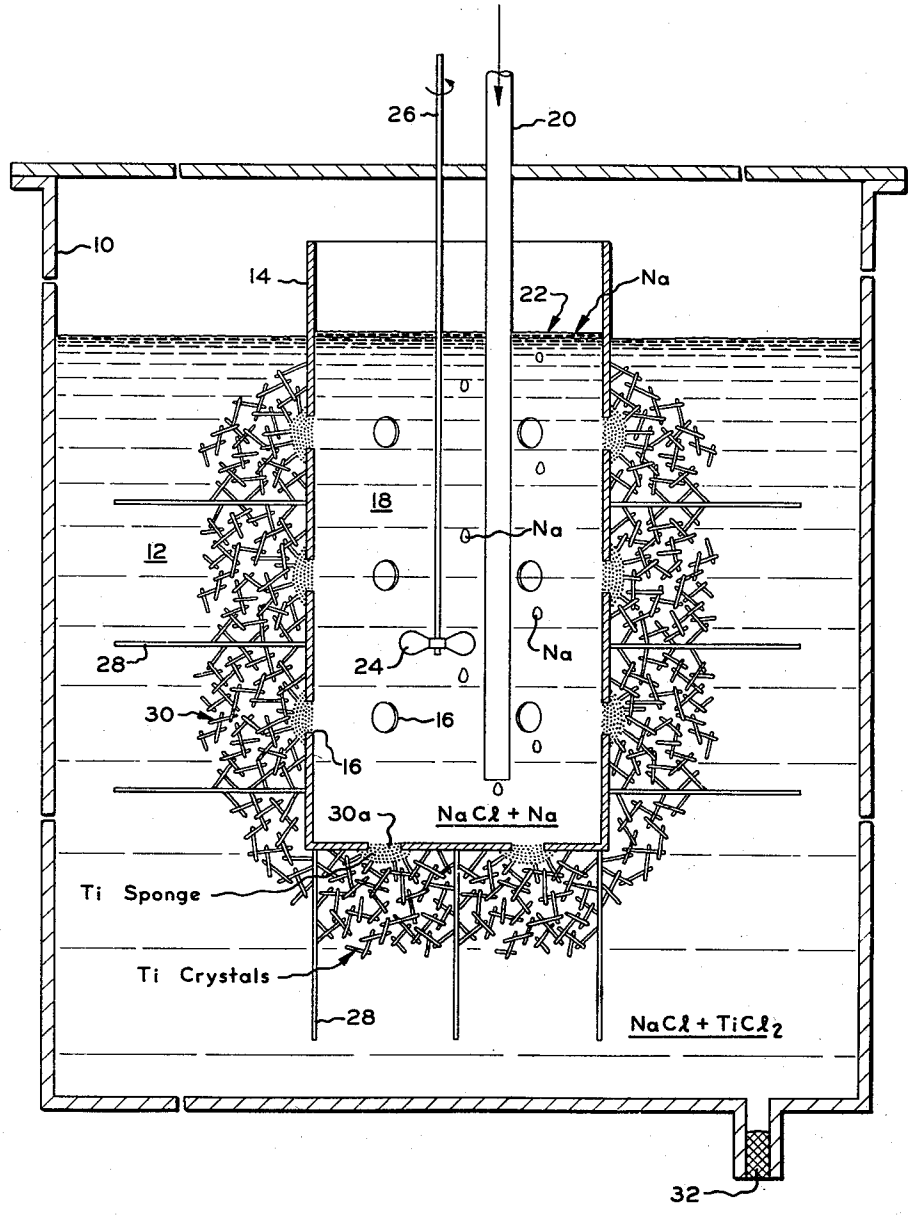
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METHOD OF PRODUCING TITANIUM

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METHOD OF PRODUCING TITANIUM

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This invention relates to the production of titanium and more particularly to the production of titanium by a process wherein a titanium compound is dissolved in a fused salt and is reduced to crystalline titanium metal by the addition of a molten metal reducing agent. This application is, in part, a continuation of our copending application Serial No. 373,512, filed August 11, 1953, and is, in part, a continuation of our copending application Serial No. 434,648, filed June 4, 1954.

