. and the Columbia-Southern Chemical Co. of Pittsburgh (a subsidiary of the Pittsburgh Plate Glass Co.) applied jointly in 1955 to the U.S. Government to supply 5,000 short tons a year for five years (28).

The titanium industry has grown very rapidly in the U.S.A. (see Table 1). In addition, 250 tons of sponge titanium were imported from Japan in 1954 (19; 27). Until 1955 all the titanium sponge in the U.S.A. was produced by E. I. du Pont de Nemours and Co. Inc., Titanium Metals Corporation of America, and the U.S. Bureau of Mines. In 1954, E. I. du Pont de Nemours and Co. Inc. and Titanium Metals Corporation of America produced about 2,500 short tons each with the Bureau of Mines producing about 150 short tons. Taking into consideration the contracts mentioned above, continued rapid growth of the industry is assured.

Table 1. Production of Sponge Titanium in the U.S.A.

Year	1950	1951	1952	1953	1954
Production (short tons)	100	700	1,075	2,250	5,250

Since titanium was first produced commercially, prices have continually fallen. Between 1952 and 1955 sheet titanium dropped in price from \$25 to \$13 per pound, while bars and billets dropped from \$20 to \$8.50 per pound (17).

CHAPTER III

PRESENT PRACTICE IN TITANIUM EXTRACTION

By describing present technological practice used to extract titanium metal, patents may be viewed in a better light. Most of the following has been taken from a U.S. Bureau of Mines Report of Investigations (10) but, nevertheless, is illustrative of general practice where titanium is obtained by the magnesium reduction of titanium tetrachloride (see Figure 1.)

Chlorination of the Ore.--Titanium bearing material is ground to 200 mesh, mixed with ground charcoal or petrol cake and pitch, briquetted, and baked at temperatures of 500 to 800°C. Batches of the briquettes are then charged medium hot into a chlorinator where chlorine gas is passed over them. A condensing system is situated adjacent to the chlorinator. This consists of a hot cyclone dust chamber, in which flue dust is deposited, followed by a condensing chamber, held at about 220° C, in which iron chloride condenses. A silica brick-lined iron tower, filled with porcelain pebbles, is used next to condense titanium tetrachloride and residual aluminum and iron chlorides. It is sprinkled internally with raw, cool titanium tetrachloride which is drawn from a tank at the base of the tower and passed through a heat exchanger. Iron and aluminum chlorides form a sludge in the collecting tank and are separated periodically. The titanium tetrachloride contained in the sludge is distilled off.

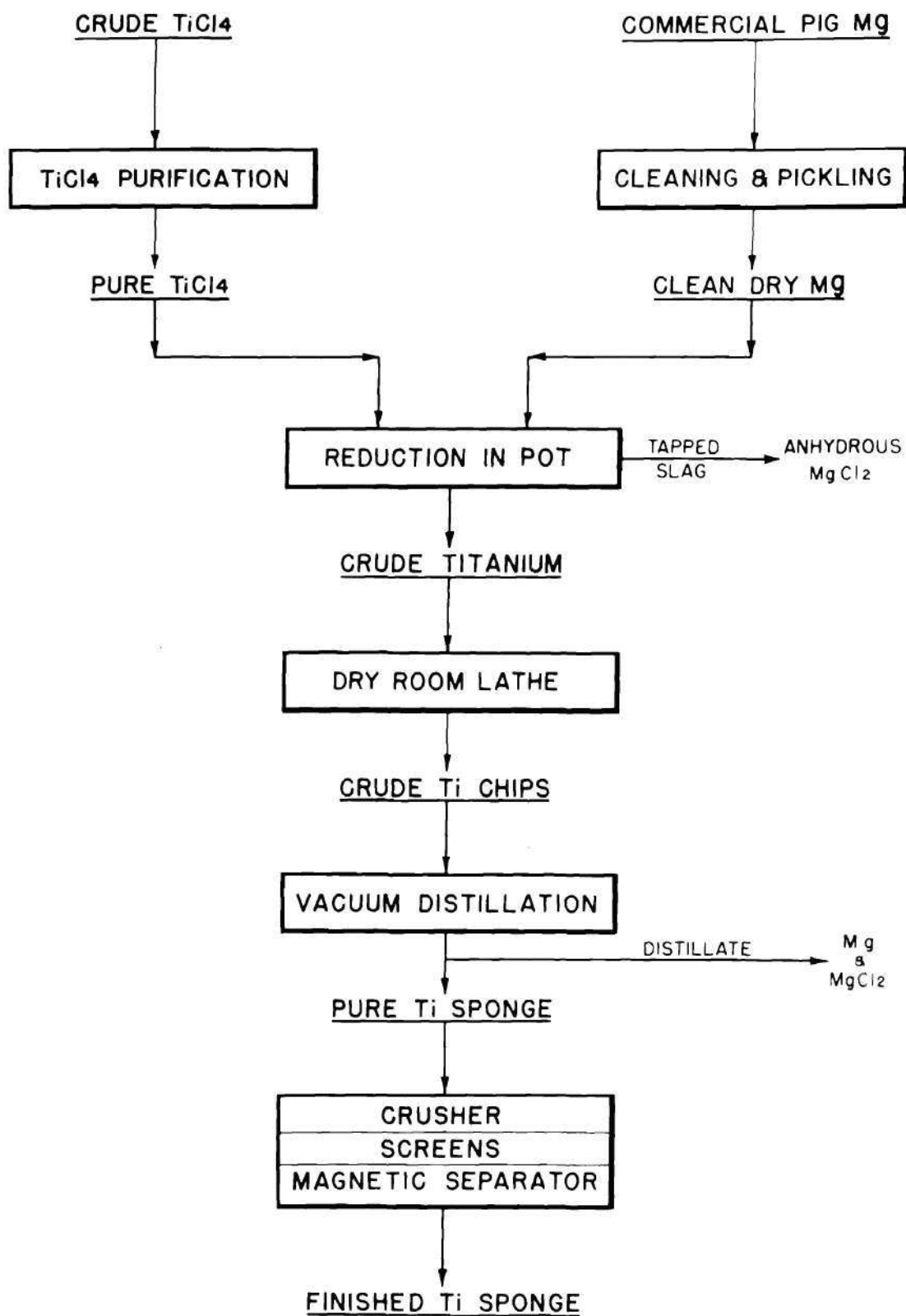


Figure 1. Flow Sheet for Titanium Sponge Production
 "Reprinted from Bureau of Mines Report of Investigations 5141."

The method of briquetting is not used by Titanium Metals Corporation of America and, instead, the paste mixture is poured onto a rotating hearth which passes through a brick firing kiln. Conditions in baking are critical for the following chlorination step. If the baking temperature is not high enough, residual hydrogen, originating mostly from the pitch, brings about the formation of excessive quantities of hydrogen chloride in the chlorination. Besides causing chlorination losses, this causes a problem of hydrogen chloride disposal.

Purification of Crude Titanium Tetrachloride.--Crude titanium tetrachloride, as obtained above, contains silicon chloride, chlorine, phosgene, sulphur chlorides, vanadyl chloride and iron chlorides as the principle impurities. These must be removed because of the deleterious effects of impurities on the mechanical properties of titanium (see CHAPTER IV). The first three are distilled off as a light fraction together with other volatile impurities. The latter three are reduced to less volatile and more insoluble compounds by treatment with copper powder, hydrogen sulphide, or vegetable oils (3).

The following method is used by the U.S. Bureau of Mines (10): A batch of about 4,400 pounds of crude titanium tetrachloride is heated to between 90 and 100° C and hydrogen sulphide added to the agitated charge at the rate of one pound per hour until slightly more than the theoretical amount (found by treatment of a sample) has been added. The batch is allowed to flow by gravity into a fractionating still where 150 pounds of lights (determined by economic balance) are distilled off. The batch

is then transferred by gravity to a pot still where pure titanium tetrachloride is distilled off. The residue is removed periodically after a baking period.

Table 2. Analysis of Residue

Element	Fe	V	Si	Ti	Cl	S
% by wt.	5.7	0.72	0.61	36.6	39.46	16.51

Table 2 shows the composition of the baked residue.

Magnesium Reduction.--Magnesium ingots, weighing about 20 pounds each and with the sum of aluminum, copper, iron, manganese, nickel and silicon less than 0.2%, copper less than 0.02% and nickel less than 0.001%, are pickled in 3 to 3.5% hydrochloric acid. When they appear bright and effervescence ceases, they are removed, flushed with water, blown over with compressed air, and dried with cloths.

