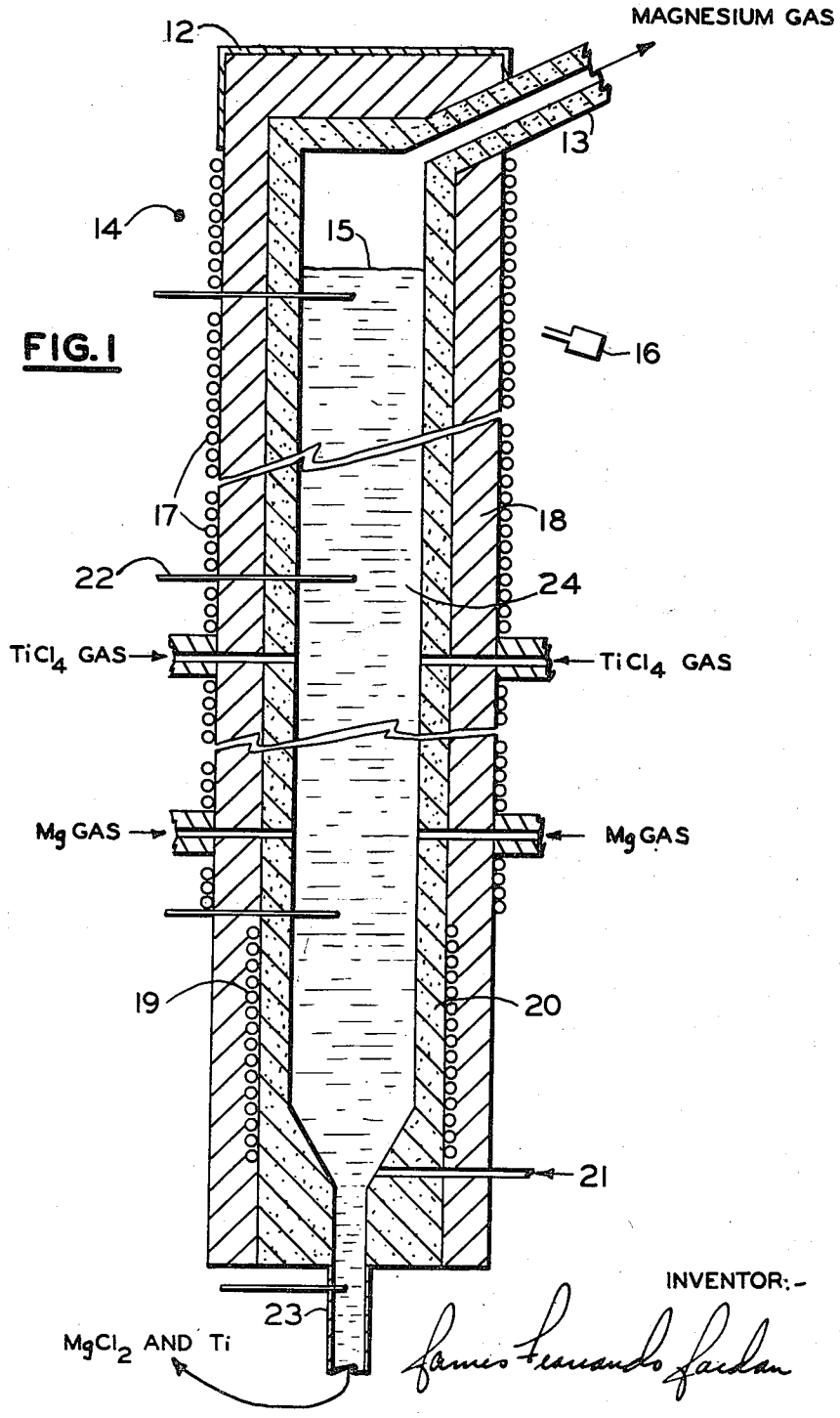
Aug. 4, 1953 J. F. JORDAN 2,647,826

TITANIUM SMELTING PROCESS

Filed Feb. 8, 1950 2 Sheets-Sheet 1

FIG. 1



INVENTOR:-

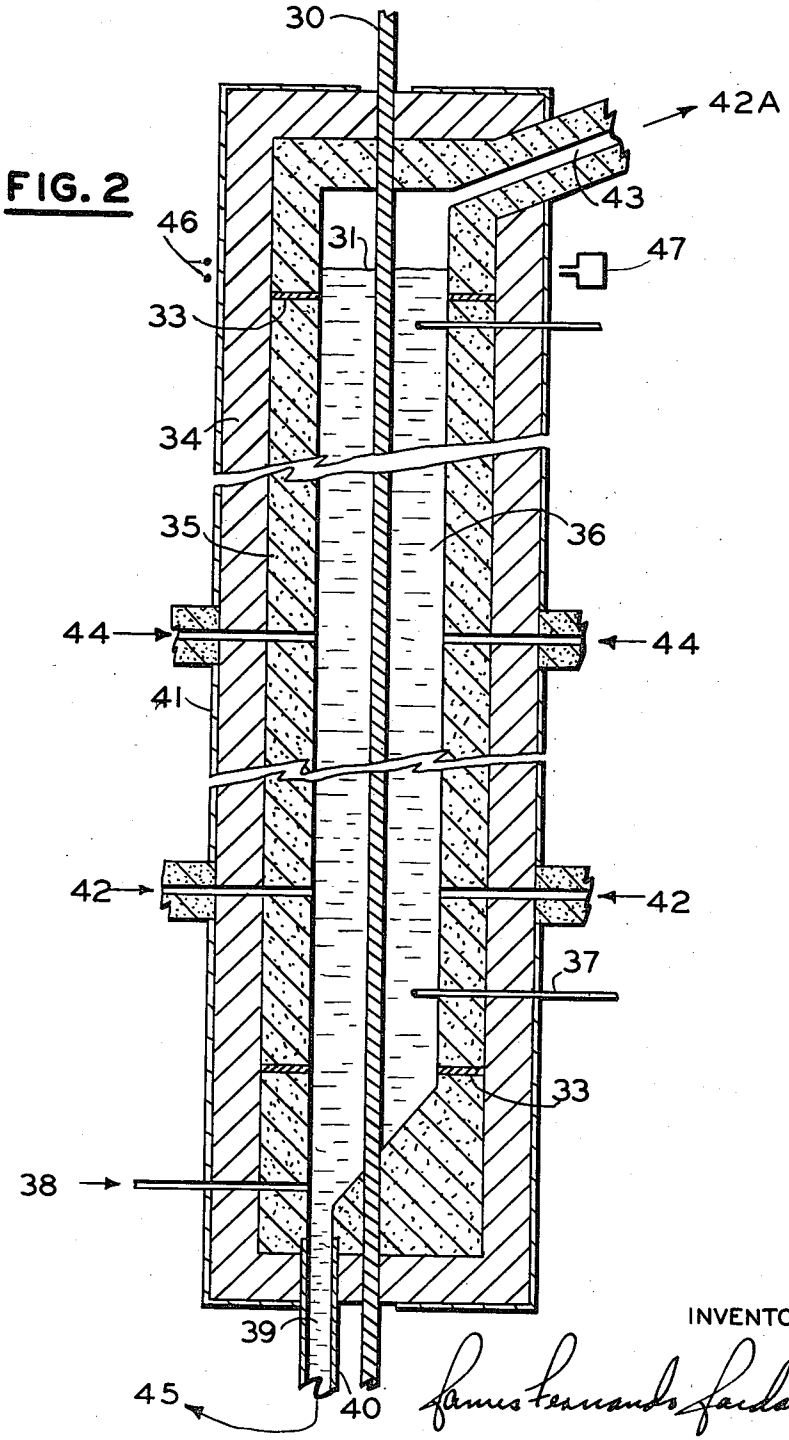
James Fernando Jordan

Aug. 4, 1953 J. F. JORDAN 2,647,826

TITANIUM SMELTING PROCESS

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FIG. 2



INVENTOR:-

James Fernando Jordan

Patented Aug. 4, 1953

2,647,826

UNITED STATES PATENT OFFICE

2,647,826

TITANIUM SMELTING PROCESS

James Fernando Jordan, Huntington Park, Calif.

Application February 8, 1950, Serial No. 143,000

1 Claim. (Cl. 75—84)

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This application is a continuation-in-part of my application, Serial No. 132,683, filed on December 13, 1949, now abandoned.

My invention relates to titanium metallurgy wherein a titanium compound is reacted with a metallic reducing agent to form titanium.

The production of ductile titanium by processes wherein a titanium compound is reacted with a metallic reducing agent is surrounded by numerous difficulties. At the root of most of these difficulties lies the fact that titanium metal containing any appreciable amount of oxygen and/or nitrogen is brittle, and that, at elevated temperatures, titanium metal will absorb these gases, either by direct contact therewith or by contact with refractories containing them.

