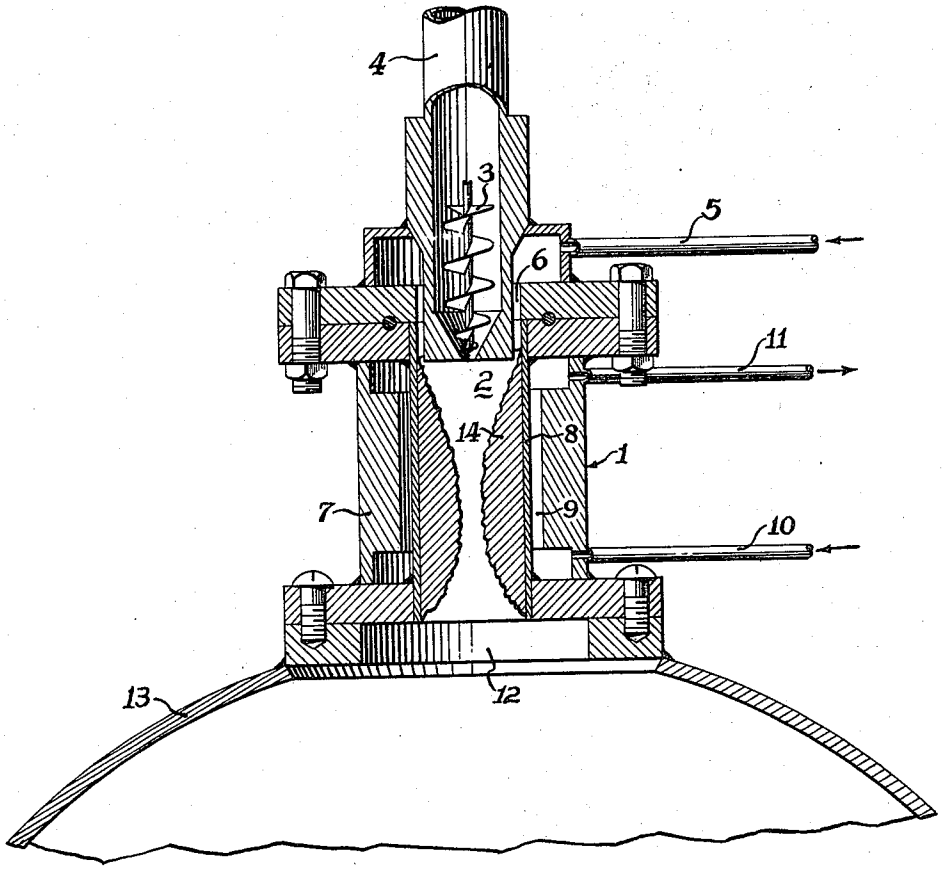
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REDUCTION OF METAL HALIDES

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REDUCTION OF METAL HALIDES

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This invention relates to metal halide reduction, and more particularly to the production of fourth group and other metals by reduction of a halide thereof. More especially, it relates to the preparation of titanium metal in molten state and lower halides of said metal by the direct reduction of titanium tetrachloride with a reducing metal such as sodium in a continuous pressurized flow reactor.

This application is a continuation-in-part of my copending application Serial No. 469,119, filed November 16, 1954, now abandoned.

Titanium metal is commercially produced and marketed in the form of particles of porous sponge. This material, as produced in the reduction reactor, is in massive state and contaminated with reaction by-product. A significant portion of the expense and effort involved in the production process deals with the finishing operations to effect removal of by-product (by vacuum distillation or leaching) and break-up of the massive sponge into useful sized particles. The success of the process depends to a large extent on the ability to exclude impurities such as oxygen and nitrogen from the titanium during its processing in the various stages or steps of the process. The size reduction treatment of the titanium metal presents a major problem because of the ductility of titanium. The temperature-time cycles of the process are such that only high alloy steels appear useful for fabricating the reactors used. Also, the extreme service conditions of the equipment result in a high consumption of alloy steel in warped and corroded equipment per pound of titanium produced, and constitutes an important factor in the process cost of titanium. Finally, the titanium product obtained still leaves much to be desired because of its sponge-like state and inherently high surface area which renders such product highly sensitive towards objectionable surface contamination by atmospheric constituents.