Mild steel reactor pots (see Figure 2) are loaded with about 330 pounds of ingots in a dry room and the lids welded on and tested for leaks. A particular pot is purged with helium and then filled at $\frac{1}{2}$ p.s.i.g. The pot is then lowered into a furnace and connections made with a titanium tetrachloride feed line, helium line, vent line, dry air cooling line, and a line to a moisture trap. A temperature controller on the furnace burner is set at 750° C and, when some of the magnesium has melted, the moisture trap is disconnected, and, with the helium pressure maintained at $\frac{1}{2}$ p.s.i.g. titanium tetrachloride is fed in initially at the rate of 30 pounds per hour. After a delay of about 5 to 20 minutes, when the reaction starts, the feed rate is stepped up to 200 to 250 pounds per hour,

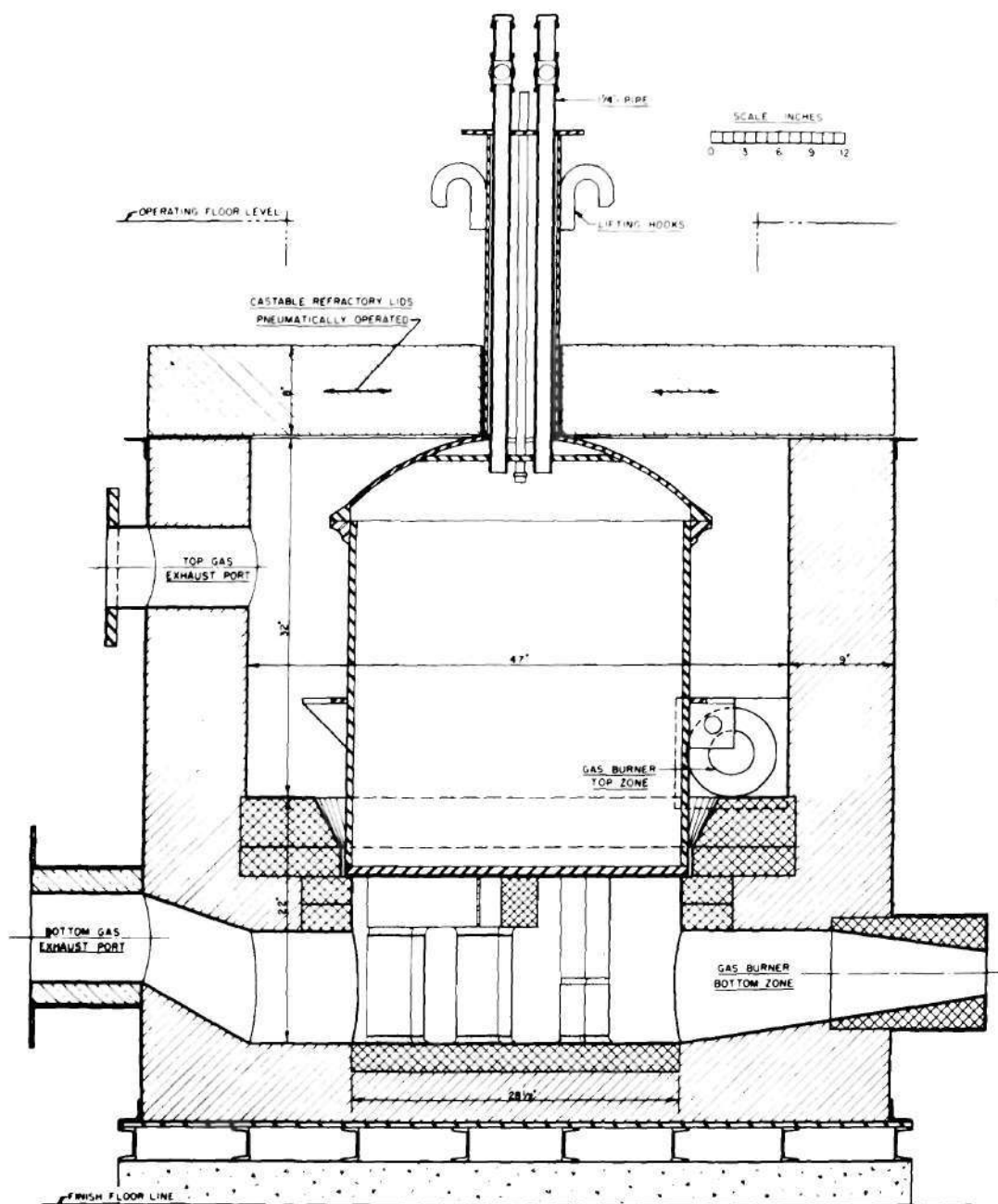


Figure 2. Cross Section of Reduction Pot and Furnace
 "Reprinted from Bureau of Mines Report of Investigations 5141."

this rate of feed having been found experimentally to give the best quality sponge. The furnace burner is shut off when the reaction generates enough heat to maintain the desired temperature of 750 to 800° C. 1,070 pounds, being equivalent to about 83 to 85% of the stoichiometrical quantity required to satisfy the reaction, $\text{TiCl}_4 + 2 \text{Mg} = \text{Ti} + 2 \text{MgCl}_2$, are charged to the pot. The excess magnesium present prevents the reactions, $\text{Ti} + 3\text{TiCl}_4 = 4\text{TiCl}_3$, $\text{Ti} + \text{TiCl}_4 = 2\text{TiCl}_2$, $2\text{TiCl}_3 = \text{TiCl}_4 + \text{TiCl}_2$, from occurring to any significant extent. The presence of lower chlorides is undesirable, because they are partly soluble in fused magnesium chloride and tend to condense on the reactor lid with obstruction of the feed lines.

After 40% of the titanium tetrachloride has been added, a first tapping of molten magnesium chloride is made. A water cooled plug is removed from an outlet at the base of the vessel and a portable burner directed at the spout to soften the locally solidified magnesium chloride. When soft enough, a tapping rod of mild steel is hammered through the hole, withdrawn, and the molten magnesium chloride allowed to flow down a launder into a slag barrel. At the first sign of helium blowing out, the water cooled plug is replaced.

The feed rate is usually decreased to 180 pounds per hour after the first tapping and maintained until the end of the run. Magnesium chloride is again tapped after 60% of the titanium tetrachloride has been added. When all the titanium tetrachloride has been added, the burner is again turned on and the temperature of the reduction pot held at 780 to 850° C for one hour. A final tapping is then made to remove as much magnesium as possible from the pot. The pot is cooled with air in the furnace,

removed, and allowed to cool for about 24 hours. At the end of the cooling period, the weld on the lid is ground off and the pot removed to a dry room to be opened.

The physical aspects of the reduction reaction have been studied by Wartman and others (31). They found that, at first, virtually all of the titanium is formed in a ring attached to the walls of the reactor. As the reaction progresses, the ring of deposited metal continues to extend farther up the wall and also outward toward the centre.

Removal of the Titanium Sponge.--The crude titanium sponge is removed by chucking the reactor on a lathe and cutting the mass away into chips with a cutting tool. Since the magnesium chloride present is extremely hygroscopic, and since the subsequent operation is vacuum distillation of the remaining magnesium and magnesium chloride, the oxygen in any moisture absorbed would find its way into the finished product. This is why the operation is carried out in a dry room. The contents are turned out into chip baskets leaving a 3/4 inch thickness of sponge on the bottom and sides of the reactor to prevent as much iron pick up as possible. The reduction cycle is now repeated.

Vacuum Distillation of Magnesium and Magnesium Chloride (32).--The chip basket from the above operation and containing crude titanium chips is suspended inside a retort (see Figure 3) which is preliminarily evacuated to less than 200 microns, the basket having been exposed to undried air for only one to two minutes. The retort is then placed in a furnace which is evacuated, the vacuum being maintained at 27 inches of mercury. The retort is evacuated to 75 microns and the furnace heat turned on.

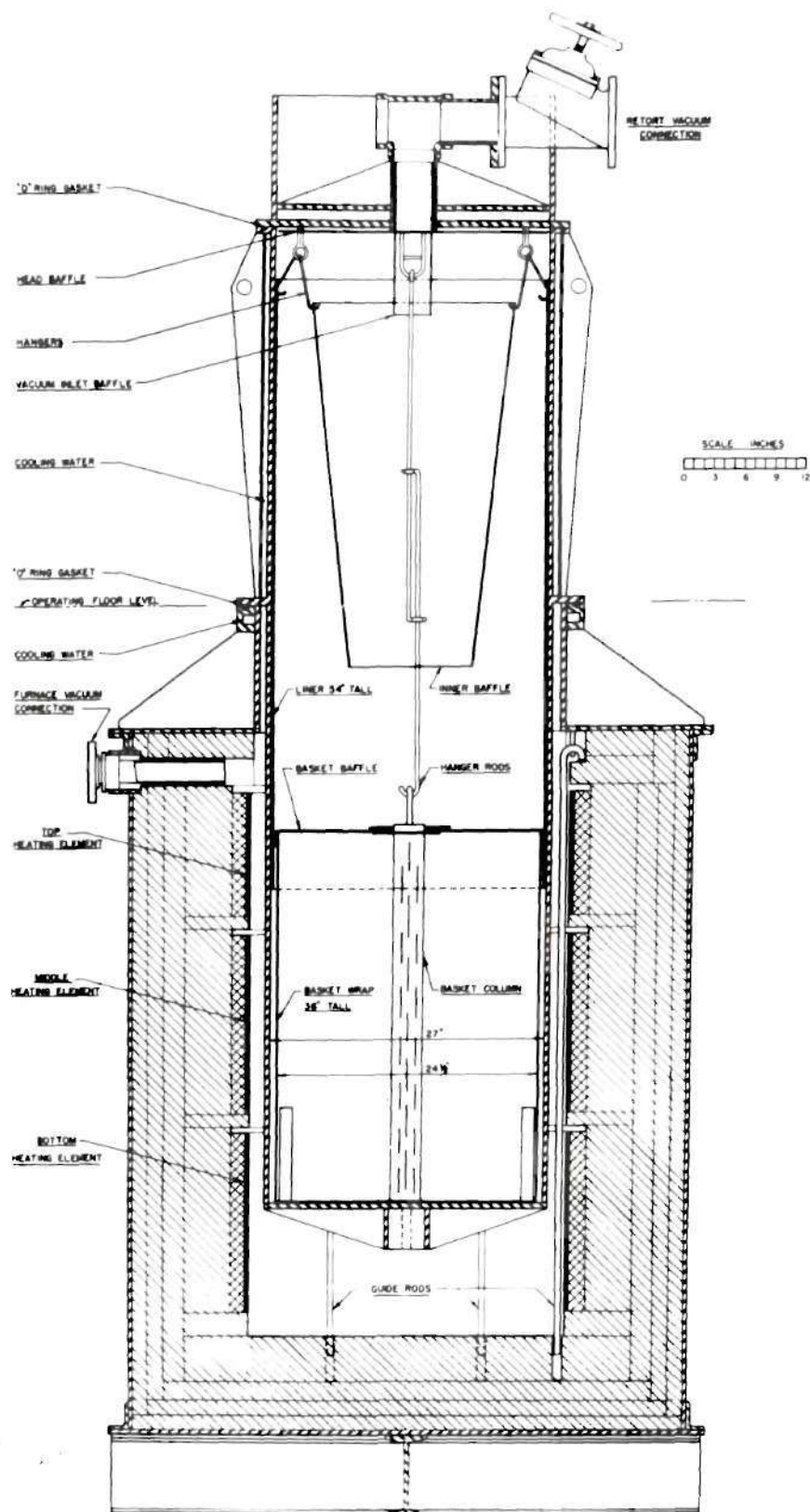


Figure 3. Cross Section of Vacuum Furnace and Distillation Retort
 "Reprinted from Bureau of Mines Report of Investigations 5141."

