May 10, 1960 J. L. VAUGHAN 2,936,232

METHOD OF PRODUCING TITANIUM

Filed Dec. 31, 1954

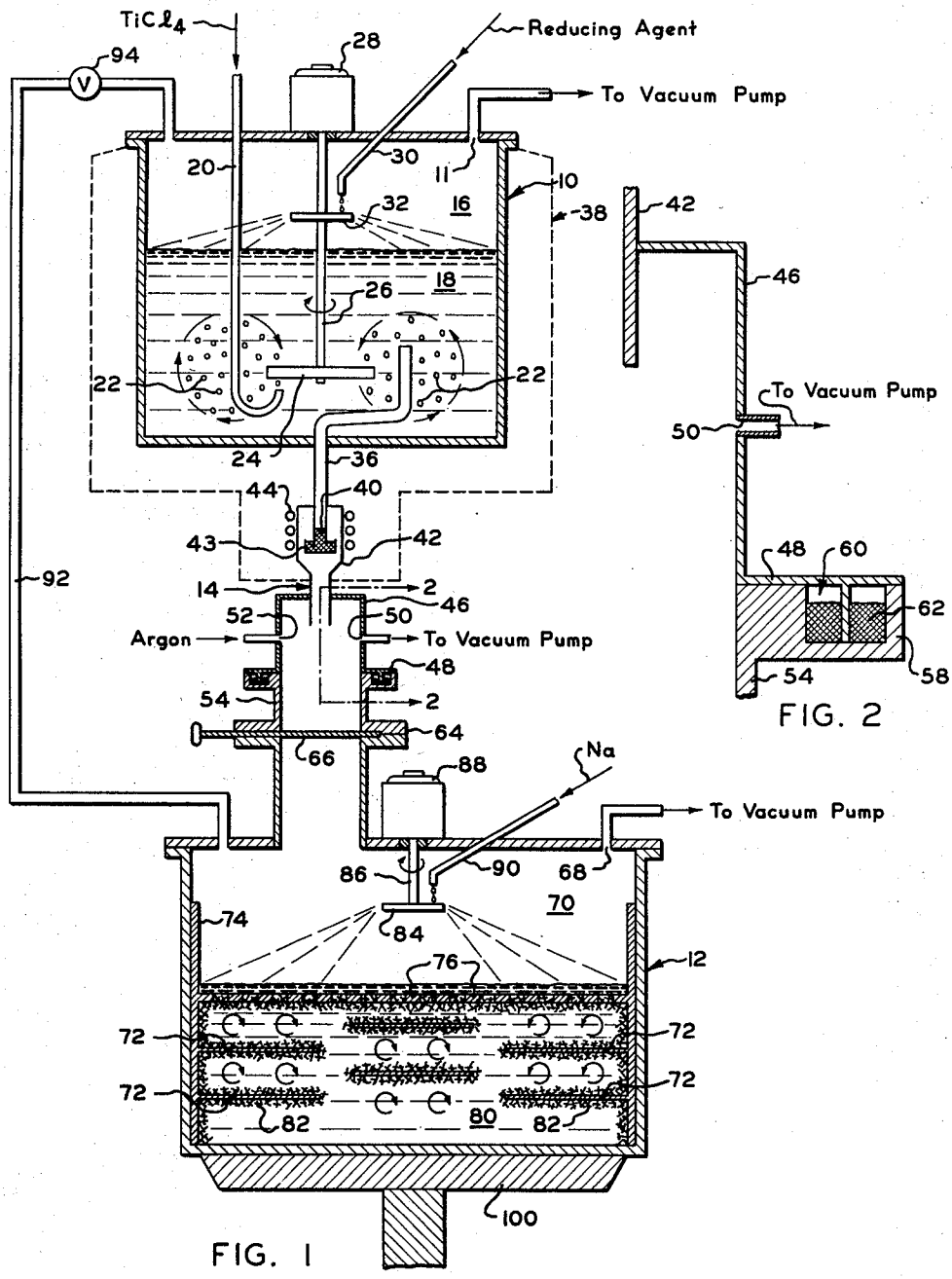


FIG. 2

FIG. 1

INVENTOR.
James L. Vaughan
BY
Oliver W. Hayes
ATTORNEY

United States Patent Office 2,936,232
Patented May 10, 1960

2,936,232

METHOD OF PRODUCING TITANIUM

James L. Vaughan, Needham, Mass., assignor to National Research Corporation, Cambridge, Mass., a corporation of Massachusetts

Application December 31, 1954, Serial No. 479,086

2 Claims. (Cl. 75—84.5)

This invention relates to the production of metals and more particularly to the production of refractory metals such as titanium and the like.

A principal object of the present invention is to provide an improved apparatus and process for the production of titanium and like metals by the multi-stage reduction of a like metal compound contained in a molten halide bath.