These difficulties have forced titanium metallurgy to develop along lines wherein every effort is directed towards keeping the metal out of contact with these gases or compounds containing these gases. In general, ductile titanium metallurgy involves the production of titanium powder or sponge that is free from oxygen and nitrogen, and then, by either powder metallurgy methods or by continuous ingotting methods, consolidating the titanium into oxygen and nitrogen-free shapes. My invention concerns the step wherein an oxygen and nitrogen-free titanium powder is to be produced.

Most successful methods of producing oxygen and nitrogen-free titanium powder involve a reaction between a titanium halide, such as the tetrachloride or the iodide, and a metallic reducing agent, such as magnesium or sodium. The reactions are carried out in an inert atmosphere in a bomb, a device that does not lend itself to the large scale production requirements posed by the current demand for ductile titanium; furthermore, such reactions within a bomb result in the wastage of a considerable amount of the reducing agent, due to the lack of intimate contact between reactants. Furthermore, such reactions within a bomb tend to yield a sponge, rather than the desired powder form. My invention has for its object the production of a titanium powder that is essentially free from oxygen and nitrogen, while efficiently utilizing the reducing agent. Other objects will be apparent in the specification and claim.

In my process, I carry out the reduction reaction by dispersing the reactants in a reaction media, so that the precipitated titanium powder remains dispersed throughout said media during and after the reaction. In my process, the excess reducing agent is recovered in a form that

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may be immediately recycled back into the reaction; furthermore, my process readily lends itself to continuous operation.

In using magnesium as a reducing agent for titanium tetrachloride, I carry out my process by first partly filling a reaction vessel with a bath of molten magnesium chloride, said bath being maintained at a temperature in the range between the boiling point of magnesium and the boiling point of magnesium chloride, said bath being preferably in the form of a column of molten magnesium chloride. Into this bath of molten magnesium chloride I continuously and slowly introduce titanium tetrachloride gas and magnesium gas, being careful to introduce both gases so that they are dispersed in said molten chloride before any substantial reaction takes place between the gases. I prefer to introduce the reactant gases at, or near, the base of the reaction media, molten magnesium chloride, so that the ensuing reaction between said gases takes place as said gases rise thru the media.

In order that the reaction between said gases be driven to completion, I introduce an excess of either magnesium gas or titanium tetrachloride gas into the media, said excess being figured in accordance with the reaction where

$$TiCl_4 + 2Mg \rightarrow 2MgCl_2 + Ti \qquad (1)$$

In my preferred embodiment, I introduce gaseous magnesium in excess of Reaction 1 near the base of a reaction media consisting of a column of molten magnesium chloride, and I introduce the tetrachloride gas into said column at a point that is above the point whereat I am introducing the magnesium gas, so that the rising magnesium gas is well dispersed in said media before said tetrachloride gas is introduced into said media, so that the titanium powder precipitated by Reaction 1 is well dispersed in said media, so as to avoid the production of titanium sponge. It is to be expected that the agitation arising from the reactant gases moving up thru said media will keep said precipitated titanium powder well dispersed in said media. If the precipitated titanium powder tends to settle, the settling action may be prevented by introducing an inert gas, such as helium, into the base of said media, so as to provide the required agitation.

As the dispersed magnesium gas and tetrachloride gas rise thru the reaction media, contacting bubbles of the reactant gases will collapse as Reaction 1 yields, in my preferred embodiment, a small amount of magnesium gas (the excess) and

the precipitated titanium wetted by the molten magnesium chloride produced by Reaction 1. The wetted titanium powder moves into the body of the bath of reaction media, and the excess magnesium gas rises thru the media to pass thereout. The excess magnesium gas may be condensed after emerging from the media, or said gas may be immediately recycled back into said media near the base thereof.

Reaction 1 is exothermic at the temperature of the reaction media, and with the reactants being supplied to said media in their gaseous form, the reaction will supply sufficient heat to maintain the media at the required temperature; however, the heat characteristics of the reaction vessel will depend upon the design of the vessel, that is, will depend upon the ability of the vessel to conserve heat.

The introduction of the gaseous reactants into the media may be continued until the bath of magnesium chloride has increased in volume until the reaction vessel is substantially full, whereupon the introduction of the reactants may be stopped, and the molten magnesium chloride containing dispersed titanium may be removed from said vessel. The titanium particles may be separated from most of the magnesium chloride by either settling or centrifuging the molten chloride, and the remaining chloride may be removed from the titanium by distillation or by treatment with cold, dilute HCl, and, finally, water.