The optimum time-temperature relation for distilling off the magnesium and magnesium chloride is about 940°C for 31 hours. Longer times are required at lower temperatures. Heating is then stopped and, when the temperature is below 870°C , the vacua on the furnace and retort are released simultaneously, dry air being allowed to enter the furnace and helium, at 1.5 p.s.i.g., the retort. The retort is then lifted from the furnace and placed in a cooling rack. After 22 hours in the cooling rack, the helium line is removed and atmospheric air allowed to diffuse into the retort. After another hour, low pressure dry air is allowed to flow through the retort for 30 seconds and then a pressure of 5 p.s.i.g. is maintained for an hour. This procedure is to condition the titanium to air and to slowly oxidize any finely divided magnesium so as to minimize the risk of fires while unloading. The chip basket is then removed from the retort and allowed to air condition for another six hours. The magnesium and magnesium chloride, which condense on water cooled baffles suspended above the chip basket, are scraped off. The scraped baffles are placed in an acid pickling vat, allowed to soak until the acid reaction ceases, rinsed with water, wiped with clean cloths, and placed in a drying oven until needed. The retort and retort head are cleaned with wire brushes and blown out with air.

Sponge titanium is removed from the basket with a cement chipper and is fed continuously to a jaw crusher with manganese jaws. The crushed sponge is screened, passed over a magnetic drum, and packed in air tight drums.

Leaching.--An alternative method of separating magnesium and magnesium chloride from crude titanium sponge is by leaching with acid. The method

has the disadvantages that large amounts of magnesium and magnesium chloride go to waste and there is a tendency to oxygen pick up inherent in the process. The leaching method was originally used by the Bureau of Mines but gave way to the vacuum distillation method on its development. The leaching method was being used by Titanium Metals Corporation of America in 1954. It seems, therefore, that neither method has an overwhelming economic advantage.

The Bureau of Mines procedure was to leach titanium chips from the boring process with hydrochloric acid, a pH of less than two being maintained at all times. Two leachings, with an intermediate grinding, were effected. The second one was with 20% HCl acid. To minimize oxygen pick up, the temperature during the first leaching was kept below 25° C and, during the second, below 45° C. Continuous agitation obviated any local heating. After washing with water and mechanically removing as much of this as possible, the chips were dried in a drum drier with air at room temperature.

Melting and Ingot Formation.--When titanium was first produced commercially, massive ductile titanium was formed by conventional powder metallurgy techniques. The titanium was sintered in vacuo or under a noble gas atmosphere. The method is now obsolete. It suffered from the disadvantage that ingots tended to retain magnesium in the centres and often proved defective.

Three methods of melting titanium chips to form ingots have been used. A vacuum or noble gas atmosphere is common to all three. In the first method titanium is melted in a graphite crucible in the arc from a graphite electrode. Carbon contamination, which goes up to 1% and more,

is a drawback. However, melting in graphite by high frequency induction is established as standard practice for the remelting of scrap and to produce castings (33).

Secondly, titanium is melted in a water cooled copper crucible or sleeve (which it does not wet) in the direct current arc struck between a water cooled tungsten (or other metal) electrode and a molten pool of titanium at the top of the ingot. In both these first two methods, titanium chips are added continuously to the molten pool of titanium formed by the arc.

Thirdly, ingots are produced by arc melting in a water cooled copper crucible. In this case consumable electrodes of pressed sponge are used. Electrical energy is applied close to the lower ends of the electrode bars by means of water cooled rolls or slip jaws. Usually, the ingots so formed are used as consumable electrodes in a second melting. An ingot can be continually lowered so as to keep the surface of the titanium pool adjacent to the arc at a constant level or the electrode can be gradually raised as the level of the titanium pool rises. The latter method is more convenient for large ingots by obviating the use of heavy machinery. The third method is now gaining recognition as the best technological practice and is ousting the other methods.

An ingot weighing about 300 pounds was formed from sponge chips for the Bureau of Mines by Republic Steel Corporation (34). The ingot was melted under an inert gas atmosphere in a water cooled copper crucible, 12 inches in diameter. A direct current arc was obtained using a water cooled thoriated tungsten electrode, 1 inch in diameter. The electrode was fixed to a centrally located shaft at an angle, so as to describe a

circular path, 6 inches in diameter, during melting. Electrode rotation was regulated in accordance with the build up in the melt and the rate of electrode retraction was governed by an automatic arc- voltage control.

Before evacuation, approximately 10 pounds of sponge were placed in the bottom of the crucible for arc initiation. The system was closed and evacuated to a pressure of about 100 microns and then backfilled to atmospheric pressure with an atmosphere containing 80% helium and 20% argon. A continuous flow of this gaseous mixture was maintained throughout the melting cycle. After backfilling, the arc was initiated on the loose sponge which was melted before the feed mechanism was started.

All the sponge, sized within fixed limits, was vacuum dried for 6 to 12 hours and loaded into feed bins which supplied the vibratory feed mechanism. The rate of feed for the first hour of melting was set at 20 to 40 pounds of material per hour. After 50 pounds had been melted, the rate of feed was increased periodically until it had reached the maximum rate of 70 to 80 pounds of material per hour. The melting time required was about seven hours. An operator, observing the melt through a pyrex window, was able to change the rate of feed and control the arc, when necessary. The ingot was allowed to cool for 30 to 45 minutes before removal from the crucible. Ingot shrinkage and lack of wetting action or adhesion between molten titanium and cold copper made removal a simple operation.

CHAPTER IV

FACTORS TO BE CONSIDERED IN PATENT APPRAISAL

Two main considerations are encountered when endeavouring to appraise a patent. The first is concerned with the possibility of the process and requires knowledge of the physical properties of reactants and products so as to help in solving (if there is a solution) mechanical handling problems. The second is concerned with production costs. The costs of starting materials and end products, capital equipment, and labour must be determined. To be of any significance, a patented process must be an improvement on those processes which are presently used and must conform to the necessary product specifications.

Raw Materials.--Titanium is the ninth ranking element in the earth's crust. There is, consequently, no shortage of titanium ores. Ilmenite, a combined titanium iron oxide, and rutile (titanium dioxide) are, by far, of greatest commercial importance. As rutile deposits are limited, the majority of the titanium is, and will be, produced from ilmenite which contains about 32% titanium and 37% iron (1). This is well illustrated by the 1953 figures for the mining of the respective ores. The World supply of rutile was 42,000 short tons and the World supply of ilmenite about 800,000 short tons (3). The majority of this was used to make titanium oxide pigments.

Although sulphuric acid is used to remove iron from ilmenite in the production of pigments (a paying proposition because of the high

price of pigments), it is a wasteful process. Direct chlorination of ilmenite would involve the production of large quantities of ferric chloride, most of which would go to waste, despite its large market in sewage disposal.

By far the most important iron separation process in operation at the present time uses the selective arc reduction of the iron oxide content with the production of pig iron and a high titanium slag. Kenecott Copper Corporation and the New Jersey Zinc Co. erected a \$30 million smelter in 1951 which produces about 250,000 tons of slag a year containing 70% titanium dioxide. 175,000 tons of pig iron a year are produced in the process. The slag, containing a small amount of iron, is in a very convenient state for chlorination.

Purity and Hardness.--Titanium has a strong affinity for oxygen, nitrogen, and hydrogen. These gases have a considerable embrittling effect, even in small concentration. Hydrogen can be removed by heating in a high vacuum and as titanium nitride dissociates at very high temperatures, some nitrogen is removed in the arc melting process (35). Nitrogen is about three times as active as oxygen in its hardening effect (35). As there is no means of removing oxygen once it contaminates the metal, the only alternative is to avoid oxidation in production and processing. Whenever the metal is heated to a high temperature it must be surrounded by a vacuum or a noble gas atmosphere.

In the vast majority of applications, titanium is required to be in a ductile state and, consequently, attention has to be paid to preventing impurity pick up. Specifications for sponge titanium have

become more stringent since its advent on a commercial scale. The specifications imposed by the Government in 1954 under its revolving fund program are indicated (Table 3). In addition, the hardness of type A was to be below 160 B.H.N. and of type B to be below 170 B.H.N. (10).

Table 3. Specifications for Sponge Titanium

Element	Ti % (min.)	Fe % (max.)	N % (max.)	Cl % (max.)	Mg % (max.)	C % (max.)
Type A	99.3	0.30	0.03	0.15	0.10	0.15
Type B	99.3	0.25	0.03	0.15	0.50	0.07

Mechanical Handling.--See comments on patent (8).

Undesirable Characteristics of the Magnesium Reduction Process as Presently Operated.--The magnesium reduction process is a batchwise operation. The advantages over this of continuous operation have long been known.

There is some iron contamination from the walls of the mild steel reactor vessels. This is partly eliminated by leaving a shell of sponge on the sides of a reactor after the first 'heat.' The boring operation for removing sponge from the reactors is costly.

Problems of Electrolysis.--Many difficulties have been encountered in attempting to develop electrolytic processes. The first U.S. patent application was not until 1952. Although some success has been achieved, it is unlikely that the conventional reduction processes will be replaced. This is largely due to the high cost of the materials forming electrolytic baths and to the complexity of proposed methods.

