

March 25, 1958

G. R. FINDLAY

2,828,199

METHOD FOR PRODUCING METALS

Filed Dec. 13, 1950

4 Sheets-Sheet 2

FIG. 4

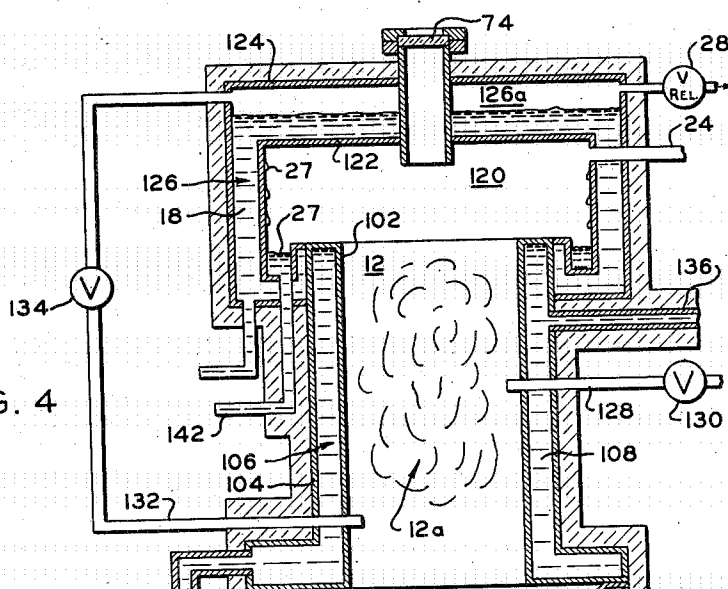
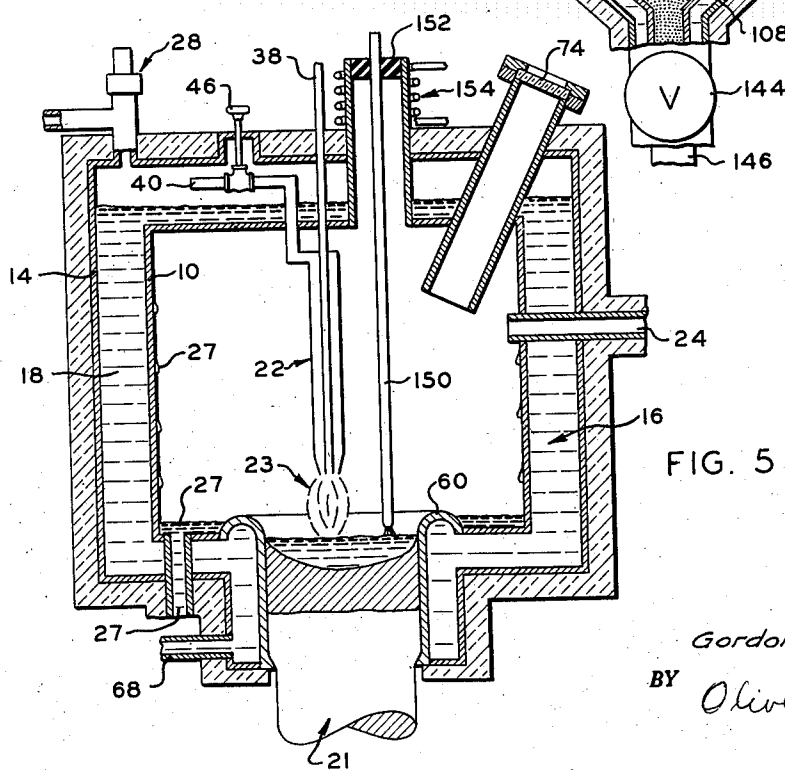


FIG. 5



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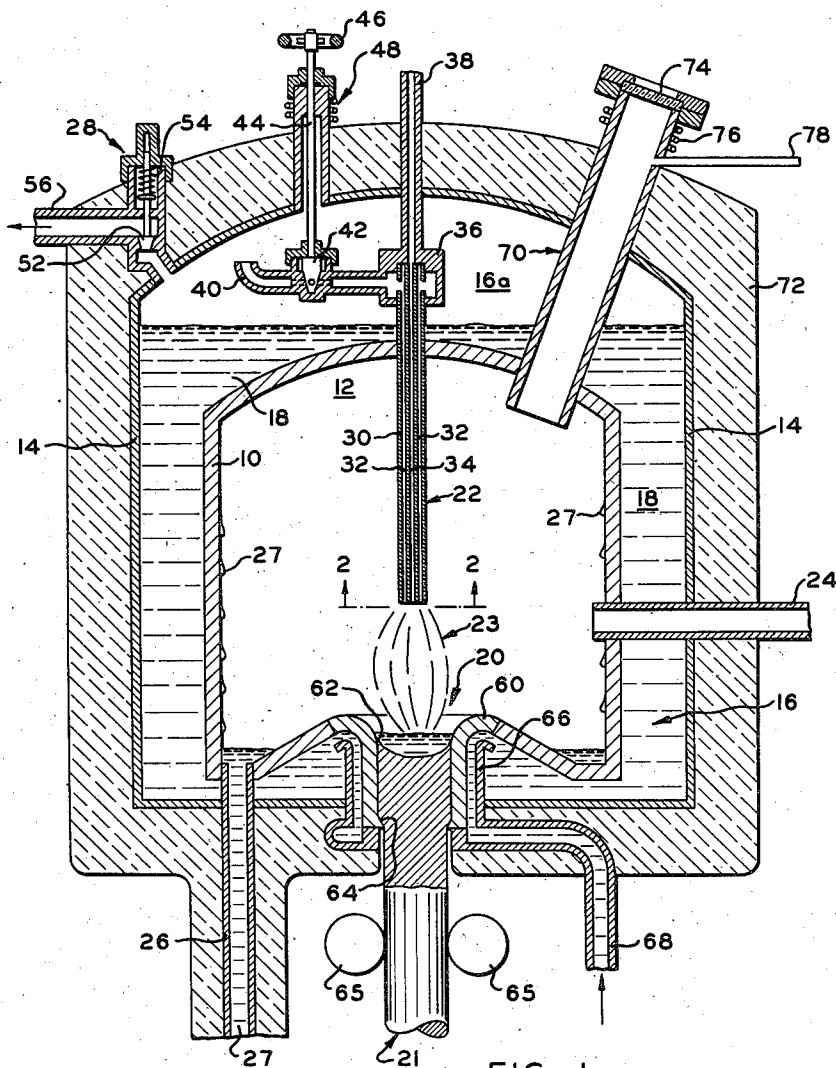