Another object of the invention is to provide an improved apparatus and process of the above type which is particularly adapted to large-scale commercial operation with high rates of production.

Still another object of the invention is to provide an improved process and apparatus of the type generally described in the copending application of Hnilicka, Serial No. 461,981, filed October 13, 1954, now Patent No. 2,847,205, granted August 12, 1958.

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

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

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

Fig. 1 is a diagrammatic, schematic drawing illustrating one preferred embodiment of the invention; and

Fig. 2 is a diagrammatic, enlarged detail of another portion of Fig. 1.

The production of titanium and related metals is accompanied by many difficulties. It is the intention of the present invention to provide an improved apparatus and process providing for multi-stage reduction of a titanium compound. In an earlier stage reactor, it is intended that titanium tetrachloride be partially reduced by a reducing agent to lower chlorides while contained in a molten halide bath. Transfer means are provided which carry the reacted bath in an uncontaminated state from the earlier stage reactor to a separate later stage reactor for further reduction of the titanium lower chlorides to metallic titanium.

In order to achieve the objects set forth, the earlier stage reactor, which for convenience will be referred to hereinafter as the first stage reactor, is designed to accomplish the reduction of titanium tetrachloride to lower chlorides in the following manner. The first stage reactor is adapted to form a chamber within which to locate a molten halide bath containing lower chlorides of titanium. The molten halide bath is preferably sodium chloride but may be one or more of the halides of the class consisting of alkali metal halides and alkaline earth metal halides. Evacuation means are provided for

ridding contaminants, but it is permissible to provide for other means which will provide an inert atmosphere. The first stage reactor is further provided with means for introducing titanium tetrachloride below the surface of the molten halide bath where an agitator means is located to provide intimate contact between the titanium tetrachloride and the lower chlorides of titanium, preferably the dichloride, contained in the bath. The reaction which results may be represented as:

$$TiCl_4+TiCl_2\rightarrow 2TiCl_3$$

The agitator means is further adapted to circulate the bath so that the $TiCl_3$ product is made available to react with a reducing agent which is fed into the halide bath at a point or zone spaced apart from the point or zone where titanium tetrachloride is introduced. The rate at which circulation is carried out is that which preferably produces an amount of lower chloride of titanium per cycle which is less than 1 weight percent of the amount of bath being circulated. The reducing agent is preferably sodium but may be one or more metals from the class consisting of lithium, sodium, potassium, magnesium and calcium. It is preferred that the amount of reducing agent used be stoichiometrically less than that required to reduce the total titanium halide content within the bath below titanium dihalide. In this manner a preferred average titanium valence of 2.2 is maintained. At the same time, the preferred mole ratio of sodium to titanium tetrachloride feed is maintained at less than 1.8 to 1.0. In this manner a desired overall reaction which may be represented as

$$2TiCl_3+2Na\rightarrow 2NaCl+2TiCl_2$$

is substantially achieved. However, some titanium dichloride and trichloride will contact the sodium so that titanium fines are also produced in a manner represented as:

$$TiCl_2+2Na\rightarrow 2NaCl+Ti$$

$$TiCl_3+3Na\rightarrow 3NaCl+Ti$$

In order to digest the fines, which at this stage are undesirable, to a soluble lower chloride, more preferably the dichloride, the bath is allowed a residence time on the order of two hours in situ before transferring it through transfer means to the later stage reactor for further reduction of the lower chlorides to metallic titanium. The digestion reaction may be represented as:

$$Ti+2TiCl_3\rightarrow 3TiCl_2$$

The preferred transfer means is arranged to facilitate an uncontaminated transfer of the molten halide bath and is further provided with means for forming a frozen salt plug capable of sealing off the first stage reactor.

Within the second stage reactor, of which there may be more than one to increase production, a reducing agent, again preferably sodium, is introduced to the surface of the molten salt bath and reacts with the lower chlorides contained in the molten halide bath to form metallic titanium. This reaction may be represented as:

$$TiCl_2+2Na\rightarrow 2NaCl+Ti$$

The second stage reactor is also preferably provided with baffle means with which to encourage growth of metallic titanium in crystalline form by restricting and minimizing convection current activity. Preferably the baffle means will be in the form of a removable lattice structure of horizontal convection current baffles.