Some of the difficulties have been discussed (36) and are outlined as follows:

The choice of suitable electrolytes is limited, for price reasons, to chlorides and fluorides. Titanium tetrafluoride is unsuitable but the double fluorides of titanium with potassium, sodium, and lithium could be considered. Sodium, potassium, and lithium fluotitanates can be obtained from aqueous solution and all dissociate in alkali fluoride and titanium tetrafluoride.

No fusion electrolysis, whether chloride or fluoride, can be operated successfully with graphite or carbon anodes (37) unless the bath contains oxides to avoid anode effect which is for the main part caused by a halogen or halogenide gas skin adhering to the graphite and which stops the flow of current.

While the fluoride electrolysis requires the presence of considerable quantities of oxide in the electrolyte, which is decomposed by the current and from which the metal is deposited exclusively, much less is needed for chloride electrolysis. The large amount of oxide used in fluoride electrolysis practically rules out the method (with graphite anodes) on account of sponge contamination by dissolved oxide.

Titanium tetrachloride is not appreciably soluble at atmospheric pressure in fused sodium chloride, calcium chloride, magnesium chloride, barium chloride, or stannous chloride nor in any carrier salt at temperatures in excess of 500°C . This rules out the use of titanium tetrachloride as bath constituent in any fusion electrolysis above that temperature. It has been demonstrated (38) that the lower titanium chlorides,

titanium trichloride and titanium dichloride, are soluble in various carrier salts and that suitable electrolytes can be obtained with these. Electrolytes of this nature are especially promising when titanium scrap anodes are used.

Extensive experimentation has been performed by the U.S. Bureau of Mines (39) to find suitable electrolytes from which titanium may be electro deposited. Of the aqueous, non aqueous, and fused salt electrolytes tested, metal was produced in only the fused salt electrolytes, the major product being sponge metal. Trial of all the other electrolytes resulted only in partial reduction of the metal ions. The conclusion was reached that sponge metal can be produced in any inorganic fused salt electrolyte that does not contain an ion more easily reduced than titanium and that has a low enough fusion point to permit the retention of the titanium halide contained in the electrolyte. In no system investigated was pure metal obtained from readily available and cheap raw materials.

CHAPTER V

PATENT CLASSIFICATION

35 patents of processes for the manufacture of titanium have been divided into five classes on account of certain similarities existing among them. These similarities are mostly chemical in nature and this has been made the basis for the division.

Direct Reduction of Titanium Halide. Patents (5; 6; 7; 8; 11; 13; 14; 15; 16; 18; 19; 21; 24)

The outstanding features of this class are the attempts in patents (8; 13; 14; 21) to continually remove solid reaction product from reaction vessels, in patents (11; 13; 14) to reduce to a minimum surface contact between reactor surfaces and metallic titanium so as to avoid welding, in patent (19) to combine the conventional operations of reduction and vacuum separation, and in patent (24) to produce ingots continually from the tetrahalide in one operation, thus eliminating the present three steps of reduction, vacuum separation, and arc melting.

Patent (5).--Titanium tetrachloride vapour is passed into a bath of fused potassium chloride on the surface of which is floating a layer of molten sodium. An atmosphere of hydrogen is effected.

Titanium produced by this method would be contaminated with hydrogen.

Patent (6).--Titanium tetrachloride is reduced by fused magnesium under a noble gas at substantially atmospheric pressure (see Figure 4). For further details see CHAPTER II.

Patent (7).--A steel basket with a perforated base rests on a supporting ring some distance from the base of a steel container. The container is heated to 200 to 300° C and titanium tetrachloride is introduced through a side conduit to purge the air. The temperature is then raised to 750 to 900° C and molten metal (magnesium, sodium, etc.) from a heated pot is allowed to run in at such a rate as to react before reaching the basket. A titanium tetrachloride pressure of one to five p.s.i.g. is maintained. Magnesium chloride drains out of the basket and may be run off periodically through a hole in the container. When sufficient reaction product has accumulated, the apparatus is cooled, titanium tetrachloride vapour purged, and the contents removed. By using two containers, the method may be made semi continuous as metal can be run into the containers alternately.

Since titanium chloride is always in excess, the method would lead to the formation of lower chlorides as well as titanium (40).

Patent (8).--Molten magnesium and titanium tetrachloride are supplied continuously to a reaction chamber in which a noble gas and/or tetrachloride atmosphere is maintained. A screw conveyor continuously removes the reaction product before it can solidify and delivers it to a drainage screen where some magnesium chloride drains off. It is then passed on to an arc melting furnace where the remaining magnesium and magnesium chloride vaporizes and is condensed on the cooled refractory walls. A

June 25, 1940.

W. KROLL

2,205,854

METHOD FOR MANUFACTURING TITANIUM AND ALLOYS THEREOF

Filed July 6, 1938

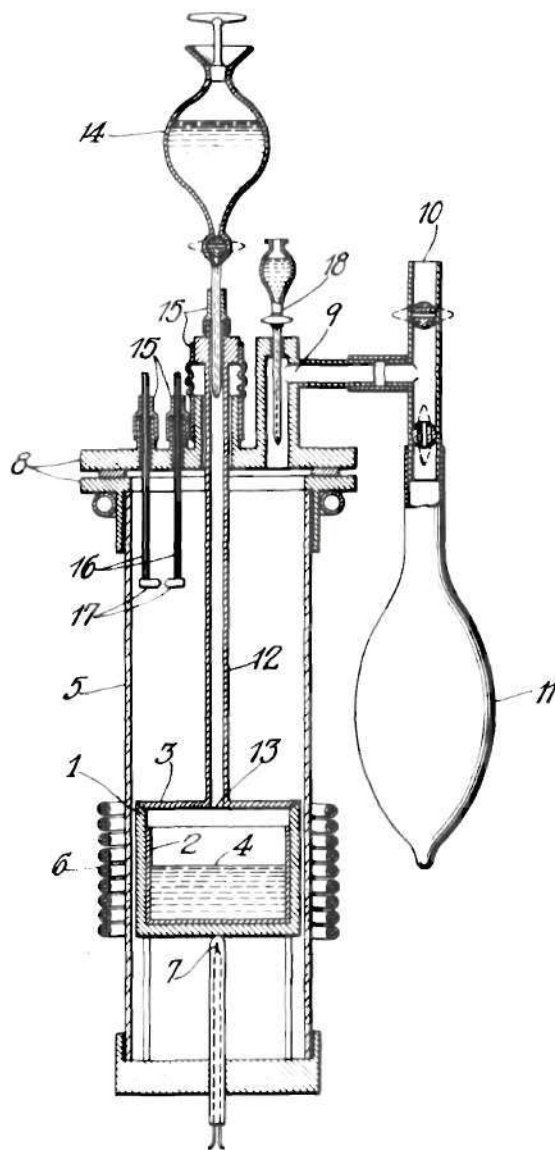


Figure 4. Diagram Illustrating Patent (6)

INVENTOR.

WILHELM KROLL.

BY

ATTORNEYS

collecting ring gathers the condensed vapours whence they run into an external vessel. An inert atmosphere prevails throughout.

Kroll (40) has pointed out some difficulties. At the operating temperatures of the magnesium and sodium reduction methods (i.e. above 720°C) titanium readily welds to every thing it touches. At the maximum temperature of the reduced sponge (about 975°C) even the best cobalt-bearing high temperature alloys would not serve as a conveyor. Each one of the two phases involved, reduction and arc melting, is already so cumbersome in itself that synchronizing both as to momentary needs of reduction and melting would make joint operations impossible. The condensation of liquid chloride up to $1,450^{\circ}\text{F}$ creates various problems with the feeding device of the hot sponge, with the electrode movements, and with the joints which have to operate reliably above 720°C . Finally, when using direct current for the arc, there may be trouble with electrolysis of the chloride.

Patent (11).--An open ended vessel with an apertured base is partly submerged in a molten halide salt bath so that the surface of some molten magnesium contained in the vessel rises to the vessel rim. The whole is contained in a closed container and a noble gas atmosphere pervades this container. With a temperature of 750 to $1,100^{\circ}\text{C}$, titanium tetrachloride is introduced onto the magnesium surface and, upon depletion of the metal, the vessel is removed, together with adhering titanium sponge. The sponge is removed and treated in a conventional manner.

It is difficult to see any advantage to be gained over the Kroll Process. Although the sponge can be removed more easily, this is countered

by the greater complexity of operation.

Patent (13).--Magnesium, in the form of slugs, finely divided, or molten and titanium tetra chloride are admitted to a central vortex which is formed in a bath of molten magnesium chloride by a paddle which projects through the base of the containing vessel. With a temperature of 800 to 900° C, and with an inert gas atmosphere, sponge titanium is formed and sinks to the bottom of the vessel and may be removed through a hole in the base. Magnesium chloride overflows continuously through a side arm. The reaction mixture in the vortex does not come into contact with the vessel walls.

Some comments have been made on the process (40):

. . .but as soon as titanium sponge is formed, the 'heavy medium' thus created behaves differently. The magnesium-impregnated titanium sponge will then either drop down to the bottom or it will hit either the walls or the impeller with subsequent welding or agglomeration of particles. There is the problem of the material of construction of the impeller.

Patent (14).--Drops of liquid magnesium are allowed to fall onto the surface of liquid titanium tetrachloride at or near its boiling point of 136° C. The globules stay on the surface until becoming solid when they sink to the bottom of the vessel. They may then be removed continuously. The liquid is given a suitable motion mechanically to prevent the drops from coming into contact with the walls of the containing vessel.

Advantages claimed are that heat requirements are small and specifications for constructional materials are not stringent.

It has been remarked (40) that:

Since an excess of halide, this is certainly quite a good method for producing lower halides, which probably do not stick together, but no pure metal could possibly be made in this way except by subsequent disproportionation of the reaction product at high temperatures.

Since in experiments by the patentee the reaction product was heated to high temperatures during the vacuum separation of the magnesium chloride, disproportionation would occur.