My preferred embodiment involves the use of my process in a continuous manner. Figures 1 and 2 show apparatuses in which such a continuous operation may be carried out.

In Figure 1, molten magnesium chloride column **24** is shown in a reaction vessel. Lining **20** may be carbon or graphite, said lining **20** being supported by refractory **18**. While I show lining **20** as carbon, other lining materials may be employed: titanium, for example. The level of bath **24** is shown as surface **15**, said surface **15** being shown under the indicating control of X-ray or radioactive source **14** and Geiger-Müller counter **16**; that is, as surface **15** rises or falls, the energy indicated by counter **16** rises or falls.

The temperature of media **24** within the reaction vessel formed by lining **20** is controlled by controlling the heat being introduced into, or removed from, lining **20** by induction coil **17**; that is, coil **17** is a pipe thru which cooling water passes, so that when high frequency current is passing thru coil **17**, lining **20** is being heated, and when no current is passing thru coil **17**, lining **20** is being cooled. The temperature of media **24** below the point whereat the magnesium gas is being introduced is under the controlling influence of cooling coil **19**.

In operation, the process pictured in Figure 1 proceeds as follows: with molten magnesium chloride column **24** above the boiling point of magnesium and below the boiling point of magnesium chloride, magnesium gas is slowly and continuously introduced at the indicated level and thru the indicated ports. Said magnesium gas should be introduced so that said gas immediately becomes dispersed in media **24**, an action that is facilitated by the use of a plurality of introduction ports at the indicated level. With the magnesium gas being introduced in a uniform and continuous manner, the titanium tetrachloride is slowly and continuously introduced into column **24** by means of the indicated $TiCl_4$ ports, and, in order to facilitate the dispersal of

said titanium tetrachloride in column **24**, a plurality of $TiCl_4$ ports should be used. The distance between the magnesium gas and the tetrachloride gas ports in column **24** should be in keeping with the stipulation that said magnesium gas should be well dispersed in media **24** before the tetrachloride gas in introduced in media **24**.

The two reactant gases will now react as they contact during their rise to surface **15**, resulting in the precipitation of titanium particles within media **24**, and also resulting in the production of more media **24**.

The excess magnesum gas passes out of the reaction vessel via outlet **13**.

As Reaction 1 releases magnesium chloride, surface **15** rises within the reaction vessel, said rise being indicated by counter **16**. Using the indications of counter **16** as a guide, the level of surface **15** may be maintained at a substantially uniform position by drawing off molten magnesium chloride containing titanium particles at the base of column **24** via outlet pipe **23**, said pipe **23** being connected to a suitable control valve (not shown) that is capable of handling molten magnesium chloride. In order to simplify the problems associated with the maintenance of a valve at high temperature, the molten chloride is shown being cooled by pipes **19** as said molten chloride passes from the Mg-gas ports down to pipe **23**, said pipes **19** containing circulating water. The cooling action of pipes **19** may be caused to lower the temperature of outflowing chloride to around 1500° F., even though said cooling may cause a certain amount of solidified chloride to accumulate on the wall of the vessel.

Control over the cooling action of waterpipe **19** may be attained by regulating the water pressure in pipe **19** in accordance with temperature readings obtained by immersed thermocouples **22** located at the beginning, and at the end, of the cooling zone within the influence of pipe **19**. Control over the temperature of the reaction zone within column **24** may be attained by controlling device **17** in accordance with temperature readings obtained by immersed thermocouples **22** located within said zone, said thermocouples **22** being connected to pyrometers (not shown).

In the event that the dispersed titanium settles in column **24** more rapidly than the molten chloride in which it is dispersed, then an inert gas **21**, such as helium, may be introduced into the base of column **24** with sufficient force to maintain the desired dispersion.

It is to be noted that the continuous process of Figure 1 involves the counter-current flow of the reactants and the resultants thru the reaction media; that is, the reactants, magnesium and tetrachloride gases, flow up, while the resultants, titanium and magnesium chloride, flow down. This counter-current flow has certain valuable advantages; for example, the presence of the lower chlorides of titanium in the molten chloride being discharged by pipe **23** is thereby prevented, due to the fact that the molten chloride is brought into substantial equilibrium with magnesium gas before being discharged thru pipe **23**.

