

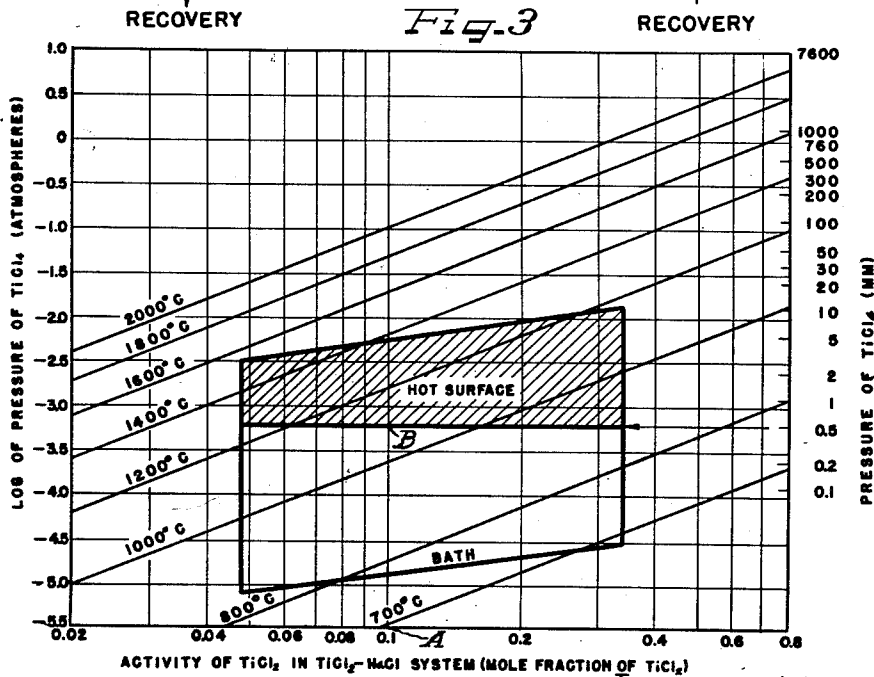
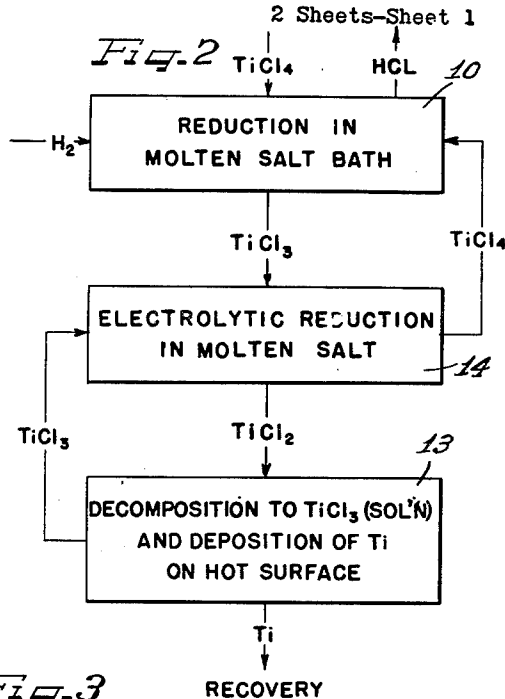
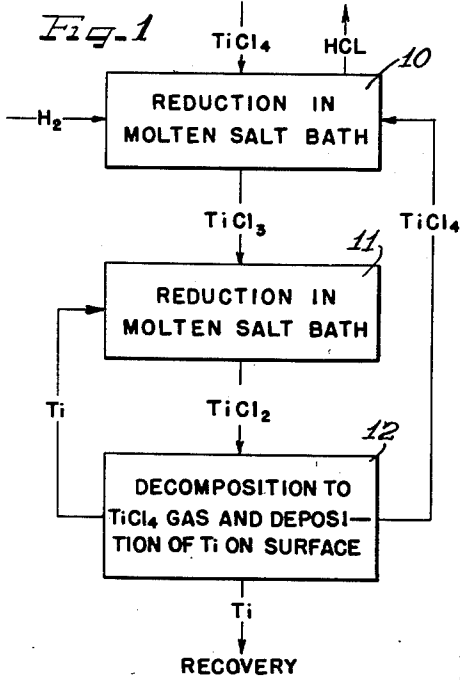
April 12, 1955

