Nov. 17, 1959 M. P. NEIPERT ET AL 2,913,332

PRODUCTION OF TITANIUM METAL

Filed April 5, 1957 2 Sheets-Sheet 1

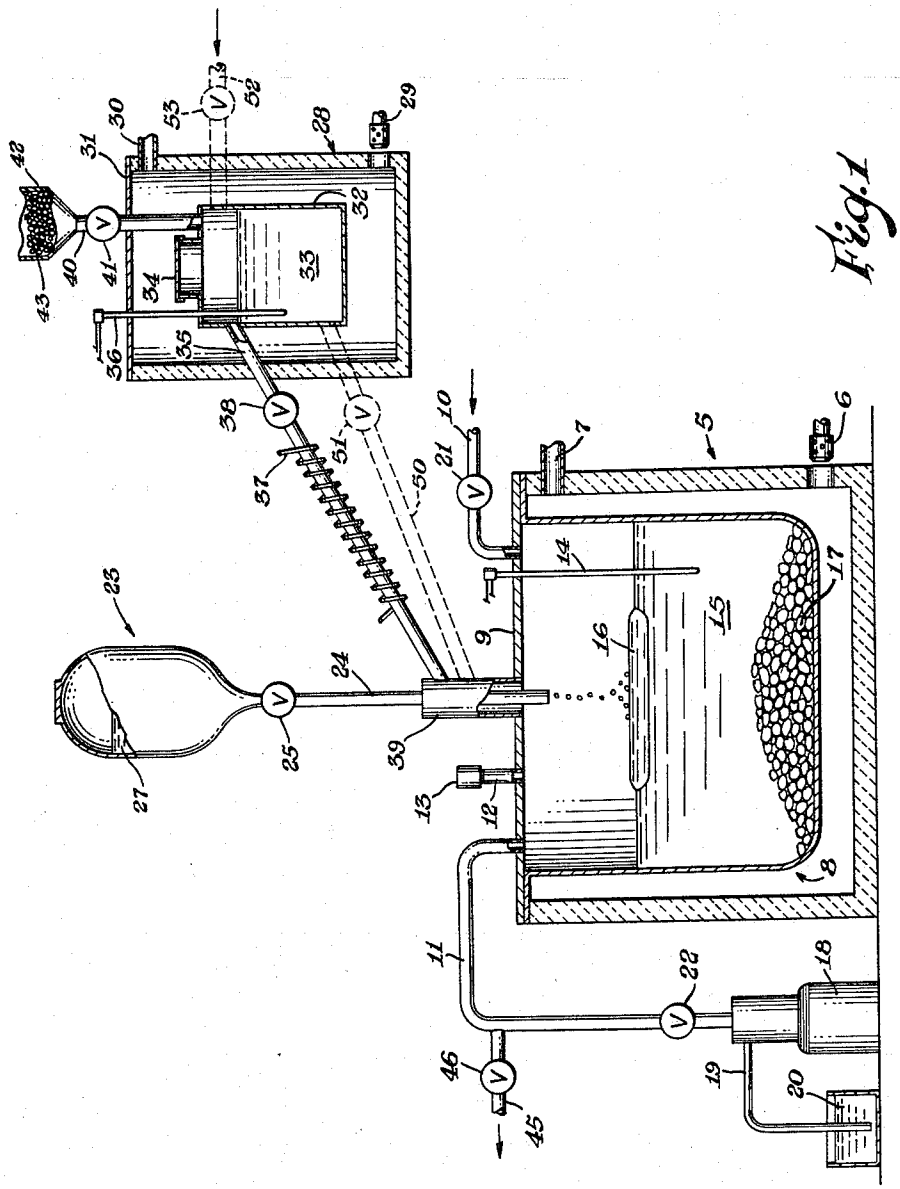


Fig. 1

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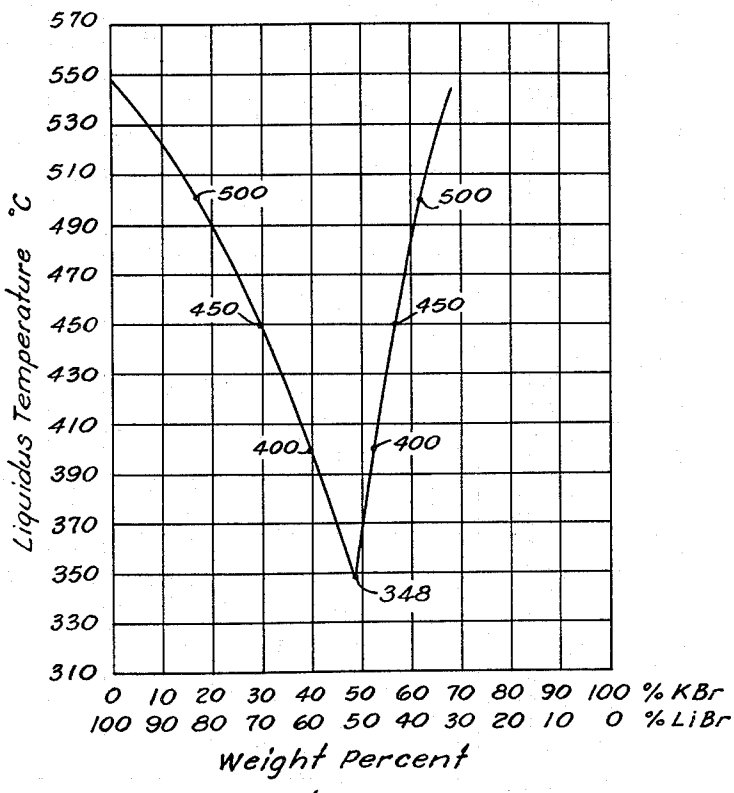


Fig. 2

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United States Patent Office 2,913,332 Patented Nov. 17, 1959

2,913,332

PRODUCTION OF TITANIUM METAL

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Application April 5, 1957, Serial No. 650,887

7 Claims. (Cl. 75—84.4)

The invention concerns generally the production of titanium metal and more particularly the production of titanium metal by the reaction of titanium tetrabromide or titanium tetrachloride with molten lithium in a molten salt bath.

It has been suggested that molten lithium may be made to reduce titanium from its halides, the temperature proposed being at least 800° and preferably about 850° C. Such high temperatures are required to remove the by-product lithium halide which forms about the lithium, which, if not removed, reduces the rate of reaction to one which is too slow to be practical. These high temperatures render the methods difficult to carry out. Even when reacted at the high temperatures required, the reaction is undesirably slow. Furthermore, attempts to employ temperatures much below about 800° C. have resulted in the titanium being formed as an undesirable fine powder rather than as a desirable coherent mass of titanium.

There is a desideratum in the art of titanium production for a method of producing titanium in a coherent mass from a readily available titanium salt by the action of a reducing metal at a relatively low temperature, e.g., not over about 550° C.

The principal object of the invention is a fulfillment of this need. The method by which this and related objects are accomplished will be made apparent by the following description and drawing.