FIG. 1

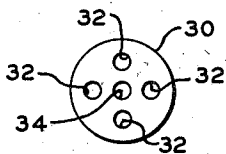


FIG. 2

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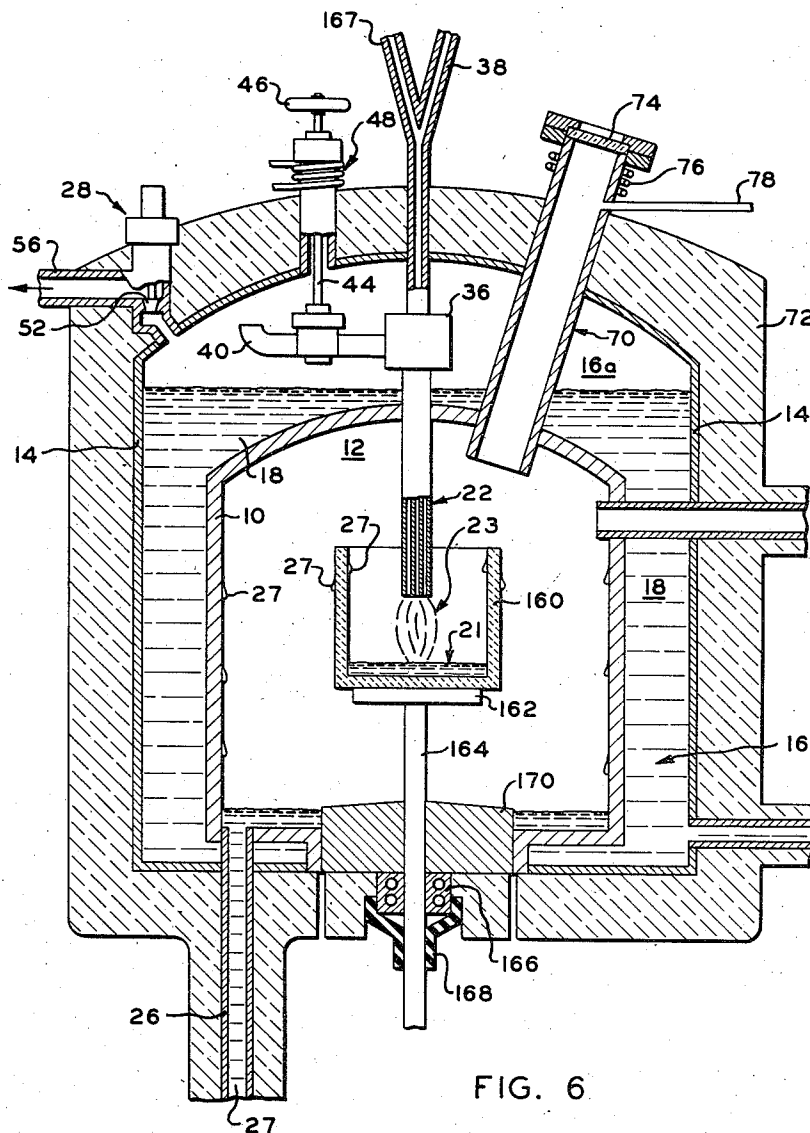


FIG. 6

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2,828,199

METHOD FOR PRODUCING METALS

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Application December 13, 1950, Serial No. 200,606

18 Claims. (Cl. 75—29)

This invention relates to the production of metals and more particularly to the production of metals in a high state of purity. This application is in part a continuation of my copending application, Serial No. 140,339, filed January 24, 1950, now abandoned, and in part a continuation of my copending application, Serial No. 189,917, filed October 13, 1950.

A principal object of the present invention is to provide improved processes for the production of metals and alloys thereof, and particularly metals, from the group consisting of titanium and zirconium, and alloys thereof, by the reduction of either a titanium tetrahalide or a zirconium tetrahalide.

Another object of the invention is to provide improved processes of the above type which are continuous in operation and which result in great savings of power necessary to achieve the desired metal production.

Still another object of the invention is to provide such processes for the production of titanium or zirconium or alloys thereof, these processes being simple to operate, having extremely high thermal efficiency, and producing the metal in pure ductile form.

Still another object of the invention is to provide processes of the above type where the product metal can be formed as a powder, as a compacted sponge, or as an ingot.

These and other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and the order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein:

Fig. 1 is a diagrammatic, schematic, sectional view of one preferred form of the invention;

Fig. 2 is a fragmentary view of a portion of the apparatus of Fig. 1 taken along the line 2—2;

Fig. 3 is a flow sheet showing one preferred arrangement of auxiliary equipment and the order of the various steps in the process;

Fig. 4 is a fragmentary, schematic, sectional view of another embodiment of the invention;

Fig. 5 is a fragmentary, schematic, sectional view of still another embodiment of the invention; and

Fig. 6 is a fragmentary, schematic, sectional view of still another embodiment of the invention.

In general the present invention relates to the production of metals by the reduction of a reducible compound thereof. It is preferably directed to the production of refractory materials and is of particular utility in connection with the production of titanium or zirconium. In practicing the process the reaction is preferably carried out in a reaction zone in a reaction chamber which

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has an atmosphere inert to the reduced metals at high temperatures. In the case of titanium or zirconium this inert atmosphere is preferably a vacuum or an atmosphere of an inert gas such as argon. The reducible metal compound, for example a titanium tetrahalide, is preferably

introduced into the reaction zone in a fluid phase and preferably in a liquid or gas phase, the latter being the most preferred embodiment. Accordingly, the reducible metal compound is preferably one which can be volatilized at a temperature below its decomposition temperature. A reducing agent is also introduced into the reaction chamber, this reducing agent being also preferably in the fluid phase, such as a liquid or gas phase, the latter being also preferred. In a preferred embodiment of the invention the reducing agent is selected so as to have a sufficiently high heat of reaction with the reducible metal compound as to melt the reduced metal and vaporize the by-product of the reaction. The reducible metal compound and the reducing agent are preferably mixed as they enter the reaction zone so that complete reduction of the reducible metal compound is achieved with coalescing of the metal and vaporization of the by-product due to the high heat of the reaction. The rate of introduction of the reducible metal compound and the reducing agent is such that the heat of reaction is sufficient to achieve the coalescing of the metal and the vaporization of the by-product despite heat losses from the reaction zone. In a preferred embodiment of the invention this heat is sufficient to completely melt the product-metal and form a solid ingot.

When titanium is the desired end product, the reducible metal compound comprises a titanium tetrahalide and preferably titanium tetrachloride. With this compound the reducing agent preferably comprises an alkali metal and particularly sodium. Without intent to limit the invention it will be initially described in terms of the reduction of titanium tetrachloride by metallic sodium.

In the process as practiced with the preferred titanium tetrachloride and the sodium mentioned above, these two materials are introduced into the reaction zone in gas phase and the walls adjacent the reaction zone are maintained sufficiently hot so that the introduced sodium and titanium tetrachloride and the by-product sodium chloride remain in gas phase in this reaction zone. This permits collection of the product titanium adjacent the reaction zone, the surface of the collected titanium exposed to the vapors in the reaction zone being at a temperature above the condensation temperature of the byproduct sodium chloride.

In the preferred operation of the above process the reactant titanium tetrachloride and sodium are introduced with thorough mixing of the gases, this mixing preferably taking place as these two reactants enter the reaction chamber so as to cause them to react violently with a highly exothermic reaction. In one preferred form of the invention the reacting gases are directed against the surface of a mass of titanium so that the heat of the reaction is directed towards this surface to coalesce the reduced titanium on the surface of the mass, and to prevent condensation of the by-product sodium chloride on this surface. This mass of titanium is preferably an ingot, and the reacting gases preferably maintain the top of the ingot molten so that the reduced titanium coalesces on the surface of this ingot. In other forms of the invention the heat of the reaction forms a coalesced mass in the form of a sponge or compact powder, while in still other embodiments of the invention the heat of the reaction is used solely to vaporize the by-product sodium chloride. In all embodiments of the invention, however, the vaporized by-product sodium chloride is either removed from the reaction chamber or is condensed on the walls thereof. In this latter case, the point of condensa-

tion of the by-product sodium chloride must be separate from the point of collection of the resultant titanium, if the titanium is to be produced in pure form.