Patent (15).--Powdered magnesium and titanium tetrachloride are fed into a graphite reaction crucible which is disposed on an axle (so that it might be inverted) under a dome shaped hood. The hood is suspended from a crane so that its open end is below the surface of a fused salt bath, a suitable composition being 15-25% magnesium chloride, 20-25% calcium chloride, 1% calcium fluoride, and the balance sodium chloride. The reactants are introduced as fast as they will react, titanium tetrachloride being added at such a rate that it is about 90-95% of the stoichiometrical requirement. The reaction is carried out below an inert atmosphere. Changes of level of the bath indicate the pressure of titanium tetrachloride under the dome. This fact can serve as a control device for reactant addition. Molten magnesium chloride overflows into the bath. When the crucible is full of sponge it is inverted and the sponge falls into a wire basket which may be baled out with a hook. The sequence is repeated.

The bath surface will be oxidized so that oxygen will be transferred to the sponge but, apart from this, there is the question as to whether the sponge will drop out of the crucible (40).

Patent (16).--Titanium tetrachloride is admitted into a graphite lined vessel, which contains a cupro magnesium alloy at about 950°C , through a graphite tube reaching almost to the bottom of the vessel. A helium atmosphere is established previous to this by purging before heating up the vessel. The titanium tetrachloride addition is controlled by a pressure mechanism. After adding to 1% in excess of the stoichiometric amount needed, the vessel is heated for a further hour and the contents allowed to run out through a hole in the vessel base. A lower layer of an alloy with the composition, 77.7% copper, 22% titanium, 0.2% iron, 0.1% magnesium and 0.04% carbon is formed. Magnesium chloride forms an upper layer.

Patent (18).--Magnesium gas and titanium tetrachloride gas are admitted near the base of a column of molten magnesium chloride which is maintained at a temperature between the boiling point of magnesium and the boiling point of magnesium chloride. The temperature is controlled by a water cooled induction coil. By using an excess of magnesium, particles of titanium appear dispersed in the salt. These may be separated by settling or by centrifugation and purified in a conventional manner. The column lining may be of graphite or titanium for example.

Graphite has been shown to disintegrate in contact with the reagents used, plugging of the reducing agent inlet would be difficult to avoid, and the problem of moving the hot reaction product has not been solved (40).

Patent (19).--Magnesium and titanium tetrachloride are reacted in a reaction zone which is situated about half way up a vertical cylindrical

vessel (see Figure 5). Apertures in the bottom of the metal base defining the zone allow of the passage through them of magnesium chloride but not of magnesium titanium. An atmosphere of an inert gas or of titanium tetrachloride is effected and magnesium billets and the tetrachloride are introduced continuously through the top of the vessel. The reaction zone is heated by a surrounding furnace. In an example, magnesium and titanium tetrachloride are added continuously with 20% excess magnesium. The temperature, initially at 725°C , is held between 900 and 980°C during the reaction period. The apparatus is then cooled to 25°C and the titanium removed. A metal recovery of 95% with a purity of over 99% is obtained. 87.7% of the magnesium chloride formed drains through the apertures. Most of the remainder distills off and is condensed in a condenser leading off from the vessel above the reaction zone.

The method looks very promising provided that there is not too much magnesium chloride in the sponge to cause difficulties in the following arc melting step. There is a small chance of oxygen pick up and heat requirements are modest.

Patent (21).--Titanium tetrachloride gas is introduced through a pipe at the top of a cylindrical vessel in such a manner as to atomize molten magnesium which may be formed by passing magnesium wire through an electric arc or by other means. The two reactants, in stoichiometric proportion, produce titanium in the inert atmosphere of the vessel and at the operating temperature of about $1,400$ - $1,600^{\circ}\text{F}$. A screw conveyor removes the reaction product from the bottom of the vessel.

The conditions are conducive to the formation of subchlorides. There might be some difficulty in mechanically handling the product.

Dec. 22, 1953

C. K. STODDARD ET AL

2,663,634

PRODUCTION OF TITANIUM METAL

Filed May 27, 1950

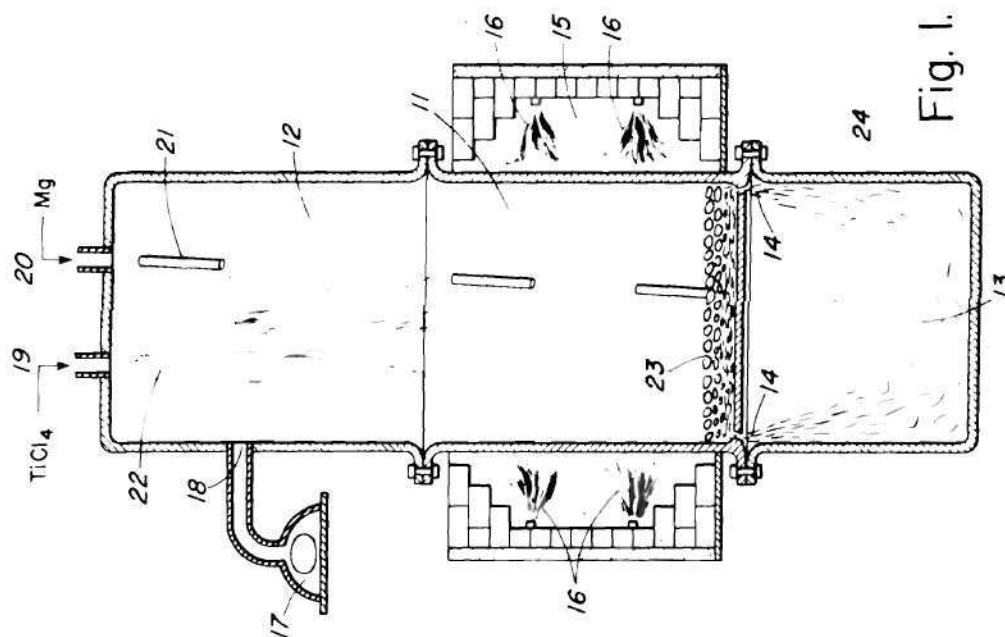


Fig. 1.

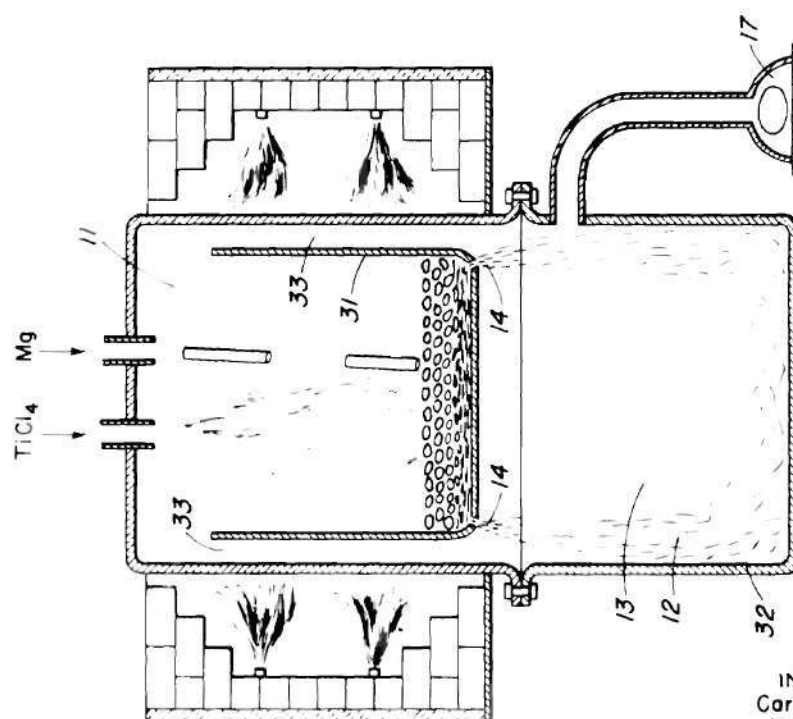


Fig. 2.

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Figure 5. Diagram Illustrating Patent (19)

Patent (24).--Magnesium and titanium tetrachloride gases are fed into a column of molten salt (such as magnesium fluoride, calcium fluoride, calcium chloride, or a mixture thereof) which is at a temperature above the melting point of titanium. Molten particles of titanium form in the column and settle to join a molten pool of titanium which forms the top of an ingot that is being continually withdrawn. Magnesium chloride, also produced in the process, is liberated as a vapour and may be condensed.

In the above patents magnesium and titanium tetrachloride are in most cases included in particular embodiments of the processes. Other reducing metals and other tetrahalides are often given as alternatives. For verification of this, recourse must be had to the patents. For price reasons, sodium, magnesium, and titanium tetrachloride are the only feasible reactants.

Oxide Reduction. Patents (1; 4; 9; 10; 23; 29; 35)

Patents (1; 4; 9; 23; 35) are concerned with the direct reduction of titanium oxide by reducing metals. Patent (9), starting with impure titanium such as might be produced by patent (23), may be considered as an adjunct to that patent. Patent (29) also begins with impure titanium which, however, is specified as being obtained by direct reduction of the oxide with carbon. In patent (10) titanium oxide is directly reduced but this is only an intermediate step in the preparation of titanium tetraiodide. It can, therefore, be considered as supplementing patents (3; 17).

Patent (1).--A grey-black oxide of titanium is heated in the presence of aluminum.

Patent (4).--Refractory metals may be produced by heating in a hermetically sealed container a metallic oxide, an alkaline earth metal halide, and a calcium-magnesium alloy.

Patent (9).--Compacts of sponge titanium are immersed in a molten alkaline earth metal and heated to $1,000^{\circ}$ C. Besides being a sintering operation, some of the oxide remaining in the sponge as impurity is reduced.

The sintering method of producing massive ductile titanium has been superceded by the arc melting method (see CHAPTER II).