The invention is based on the discovery that by suitably adding liquid titanium tetrabromide or tetrachloride to lithium metal suspended in a molten salt bath comprising a mixture of halides selected from the alkali and alkaline earth metal halides coherent titanium metal is continuously produced at a temperature as low as the melting point of the bath. The preferred bath to employ comprises a mixture of potassium bromide and lithium bromide when titanium tetrabromide is employed or potassium chloride and lithium chloride when titanium tetrachloride is employed. Impurities normally present in such salt baths, e.g., trace amounts of salts of iron, and salts of calcium, and magnesium other than the halides may be present.

By slowly dropping liquid titanium tetrabromide or titanium tetrachloride onto the molten salt bath containing the molten lithium, a continuous reaction is caused to take place between the titanium tetrabromide or tetrachloride and the lithium at or above the ignition temperature of lithium in the tetrahalide employed to produce a mass of coherent titanium rather than a fine powder. The ignition temperature of lithium in titanium tetrabromide is about 200° C. and in titanium tetrachloride about 185° C. and is evidenced by a glow in the area of contact of the reactants, referred to hereinafter as the zone of reaction. The glow is the composite effect of scattered scintillating points in the reaction to which reference is made hereinafter as hot spots. The continuous presence of hot spots indicates that the rate of feed of the titanium tetrabromide or tetrachloride is within the proper range, whereas the absence or marked irregularity of hot spots in the presence of sufficient lithium metal indicates too slow or too rapid a rate of feed of the titanium tetrabromide or tetrachloride.