Our aforesaid applications disclose a process for producing high yields of crystalline titanium wherein a molten reducing agent is fed to the upper surface of a molten bath of a lower halide of titanium dissolved in a fused salt. The process is so conducted as to form at the outset a thin crust of sintered titanium fines over the bath, adhering to the walls of the container and any other supporting structure that may be present. This porous layer of sintered fines acts as a barrier for segregating on its upper side a layer of fused salt in which the reducing agent is concentrated but in which the titanium halide content is low, this layer grading into the remainder of the bath in which the relative concentrations of reducing agent and titanium halide are reversed. This concentration gradient is maintained through the remainder of the process and constitutes an important condition of its operation. The sintered porous titanium barrier further performs the important function of a supporting bed from which titanium crystals grow downwardly into the titanium-halide-rich portion of the bath as the process continues.

An object of this invention is to provide a specific embodiment of the aforesaid process wherein the portion of the bath in which the reducing agent is concentrated may be maintained interiorly of the bath and below its surface, extending into the lower portion of the bath so that the titanium halide content of the bath may be more completely and efficiently utilized in the crystal growing operation. Another object is to provide such an embodiment in which the reducing agent may be more efficiently distributed through the portion of the fused salt bath which is substantially free of titanium halide. Other objects and advantages will be apparent from the ensuing detailed description, taken in connection with the accompanying drawing, the figure of which is a diagrammatic, schematic drawing illustrating one embodiment of the invention.

For simplicity of description and without intent to limit the invention thereby, it will be assumed, in the following discussion of the invention, that the reducing agent is sodium, that the titanium lower halide is a titanium lower chloride, and that the fused salt is sodium chloride. In accordance with our present invention, a foraminous shield or barrier is provided extending vertically within the fused salt bath. This shield either itself surrounds or, in combination with a wall portion, segregates a portion of the bath into which liquid sodium is fed. Preferably this shield takes the form of a cylinder, hemisphere or the like, open at the top and extending down into the

bath from above its upper surface. Preferably also it is of metal and may be formed of sintered titanium fines or "sponge." The liquid sodium feed tube preferably extends downwardly within the portion of the bath segregated by the shield to adjacent its lowermost portion.

The portion of the bath segregated by the shield constitutes essentially molten sodium chloride and the sodium fed thereto has little or no titanium chloride content. This may be accomplished initially by filling the area within the shield with a solid plug of sodium chloride which is melted after fused sodium chloride (with dissolved titanium lower chloride) is fed into the surrounding portion of the container. The foraminous shield then prevents substantial circulation of titanium chloride into the fused sodium chloride in its interior. Alternatively, the portion of the bath segregated by the shield may initially have the same concentration of titanium lower chloride as the remainder of the bath. In this case, the initial feed of sodium into this portion of the bath soon eliminates substantially all of the titanium chloride therein by reaction therewith to form titanium fines, these fines either sinking to the bottom of this portion or adhering to the shield as a porous, spongy layer.

As the feed of the sodium continues, the sodium concentration of this portion of the bath approaches saturation, and a sodium concentration gradient is established through the shield to the surrounding portion of the bath. Hence, the conditions for crystal growth as described in our aforesaid prior applications are established. The crystals grow outwardly from the exterior of the shield or from a layer of titanium sponge which may initially form thereover. Thus the shield acts as a supporting bed from which the crystals grow.

Since the point of sodium feed is preferably adjacent the bottom of the bath, the maintenance of a nearly saturated solution of sodium in sodium chloride is promoted and crystal growing conditions are established throughout the depth of the bath, thus providing efficient utilization of the entire titanium lower halide content within the bath outside the shield. Furthermore, the portion of the bath within the shield may be stirred to promote a thorough circulation and distribution of the sodium therein.

If desired, feed of sodium within the shield may be supplemented by feed of sodium also to the upper surface of the bath outside the shield. In this case, there will be established on the upper surface of the bath a porous layer of titanium sponge between the shield and the container wall, the sponge layer serving to segregate above it a layer of fused salt high in sodium and low in titanium chloride. Crystal growth from the lower portion of this horizontally extending sponge layer can proceed simultaneously with the growth of crystals outwardly from the shield.