Prior attempts to produce melted titanium particles or nodules have been undertaken, of which the batch type reduction of titanium by sodium metal, described by M. A. Hunter (J.A.C.S., 32, 334, 1910) need only be mentioned. In that process, titanium tetrachloride and sodium were reacted in a high pressure bomb heated to red heat. Even with a very high pressure bomb construction, the reaction fails to be completely contained within the reactor and is considered to be almost instantaneous, taking place with the force of an explosion. That such a process has not been commercially utilized for titanium metal production is evident. The design of pressure reactors necessary to operate at red heat in the pressure range which results from this reaction is possible even today only in small size reactors. Furthermore, the reaction as effected in the hot bomb occurs at such high pressures and temperatures that it is too hazardous to undertake beyond a small scale or on an experimental basis.

Again, in the production of refractory or high melting

metals from groups II, III, IV, V and VI of the periodic table by reduction of their halides, the most common procedures deposit them in solid form, as decomposition products on a hot wire or other surface, as cathodic deposits, or as sponge or powders. Their recovery in pure form necessitates the costly mechanical removal of surface deposited products. The sponge product is notably difficult to remove from the reactors as is conversion thereof to useful form by vacuum distillation, leaching and melting. The fine powders produced are frequently pyrophoric and hence difficult to handle and recover free of undesired contaminants.

The fabrication of the elements, especially the true metals, into useful shapes requires a certain degree of ductility and formability. This property has in turn been found directly proportional to the purity. For this reason, it is evident that the best preparative processes comprise those which convert the elemental product quickly to a dense or massive form of low surface area, such as an ingot, with a minimum of handling and exposure to contaminating environment, especially air. With this in mind, several schemes have been devised to produce these refractory materials directly in the molten state so that ingots of the product can be recovered. Such processes are fraught with considerable difficulties, as the work on producing titanium metal illustrates.

It is among the objects of this invention to overcome these and other disadvantages of prior titanium and other metal producing operations and to provide novel methods and means for attaining these objects. One broad objective of this invention is to provide a continuous high production rate method for reducing the halides of certain refractory metal elements. Another general object is to provide suitable controls over the reduction reaction to obtain varying degrees of reduction whereby, as desired, several types or forms of products can be obtained. A further object is to avoid recourse to the large, costly high pressure vessels required by prior art methods and as a consequence, the disadvantages which a batch operation would entail. A still further object is to produce these refractory elements in the molten state whereby they can be easily removed from the reaction chamber as desired and under conditions where substantially no contamination due to process steps will occur.

It is among the particular objects to produce various metals and subhalides thereof, including especially molten titanium particles, and by a continuous, commercially adaptable type of process; to provide an improved, novel process in which the reduction reaction can be carried out at a minimum pressure and in an externally cooled reactor wherein reactants are mixed and reacted within a relatively small reaction zone so that one obtains large capacity by increased density of the reacting system; to carry out the reaction in the presence of liquid phases and within a reaction zone having solid metallic titanium walls, and from which zone reaction products discharge directly into an inert fluid maintained under a lesser or atmospheric pressure in a conventional type vessel. Further objects and advantages of the invetnion will be apparent from the ensuing description as well as from the accompanying illustrative drawing in which is shown a vertical, cross-sectional view of one form of apparatus in which the invention can be carried out.

These and other objects are attained in this invention which comprises separately charging under pressure and in the fluid state into an externally cooled reaction zone a reducing metal reactant and a halide of a high melting metallic element from groups II, III, IV, V and VI of the periodic table, mixing and reacting said halide and reducing metal reactants in said zone, during the reduction reaction removing sufficient heat from the reactor walls through said external cooling to form a coating

of at least one solidified reaction product on and over the inner walls thereof to decrease the cross-sectional area of said zone, developing a reaction zone back pressure stabilized at the pressure at least equal to the vapor pressure of a halide of said reducing metal at the melting point of the product metal, regulating the reactant feed rates to maintain essentially stoichiometric requirements of reactants, discharging molten reduction products of the halide metal reactant formed in said zone into an inert fluid within an associated collecting zone which is maintained under a lesser pressure, and recovering in separated state the resulting reduction product and associated salt byproduct discharged into said collecting zone.