In preferred forms of the invention, as mentioned previously, the heat of the reaction is such that the by-product sodium chloride is vaporized and the titanium is melted. The heat available for accomplishing these ends is a function of the heat of reaction, the radiation heat losses, and the temperature of the entering sodium and titanium tetrachloride. In order that there will be an excess of heat available for achieving the vaporization of the sodium chloride and for melting the product titanium, it is preferred that the sodium and titanium tetrachloride be introduced in gas phase. In order to limit the amount of refractory metals that must be used in the reaction chamber, one preferred embodiment of the invention contemplates the condensation of the sodium chloride in a portion of the reaction chamber separate from that portion thereof in which the product titanium is collected.

Referring now more particularly to the drawings, where like numbers refer to like elements in all the figures, the apparatus comprises a reaction vessel 10 defining therein a reaction chamber 12. Surrounding the reaction vessel 10 there is preferably positioned a second vessel 14, the space 16 between these two vessels being arranged to hold a liquid heat-exchange medium 18. Near the bottom of the reaction chamber 12 there is located an ingot-forming mold 20 in which a titanium ingot 21 is formed during the reaction. For achieving intimate mixture of the titanium tetrachloride and sodium vapors there is provided a "torch" 22 which separately feeds the two vapors into the reaction chamber and directs these two vapors together as they enter the chamber so as to form a flame 23 in which the reduction takes place. This flame 23 serves as the reaction zone and achieves complete reduction of the titanium tetrachloride to metallic titanium. Since the flame 23 is directed towards the ingot mold 20, the resultant titanium is caused to impinge on the surface of an ingot in the mold and to coalesce on this surface, the flame being sufficiently hot to maintain at least the upper surface of the ingot in molten condition.

The reaction chamber 12 includes a vacuum-pumping port 24 connected to a suitable vacuum-pumping system, not shown, which can evacuate the reaction chamber 12 to a low free air pressure on the order of less than .001 mm. Hg abs. Located near the bottom of the reaction chamber, and spaced to one side of the ingot mold, is an outlet pipe 26 for removing liquid sodium chloride 27.

The vapor pressure of the heat-exchange medium 18 is controlled by a pressure relief valve, generally indicated at 28, the setting of this pressure relief valve 28 controlling the temperature of the liquid heat-exchange medium as a function of the vapor pressure in the space 16a thereabove. The liquid heat-exchange medium, as indicated previously, is preferably sodium since sodium has excellent thermal conductivity at high temperatures, and also since it must be vaporized for use in the preferred reaction described above. In the preferred arrangement shown the sodium vapors existing in the space 16a above the surface of the liquid sodium 18 are used as a source of supply for the sodium vapors fed to the torch 22. This torch 22 comprises, in the preferred form shown, a rod 30 preferably formed of a refractory metal, such as molybdenum, having a plurality of holes 32 near the periphery thereof (see Fig. 2). A central hole 34 is also provided in the rod 30, the holes 32 being for the purpose of feeding sodium vapors into the reaction zone, and the hole 34 being for the purpose of feeding titanium tetrachloride vapors into the reaction zone. This "torch" provides a short flame in which there is thorough intermixing of the sodium and titanium tetrachloride vapors. This flame 23 is preferably a forced diffusion type of flame which achieves complete reaction, in a highly concentrated zone, between the sodium and titanium tetrachloride vapors. The sodium vapors are fed to the holes 32 by means of a

distributing collar 36 in communication with the upper ends thereof; while titanium tetrachloride vapors are fed to the hole 34 by means of a tube 38 connected to the upper end of this hole 34. A pipe 40 leads from the space 16a above the level of the molten sodium, this pipe 40 being connected to the collar 36 and the flow of sodium vapor through this pipe being controlled by a valve 42. This valve 42 is preferably provided with a long stem 44 having an exteriorly positioned operating handle 46 and a water-cooled seal 48.

The pressure relief valve 28 for controlling the vapor pressure of the sodium in the chamber 16 comprises a valve 52, the degree of opening of which is controlled by a pressure responsive device, such as a spring 54. A pipe 56 is included for permitting escape, to a suitable receptacle, of excess sodium vapors generated in space 16a by the exothermic reaction which occurs within the reaction chamber 12.

The mold 20 in which the titanium ingot 21 is formed comprises a curved flange portion 60 surrounding a central cylindrical portion 62, these two portions being preferably integral and formed of a refractory metal, such as molybdenum. At the bottom of the central cylindrical section 62 there is included a reducing die 64 which reduces the diameter of the titanium ingot 21 as it is withdrawn by a pair of rolls 65. This reducing die 64 thus serves as a vacuum seal to prevent passage of air into the reaction zone between the boundaries of the forming ingot and the mold surface. Surrounding the mold is a liquid sodium guide 66 which serves to cause flow of liquid sodium into heat-exchange relationship with the exterior surfaces of mold portions 60 and 62, this sodium being introduced through a pipe 68 and, in one preferred form of the invention, the entering liquid sodium being at a lower temperature than the remainder of the sodium 18 in the space 16 so as to remove heat from the mold walls at a high rate.

A sight tube 70 is positioned near the top of the reaction chamber, this sight tube extending through the inner and outer vessels 10 and 14 respectively, and through a layer of insulation 72 which preferably surrounds the whole apparatus. At the top of the sight tube there is provided a sight glass 74 adjacent to which is positioned a water-cooling coil 76. Argon or other inert gas is preferably introduced through a pipe 78 so as to cause a flow of argon gas down the sight tube 70 to remove any vapors which might otherwise diffuse up the tube 70 and condense either as a smoke within tube 70 or as a coating on the inner surface of the sight glass 74. The sight glass 74 is preferably also provided with a wiper (not shown) for removing from the inner surface of the sight glass any condensed material which reaches the sight glass despite the argon flow.