Referring now to the drawing, there is illustrated one method of practicing the invention wherein **10** represents the reactor containing a charge of fused salt **12**, this fused salt **12** preferably comprising sodium chloride and containing a dissolved mixture of titanium dichloride and titanium trichloride. Positioned within the fused salt bath is a hollow perforated body **14**, in the form of a vertically extending cylinder, which is preferably formed of titanium and contains a plurality of perforations **16**. This perforated titanium cylinder **14** defines a space **18** which extends downwardly an appreciable distance into the fused salt bath. This space **18** is maintained essentially free of titanium chlorides, at least after the reduction reaction has proceeded for a short period of time. A feed pipe **20** is provided for feeding sodium near the bottom of cylinder **14**, excess sodium floating to the surface as indicated at **22**. A stirrer **24**

carried by a shaft **26** is preferably included for assisting in dissolving the sodium within the space **18**. Rods or fins **28** may be provided on the outside of the cylinder **14** to assist in supporting the growing mass of titanium crystals **30**. As shown in the drawing, each of the holes **16** is filled by a thin layer of titanium sponge **30***a* serving as a porous diaphragm for isolating the titanium-chloride-free salt **18** from the titanium-chloride-containing salt **12**.

In the operation of the device illustrated in the drawing, the cylinder **14** is positioned in the reaction chamber **10**. In one method of operation, this cylinder **14** is initially filled with a solid casting of sodium chloride. A molten mixture of sodium chloride and titanium lower chlorides (trichloride and dichloride) is then poured into the reactor to about the level indicated, this mixture preferably being formed by the partial reduction of titanium tetrachloride with sodium.

This molten mixture is preferably prepared in a separate reactor by reacting 1.7 moles of sodium with each mole of titanium tetrachloride to form a solution of titanium lower chlorides in sodium chloride. The resultant titanium chloride content (excluding the by-product sodium chloride) is approximately 30 mole percent titanium trichloride and 70 mole percent titanium dichloride. This relatively high proportion of titanium trichloride has been found highly desirable, since equilibrium studies indicate that the relative concentration of titanium trichloride in the mixture of titanium chlorides should be greater than about 11 mole percent. If this it not done, there is a possibility of producing some free titanium metal in the form of powder suspended in the fused salt. This free titanium powder can sinter to pipe walls and the like and drastically affect the flow of fused salt. However, if the titanium trichloride concentration (relative to the dichloride) is maintained above about 11 mole percent, any free titanium produced will be subsequently consumed by reaction with the titanium trichloride.

This molten mixture is preferably at a temperature of about 850° C. to 950° C. and will melt the sodium chloride inside the cylinder **14** so that the perforated cylinder **14** will thus at least initially separate an essentially titanium-chloride-free salt mass from a mass of salt containing dissolved titanium chloride. Sodium is then fed to the interior of the cylinder, the sodium going into solution and diffusing outwardly through the holes **16**. As the sodium diffuses outwardly, it will meet inwardly diffusing titanium chloride with which it will react to form titanium powder. Since this powder will be formed at the holes **16**, it will rapidly collect around these holes **16** to form a partially sintered sponge **30***a*, the sintered sponge serving to prevent gross flow of salt inwardly or outwardly through these holes while permitting diffusion of ions therethrough. Further feed of sodium to the thus isolated interior of cylinder **14** will provide a high concentration of dissolved sodium adjacent the inner side of the porous sponge **30***a*. This concentration gradient will decrease outwardly through the holes **16**, thereby establishing conditions for the growth of large crystals. Titanium crystals of large size will accordingly start to form on the outside of the sponge **30***a*, these titanium crystals forming an interlaced mass which, in itself, will provide an additional barrier to gross circulation of the solution adjacent the outer surface of the cylinder **14**. The growing mass of crystals will then also aid in maintaining the sodium concentration gradient, this gradient extending gradually outwardly from the cylinder as the crystals grow thereon. Accordingly, the growing mass of crystals can additionally serve as an extension of the initial permeable titanium layer, thus permitting the sodium concentration gradient to be carried out into points of the bath far removed from the perforated titanium cylinder **14**. During the latter stages of the run, some circulation of the titanium dichloride solution may be employed to assure substantial utilization of the dissolved titanium dichloride. When the reduction has been completed, a frozen salt plug (indicated at **32** at the bottom of the reactor) may be melted to allow drainage of the spent salt therefrom. This drains the great bulk of the salt away from the titanium crystal mass, this mass then being cooled and leached in acidified water to remove residual salt and any unreacted reactants such as the lower chlorides of titanium and sodium.