Referring now to the drawings, shown in Fig. 1 is one preferred arrangement of elements embodied in the present invention. The earlier or first stage reactor is shown at **10**, available to feed a later or second stage reactor **12** through a transfer means **14**. The first stage reactor **10**,

which is adapted to be evacuated through means **11**, comprises a chamber **16** within which is achieved partial reduction of titanium tetrachloride to a solution of lower chlorides in a molten halide bath. Located to the outside of first stage reactor **10**, and extending down part way on the transfer means **14**, is a means **38** for removing excess heat from the molten halide bath and also for supplying heat when desired. In producing the desired partial reduction, titanium tetrachloride is preferably introduced below the surface of the molten halide bath by means **20** which is preferably a tube. The molten halide bath **18** is preferably a halide or eutectic mixture of halides chosen from the class consisting of alkali metal halides and alkaline earth metal halides. In one preferred embodiment, sodium chloride is used. The titanium tetrachloride introduced to the bath, and represented after its introduction by bubbles **22**, is brought into intimate contact with the lower chlorides of titanium, preferably the dichloride, in a first zone through the action of agitator means **24** to form titanium trichloride. Agitator means **24** is suspended in the molten halide bath **18** by a shaft **26** which is in turn driven by a motor **28**. Agitator means **24** is preferably a turbine and is adapted to circulate the titanium trichloride which is formed in a first zone to a second zone preferably located at the surface of bath **18**. The reducing agent is preferably introduced into chamber **16** by a means **30** which comprises a pipe and is uniformly distributed to the surface of molten bath **18** through the agency of spinning disc **32**. As a result of so contacting the reducing agent, preferably sodium, with titanium trichloride and titanium dichloride, additional lower chlorides are formed in the molten halide bath **18** along with titanium fines. The molten halide bath **18** is retained in situ until such time as the titanium fines have been digested again to lower chlorides of titanium, which will preferably go into solution with the said molten halide bath.

The transfer means **14** preferably comprises a rigidly positioned pipe member **36**, one end of which penetrates the bottom of the first stage reactor **10**, extending up from the bottom of the reactor **10** to a height slightly above that a which the agitator means **24** is suspended. Transfer means **14** is provided with means for forming a frozen salt plug represented at **40** which preferably comprises a trap means **42** and freezing coils **44**. The trap means **42** is illustrated as including a sump **43** for collecting a charge of molten salt which can be frozen by coils **44** to plug the end of pipe **36**. Additional molten salt flowing down pipe **36** after freezing of the bottom plug will also be frozen, at least near the bottom of pipe **36**. The lower end of trap means **42** extends into sealing means **46**, the lower end of said sealing means **46** being adapted to form a vacuum seal **48** with a corresponding seal means **54** of the second stage reactor **12**. Sealing means **46** is provided with means **50** and **52** for evacuating and/or flushing said sealing means with an inert gas such as argon. In order to protect the sealing qualities of vacuum seal **48**, which would be adversely affected by heat given off from the molten halide bath during transfer, the walls of sealing means **46** are preferably of light construction and comprise a material having relatively low heat conductance, thereby forming an effective heat break.

For the sake of clarity, Fig. 2 is provided to show the details of vacuum seal **48**. The second stage sealing means **54** is provided with a channeled flange **58**, the channel **60** of which is adapted to contain a meltable metal sealing material **62**, into which material the lower end of sealing means **46** is adapted to be inserted after sealing material **62** (e.g., solder or the like) has been melted by a suitable heater (not shown). When the seal is in position, the solder **62** is again frozen to complete the seal.

Returning now to Fig. 1, seal means **54** is preferably a hollow extension of the second stage reactor **12** which

is provided with vacuum closure **64** adapted to be opened through manipulation of sliding door **66**. This arrangement facilitates evacuating or, if preferred, purging of chamber **70** with inert gas prior to positioning reactor **12** to receive the molten halide bath, transferred from the first stage reactor **10**.

Second stage reactor chamber **70** is adapted to be evacuated through the pipe means **68**. Located within the chamber **70** are baffle means **72** adapted to restrict convection current activity within molten halide bath **80**. Preferably the baffle means **72** is constructed so as to form a removable lattice structure, the horizontal convection current baffles **72** thereof being supported by support **74** located within chamber **70**. It is also preferred that the removable lattice support **74** be provided with a perforated horizontal member **76** located above the horizontal convection current baffles **72** and adapted to support an initially formed metallic titanium crust. The second stage reactor **12** is further provided with means **84** for introducing a reducing agent, preferably sodium, to the surface of the molten halide bath **80**. This introducing means **84** is preferably in the form of a spinning disc which is supported by shaft **86** driven by electric motor means **88**. A pipe **90** is provided for supplying the reducing agent from an outside source (not shown) to spinning disc **84**. A positioning means **100**, one preferred embodiment of which is a hydraulic lift, is utilized to properly align and contact the second stage reactor **12** with transfer means **14**, thereby insuring that vacuum seal **48** is secured and that a vacuum-tight passage is had for transfer of the molten halide bath from first stage reactor **10** to second stage reactor **12**. In order to expedite transfer of the molten halides from the first stage reactor **10** to the second stage reactor **12**, pressure-equalizing pipe **92** is provided, to be opened or closed by valve **94**.