J. GLASSER

2,706,153

METHOD FOR THE RECOVERY OF TITANIUM

Filed April 19, 1951



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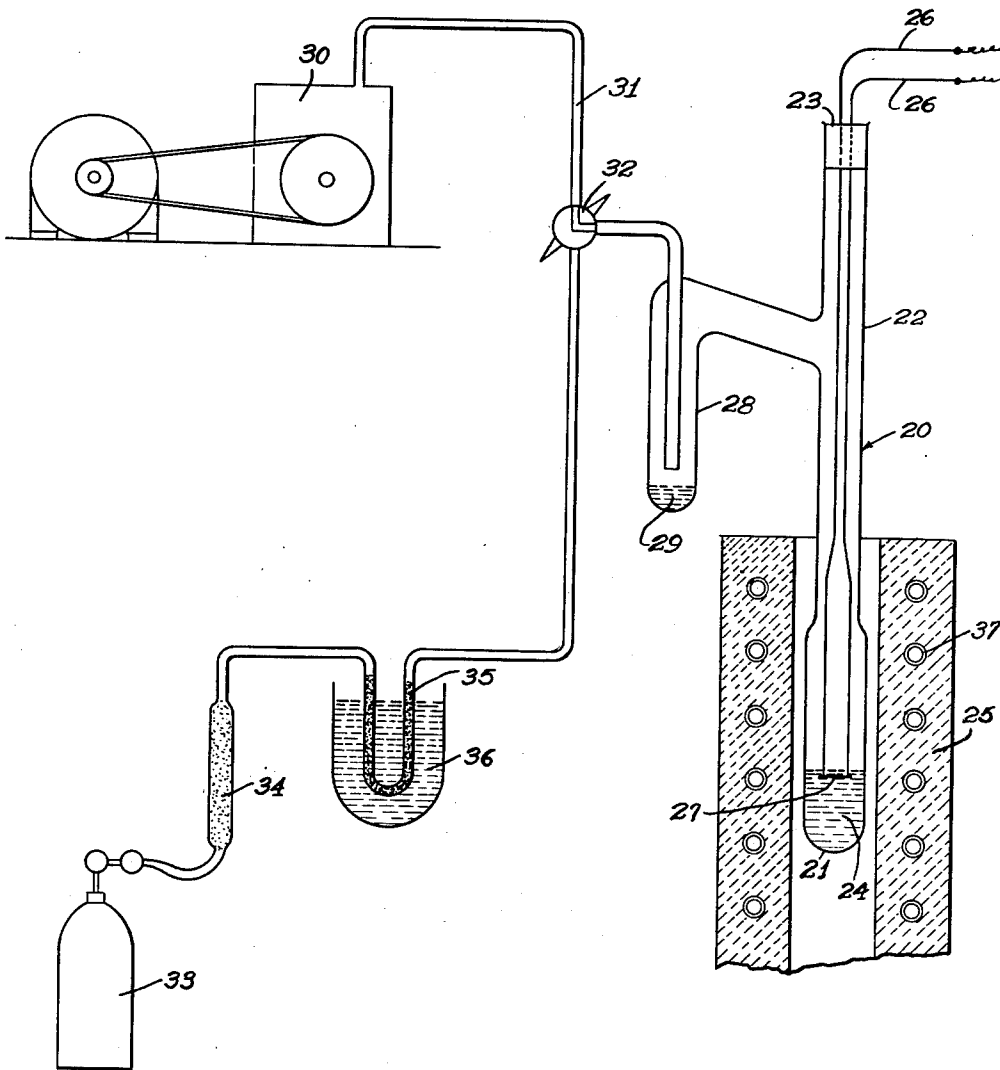
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2 Sheets-Sheet 2

Fig. 4



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2,706,153

METHOD FOR THE RECOVERY OF TITANIUM

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3 Claims. (Cl. 75—84)

The present invention relates to a method for the recovery of substantially pure, metallic titanium in crystalline form.

Metallic titanium has long been one of the more difficult metals to recover in substantially pure form. While the ores in this metal are quite plentiful, conventional processes for ore reducing are not adaptable to the recovery of titanium because of the inherent stability of the titanium oxide present in the ore and the reactivity of titanium metal in its elemental form. While processes have been developed for the recovery of titanium in elemental form, these processes usually involve the recovery of crystalline titanium in the form of extremely small particles. These particles are inherently unstable and even pyrophoric, readily oxidize in the presence of air or water, and even react with nitrogen from the air to form titanium nitrides.

An object of the present invention is to provide a method for the recovery of titanium in which the metallic titanium is deposited in the form of relatively large, ductile crystals which are relatively stable to air, water, and other reagents which ordinarily attack the finely divided crystals of titanium recovered in previously practical processes.

