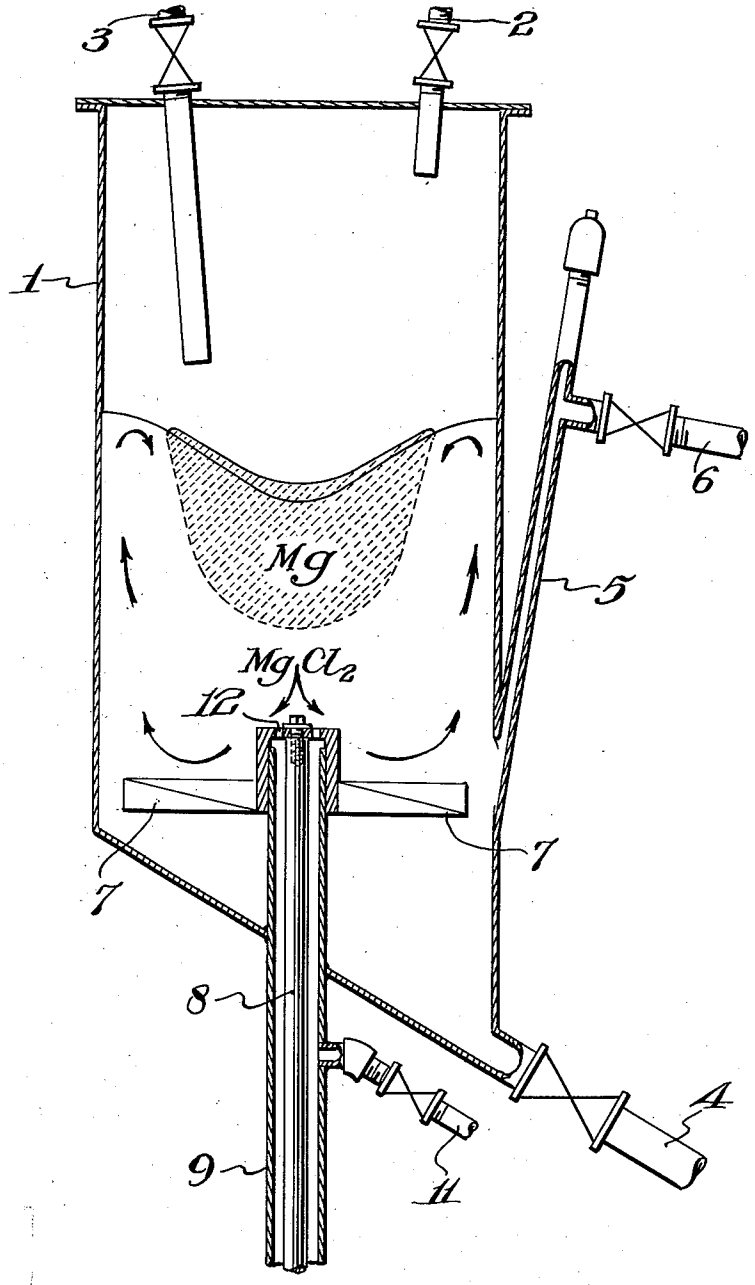
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PRODUCTION OF METALS

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PRODUCTION OF METALS

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This invention relates to the preparation of titanium and zirconium metals by reduction of their halides. More particularly it relates to novel methods for preparing such metals in relatively pure, elemental state by reduction of a halide thereof, especially a tetrachloride, with a particular type of metallic reducing agent.

Titanium and zirconium, due to their previous commercial scarcity, have been classed as "rare metals." Their unavailability has been due to the difficulties encountered in prior attempts to separate them from their ores or compounds. Due to their potential importance for use in aviation and other fields, they are now of first-rank importance.

The classical sodium reduction method for producing titanium comprises the heating of titanium tetrachloride and metallic sodium in a steel bomb. The sodium reacts with the chloride to produce sodium chloride and free elemental titanium and the possibility of contamination of the titanium with oxygen is avoided in such process. More recently other metallic reducing agents have been suggested for use, including those of calcium, magnesium, aluminum and potassium. The reducing metal must in such instances be highly reactive, must not alloy appreciably with the metal being produced, and the chloride by-product must be capable of ready separation from the metal. Magnesium is especially suited for this purpose, since it does not alloy with titanium and is commercially available in large quantities. Zirconium halides react with magnesium and the other reducing agents mentioned in somewhat analogous fashion.

