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F. J. SCHULTZ ET AL

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ELECTROLYTIC METHOD FOR REFINING TITANIUM METAL

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Fig. 1.

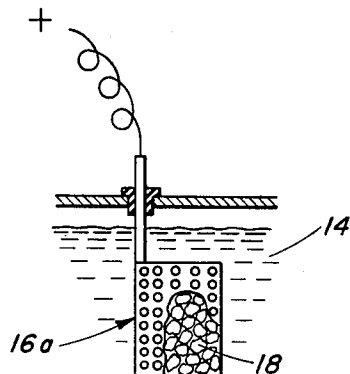
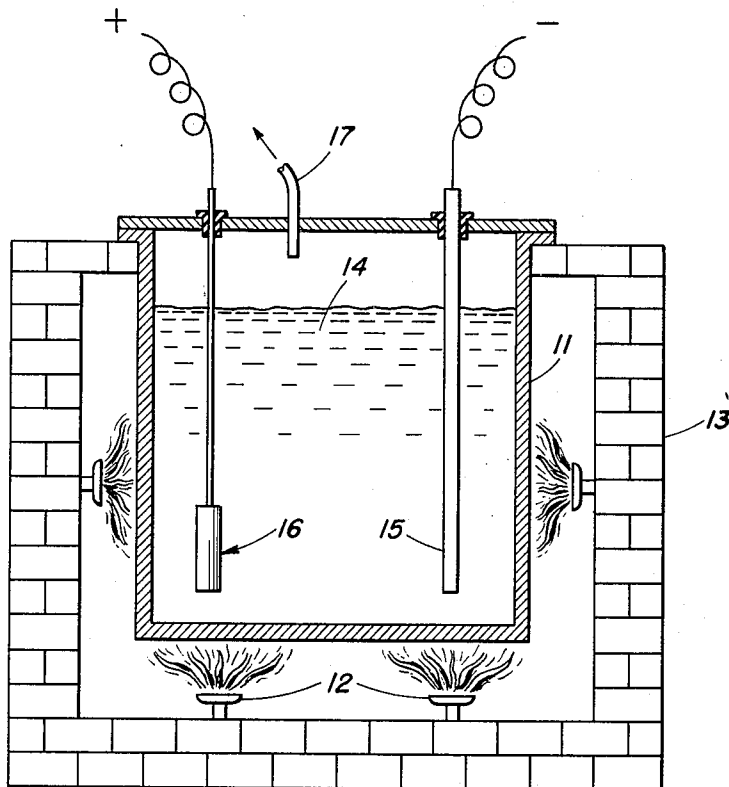


Fig. 2.

INVENTORS
Frank J. Schultz
Thomas M. Buck

BY

Charles F. Kugel
ATTORNEY

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ELECTROLYTIC METHOD FOR REFINING
TITANIUM METAL

Frank J. Schultz, Fords, and Thomas M. Buck, Plainfield,
N. J., assignors to National Lead Company, New York,
N. Y., a corporation of New Jersey

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This invention relates to a method for refining impure metal. More specifically it relates to an electrolytic method for refining titanium metal.

Titanium metal has been prepared by a number of methods including the chemical reaction between titanium halides and various metallic reducing agents. The titanium metal prepared by this procedure is often contaminated with impurities and it is desirable to have a method for refining such impure titanium metal.

It has been found that it is difficult to refine electrolytically impure titanium metal since titanium is multi-valent and, therefore, forms a number of valence states in the electrolytic medium used for such a refining process. For example, it is possible to form quadrivalent, trivalent, and divalent compounds such as titanium tetrachloride, titanium trichloride, and titanium dichloride. Furthermore, an aqueous solution may not be used as the electrolytic medium because reduced titanium salts may react with water. With respect to using molten salt electrolytes, it has been found that reduced titanium compounds such as titanium dichloride and titanium trichloride are soluble whereas titanium tetrachloride is not. With such a variety of titanium compounds having different valence states, i. e. titanium tetrachloride, trichloride and dichloride, it is difficult to refine impure titanium metal by such a process.

An object of this invention, therefore, is to provide a method for refining impure or crude titanium metal by an electrolytic process which is simple and economical to operate. A still further object of the instant invention is to provide an electrolytic refining process for the production of titanium metal which produces substantially pure and ductile titanium metal. These and other objects will become apparent from the following more complete description of the instant invention.

Broadly this invention contemplates a method for refining titanium metal which comprises passing electric current through an electrolytic cell having a cathode, and a molten halide salt electrolyte containing reduced titanium chlorides and employing impure titanium metal as the anode. By the term "reduced titanium chlorides" we mean titanium dichloride and titanium trichloride. The titanium metal employed as the anode is composed of the impure or crude titanium metal to be refined. The fused salt electrolyte should contain a concentration of from 0.1 to 5.0 molal reduced titanium chlorides of which at least 40% is titanium dichloride. The refining process should be carried out by maintaining during the passage of said current an anode current density from 0.01 to 3.0 amperes per square centimeter, and a cathode current density of at least 0.1 ampere per square centimeter but not exceeding five times the numerical molality of the reduced titanium chlorides present in the electrolyte.

