

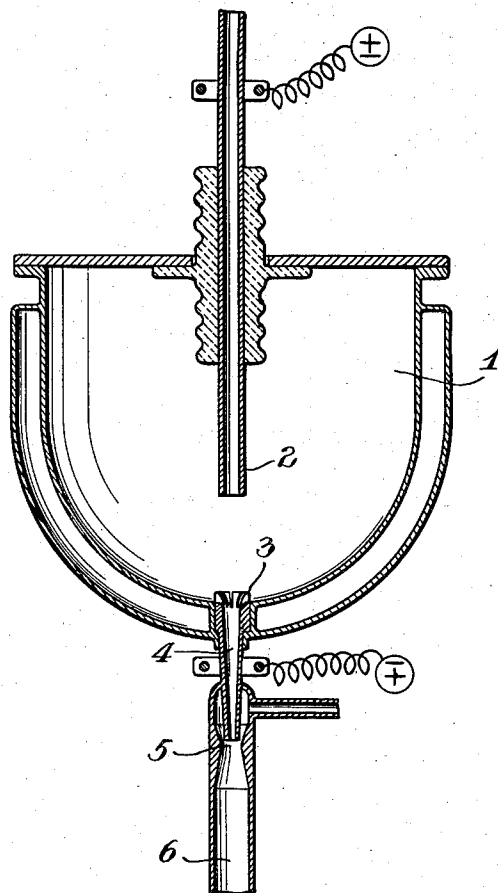
Nov. 11, 1958

KOJIRO ISHIZUKA

2,860,094

PROCESS FOR THE RECOVERY OF METALLIC TITANIUM

Filed March 18, 1954



1

2,860,094

PROCESS FOR THE RECOVERY OF METALLIC TITANIUM

Kojiro Ishizuka, Ashiya City, Japan

Application March 18, 1954, Serial No. 417,108

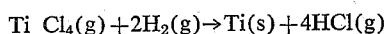
1 Claim. (Cl. 204—164)

The present invention relates to a process for recovering metallic titanium from tetrachloride, wherein titanium tetrachloride is mixed with hydrogen in excess of stoichiometrical amount, and a substance of high electrical conductivity, for instance, minute particles of metallic titanium or low grade titanium tetrachloride is admixed therewith, and the mixture thus obtained is then ejected from one electrode towards the other, receiving electrode having a hole, whereby metallic titanium is recovered from titanium tetrachloride.

The object of this invention is to provide a process, wherein metallic titanium is obtained extremely easily from a technical and economical point of view, in a simpler and continuous operation and with an extraordinarily lower equipment cost per unit production equipment, as compared with the Kroll process where metallic magnesium is used.

Hitherto, various investigations have been conducted on the process for obtaining metallic titanium from the titanium tetrachloride formed by treating titanium-containing materials with chlorine. However, the process which is now being employed in the industrial practice is one which comprises reacting titanium tetrachloride with metallic magnesium in an inert gas at elevated temperatures, which requires, however, an abundant quantity of metallic magnesium of high purity, and besides the operation is not easy. Furthermore, the present day operation is batchwise, and in addition high electric power is required for the recovery of metallic magnesium from magnesium chloride then formed. Hence, this process is not yet sufficiently satisfactory, particularly in view of achieving low production cost.

It has been already well-known that titanium tetrachloride reacts with hydrogen at high temperatures above 2000° C. to produce metallic titanium according to the following equation:



It is, however, extraordinarily difficult to obtain metallic titanium industrially in the above mentioned reaction. For instance, in the process as has been developed lately, wherein the reaction is carried out in an electric furnace, colloidal material is employed for electrodes entering the metallic titanium. This process not only lowers the purity of the titanium, but also it is difficult to equip a quenching apparatus therein and thus the production efficiency is extremely low so that the industrial practice is not easy.

The present inventor has made an exhaustive investigation on an industrial process for obtaining metallic titanium practically in such a reaction as described above, and completed this invention, which enables an accurate and continuous production of metallic titanium at extremely low production cost and easily, by rapidly cooling the product obtained by directly subjecting titanium tetrachloride and hydrogen gases to electrical discharge. In particular, since the titanium tetrachloride and hydrogen have high electrical resistance and consequently in-

2

ulating property, the stability of electric arc is not only difficult to attain, but the electric power consumed between both electrodes is also very low, so low that an industrial practice is almost impossible. The present invention is however an excellent process, wherein substances are admixed in the gas stream, such as not lowering the purity of metallic titanium to be formed, for instance, minute particles of metallic titanium or of low grade titanium chloride, in order to improve thereby the electrical conductivity of the mixture. And the mixture thus improved in the conductivity is ejected from one electrode toward the other perforated electrode intended to receive the jet in order to effect electrical discharge by passing heavy electrical current between the said electrodes, whereby metallic titanium is produced.

It is an extremely easy task to maintain titanium tetrachloride having a boiling point of about 139° C. in gaseous state, and it is likewise very simple to control the mixing proportion between the titanium tetrachloride and hydrogen. The control of the flow rate of the aforementioned minute particles lowering the electrical resistance of the mixed gas stream of both gases, is also quite easy. Moreover, the adjustment of the discharge voltage is also easy by providing a device for moving one electrode up and down, with the other receiving electrode fixed, and the quenching of the reaction product and excess of hydrogen having passed through the perforated receiving electrode, as well as maintaining high yield of the product are likewise easy.