Several disadvantages attend these prior methods for obtaining metallic titanium or zirconium. In preparing titanium, for example, the reduction is generally effected at temperatures ranging from 750–1100° C. with formation of the titanium in sponge form together with a metal halide by-product in liquid or molten condition. This sponge forms upon and tenaciously adheres to the internal walls of the reactor to eventually "grow" or bridge across its upper or top portion. Due to the reactivity of titanium at high temperatures with oxygen, hydrogen, nitrogen and water vapor, the sponge must be cooled to below the reaction temperature of the titanium before an attempt to remove and recover such sponge from the reaction vessel can be undertaken. A considerable amount of time is thus consumed and prolonged interruptions are encountered in these operations. Consequently, these steps of heating the charge, carrying out of the reaction,

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cooling the final product, and discharging it from the reactor, have rendered this prior non-continuous type of operation unattractive and economically disadvantageous for commercially exploiting titanium and zirconium manufacture.

It is among the objects of this invention to overcome these and other disadvantages characterizing prior titanium and zirconium metal-producing operations. A primary object is to provide a novel, commercially useful and continuous type of operation for producing these metals through reduction of their halides which will be free from the disadvantages of such prior procedures. Additional, specific objects of the invention are to provide a novel, simplified method and apparatus wherein objectionable adherence of the metal sponge reaction product to the walls of the reactor can be readily obviated and from which the sponge can be readily recovered during the process without recourse to the periodic shutdowns which prior methods and apparatus have necessarily entailed; and to provide a novel process in which a more accurate, effective control can at all times be exercised over the reduction operation itself and more particularly over the density characteristics of the sponge metal reaction product recovered therefrom. Other objects and advantages of the invention will be apparent from the ensuing description as well as from the accompanying drawings in which there is shown a vertical, sectional view of one useful form of apparatus in which the invention can be carried out.

These objects are attained in this invention which broadly comprises reducing in an inert gaseous atmosphere and at an elevated temperature within a reaction zone a halide of titanium or zirconium with a metallic reducing agent, and during said reduction suspending said reducing agent upon the surface of a metal salt bath maintained under vortical motion within said zone.

In a more specific and preferred embodiment, the invention comprises reducing titanium tetrachloride with magnesium in an atmosphere of argon and at temperatures ranging from 850–1000° C. within a reaction zone, throughout said reduction floating said magnesium on the surface of a liquid magnesium chloride bath maintained at a constant level and in vortical motion within said zone, and during said reduction withdrawing therefrom titanium metal sponge formed therein.

Referring to the drawing, there is shown a reaction vessel 1 constructed preferably of cor-

rosion-resistant steel or other metal or alloy capable of withstanding relatively high temperatures and attack from corrosive fluids, and which can be heated to any desired temperature through the medium of a surrounding electrical or other suitably-associated heating or furnacing means (not shown). Valved inlets 2 and 3 are provided in the upper, top portion of said reactor through which inlets, respectively, a metal halide reactant and a reducing metal can be separately fed at controlled rates into the reactor for reaction therein. A valve controlled outlet or drawoff 4 is provided in the base of said reactor, through which outlet metal sponge and other reaction products formed within the reactor can be conveniently discharged, either continuously or semi-continuously, from the reactor. A liquid level control element 5 provided with an overflow pipe or spout member 6, which is in open communication with the interior of the reactor, is also provided in the base of said reactor, whereby a substantially constant level of a metal salt bath can be maintained within the reactor and for a purpose to be presently described. Suitably mounted for rotation within the base of the reactor and well below the surface or level of its contained metal salt bath is a conventional blade or paddle type agitator 7. The drive shaft 8 to which its paddle members are secured is driven at any desired, controlled rate of speed by means of a conventional motor or other driving means (not shown). Arranged in concentric, spaced relationship about the shaft 8 is an annular casing 9 adapted to form a passage 10 having an inlet 11 and an outlet 12 through which passage an inert gas, such as argon, from a suitable source of supply (not shown) can be fed, as desired, into the system to maintain an inert atmosphere within the reactor and concurrently prevent leakage of atmospheric or other objectionable reactive gases into said reactor and the system.