Broadly the invention comprises producing titanium metal by slowly adding a titanium halide consisting of either the tetrabromide or tetrachloride to a molten salt mixture comprising halides of alkali and alkaline earth metals and containing lithium metal in an atmosphere comprising an inert gas. It is preferred that the lithium metal be present in excess of the stoichiometric quantity required for the reatcion:

$$TiBr_4(\text{or } TiCl_4)+4Li \rightarrow 4LiBr(\text{or } 4LiCl)+Ti$$

The baths employed are those having a melting point of not over about 550° C., and preferably between about 400° and 450° C. Eutectic mixtures of alkali and alkaline earth metal halides are particularly suitable in the practice of the invention because of their generally lower melting points. A bath comprising either lithium bromide and potassium bromide or lithium chloride and potassium chloride of which the halogen is the same as that of the titanium halide being used, is preferred over a bath comprising the halides of more than one halogen, e.g., a mixture of bromides and chlorides and/or iodides. The presence of halides containing the same halogen provides a more simplified subsequent recovery of bath components, as by electrolysis, the iodides being particularly undesirable for purposes of recovery since they volatilize at or below the temperature of the electrolysis. Caesium and rubidium halides are usually not employed because of their relatively higher cost and sodium halides are usually not employed to any substantial extent because they tend to raise the melting point of the bath.

The melting points of some binary, ternary, and quaternary eutectic mixtures of halides of alkali and alkaline earth metals suitable for practicing the invention are set out in tabulated form below:

Components of eutectic mixture:	Melting point of eutectic mixture in ° C.
LiCl and CsCl	322
LiCl and RbCl	312
LiCl and KCl	352
LiBr and CsBr	255
LiBr and KBr	348
LiBr and NaBr	525
LiI and CsI	204
LiBr and $SrBr_2$	453
LiBr, CsBr, and NaI	252
LiCl, KCl, and NaCl	362
LiCl, NaCl, and CsCl	320
LiCl, NaCl, and RbCl	318
LiCl, KF, and KCl	351
$BaCl_2$, KCl, and $CaCl_2$	440
KCl, NaCl, and $MgCl_2$	396
KCl, NaCl, $BaCl_2$, and $MgCl_2$	410

Fig. 1 of the drawing shows an elevation largely in section of one type of apparatus which is suitable for the practice of the invention.

Fig. 2 shows a phase diagram of a prefererd binary salt mixture for practicing the invention.

Referring to Fig. 1 in more detail, there is shown a first furnace setting 5 having gas burner 6 and flue gas outlet 7 in the walls thereof. In furnace setting 5 is reactor 8 having removable top 9. In openings provided therefor in top 9 are inert gas inlet line 10 having valve 21 therein, exhaust or gas outlet line 11 provided with valve 22, sight glass tube 12 supporting sight glass 13, and thermocouple 14. Inert gas line 10 is attached to a source of inert gas (not shown). Outlet line 11 is connected to safety tank 18. Tube 19 from tank 18 opens into liquid trap 20. Exhaust line 45, connected to an evacuation means (not shown) and containing valve 46 therein, provides a means for evacuating the system.

Reservoir 23 is provided for holding a supply of titanium tetrachloride or molten titanium tetrabromide 27. Pipe 24 leads therefrom into reactor 8 and valve 25 there-

in provides a means to control the rate of flow of the titanium halide 27 into reactor 8.

Second furnace setting 28, having gas burner 29 and flue gas outlet 30 in the walls thereof and removable cover 31 thereon, provides a means for heating still pot 32 positioned therein and adapted to hold lithium metal 33 to be vaporized. Pot 32 is provided with removable cover 34, outlet line 35 having valve 38 therein, thermocouple 36, and particulated solid lithium feed-line 40 containing valve 41, leading from reservoir 42 containing solid lithium particles 43. Around outlet line 35 are heat-control coils 37 connected to a source of circulating medium (not shown). By controlling the temperature of outlet line 35 by means of coils 37, the vaporous lithium is converted to a liquid but is not permitted to solidify. Outlet line 35 opens into annular duct 39 which is positioned about the lower portions of pipe 24 and opens into reactor 8.

