April 14, 1959 C. L. SCHMIDT ET AL **2,882,143**

CONTINUOUS PROCESS FOR THE PRODUCTION OF TITANIUM METAL

Filed April 16, 1953 2 Sheets-Sheet 1

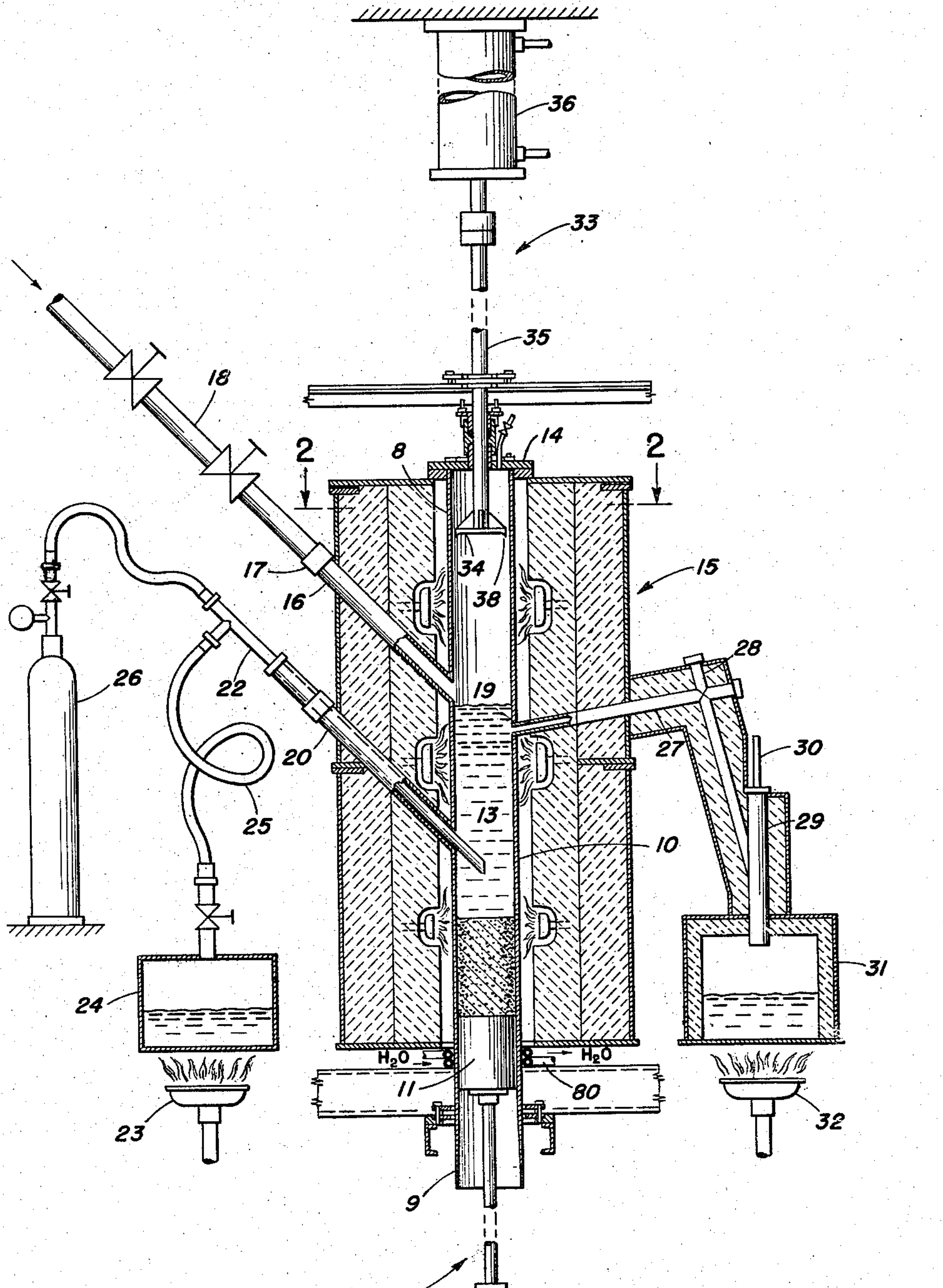

Fig. 1.

