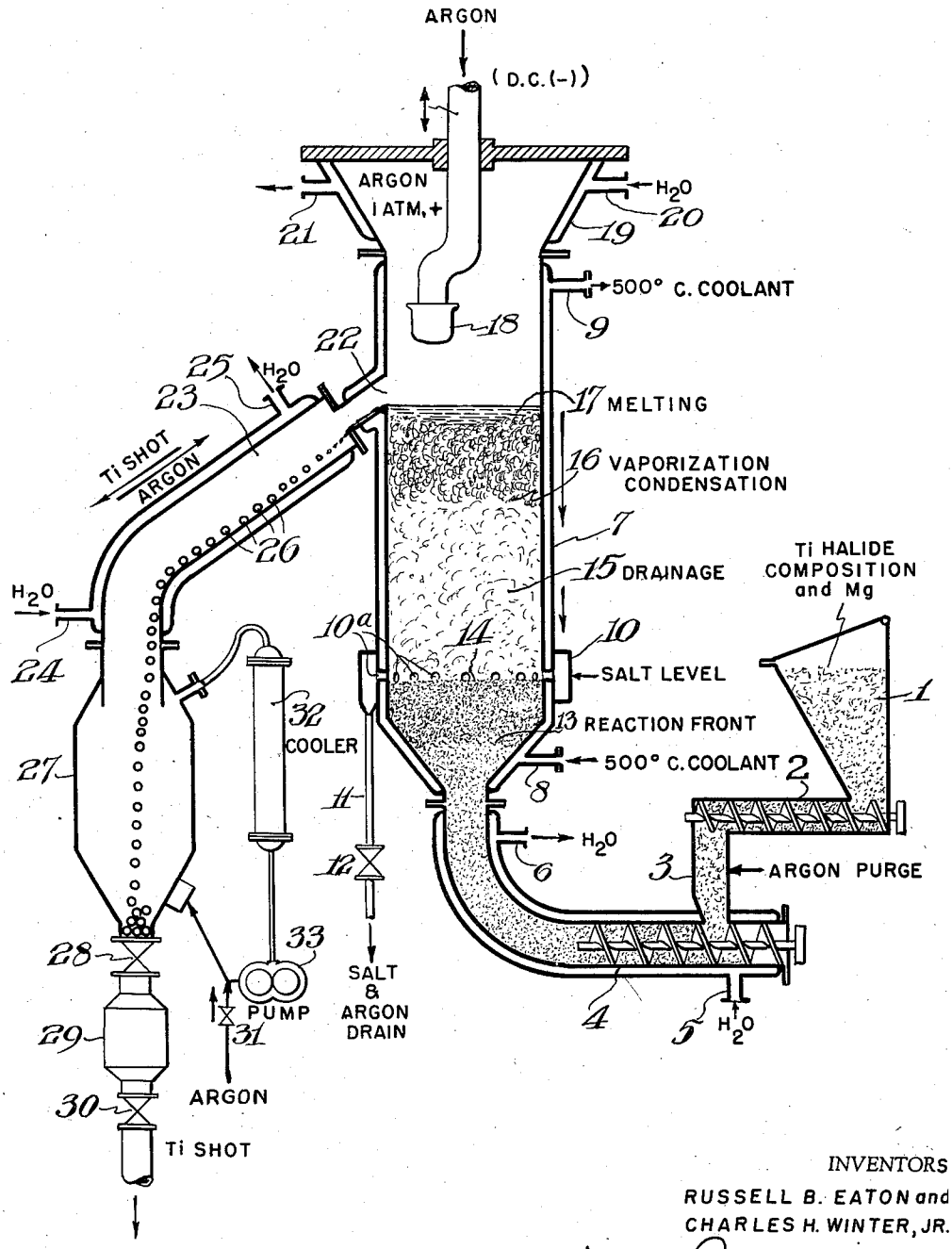
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METHOD OF PRODUCING GROUP IV-A METALS

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METHOD OF PRODUCING GROUP IV-A METALS

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This invention relates to a process for the preparation of the group IV–A metals. More especially, this invention relates to an integrated continuous process for the preparation of titanium metal.