The preferred operation of the device of Fig. 1, and the arrangement of the auxiliary equipment, is illustrated best in the flow diagram of Fig. 3 wherein like members refer to like elements in the other figures. In this Fig. 3 there is provided a storage chamber 80 for holding the reducible metal compound A (e. g. titanium tetrachloride). A supply tank for holding the molten metallic reducing agent B (e. g. sodium) is indicated at 82. A pump or valve 84 is included for feeding the titanium tetrachloride from the supply 80 to a vaporizer 86 therefor, while a pump or valve 88 is included for transferring molten sodium from supply 82 to the space 16 surrounding the reaction vessel 10. For electrolyzing the sodium chloride reaction product the pipe 26 leads to an electrolysis chamber 90, the sodium formed in this chamber 90 being piped to supply 82 through a filter 91 for removing impurities such as oxides. The chlorine generated in chamber 90 is piped to a reaction vessel 92 in which the titanium tetrachloride is formed by reaction with titanium dioxide and carbon. This manufacture of titanium tetrachloride is well described in chapter 17 of "Titanium, Its Occurrence, Chemistry and Technology,"

by Barksdale, published (1949) by the Ronald Press Co., New York. The resultant crude titanium tetrachloride is then piped to a crude storage tank 93 at which point a purifying agent such as oleic acid may be added. From the crude storage tank the crude titanium tetrachloride goes to a stripper 94 where some impurities, such as silicon tetrachloride, are removed. It then passes through a fractionation column 95, and the thus purified titanium tetrachloride is then pumped to storage chamber 80. For initially heating the sodium in the space 16 to a desired high temperature on the order of 1000° C. there is provided a heater 96 which heats the sodium to 1000° C., the vapors of the sodium condensing at the top of the space 16 and the condensed sodium being recirculated through the heater until the sodium in space 16 has been brought up to the desired temperature. If desired, separate condensers 97 and 98, for unreacted sodium and unreacted titanium tetrachloride, respectively, may be provided in the vacuum pumping line 24 leading to a vacuum pumping system schematically indicated at 99.

In the operation of the device shown in Figs. 1, 2, and 3, the supply chambers 80 and 82 are filled with titanium tetrachloride and sodium, respectively, some of the sodium being fed to space 16 so as to fill this space to the level indicated. Heater 96 is energized to heat the sodium in space 16 to the desired temperature, preferably about 1000° C. During the heat-up time the reaction chamber 12 is preferably being evacuated by means of vacuum pump 99 to a free air pressure on the order of less than about 1 micron Hg abs. In lieu of evacuating chamber 12 it may be purged of air by sweeping with argon introduced through pipe 78 at a pressure slightly in excess of atmospheric pressure.

When the reaction chamber 12 has been brought to its desired temperature of about 1000° C. the feed of argon through pipe 78 and down the sight tube 70 is commenced. The valve 42 is opened to allow sodium vapors to enter the distributing collar 36 and to pass down the outer holes 32 in the "torch" 22. At the same time the titanium tetrachloride is fed into the pipe 38 by pumping titanium tetrachloride from the supply tank 80 to the vaporizer 86. The thus vaporized titanium tetrachloride enters the central hole 34 in the "torch" 22 and mixes intimately with the sodium as the two vapors issue from the end of the torch. The feed of the sodium and the titanium tetrachloride vapors is preferably accomplished with a stoichiometric relationship therebetween. If desired an excess of sodium may be fed to the reaction zone, this excess being helpful in preventing formation of lower chlorides resulting from incomplete reduction of the titanium tetrachloride. During the travel of the titanium tetrachloride vapor down pipe 38 and through the hole 34 in the torch, this vapor is preferably super-heated by the heat of the reaction chamber to a temperature on the order of about 1000° C. The two hot vapors issuing from the end of the torch ignite with a highly exothermic reaction to give an intensely hot flame 23 in which the sodium reduces the titanium tetrachloride to metallic titanium with sodium chloride as a by-product. The flame temperature is preferably about 2000° C. so that the titanium formed therein is subjected to a temperature above its melting point. This flame is directed towards the top of the ingot 21 in the mold 20 and maintains the upper surface of this titanium ingot in molten condition. The metallic titanium formed by the reduction reaction is driven by the flame, and the initial velocity of the reactants, towards the surface of the ingot where it coalesces on the surface of this ingot. Since the temperature of the flame 23 is extremely high the by-product sodium chloride 27 remains in the vapor phase and is completely separated from the metallic titanium formed in the flame. The sodium chloride 27 is condensed on the walls of the reaction chamber, runs down these walls and is withdrawn

from the reaction chamber 12 by means of pipe 26. This sodium chloride 27 passes to the electrolysis chamber 90 where it is electrolyzed, by usual techniques, to sodium and chlorine. The resultant sodium is recirculated to the sodium supply 82 while the chlorine is passed to the reaction chamber for forming titanium tetrachloride by reaction with carbon and titanium dioxide. This titanium tetrachloride is then purified and fed to the titanium tetrachloride supply 80. Any unreacted sodium and titanium tetrachloride are separately condensed in condensers 97 and 98 and fed back to their respective supplies.

During the reaction the total pressure in the system is maintained at about atmospheric pressure by the argon which travels down sight glass tube 70, this argon being removed at a constant rate by the pump 99. The vapor pressure of the sodium in space 16 is maintained essentially constant during the process by the operation of the pressure relief valve 28. The sodium vapors which pass through pressure relief valve 28 are condensed in condenser 97 and then fed back to the sodium supply 82. The heat of condensation of the sodium may conveniently be utilized for vaporizing the titanium tetrachloride and maintaining the sodium supply molten by use of a suitable heat-exchange device (not shown).

As the titanium, formed in the flame 23, coalesces on the upper surface of the ingot 21 in the mold 20, the size of the ingot increases. Consequently, the ingot is withdrawn by rolls 65 as the titanium is added to the ingot, the level of the top of the ingot being preferably kept constant during this withdrawal. The control of the ingot withdrawal may be achieved by the use of thermocouples (not shown) which measure the temperature in the mold wall 62 and thus indicate the level of titanium therein.

Referring now to Fig. 4 there is shown still another embodiment of the invention wherein the desired end product of the reaction is a powder rather than an ingot. This embodiment will also be particularly described in connection with the formation of titanium powder by the reduction of titanium tetrachloride with sodium without intent to limit the scope of the invention thereby. This aspect of the invention is of particular importance where the resultant titanium is to be used for the manufacture of articles by powder metallurgy techniques or for making alloys by melting a mixture of titanium powder and another metal in powdered or solid form. In the Fig. 4 embodiment of the invention the reaction between the introduced titanium tetrachloride and sodium takes place as a relatively diffuse reaction in a relatively large reaction zone. In this embodiment the heat of the reaction per gram of reactants is the same as that in the previously discussed process. However, the heat is not so concentrated and is not directed against the collected titanium powder. Consequently, the titanium powder is not appreciably melted by the heat of reaction after it has been formed. However, the heat of reaction is used to maintain the temperature of the reaction zone and the point of collection of the titanium powder at a temperature above that at which the by-product sodium chloride will condense.

In Fig. 4 where like numbers refer to like elements in the other figures, the reaction chamber 12 is defined in part by a reaction vessel 102 which is preferably surrounded by a second vessel 104, these two vessels providing therebetween a space 106 in which a heat-exchange liquid 108 is positioned. Below the reaction chamber 12 is a titanium-powder-collecting chamber 110 which is also surrounded by two vessels 114 and 116, defining therebetween a second heat-exchange liquid space 118 in which the heat-exchange liquid 108 can circulate to permit maintenance of an even, high temperature at the walls defining the chambers 12 and 110. At the top of the chamber 12 is positioned a third chamber 120 into which the unreacted starting materials and the by-product

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sodium chloride move prior to leaving the system. Chamber 120 is also preferably defined by two vessels 122 and 124 between which there is provided a space 126 in which a second heat-exchange liquid is confined. This second heat-exchange liquid is preferably the sodium 18 used as the reducing agent. The titanium tetrachloride is preferably introduced, in the form of a gas, into the reaction chamber 12 through a pipe 128, the flow thereof being controlled by a valve 130. The sodium 18, also preferably in the form of a vapor, is preferably introduced, through a pipe 132, in to the reaction chamber at a point below the pipe 128, the flow of sodium vapor being controlled by a valve 134. This pipe 132 preferably leads from the space 126a above the level of the liquid sodium in space 126.

