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ELECTROLYTIC PRODUCTION OF TITANIUM

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Fig. 1.

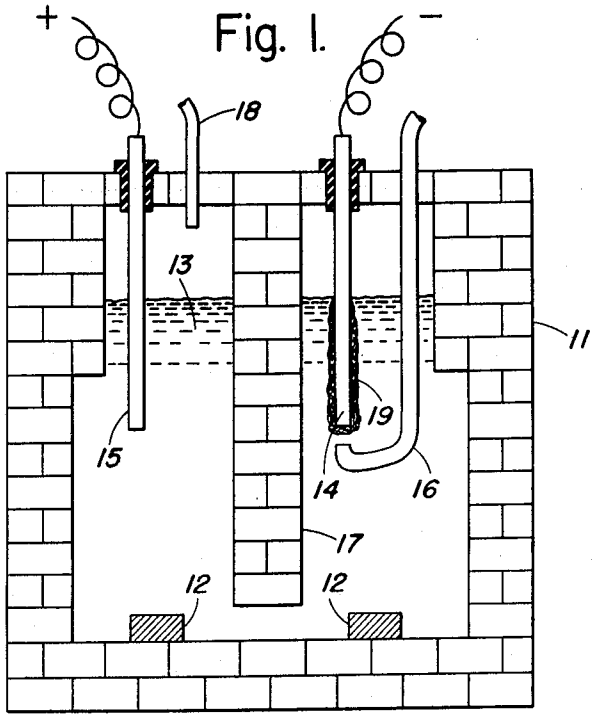
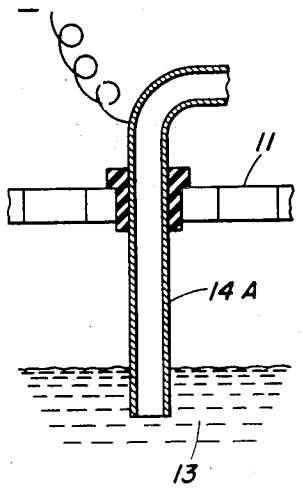


Fig. 2.



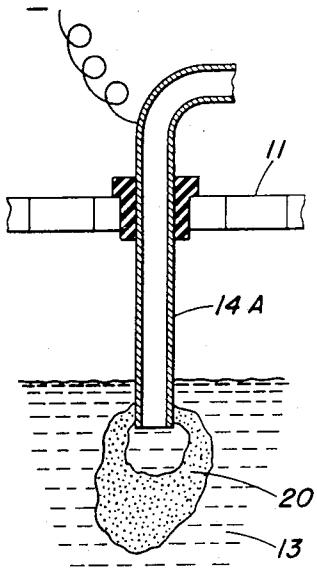


Fig. 3.

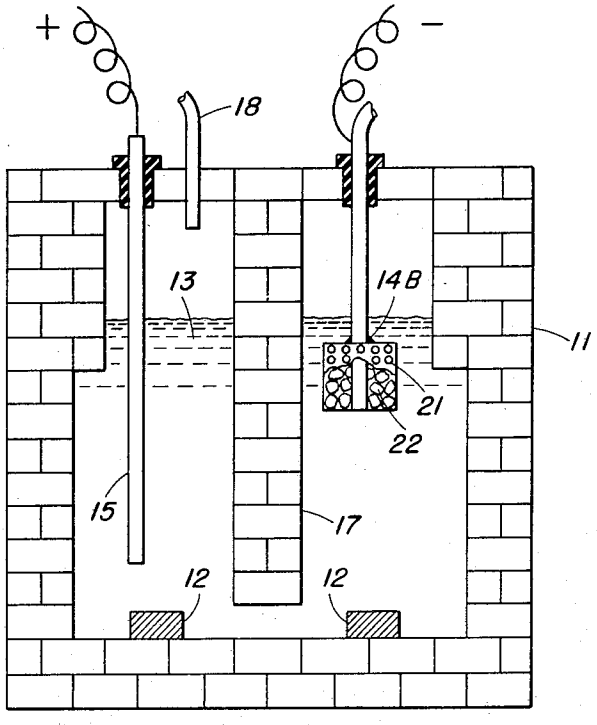


Fig. 4.