Patent (10).--A titaniferous iron ore is heated to a high temperature in the presence of sufficient powdered or granulated aluminum to reduce the oxide to metal (thermit reaction) and to form an aluminum alloy with as high a content of titanium as possible. Using rutile, an alloy containing about 70% titanium is obtained. The alloy is dissolved under reflux in a non-polar solvent containing iodine. After distilling off the solvent, sufficient potassium iodide is added to form potassium aluminum iodide. Titanium tetraiodide and the remaining iodine are then distilled off. The titanium tetraiodide is thermally decomposed to produce titanium and iodine is recovered from the various iodides.

Patent (23).--A mixture of titanium dioxide of high purity and ground to pass a 100 mesh sieve, distilled magnesium of highest purity in 100% excess, and dehydrated calcium chloride is placed in a crucible (preferably of iron lined with calcium or magnesium oxides) with an air tight cover. After evacuating to a high vacuum, argon gas is introduced at slightly above atmospheric pressure and the mixture heated to $1,000^{\circ}$ C for

30 minutes. The crucible is cooled, opened, and placed under water. A stirrer is centered in the crucible and hydrochloric or acetic acid is added to dissolve the excess magnesium. After all the solid matter has been loosened, the empty crucible is removed and the remaining liquid stirred to dissolve every thing but the titanium powder. The slurry is allowed to settle for an hour, the supernatant liquid syphoned off, and the powder further washed with acid and water. The powder is filtered and dried under vacuum conditions. It is then mixed with nitrogen free calcium (obtained by melting calcium with scrap titanium) in 100% excess and calcium chloride. The mixture is treated in a similar fashion to the one above. It is claimed that expensive calcium is conserved by using it in conjunction with magnesium.

Patent (29).--It is known that impure titanium can be produced by reduction of the oxide with carbon in an electric furnace. Such titanium, containing mostly carbon as impurity, is heated near the open end of a refractory tube (e.g. molybdenum) in the form of small lumps. Mixed alkali titanous fluoride contained in a refractory boat is situated at the closed end of the tube. The salt, on heating, vaporizes and the vapours pass over the impure titanium into an outer mullite tube concentric with the inner tube and having an open end at the same end as the inner tube. Titanium condenses in this cooled end of the outer tube. The whole apparatus is evacuated, the excess vapours being drawn off and condensed. An experimental vacuum of 0.001 m.m. of mercury has been used. The process conforms to the reaction: $6\text{KF}(\text{v}) + 3\text{TiF}_3(\text{v}) + 2\text{Ti}(\text{s}) \rightleftharpoons 5\text{TiF}_3(\text{v}) + 6\text{K}(\text{v})$ which is driven to the right at high temperatures.

Patent (35).--Titaniumdioxide is reacted with ten times its weight of sodium- calcium sludge (containing about 20% calcium), obtained in a Downs Cell, in a suitable vessel. After heating at 900°C for one and a half hours, the temperature is raised to $1,100^{\circ}\text{C}$ when sodium distills off and is condensed, providing a valuable by-product. The remaining mixture is leached with alcohol and dilute acid, washed with water, and dried. A purity of 95% is claimed and the suggestion made that further purification be effected by other means.

In view of the fact that the last traces of oxygen, once present in sponge titanium, cannot be removed without going via an intermediate compound (see CHAPTER IV), the impure titanium produced by direct reduction of the oxide can only provide a starting point for the production of the tetraiodide (or other halide) and subsequent thermal decomposition to very pure titanium which has a limited demand.

Reduction by Sodium Amalgam. Patents (12; 20; 25; 28)

Three patents (12; 25; 28), by the same patentees, relate to the reduction of titanium tetrachloride by sodium in the form of sodium amalgam. Patent (20) may be considered an appendage to patent (12).

Patent (12).--Sodium amalgam (preferably containing about 0.2% sodium), from a conventional mercury- chlorine cell, is agitated with titanium tetrachloride in a reactor plant under an inert gas atmosphere. The temperature is maintained between 100 and 300°F . Sodium is in slight excess. The depleted amalgam passes out of the plant together with a powdery reaction product of sodium chloride, titanium, and titanium subchlorides.

The mixture is next passed to a mercury filter where about 99% of the spent amalgam is recovered and recycled to the cell. About 80% of the sodium chloride in the reaction product is vaporized, or drained off as liquid, in a separating furnace. The reaction product from the separating furnace, now containing about equal parts by weight of sodium chloride and titanium, is passed to a melting furnace where the remaining sodium chloride distills off and ingots or castings are formed. Alternatively the sodium chloride may be separated by leaching with water.

Patent (20).--The powdery reaction product formed in patent (12) is compressed against a conical perforate barrier converging in the direction of the compressive force. Substantially all the mercury is pressed out at a temperature below the melting point of sodium chloride. The mass is next compressed into the bore of a cylindrical perforate barrier (a continuation of the conical barrier). Here, with the temperature maintained above the melting point of sodium chloride, some of the sodium chloride is removed. The mass is finally extruded in rod form. Rods may be used as consumable electrodes in an arc melting furnace where the remaining sodium chloride distills off.

Patent (25).--As a further development of patent (12), titanium tetrachloride is introduced below the surface of a liquid pool of amalgam containing 0.794% sodium and the mixture agitated at 140° C. Amalgam with 0.541% sodium is recovered by filtration. Mercury remaining in the reaction product is distilled off in an argon atmosphere at 600° C for 16 hours. Sodium chloride is volatilized by treatment at a pressure of

0.2 microns at 800 to 900° C for two hours. About 88% of the titanium is recovered. By carrying out the reaction in the presence of excess titanium tetrachloride, the method may be used to produce lower chlorides. Amalgams with composition ranges of 0.05-2.5% and 10-50% are preferred because their boiling points are less than 180° C.

Patent (28).--A further development of patent (25) aims at minimizing the production of subchlorides.

Sodium amalgam is pumped through a reactor and titanium tetrachloride is added well below the surface (see Figure 6). The reaction product, with a mercury-titanium ratio of about 0.25, floats to the surface and may be removed mechanically, such as with a screw conveyor. The mole ratio of sodium to titanium tetrachloride should not be less than four. By maintaining the sodium content above three atomic per cent and if the reacting amalgam is agitated, an 80% yield is assured. The reaction temperature may lie between 100° C and the amalgam boiling point. Purification of the reaction product may be effected by the procedure used in patent (25).

The following advantages are claimed for the amalgam process:

- (a) Amalgam is more easily handled than a pure reducing metal.
- (b) Temperature and pressure conditions are less rigid.
- (c) Intimate contact of sodium and titanium tetrachloride by agitation is simply effected.
- (d) Contact with mercury deactivates the finely divided titanium.
- (e) Heat transfer problems are avoided.
- (f) The vigour of the reduction reaction is diluted.
- (g) Sodium as an amalgam is less costly than as the pure metal.

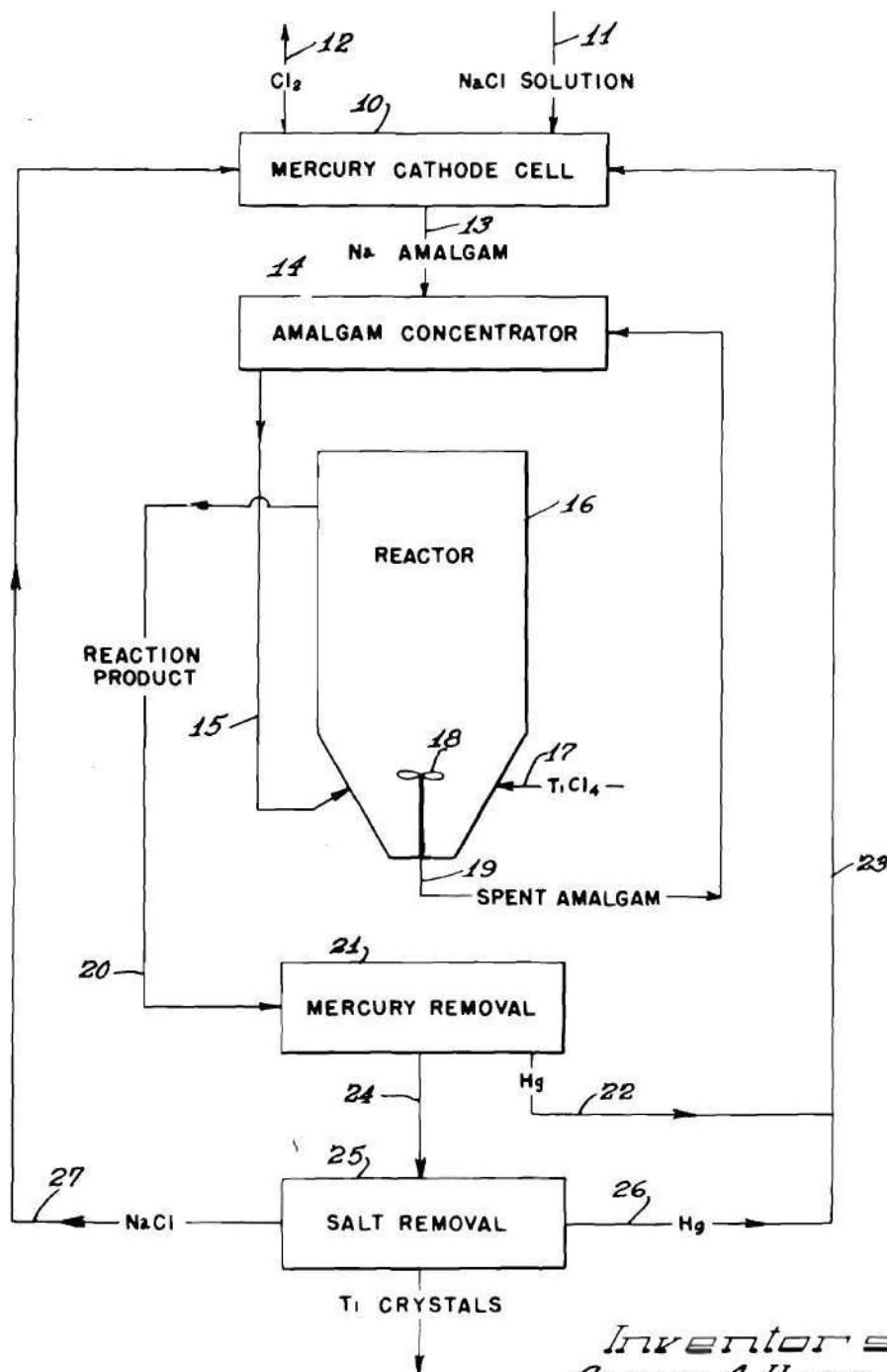
Nov. 18, 1952

C. A. HAMPEL ET AL

2,618,550

METHOD FOR THE PRODUCTION OF TITANIUM

Filed Jan. 4, 1952



Inventors
CLIFFORD A. HAMPEL
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Niel Sherman, Morani, Glass & Sniggen
Attys.