In the operation of the Fig. 4 device the heat-exchange liquid 108, which is preferably a metal or a metal salt (for example, lead, sodium chloride, or a suitable eutectic) is heated by external heaters of the type schematically indicated in Fig. 3. The heat-exchange liquid 108 is circulated to and from a suitable heating means, such as a heat exchanger, by means of pipes 136, 138 and pipe 140 connecting the spaces 106 and 118. Heating of the heat-exchange liquid 108 is preferably continued until it reaches a temperature of approximately 1200° C. If the heat of heat-exchange liquid 108 is not sufficient to raise the sodium temperature up to about 1000° C. the sodium can also be heated initially by heaters of the type schematically indicated at 96 in Fig. 3. The chambers 12, 110 and 120 are then evacuated to a low free air pressure by means of a vacuum pumping system connected to the exit pipe 24. If desired, a partial pressure of argon of a few millimeters Hg abs. may then be introduced into these three chambers. When the desired temperatures and pressures have been obtained in the system the valves 130 and 134 are opened, permitting stoichiometric flow of titanium tetrachloride and sodium, respectively, into the reaction chamber 12. These introduced vapors mix and give a diffuse reaction in the area shown at 12a, the heat of the reaction being primarily dissipated by radiation to the walls of the reaction chamber 12 where it is transferred to the heat-exchange liquid 108. Due to the circulation of heat-exchange liquid 108, it maintains the walls of reaction chamber 12 and the titanium-powder-collecting chamber 110 at a uniform high temperature, preferably at least 1200° C. The product titanium 111, due to its formation in a diffuse gas phase reaction, is in the form of a powder, this powder falling from the reaction chamber 12 to the collection chamber 110 where it is collected. The by-product sodium chloride is prevented from condensing on the walls of chambers 12 or 110, or on the produced titanium due to the high temperature maintained at these points by means of the heat-exchange liquid 108 and the relatively low total pressure, on the order of less than about 5 mm. Hg abs., maintained within chambers 12, 110, and 120. However, since the walls 122 of the third chamber 120 are at about 1000° C. the sodium chloride 27 will condense thereon so that it may be removed in liquid phase through a pipe 142 provided for this purpose. Any unreacted sodium or titanium tetrachloride cannot condense in any portion of the apparatus due to the high temperature of the interior thereof, and is withdrawn through the pipe 24 where these materials can be separately condensed. Depending upon the amount of radiation loss from the apparatus and the rate of feed of the reactant materials, the heat-exchange liquid 108 can be additionally heated or cooled to maintain its temperature relatively constant at a sufficiently high level so that the walls of the chambers 12 and 110 are above the condensation temperature of the sodium chloride at the pressure existing in the system.

The resultant titanium powder can be collected in a batch and removed after the apparatus has been shut

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down, or can be continuously or intermittently removed by means of an air lock mechanism schematically indicated at 144. In a preferred embodiment, the air lock mechanism 144 comprises a valve which intermittently discharges the titanium powder into a pipe 146. From the pipe the titanium powder may be put into cans having an inert atmosphere. Equally, it may be compacted and sintered into a rod or other shaped object as a final form or for use as a consumable electrode in an arc-melting process. Alternatively, it can be fed as a free powder or as a partially compacted powder to an arc or other melting chamber where it may be melted into a compacted sponge or an ingot. In any case the titanium powder should not be exposed to air until it has been compacted to a coarse powder, sponge, or ingot since, as originally formed, it will be highly absorptive to oxygen and may be spontaneously inflammable in air.

In accordance with the Fig. 4 embodiment of the invention it should be pointed out that the countercurrent flow of the titanium tetrachloride and sodium vapors is preferred since the highest concentration of sodium vapors is at the bottom of the reaction zone 12. Thus any relatively less volatile lower chlorides formed during the reduction step will tend to fall through a progressively higher concentration of sodium vapors so that they are completely reduced before they fall beyond pipe 132 through which the sodium vapors enter.

While the operation of the device of Fig. 4 has been discussed in connection with the use of separate heaters for bringing it up to the desired starting temperature, it should be apparent that the initial temperature may be achieved by burning two introduced gases, such, for example, as by introducing acetylene through pipe 132 and introducing oxygen through pipe 128.

In still another embodiment of the invention, illustrated in Fig. 5, additional heat is added to the heat of reaction to assist in heating the titanium produced by the reaction. This additional heat is in the form of an electric arc and may serve one or both of two functions. The first of these functions is to assure complete and thorough melting of the titanium formed in the reaction. This is particularly helpful in some cases when the reaction is first started and it is desired to assure the presence of a molten pool of titanium on the ingot in the mold at the start of the run. The second function can be the melting of a second metal in the form of a solid added to the metal at the top of the ingot so as to form an alloy with the produced titanium. In this case the electrode used for striking the arc is preferably a consumable electrode of the alloying metal.

Referring now specifically to Fig. 5, where like numbers refer to like elements in the other figures, the device of Fig. 1 is modified by the addition thereto of an electrode 150 slidably mounted in an insulating member 152 carried by a water-cooled flange 154. The remainder of the Fig. 5 embodiment of the invention is preferably otherwise made identical with the construction of the Fig. 1 embodiment of the invention. In the use of the Fig. 5 embodiment the arc from electrode 150 to the ingot 21 is preferably started before the sodium and titanium tetrachloride vapors are fed to the "torch" 22 so that the surface of the ingot 21 will initially be molten. This has the advantage that the initially formed titanium will have a very hot surface on which to impinge and will not tend to be scattered as a smoke throughout the system. When the electrode 150 is solely for the purpose of adding additional heat to the titanium ingot, it is run at a sufficiently low power level or is water-cooled so as not to contaminate the ingot. The reverse is, of course, true when the electrode is to be consumed by the arc.

In still another embodiment of the invention the process is operated as a batch process, the product titanium being obtained as a compacted powder, as a partially

melted sponge, or as an ingot. This form of the invention is illustrated in Fig. 6 in connection with a modification of the Fig. 1 apparatus. In Fig. 6, where like numbers refer to like elements in the other figures, the ingot-forming mold is replaced by a crucible 160 carried by a support 162 on the end of an operating rod 164. The rod 164 extends through a removable door 170 provided with a water-cooled block 166 and a vacuum seal 168. The movement of the rod 164 is preferably controlled by a suitable means, not shown, which can be manually or automatically operated for raising and lowering the crucible 160. Fig. 6 embodiment also includes a pipe 167 through which the vapors of a reducible compound may be introduced into the reaction zone along with the titanium tetrachloride.