Titanium metal is presently commercially produced by utilizing magnesium reduction of titanium tetrachloride. This process is a batch operation in which the various steps necessary for the production of the metal are carried out in various places and at various times. Batch processes of this type require extensive handling of the metal and the by-product materials are therefore wasteful in time, effort, and equipment, and encourage contamination of the product metal.

Integrated continuous processes for titanium metal have been proposed of which U. S. P. 2,564,337 is an example. According to that process, as described, the following steps are required: (*a*) the halide and reducing metal reactants are fed into a reactor; (*b*) reaction occurs and the titanium product metal settles downwardly; (*c*) then it is recovered and moved upwardly; (*d*) it is drained and moved horizontally and downwardly; (*e*) it is stored in a bin; (*f*) it is moved horizontally, and (*g*) then dropped vertically into the purification and melting furnace. These integrated movements in different pieces of apparatus require that the equipment be complex and expensive. Also, in the arc melting, of a mixture of the liquid by-product and titanium metal, splashing of the titanium, because of sudden vaporization of the by-product, causes the liquid titanium to contact the electrode, the liquid titanium attacks the electrode structure and carries impurities such as carbon or tungsten into the product metal. Large ingots of pure titanium may be considered ill adapted for purposes wherein it is necessary to have an alloy of titanium. The large ingot form is not easily handled and requires comminuting for the production of homogeneous alloy ingots by remelting alloy mixtures.

In the above mentioned processes the ratio of the reactants are not under control; that is, the reducing metal either exists, (1) in the first instance, in large excess to which is added the titanium tetrahalide; or, (2) in the second case, the titanium halide atmosphere exists within the reactor and the reducing metal magnesium is added to that atmosphere. In both of these no control over the actual amount of reactant taking place in the reaction is maintained. Also, the amount of reactive heat is not under control. The reaction between the reducing metal such as magnesium and titanium tetrachloride releases a large amount of heat. Therefore, the reaction must be controlled within limits of size and shape for the heat release capacity of the apparatus because extreme temperatures will cause reaction between the produced titanium and the reactor walls which are commonly made of iron.

It is among the objects of the present invention to provide a process in which the required movements of the reactants and products are simplified. Another object is to provide a process which requires simple and

inexpensive apparatus. Other objects are to provide a process in which the product metal is produced in a form suitable for maximum utilization in the metal industry without subsequent handling step. It provides a process wherein the reactive heat and the heat provided for melting of the metal assist in separating the by-products and unreacted materials from the product metal. Also, an integrated continuous process is provided in which there is an upward movement of all materials during feeding, reaction, separation, and melting. Other objects will become apparent as the description proceeds.

The above and other objects are accomplished by this invention which includes a continuous process for producing solid forms of refractory metal which comprises continuously and forcibly feeding premix charge of solid reducing metal and solid halide salt composition containing a halide of the refractory metal upwardly into a cooled-wall reactor, controlling the rate of said feed to establish and maintain a reaction zone at a temperature above the melting point of the halide salt portion of the reaction mass and within the lower portion of said reactor, removing fluid halide salt by-product and any ancillary vapors from the reactor through at least one port situated above the said reaction zone and below a superincumbent melting zone, maintaining an effective pressure of inert gas above said melting zone and a flow of said gas downwardly to the said by-product removal port, melting the solid product metal into a pool within said superincumbent melting zone by means of an electric arc, and draining the molten metal into an associated zone for solidification into the desired form. In one particular embodiment this invention comprises a continuous process for producing titanium metal shot which comprises continuously and forcibly feeding premixed charge of solid particles of magnesium and solid particles of a titanium subchloride, with a chlorine to titanium atom ratio less than 4, associated with sodium chloride upwardly into a cooled wall reactor, controlling the rate of said feed to establish and maintain a reaction zone within the lower portion of said reactor, removing fluid magnesium chloride and sodium chloride, and argon vapors, from the reactor through at least one port situated above the said reaction zone and below a superincumbent melting zone, maintaining an effective pressure of argon above said melting zone and a flow of said argon downwardly to the said removal port, melting the solid titanium into a pool within said superincumbent melting zone by means of an electric arc, and draining the molten titanium into an associated zone for solidification into titanium shot.