Figure 6. Diagram Illustrating Patent (28)

Some comments by Kroll (41) on patent (12) point out some flaws in the amalgam process:

Separation of the mercury from the sodium chloride by evaporation in a vacuum, as well as the ultimate separation of mercury from sodium chloride and from the sponge at temperatures in excess of 850°C in vacuo and the transfer of the pyrophoric material to the various kinds of equipment in absence of air, might bring insurmountable difficulties. It is not clear why mercury should be introduced into the reduction cycle since sodium itself reduces at low temperatures. If, under these conditions, titanium crystals can be obtained and if the reacted mixture does not cake so that it can be transferred to a reaction tank in absence of air where it could be lixiviated with liquid ammonia, such a method might be developed for continuous operation.

Electrolysis. Patents (22; 30; 31; 32; 33; 34)

Six patents, all of which have been assigned to Horizons Titanium Corporation, are concerned with the production of titanium by electrolysis. Patents (30; 31; 32) are by the same patentee and are similar. Patents (33; 34) propose ways of keeping the electrolytic bath compositions in patents (30; 31; 32) constant, so as to make the processes continuous.

Patent (22).--A fused mixture of pure titanium monoxide and one or more alkaline earth halides, with or without an admixture of alkali metal chloride, is electrolyzed under an inert atmosphere. The anode and cathode areas are physically separated.

An example is the electrolysis of calcium chloride and titanium monoxide in a graphite crucible at 780 to 925°C . The graphite crucible may act as an anode. Sponge titanium collects on a graphite or metal cathode which is suspended in the bath. The sponge, which may be removed from the cathode periodically, is washed and dried at 100°C in an inert

atmosphere, followed by melting in a conventional manner. Absence of higher oxides is essential; otherwise deposition of some titanium monoxide occurs at the cathode. If the solubility of titanium monoxide is exceeded, particles of it will be carried over to the cathode. The concentration of titanium monoxide is maintained either by using sintered titanium monoxide anodes or by adding lumps to the bath close to the anode. In a compartmental cell, in which diaphragms of zircon or graphite are used, titanium monoxide may be present in solid form in the anode compartment.

Patent (30).--Titanium produced by patent (22), being finely divided, is easily contaminated by oxygen and nitrogen.

An electrolytic bath is composed of 2 to 30% of at least one alkali metal fluotitanate and at least one alkali metal halide (other than fluoride) with titanium monoxide added to maintain saturation. The constituents must be anhydrous and of high purity. A carbonaceous anode, such as a graphite cell, and an iron (or other metal) cathode decompose the electrolyte into carbon monoxide, which is liberated at the anode, and sponge titanium, which is deposited on the cathode. The temperature may be in the range 550 to 950° C but, if the cell is not compartmentalized, the sponge is prone to contamination by carbon monoxide above 800° C. The same precautions with regard to titanium monoxide addition are observed as in patent (22). A metal recovery of about 95% is achieved.

The presence of a fluotitanate results in the production of a coarser sponge.

Patent (31).--The decomposition of the titanium fluoride content of the fluotitanate in patent (30) necessitates frequent replacement of the

bath and renders the method commercially unattractive.

Electrolysis is effected without decomposition of the fluotitanate by continual addition of titanium tetrachloride to a bath of similar composition to that in patent (30), but with no titanium monoxide content. A voltage, lying below the decomposition voltage of the fluotitanate and above that of the titanium tetra chloride, is established.

The titanium tetrachloride, diluted with argon, is introduced through a hollow graphite rod (which may also act as anode), with perforations near the lower end, close to the anode and at a suitable rate. The temperature is maintained at 600 to 650° C to allow of greater retention of titanium tetrachloride in the bath. A titanium recovery of about 90 to 95% is achieved.

Patent (32).--A solid solution of titanium carbide and titanium monoxide is electrolyzed in a bath similar to the ones used in patents (30; 31), presence of a fluotitanate having the advantages mentioned. The ratio of titanium carbide to titanium monoxide should be less than one, otherwise formation of a fine dispersion of carbon particles results in sponge contamination. A carbonaceous anode will tend to take up the oxygen from any excess titanium monoxide. The solid solution is preferably added near the cathode so that carbon monoxide liberated in the reaction is remote from the sponge deposit. In an optimum range of about 100° C between 600 and 850° C carbon monoxide is produced from the anode and from the solid solution. Above this range, free chlorine is formed, while below it, titanium tetrachloride tends to appear. A metal recovery of about 87% is obtained.

Patent (33).--Electrolysis of the fused salt baths in patents (30; 31; 32) is uneconomical, because of the high cost of the starting materials.

A bath containing 2 to 30% of a fluotitanate, as in patents (30; 31; 32), but without addition of titanium monoxide etc., is electrolyzed in similar cells to the ones described. Chlorine gas, which is evolved at the anode, is reacted with hydrogen to form hydrogen chloride which is reacted with cooled, spent electrolyte and titanium source material in aqueous or other solution at 100° C. The mixture is then evaporated and fluotitanate and alkali chloride crystals obtained separately. These, after drying, are returned to the cell. Source material should be as pure as possible to prevent build up of extraneous impurities.

Patent (34).--Chlorine from the electrolytic cell in patent (33) is reacted with a titaniferous source material, such as rutile or titanium slag concentrates, and carbon (see Figure 7). Titanium tetrachloride which is produced is reacted with spent electrolyte in solution at 100° C and the mixture is evaporated. Fluotitanate and alkali chloride crystals are dried and returned to the cell.

All the patents in this group are founded on an experimental basis. The last patent, being a development of previous ones, is the most commercially economical one. Drawbacks are high energy requirements for evaporating the renovated electrolyte solution and for heating the electrolyte to the bath temperature.

Thermal Decomposition of Titanium Halides. Patents (2; 3; 17; 26; 27)

Patents (2; 3; 17) are concerned with halide decomposition at vapour solid interfaces while patents (26; 27) include liquid salt

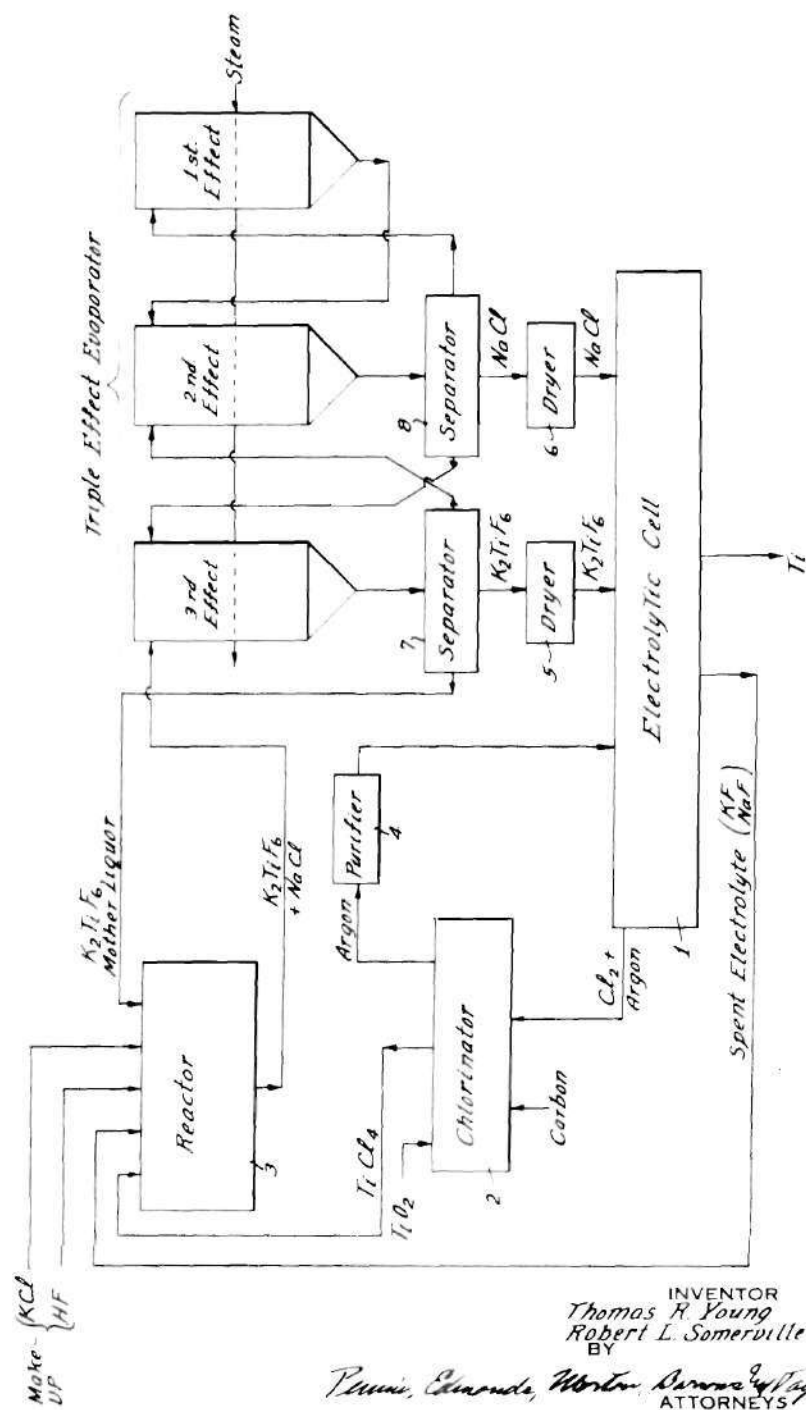
Jan. 17, 1956

T. R. YOUNG ET AL

2,731,406

PREPARATION OF ELECTROLYTE

Filed Jan. 21, 1953



INVENTOR
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Reini, Edwards, Morton, Somerville & Taylor
 ATTORNEYS

Figure 7. Diagram Illustrating Patent (34)

media as essential parts of the processes.