In our process, as previously noted, the porous shield or barrier which at least includes titanium fines and which produces a concentration gradient of reducing agent in the fused salt plays an important part. This shield not only acts as a crystal growing bed and support but also appears to function as a distributor for the reducing agent to the zone of crystal growth in such manner that crystal formation proceeds at a rate considerably faster than can be accounted for by the molecular diffusion rate of the reducing agent in fused salt. The crystal growth is also accomplished without substantial formation of free titanium fines in the bath once the crystal growing starts. Localization of the reducing agent in the zone of crystal growth can be accounted for by the fact that the reducing agent must initially pass through the shield or barrier from which the crystals grow, but the speed of the reaction indicates that the barrier supplements this function with some further action in distributing and directing the reducing agent to the locale of the crystal growing.

The mass transported in a fluid system by simple molecular diffusion can be expressed as mass transported per unit area per unit time under unit concentration gradient across unit distance. This quantity is called the "diffusion coefficient" and is a constant for a given system depending on viscosity, temperature, pressure, etc. A consideration of the basic properties of the liquid Na:NaCl system leads to a calculated value in the range of 10^{-5} to 10^{-4} for the molecular diffusion coefficient of sodium through sodium chloride. However, a series of experiments of the rate of transport of sodium through sodium chloride in a metal tube indicated that the observed transport of sodium at 850° C., under the conditions of our invention, is on the order of 10^{-2} to 10^{-3}, which is one to two orders of magnitude greater than that calculated for molecular diffusion. Additionally, this observed sodium transport is not constant but is dependent on experimental conditions which have no appreciable effect upon the molecular diffusion coefficient.

In these experiments, nickel tubes were mounted vertically in a furnace. The tubes were filled with molten sodium chloride and on top of the sodium chloride there was provided a layer of molten sodium. Accordingly, the nickel tubes spanned a concentration gradient of sodium in sodium chloride. At the end of predetermined periods of time, the bottom portions of the tubes were pinched off and separated from the remainder of the tubes. The salt in these bottom portions was then analyzed for metallic sodium content. From the actual sodium content, "apparent" diffusion coefficients were calculated as follows:

Tube Length, cm.	Inner Tube Diameter, inches	"Diffusion" Time, seconds	"Apparent" Diffusion Coefficient, cm.²/sec.
10	¼	3,600	0.0055
10	3/16	900	0.0110
10	3/16	3,600	0.0070
10	3/16	14,400	0.0039
15	3/16	3,600	0.0095
15	3/16	14,400	0.0060
10	⅛	3,600	0.0076

From a study of the above data, it is evident that the "apparent" diffusion coefficient is at least fifty to one hundred times the estimated molecular diffusion coeffi-

cient. There are also other anomalies in these data. Thus the "apparent" diffusion coefficient is found to vary with the time available for transport and is also a function of the length of the path available for transport and the tube diameter.

This dependence of the "apparent" diffusion coefficient on time and distance is not characteristic of molecular diffusion. However, these variations in sodium transport are compatible with the rate at which sodium can be generated at a distance, assuming electrochemical reactions at the walls of the tubes and subsequent electron transport by the walls. The observed rate of transport of sodium and the observed variations in the rate of transport both approximately fit an electrochemical mechanism. Thus, in the sodium diffusion experiments, the rate of transport of sodium down the tube and of chloride ions from the bottom to the top of the tube is consistent with rates which would be experienced in a concentration cell, with an electrical potential difference between salt saturated with sodium at the top and salt containing less sodium at the bottom.