In the production of titanium metal in an apparatus of the type just described, a titanium halide such as titanium tetrachloride can be subjected to reduction with a metal such as magnesium. In such operation a metal salt bath, preferably magnesium chloride, is initially formed in the reactor 1, to be retained therein, by means of element 5, at a controlled level, and subjected to vortical motion by means of the agitator 7. Thus, sufficient solid magnesium chloride is first placed within the reactor and heat applied thereto to induce its melting and liquefaction. Paddle agitator 7 is then set in motion and at a rate of speed which is adapted to establish a circulatory motion in the top of the liquid bath from the side walls of the reactor towards the center and thence downwardly so that a liquid vortex is formed at such center. At the same time and throughout the subsequent reducing operation, temperatures ranging from about 800–900° C. preferably prevail within the reactor which is in closed condition and under an inert atmosphere of argon introduced via conduit 9 and inlet 11. Magnesium metal in either molten, slug or other finely-divided condition is then fed via inlet 3 onto the surface of the magnesium chloride where it floats upon and collects at the center of the vortex to quickly melt under the prevailing temperatures. Surface movement of the salt bath from the reactor side walls towards the reactor center causes the floating, molten magnesium to accumulate on the top, central portion of the bath and thus remain out of contact with such reactor walls. At the same time, the axial down-draft of the bath liquid is maintained at a rate which is insufficient to submerge the pool of molten reducing metal. The reactant metal thus remains at the surface of the bath out of contact with said reactor walls but in constant contact with the titanium tetrachloride being continuously introduced into the reactor via the inlet 2 and in quantity which will provide and maintain a constant atmosphere of that halide over the surface of the molten reducing metal. The magnesium reacts with the titanium tetrachloride to liberate titanium metal and at the same time forms additional quantities of magnesium chloride which, being of greater density than the metal itself, sinks below the surface of the magnesium and joins the supporting magnesium chloride bath to be thus removed from the zone where it might interfere with the intimate contact desired to be effected between the magnesium metal and titanium tetrachloride. As the magnesium chloride bath increases, it gradually overflows and is removed from the reactor via overflow spout 6. As magnesium metal is consumed during the reaction, additional quantities of that metal can be continuously or intermittently added to the reactor via inlet 3. The titanium metal reaction product can be allowed to collect, by settling through the molten magnesium chloride bath, as finely-divided sponge in the bottom of the reactor and periodically removed therefrom for separation and recovery through discharge outlet 4. Preferably, however, it is continuously removed from the reactor through said outlet together with a portion of the liquid magnesium chloride. It can then be subjected to conventional water washing or other form of leaching treatment, or may be vacuum-distilled to remove magnesium chloride and other undesired impurities to obtain the final, desired pure metal. Thereafter, the metal can be formed into ingots or briquettes and subsequently fabricated into the desired titanium metal or alloy.

To a clearer understanding of the invention, the following specific examples are given. These are merely illustrative and are not to be construed as in limitation of the invention:

Example I

Titanium metal was produced through reduction of $TiCl_4$ with magnesium. An apparatus of the type shown in the accompanying drawing was employed in such reduction. This apparatus consisted of a cylindrical, corrosion-resistant steel reaction vessel 24'' high, having an internal diameter of 10'' and provided with a paddle agitator in its base, the blades of which had an overall length of 8'' and were 1⅜'' in width. This agitator was connected to a motor driven at 130 R. P. M. During the operation an argon atmosphere prevailed within the reactor, such gas being added thereto at a rate of one cubic foot/hr. During said operation also, the reactor was maintained at 850° C. by means of an electric heating element in which it was enclosed.

At the commencement of the operation, solid magnesium chloride was charged into the reactor and melted therein to liquid condition. Rotation of the agitator was then effected with the speed of its paddles being so regulated as to create a vortex in the center of the molten magnesium chloride. At the sides of the vessel, the magnesium chloride reached to a height of 11'' from