Another object of the present invention is to recover titanium by selective deposition of metallic titanium from a liquid phase system.

Still another object of the present invention is to provide a method for the recovery of titanium from lower titanium halides.

I have now discovered that if the proper reaction conditions are observed, metallic titanium can be deposited upon a heated surface from a liquid bath containing lower halides of titanium. By "lower halides of titanium" I mean to include the relatively unstable halides such as titanium dichloride and titanium trichloride which result from the partial reduction of the more stable titanium tetrachloride. The process is also applicable to the recovery of metallic titanium from titanium dibromide and tribromide. The crystals of titanium metal which are obtained by this process are relatively large, ordinarily being well in excess of 100 microns in diameter. Crystals of this size are considerably more stable to air, oxidizing gases, and other reactants than are crystals whose dimensions are on the order of 1 to 10 microns.

A further description of the present invention will be made in connection with the attached sheets of drawings in which:

Figure 1 is a diagram of the mechanism of a reaction according to the present invention;

Figure 2 is a diagram of another reaction mechanism which may be employed;

Figure 3 is a graph showing the equilibrium gas pressures of titanium tetrachloride over a titanium dichloride-sodium chloride system as employed in the process of Figure 1 at various concentrations and temperatures; and

Figure 4 is a schematic diagram of one type of apparatus which may be employed in the practice of the process.

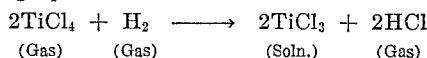
In the embodiment of the process illustrated in Figure 1, I have illustrated a reduction stage 10 in which a supply of titanium tetrachloride and hydrogen gas are introduced into a molten salt bath. The salt used in the bath should have a melting point below about 1000° C. so that the proper temperature differentials may be maintained within the process. Salts of alkali metals, and alkaline earth metals, as well as magnesium salts may be

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employed for this purpose. The most common salt bath which may be employed consists of sodium chloride, but it will be appreciated that other salt baths such as sodium bromide, calcium chloride, calcium fluoride, magnesium chloride, and the like may similarly be employed.

One of the advantages of employing a molten salt bath for the partial reduction of titanium tetrachloride to a lower halide of titanium resides in the fact that lower temperatures can be employed where the bath is used. For example, if titanium tetrachloride is reacted with hydrogen in the absence of the salt bath, temperatures on the order of 1200° C. must be employed. On the other hand, by using a molten salt bath as the vehicle for the reaction, temperatures only slightly above the melting point of the salt, for example, temperatures of about 900° C., will be sufficient for the reaction. A more important advantage arising from the use of a salt bath for the partial reduction of titanium tetrachloride to titanium trichloride is the fact that the reaction goes more completely, and the recovery is quantitative, since the trichloride is dissolved in the salt bath as soon as it forms, thus reducing possible losses through volatilization. Another advantage of the present process is the fact that the purity of the raw materials is not critical.

The reduction of titanium tetrachloride by means of hydrogen at relatively low temperatures and normal pressures produces both titanium trichloride and titanium dichloride, with the former predominating according to the following equation:

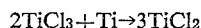


The above reaction is carried out in an air-free, non-oxidizing atmosphere, and preferably in an atmosphere of hydrogen, argon, helium, neon, or other inert gas.

In place of the hydrogen reduction of titanium tetrachloride to yield lower halides of titanium, a suitable starting material for the process of the present invention can be prepared by partially reducing titanium tetrachloride by means of other reducing agents, as, for example, metallic sodium, metallic magnesium, or metallic titanium, all of these being used under a protective atmosphere of an inert gas. Impure titanium can be used as a reducing agent, and in these circumstances, the process would be one for purifying impure titanium or its alloys to recover pure titanium.

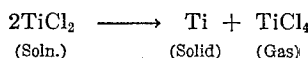
The titanium trichloride produced in the reduction stage 10 is further reduced to the dichloride in a second reaction stage 11. For purposes of convenience, the two reduction stages 10 and 11 have been illustrated in separate zones in the drawings, to illustrate more clearly the mechanism of the reaction. It will be understood that both reduction reactions can be, and preferably are, carried out concurrently in a closed system under a protective atmosphere of a non-oxidizing gas such as hydrogen.