Figure 2 shows another reaction vessel wherein my process may be carried out in a continuous manner. Here, molten magnesium chloride column **36** is retained within graphite lining **35**. Graphite lining **35** is supported by refractory **34**, which, in turn, is supported by shell **41**. The heating means for the vessel of Figure 2 is

graphite or carbon resistance electrode **30**, said electrode **30** being heated, as required, by the passage of electricity therethrough. Electrode **30** is shown in contact with lining **35** at both ends of the reaction vessel; and, in order to prevent lining **35** from shorting electrode **30** out, insulators **33** are located at both ends of said vessel—alternatively, said electrode **30** may be insulated from lining **35** at the points whereat said electrode **30** passes thru said lining **35**.

With the column of molten magnesium chloride **36** heated to the reaction temperature, my process may be placed in operation in the vessel of Figure 2 by continuously and slowly introducing magnesium gas **42** into media **36** in the indicated manner and position, and then introducing the tetrachloride gas **44** into media **36** at a point above where gas **42** is being introduced, said gases **42** and **44** being introduced so that they are dispersed in media **36**.

With magnesium gas **42** being added in excess of the requirements of Reaction I, said reaction will proceed as substantial and widespread contact takes place between the ascending gases; the height of the column of media **36** over the position whereat gas **44** is being introduced being such that gases **42** and **44** will have time to contact to effect the substantial completion of Reaction I before said gases reach surface **31**. The excess of magnesium gas **42A** leaves the reaction vessel via opening **43**.

As Reaction I releases magnesium chloride to column **36**, the level of surface **31** rises, an action that may be followed by an arrangement of two X-ray or radioactive sources **46** and Geiger-Müller counter **47**, arranged so that when surface **31** rises or falls, the energy reaching counter **47** rises or falls. Operated in accordance with the indications of counter **47**, the surface **31** of column **36** is maintained at the desired level by withdrawing molten magnesium chloride containing titanium out of the bottom of column **36** via pipe **40**; products titanium and magnesium chloride **45** being shown leaving column **36** as stream **39**. The withdrawal of molten chloride containing titanium thru pipe **40** may be controlled by a valve (not shown); however, the molten chloride containing titanium should be cooled to a temperature just above the melting point of magnesium chloride before being permitted to pass thru said valve.

The titanium dispersal within media **36** may be aided by the introduction of an inert gas, such as helium, at or near the base of column **36**, such as gas **38**.

The temperature situation within column **36** may be watched by pyrometers (not shown) connected to thermocouples **37**, and column **36** may be cooled by burying water pipes (not shown) in lining **35** or refractory **34**.

The magnesium gas and titanium tetrachloride gas employed in my process may be produced in generators which evaporate liquid magnesium and liquid tetrachloride to produce the desired gas form. Stills for generating such gases have been described in technical literature.

Means for metering said gases as they pass from still to reaction vessel are available; one of the simplest methods being the use of a standardized orifice, said orifice being standardized on the basis of the determined put-through at a given temperature and pressure.

While my preferred embodiment envisions the use of magnesium gas and tetrachloride gas as the form in which the reactants are introduced into the reaction media, said reactants may also be introduced into the media in the form of liquids, and, in the case of the magnesium, even as a powdered solid. One advantage of introducing the reactants as liquids is that the very large expansion that takes place as said liquids are suddenly lifted above their boiling points results in an explosive dispersal of the resulting gases; another advantage is that equipment for metering a liquid is simpler than high temperature devices for metering a gas. The introduction of magnesium powder into the media is feasible only when a magnesium powder is available that is essentially free from oxides and/or nitrides. The introduction of magnesium powder into the media may be accomplished by feeding said powder into a high velocity stream of an inert gas, such as helium, that impinges into said media.

While Figures 1 and 2 show, and I have pointed out the advantages of, a counter-current flow of the reactants and resultants thru my reaction media, my process may be carried out with the reactants and resultants flowing thru said media concurrently with respect to each other, and, when operating my process on a batch basis, the direction of flow of the reactants and resultants may be entirely at random with respect to each other. For example, a concurrent flow of the reactants and resultants may be obtained by modifying the vessels shown in Figures 1 and 2 so that the molten magnesium chloride containing dispersed titanium leaves the columnar media by overflowing at the top of said column, instead of being withdrawn at the bottom of said column.