INVENTORS
Charles L. Schmidt
Carl K. Stoddard
BY
Charles F. Kaegebehn
ATTORNEY

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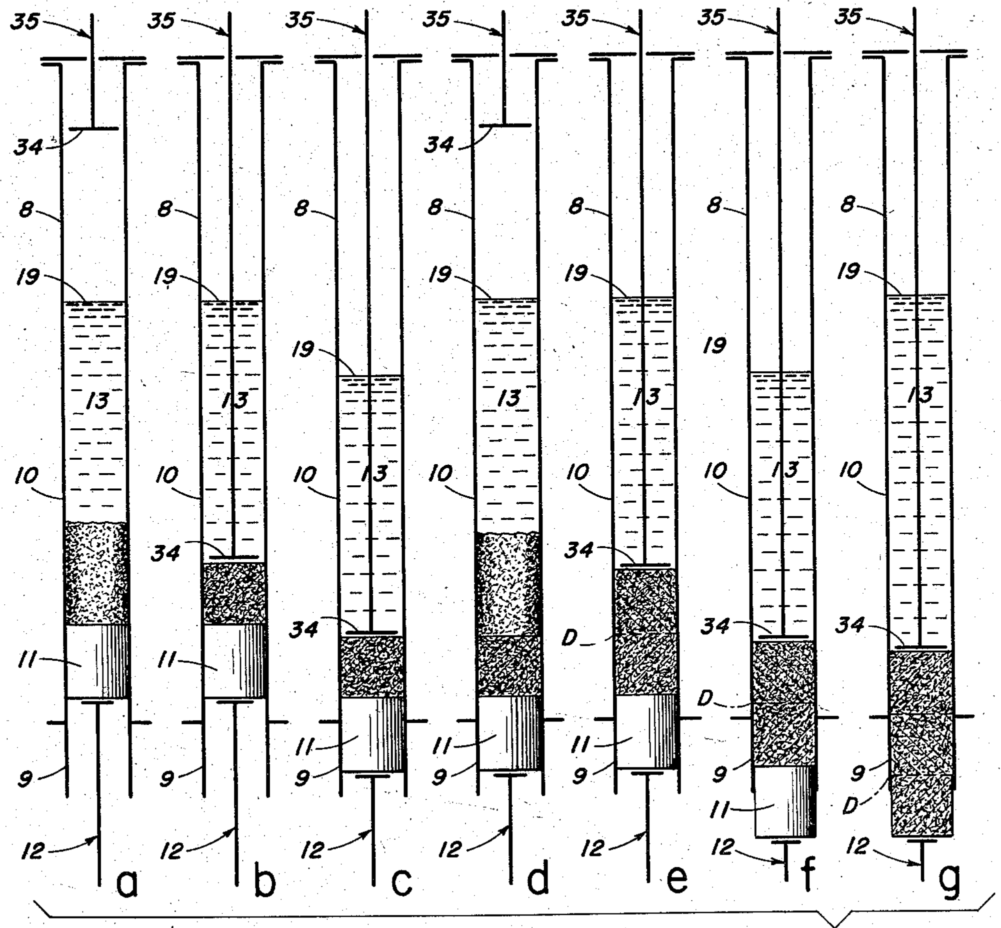

Fig. 3.

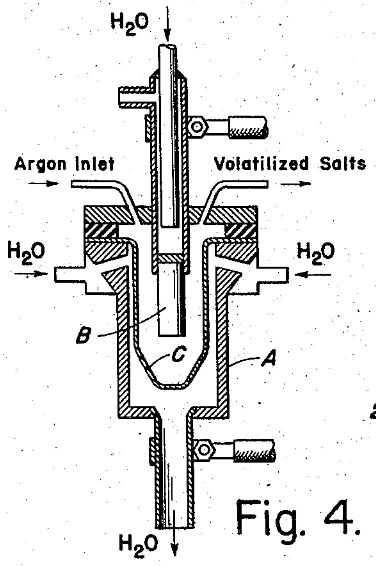

Fig. 4.

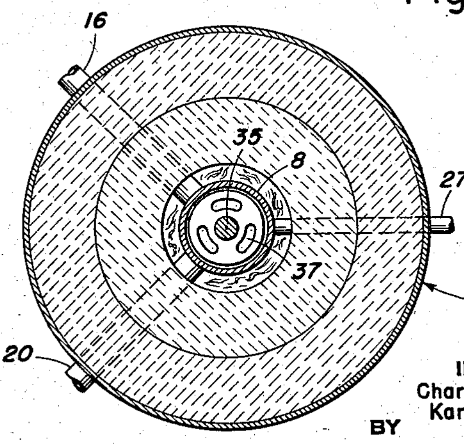

Fig. 2.

INVENTORS
Charles L. Schmidt
Karl K. Stoddard
BY
Charles F. Kaegebehn
ATTORNEY

2,882,143
Patented Apr. 14, 1959

2,882,143

CONTINUOUS PROCESS FOR THE PRODUCTION OF TITANIUM METAL

Charles L. Schmidt, Fair Haven, N.J., and Carl K. Stoddard, Henderson, Nev., assignors to National Lead Company, New York, N.Y., a corporation of New Jersey

Application April 16, 1953, Serial No. 349,222

10 Claims. (Cl. 75—84.5)

This invention relates in general to a method for producing a refractory metal from a refractory metal halide and specifically, to an improved process and means for producing a titanium metal compact of continuous length by reacting titanium tetrachloride with molten alkali metals or alkaline earth metals including magnesium.

In general, the processes which have heretofore been developed for producing titanium metal by reduction of titanium tetrachloride with alkali metals and alkaline earth metals including magnesium have been, for the most part, "batch" type operations. For example, the Kroll Patent No. 2,205,854, June 25, 1940, and the Schlechten et al. Patent No. 2,482,127, September 20, 1949, describe methods for producing titanium metal by reacting titanium tetrachloride with a molten alkaline earth metal in a reaction pot whereby a titanium metal product is formed which comprises a hard metallic sponge-like mass of material. It is characteristic of these processes that the metallic sponge adheres tightly to the walls of the reaction pot and can be removed therefrom only at great expense, loss of time and impairment of the quality of the titanium metal. Other examples of current efforts to produce titanium metal are the Maddex Patent No. 2,564,337, August 14, 1951, and the Winter, Jr., Patent No. 2,586,134, February 19, 1952, each of which is directed towards the production of refractory metals in a manner to avoid the distinct disadvantages of a batch type process.

In all of the aforementioned and similar processes heretofore used, the metal is formed in small batches and/or by resorting to complicated and expensive apparatus. As a result, the production of refractory metal and in particular titanium metal, has been slow, laborious and at great expense.

An object of the present invention is to provide an improved process for the preparation of a refractory metal by the reaction of a refractory metal halide with a molten alkali metal or alkaline earth metal including magnesium wherein the recovery of the refractory metal is substantially continuous, direct and economical.

A further object of the invention is to provide an improved method and means for producing a high quality refractory metal compact in a substantially continuous operation.

Another object of the invention is to provide an improved method for reacting titanium tetrachloride and liquid magnesium metal in a manner to form, consolidate and recover titanium metal as a titanium metal compact of substantially continuous length.

A still further object of the invention is to form a titanium metal billet which may be used as an electrode in an arc furnace to separate the metal from salt inclusions.