In the operation of the Fig. 6 device the procedures can be the same as those described in connection with Fig. 1. However, in the Fig. 6 embodiment of the invention the crucible 160 is lowered as the titanium 21 is formed therein. By controlling the rate of feed of the reactants, the amount of heat loss from the crucible 160, and the distance between the flame emanating from the "torch" 22 and the product titanium, the physical characteristics of the resultant titanium may be widely varied. When the radiation heat losses are low, the rate of reactant feed is high, and the "torch" is close to the mass of formed titanium, the formed titanium will be completely melted and a solid ingot will result. When the heat is somewhat less, such as is the case when the rate of reactant feed is less, when the space between the "torch" and the mass of titanium is greater, or the heat loss is higher, the formed titanium will be produced as a more or less compacted sponge. When the temperature is even lower the titanium will be produced and collected as a powder.

As can be seen from the above discussion of the Fig. 6 embodiment of the invention, the crucible 160 serves to define the reaction zone. This crucible can be formed of a refractory such as zirconia which will not contaminate the product metal and is preferably heated gradually to the operating temperature of 1200° C. or above so as to avoid heat shock. This may be easily achieved by burning sodium and chlorine vapors in the "torch" 22 prior to the introduction of the titanium tetrachloride. During the operation of the reduction of the titanium tetrachloride, the crucible is preferably maintained at a sufficiently high temperature so that the by-product sodium chloride will not condense on the inner wall of the crucible 160. If some sodium chloride does condense on this inner wall at the start of the reduction step, it is vaporized therefrom by the heat of the reaction as the crucible is lowered during the build-up of the mass of titanium in the crucible.

While the invention has been specifically described in connection with the use of the preferred titanium tetrachloride as the reducible product-metal compound and the preferred sodium as the metallic reducing agent, numerous other materials may be employed. The essential attributes for the metallic reducing agent (B in Fig. 3), which enable it to achieve a satisfactory reduction of a reducible product-metal halide, are set forth below:

(1) The heat of reaction of the metallic reducing agent with the reducible product-metal halide must be great enough, at a temperature corresponding to the melting point of the product-metal, to supply at least enough heat for:

(a) The total heat capacity of the reactant materials and the by-products of the reaction between the pre-heat temperature and the melting point of the product-metal;

(b) The heat of vaporization of the by-product halide of the metallic reducing agent;

(c) The heat of fusion of the product-metal (where a coalesced product is desired);

(d) The heat loss in the "cold mold" 20 or its equivalent; and

(e) The radiation heat loss from the reaction flame.

(2) The free energy change of the reaction (ΔF), at a temperature corresponding to the melting point of the product-metal, must be favorable or a satisfactory yield must be possible by regulation of the pressure at which the reaction is carried out.

(3) The vapor pressure of the halide of the metallic reducing agent, which is a by-product of the reaction, shall be high in comparison with the vapor pressure of the product-metal at the melting point of the product-metal so as to achieve vaporization of this halide of the metallic reducing agent.

(4) The vapor pressure of the metallic reducing agent should be high because of the necessity for:

(a) Vaporizing the metallic reducing agent for the reaction; and

(b) Preventing the metallic reducing agent from remaining in the product-metal, particularly if there is any appreciable solubility of the two metals.

(5) The chosen metallic reducing agent should have no solubility, or very little solubility, in the product-metal at the melting point of the product-metal and, in addition, the metallic reducing agent should not react with the product-metal to form intermetallic compounds.

(6) It is not essential, but it is considered important from an economic standpoint, that the metallic reducing agent

(a) Have a low melting point;

(b) Have a small ratio of atomic weight to valence;

(c) Be easy to prepare from its halide by means such as electrolysis;

(d) Be capable of being prepared in, or purified to, a high state of purity free from nitrides and oxides in particular;

(e) Be noncorrosive or nonreactive with available materials of construction at the temperatures required;

(f) Be relatively abundant so that the capital investment in metallic reducing agent required for circulation in the system be low;

(g) Have good thermal conductivity; and

(h) Have a low heat of vaporization.

In preferred forms of the invention the reducible product-metal compound (A in Fig. 3) is a product-metal halide and preferably meets the following requirements:

(1) The product-metal halide is preferably volatile and preferably has a boiling point less than about 800° C. The product-metal halide does not decompose into lower halides at its volatilization temperature.

(2) The product-metal halide must be capable of being purified to a high degree to remove product-metal oxide or oxyhalide salts. The product-metal halide should have a vapor pressure or boiling point substantially different from any oxide or oxyhalide salt that the product-metal might form so that purification of the product-metal halide can be effected by distillation.

(3) The product-metal should have a vapor pressure which is low at its melting point and is low with respect to the pressure in the reaction zone to minimize loss of the product-metal by evaporation.

(4) The product-metal halide should have a satisfactory high heat of reaction with the chosen reducing agent.

When materials other than the preferred titanium tetrachloride and sodium are used, the temperature of the walls of the reaction chamber is adjusted so that it is above the melting point of the by-product compound formed during the reducing reaction and below that temperature at which the vapor pressure of the by-product compound is an appreciable portion of the total pressure in the reaction chamber. In order to achieve the above operating conditions it is only necessary to control the rate of heat removal by controlling the vapor pressure

above the heat-exchange medium surrounding the reaction chamber in the Fig. 1 form of the invention.

While the invention has been described primarily in connection with the manufacture of pure metals, it is equally adaptable to the manufacture of alloys. In this latter case a mixture of two reducible metal compounds may be fed into the reaction zone through the pipe 38 so that the two metallic compounds may be simultaneously reduced to form the desired binary alloy. Equally, tertiary and quaternary alloys may be formed, if desired, by the above process.

The following table lists a number of the various reducible compounds that can be introduced into the reaction zone so as to achieve a codeposition of these compounds to form alloys with the primary metal being produced in the reaction zone. This table gives, along with these compounds, the temperatures at which they have a vapor pressure of one atmosphere.

Table I

Alloying Element	Reducible Compound	Boiling Point, °K., 1 atm.
Aluminum	Aluminum Chloride (Anhydrous)	720
Silicon	Silicon Tetrachloride	330
Carbon	Carbon Tetrachloride	350
Zinc	Zinc Tetrachloride	604
Tin	Tin Tetrachloride	386
Hafnium	Hafnium Tetrachloride	590
Chromium	Chromium Trichloride	1,220
Molybdenum	Molybdenum Pentachloride	541
Tungsten	Tungsten Pentachloride	549
Vanadium	Vanadium Tetrachloride	437
Columbium	Columbium Pentachloride	516
Tantalum	Tantalum Pentachloride	507
Manganese	Manganese Chloride (Anhydrous)	1,463
Iron	Ferrie Chloride	592
Cobalt	Cobaltous Chloride	1,323
Nickel	Nickelous Chloride	1,260
Phosphorous	Phosphorous Pentachloride	439
Sulphur	Sulphur Dichloride	332

For convenience of illustration these reducible compounds of the alloying elements have been listed as the chlorides of the various alloying elements. In some cases the other halides may be preferable in view of their higher vapor pressures or other desirable characteristics. Equally, other reducible compounds thereof may in some cases be superior.

These compounds of the alloying elements may be mixed with the reducible compound of the primary metal at numerous points in the system. For example, in the manufacture of titanium alloyed with molybdenum, titanium tetrachloride is preferably the reducible compound of the primary metal, and molybdenum pentachloride is the compound of the alloying metal. In this case these two compounds may be:

(a) Mixed in liquid phase in the desired alloying proportions, flash vaporized, and then fed into the reaction zone as a mixed vapor;

(b) Separately vaporized and mixed in the desired proportions prior to introduction into the reaction zone; or

(c) Separately introduced, preferably in vapor phase, into the reaction zone.