For refining impure titanium metal to produce ductile titanium metal of exceptional quality, it is desirable to have at least 70% of the reduced titanium chlorides in the electrolyte present as titanium dichloride, the re-

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mainder being titanium trichloride. Furthermore it is preferred in such instances to have present a concentration in said electrolyte of from 0.3 to 2.0 molal reduced titanium chlorides. The anode current density preferably should be from 0.1 to 0.3 amperes per square centimeter and the cathode current density from 0.2 to 1.5 amperes per square centimeter during the passage of the current through the cell.

Fig. 1 is presented to illustrate more clearly in cross section the type of electrolytic cell which has been successfully used in refining titanium metal according to the instant invention. Referring to Fig. 1, the electrolytic cell consists of container 11 which is heated externally by gas flames 12 in furnace 13. The halide salt electrolyte 14 is placed in the container. A cathode 15 is inserted into the cell and extends down into the electrolyte. The cathode may be composed of any suitable material such as nickel. The anode 16 consists of impure titanium metal which is to be refined. The cell is further provided with vent 17 to permit the removal of any gaseous products.

The particular type of anode is unimportant and substantially any sintered, pressed or solid form may be used. It is particularly desirable to consolidate as by sintering or pressing finely divided impure titanium metal to be refined into the form of a compacted mass, for instance rods, sheets, bars and the like. These compacted masses are then immersed into the fused salt bath as the anode. However, many other methods may be used to prepare the anode for example, suspending the impure titanium metal in the fused salt bath by providing a container such as a metallic basket, e. g. one constructed of nickel or other suitable material in which the impure titanium metal may be placed. Fig. 2 shows pieces of impure titanium metal 18 in such a metallic anode basket 16A.

The halide salt electrolyte preferably comprises a molten halide mixture of alkali or alkaline earth metals or magnesium. It is particularly desirable to employ the chlorides of said metals because of the economics involved. These halides may be employed singly or in combinations. Mixtures of these halides which form low melting point eutectics are most convenient to employ.

The halide salt electrolyte should contain reduced titanium chlorides in concentration from 0.1 to 5.0 molal, of which at least 40% is titanium dichloride. In order to make ductile metal or exceptional quality the halide salt electrolyte should contain reduced titanium chlorides in concentration from 0.1 to 5.0 molal, preferably from 0.3 to 2.0 molal, the reduced titanium chlorides being at least 70% titanium dichloride. If the percentage of titanium dichloride is less than 40%, a titanium metal product is obtained which is no purer than the starting titanium metal and hence no refining is performed.

An atmosphere of argon or other inert gas is preferably maintained above the molten salt bath in order to prevent contamination of the titanium values by the outside atmosphere.

In order to carry out the process of the instant invention the impure titanium metal which acts as the anode is introduced into the fused salt bath which contains reduced titanium chlorides. An electric current is then passed through the cell. The impure titanium metal at the anode is then converted to solubilized titanium chlorides which are transferred through the salt bath to the cathode where they are reduced and deposited as titanium metal. The impurities originally present in the impure metal at the anode are released during the solubilization process and may settle out as a sludge in the bottom of the cell. The titanium metal at the anode

therefore is solubilized, transferred and subsequently deposited on the cathode in a purified state.

In operating the cell it is necessary to maintain current densities which fall within certain limits in order to refine impure titanium metal. It has been found that it is necessary to maintain an anode current density from 0.01 to 3.0 amperes per square centimeter and a cathode current density of at least 0.1 ampere per square centimeter but not in excess of five times the numerical molality of the reduced titanium chloride present in the electrolyte. If the anode current density is less than 0.01 ampere per square centimeter, the rate of titanium metal refined is excessively slow and therefore the throughput efficiencies are excessively low. If an anode current density exceeds 3.0 amperes per square centimeter, there is too much opportunity for titanium dichloride present in the salt electrolyte to be converted to titanium trichloride which results in the titanium values being chlorinated instead of producing titanium metal. The current densities of the electrodes are dependent on both the current passing through the cell and the effective electrode area, that is that portion of the surface area of the electrode at which electrolysis actually occurs. If the cathode current density is less than 0.1 ampere per square centimeter, titanium metal will not be deposited. If the maximum current density is exceeded, metals other than titanium, that is, those from the fused salt electrolyte will be deposited.

For ductile titanium metal of exceptional purity the anode current density should be from 0.1 to 0.3 ampere per square centimeter and the cathode current density from 0.2 to 1.5 amperes per square centimeter.