These and other objects of the instant invention will become more apparent from the following more complete description and the accompanying drawings in which:

Figure 1 is a front elevation in section of the apparatus of this invention for producing a titanium metal compact substantially continuously.

Figure 2 is a transverse sectional view of the apparatus on line 2—2 of Figure 1.

Figure 3 is a diagrammatic view of the sequence of operations of the apparatus of Figure 1; and

Figure 4 is a diagrammatic view of an electric arc furnace utilizing a billet-electrode for separating and recovering the pure metal from salt inclusions.

In its broadest aspects, the present invention relates to an improved process for preparing a refractory metal substantially continuously by reacting a halide of the refractory metal with a molten metallic reducing agent in a molten salt bath to form the refractory metal in the molten salt bath; and periodically consolidating the refractory metal in the bath to form and expel therefrom a refractory metal compact of continuous length.

More specifically, in accordance with the instant invention, the substantially continuous production of a refractory metal such as, for example titanium metal, is effected by providing a molten salt bath in a reaction chamber having an open bottom end, charging the molten salt bath with magnesium metal and introducing titanium tetrachloride to form titanium metal dispersed throughout the molten salt bath; and periodically consolidating the titanium metal to form a titanium metal compact in the bath which is expelled from the bath and from the bottom end of the vessel as a single integrated titanium metal compact of continuous length, sometimes referred to hereinafter as a titanium metal billet.

In one specific embodiment of the invention involving the preparation of substantially pure titanium metal, a molten salt bath comprising a molten metal halide, preferably magnesium chloride, is provided within a suitable reaction vessel which, as shown especially well in Figures 1 and 2, is an open ended metallic reaction vessel **8** formed of stainless steel or other suitable type of metal and substantially circular in cross section. The inside diameter of the vessel may be uniform throughout its length, but superior results have been achieved by forming the lower end, sometimes hereinafter referred to as the tail-pipe portion **9** thereof, as shown in Figure 1 with a slightly expanding internal diameter so that the metal billet may free itself from the walls of the vessel as the billet is expelled therefrom. An increase in internal diameter of the lower end of the tail-pipe portion **9** of the vessel, compared to the upper end thereof, of about 0.2 inch in approximately 20 inches has been found satisfactory for a vessel having an inside diameter of approximately 6 inches.

The inside of the reaction vessel above the tail-pipe portion **9** thereof constitutes a reaction chamber **10**, the bottom end of which is open but provided with slidable and removable closure means **11** which is preferably in the form of a metal end-plug arranged to fit up into the open bottom end of the reaction chamber **10** and to be removably held therein by suitable retaining means such as indicated generally at **12** in the drawings. The retaining means **12** may for convenience comprise a hydraulically operated jack arranged immediately beneath the removable end-plug **11** and adapted to support the latter in the open bottom end of the reaction chamber during the initial part of the reaction; and subsequently, following removal of the end-plug, to engage and support the lower extremity of the continuous billet of titanium metal as it is being expelled from the open bottom end of the reaction chamber.

Although a removable end-plug **11** and hydraulic jack **12** are quite satisfactory, it is within the purview of the invention to substitute a hydraulically operated ram or mechanically equivalent means both for initially closing the open bottom end of the reaction chamber and supporting the lower extremity of the billet.

The salt bath **13** is composed of a halide salt of a metal or metals selected from the group consisting of the alkali metals and alkaline earth metal including magnesium. It will be found convenient, whenever practical, to employ a product of the reduction as the salt bath, for instance when titanium tetrachloride is being reduced with magnesium, the salt bath may be composed of magnesium chloride. The salt bath materials may be introduced into the reaction chamber **10** before the cover **14** is put in position, or may be charged into the chamber by way of the reducing metal feed pipe, hereinafter described; and are maintained in a molten condition therein by heat exchange means which, as shown especially well in Figure 1, may comprise a substantially concentric furnace **15** arranged around and extending longitudinally of the reaction vessel and embodying a plurality of heating units of varying capacity to provide the heat necessary to maintain the molten salt bath at a preferred temperature hereinafter described.

In this connection it will be seen that the lower end of the furnace **15** terminates at approximately the bottom end of the reaction chamber **10** whereby the tail-pipe portion **9** of the reaction vessel is unheated, its overall length being such that the retention time of the billet in this relatively cool portion of the reaction vessel will correspond substantially to the time required for the titanium metal billet to cool down sufficiently both to freeze the salts entrained in the billet; and to preclude contamination of the billet by the oxygen in the atmosphere. In this connection auxiliary cooling means such as for example cooling coils **80** may be arranged around the upper end of the tail-pipe portion **9** to accelerate the dissipation of heat therefrom, if necessary, and hence provide positive control of the temperature in this critical region of the reaction vessel.

As indicated by the size and arrangement of the heating units of the furnace **15**, the latter is designed in a manner to heat the reaction chamber, and hence the salt bath non-uniformly whereby the temperature of the salt bath adjacent the lower end of the reaction chamber **10** is at a minimum value corresponding substantially to the freezing temperature of the salt bath; and increases substantially uniformly upwardly to a maximum temperature in the upper regions of the bath for most efficient reaction between the halide of the refractory metal and the reducing metal. This temperature range will vary, of course, depending upon the melting points of the materials used to form the salt bath. In particular, when magnesium chloride is employed as the salt bath, the temperature gradient of the bath varies from the freezing temperature of the salt bath of about 712° C. adjacent the bottom end of the reaction chamber **10** to an upper temperature of from about 880–890° C. adjacent the top of the bath, the preferred average temperature of the salt bath in the reaction chamber being about 800° C. As pointed out above, the lowest temperature of the salt bath is substantially adjacent the bottom end of the chamber **10**, corresponding to the lower end of the furnace **15**, so that at and below this point the molten salt bath will freeze and automatically form an effective seal between the compact being formed in the open bottom end of the reaction chamber and the inner walls thereof.