One particular embodiment of our invention will now be described in connection with the vertical cross-sectional view illustrated in the accompanying figure of the drawing showing equipment suitable for carrying out this process.

The reacting components of the premixed charge are stored in bin 1. This premixed charge consists of the reducing metal and the titanium halide. The titanium halide composition, preferably in small particles for ease of mixing, comprises a titanium subchloride, with a chlorine to titanium atom ratio less than 4 associated with at least one chloride selected from a class consisting of the chlorides of the alkali or alkaline earth metals. The reducing metal, preferably in the form of small solid particles, is selected from the class consisting of alkali or alkaline earth metals and preferably magnesium partibles. These two reacting constituents are mixed in predetermined proportions to produce the titanium metal; that is, with sufficient reducing metal to accept the chlorine of the titanium halide and reduce it to the metal.

Bin 1 discharges through a conveyor 2 into an open conduit 3 leading to another conveyor. In this open con-

duit the material falls freely and section 3 serves as a barrier to prevent the inadvertent flareback of the reaction up into the storage bin. Section 3 has an argon purge which prevents contamination of the produced metal by absorbed or occluded air. The conduit 3 is connected to the feeding section 4, which is a water-cooled conduit leading to the lower portion of the reaction chamber 7. The feed conduit 4 contains a screw force feeding mechanism having a regulatable speed to control the rate of feed of the premix charge. The walls are water cooled with water entering inlet 5 and exiting at port 6. The reactor vessel 7 is cylindrical in form with an outer jacket as cooling means. The coolant enters that section at port 8 and leaves at port 9. The entire section is cooled with a heat transfer salt to about 50° C. above the melting point of the by-product salt. The lower portion of the reactor is provided with a conical bottom as shown.

Near the lower end the reactor has a number of by-product halide salt removal ports 10*a* leading through the cooled section to an exterior bustle pipe 10 which drains by line 11 and valve 12 to an exterior catch basin not shown. This is the by-product salt and argon removal section. The premix feed enters through the conduit 4 into the conical bottom of the reaction vessel and within this section the rate of feeding is controlled so that a reaction front is stabilized as shown at point 13. The products of the reaction and the reaction mixture are then pushed by the screw action upwardly in the reactor and when the molten salt has reached the level of the removal ports, a salt level 14 is stabilized. Above the level of 14 the mass of titanium metal contains molten salt draining from the metal and from the outer zone above the drainage section 15.

As the metal moves upwardly in the conduit it then passes from the drainage section into a hotter zone in which the temperature exceeds the boiling point of the by-product salt. The by-products are vaporized and this vapor partially condenses to the liquid form as it progresses downwardly to the drainage section. As the metal product is pushed upwardly by the incoming feed it then approaches the melting zone 17. The melting is accomplished by the arc electrode 18 fitted into a water cooled head 19 to which cooling water is fed through port 20 and leaves through port 21. Power from a D. C. source is supplied to the electrode, from a source not shown with the electrode at a negative potential and the vessel walls at the positive potential. The conduit 7 has a molten metal discharge port 22 which establishes the level of the molten pool. The molten metal leaving port 22 then falls into a cooling and shotting section 23 which is a water-cooled conduit leading to a storage bin. Water is furnished to the jacket through port 24 and leaves through port 25. The molten metal is continuously formed by the arc melting operation and the metal for the melting operation is continuously fed into the zone by the action of the force feed of the reactants at the lower portion of the reactor. The solidified titanium shot 26 from the solidification conduit fall into an argon purged bin 27 that may be emptied through valve 28 into an intermediate bin 29 which allows discharge of the product metal through valve 30 without substantial loss of argon. The bin 27 is purged of any amount of by-product by an argon flow makeup coming in through line 31 into the recirculation system consisting of a pump 33 and a cooler 32. The argon pressure within bin 27 causes it to flow back through conduit 23 into the head of the melting section. This argon pressure within the melting head section supplies a flow of argon around the edges of the molten pool where a leaking type of seal is obtained. This flow of argon down through the metal mass prevents the by-product salt from entering into the melting section and assists in the vaporization and drainage of the by-product salt from the metal as it follows its upward course. Loss of this small leakage of argon may be avoided by providing that the salt and argon removed through line 11 enter a sump wherein the gas may be taken from a overhead level.