Where the alloying compound is to be used only in small quantities, and it has a relatively low vapor pressure, it may conveniently be introduced into the reaction zone by passing the vapors of the primary metal compound over the alloying metal compound which is heated to a temperature sufficient to give the correct partial pressure of the alloying compound in the vapor stream entering the reaction chamber. Thus, for example, when manganese chloride is the alloying compound and a titanium alloy of approximately three percent manganese is desired, vapors of titanium tetrachloride at a temperature of 880° C. and a pressure of 20 lbs./in.² gauge should be allowed to come to equilibrium

over a mass of manganese chloride heated to a temperature of about 880° C. These temperatures will give the correct partial pressures of these two compounds (40.8 mm. MnCl₂, 2360 mm. TiCl₄) so that the resultant metal formed in the reaction zone will be a titanium alloy containing the desired three percent manganese.

When using alloying elements, such as aluminum and chromium, which have high vapor pressures at the melting point of the primary metal, for example titanium, it is necessary to use an amount of the alloying element compound in excess of that which is stoichiometrically correct for forming an alloy of a predetermined composition. This is due to the loss, by vaporization, of a portion of the reduced alloying element. The excess required can be readily determined by experimental runs with careful analysis of the final product.

The general principles controlling the formation of the binary systems discussed above are equally applicable to the formation of tertiary and quaternary alloys. To form these multielement alloys it is only necessary to introduce several of the reducible alloying compounds along with the primary metal compound, such as the titanium tetrachloride. When used in the claims, the word "metal" is intended to include alloys thereof as well as the pure metal.

It is equally feasible to introduce the alloying element in vapor, liquid or solid phase as the element rather than as a reducible compound thereof. This aspect of the invention was discussed previously in connection with the description of Fig. 6 above. This embodiment of the invention is particularly applicable in those cases where the alloying element is normally a gas, such as is the case where small predetermined quantities of oxygen or nitrogen are to be added to the primary metal (e. g., titanium) to increase its hardness or strength.

While the invention has been described in connection with the manufacture of pure metals or alloys thereof, it can be equally practiced in connection with the formation of lower halides, although this is a less preferred embodiment of the invention. The formation of lower halides can be considered as being of considerable importance in the production of starting materials for certain electrolytic processes. In the formation of these lower halides, for example the formation of titanium trichloride, the apparatus of Fig. 6 is particularly useful. In this modification of the invention the rate of feed of the titanium tetrachloride and the sodium is so adjusted that only partial reduction is achieved, the quantity of sodium fed being stoichiometrically correct for forming titanium trichloride, but being insufficient for forming titanium dichloride or metallic titanium. In this case the by-product sodium chloride is collected within the crucible 160 at a temperature of about 1000° C., and the titanium trichloride is condensed at a temperature of about 900° C. on the walls of the vessel 10. This titanium dichloride is preferably removed in a more or less continuous manner by a scraper mechanism and ejected through a suitable airlock system of the type schematically shown at 144 in Fig. 4. If desired, the resultant titanium trichloride can be fed directly into a suitable electrolysis chamber.

In the above discussion of the various embodiments of the invention the flow sheets have been shown with circulation of liquid compounds, such as titanium tetrachloride, between the various portions of the apparatus. In some cases the reducible compounds are solid at room temperature or at elevated temperatures. In such cases the materials can be handled as solids or can be handled as liquids under super atmospheric pressure. Additionally, these materials can be circulated as vapors at elevated temperatures and under reduced pressure, where necessary. In all cases contamination of the recycled materials should be kept to an absolute minimum. When titanium is being produced the purging action of the initially formed titanium on any oxygen in the system gives

a very pure material for recycling and, if proper precautions are taken, the addition of oxygen to the subsequently formed titanium is a minimum so that this subsequently formed titanium is of extremely high purity.

While one preferred recycling system has been outlined previously in the discussion of Fig. 3, numerous modifications may be made in this system. For example, the sodium chloride by-product may be treated, at low pressures, with calcium carbide to give sodium and calcium chloride. The calcium chloride can be burned in air to give calcium oxide and chlorine, while the calcium oxide can be converted to calcium carbide by reacting with carbon in an electric furnace.

Since certain changes may be made in the above process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description, or shown in the accompanying drawings, shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. In a process for producing a product metal selected from the group consisting of titanium, zirconium, hafnium, vanadium, columbium, tantalum, chromium, molybdenum, tungsten, iron, cobalt, nickel and mixtures thereof by reduction of a halide of the product metal with a metallic reducing agent selected from the group consisting of lithium, sodium, potassium, magnesium and calcium, the improvement which comprises mixing at least one halide and the reducing agent each in fluid phase in a reaction zone so that they react with intense heat to form a highly heated reaction flame which is at a temperature above the melting point of the product metal and above the vaporization temperature of the by-product halide, directing said flame against a body of the product metal to maintain the surface of the product metal at an elevated temperature above the vaporization temperature of the by-product halide and to collect the product metal in the flame on the hot product metal surface, the elevated temperature being due substantially to the reaction heat and the superheat of the reactants, and separately withdrawing the product metal and the by-product halide from the reaction zone.

2. In a process for producing a product metal selected from the group consisting of titanium and zirconium by reduction of a halide of the product metal with a metallic reducing agent selected from the group consisting of lithium, sodium, potassium, magnesium and calcium, the improvement which comprises mixing the halide and the reducing agent each in fluid phase in a reaction zone so that they react with intense heat to form a highly heated reaction flame which is at a temperature above the melting point of the product metal and above the vaporization temperature of the by-product halide, directing said flame against a body of the product metal to maintain the surface of the product metal at an elevated temperature above the vaporization temperature of the by-product halide and to collect the product metal in the flame on the hot product metal surface, the elevated temperature being due substantially to the reaction heat and the superheat of the reactants, and separately withdrawing the product metal and the by-product halide from the reaction zone.

3. The process of claim 2 wherein an alloy of said product metal is formed by coreducing a halide of at least one of the elements aluminum, silicon, carbon, zinc, tin, hafnium, chromium, molybdenum, tungsten, vanadium, columbium, tantalum, magnesium, iron, cobalt and nickel.

4. The process of claim 2 wherein the by-product halide is at least partially collected on the walls of a reaction chamber surrounding the reaction zone.

5. The process of claim 2 wherein the reaction zone is initially heated by burning sodium and chlorine therein.

6. The process of claim 2 wherein the product metal is collected as a partially sintered body.

7. The process of claim 2 wherein the product metal is collected in molten form and an alloying metal is added to the molten product metal.

8. The process of claim 2 wherein a mass of product metal in the reaction zone is initially heated by means of an arc.

9. The process of claim 2 wherein said product metal halide comprises titanium tetrachloride and said metallic reducing agent comprises sodium.

10. The process of claim 2 wherein said product metal halide is titanium tetrachloride and said metallic reducing agent is sodium.