The titanium trichloride, dissolved in a molten salt bath maintained at temperatures above its melting point, is reduced by elemental titanium according to the following equation:



The next stage of the process involves the decomposition of the titanium dichloride produced in the previous reaction to metallic titanium by selective deposition upon a hot surface. Titanium dichloride and titanium trichloride are soluble in each other and each is soluble in the molten salt bath. This feature permits the deposition of metallic titanium from a purely liquid system instead of from vapor phase, as has previously been done. The decomposition of the titanium dichloride to metallic titanium has been indicated in Figure 1 of the drawings in the stage designated by reference numeral 12.

In the decomposition stage 12, the titanium dichloride is thermally decomposed to yield metallic titanium according to the equation:



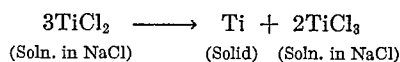
A portion of the titanium which is recovered from the deposition is returned to the reduction stage 11 to assist

in the reduction reaction, and the titanium tetrachloride produced by the decomposition of the dichloride can be reacted with additional amounts of hydrogen to produce the trichloride as illustrated in the drawings.

In the embodiment of the invention illustrated in Figure 2 the disproportionation of titanium trichloride to the dichloride and tetrachloride is carried out by an electrolytic reduction process. This process consists in immersing a pair of inert electrodes into the fused salt bath containing the titanium trichloride dissolved in the bath, whereby the trichloride undergoes a disproportionation reaction to form titanium dichloride at the cathode and titanium tetrachloride at the anode.

In stage 13, Figure 2, the dichloride formed at the cathode is disproportionated to titanium and titanium trichloride at a hot surface by virtue of keeping the trichloride concentration very low in the catholyte. The trichloride from stage 13 is recirculated to the electrolytic reduction stage 14 for the purpose of minimizing the concentration of the trichloride in the catholyte.

Titanium dichloride is disproportionated to titanium trichloride and metallic titanium in stage 13 according to the following equation:



Thermodynamic calculations show that the above reaction will proceed only if the concentration of the trichloride is maintained sufficiently low at a given temperature. The following table shows the mole fraction of TiCl_3 in equilibrium with 0.1 mole fraction of the TiCl_2 dissolved in molten NaCl:

Temp. (°K.)	Mole fraction TiCl_3 with 0.1 M. F. TiCl_2
900.....	0.0002
1,000.....	0.003
1,100.....	0.006
1,200.....	0.024
1,300.....	0.067
1,400.....	0.147
1,500.....	0.18

As the disproportionation reaction is favored by elevated temperatures, a convenient method for carrying out the reactions in stages 14 and 13 consists in first forming the dichloride in the electrolytic reduction stage 14 at a temperature just above the melting point of the salt, and subsequently disproportionating the dichloride produced at temperatures from 300° to 500° C. above the melting point of the salt.

The concentration of TiCl_3 in the disproportionation reaction mixture should be less than 0.05 mole fraction, and preferably less than 0.01 for 0.1 mole fraction of TiCl_2 . One method by which the concentration of TiCl_3 could be held at a minimum consists in combining stages 13 and 14, and locating the hot body upon which the titanium is to be deposited in close proximity to the cathode. In the process of Figure 2, there is no need for atmosphere control, in that the control comes in the composition of the bath.

One of the essential considerations in the practice of the processes of Figures 1 and 2 is the maintenance of a stable salt bath. It is of prime importance to keep the bath stable so that the thermal decomposition of the lower halides of titanium to metallic titanium takes place at the surface of the hot body which is introduced into the bath instead of within the bath itself. The minimum temperature of the bath will be determined by the melting point of the salt, while the maximum temperature which can be employed in the bath will be limited by the temperature differentials to be observed between the bath temperature and the temperature of the heated body upon which the titanium is deposited.

In Figure 3 of the drawings, there is illustrated a graph showing the correlation between several of the factors involved in maintaining a stable fused bath of sodium chloride and titanium dichloride in the process of Figure 1. In the graph, the abscissae represent the activities of titanium dichloride in a mixture of titanium dichloride and sodium chloride. The activity coefficient of titanium dichloride was assumed to be unity, so that the activity

will be equal to the mole fraction of titanium dichloride in the system.

The ordinates of the graph represent the equilibrium pressures of titanium tetrachloride over the titanium dichloride-sodium chloride system.

Another important consideration in the practice of the present process is the control of the pressure of titanium tetrachloride over the system. The partial pressure should be less than 10 millimeters of mercury but more than .01 millimeter of mercury, and preferably from .2 to 5 millimeters.