By referring to the graph of Fig. 2, the temperatures at which various percentages compositions of potassium bromide and lithium bromide are completely molten are shown and designated as the liquidus temperature. It will be observed that a weight percentage composition of 47 percent of KBr and 53 percent LiBr, the eutectic mixture, is molten at 348° C. The percentage composition which is molten at any given temperature is shown between the upwardly (the right and left) diverging segments of the curve. As the temperature is increased, the range of percentage composition which is molten at a given temperature is increased. Therefore, the range of percentage composition permitted, when employing this bath to practice the invention, is that shown between the segments of the curve at the temperature on the graph which corresponds to the temperature of the bath employed. For example, at 400° C. and above, all compositions are molten which comprise from 39 percent KBr and 61 percent LiBr to 53 percent KBr and 47 percent LiBr. At 450° C. and above, all compositions are molten which comprise from 30 percent KBr and 70 percent LiBr to 57 percent KBr and 43 percent LiBr.

In practicing the invention, a bath composed of two or more halide salts of alkali and/or alkaline earth metals, is made up in reactor 8. Preferably a mixture which is molten at not over about 450° C. is used, e.g., the mixture of 57 percent KBr and 43 percent LiBr (as shown in Fig. 2) or 65 percent KCl and 35 percent LiCl by weight, which is completely molten at about 450° C.

Lithium metal, usually of commercial grade for purposes of convenience and economy, is added to still pot 32 by removing covers 31 and 34 or placing particulated lithium in reservoir 42 and, by opening valve 41, adding it through feed tube 40. The lithium metal is vacuum distilled by partially evacuating the system by closing valves 41, 21, 22, and 25 and opening valve 46 in line 45. The lithium metal is then melted and vaporized in pot 32 and the evolved vapor condensed by means of coil 37 as it passes through pipe 35 thereby forming liquid lithium which follows through annular duct 39 directly onto molten salt bath 15. The lithium forms in a pool or layer 16 at or near the top of the molten salt bath below pipe 24 leading from titanium halide reservoir 23. After pool 16 is of sufficient quantity to sustain the reaction with the titanium halide for a desired time, say 0.5 to 8.0 hours, valves 46 and 38 are closed. Reactor 8 is then heated to a temperature at which the salt mixture is somewhat above its melting point.

A flow of inert gas is provided by opening valve 21 in line 10 and valve 22 in line 11 to create a protective atmosphere above the lithium layer and the exposed surface of the molten salt bath. The inert gas outlet 19 which leads to safety tank 18 and thence to a liquid seal, e.g., one of mercury, sulfuric acid, or a heavy oil, in trap 20 prevents any back pressure in the system from forcing liquid from trap 20 into reaction chamber 8.

Liquid titanium tetrabromide or titanium tetrachloride is then added slowly, by partially opening valve 25, preferably dropwise, say from 3 or 4 to 10 drops per second, to the mixed molten halides containing lithium metal in the reactor. The proper rate of feed of the titanium halide is attained by maintaining ignition condition between the lithium and the halide as evidenced by the more or less continuous existence of hot spots in the zone of reaction.

The apparent capillary attraction between the lithium and the halide bath and the movement resulting both from the heat of the exothermic reaction between the lithium and the $TiBr_4$ or $TiCl_4$ and the difference in density among the various reactants and products produces sufficient intermingling of the bath with the lithium and $TiBr_4$ or $TiCl_4$ in the zone of reaction to result in dissolution by the bath of the LiBr or LiCl being formed, thereby preventing the concentration of the LiBr or LiCl thus formed in the zone of reaction from interfering with a continuous and substantially complete reaction.

The titanium sponge, together with a small amount of entrained LiBr or LiCl, depending upon the halide used, is formed and settles to the bottom of the reactor as indicated at 17. The greater portion of the LiBr or LiCl formed is dissolved by the bath and becomes part thereof.

The titanium sponge is then removed from reactor 8 as by taking off cover 9 and raking the titanium metal from the reactor. The metal may be thereafter separated from substantially all foreign material by vacuum distillation or other known purification means.