Summarizing the foregoing process, the titanium halide composition and magnesium metal are reacted at a controlled rate to produce an integrated network of sponge titanium metal. As this product is pushed upward by incoming feed the bulk of the by-product salt is removed through a bustle ring to establish a maximum liquid salt level within the reactor. Further drainage of the sponge titanium above the salt level is obtained by substituting argon gas for the salt within the voids. Vaporization of the residual salts from the sponge metal occurs as the mass approaches the shallow pool of molten titanium metal maintained by an arc at the upper portion of the equipment. Internally, condensation of the vaporized salt occurs in that portion of the equipment beneath the vaporization zone but above the salt liquid level. Argon is introduced at a pressure slightly above the removal pressure to the vapor space above the liquid titanium metal. This argon serves to prevent volatile material rising through the imperfect seal between the liquid titanium metal pool and the cool equipment shell. This argon leaves the equipment along with the liquid by-product salt and may be recycled. The liquid titanium metal is continuously removed from the shallow pool by overflowing to a water-cooled conduit. This liquid titanium metal on freezing forms small globules resembling shot material.

It will be understood therefore that in this continuous process and its sequence of operations, there is provided a gradual temperature rise of the material and, in addition to withdrawing salt from the product outlet zone near the base of the reaction chamber, undrained contaminants are also vaporized as they are carried into the melting zone; these vapors are condensed internally below the distillation zone and directed downward to the by-product outlet with the aid of inert gas escaping downward within the chamber from the head maintained in the melting zone.

The following example will show one mode of operation of this invention, but this is intended as illustrative only not as a limitation thereof.

Example

A reactor similar to that shown in the figure of the drawing, which included a vertical steel cylinder, 24 inches in diameter by 48 inches tall. It was equipped with an arc melting head and arranged for screw feeding of particles of titanium subchloride associated with sodium chloride of the composition represented by the formula $TiCl_{2.5}.1.5NaCl$ and magnesium particles through a conical bottom having a 6-inch diameter inlet. The particle sizes of the magnesium and titanium subchloride salt composition were adjusted so that the reaction propagation rate was 10 to 30 inches per minute. The reactor after sweeping with insert gas was fed this mixture at the rate of 8500 pounds per hour or 7500 lbs./hour of titanium containing salt and 1000 pounds per hour of magnesium metal shot. The upward velocity of this mixture through the 6-inch entrance to the feed cone was calculated to be approximately 100 inches per minute. The reaction was started by lowering the arc melting electrode and striking an arc against the rising premixed charge. The arc electrode was retracted to the melting position as soon as the reaction was started. As the titanium metal sponge product rose above the salt tapping bustle pipe, by-product salt issued from it at a rate of approximately 6900 pounds per hour. During the above operations a stream of argon gas was introduced to the top of the unit at a rate of 150 cubic feet per hour. This argon gas left the unit via the salt tapping pipe, along with a small amount of excess magnesium.

As the mass of titanium sponge approached the overflow port, the arc was restarted, and a pool of liquid titanium metal established. As the liquid titanium metal rose above the exit port, it was conducted by means of a water-cooled copper chute into the gas tight receiver from which solidified and cooled pellets were periodically discharged through a lock arrangement to the atmosphere. It was found that the production rate was approximately 1500 pounds per hour, and that the power requirement was approximately 1500 kilowatts at 40 volts D. C. The electrode was maintained negative as in established arc melting practice.