Patent (2).--Highly refractory metals may be obtained by heating sulphides of the metals to their decomposition temperatures in a vacuum. Volatilized sulphur is removed.

This patent does not pertain directly to the preparation of titanium and any obtained in this way would be heavily contaminated with sulphur.

Patent (3).--Metals of the first undergroup of the fourth column of the periodic system may be precipitated on an incandescent body which is situated in an atmosphere containing at least one iodide of the metals to be precipitated.

Patent (17).--As the incandescent body in patent (3) is a wire through which an electric current flows, there is some difficulty in controlling the current as titanium metal is gradually deposited on the wire.

In an improvement of the process, a shell for the deposition of titanium is heated by radiation from a heating element disposed inside the shell (see Figure 8). The shell is positioned inside a vessel which may be evacuated. Graphite, molybdenum, or titanium may be used to construct the shell.

After evacuating, and degassing by heating up to the operating temperature of $1,200^{\circ}\text{C}$, a titanium halide (bromide or iodide) is admitted continuously. Iodine is removed through a line leading to a condenser.

Patent (26).--Titanium dichloride is decomposed by an electrically heated plate of a refractory substance (such as tungsten, molybdenum, titanium,

May 1, 1951

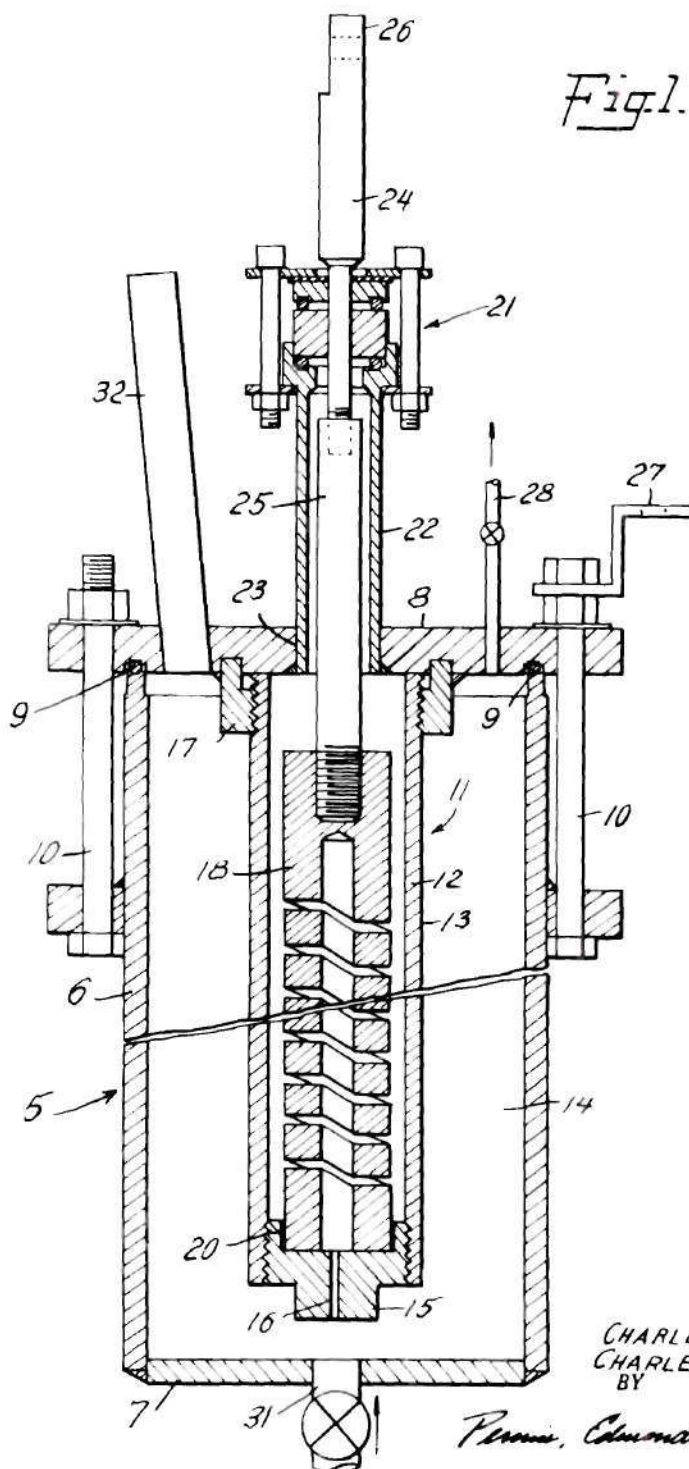
C. L. SCHEER ET AL

2,551,341

APPARATUS FOR THERMAL DECOMPOSITION OF METAL HALIDES

Filed Nov. 22, 1949

2 Sheets-Sheet 1



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Figure 8. Diagram Illustrating Patent (17)

or graphite) situated in a solution of the dichloride in a molten salt bath (melting point less than $1,000^{\circ}\text{C}$). Salts of alkaline earths, alkali, and magnesium may be used. The dichloride may be obtained by introducing titanium tetrachloride and hydrogen to the bath. Titanium dichloride and titanium trichloride are formed and the latter is further reduced either by the deposit of titanium on the plate or by electrolytic means. Best results have been obtained with a temperature differential of 100 to 300°C between the hot plate and the bath and with a titanium tetrachloride pressure of 0.01 m.m. of mercury over the bath. Titanium crystals formed on the hot plate may be leached with water on removal.

Patent (27). The disadvantage of the requirement of subsequent melting and ingotting of the titanium produced in patents (3; 17) is avoided.

A titanium halide is introduced near the base of a molten pool of calcium chloride, calcium fluoride, magnesium fluoride, or a mixture thereof. The temperature of the pool lies between the melting point of titanium and the boiling point of the pool contents, $3,500^{\circ}\text{F}$ being recommended for titanium tetraiodide decomposition and $3,900^{\circ}\text{F}$ for titanium tetrachloride or tetrabromide decomposition. Decomposition of the halide into molten particles of titanium and into halogen gas occurs and the particles settle and join a pool of molten titanium which constitutes the upper part of a moving ingot. Heat is supplied by means of an arc struck between a water cooled, tungsten tipped, carbon electrode and the titanium pool. The containing vessel is water jacketed so that its inner surface is protected from the bath and from free halogen by a crust of solidified salt.

Kroll (41) has commented on patent (17):

. . . but it would eliminate only one of the main drawbacks of the iodide method. The others are: high energy requirements, difficulties in heat dissipation, the batch operation, and the necessity of starting from a rather pure titanium which is only partly used up.

Because very pure titanium can be produced by the iodide method (patents (3; 17)), it has found commercial use in the purification of titanium produced by other methods. It cannot, however, compete in the production of a cheap constructional metal.

The energy requirements in patent (27) are excessive and it is unlikely that such corrosive fluids could be handled at the operating temperatures.

CHAPTER VI

CONCLUSIONS

The 35 patents, that have been considered, are seen to have fallen into five distinct classes. A complete economic analysis of each patent has not been attempted. This would be difficult of accomplishment. Conclusions of a general nature have been reached instead.

Many of the patented processes are either impossible of operation or are unable to produce titanium to the required specifications. Where this is the case, remarks have been made in the text.

Patents in the first class, "Direct Reduction of Titanium Halides," provide the only feasible processes for the production of a cheap constructional metal with the required purity. The only real competitors are patents in the fourth class, "Electrolysis." However, patent (34), the most promising in this category does not result in a saving in titanium containing raw material which is titanium tetrachloride. The cost of electrolytic magnesium and sodium (the only reducing metals which are cheap enough) and the cost of operating the conventional reduction process are favourable when set against the costs of the heat requirements of the continued renovation of the electrolytic bath and of the accompanying evaporation process.

In the second class, "Oxide Reduction," the patents are of no significance in the production of a constructional metal in spite of economic advantages. This is because the metal is embrittled by remaining

traces of oxygen. Titanium produced in this way may be used in the formation of titanium alloys in which the presence of oxygen might not have such a deleterious effect. Another outlet for this oxygen contaminated titanium might be as a raw material in the production of very pure titanium by a method in the fifth class, "Thermal Decomposition of Titanium Halides." Pure titanium produced in this way has limited uses, chiefly in laboratories. The extent of its use in the field of atomic energy is not known. Economically, the process is far from being a competitor in the production of structural titanium.

Processes in the third class, "Reduction by Sodium Amalgam," may also be eliminated as competitors. The disadvantages of handling large quantities of expensive mercury and separating this from the reaction product are prohibitive.

Not counting the 'Kroll Process,' which has been developed into present conventional usage, the most promising patents, in the authors opinion, in each class are as follows:

- (a) Patent (19),
- (b) Patent (35),
- (c) Patent (28),
- (d) Patent (34),
- (e) Patent (17).

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