Roughly then, the bottom end of the reaction chamber **10** corresponds substantially to the freezing level of the salt bath within the reaction vessel. Since collection and compacting of the titanium metal is carried out in the molten salt bath, the freezing level of the molten salt bath represents the very lowest point in the reaction chamber at which the titanium metal compact may be formed. Preferably, however, the end-plug **11** which serves temporarily as the bottom end-closure of the reaction chamber and against which the formation of a titanium metal campact is initiated, is located within the reaction chamber at a point somewhat above the ffreezing level of the molten salt bath, and highly satisfactory results have been achieved when the end-plug **11** has been located at a point in the chamber at which the temperature of the magnesium chloride salt bath is from about 715–720° C.

The reducing agent such as magnesium, calcium, sodium or other metal having a reducing potential greater than titanium may be charged into the molten salt bath from the top thereof either in the form of solid metal or in a molten condition.

Preferably magnesium metal is used as the reducing metal and is charged into the reaction vessel in the form of solid rods or bars by way of a delivery pipe **16**, one end of which intersects the wall of the reaction vessel and the opposite end of which is connected, by means of a flanged coupling **17** or the like, to an air lock, indicated generally at **18**, whereby the rods of magnesium metal may be introduced successively into the delivery pipe while excluding air from entering the reaction chamber. In the preferred construction shown, the longitudinal axis of the delivery pipe **16** extends upwardly at an angle of substantially 45° with the longitudinal axis of the reaction vessel, the inner end of the delivery pipe intersecting the wall of the reaction vessel at a point above the top surface **19** of the molten salt bath **13**.

The halide of the refractory metal, in this instance vaporous titanium tetrachloride, may be introduced in either of two ways i.e. either above the upper surface of the molten salt bath or beneath the upper surface of the bath. Preferably the titanium tetrachloride is fed into the molten salt bath **13** below the upper surface **19** thereof, and to this end a feed pipe **20** is provided which intersects the wall of the reaction vessel at a point well below the upper region of the salt bath, the longitudinal axis of the feed pipe **20** extending upwardly at an acute angle with the longitudinal axis of the reaction vessel. Although the feed pipe **20** is shown, for simplicity, substantially in the plane of the delivery pipe **16**, it will be understood that the two pipes may be in different vertical planes.

The titanium tetrachloride feed pipe **20** may be a metal pipe fixedly secured to the wall of the vessel and terminating at its inner end substantially flush with the wall of the reaction chamber. In the preferred construction, however, the feed pipe is a composite member comprising the fixed metal pipe **20** and a telescoping metal lance **22** which is slidable longitudinally within the metal pipe **20** and which is of such length that during the reaction period the inner end of the lance may be extended into the molten salt bath substantially to the center thereof. It has been found that this expedient obviates any tendency there might be for the titanium metal sponge to form at the intersection of the feed pipe with the wall of the chamber or longitudinally of the walls thereof.

As pointed out above, the titanium tetrachloride is fed into the bath preferably at a point below the upper surface thereof and although the titanium tetrachloride may be in liquid form, it is preferred to use gaseous titanium tetrachloride. To this end suitable heating means, indicated generally at **23**, may be provided for vaporizing a source **24** of liquid titanium tetrachloride which is connected by means of a flexible connection **25** to the movable lance **22** of the feed pipe **20**. In addition, the feed pipe **20** is wrapped or otherwise covered with suitable heat insulating material.

Since the presence of oxygen in the reaction vessel during the reaction is exceedingly detrimental to the quality of titanium metal produced, the titanium tetrachloride feed pipe is carefully sealed against the admission of oxygen into the reaction vessel. As one expedient to this end suitable apparatus, indicated generally at **26**, is connected to the outer end of the lance **24** to maintain helium or a similar inert gas in the lance at all times so that whatever the vaporous titanium tetrachloride feed is shut off, sufficient helium gas is present in the lance to preclude the entry of air or oxygen into the molten salt bath. In like manner, the inert atmosphere within the lance precludes admission of the molten salt bath up into the open inner end thereof. The vertical distance from the inner end of the lance **22** of the titanium tetrachloride feed pipe **20** to the upper surface **19** of the salt bath **13** may vary to some degree, and unusually successful operation of the reactor has been achieved when the feed pipe lance enters the bath at a point nearer the bottom than the top of the bath.

In this connection the level **19** of the admixture of molten salts and molten magnesium metal is maintained throughout the reaction at a predetermined height within the reaction chamber by overflow control means comprising a tap pipe **27**, the inner end of which, as shown especially in Figure 1, intersects the wall of the reaction chamber at substantially the height selected for the preferred level of the molten salt. The tap pipe **27** slopes upwardly at a slight angle, preferably 5° or 10°, to the horizontal axis of the vessel and its outer end is open or provided with a removable closure to permit the introduction of a clean-out rod or the equivalent for clearing the tap pipe in the event it becomes clogged. Intersecting the tap pipe adjacent its outer end is the upper open end of a tap pipe extension **28** which slopes downwardly at an obtuse angle with the longitudinal axis of the vessel and intersects at its lower end a substantially vertical delivery pipe **29**, the upper end of which is provided with a delivery pipe extension **30** of reduced diameter also open at its upper end. The upper open ends of the respective extension pipes **28** and **30** provide access to the interiors of the respective pipes for rodding or clearing the latter of any condensed materials deposited therein and during normal operation would be capped to exclude the admission of air to the reaction chamber. Specifically, the material which overflows from the molten bath comprises, in the main, molten magnesium chloride which is formed by reaction of the reduced chlorides of titanium with the molten magnesium metal. Hence, as the reaction proceeds the level of the molten magnesium chloride rises until it overflows into the tap pipe **27** and thence by way of the tap pipe extension **28** and delivery pipe **29** into a recovery vessel **31**. Since solidification of the molten magnesium chloride within the aforementioned pipes would clog the pipes, the latter are designed not only so that they may be readily rodded but are preferably insulated and heated by external heating means such as indicated generally at **32** to insure free flow of the molten magnesium chloride therethrough.