In such a concentration cell, electrons are furnished at the top of the cell (e. g., the nickel tube) by ionization of dissolved sodium, these electrons traveling down the tube and liberating sodium at the points of lower sodium concentration. The resultant excess negative chloride ions at the bottom of the cell and positive sodium ions at the top of the cell will migrate toward each other. Since the migration of sodium ions and chloride ions in the existing electrical potential difference is much faster than molecular diffusion of sodium, the above-postulated concentration cell mechanism can explain a transport of sodium which is much faster than would be indicated if true molecular diffusion were controlling.

Comparing the tubes in the foregoing experiments with the network of cores in the shield or barrier, it will be apparent that a positive sodium distributing action is indicated for the barrier. If the transport of sodium through the porous barrier operates at least in part by electron transfer, the mechanism would be as follows: Due to the concentration gradient of sodium between the saturated solution of sodium in sodium chloride and the solution of titanium chloride in sodium chloride, an electrical potential difference is set up in the fused salt bath. This electrical potential difference is similar to the electrical potential difference existing in the simple sodium concentration cell since the concentration of sodium in the titanium chloride solution is very low. The electrons resulting from the ionization of dissolved sodium are conducted by the metal of the barrier, under the influence of the electrical potential difference, to points in the titanium chloride solution where the electrons may act to cause deposit of titanium atoms. The electrons can deposit titanium either directly or indirectly by release of sodium atoms which in turn react with titanium chloride to deposit metallic titanium on the barrier.

Since the barrier is porous, chloride ions and sodium ions are free to migrate therethrough, these ions traveling under the existing potential difference at a much higher rate of speed than in true molecular diffusion. As the titanium crystals grow on the barrier, these crystals in turn act as an extension of the barrier so that electrons can be carried to the farthest tips of the growing crystals. Observed titanium production rates, wherein sodium was introduced on one side of a porous barrier and titanium crystals were grown on the other side of the barrier, have been compared with theoretical titanium production rates, assuming the transport of sodium by the concentration cell mechanism. The actual titanium production rates were of the same order of magnitude as the calculated rates based on this theoretical mechanism.

While we are not certain of the exact mechanism of sodium transport accomplished by the porous barrier, it could be either a surface wetting transfer or the above-discussed electron transfer or perhaps a combination of both. Sodium contacting the metal surface of the barrier could, by wetting action on that surface, migrate downwardly and outwardly over the forming crystals. This would also tend to direct sodium feed to the point of crystal growth.

While a specific example of the invention has been discussed above, numerous alternative embodiments of the described apparatus and process may be employed without departing from the spirit of the invention. The barrier or shield 14, for example, can be a fine mesh screen or a sintered titanium sponge. Equally, the barrier 14 can be modified greatly. For example, it can be rectangular in cross section or of any other convenient shape. More than one feed tube can be provided for each barrier if so desired. Other shapes and dimensions for the barrier can obviously be employed, as well as using a plurality of such barrier elements for each fused salt bath. The temperature of the reaction mass may be varied widely from slightly above the melting point of the salt to temperatures on the order of 1000° C. and above. Numerous reducing agents other than the sodium may be employed. For example, potassium, calcium, magnesium, lithium or various combinations of these elements may be utilized. From the standpoint of low cost of operation, sodium or magnesium is preferred. Other halides of titanium may be utilized although, from the standpoint of cost, ease of handling, etc., the tetrachloride is preferred as starting material.

The process may be practiced with continuous or intermittent feed of titanium chloride, either as such or dissolved in fused salt. In such case, an intermittent or continuous overflow of fused product salt will normally be provided at a point in the reactor where the fused salt is relatively low in titanium chloride. While agitation of the titanium chloride bath should be minimized, particularly while the initial sintered titanium layer is forming, some slight circulation of the bath may be provided at later stages of the process to facilitate complete reaction between the contained titanium chlorides and sodium.