In a more specific embodiment, the invention comprises continuously producing molten titanium metal by separately charging under pressure titanium tetrachloride and sodium while both are maintained in the liquid state into an externally cooled reaction zone, mixing and reacting said tetrachloride and sodium reactants within said zone and forming a deposit of solid titanium metal upon the internal walls thereof, continuing said deposition until the cross-sectional area of said zone is decreased and restricted to the point of developing a back pressure therein stabilized at the pressure at least equal to the vapor pressure of sodium chloride at the melting point of the titanium metal, controlling the reactant feed rates so as to maintain essentially stoichiometric proportions of reactants in the system, expelling molten titanium metal and fluid sodium chloride by-product formed in the reaction zone into an inert fluid within a collecting zone which is maintained under lesser or atmospheric pressure, and thereafter separating and recovering said titanium product from said by-product.

Referring to the drawing, involving one adaptation of the invention, a suitable liquefiable reducing metal, such as sodium, is pumped from a source of supply (not shown) under pressure to a suitable metal type reactor 1 which preferably is of relatively small dimension and is capable of withstanding relatively high pressures, temperatures and corrosive conditions. The reducing metal discharges into a cylindrical reaction zone 2 from a suitable nozzle or fluid reactant mixing arrangement 3 forming the outlet of the sodium supply conduit 4. Concurrently, the titanium halide reactant, preferably titanium tetrachloride, is charged, in liquid state and metered, at a regulated rate under pressure into said zone from a supplying conduit 5, to discharge therein from an inlet 6 in a direction tangential to the inner surface of the reactor so that intimate mixing of reactants will take place upon their introduction into the reaction zone 2. This zone can comprise an outer steel shell 7, an inner reinforced wall 8 of copper or other suitable metal having high heat conductivity, and a channel means 9 interposed between said shell and wall through which means a suitable heat exchange cooling fluid or refrigerant of conventional type can be continuously passed from an inlet 10 and to outlet 11 to maintain the wall 8 in desired, relatively cool condition throughout the reduction. Alternatively, suitable cooling coils (not shown) can be disposed about said wall to induce such cooling, and, if desired, can be used in conjunction with the cooling medium supplied to said channel. An outlet 12 is provided for the reaction zone, which outlet is in open communication with and discharges into a conventional type metal collection chamber 13 adapted to be maintained under substantially atmospheric pressure and an inert atmosphere of argon, helium or other suitable rare gas and wherein the titanium metal product and reaction by-product may be cooled and collected.

In operating an apparatus of the type just described, employing titanium tetrachloride and sodium metal in their liquid form as reactants, these are introduced by pumping into the reactor 1 and reaction zone 2 via conduits 5 and 4, respectively, where they initially react to form sponge titanium metal and by-product vapor, with the reaction chamber pressure substantially one atmosphere. The sponge, titanium metal builds up initially therein as a progressively increasing mass 14 on the interior of the reaction zone walls 8 being simultaneously cooled by passage of water or other suitable coolant from inlet 10 through channel 9 and outlet 11. During this initial building-up period, the reactor chamber pressure remains essentially at one atmosphere, but as the build-up of titanium sponge on the wall 8 increases, restriction of the passage of the product liquids and gases through the reaction zone 2 takes place and the decreased area for exhaust of the products and by-products develops a back pressure supported by the pumps which produces the feed pressure for the liquid reactants. When the back pressure within the reactor becomes sufficient to retain a sufficient percentage of the sodium chloride in the liquid state (to provide sensible heat to elevate the temperature to about 1680° C.), the titanium metal built up on the interior surfaces of the reactor walls 8 begins to melt and is blown out of the reaction zone and into the collector 13. The interior configuration of the reaction zone becomes stabilized because if the amount of titanium metal removed per unit time becomes excessive, then the reaction zone cavity increases in size and the pressure within the system drops. Therefore, the temperature will drop because of the vaporization of sodium chloride, and this, in turn, causes titanium metal to again solidify and build up on the wall 8. By this means, the reactor will become automatically stabilized at a minimum pressure and at a temperature closely adjacent to the melting point of the titanium metal. A slight excess usually not more than 10 wt. % of sodium metal reductant is preferably utilized to insure that the titanium metal product is free of lower chlorides.