Since molten magnesium metal has a lower specific gravity than that of molten magnesium chloride, one would expect it to float on the surface of the latter and be lost through the tap pipe **27**. However, it is postulated and has been substantiated by evidence that particles of titanium metal attach themselves to the globules of molten magnesium metal, thereby increasing the specific gravity of the latter such that the globules of molten magnesium metal migrate toward the bottom of the bath. Consequently, no significant amount of molten magnesium metal is carried out of the bath by way of the overflow pipes.

Pursuant to the objects of the invention, the titanium metal which is formed in the bath by reaction of the reduced chlorides of titanium i.e. the dichlorides and trichlorides, with the globules of molten magnesium metal, is periodically consolidated, that is to say, brought together into the form of a single compact mass of material comprising substantially pure titanium metal. In brief the consolidation of the titanium metal is effected by a ramming operation characterized by the use of a reciprocable piston-like ram, hereinafter described, adapted to make a smooth runnng fit in the cylindrical reaction chamber **10** and to be moved downwardly periodically through the molten bath **13**, thereby to collect a major portion of the titanium metal therein and carry it downwardly to the bottom of the bath; and thereupon or subsequently to compress the titanium metal against the upper end of the aforementioned removable end-plug **11** (or a previously formed compact of titanium metal) at the bottom of the reaction chamber with sufficient pressure to expel therefrom a large proportion of the inclusions of molten magnesium and/or molten salt and form a substantially solid titanium metal compact. In addition to its function of periodically collecting and compressing the titanium metal into the form of a compact within the molten salt bath, the ram serves also to integrate and expel successive titanium metal compacts from the bath by way of the open bottom end of the reaction chamber as a titanium metal billet of continuous length.

Referring to the drawings, the piston-like ram is indicated generally at **33** and comprises a ram-head **34** and a ram-head operating rod **35**. The ram is preferably actuated by hydraulic means, which is indicated generally at **36**, and is capable of applying pressure to the ram-head **34** for compacting the titanium metal against the end-plug **11** in the bottom of the reaction chamber **10**. The ram-head is a disc shaped member of a diameter to make a smooth running fit inside the reaction chamber. Since it is desirable to avoid trapping molten magnesium chloride in the titanium metal compact or on the top of the ram-head, the latter is provided with a plurality of apertures **37** which extend therethrough. Thus, as the ram-head is moved down through the molten bath **13**, the apertures **37** in the ram-head permit the molten material to pass upwardly above the ram-head while the imperforate portion of the ram-head collects and carries the titanium metal in the bath to the bottom of the reaction chamber where the particles of titanium metal are compressed by the ram-head to form a compact substantially free of the molten salt materials. Upon drawing the ram-head upwardly through the bath, the molten salt materials in the bath may pass down through the apertures in the ram-head so that when the latter is in its original uppermost position in the chamber **10**, substantially no molten material is retained on the top of the ram.

The ram-head **34** may also be provided with a cutting edge **38** which, as the ram-head is forced downwardly into the bath, serves to cut through and/or dislodge any particles of titanium metal which may be clinging to the walls of the reaction chamber.

As pointed out above, the temperature of the salt bath varies throughout the bath and is critical for the successful operation of the reactor. This is particularly true of the temperature of the bath at the lower end of the reaction chamber where freezing of the salt bath must occur in order to insure a seal between the compact being formed and the open bottom end of the reaction chamber. For a magnesium chloride bath the freezing point is about 712° C. which is, therefore, the maximum permissible temperature of the bath at the open bottom end of the reaction chamber. If other salts are employed, then the freezing temperature of the bath would be different. For example, if a sodium chloride bath is employed, then the maximum temperature of the bath at the open bottom end of the reaction chamber would be about 801° C.

The process by which the titanium metal billet is formed using the apparatus of this invention is illustrated especially well in Figure 3 and described briefly as follows: The reaction vessel is made ready for operation by raising and securing the ram-head **34** in its uppermost position in the reaction chamber, as shown in Figure 3*a*, and adjusting the hydraulic jack **12** so as to hold the steel end-plug **11** tightly in place in the bottom end of the reaction chamber **10** and preferably at a point at which the temperature of the bath is slightly above freezing as for example about 715–720° C. If available, it is preferred to drop a piece of titanium metal sponge into the reaction chamber onto the top of the end-plug **11** to serve as a starting material on which to form a compact in which instance the end-plug **11** would be located further down in the chamber so as to bring the titanium metal sponge at the aforesaid temperature level.

The molten salt bath **13** in the reaction chamber is prepared by adding crushed anhydrous magnesium chloride to the reactor and then heating the reactor to melt the anhydrous magnesium chloride and establish an average temperature in the molten salt bath of about 800° C. Heat is also applied to the magnesium chloride recovering vessel **31** to bring it up to a temperature of about 800° C., and similarly heat is applied to the titanium tetrachloride feed pipe **20** and the magnesium chloride overflow pipes to prevent solidification of the respective compounds therein.

After purging the entire system of oxygen and other deleterious gases, a hose from the helium source **26** is attached to the lance **22** of the titanium tetrachloride feed pipe **21** to maintain a continuous purge of helium gas therein. The lance **22** is moved downwardly in the feed pipe **21** until its lower end is advanced into substantially the center of the molten salt bath in the reaction chamber whereupon valves of the titanium tetrachloride vaporizing chamber **24** are open to admit vaporous titanium tetrachloride into the feed pipe. For optimum performance, the titanium tetrachloride vaporizing chamber should be kept at a temperature from between 500–600° C. and the feed pipe at a temperature between 300–400° C.