The reactions described in connection with Figure 1 are carried out in a closed system, i. e., one in which the ambient pressure throughout the system is carefully controlled. The control of the pressure of titanium tetrachloride over the system may be accomplished by providing a cold trap containing a liquid supply of titanium tetrachloride. In a large system, the partial pressure of the titanium tetrachloride over the system will closely approximate the vapor pressure of the titanium tetrachloride at the temperature of the cold trap. Thus, for example, in such a system the partial pressure of titanium tetrachloride can be maintained at a value of about 0.5 millimeter by providing a supply of liquid titanium tetrachloride at a temperature of -20° C. in communication with the system.

An important consideration in the practice of the processes of both Figures 1 and 2 is the temperature differential to be maintained between the surface of the hot body upon which the deposition of titanium is to be accomplished, and the temperature of the bath. I have found that for best results this temperature differential should be at least 100° C., and preferably on the order of 300° C.

The body upon which the titanium is to be deposited should be a refractory substance having a melting point well above the temperature of the bath. As an example, the heated metal body can take the form of an electrically heated filament of tungsten, molybdenum, or titanium. Alternatively, solid rods of these metals, as well as graphite rods, may be used as the surfaces upon which the titanium is selectively deposited.

It is particularly important for proper deposition in the process of Figure 1 that the hot body be introduced into the surface of the bath very carefully, so that the surface of the heated body is immersed only to a depth less than that at which the static head of the bath exceeds the difference between the equilibrium pressure of titanium tetrachloride at the temperature of the hot surface and the pressure of titanium tetrachloride above the system.

The following example illustrates the manner in which the proper operating conditions are obtained for the process of Figure 1 from the graph of Figure 3. For the purposes of the example, it will be assumed that the pressure of the titanium tetrachloride over the system is maintained at a value of 0.5 millimeter, and that the mole fraction of titanium dichloride in the titanium dichloride-sodium chloride system is 0.1. The latter composition is represented by the vertical line extending from the point A along the abscissa of the diagram. At this concentration, the minimum temperature of the hot surface or the maximum temperature of the bath can be determined by the intersection with the line from the point A of the horizontal line representing an equilibrium pressure of 0.5 millimeter. This point of intersection has been labeled as point B. The corresponding temperature is then determined by extrapolating between the parallel sloping temperature lines indicated on the drawing, and in this instance is found to be approximately 1100° C.

The shaded area of the diagram represents the temperatures to be employed on the heated body for deposition purposes. Theoretically, the temperature of the heated body need be only slightly higher than the temperature of the bath, but in practice it is impossible to control the temperature to such a fine degree. Consequently, for best results, I have found that a minimum temperature differential of 100° C. should be maintained between the bath and the hot surface. In the cited example, the temperature for the hot surface would be at least 1200° C., and preferably about 1300° C. with the bath below 1100° C., but above its melting point.

An apparatus suitable for carrying out the process of Figure 1 has been illustrated in Figure 4. The apparatus there shown includes a reaction vessel 20 having a large diameter bulb portion 21 and a reduced diameter neck

22. The vessel 20 is sealed from the atmosphere by means of a seal 23 inserted in the end of the neck 22.

The bulb 21 contains a liquefied bath 24 of titanium subhalides in admixture with sodium chloride. To attain the temperatures required to keep the bath 24 molten, the bulb 21 is disposed in an electrically heated split tube furnace 25 containing heating elements 37.

A pair of conductors 26 connected to a source of current, not shown, extend through the seal 23 and are joined at one end of a refractory filament 27. The depth to which the filament 27 is immersed in the bath is less than that at which the static head of the bath exceeds the difference between the equilibrium pressure of titanium tetrachloride at the temperature of the filament and the pressure of titanium tetrachloride over the system, as previously explained. After the bath 24 has reached the proper operating temperature, it is possible to discontinue heating by means of the furnace 25, as the heat dissipated from the filament is usually sufficient to maintain the bath molten.

The control of the partial pressure of titanium tetrachloride over the system is accomplished by providing a cold trap 28 in communication with the reaction vessel 20. A liquid body of titanium tetrachloride 29 is maintained at a suitably low temperature, normally on the order of -20°C ., where the vapor pressure of titanium tetrachloride approximates the desired pressure of titanium tetrachloride over the system. Thus, as titanium tetrachloride vapors are evolved from the highly heated bath 24, the vapors condense in the cold trap 28, thus effectively maintaining the pressure of titanium tetrachloride over the system at the vapor pressure of titanium tetrachloride at the temperature of the cold trap.