For a clearer understanding of the invention, the following specific examples are given. These are not to be construed as in limitation of the underlying principles and scope of the invention.

EXAMPLE I

A reactor of the type shown in the drawing, having a cylindrical 10 inch long, 2 inch diameter reaction zone with a ½" thick copper water-cooled wall, was operated for 27 minutes to demonstrate steady state operation. Liquid titanium tetrachloride and liquid sodium were pumped to the reactor at about 1.5 gallons per minute each. They spontaneously reacted and the pressure increased rapidly to 150 lbs. per sq. in. gauge after only a few seconds of operation. After 27 minutes, the reactor depleted the feed tanks and the reactor was shut down. 152 lbs. of fused titanium metal particles of up to about 20 mesh were obtained after cooling the apparatus and leaching the products with dilute nitric acid. The titanium metal particles were examined and found to be roughly droplet in shape and to have a density equal to 4.5 grams per milliliter or equivalent to solid titanium metal. A sample of this material, melted in an arc furnace, tested to a Brinell hardness number of 120 to establish the eminent suitability of the product for usual titanium metal applications.

In the foregoing example, the reaction was run at a rate of about 300 lbs. of titanium per hour with a cross-sectional area in the reactor of about .02 sq. ft. which represents a rate of about 15,000 lbs. of Ti per hour per sq. ft. of cross-sectional area of reactor. Additional experiments demonstrate that rates equivalent to about 250,000 lbs. per hour per sq. ft. are attainable. These rates are many orders of magnitude larger than that obtained in the present commercial methods of producing titanium metal.

EXAMPLE II

Partial reduction of titanium tetrachloride

An apparatus having the general design of Figure 1 was used. The reaction chamber was enclosed in a hollow copper cylinder 30" long having a 2" I.D. with walls

1" thick (8 in Fig. 1). Cooling was obtained by circulating molten sodium through the surrounding jacket. Provision was made for pumping liquid sodium as a reducing agent into the reaction zone at a constant rate of close to 5.3# per minute. Another pumping installation feed $TiCl_4$ at close to 26.5#/min. The reaction was spontaneous. The pressure rose to 300 p.s.i. in 20 seconds and a dynamic equilibrium was established with pressure ranging from 200 to 500 p.s.i.g. The temperature measured first at the exit of the reaction zone by means of optical pyrometry rose quickly to around 1400° C. indicating that some of the sodium chloride was probably boiling. After 16 minutes the reagent supply became exhausted and the run was terminated, the apparatus cooled over a period of several hours and examined. The receiver contained a black solid which was analyzed and had the composition $TiCl_{2.3}$1.65NaCl. It melted around 500° C. to a homogeneous liquid with a few particles of solid titanium in the bottom. The reaction chamber was cut in half along its axis and was found to be lined with titanium metal, partly sponge-like with the internal opening still present and lined with solid titanium which clearly had been at melting temperatures during the run. The main product, comprising a solution of lower titanium chlorides was useful in production of titanium metal by electrolytic methods or it could be fed molten, along with additional sodium, to be reduced to molten titanium by the method of this invention.

EXAMPLE III

Reduction of silicon tetrachloride

An apparatus similar to that of Fig. 1 was fitted with a pre-cast hollow cylinder of silicon 10" long to serve as the initial "Skull" 14. This cylinder extended to within 2" of the inlet port 6 and the central opening or bore was about ¾" in diameter. The collecting chamber was provided with a silica pot about 12" in diameter and 2' high and located just under the reactor outlet and in contact with the cooled bottom of vessel 13 (Fig. 1). Liquid sodium cooling was employed in the reactor jacket. The cooling jacket temperature was initially set at 300° C. Positive displacement pumps for sodium and silicon tetrachloride were set to deliver 10#/min. of Na and 16.0#/min. of $SiCl_4$, this being a small stoichiometric excess of sodium. With the reaction chamber at 300° C. and well purged with argon, both pumps were started. The reagents reacted at once and a rapid temperature rise occurred. The flow and cooling of the coolant sodium were increased and controlled to keep the sodium leaving the jacket between 125° and 300° C. The pressures developed were between 200 and 500 p.s.i.g. After a run of 35 minutes, the apparatus was cooled under argon purge and opened. The silica pot had collected about 65 pounds of molten silicon which had settled to the bottom and solidified into an ingot. Most of the sodium chloride was in the pot above the Si while some had spattered or condensed outside the pot in the collecting chamber. Examination of the reaction chamber showed the silicon cylinder still in place covering the copper walls. The center bore however was enlarged at the top and tapered toward the outlet. Its surface had an irregular fused appearance.