As an alternative method of practicing the invention, liquid lithium metal, if in sufficiently pure state, may be employed directly without the intermediate step of distillation. When such alternative method is employed, lithium metal is placed in pot 32 as in the above described embodiment, but valve 38 in outlet line 35 is maintained in a closed position and valve 51 in outlet line 50 (shown by broken lines in Fig. 1 leading into chamber 39) is opened. The lithium metal is melted but not vaporized in reactor 32. Inert gas is introduced through line 52 by opening valve 53 therein (shown by broken lines in Fig. 1) to create positive pressure for forcing liquid lithium down line 50.

Another mode of practicing the invention is to distill a commercial grade lithium into a storage reservoir, heated to maintain the distilled lithium in a liquid state, and thereafter to use the thus-distilled lithium in the manner described in the above paragraph.

The following examples are illustrative of the practice of the invention.

Example 1

A mixed salt was prepared by admixing 648 grams of LiBr with 859 grams of KBr in an apparatus of the type shown in the drawing. This is a 43 percent LiBr-57 percent mixture by weight. The apparatus was partially evacuated by opening valve 46 and applying a vacuum pump to line 45.

175 grams of commercial lithium metal were distilled from reactor 32, condensed in line 35 to liquid, and run directly into reactor 8 containing the molten mixed bromide salts. Valve 38 was then closed. The bath in reactor 8 was then heated to 450° C. to form bath 15; valve 46 was then closed and valve 22 opened. Inert gas was admitted through inlet 10 to the reactor thereby displacing the air therefrom. $TiBr_4$ in reservoir 23 was then added dropwise into the reactor by partially opening valve 25. As the reaction proceeded the reduction of titanium tetrabromide by the action of the lithium was effected, producing titanium sponge and LiBr. The LiBr percentage of the bath accordingly increased as the operation continued. After a total of 1587 grams of titanium bromide was added, valve 25 was closed. The reaction was thereby stopped. Cover 9 was removed and the titanium sponge thus formed was removed from the bath by raking it out. The adhering salts were removed from

the sponge by vacuum distillation according to known practice. 139 grams of titanium metal were recovered. An analysis was carried out for the following elements in the thus-formed titanium metal with the following results: 0.1 percent Fe; 0.22 percent C.; 0.096 percent N; no Li; balance substantially titanium.

In Example 1, the percentage of LiBr in the bath had not reached 71 percent so that a temperature of 450° C., as shown by Fig. 2, was clearly satisfactory since the salt remained molten at that temperature. Had it been desirable to continue the reaction after the percentage of LiBr in the bath had reached or exceeded 71 percent, the temperature then might have been raised to maintain the salts in molten state. Although it may be observed by again referring to Fig. 2 that at 547° C. a LiBr-KBr bath remains molten which contains between about 32 percent and 100 percent LiBr, such a bath is not preferred because of the high temperature requirement. In the interests of economical and efficient operation, it is advisable periodically to revivify the bath by withdrawing a portion of the bath in which the LiBr content has thus increased and add enough KBr to make the percentage composition again about 40 to 45 percent LiBr and 60 to 55 percent KBr.

The withdrawn portion of the bath then may be electrolyzed at a potential sufficient to decompose the LiBr but not the KBr, Li metal thereby being recovered at the cathode which may be subsequently used for replenishing the Li metal supply in pot 32 that had been consumed in the reduction reaction. Bromine is liberated at the anode and may be used to make more $TiBr_4$ for addition to reservoir 23. The KBr remaining after electrolysis of the LiBr component of the withdrawn portion of the bath may be used for further addition to bath 15.

Example 2

The KBr—LiBr bath of Example 1 was again prepared. The bath was heated to 547° C. The apparatus was partially evacuated and 292 grams of commercial lithium were vaporized from pot 32 and the vapor condensed to liquid lithium in tube 35 and led into the bromide bath in reactor 8; thereafter valve 38 was closed as in Example 1. An atmosphere comprising an inert gas was provided in reactor 8 as in Example 1 and the temperature of the bromide bath therein raised to and maintained at about 547° C. while 2580 grams of titanium tetrabromide in reservoir 23 were added dropwise, by opening valve 25 and controlling the rate of flow thereby over a 50 minute period. The titanium sponge which was formed was removed from the reactor together with some occluded salt and the salt removed therefrom by vacuum distillation as in Example 1. 332 grams of purified titanium were recovered. This was a 99 percent yield based on the titanium recovery theoretically possible.