The solid titanium halide composition comprises a titanium sub-chloride with a chlorine to titanium ratio less than 4 associated with at least one chloride salt selected from the class consisting of the chlorides of the alkali or alkaline earth metals. The titanium halide composition reactant may be obtained from several sources of which the following are illustrative: (1) the addition of pure sub-chloride to the associated salt; (2) the formation of a salt mixture by the reduction of titanium tetrachloride with the proper amount of a reducing metal; and (3) the reduction of titanium tetrachloride by hydrogen in the presence of a molten salt as an absorbing medium. In the solid state, then the composition is comminuted to the proper size for the desired reaction rate. The preferred salt composition contains up to 50 mol per cent titanium sub-chloride having chlorine to titanium atom ratios between 2 and 3 inclusive. The preferred associated salt is sodium chloride. It is contemplated that several associated salts may be combined to produce molten salt mixtures, resulting from the reduction process, which have low melting points. For the production of pure titanium no associated salt component other than titanium may be included which is reducible either by the reductant metal such as magnesium or the titanium metal product. It is contemplated that for the production of titanium alloys that the halide salt composition may contain either the metal or metal halide of the material desired in the titanium alloy, for instance iron chloride may be included if a titanium-iron alloy is desired, or, nickel chloride, tungsten chloride, aluminum chloride, or other various alloying materials as may be desired in the final alloy product.

The solid reducing metal is selected from the class consisting of alkali or alkaline earth metals and preferably is magnesium. The preferred reductant, magnesium particles or droplets to be applied in the reduction system may be produced by agitation, shotting, atomization, from reduction reactions which produce particulate magnesium, and from the usual commercial sources. The particle size desired may be obtained from these sources by control of the variants available in the various production methods. The reactants are mixed in the proportions required to produce titanium metal and by-product salt. The particle size of the reducing metal and the titanium subchloride composition are adjusted to obtain a desired reaction propagation rate. This together with the method of adjusting the feeding rate allows complete control over the rate of production of a reactor unit. With the example shown the following conditions obtain during the period of stable operation: (1) the rising rate of the titanium metal sponge was .65" per minute; (2) rising rate of the liquid titanium was .32" per minute; (3) estimated downward superficial vapor velocity from the distillation zone was about 1.5 ft. per second.

Although this process has been discussed as applied to titanium as the metal to be produced, it is also applicable for the production of the group IV–A metals in general; that is, titanium, zirconium, and hafnium; and may be extended to other metals wherein a solid halide or metal salt may be reacted with a reducing agent to produce a solid metal structure and a by-product material which is molten and vaporizable below this

melting temperature. The preferred titanium salt utilized in the operation is a sub-chloride as previously discussed, and it is preferred because of the economic advantage obtained when utilizing this common halogen component. In certain cases the other solid halides of the halogens (bromine and iodine) may be utilized, but because of their economic position the titanium salts of these elements are not preferred. With zirconium metal as a further example of group IV–A, the tetrachloride salt may be utilized because it is a solid which may be mixed with the magnesium particles to produce a premixed charge suitable for the operation of the method of this invention. Certain factors are to be considered in the choice of the metal salt reactant and the reductant utilized in our process. The metal salt should be solid at temperatures prevailing in the reactor feeding process. The reductant should be solid at this same temperature. The by-product salt obtained from the reaction should melt and be vaporized below the melting temperature of the product metal. Also, the reductant metal should be vaporized below this temperature if a pure product metal is desired. In the operation of this process to produce alloys of the product metal, it is permissible to add the alloying element either as particles of metal; or if the product metal may be obtained by reduction of a salt by the reducing agent employed, then a salt of the alloying ingredient may be added to the charge whereupon both the product metal and the alloying metal will be obtained by the reduction and an alloy produced in the melting step.