Because the preferred reaction system is contained within a solidified reaction product skull, disadvantageous contact is eliminated of all materials of construction such as carbon, graphite, carbon black, refractories, steel, etc., at high temperature with corrosive reactants and contamination of the product arising therefrom. For example, when producing titanium metal the titanium reaction skull is contained within an externally cooled metal shell which is held below any possible reaction temperature. These combine to produce a reactor construction which guarantee product purity equaling the purity of the reactants, and the titanium product, due to its dense structure, can be readily treated conveniently (by such means as leaching, vaporization, or vacuum distillation) to effect final purification and production of a product of maximum purity.

As already indicated, the cooled inner wall 8 of the reactor is preferably constructed of high heat conductivity metal such as copper or silver. Alternatively, it can consist of a suitable material such as steel or refractory metals such as tantalum, molybdenum, tungsten, etc., having high alloying temperatures. While the reactor is preferably cylindrical in form, with a length of several diameters, other forms and shapes, such as nozzles, area-dynamic shapes, etc., are also adaptable for use. Mixing of the reactants by recourse to jets, nozzles, tangential streams, sheeted streams, opposing jets, etc., or the like, can be effected.

Although the invention has been illustrated as applied to certain adaptations utilizing titanium and silicon chlorides and sodium as reactants, it is not restricted thereto. As already indicated, it is generally applicable to the reduction of the various halides and subhalides of refractory elements obtainable in liquid or gaseous form from groups II, III, IV, V and VI of the periodic table of elements with various fluid phase reducing metal reactants. Also, suitable modifications in operating conditions, such as varying amounts of reactant preheats and changes in temperature and pressure of reaction can be conveniently resorted to so that employment can be made of such other alkali or alkaline earth reducing metals as Mg, K, Li, Ca, Sr, Ba, etc., and the various fluid halides of said refractory elements, especially their chlorides. Refractory elements obtainable herein whose halides (chlorides, bromides, iodides, fluorides) can be reduced in the process include beryllium, boron, scandium, yttrium, silicon, titanium, zirconium, halfnium, thorium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, etc. These halides can be reduced singly or in admixture with each other to form desired alloys, intermetallic compounds, and lower valent halides.

The halides of these elements particularly useful in this process are those which are obtainable in fluid (vaporous or liquid) form at temperatures in the feasible pumping and metering range. Low melting halides such as $TiCl_4$, $SiCl_4$, $NbCl_5$, $TaCl_5$, etc., are easiest to handle but any halide which is fluid at 800° C. or below can be used. As noted, the gaseous halides, especially SiF_4 are contemplated as useful. Many of the higher melting, or subliming halides, such as $ZrCl_4$, may be liquefied by being dissolved in an alkalinous metal halide salt, preferably a chloride of the alkali or alkaline earth metal. A particularly useful example of such salt solution comprises the various compositions from mixtures of $TiCl_3 \cdot NaCl$ and $TiCl_2 \cdot 2NaCl$ which melt below about 550° C. All the normal halides are useful but the preferred are the chlorides and the lower melting or gaseous fluorides. The lower halides, such as $TiCl_2$, $TiCl_3$, $CrCl_3$, CrF_2, being generally too high-boiling, are liquefied at lower temperatures by solution in NaCl, KCl or other alkali or alkaline earth metal chlorides or halides. Typical examples of directly useful refractory metal halides include BCl_3, BF_3, $BeCl_2$, $ScCl_3$, $ScBr_3$, YCl_3, SiF_4, $SiCl_4$, $TiCl_4$, $NbCl_5$, NbF_5, $NbBr_5$, NbI_5, TaF_5, $TaCl_5$, $TaBr_5$, VCl_4 $MoCl_5$, WCl_5, WF_5 and WBr_5, etc. Examples of the higher melting halides which may be used in salt solution are: $TiCl_2$, $TiCl_3$, $ZrCl_4$, $HfCl_4$, $ZrCl_3$, $ThCl_4$, $NbCl_3$, $TaCl_3$, CrF_2, $CrCl_2$, etc. In some instances, the higher melting halides are not very soluble in the carrier salt chosen. It is often feasible therefore to increase the concentration of this reactant by suspending finely divided solid halide particles in the molten salt and feeding this suspension to the reactor.