The magnesium metal in the form of ½ pound sticks is then added into the reaction chamber **10** from the air lock **18** in the top thereof, the vaporous titanium tetrachloride being concurrently fed into the bath initially at a relatively low rate and subsequently at an increased rate as the reaction proceeds. The magnesium metal is preferably added in amounts of 5% excess over the theoretical amount to reduce the titanium tetrachloride introduced.

After feeding a predetermined quantity of titanium tetrachloride into the bath **13** to form an appreciable amount of titanium metal, the titanium tetrachloride feed is cut off by means of a valve as shown in Figure 1, and the feed pipe lance **22** is withdrawn from the bath. During this time helium under slight pressure is maintained in the feed pipe lance to preclude entry of the molten bath material.

The ram-head is then released and moved down forcefully into the molten bath **13**, as indicated diagrammatically in Figure 3*b*, to collect the titanium metal therein and compress it against the end-plug **11** (or titanium metal sponge) in the bottom of the reaction chamber whereupon the ram is withdrawn and titanium tetrachloride is again fed into the molten salt bath to form additional titanium metal therein which is subsequently collected and compressed into intimate contact with the previously formed metal in the bath by subsequent ramming action of the ram.

The periodic feeding of titanium tetrachloride into the bath to form titanium metal and the collection, compression and integrating of the titanium metal is continued until a titanium metal compact of appreciable thickness is formed in the bottom of the reaction vessel. Thereafter, the titanium metal compact is expelled from the reaction chamber in the manner hereinafter described.

Referring again to the action of the ram, compression and integration of the titanium metal is effected by the force applied thereon by the ram while the titanium metal is being held from displacement from the reaction chamber by the aforesaid hydraulic jack and/or by freezing of the titanium metal to the walls of the chamber.

Preferably the force applied on the titanium metal is sufficient not only to compact and integrate the metal but to force therefrom molten magnesium metal and/or molten salts which may be trapped in or between the particles of titanium metal. In accordance with this practice, a compact of relatively dense substantially pure titanium metal is insured. By way of example, the pressure applied by a ram adapted to form a titanium metal compact substantially 6 inches in diameter is of the order of from 30 to 175 pounds per square inch.

Expulsion of the compacted titanium metal from the open bottom end of the chamber is effected by the force of the ram when the resistance to displacement of the titanium metal compact is either removed or decreased to a value less than the force being applied thereon by the ram i.e. by the pressure differential between the ram and the compact supporting means.

A characteristic feature of the invention is the production of a titanium metal billet of continuous length. To this end the hydraulic jack **12** is adapted initially to hold the metal end-plug **11** securely in the bottom end of the reaction vessel against the compression force of the ram during repeated ramming actions of the ram-head, as hereinabove described, until a metal compact of appreciable size has been formed in the chamber as shown in Figure 3*b*. Thereafter the hydraulic jack is lowered by a fractional amount of the thickness of the compact in the chamber, whereupon the ram-head is moved down forcefully against the titanium metal compact in the chamber, as shown diagrammatically in Figure 3*c*, to break the compact from the walls of the chamber, if necessary, and expel the compact from the molten salt bath by a fractional amount substantially equal to the amount by which the hydraulic jack has been lowered, the upper portion of the compact remaining in the bath.

In so doing, the metal end-plug **11**, which has been released by the jack, is also displaced downwardly from its initial position in the tail-pipe portion **9** of the vessel to a lower position. During the formation of the compact its lower extremity is substantially adjacent the freezing level of the molten salt bath in the reaction chamber, and hence a relatively thin skin of frozen salt forms between the lower end of the compact and the walls of the reaction chamber, and this thin skin of frozen salt adheres slightly both to the metal compact and the walls of the chamber and hence serves not only to hold the compact temporarily within the reaction chamber but also to seal off the lower end of the reaction chamber against the egress of the molten salt during expulsion of the titanium metal compact therefrom.

Following fractional expulsion of one compact from the reaction chamber, the periodic feeding of titanium tetrachloride and magnesium metal to the reaction chamber is resumed and accompanied by periodic ramming actions of the ram until a second titanium metal compact is formed in the reaction chamber, as shown in Figures 3*d* and 3*e*, the compression force of the ram being sufficient not only to expel molten magnesium metal and/or molten salt bath from the compacted metal but also to integrate the metal of the second compact with the metal of the upper portion of the preceding fractionally displaced metal compact.

Upon completion of the second titanium metal compact, the hydraulic jack is again lowered to release the end-plug 11 whereupon the ram is brought down into contact with the second compact, as shown in Figure 3*f*, thereby forcing a fractional part thereof downwardly out of the open bottom end of the reaction chamber in the manner hereinabove described.

The feeding and ramming actions are thus repeated in succession, thereby successively forming and integrating titanium metal compacts in the reaction chamber, which are expelled therefrom as a titanium metal billet of continuous length.

In actual practice the metal end-plug 11, which is initally disposed between the hydraulic jack and the first metal compact, is removed as soon as the titanium metal billet is long enough to permit the hydraulic jack to engage directly against the leading end of the billet for supporting the latter while successive compacts are formed and integrated on the upper end thereof within the salt bath, as shown in Figure 3*g*.