The reactor 7 shown in the drawing and applied in the example was a cylindrical vessel, but this shape is not critical, and rectangular, square, or other shape vessels may be equally satisfactory. The reactor was operated in a vertical position with the reactants being fed into the lower portion. In the broader aspect the reactor may be in inclined positions up to nearly the horizontal position with the limitation that the flow of the reactants to the final product is in an upwardly direction.

This invention allows complete control over the rate of production of titanium metal because the reaction rate may be controlled as previously discussed by the sizing of the reactants. The feed rate is controllable over wide limits and therefore may be stabilized at that value set by the reactivity of the premix charge in order that a stable reaction front, as shown in the drawing at 13, may be established. With a given type of reaction feed the rate of production per reactor unit will depend upon the size of the equipment. In this process the material enters an in-line processing unit at the base as reactants and the desired metal is discharged from the upper portion as a finished product eminently suitable for the metallurgical uses. The shot form of titanium is particularly useful for producing a feed for a melting furnace to produce pure or alloyed metal. Their solid shape gives a low area to volume relationship and because of the solid structure produces a very stable material for storage. The complete processing of the material of the reactants to the finished product is done within one equipment unit and no intermediate discharging, handling, comminuting or vacuum equipment is necessary.

We claim as our invention:

1. A continuous process for producing a solid form of group IV–A refractory metal selected from the group consisting of titanium, zirconium, and hafnium, comprising forcibly and continuously charging a mixture comprising predetermined amounts of a solid reducing metal selected from the group consisting of alkali, alkaline earth metals and magnesium, and a solid metal halide salt of said refractory metal upwardly into a cooled wall reactor for reaction therein at an elevated temperature, charging said mixture at such a rate that a reaction zone is established and maintained within the lower portion of said reactor at a temperature above the melting point of the halide salt portion of the mass undergoing reaction

and below the vaporization temperature of the refractory metal under production and said reducing metal, maintaining a superincumbent melting zone above said reaction zone to form a molten pool of said refractory product during said reaction, removing fluid halide salt reaction by-product and ancillary vapors from the reactor through a withdrawal outlet arranged above said reaction zone and below said melting zone, flowing an inert gas at a positive pressure downwardly in said reactor and through said melting zone, around the edges of said molten pool, and out said by-product withdrawal outlet, subjecting the solid refractory metal product obtained in the reactor to arc melting to form a molten pool thereof within said superincumbent melting zone, and draining said molten metal product from said pool into an associated collecting zone for solidification and recovery.

2. A continuous process for producing a solid form of titanium metal, comprising forcibly and continuously charging a mixture of predetermined amounts of a solid reducing metal selected from the group consisting of alkali, alkaline earth metals and magnesium, and a solid metal halide salt composition containing a halide of titanium and a halide of a metal selected from the group consisting of alkali and alkaline earth metals, upwardly into a cooled wall reactor for reaction therein at an elevated temperature, charging said mixture at such a rate that a reaction zone is established and maintained within the lower portion of said reactor at a temperature above the melting point of the halide salt portion of the mass undergoing reaction and below the vaporization temperature of titanium and said reducing metal, maintaining a superincumbent melting zone above said reaction zone to form a molten pool of said refractory product during said reaction, removing fluid halide salt reaction by-product and ancillary vapors from the reactor through a withdrawal outlet arranged above said reaction zone and below said melting zone, flowing an inert gas at a positive pressure downwardly in said reactor and through said melting zone, around the edges of said molten pool, and out said by-product withdrawal outlet, subjecting the titanium product obtained in the reactor to arc melting to form a molten pool thereof within said superincumbent melting zone, and draining said molten titanium product from said pool into an associated collecting zone for solidification and recovery.