Again, while particular reaction temperatures have been mentioned, in general, the temperature of the inner surface of the deposited metal or product will approximate the melting point of such product or metal. For example, in the instance of scandium, a temperature of about 1200° C. is realized; in the instance of silicon, a temperature of

about 1450° C. is obtained; in titanium production a temperature of about 1680° C. is encountered; and with zirconium, about 1900° C. is attained. For more refractory metals, such as boron, niobium, molybdenum, tantalum, tungsten, temperatures, respectively of 2300, 2620, 2996 and 3370° C. are contemplated.

Generally, however, since the products of the reaction are continuously and rapidly removed from the relatively small reaction chamber, it is quite important that they be in fluid, preferably liquid condition. In consequence, the reaction zone temperature should be at least equal to the melting point of any of the products formed in a given reaction. When, as noted, metals are being formed, the limiting temperature is usually the melting point of the metal. Even when partial reduction of the refractory metal halide is practiced, a portion of the refractory metal halide is reduced to the element and deposits on the inner wall of the reactor. The reaction zone must be maintained above this temperature or the discharge path of the chamber will freeze shut. The melting points of the product salts can be modified by using other salts of the same class as reagent carriers or by employing a mixture of reducing metals.

In this process, several means are available for maintaining the essential temperature in the reaction zone. The cooling rate can be controlled both by varying flow of cooling liquid and the area of chamber surface available. The size and geometry of the reactor can be designed to give optimum controlling conditions when basic data is known. Even where such dates are not available, normal experimentation will lead to the desired conditions. In most cases where complete reduction is involved large amounts of heat must be removed either to prevent melting through the reactor wall or to cause proper restriction of reactant mixture flow to prevent undue vaporization of by-products. Another temperature control is available in the reactants themselves. Feeding of liquid halides and reducing metals rather than gaseous reactants reduces the heat of reaction by their heat of vaporization. In many instances, additional heat is needed to maintain proper temperatures. Preheating of the reactants serves this purpose. Thus, when salt solutions of the lower chlorides are being reduced, the remaining heat of reaction is low and in view of the heat capacity of the carrier salt, a high feed temperature is indicated. Such salt solutions may be pumped at about 500–600° C. and thereafter passed through heat exchanges to pick up the required heat, that is, sufficient to maintain a heat balance in relation to the reaction and cooling which will produce fluid products. When a titanium subchloride-alkali metal chloride salt composition such as $TiCl_{2-3}$.NaCl is being prepared, a $TiCl_4$:Na ratio of 1:1 to 1:2 can be used.

The products of the reaction may be collected together or separately. Thus, when titanium and sodium chloride are produced they can be cooled and separation means applied to the combined products, or the products may be discharged from the reactor into a hot collector wherein the Ti product can be separated from the vaporous by-product by sedimentation or other solid-vapor separation means. Since the reactor is such a relatively small proportion of the system, it can be modified at little expense to provide for changing the capacity and yield characteristics. The process is advantageously continuous rather than batch and requires fewer components compared to the multiple step procedures in existing processes. The reaction system is inherently self-corrective because the formation of the skull within the reaction zone controls the pressure within the reactor and size of the reaction space. The reaction zone configuration stabilizes at a pressure which exceeds the vapor pressure of the reducing metal halide salt at the melting point of the refractory metal present.