A pump 30 is connected to the system by means of a vacuum line 31 and a valve 32 to evacuate the system in order to have only titanium tetrachloride in the system.

A vessel of helium 33 is provided to introduce an inert gas into the system when the filament 27 is to be withdrawn from the vessel 20. The helium gas is purified by passage through a desiccant 34, and an adsorbent material such as activated charcoal 35 disposed in a bath of liquid air 36 before being introduced into the vessel 20.

While not shown in the schematic drawing, it will be understood that means will be provided in the vessel 20 to adjust the depth to which the filament 27 is immersed within the bath 24 without affecting the pressure within the system.

To illustrate the actual operating conditions of the deposition, the following example is submitted.

A bath was formed containing 20% titanium dichloride and 80% by weight sodium chloride. An electrically heated tungsten filament, was then positioned to a depth of about $\frac{1}{4}$ inch below the surface of the bath. The partial pressure of titanium tetrachloride over the system was maintained at 0.5 mm., and a bath temperature of 900°C . was used. The temperature of the filament was in the neighborhood of 1200°C .

As soon as the deposition commenced, the apparent resistance of the tungsten filament decreased. Eventually, the current drawn by the filament became more or less constant.

When the tungsten filament, with the elemental titanium deposited thereon was withdrawn from the bath, it was found that approximately one half of the titanium originally present in the bath had been converted to metallic titanium.

The crystalline size of the titanium particles recovered was in the neighborhood of 200 microns. These crystals are ductile, stable in air, and can be leached with aqueous reagents without substantial deterioration.

The process of the present invention is also amenable to operation in a continuous manner. For example, a heated refractory metal wire may be guided through the molten bath at a predetermined distance below the level of the bath, and the titanium removed continuously as a deposit on the refractory metal wire.

It will be understood that modifications and variations may be effected without departing from the scope of the novel concepts of the present invention.

I claim as my invention:

1. In a method of recovering titanium from a system consisting essentially of a titanium dihalide dissolved in a molten alkali metal salt bath, and a source of a liquid titanium tetrahalide, the halogen of each of said halides being the same and being selected from the group con-

sisting of chlorine and bromine, said liquid tetrahalide being in open communication with said bath to provide a partial pressure of said titanium tetrahalide over said bath, the steps comprising immersing an independently heated refractory metal surface in said molten bath, maintaining said bath at a temperature of between its melting point and 1100°C . and said refractory body at a temperature of at least 100°C . above that of said bath, limiting the depth of immersion of said refractory surface to less than that at which the static head of the bath over said refractory surface exceeds the difference between the equilibrium pressure of said titanium tetrahalide at the temperature of said heated surface and the pressure of said titanium tetrahalide over said bath, and maintaining said temperature differential to effect decomposition of said titanium dihalide to titanium metal and consequent deposition of said titanium metal on said heated surface.

2. In a method of recovering titanium from a system consisting essentially of titanium dichloride dissolved in a molten sodium chloride bath and a source of liquid titanium tetrachloride in open vapor communication with said bath to provide a partial vapor pressure of titanium tetrachloride over said bath, the steps comprising immersing an electrically heated refractory wire in said molten bath, maintaining said bath at a temperature of between its melting point and 1100°C . and said wire at a temperature of at least 1200°C ., limiting the depth of immersion of said wire in said bath to less than that at which the static head of said bath over said wire exceeds the difference between the equilibrium pressure of said titanium tetrachloride at the temperature of said wire and the pressure of said titanium tetrachloride over said bath, maintaining a temperature differential of at least 100°C . between said wire and said bath to effect decomposition of said titanium dichloride to titanium metal and consequent deposition of said titanium metal on said heated wire.

3. In a method of recovering titanium from a system consisting essentially of titanium dichloride dissolved in a molten alkali metal salt bath, and a source of liquid titanium tetrachloride, said liquid titanium tetrachloride being in open vapor communication with said bath to provide a partial pressure of said titanium tetrachloride over said bath, the steps comprising immersing an independently heated refractory surface in said molten bath, maintaining said bath at a temperature of between its melting point and 1100°C . and said refractory surface at a temperature at least 100°C . above that of said bath, limiting the depth of immersion of said refractory surface to less than that at which the static head of the bath over said refractory surface exceeds the difference between the equilibrium pressure of said tetrahalide at the temperature of said heated surface and the pressure of said titanium tetrachloride over said bath, and maintaining said temperature differential to effect decomposition of said titanium dichloride to titanium metal and consequent deposition of said titanium metal on said heated surface.

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