As pointed out above, while the hydraulic jack 12 and metal end-plug 11 provide satisfactory means for initiating the formation of the titanium metal billet and subsequently supporting the latter as it is expelled from the bottom end of the reaction chamber, an equivalent means may comprise a hydraulically or mechanically actuated ram arranged to act in opposition to the ram of the reaction chamber. In this connection it is within the purview of the invention to coordinate the actions of the respective rams such that during the formation of titanium metal compacts in the reaction chamber, equalized pressure will be maintained between the titanium metal compact and the lower ram to prevent expulsion of the compacts from the reaction chamber and to expel molten magnesium metal and/or the molten salts from the compacts; whereas, for expulsion of the billet a pressure differential is maintained between the two rams, in a direction to expel the titanium metal billet from the open bottom end of the reaction chamber.

It will be evident that the ramming action of the ram-head serves successively to collect titanium metal in the molten bath and compress it into the form of compacts of titanium metal; and that with each periodic expelling action of the ram, a portion of the compact already formed in the molten salt bath is forced out, that is to say, expelled from the bottom end of the reaction vessel as a fractional part of a billet. Under properly controlled conditions the reactor may be run uninterruptedly, thereby expelling a titanium metal billet of high titanium metal content.

The billet comprises, in the main, substantially pure titanium metal and relatively minor amounts of frozen salt which may be separated from the pure titanium metal by well known leaching and/or distillation techniques. It is also within the purview of the invention to recover the titanium metal by heating the billet to a temperature sufficient to volatilize the salts and melt the titanium metal. One way this may done quite effectively is to make the billet one electrode of an arc furnace A such as shown in Figure 4 and form an arc between the billet-electrode B and a second electrode of the furnace such as the copper crucible C. At the temperature of the arc the salts in the billet are volatilized off and the titanium metal melted to form a substantially pure metal ingot free of salt inclusions. During this treatment the volatilized chlorides are continuously swept out of the crucible by circulating an inert gas therethrough.

A typical run made with the apparatus described above was carried out as follows: 80 pounds of anhydrous magnesium chloride was introduced into the reaction vessel and heated for a period of substantially 5 hours until the magnesium chloride formed a molten bath within the reaction vessel. Helium gas was then introduced into the system to purge the system of any oxygen whereupon one-half pound sticks of magnesium metal were fed discontinuously into the bath over a period of 76 hours and at a rate of about 0.16 pound per minute so as to maintain substantially 5% excess of magnesium in the bath throughout the run, the total amount of magnesium fed into the bath being about 155 pounds. During this time substantially 574 pounds of vaporous titanium tetrachloride was fed into the bath in substantially 20 pound increments at a point substantially two feet beneath the upper surface thereof.

After each 20 pound increment of titanium tetrachloride had been fed into the bath, the ram was operated periodically to collect and compress the titanium metal in the bath and form a compact, and subsequently the hydraulic jack was lowered by a fractional amount of the thickness of a single compact and the ram operated to expel the integrated titanium metal compact by a corresponding amount from the molten salt bath. Thus, by successive ramming and expelling actions of the ram, successively formed compacts were integrated and expelled from the reaction vessel as a titanium metal billet measuring substantially 66" in length and of a diameter corresponding substantially to the inside diameter of the reaction chamber. The titanium metal billet analyzed as comprising from about 85% to 90% titanium metal by weight.

A portion of this billet was shaped in the form of an electrode approximately 5/8 square inch in cross section and about 6 inches long. This electrode, containing about 90% titanium metal, by weight, was then mounted in an arc furnace as one electrode of the furnace as shown diagrammatically in Figure 4. A current of about 200–300 amperes at from about 20–30 volts was passed through the billet-electrode and a second electrode of the arc furnace thereby developing a high temperature in the furnace. After maintaining the arc for a period of about two minutes substantially 1/6 of the billet-electrode was melted away, the frozen salts in the electrode being volatilized and carried out of the furnace by argon gas which was circulated through the furnace under about 2 pounds pressure. The molten titanium metal accumulated in the bottom of the furnace in the form of a substantially pure titanium metal button weighing about 30 grams.

From the foregoing description it will be manifest that the process and apparatus of the present invention provides a relatively simple, inexpensive and highly productive method for producing titanium metal of high purity and ductility; and that the titanium metal billet is extruded as a continuous length of substantially solid metal from which impurities may be readily removed at minimum expense, thereby precluding the high losses of metal, time and equipment which have characterized earlier batch methods for producing refractory metals.

While this invention has been described and illustrated by the examples shown, it is not intended to be strictly limited thereto, and other variations and modifications may be employed within the scope of the following claims.

We claim:

1. A process for producing a refractory metal compact which comprises: providing a reaction bath consisting of a molten halide salt of a metal selected from the group consisting of the alkali metals and alkaline earth metals including magnesium; introducing a reducing metal into said molten metallic salt bath; feeding a chloride of said refractory metal to said molten metallic salt bath and reacting said chloride with said reducing metal to form refractory metal particles in said bath; consolidating and positively compacting the refractory metal particles in said bath to produce a relatively dense refractory metal compact therein; and recovering said relatively dense refractory metal compact by applying pressure on said compact, thereby expelling said compact from said bath.

2. A process for producing a titanium metal compact which comprises: providing a bath consisting of molten magnesium chloride; introducing magnesium metal into said magnesium chloride bath to form molten magnesium metal in said bath; feeding titanium tetrachloride into said bath; and reacting said titanium tetrachloride with said magnesium metal to form titanium metal in said bath; periodically collecting and compressing the titanium metal in said bath to produce a relatively dense titanium metal compact therein; and recovering said titanium metal compact by applying pressure to said compact, thereby expelling said compact from said bath.

3. A process for producing a titanium metal compact which comprises: providing a bath consisting of molten magnesium chloride; introducing magnesium metal into said magnesium chloride bath to form molten magnesium metal in said bath; feeding titanium tetrachloride into said bath; and reacting said titanium tetrachloride with said magnesium metal to form titanium metal in said bath; periodically collecting the titanium metal in said bath and compressing the collected titanium metal with a compression force sufficient to expel substantially all in-

clusions of said molten salt from said collected titanium metal and form a relatively dense titanium metal compact in said bath; and recovering said titanium metal compact by applying pressure thereto, thereby expelling said titanium metal compact from said bath.