3. A continuous process for producing titanium metal shot which comprises continuously and forcibly feeding a premixed charge of predetermined amounts of solid particles of magnesium, and solid particles of a titanium sub-chloride having a chlorine to titanium atom ratio of less than 4 and sodium chloride, upwardly for reaction into a cooled wall reactor for reaction therein at an elevated temperature, controlling the rate of said forcible feeding to establish and maintain a reaction zone within the lower portion of said reactor at a temperature above the melting point of the chloride salt by-products and below the vaporization temperature of titanium and magnesium, maintaining a superincumbent melting zone above said reaction zone to form a molten pool of said refractory product during said reaction, draining fluid magnesium chloride and sodium chloride from the reactor through at least one port situated above said reaction zone and below said superincumbent melting zone, maintaining an effective pressure of argon above said melting zone and flowing said argon downwardly around the edges of said molten pool to and out said removal port, arc melting solid titanium formed as a pool within said superincumbent melting zone, and draining the molten titanium from said pool into an associated zone for solidification into solid titanium shot.

4. A continuous process for producing a solid form of a group IV–A refractory metal selected from the group consisting of titanium, zirconium, and hafnium which comprises continuously and forcibly feeding upwardly into an externally cooled reactor a premixed reactant charge comprising predetermined quantities of a solid reducing metal selected from the group consisting of alkali, alkaline earth metals, and magnesium, and solid metal chloride salt composition containing a chloride of said refractory metal and a chloride of a metal selected from the group consisting of alkali and alkaline earth metals, controlling the rate of said feeding to establish and maintain a reaction zone within the lower part of said reactor at a temperature above the melting point of the chloride salt reaction product formed but below the vaporization temperature of said refractory and reducing metals, maintaining a superincumbent melting zone above said reaction zone to form a molten pool of said refractory product during said reaction, removing from the reactor chloride salt by-product formed in fluid state together with any ancillary vapors from at least one withdrawal point maintained above said reaction zone and below said superincumbent melting zone, maintaining a pressure of inert gas above said melting zone and flowing said gas downwardly around the edges of said molten pool to and out of said by-product withdrawal point, arc melting solid product refractory metal obtained and forming a pool thereof within said superincumbent melting zone, and draining the molten metal from said pool into an associated zone for solidification and recovery in predetermined form.

5. A continuous process for producing titanium metal in individual solid particles which comprises continuously and forcibly feeding upwardly into an externally wall-cooled reactor for reaction at an elevated temperature a predetermined reactant mixture charge comprising solid magnesium particles, solid particles of a titanium sub-chloride having a chlorine to titanium atom ratio of less than 4, and sodium chloride, controlling the rate of said feeding to establish and maintain a reaction zone within the lower portion of said reactor wherein a temperature above the melting point of said chlorides and below the vaporization temperature of said titanium and magnesium prevails, maintaining a superincumbent melting zone within said reactor and above said reaction zone to form a molten pool of said refractory product during said reaction, removing fluid magnesium chloride and sodium chloride and ancillary vapors from the reactor through at least one withdrawal point situated above said reaction zone and below said superincumbent melting zone, maintaining an effective pressure of argon above said melting zone and flowing said argon downwardly around the edges of said molten pool and to and through said removal point, arc melting solid titanium product obtained and forming a pool thereof within said superincumbent melting zone, and draining molten titanium from said pool into an associated zone for solidification into individual titanium particles.

6. A process for producing titanium metal which comprises feeding a premix of reactants comprising regulated amounts of a titanium chloride, a reducing metal selected from an alkali metal, an alkaline earth metal and magnesium, together with a chloride of a metal selected from the group of alkali and alkaline earth metals, into the bottom of a reaction chamber and a reaction zone maintained at an elevated temperature above the melting point of the chlorides present in said reactants and below the vaporization temperature of titanium and said reducing metal, the wall surfaces of which are continuously cooled, moving the formed metal product upwardly through said chamber from a reaction zone to a melting zone by the force of the oncoming feed of reactants, withdrawing reaction by-products from a discharge zone maintained at a point intermediate said reaction zone and melting zone, maintaining a head of inert gas above the melting zone sufficient to force said gas downwardly around the edges of the molten metal formed in the melting zone and against the rising metal network to replace

voids therein and to assist in discharging said by-products from said discharge zone, subjecting the metal product formed to arc melting treatment during said reaction to provide a molten pool thereof in said melting zone and withdrawing the molten metal from said pool into an associated metal solidification and recovery zone.

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