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ELECTROLYTIC PRODUCTION OF TITANIUM

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4 Claims. (Cl. 204—64)

This invention relates to the production of refractory metals. More particularly it relates to the production of high purity metal by an electrolytic process. More specifically it relates to a continuous electrolytic method for producing rare and refractory metal of high purity directly from metal halides.

There are many compounds of refractory metals which are found in nature but which are extremely difficult to reduce to the metallic state. In many instances it is relatively easy to convert such compounds to halides by halogenation processes. However in the case of such metal compounds it is difficult to produce the refractory metals from their respective halides. Included in the group of metals which fall within the class known as refractory metals are titanium, zirconium, vanadium, niobium, tantalum, molybdenum and tungsten.

Some of these refractory metals have heretofore been produced from their compounds by thermal reduction methods employing pressure and a reducing metal while others have been produced from salts such as, for instance, titanium tetrahalide by direct chemical reduction, employing metallic sodium or metallic magnesium reducing agents. Such methods for producing titanium metal are described in the literature, for instance, the Hunter process in Journal of the American Chemical Society, vol. 32, pp. 330–336, and the Kroll process in U. S. Patent No. 2,205,854. While these methods have produced such metals they suffer from a fundamental economic disadvantage in that the cost of the reducing metal employed, such as sodium or magnesium, is relatively high and the processes are expensive and cumbersome to operate.

Production of refractory metals by direct electrolysis processes on a practical basis has heretofore not been accomplished. Many of the halide salts of such metals are nonconductors and therefore cannot of themselves be electrolyzed. Therefore the use of a suitable electrolytic medium is necessary. The electrolysis of aqueous solutions of such metal compounds has to date produced only unsatisfactory results. Many of the halides of such refractory metals are either insoluble or slightly soluble in molten salt electrolytes.

An object of this invention therefore is to produce refractory metals electrolytically by a direct method from metal halides. A further object is to produce refractory metals directly by the reduction of metal halides whereby refractory metals of high purity may be produced. Another object is to produce refractory metals directly from metal halides by a continuous process. These and other objects of this invention will become apparent from the following more complete description of the instant invention.

This invention in its broadest aspects contemplates a method for the production of refractory metal in an electrolytic cell having a cathode, an anode and a fused salt electrolyte which comprises continuously introducing into said cell in the vapor state below the surface of said electrolyte a halide of the metal to be reduced, meanwhile

concurrently passing electric current through said cell at a rate synchronized with the metal halide addition so that the amount of current is sufficient to reduce the metal halide substantially directly to metal, said metal halide being added in juxtaposition to said cathode to contact the surfaces thereof.

According to the present invention, halides of such metals can be electrolytically, transiently reduced to reduced metal halides which are soluble in the molten electrolyte and the reduced metal halides are substantially immediately further reduced to metal. In this way it is possible to conduct a direct electrolysis of refractory metal halides whereby metal is formed on a continuous basis.

This invention contemplates employing as a feed material a refractory metal halide compound. Although all of the halides may be employed, it has been found however that fluorides are undesirable due to difficulties involved in handling such compounds because of the reactivity and corrosion effects on materials of construction at the temperatures employed. It is particularly desirable to employ chlorides and bromides since they are easily and economically prepared.

It is necessary to pass electric current concurrently through the cell at a rate synchronized with the rate of metal halide addition to the cell so that the amount of current is sufficient to reduce a substantial portion of the metal halide directly to metal.