Growth of titanium crystals will start on the perforated horizontal member **76** and then on the remaining parts of the baffle means **72** which are in contact with the molten halide bath **80**. This is facilitated by locating the perforated horizontal member **76** at a point or zone conveniently near where sodium enters the bath **80**. Metallic titanium deposits on a given structure in the form of an accretion which is initially fines, later followed by the growth of large crystals. In order to aid in the deposition of the titanium and, more particularly, to facilitate growth of large crystals of titanium, convection currents, which result from heating or cooling of bath **80**, are localized and minimized by the use of the baffle means **72**. The entire structure **74** is constructed so as to be removed from chamber **70** for removal therefrom of the metallic titanium product **82** and for any further processing which may be desired.

In the operation of the complete equipment illustrated in Figs. 1 and 2, first stage reactor chamber **16** and pipe member **36** are evacuated and/or purged by an inert gas such as argon. A charge of molten anhydrous metal halide containing titanium dichloride, sufficient to fill pipe means **36** and reactor chamber **16** to a point above the top of pipe **16**, is then preferably poured into the reactor. Cooling coils **44** are then operated to freeze a portion of the molten salt mixture and form the salt plug **40**. Titanium tetrachloride is then pumped in through tube **20** to enter below the surface of the molten halide bath. Agitator means **24** is then put into operation and thereafter reducing agent, preferably sodium, in an amount previously described is preferably entered into the chamber **16** through pipe **30** and distributed to the surface of the bath. Residence time requirements are satisfied and, as a result, the produced lower chlorides of titanium are dissolved in the molten salt bath.

A second stage reactor **12**, the reaction chamber **70** of which has been evacuated and provided with baffle means **72**, is aligned and positioned to form a vacuum seal at **48** with transfer means **14**. The now enclosed space in

the transfer means 14 which is located between the salt plug 40 and vacuum closure 64 is evacuated and purged with argon. Sliding door 66 is opened and operation of the cooling coil 44 is discontinued to allow the salt plug to melt. Vacuum break line 92 having been attached, valve 94 is opened and the molten halide bath passes through the transfer means 14 and into the second stage reactor chamber 70. After transfer of the molten halide bath is completed, the sliding door 66 and valve 94 are closed, and the second stage reactor may be relocated elsewhere or left in situ to further reduce the dissolved lower chlorides of titanium to metallic titanium. In either case, the first stage reactor 10 is again ready to be operated. The second stage reactor chamber 70 is filled by the transferred molten halide bath to a height above that at which the horizontal perforated member 76 is positioned. Sodium distribution means 84 is then operated and sodium is distributed to the surface of the bath 80, producing metallic titanium 82.

The apparatus described above is preferably made of Inconel or nickel so as to resist the corrosive action of titanium chlorides and sodium chloride or other halides used.

The present invention may, in addition to being used in the production of metallic titanium, be employed for the manufacture of other refractory metals by reduction of suitable compounds carried in a fused salt. It can also be used to coreduce several metallic compounds to form alloys thereof. Accordingly, when the expressions "titanium" or "metal" and the like are used in the appended claims, they are intended to include alloys as well as the pure metal.

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

What is claimed is:

1. In a multi-stage process for the production of metallic titanium from dissolved titanium chlorides contained in a molten halide bath comprising sodium chloride, the steps of feeding titanium tetrachloride to the bath below the surface thereof, agitating the bath to provide intimate contact between the titanium tetrachloride and dissolved titanium dichloride, feeding sodium to the surface of the bath in an amount stoichiometrically less than that required to reduce the total titanium chloride content within the bath below titanium dichloride, the feed of sodium resulting in the production of a mixture of titanium fines, titanium dichloride and titanium trichloride, digesting said titanium fines in the bath to titanium dichloride by reaction with dissolved titanium trichloride over an extended period of time to provide a bath whose titanium content is essentially in the form of dissolved titanium dichloride and dissolved titanium trichloride, and thereafter transferring the bath containing said titanium chlorides to a second stage for further reduction to metallic titanium, the average titanium valence being maintained above 2.0 during substantially all the extended period of time, the fused bath at the time of transfer having an average titanium valence on the order of 2.2.

2. The process of claim 1 wherein the reduction of titanium dichloride to metallic titanium is carried out in the second stage by introducing a reducing agent to the transferred bath while restricting convection current activity within said transferred bath.

References Cited in the file of this patent

UNITED STATES PATENTS

2,148,345	Freudenberg	Feb. 21, 1939
2,564,337	Maddex	Aug. 14, 1951
2,607,674	Winter	Aug. 19, 1952
2,647,826	Jordan	Aug. 4, 1953
2,706,153	Glasser	Apr. 12, 1955

FOREIGN PATENTS

694,921	Great Britain	July 29, 1953