While I have discussed magnesium as the reducing agent for the tetrachloride, certain of the alkalies may be employed as reducing agents. Sodium, for example, reacts

$$TiCl_4 + 4Na \rightarrow 4NaCl + Ti \qquad (2)$$

Sodium gas may be employed in my process by merely substituting said sodium gas for the magnesium gas reagent previously described. When using sodium gas, the reaction media consists of a bath or column of molten sodium chloride at a temperature in the range between the boiling point of sodium and the boiling point of sodium chloride. Potassium may also be used as a reducing agent in my process. In this case, the reaction media is a bath or column of molten potassium chloride at a temperature in the range between the boiling point of potassium and the boiling point of potassium chloride. With these alkali reducing agents, addition agents may be employed in the molten media in order to lower its melting point, for the boiling points of these metals are fairly close to the melting points of their chlorides. As addition agents, other chlorides may be employed, said other chlorides being introduced into the molten media with, or separate from, the reactants.

I have directed my description towards the process wherein titanium tetrachloride is to be reduced, for this titanium compound is today being widely employed as a source of titanium; however, other titanium compounds may also be employed—for example, other titanium halides, such as the fluorides, and, in such cases, the reaction media will be the fluoride of the reducing agent.

In order to meet the requirements of my process, the reaction media must be substantially inert towards the reactants. Ordinarily, the simplest media is, as has been described, one of

the resultants from the reducing reaction; however, other reaction media may be employed.

When I refer to my reaction media as being substantially inert, I mean that said media is substantially inert towards the gaseous reducing agent of my process, and I also mean that said media is substantially inert towards titanium metal in the presence of an excess of said gaseous reducing agent, so that said media does not prevent the reducing reaction from taking place. Reactions such as Reaction 1 may be presumed to be reversible, and, accordingly, it may be presumed that molten magnesium chloride, for example, will react, at least slightly, with titanium in the absence of magnesium. In certain cases, the inert media will act as a solvent for unreduced titanium compounds—for example, titanium tetrachloride will react with titanium to form lower chlorides, and said lower chlorides are soluble in molten magnesuim chloride. In certain cases, the inert media will act as a solvent for one of the reaction products—molten magnesium chloride, for example, will naturally dissolve magnesium chloride formed during the reaction.

While I prefer to maintain the precipitated titanium dispersed throughout the column of reaction media, the process may be operated so that the precipitated titanium is allowed to settle to form a concentrate of titanium particles, thus performing within the column of media the first step in the separation of titanium and media that must follow the reduction phase of the process. In this procedure, the agitation of the column of media is arranged so that the precipitated titanium can settle, the settled titanium particles being withdrawn from the base of the column of media as a concentrate of titanium particles, and the height of said column is maintained by allowing the molten media to overflow, or be removed, at the top of the media column. Thus, with Reaction 1, a concentrate of titanium particles containing a part of the molten magnesium chloride produced by the reaction is withdrawn at the base of the media column, and the balance of the molten magnesium chloride produced by the reaction is withdrawn at or near the top of the media column—the object being to produce a titanium concentrate containing the minimum amount of magnesium chloride and a magnesium chloride that is essentially free from titanium. In order to accomplish this separation within my media column, there should be zones of quiet above and below the zone of reaction wherein violet agitation is caused by moving gas. In general, this means that the media column must extend well below the lowest point within said column whereat gas or gas-forming matter is being introduced, and that said media column must extend well above that point in the column whereat moving gas is strongly agitating said column.

While the reducing gas should always be introduced into my reaction media near the base thereof, the point of introduction of the titanium compound will depend upon its nature. With a titanium compound that forms a gas within the reaction media, said compound had best be introduced into the column near the base thereof; with a titanium compound that tends to settle thru the media, said compound had best be introduced at or near the top of the column.

Having now described and shown several forms of my invention, I wish it to be understood that my invention is not to be limited to the specific form or arrangement of steps described hereinbefore, except insofar as such limitations are specified in the appended claims.

I claim as my invention:

In the process wherein titanium tetrachloride is reacted with a reducing agent selected from the group consisting of magnesium, sodium and potassium to form titanium and a chloride of said reducing agent, the improvement, which comprises: heating said reducing agent chloride to form a molten pool of said reducing agent chloride at a temperature that lies above the boiling point of said reducing agent and below the boiling point of said reducing agent chloride; introducing and dispersing said reducing agent within said molten pool at a point that lies below the point at which said titanium tetrachloride is being introduced into and dispersed within said molten pool, so as to form titanium particles dispersed within said molten pool as said reducing agent and said titanium tetrachloride contact each other within said molten pool; and withdrawing molten reducing agent chloride containing titanium particles from said molten pool at a point that lies below the point at which said reducing agent is being introduced into said molten pool.

JAMES FERNANDO JORDAN.

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