It has further been discovered that refractory metals and particularly titanium and zirconium metals of exceptional purity which are ductile may be produced by the instant invention if the reduction of the metal halide is confined to the immediate vicinity of the cathode. The term "confined to the immediate vicinity of the cathode" means that the reduced metal halide, for example, reduced titanium chlorides, that is, titanium dichloride and titanium trichloride which are formed in the transitory state, immediately upon the introduction of metal halides into the molten salt electrolyte, are not permitted to diffuse throughout the molten salt electrolyte but are momentarily maintained directly in the immediate vicinity of the cathode whereby the metal halide values are immediately reduced to metal. Methods by which the reduction of metal halides to metal may be confined to the immediate vicinity of the cathode will be described in detail later in the specification.

It has further been found by concurrently adding electric current through the cell at a rate synchronized with the metal halide addition that the current efficiency of the cell is decidely increased. When employing halides of refractory metals which possess a multiplicity of valence states, an increase in the concentration of reduced metal halides in the salt bath which is obtained by adding current at a rate which falls behind a synchronized and concurrent rate results in excessive diffusion of the reduced halides throughout the electrolyte and permits rehalogenation of the reduced halides formed. Such diffusion which results in rehalogenation of the reduced halides decreases the current efficiency decidedly.

In carrying out the process of the instant invention it is preferred to add the metal halide in vapor form to the cell. In order to add some of the compounds at a substantially constant rate it is convenient to meter some of the compounds while they are in either the liquid or solid state.

In order to describe more clearly the details of the instant invention the process will be specifically illustrated by describing the production of titanium metal from titanium tetrahalide and more particularly from titanium tetrachloride.

The process of the instant invention may be described in more detail by use of the following figures in which

Fig. 1 shows a cross section of an electrolytic cell; Fig. 2 a cross section of a preferred hollow cathode arrangement; Fig. 3 a cross section of the metal deposit built up on the end of the hollow cathode; Fig. 4 a cell in cross section showing another arrangement for confining the reduction of titanium tetrahalide to the immediate vicinity of the cathode.

The apparatus shown in Fig. 1 consists of a cell container **11** heated by graphite electrodes **12**. The cell container is filled or partially filled with electrolyte **13**, in which is suspended cathode **14** and anode **15**. A conduit **16** is inserted into the cell which terminates in juxtaposition to the bottom portion of cathode **14**. This conduit is used for the introduction of titanium tetrachloride. A barrier **17** extending beneath the surface of the molten electrolyte separates the cathode **14** from the anode **15**. A vent **18** is provided to permit removal of gaseous products from the anode section of the cell. The cathode **14** is coated with a deposit of titanium metal **19**.

In operating the cell shown in Fig. 1, titanium tetrachloride vapors are passed into the cell through conduit **16** concurrently at a rate synchronized with the passage of the current through said cell and titanium metal is substantially immediately and directly deposited on the cathode. The electrolyte used in this cell is a fused halide salt of an alkali or alkaline earth metal including magnesium, particularly the chlorides of said salt.

In Fig. 2 is shown a cathode having a central bore, i. e. a hollow cathode. When such a cathode is employed in the electrolytic cell the bore acts as a conduit, and titanium tetrachloride is passed through the bore and enters the cell at the bottom of the cathode. The hollow cathode in Fig. 2 consists of a tantalum or nickel metal hollow tube **14A**. In operating a cell containing this particular type of cathode, the titanium tetrachloride gas is passed downwardly through the tube **14A** and enters the fused salt bath **13** at the bottom of the cathode.

In Fig. 3 is shown the same cathode described in Fig. 2. which has been in operation for a period of time. The titanium metal which is formed by the immediate and direct reduction of titanium tetrachloride is built up on the bottom of the cathode as a coarse titanium metal porous mass **20**. As the metal deposit increases in size as the reaction proceeds, a central portion of the mass of titanium metal apparently redissolves and eventually a hollow portion in the center of the titanium metal porous mass is formed. This formation of a porous titanium metal mass effectively confines the reduction of the titanium tetrachloride to titanium metal to the immediate vicinity of the cathode. In such an arrangement substantially none of the titanium values escapes beyond the boundaries of the titanium metal mass.