In order to describe more fully the invention, the following examples are presented:

EXAMPLE 1

An electrolytic cell of the type shown in Fig. 1 was used to refine impure titanium metal. A chloride salt electrolyte consisting of 7300 grams of strontium chloride and 2700 grams of sodium chloride was introduced into the cell and heated at a temperature of 700° C.

The electrolyte was charged with 1425 grams titanium dichloride and 463 grams titanium trichloride equivalent to a concentration of approximately 1.5 molal reduced titanium chlorides. About 75% of the total reduced titanium chlorides was titanium dichloride and the remainder titanium trichloride. The impure titanium metal which was to be refined was compressed into the form of a solid cylindrical anode by sintering and the impure titanium metal anode was inserted into the electrolyte. The impure titanium metal which had been prepared by the process described in U. S. Patent No. 2,205,854 had a Brinell hardness number of 361. A spectrographic analysis of the impure metal is reported in Table I.

An electric current of 65 amperes at an impressed voltage of 1.6 volts was then passed through the electrolytic cell. The cell was run with a cathode current density of 1.0 ampere per square centimeter and an anode current density of 0.25 ampere per square centimeter. The cell resistance was approximately 0.02 ohm.

The impure titanium metal at the anode was then converted to solubilized reduced titanium chlorides which were transferred through the fused salt electrolyte to the cathode at which point they were electrolytically reduced to titanium metal which was deposited on the cathode. The impurities which were present in the titanium metal forming the anode settled out as sludge material in the bottom of the cell.

The purified titanium metal which had deposited at the cathode was removed from the fused salt bath and leached with dilute hydrochloric acid. The metal was then washed with distilled water and dried at 50-60° C. The purified metal was then melted in an arc furnace to produce a metallic mass which had a Brinell hardness number of 204 and which was much purer than

the impure starting material as indicated by the spectrographic analysis also recorded in Table I.

EXAMPLE II

Another sample of impure titanium metal having a Brinell hardness number of 420 was refined electrolytically in the manner identical to that described in Example I. Again the impure titanium metal was sintered into the form of a cylindrical solid and the impure titanium metal anode inserted into the fused salt electrolyte. The operating conditions for this refining process were identical to those described in the previous example. The purified titanium metal which deposited at the cathode in this experiment was also melted into a metallic mass and had a Brinell hardness number of 212. The impure starting metal and the purified metal deposited at the cathode were analyzed spectrographically as reported in Table I.

Table I
SPECTROGRAPHIC DATA

	Example I		Example II	
	Impure Ti	Refined Ti	Impure Ti	Refined Ti
Percent Si.....	0.12	0.08	0.1	0.06
Percent Fe.....	0.25	0.001	0.03	0.001
Percent Al.....	0.02	0.01	0.1	0.05
Percent Sn.....	0.004	<0.001	<0.001	<0.001
Percent Mg.....	0.05	0.0007	0.01	0.001
Percent Mn.....	0.14	0.04	0.002	0.001
Percent Cr.....	0.6	0.06	0.004	0.003
Percent Ni.....	0.02	<0.001	0.03	0.01

It has been shown by the description and the examples presented above that impure titanium metal may be refined by passing electric current through an electrolytic cell in which the impure titanium metal acts as the anode and in which the molten salt electrolyte contains reduced titanium compounds. Furthermore it has been established that high purity ductile titanium metal may be produced by an electrolytic refining process which is simple and economical to operate.

While this invention has been described and illustrated by the examples shown, it is not intended to be strictly limited thereto and other modifications and variations may be employed within the scope of the following claims.

We claim:

1. Method for refining titanium metal which comprises passing electric current through an electrolytic cell having an anode and a cathode and a molten halide salt electrolyte, employing impure titanium metal as the anode in said cell, said electrolyte being composed of at least one compound selected from the group consisting of the halide salts of alkali metals, alkaline earth metals, and magnesium, said electrolyte further containing soluble titanium compounds selected from the group consisting of titanium dichloride and titanium trichloride in concentration from 0.1 to 5.0 molal, said soluble titanium compounds comprising at least 40% titanium dichloride, and maintaining during the passage of said current an anode current density from 0.01 to 3.0 ampere per square centimeter, and a cathode current density in amperes per square centimeter ranging from 0.1 up to 5 times the numerical molality of the soluble titanium compounds.

2. Method for refining titanium metal which comprises passing an electric current through an electrolytic cell having an anode, cathode and a molten halide salt electrolyte, employing impure titanium metal as the anode in said cell, said electrolyte composed of at least one compound selected from the group consisting of the halide salts of alkali metals, alkaline earth metals, and magnesium, said electrolyte containing soluble titanium compounds selected from the group consisting of titanium dichloride and titanium trichloride in concentration from 0.3 to 2.0 molal, and maintaining during the passage of said current an anode current density from 0.1 to 0.3 am-

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peres per square centimeter and a cathode current density from 0.2 to 1.5 amperes per square centimeter.

3. Method according to claim 2 in which the soluble titanium compounds comprise at least 70% titanium dichloride.

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