its base, whereas at the center it reached a height of 7". In other words, the vortex was 4" deep. Upon achieving such liquid vortex and motion, slugs of magnesium were introduced into the reactor through the inlet provided therefor and at the rate of one slug per minute (equivalent to 5 pounds of magnesium metal per hour). This magnesium collected at the center of the vortex to be quickly melted under the high temperature conditions obtaining within the reactor. The molten metal floated on the magnesium chloride, at the vortex, and much as an iceberg floats in water; i. e., since the specific gravity of magnesium is about 75% that of magnesium chloride, about 75% of the metal was submerged in the salt bath support. Simultaneously, liquid titanium tetrachloride, at the rate of 19.5 pounds per hour, was added continuously to the reactor, to become immediately vaporized upon encountering the high (850° C.) temperature within the reactor. Upon contact of this $TiCl_4$ vapor with the magnesium metal in the argon atmosphere, titanium metal was formed which settled to the base of the reactor and was continuously withdrawn therefrom through its outlet together with small amounts of $MgCl_2$ liquid. Meanwhile, additional magnesium chloride was being formed during the reaction and any excess or overflow thereof was removed by means of the overflow outlet also provided in the base of the reactor.

The titanium sponge metal thus produced, on analysis, had the following approximate composition:

Constituent	Percent by Weight	Pounds/ Hour
Titanium	53.6	4.5
Magnesium	5.4	0.45
Magnesium chloride	24.4	2.05
Titanium Subchlorides, etc.	16.6	1.40
Total	100.0	8.40

The recovered sponge was treated under vacuum distillation to remove the $MgCl_2$ and other impurities present, to result in the recovery of substantially pure titanium metal from the operation.

Example II

Example I was duplicated, except that stoichiometric proportions of magnesium and sublimed zirconium chloride were employed in the reaction and a temperature of 825° C. existed in the reactor. From this operation a pure zirconium metal product was recovered.

While described above in its application to certain specific and preferred embodiments, the invention is not restricted thereto. Generally, use is contemplated herein of any reducing metal which is more electropositive than the titanium or zirconium being produced. Metals especially useful for this purpose include those which, in aqueous solutions, would have electrode potential values of 1.70 or greater as shown by the electromotive force series. Of these, the alkali and alkaline earth metals are especially useful because their electrode potentials are all greater than 2.0, a fact which insures rapid reaction at the 750° C. or higher temperature usually employed herein. Among specific examples of such useful and contemplated reducing metals are magnesium, calcium, barium, strontium, aluminum, sodium, potassium or lithium. These are molten at 750° C. or higher and have relatively low specific gravities enabling them to be floated on the most suitable metal halide salt baths. Of those mentioned, calcium and magnesium are preferred, magnesium being most preferred for use in view of its high potential and production in the reaction of a residue easily separated from the metal being produced.

A variety of metal halide salts can be employed as the molten metal bath, provided they are substantially inert with respect to the reactants employed. However, certain restrictions exist as to the combinations of employable supporting bath and reducing metal. The relative densities of the reducing metal and the supporting metal salts and the pressures maintained within the reaction vessel are most critical. The metal must be less dense than the support; and both must be liquid within the same temperature and pressure range. Preferably, the bath salt used comprises the same salt as that which is or will be produced in the reduction reaction. For example, when reducing $TiCl_4$ with magnesium, the magnesium is preferably floated on a melt of magnesium chloride; and when calcium or other alkaline earth metals are resorted to as reducing agents, a melt of the corresponding alkaline earth metal halide, especially a chloride, is preferred for employment. Similarly, sodium may be supported on sodium chloride, when the sodium reduction method is resorted to; potassium on potassium chloride, and calcium on calcium chloride, etc. Alternatively, magnesium may be floated on its bromide salt and sodium or potassium on their respective bromide or iodide salts, etc. Neither magnesium nor sodium, however, may be used with their fluorides at atmospheric pressure because the fluorides are solid at a temperature where the metals volatilize. However, such systems can be resorted to with addition of a lower melting halide salt, such as sodium or potassium chlorides. Oxygen-containing compounds are not desirable for use in the invention because of their reactivity with titanium or zirconium and the undesired contamination which would result of the metal being produced. Except for these restrictions of density and melting temperatures, any combination of reducing agent and molten liquid metal halide support can be generally employed in the invention.