11. In the process wherein the tetrachloride of titanium is reacted with an alkali metal reducing agent to form titanium as a product metal and a by-product chloride of said reducing agent within a reaction zone having an atmosphere that is substantially inert towards the product metal, the improvement, which comprises: mixing and reacting a stream of said tetrachloride in vapor phase with a stream of said reducing agent in vapor phase within said reaction zone to form a product stream consisting essentially of particles of said product metal entrained in said by-product chloride in vapor phase, the temperature of said product stream being above the boiling point of said by-product chloride, said temperature being due essentially to the heat of said reaction and the heat content of said reactants; directing said product stream into contact with the surface of a mass of said product metal so that particles of said product metal contained in said product stream contact and collect on said surface, said reactants being introduced into said process at a sufficiently fast rate and at a sufficiently high preheat temperature to cause said product stream to maintain said surface at a temperature that lies above the boiling point of said by-product chloride despite heat losses from said process; and separately withdrawing the product metal collected on said surface and said by-product chloride in vapor phase from said process.

12. In a process for producing titanium by reduction of a titanium tetrahalide wherein the reduction is accomplished in a reaction zone in a reaction chamber having an atmosphere which is substantially inert to the product titanium, the improvement which comprises introducing said titanium tetrahalide in vapor phase into said reaction chamber at a controlled rate, introducing a metallic reducing agent in vapor phase into said reaction chamber at a controlled rate with thorough mixing of said two introduced materials in the vapor phase so that they react with intense heat to reduce the titanium tetrahalide to titanium, said metallic reducing agent being selected from the group consisting of the alkali metals and alkaline earth metals, said reducing agent being introduced in sufficient quantity to achieve substantially complete reduction of the introduced product metal halide and to maintain some excess reducing agent vapor in the reaction chamber, said materials being introduced at a sufficiently fast rate and at a sufficiently high temperature so that the temperature of the reaction zone is sufficient to maintain molten the product titanium and to vaporize the by-product halide despite heat losses from the reaction chamber, the temperature of the reaction zone being due essentially to the reaction heat and the superheat of the reacting materials, said materials being directed against the surface of a mass of the product titanium so that the heat of the reaction is directed towards said surface to maintain said surface molten and the product titanium is collected on said molten surface, and condensing said by-product halide separately from the molten titanium surface.

13. In a process for producing titanium by reduction of a titanium tetrahalide with a metallic reducing agent from the group consisting of the alkali metals and the

alkaline earth metals, the improvement which comprises mixing vapors of the tetrahalide and a stoichiometric excess of vapors of the reducing agent in a reaction zone so that the vapors react with intense heat to reduce the tetrahalide to liquid titanium with the formation of a halide of the reducing agent as a by-product vapor, directing the liquid titanium and vaporous by-product halide against a liquid titanium surface superimposed on a solid titanium surface to separate liquid titanium from the reaction products, simultaneously removing heat from the solid titanium surface to solidify liquid titanium at the solid-liquid interface, and separately withdrawing the product titanium and the by-product halide from the reaction zone.

14. In a process for producing titanium by reduction of a titanium tetrahalide with a metallic reducing agent from the group consisting of the alkali metals and the alkaline earth metals, the improvement which comprises mixing vapors of the tetrahalide and vapors of the reducing agent in a reaction zone so that the vapors react with intense heat to form a highly heated reaction flame which is at a temperature above the melting point of titanium and above the vaporization temperature of the by-product halide, directing said reaction flame against the surface of a titanium body to maintain said surface molten by transfer of heat from the flame to the surface and to collect on the molten titanium surface liquid titanium carried in the flame, simultaneously removing heat from the titanium body to solidify liquid titanium at the solid-liquid interface, and separately withdrawing the product titanium and the by-product halide from the reaction zone.

15. In a process for producing a group IV metal from the class consisting of titanium and zirconium by reduction of a group IV metal tetrahalide with a metallic reducing agent from the group consisting of the alkali metals and the alkaline earth metals, the improvement which comprises mixing vapors of the tetrahalide and vapors of the reducing agent in a reaction zone so that the vapors react with intense heat to form a highly heated reaction flame which is at a temperature above the melting point of the group IV metal and above the vaporization temperature of the by-product halide, directing said reaction flame against the surface of a group IV metal body to maintain said surface molten by transfer of heat from the flame to the surface and to collect on the molten group IV metal surface liquid group IV metal carried in the flame, simultaneously removing heat from the group IV metal body to solidify liquid group IV metal at the solid-liquid interface, and separately withdrawing the product group IV metal and the by-product halide from the reaction zone.

16. In a process for producing zirconium by reduction of a zirconium tetrahalide with a metallic reducing agent from the group consisting of the alkali metals and the alkaline earth metals, the improvement which comprises mixing vapors of the tetrahalide and vapors of the reducing agent in a reaction zone so that the vapors react with intense heat to form a highly heated reaction flame which is at a temperature above the melting point of zirconium and above the vaporization temperature of the by-product halide, directing said reaction flame against the surface of a zirconium body to maintain said surface molten by transfer of heat from the flame to the surface and to collect on the molten zirconium surface liquid zirconium

carried in the flame, simultaneously removing heat from the zirconium body to solidify liquid zirconium at the solid-liquid interface, and separately withdrawing the product zirconium and the by-product halide from the reaction zone.

17. In a process for producing titanium by reduction of a titanium tetrahalide wherein the reduction is accomplished in a reaction zone in a reaction chamber having an atmosphere which is substantially inert to the product titanium, the improvement which comprises introducing said titanium tetrahalide in vapor phase into said reaction chamber at a controlled rate, introducing a metallic reducing agent in vapor phase into said reaction chamber at a controlled rate with thorough mixing of said two introduced materials in the vapor phase so that they react with intense heat to reduce the titanium tetrahalide to titanium, said metallic reducing agent being selected from the group consisting of the alkali metals and magnesium, said reducing agent being introduced in sufficient quantity to achieve substantially complete reduction of the introduced product metal halide and to maintain some excess reducing agent vapor in the reaction chamber, said materials being introduced at a sufficiently fast rate and at a sufficiently high temperature so that the temperature of the reaction zone is sufficient to maintain molten the product titanium and to vaporize the by-product halide despite heat losses from the reaction chamber, the temperature of the reaction zone being due essentially to the reaction heat and the superheat of the reacting materials, said materials being directed against the surface of a mass of the product titanium so that the heat of the reaction is directed towards said surface to maintain said surface molten and the product titanium is collected on said molten surface, and condensing said by-product halide separately from the molten titanium surface.

18. In a process for producing a metal selected from the group consisting of titanium and zirconium by reduction of a tetrahalide of said metal with a metallic reducing agent selected from the group consisting of the alkali metals and magnesium, the improvement which comprises mixing vapors of the tetrahalide and vapors of the reducing agent in a reaction zone so that the vapors react with intense heat to form a highly heated reaction flame which is at a temperature above the melting point of the metal and above the vaporization temperature of the by-product halide, directing said reaction flame against the surface of a body of said metal to maintain said surface molten by transfer of heat from the flame to the surface and to collect on the molten metal surface liquid metal carried in the flame, simultaneously removing heat from the metal body to solidify the liquid metal at the solid-liquid interface, and separately withdrawing the product metal and the by-product halide from the reaction zone.

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