4. A process for producing a titanium metal compact which comprises: providing a bath consisting of molten magnesium chloride; introducing magnesium metal into said magnesium chloride bath to form molten magnesium metal in said bath; feeding titanium tetrachloride into said bath; and reacting said titanium tetrachloride with said magnesium metal to form titanium metal in said bath; periodically collecting the titanium metal in said bath and compressing the collected titanium metal with a compression force sufficient to expel substantially all inclusions of said molten salt from said collected titanium metal and form a relatively dense titanium metal compact in said bath; forming and integrating titanium metal compacts successively in said bath to produce a single billet of titanium metal; and recovering said single billet of titanium metal by applying pressure to said successively formed titanium metal compacts in said bath, thereby expelling a fractional part of each successively formed compact from said molten salt bath.

5. A process for producing a titanium metal compact which comprises: providing a bath consisting of molten magnesium chloride in a reaction chamber; introducing magnesium metal into said magnesium chloride bath to form molten magnesium metal in said bath; heating said bath in a manner to provide a temperature gradient in said bath ranging from the freezing point of said magnesium chloride adjacent the bottom of said reaction chamber to a temperature of about 840° C. adjacent the upper end thereof; feeding titanium tetrachloride to said magnesium chloride bath and reacting said titanium tetrachloride with said magnesium metal to form titanium metal in said bath; periodically collecting and compressing the titanium metal into the bottom of said reaction chamber at a level above the freezing point of said magnesium chloride bath to produce a relatively dense titanium metal compact therein; and recovering said titanium metal compact by applying pressure thereto, thereby expelling said titanium metal compact from said bath.

6. A process for producing a titanium metal billet which comprises: providing a bath consisting of molten magnesium chloride in a reaction chamber having a removable end-closure at one end; introducing magnesium metal into said magnesium chloride bath to form molten magnesium metal in said bath; heating said bath in a manner to provide a temperature gradient in said bath ranging from a temperature slightly above the freezing point of said magnesium chloride adjacent the removable end-closure of said reaction chamber to a temperature of about 840° C. adjacent the upper end of said reaction chamber; feeding titanium tetrachloride to said magnesium chloride bath and reacting said titanium tetrachloride with said magnesium metal to form titanium metal in said bath; periodically collecting and compressing the titanium metal into the bottom end of said reaction vessel against said removable end-closure to produce successively relatively dense titanium metal compacts therein; integrating the successively formed compacts in said bath to produce a single billet of titanium metal; and recovering said titanium metal billet by applying pressure to said successively formed titanium metal compacts in said bath, thereby simultaneously displacing said removable end-closure from the bottom end of said reaction chamber and expelling a fractional part of each successively formed titanium metal compact from said bath.

7. A process for producing titanium metal compact which comprises: providing a bath consisting of molten magnesium chloride in a reaction chamber having a removable end-closure adjacent its bottom end; introducing magnesium metal into said magnesium chloride bath to form molten magnesium metal in said bath; feeding titanium tetrachloride to said magnesium chloride bath and reacting said titanium tetrachloride with said magnesium metal to form titanium metal in said bath; periodically collecting the titanium metal in said bath; compressing the collected titanium metal in said bath against said removable end-closure by providing equalized pressure between said compact and said removable end-closure to oppose displacement of said removable end-closure from said reaction chamber, said compression force being sufficient to expel substantially all inclusions of said molten salt from said collected titanium metal and form a relatively dense titanium metal compact in said bath; and recovering the titanium metal compact from said bath by providing a pressure differential between the compact and the displaceable end-closure in a direction to effect displacement of said removable end-closure, thereby simultaneously to displace the titanium metal compact and the displaceable end-closure from said reactor chamber.

8. A process for producing a titanium metal billet which comprises: providing a bath consisting of molten magnesium chloride in a reaction chamber having a displaceable end-closure; introducing magnesium metal into said magnesium chloride bath to form molten magnesium metal in said bath; feeding titanium tetrachloride into said magnesium chloride bath at a point remote from the upper surface thereof and remote from the adjacent walls of said reaction chamber to form the reduced chlorides of titanium in said bath; reacting said reduced chlorides of titanium with said magnesium metal to form titanium metal in said bath; concurrently withdrawing molten magnesium chloride from said reaction vessel so as to maintain said bath at a predetermined level in said vessel; periodically collecting and compressing the titanium metal in said bath against the displaceable end-closure in said reaction vessel to produce a relatively dense titanium metal compact in said bath; exerting pressure on said compact simultaneously to displace said end-closure from said reaction chamber and simultaneously expel a fractional part of said titanium metal compact from said bath; subsequently periodically collecting and compressing additional titanium metal onto the fractional part of the preceding compact remaining in said bath to produce and integrate a succeeding titanium metal compact on the preceding compact, thereby to form a billet and recovering said billet by exerting pressure on the upper end thereof, thereby expelling said billet from said reaction chamber.

9. In a process for producing a refractory metal by reacting a multivalent halide of the refractory metal with a reducing metal in a bath consisting of a molten halide salt of a metal selected from the group consisting of alkali metals and alkaline earth metals including magnesium, the steps comprising: introducing the halide of said refractory metal into said bath to react with said reducing metal and form refractory metal particles in said bath; periodically collecting the refractory metal particles in said bath and compressing said refractory metal particles to expel said molten salt from the compressed refractory metal particles and form a relatively dense refractory metal compact in said bath and thereafter expelling the refractory metal compact from said bath.

10. A process for producing a refractory metal according to claim 1 wherein the molten metallic salt is concurrently withdrawn from said bath to maintain said bath at a predetermined level.

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