The metals which this invention is particularly useful for producing comprise titanium and zirconium. Any of their halides can be reduced in the process and those the halogen component of which has an atomic number greater than 9, i. e., chlorine, bromine, or iodine, are generally utilizable. The chlorides, such as $TiCl_4$ and $ZrCl_4$, are preferred for use since they are the most economical, practical and readily obtainable. While these chlorides are preferred, the bromides, iodides or fluorides of these metals can also be used, as already indicated. The fluorides are less desirable for employment, especially since the alkaline earth fluorides which result in the process are insoluble in water and difficult to eliminate in the subsequent purification operation. Iodides and bromides are also solid at room temperature and, though employable, are economically disadvantageous due to their relatively high cost.

The only major difference between the titanium and zirconium-producing processes is that when using the tetrachlorides at atmospheric pressures zirconium tetrachloride is a solid which sublimes at about 300° C., while titanium tetrachloride is a liquid between −30° C. and 136.4° C. Thus, the chosen method of addition of zir-

conium tetrachloride may be different. Aside from this, the involved halides may be added in any desired form, either as solids, liquids, or vapors. If added as liquids, or as solids, they become volatilized upon introduction into the heated reaction vessel.

While reactor temperatures in the range of from 800–900° C. and substantially atmospheric pressures are employed during the reaction, such temperatures and pressures are merely preferred. If desired, temperatures ranging from 750–1100° C., as well as pressures above atmospheric and to, say, from 1–3 atmospheres or higher, can be resorted to. Again, while argon has been indicated as a preferred, useful type of protective or inert gas for employment in the invention, other inert gaseous elements of group 0 of the periodic table, including helium or neon, or mixtures thereof, can be employed. Additionally, any other protective and inert gas can be used, provided such gas is free from undesirable reactants, especially oxygen and nitrogen, the presence of which is to be avoided in the system.

As an alternative to the continuous or intermittent withdrawal of the sponge metal reaction product through reactor outlet 4, withdrawal of such sponge can, if desired, be effected in the form of a spongy ingot by taking advantage of the characteristic of the titanium or zirconium reaction product to adhere to any solid surface including itself. Thus, this ingot can be started by having present at the beginning of the reaction a suitable supporting surface or "bait" material upon which the sponge product will "grow" and be subsequently withdrawn through the top of the reactor. For example, a suitable starting material, such as a rod or other form of titanium, can be suitably disposed above and inserted through the top of the reactor to descend therefrom into the vortex formed at the top of the metal halide bath and contact the pool of molten reducing metal retained in such vortex. As the reaction proceeds, this rod together with its deposit of sponge metal from the reaction can be slowly withdrawn upwardly from the reactor to proceed through a suitable cooling space and gas-sealed removal lock for withdrawal to a suitable purification stage of the process. The ingot will be somewhat porous and will contain minor amounts of magnesium chloride and magnesium metal, but the latter will continue to react with the titanium or zirconium halide to which it is exposed within the reactor and until it has passed through the gas locks or other means adapted to prevent admission of air into the reactor. The manner of withdrawal of the metal and the physical condition thereof at the time of withdrawal may be selected at will and may be determined by the use for which the metal product is designed.

A most important feature of the invention is, as already noted, the special motion which is imparted to the supporting liquid salt bath. It is due principally to this feature of the invention that the present process is rendered continuous and resort to such liquid motion will be found to obviate many of the difficulties attendant prior titanium and zirconium metal producing operations. Obviously this liquid motion and maintenance of a vortex may be achieved in a variety of ways, the simplest being by mechanical agitation and through resort to the paddle means within a reactor, such as has been described in the drawing. Various other devices and modifications of such vortex-inducing means can be resorted to. For instance, the reaction vessel equipped with a conventional paddle and drive shaft may be placed on a suitable turn-table or other media adapted to rotate said paddle; or the liquid support bath may be actually pumped out at the bottom of the reactor and returned thereto in continuous circulation at the top thereof for flow downwardly along its side walls. This will give the same effect of motion from the side walls to the center of the vessel and downward. Alternatively, such movement may be accomplished with the aid of a submerged, inverted, conical structure so arranged or positioned that there is a limited opening at the periphery of the vessel. These and other obvious modifications to the invention will be apparent to those skilled in the art.

The great advantage of this invention and its immediate value in the field of titanium and zirconium metal production will be apparent from the fact that for the first time it is possible to obtain such metals in a pure state by a continuous operation in which the raw materials may be continuously added to a reaction vessel and the sponge metal product continuously withdrawn therefrom for recovery and purification.