Additionally, the reactor can be fed with lower halides of titanium such as titanium trichloride, manufactured from titanium-bearing materials in the manner shown in the copending applications of Singleton, Serial No. 304,388, filed August 14, 1952, now Patent No. 2,770,541, granted November 13, 1956, and Singleton, Serial No. 315,461, filed October 18, 1952, now abandoned. Equally, titanium trichloride can be made by the technique described by Sherfey et al., Journal of Research of the Bureau of Standards 46, 299–300, April 1951. Additionally, the dichloride of titanium can be manufactured by numerous processes such as disproportionation of the trichloride or partial reduction of the trichloride or tetrachloride.

The present invention can be equally employed for the manufacture of titanium alloys by the coreduction of the chlorides, for example, of vanadium, chromium, manganese, iron, nickel, cobalt, columbium, tantalum, molybdenum, tungsten or silicon. The alloy may be a binary alloy or it may be an alloy containing 3 or 4 constituents. In the manufacture of alloys, the same general conditions are employed. Accordingly, when the expression "titanium" is used in the appended claims, it is intended to include alloys of titanium as well as pure titanium.

It should be additionally pointed out that the salt mixture in which the reduction is carried out may be formed of numerous halides which can be mixed halides, single halides and halides of materials other than the specific reducing agent or agents employed in the reaction. From the standpoint of simplicity of operation and ease of control, it is preferred, however, that the salt be the chloride of the reducing agent. Thus it is quite feasible to employ binary and ternary mixtures of halides having quite low melting points.

It should be pointed out, in connection with a consideration of the various salts which can be employed, that these salts should be completely anhydrous and free of any contaminants such as carbon, nitrogen, oxygen or hydrogen. This is due to the tremendous reactivity of titanium metal at temperatures on the order of 800° C. to 900° C. and above.

In the above specification, reference has been made particularly to the preferred titanium chloride, tetrachloride and dichloride. In most instances, the trichloride is equally useful and, as a matter of fact, it is extremely unlikely that any system having an appreciable concentration of one of the lower chlorides of titanium will not have at least some of the other lower chloride also present. It should be apparent that one can also employ the corresponding di-, tri- and tetra-halides from the group consisting of the iodides, bromides and fluorides of titanium.

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 drawing, shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. In the process of forming titanium crystals by the reduction of a lower titanium chloride dissolved in an inert fused salt, the improvement which comprises feeding reducing agent to a portion of the salt which is substantially free of lower titanium chloride and isolating said portion from the remainder of the bath by means of a generally vertically extending foraminous shield which prevents rapid flow of fused salt between said portion and the remainder of the bath containing lower titanium chloride, the reducing agent being fed to a portion of the salt which is substantially below the surface thereof so as to substantially saturate the portion of the fused salt to which the reducing agent is fed, the foraminous shield serving as a barrier for segregating on one side thereof the high concentration of reducing agent in the fused salt which is substantially free of titanium chloride, this high concentration of reducing agent grading into the remainder of the fused salt in which the relative concentrations of reducing agent and titanium chloride are reversed.

2. A process for manufacturing titanium wherein a titanium lower chloride is dissolved in a bath of an inert fused salt and is reduced to titanium crystals by the addition of a metallic reducing agent, the improvement of which comprises providing and maintaining in the fused salt bath a zone comprising fused salt substantially free of titanium lower chloride, said zone being laterally displaced from the portion of the fused salt containing dissolved titanium chloride and being isolated from said titanium-chloride-containing portion of the fused salt bath by means of a generally vertically extending permeable metallic diaphragm, and supplying reducing agent to said zone so as to substantially saturate said zone to which the reducing agent is fed, the diaphragm serving as a barrier for segregating on one side thereof the high concentration of reducing agent in the fused salt which is substantially free of titanium chlorides, this high concentration of reducing agent grading into the remainder of the fused salt in which the relative concentrations of reducing agent and titanium lower chloride are reversed.