The titanium recovered had a Brinell hardness number of 217. An analysis was made for the following elements in the thus-prepared titanium and were shown to be present as follows: 0.12 percent Fe; 0.067 percent C.; 0.03 percent N; no lithium; balance substantially titanium.

It has been shown by the examples above that titanium can be produced by the regulated addition of liquid titanium tetrabromide to a molten salt mixture of KBr and LiBr, at a temperature as low as the melting temperature of the bath which may be as low as 348° C., in an atmosphere of an inert gas. The flow is regulated by observing the continued presence of the hot spots which indicate that the ignition temperature is being maintained in the zone of reaction.

The titanium sponge formed thereby may thereafter be rendered substantially pure by known methods of removing the impurities e.g., by sublimation, vacuum distillation or water and acid leaching.

The process is economical of operating costs since the temperatures required for the invention are lower than those required in known processes thus requiring less fuel and resulting in less wear and maintenance of equipment. The process is economical of material costs since the lithium bromide or chloride produced may be electrolyzed to recover the lithium metal and bromine or chlorine, the lithium metal thus recovered being used directly in the process and the bromine or chlorine to make more titanium halide for use in the process. The potassium or other alkali metal halide comprising the used bath after thus removing the lithium halide by electrolysis may be used in making up more bath for use according to the invention. The percentage of titanium recovered from that theoretically possible is high. The sponge produced compares favorably with sponge produced by known processes.

Having described the invention, what is claimed and desired to be protected by Letters Patent is:

1. The method of producing titanium metal sponge which comprises adding dropwise a liquid titanium tetrahalide selected from the class consisting of the tetrabromide and the tetrachloride onto molten lithium metal present in excess of the stoiochiometric quantity required to react with the tetrahalide and suspended at the surface of a molten salt bath, to provide a reaction zone at the surface of the molten lithium having a temperature above 200° C. but not over 550° C. when the tetrabromide is employed and above 185° C. but not over 550° C. when the tetrachloride is employed, at a controlled rate of addition sufficient to maintain ignition conditions between the lithium and the tetrahalide in said reaction zone, said bath having a melting point of not over 550° C. and consisting essentially of a mixture of halides selected from the class consisting of alkali metal and alkaline earth halides.

2. The method of claim 1 wherein the tetrahalide is titanium tetrachloride and the bath consists of a mixture of LiCl and a chloride selected from the class consisting of KCl, NaCl, CsCl, RbCl, and alkaline earth chlorides.

3. The method of claim 2 wherein the tetrahalide is $TiBr_4$ and the bath consists of a mixture of LiBr and a bromide selected from the class consisting of KBr, NaCl, CsBr, RbBr, and alkaline earth bromides.

4. The method of claim 3 wherein the bath consists of a mixture of Li3r and KBr.

5. The method of claim 4 wherein the LiBr is present in an amount of between 70 and 43 percent and KBr is present in an amount between 30 and 57 percent by weight to give a melting point to the bath of not over 450° C.

6. The continuous method of producing titanium metal sponge which comprises raising the temperature of a confined molten salt bath consisting essentially of a mixture of alkali metal halides and alkaline earth halides, at least one of which alkali metal halides is a lithium halide, to a temperature between the melting point of the bath and 550° C., protecting the surface of the bath by an inert gas, introducing lithium metal to form and maintain a pool of molten lithium metal suspended in said bath a portion of which is exposed above the surface of said bath, feeding dropwise a liquid titanium tetrahalide selected from the class consisting of $TiBr_4$ and $TiCl_4$ in less than the stroichiometric quantity required to react with the lithium metal present, maintaining a reaction zone at the exposed surface of said molten lithium metal of a temperature of at least 200° C. when $TiBr_4$ is employed and at least 185° C. when $TiCl_4$ is employed.

7. The method of claim 5 wherein said lithium metal is added in the molten state to said bath.

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