I claim as my invention:

1. A method for producing a metal selected from the group consisting of titanium and zirconium which comprises reducing in an inert atmosphere and at an elevated temperature within a wall-enclosed reaction zone a halide of said metal with a metallic reducing agent having an electrode potential value of at least 1.70, throughout said reaction floating said reducing agent out of contact with the walls of said reaction zone and on the surface and in the vortex of an inert molten metal salt bath maintained in vortical motion within said zone by mechanical impelling means disposed wholly below the surface of said vortex, and withdrawing therefrom the resulting metal reaction product.

2. A method for producing a metal selected from the group consisting of titanium and zirconium which comprises reducing in an inert atmosphere and at temperatures ranging from 750–1100° C. in a wall-enclosed reaction zone, a volatile halide of said metal the halogen component of which has an atomic number greater than 9 with a metallic reducing agent having an electrode potential value of at least 1.70, which agent, during the reaction and at said temperature, forms a liquid halide by-product, throughout said reduction floating said reducing agent out of contact with the walls of said reaction zone on the surface and in the vortex of an inert metal salt bath which is maintained in vortical motion within said zone by mechanical impelling means disposed wholly below the surface of said vortex, and withdrawing therefrom the resulting metal reaction product.

3. A process for the preparation of titanium metal which comprises floating molten magnesium on the surface of a mass of molten magnesium chloride maintained within and partially filling a wall-enclosed reaction zone, maintaining said zone under an atmosphere of argon and at temperatures ranging from 800–900° C., forming a vortex within said mass and at the surface thereof by imparting motion thereto below its surface and from its periphery towards its center and thence downwardly but at a rate which is insufficient to completely submerge said molten magnesium in said chloride but maintains the magnesium within a vortex and out of contact

with the walls of said reaction zone, effecting said vortical motion by mechanical impelling means disposed wholly below the surface of said vortex, maintaining a charge of titanium tetrachloride vapors above the surface of and for reaction with said molten magnesium, and during the reaction withdrawing from said reaction zone titanium metal formed in the reaction.

4. A process for the preparation of zirconium metal which comprises floating molten magnesium on the surface of a mass of molten magnesium chloride maintained within and partially filling a reaction zone, maintaining said zone under an atmosphere of argon and at temperatures ranging from 800–900° C., forming a vortex within said mass and at the surface thereof by imparting motion thereto from its periphery towards its center and thence downwardly but at a rate which is insufficient to completely submerge said molten magnesium in said chloride but maintains the magnesium out of contact with the walls of said reaction zone, effecting said vortical motion by mechanical impelling means disposed wholly below the surface of said vortex, maintaining a charge of zirconium chloride vapors above the surface of and for reaction with said molten magnesium, and during the reaction withdrawing from said reaction zone zirconium metal formed in the reaction.

5. A process for the preparation of titanium metal which comprises floating molten sodium on the surface of a mass of molten sodium chloride maintained within and partially filling a reaction zone, maintaining said zone under an atmosphere of argon and at temperatures ranging from 800–900° C., forming a vortex within said mass and at the surface thereof by imparting motion thereto from its periphery towards its center and thence downwardly but at a rate which is insufficient to completely submerge said molten sodium in said chloride but maintains the sodium out of contact with the walls of said reaction zone, effecting said vortical motion by mechanical impelling means disposed wholly below the surface of said vortex, maintaining a charge of titanium tetrachloride vapors above the surface of and for reaction with said molten sodium, and during the reaction withdrawing from said reaction zone titanium metal formed in the reaction.

6. A process for the preparation of titanium metal which comprises floating molten calcium on the surface of a mass of molten calcium chloride maintained within and partially filling a reaction zone, maintaining said zone under an atmosphere of argon and at temperatures ranging from 800–900° C., forming a vortex within said mass and at the surface thereof by imparting motion thereto from its periphery towards its center and thence downwardly but at a rate which is insufficient to completely submerge said molten calcium in said chloride but maintains the calcium out of contact with the walls of said reaction zone, effecting said vortical motion by mechanical impelling means disposed wholly below the surface of said vortex, maintaining a charge of titanium tetrachloride vapors above the surface of and for reaction with said molten calcium, and during the reaction withdrawing from said reaction zone titanium metal formed in the reaction.

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