I claim as my invention:

1. A continuous process for producing an element selected from the group consisting of beryllium, boron, scandium, yttrium, silicon, titanium, zirconium, hafnium, thorium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten comprising reacting at an elevated temperature within an externally cooled, relatively restricted reaction zone of a reactor, a halide of said element and a reducing metal selected from the group consisting of alkali and alkaline earth metals and magnesium, effecting said reaction by charging said reactants while in liquid state under pressure into said zone, and initially reacting them therein at substantially atmospheric pressure, forming the resulting elemental reaction product as a solid deposit on the inner wall surfaces of said zone and continuing the reaction and pressure addition of reactants to decrease the cross-sectional area of the reaction zone through progressive build-up thereon of said product and to increase the reaction zone pressure to a minimum at least equal to the vapor pressure of the by-product reducing metal halide reaction product formed at the melting point of said elemental product, continuing the reaction under the dynamically stabilized reaction zone conditions of cross-sectional area, pressure and temperature and forming said elemental product in liquid state and said reducing metal halide by-product in fluid form, discharging the resulting liquid and fluid reaction products from said reaction zone into a collection zone maintained under substantially atmospheric pressure and an inert atmosphere, and recovering the fused elemental product from the metal halide by-product discharged into said collection zone.

2. A continuous process for producing titanium metal comprising reacting at an elevated temperature within an externally cooled, relatively restricted reaction zone of a reactor titanium tetrachloride with a reducing metal selected from the group consisting of magnesium and alkali metals, effecting said reaction by charging said reactants while in liquid state under pressure into said zone for initial reaction therein at substantially atmospheric pressure, forming the resulting titanium metal reaction product as a solid deposit on the inner wall surfaces of said zone and continuing the reaction and pressure addition of reactants to decrease the cross-sectional area of the reaction zone through progressive build-up thereon of said titanium metal product and to increase the reaction zone pressure to a minimum at least equal to the vapor pressure of by-product reducing metal halide reaction product formed at the melting point of said titanium metal product, continuing the reaction under the dynamically stabilized reaction zone conditions of cross-sectional area, pressure and temperature and forming said titanium metal product in liquid state and said reducing metal halide by-product in fluid form, discharging the resulting liquid and fluid reaction products from said reaction zone into a collection zone maintained under substantially atmospheric pressure and an inert atmosphere, and recovering the fused titanium metal product from the metal halide by-product discharged into said collection zone.

3. A continuous process for producing zirconium metal comprising reacting at an elevated temperature within an externally cooled, relatively restricted reaction zone of a reactor zirconium tetrachloride with a reducing metal selected from the group consisting of magnesium and alkali metals, effecting said reaction by charging said reactants while in liquid state under pressure into said zone for initial reaction therein at substantially atmospheric pressure, forming the resulting zirconium metal reaction product as a solid deposit on the inner wall surfaces of said zone and continuing the reaction and pressure addition of reactants to decrease the cross-sectional area of the reaction zone through progressive build-up thereon of said zirconium metal product and to increase the reaction zone pressure to a minimum at least equal to the vapor pressure of the by-product reducing metal halide reaction product formed at the melting point of said zirconium metal product, continuing the reaction under the dynamically stabilized reaction

zone conditions of cross-sectional area, pressure and temperature and forming said zirconium metal product in liquid state and said reducing metal halide by-product in fluid form, discharging the resulting liquid and fluid reaction products from said reaction zone into a collection zone maintained under substantially atmospheric pressure and an inert atmosphere, and recovering the fused zirconium metal product from the metal halide by-product discharged into said collection zone.

4. A continuous process for producing titanium metal comprising reacting at an elevated temperature within an externally cooled, relatively restricted reaction zone of a reactor titanium tetrachloride and sodium, effecting said reaction by charging said reactants separately and while both are in liquid state under pressure into said zone and initially reacting them therein at substantially atmospheric pressure, forming the resulting titanium metal reaction product as a solid deposit on the inner wall surfaces of said zone and continuing the reaction and pressure addition of reactants at a substantially stoichiometric ratio and constant rate, decreasing the cross-sectional area of the reaction zone through progressive build-up thereon of said titanium metal product and to increase the reaction zone pressure to a minimum at least equal to the vapor pressure of the sodium chloride by-product formed at the melting point of titanium, continuing the reaction under the dynamically stabilized reaction zone conditions of cross-sectional area, pressure and temperature and forming said titanium metal product in liquid state and said sodium chloride by-product in fluid form, discharging the resulting liquid and fluid reaction products from said reaction zone into a collection zone maintained under substantially atmospheric pressure and an inert atmosphere, and thereafter recovering the fused titanium metal product from the sodium chloride by-product discharged into said collection zone.