3. In a process of forming titanium crystals by the reduction of a lower titanium chloride dissolved in an inert fused salt, the improvement which comprises providing in a fused salt a foraminous layer comprising titanium particles which extends from adjacent the surface of the bath downwardly an appreciable depth into the bath, and feeding reducing agent to the fused salt bath on one side of the titanium layer to provide a zone which is substantially saturated with reducing agent to form reducing agent concentration gradient which extends generally horizontally through said layer, said layer serving to prevent rapid flow of fused salt from one side thereof to the other, said foraminous layer segregating on one side thereof a high concentration of reducing agent and substantially no titanium chloride in the portion of fused salt to which the reducing agent is fed, this high concentration of reducing agent grading into the remainder of the bath in which the relative concentrations of reducing agent and titanium chloride are reversed.

4. A process for manufacturing titanium wherein a titanium lower chloride is dissolved in a bath of an inert fused salt and is reduced to titanium crystals by the addition of a metallic reducing agent, the improvement of which comprises providing and maintaining in the fused salt bath a porous metallic element between the point of reducing agent feed and the remaining portion of the bath, the feed of reducing agent being below the surface of the fused salt to a portion of the fused salt which is substantially free of titanium chloride and the porous metallic element being effective to maintain a generally horizontally extending concentration gradient of reducing agent, said porous metallic element segregating on one side thereof a high concentration of reducing agent and substantially no titanium chloride in the portion of the fused salt bath to which the reducing agent is fed, this high concentration of reducing agent grading into the remainder of the bath in which the relative concentrations of reducing agent and titanium chloride are reversed.

5. In a process for producing titanium wherein a lower halide of titanium is dissolved in an inert fused salt bath and is reduced to titanium crystals by means of a metallic reducing agent selected from the class consisting of the alkali metals and the alkaline earth metals, the molten salt comprising a halide selected from the group consisting of the alkali metal halides and the alkaline earth metal halides, the improvement which comprises adding molten reducing agent to a limited portion of the fused salt bath, maintaining said limited portion essentially free of dissolved titanium lower halide, said limited portion extending a substantial distance down into said bath, isolating said limited portion from the remainder of the bath containing titanium lower halide at least partially by means of a vertically extending layer of sintered titanium particles, said vertically extending layer of sintered titanium particles segregating on one side thereof a high concentration of reducing agent and substantially no titanium lower halide in the portion of the fused salt bath to which the reducing agent is fed, this concentration of reducing agent grading into the remainder of the bath in which the relative concentrations of reducing agent and titanium lower halide are reversed.

6. In a process for manufacturing titanium wherein a solution of a lower chloride of titanium in an inert molten salt is reduced to metallic titanium by means of sodium, the improvement which comprises feeding the sodium to a limited portion of the molten salt to form an initial vertically extending layer of sintered titanium particles which separates the limited portion of the salt from the remainder thereof, the layer of titanium particles being effective to prevent rapid flow of salt through the layer so as to permit the formation of a sodium concentration gradient which extends horizontally across the layer, feeding more sodium to the limited portion of the molten salt bath to maintain the sodium concentration gradient, this concentration gradient traveling horizontally away from the point of sodium feed as a mass of titanium crystals forms on the far side of the initial titanium layer in the portion of the molten salt bath containing lower titanium chloride, and supporting the initial titanium layer in the position where it was formed in the salt bath during reduction of further titanium chloride within the salt bath, said vertically extending layer of sintered titanium particles segregating on one side thereof a high concentration of reducing agent and substantially no titanium lower chloride in the portion of

the fused salt bath to which the reducing agent is fed, the concentration of reducing agent grading into the remainder of the bath in which the relative concentrations of reducing agent and titanium chloride are reversed.

7. The process of claim 2 wherein the reducing agent comprises sodium, the lower titanium chloride comprises a mixture of titanium dichloride and titanium trichloride dissolved in sodium chloride, and the mole percentage of titanium trichloride relative to the titanium dichloride content is at least 11 percent at the start of the feed of sodium to the fused salt.

8. The process of claim 2 wherein the zone comprising fused salt low in titanium lower chloride is agitated to increase dissolution of the reducing agent in the fused salt in said zone.

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