The electrical discharge enables an extremely stable operation absolutely without interruption, when the flow rates of both gases, the down flow of minute particles, the distance between the electrodes and the flow rate and temperature of the cooling hydrogen, etc. are kept constant. Particularly in the equipment and apparatus of a large scale production capacity, a stable, simpler and extremely stable operation may be attained, in contrast with a smaller scale production unit, and thus metallic titanium may be obtained at an extremely low cost and continuously.

The hydrogen chloride formed by the hydrogen reduction may be converted into high purity hydrogen chloride by separating from other gases due to liquefaction. And the hydrogen chloride reacts with oxygen of high purity to liberate chlorine of high purity. This chlorine may be used repeatedly for the tetrachloridizing of raw titanium materials. When both the hydrogen for reduction and the oxygen for oxidation are obtained by the electrolysis of water, raw titanium oxide, water and electric power are only needed as starting materials, from which metallic titanium is recovered.

The accompanying drawings represent one example of the apparatus for carrying out the present invention, where a direct current or single phase electric source is employed. In a reaction furnace 1, an electrode in the form of a nozzle 2 is provided; a gaseous substance formed by appropriately intermixing titanium tetrachloride, hydrogen and a good electrically conductive substance, e. g. minute particles of metallic titanium and of low grade titanium chloride with one another is ejected toward a perforated electrode 3 to build up an electrical discharge between both electrodes; the reaction gas, metallic titanium formed, excess hydrogen and other substances are allowed to pass through the perforated electrode 3 and to flow down from a gas port 4; then cooling hydrogen is added from an injector 5 to the downflowing gas and substances formed to cool them rapidly thereby to suppress the reverse reaction to an extremely low extent. Thus, they are introduced through the pipe 6 to a separating vessel and separated therein.

The examples of embodiment of this invention are as shown in the following:

3

(A) A mixed gas consisting of titanium tetrachloride and hydrogen in excess of the equivalent quantity was ejected through the hole of 5 mm. in inner diameter of nozzle shaped electrode 2 toward the perforated receiving electrode 3. When electrical discharge was effected with the electrode distance kept 15 mm., an extraordinary stable discharge condition was set up at the voltage of 2,400 v. and electric current of 1.26 milliamperes, evolving high heat and the reduction of titanium tetrachloride being effected vigorously, yielding gray white powder.

The purity of titanium tetrachloride and hydrogen used was in the order of 99.9%, and the analysis of the product showed 90% metallic titanium and balance low grade chloride.

The powder thus formed was then heated at high temperature in vacuum. Substantially no low grade titanium chloride remained then and metallic titanium of 99.6% purity was obtained.

(B) The powdered substance produced in Example A was mixed with the above-mentioned mixed gas under exclusion of atmospheric air, and a definite quantity of the mixture was allowed to flow down and eject as in Example A through the electrode hole 2. Then, electric discharge was induced with the electrode distance held 50 mm. The stability of discharge condition was established under 2400 volt and current of 5 milliamperes, and the titanium tetrachloride was reduced vigorously, yielding light dark gray powder.

The analysis of the said product showed that it was composed of 90% metallic titanium and balance low grade titanium chloride.

When this powdered substance was heated in vacuum at elevated temperatures, metallic titanium of 99.65% purity was obtained, with no substantial quantity of low grade chloride remaining. Further, for carrying out the present invention, provisions were made for various conditions, such that, the upper electrode was moved up and down in an enclosed apparatus; a tungsten tip was fitted on the pointed end of the electrode; both the upper and lower perforated receiving electrodes were each pro-

4

vided with oil-cooling apparatus; metallic titanium was used for the lower perforated receiving electrode; the apparatus was provided for ejecting gases from the upper electrode hole linearly; and the apparatus for quenching the product and excess gases was provided. However, as those conditions are out of the scope of this invention, no detailed descriptions have been given.

What I claim:

Electric discharge process of producing metallic titanium by the vapor phase reaction of titanium tetrachloride and hydrogen, which consists in forming a mixture consisting of a mixed gas of titanium tetrachloride and hydrogen in admixture with minute particles of a substance of high electrical conductivity and which will not affect the purity of the metallic titanium to be produced, injecting said mixture into a bowl-shaped electric discharge reaction chamber through a nozzle-shaped electrode which extends into said reaction chamber, effecting the reaction between titanium tetrachloride and hydrogen to produce metallic titanium by subjecting said mixture to an electric discharge established between said nozzle-shaped electrode and a hollow receiving electrode which extends into said reaction chamber at the end opposite to said nozzle-shaped electrode and removing the metallic titanium produced together with the remaining reaction products from the reaction chamber through said hollow receiving electrode by means of injector means provided in said receiving electrode, and rapidly cooling the reaction products by cold hydrogen injected by said injector means.

References Cited in the file of this patent

UNITED STATES PATENTS

1,046,043	Weintraub	Dec. 3, 1912
1,065,144	Von Koch	June 17, 1913
2,709,182	Farlon	May 24, 1955
2,724,692	Akerlof	Nov. 22, 1955

FOREIGN PATENTS

721,479	Germany	June 6, 1942
---------	---------	--------------