5. A continuous process for producing titanium metal comprising separately charging liquid titanium tetrachloride and liquid sodium reactants under pressure into an externally cooled reaction zone, mixing and reacting said reactants at an elevated temperature within said zone and forming a deposit of titanium metal sponge upon inner walls thereof, continuing said formation and deposition to decrease the cross-sectional area of said zone and develop a back pressure stabilized at the pressure equal to the vapor pressure of the sodium chloride formed at the about 1680° C. melting point of titanium metal, continuing the reaction under the dynamically stabilized reaction zone conditions of cross-sectional area, pressure and temperature, and forming said titanium metal product in liquid state and sodium chloride by-product in fluid form, regulating the rate of feed of said reactants to maintain an excess of the stoichiometric requirement of sodium in the reaction zone, discharging titanium in molten state and by-product sodium chloride in fluid form from said zone and into an inert fluid in a collection zone maintained at substantially atmospheric pressure, and thereafter separating and recovering the melted titanium metal product from said by-product sodium chloride.

6. A method for reducing a halide of an element selected from the group consisting of beryllium, boron, scandium, yttrium, silicon, titanium, zirconium, hafnium, thorium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten comprising separately charging to a reaction zone while under pressure and in fluid state a reducing metal selected from the group consisting of magnesium and alkali and alkaline earth metals, and a halide of an element selected from the group consisting of beryllium, boron, scandium, yttrium, silicon, titanium, zirconium, hafnium, thorium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten, mixing and reacting said reducing metal and elemental halide reactants in said zone at an elevated temperature while removing through external cooling sufficient heat from the walls of the reaction zone to form on the interior wall surfaces of said zone a solid deposit of the element being formed in the process, continuing the charging of said reactants to said zone to decrease by progressive build-up of said deposit the cross-sectional area of said zone and to develop a reaction zone back pressure stabilized at the pressure at least equal to the vapor pressure of the by-product reducing metal halide being formed at the melting point of said element, continuing the reaction under the dynamically stabilized reaction zone conditions of cross-sectional area, pressure and temperature, and forming said elemental product in liquid state and said reducing metal halide by-product in fluid form as reaction products, discharging said reaction products into a collection zone maintained at a substantially lower pressure, and thereafter recovering the resulting reaction products.

7. A method for producing an element selected from the group consisting of beryllium, boron, scandium, yttrium, silicon, titanium, zirconium, hafnium, thorium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten comprising separately charging into a reaction zone while under pressure and in fluid state, a chloride of said element and a reducing metal selected from the group consisting of magnesium and alkali and alkaline earth metals, effecting initial reaction therein at substantially atmospheric pressure, forming a solid deposit of the resulting elemental reaction product on the inner wall surfaces of said reaction zone and through external cooling of the walls of said zone, continuing the reaction and pressure addition of said chloride and reducing metal reactants to decrease the cross-sectional area of said reaction zone through progressive build-up therein of said elemental reaction product and to increase the reaction zone pressure to a minimum at least equal to the vapor pressure at the melting point of said elemental reaction product of the by-product reducing metal chloride reaction product being formed in the process, continuing the reaction under the dynamically stabilized reaction zone conditions of cross-sectional area, pressure and temperature and forming said elemental reaction product in liquid state and said reducing metal chloride by-product in fluid form, discharging the resulting liquid and fluid reaction products from said reaction zone into a collection zone maintained under a substantially lower pressure and an inert atmosphere, and recovering the fused elemental product from the metal chloride by-product discharged to said collection zone.

8. A process for producing silicon comprising separately charging liquid silicon tetrachloride and liquid sodium reactants under pressure into an externally cooled reaction zone, mixing and reacting said reactants at an elevated temperature and within said zone and forming a deposit of solid silicon upon the inner walls of said zone, continuing said formation and deposition to decrease the cross-sectional area of said zone and develop a back pressure stabilized at the pressure equal to the vapor pressure of the sodium chloride formed at the melting point of silicon, regulating the rate of feed of said reactants to maintain an excess of the stoichiometric requirement of sodium in said zone, discharging the silicon in molten state and by-product sodium chloride in fluid form from said zone and into a collection zone maintained at substantially atmospheric pressure, and thereafter separating and recovering the silicon product from said sodium chloride by-product.

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