Titanium tetrachloride vapors are added through the hollow conductor. The reduced titanium chlorides in the transitory state are prevented from leaving the immediate vicinity of the closely packed cathodic titanium metal particles, and therefore the reduction of titanium tetrachloride to titanium metal is effectively confined to the immediate vicinity of the cathode.

In Fig. 4 the cathode **14B** comprises a hollow conductor connected to and extending into a porous container or basket **21** which contains closely packed titanium metal particles **22** also in contact with the hollow conductor.

In order to reduce titanium tetrachloride substantially directly to metal, sufficient current must be added concurrently through said cell at a rate synchronized with the rate of titanium tetrachloride addition. It has been found that theoretically sufficient current is added through the cell if about 4 faradays of electricity are concurrently passed through the cell as approximately one mol of titanium tetrachloride is introduced into the cell. In actual practice, however, it has been found desirable to add a quantity of electricity in somewhat excess of the theoretical amount in order to make up the current loss caused by side reactions in the cell. This extra quantity

of electricity will vary dependent on the cell design. With the types of cells shown in Fig. 1 and Fig. 4 it has been found desirable to add from about 4.5 to 5.0 faradays of electricity per mol of titanium tetrachloride introduced in order to maintain efficient cell operation. Theoretically if less than one mol of titanium tetrachloride is introduced into the cell for each 4 faradays of electricity which pass through the cell, other metals from the fused salt electrolyte may be deposited on the cathode with the titanium metal. When titanium tetrachloride is added in a quantity in excess of one mol for each 4 faradays of current which pass through the cell, titanium dichloride and titanium trichloride will be formed in the electrolyte and will diffuse and be transferred through the bath to the anode where they will combine with the chlorine released and will eventually be rechlorinated to titanium tetrachloride which will be released from the cell. The efficiency of such an operation will noticeably be decreased when the amount of titanium tetrachloride exceeds about 1.2 mols of titanium tetrachloride introduced for each 4 faradays of electricity.

With respect to production of metal from metal halides it must be remembered that sufficient current must be added concurrently through said cell at a rate synchronized with the rate of the metal chloride addition. The theoretical amount of electricity added per mol of refractory metal halide measured in faradays must be numerically substantially equal to the number of halide atoms present in said refractory metal halide molecule. Of course, as indicated above, the actual amount of electricity will be somewhat greater than the theoretical due to the side reactions which occur and the type of cell being used. As previously stated for each mol of titanium tetrachloride introduced it is necessary in theory to add substantially 4 faradays of electricity concurrently with the introduction of the titanium tetrahalide; in the case of molybdenum pentachloride, 5 faradays of current should be added for each mol of molybdenum pentachloride introduced. Likewise 4 faradays of current should be added for each mol of vanadium tetrachloride introduced into the cell. In all cases a small additional quantity of electricity is necessary in actual operation to overcome the effect of side reactions.

The fused salt electrolyte preferably comprises a molten halide mixture of alkali or alkaline earth metal, including magnesium, particularly the chlorides which may be employed singly or in combinations. Mixtures of these halides which form low melting point eutectics are most convenient to employ such as mixture of sodium chloride and strontium chloride or sodium chloride and magnesium chloride. The cell is operated at a relatively high current density, a typical cathode current density being about 3 amperes per square centimeter. Good results may be obtained within a broad range depending upon the cell characteristics and operating conditions. Generally, a cathode current density between 1 and 6 amperes per square centimeter has been found satisfactory. Within this current density range the metals and particularly titanium metal are deposited on and adhere to the cathode.

In order to illustrate the operation of various embodiments of this invention the following examples using titanium tetrachloride are shown.

Example 1

Using a cell similar to that shown in Fig. 1 having a conduit for the introduction of titanium tetrachloride vapors in juxtaposition to the cathode, a fused salt electrolyte consisting of 37 pounds of strontium chloride and 13 pounds of sodium chloride were added to the cell, and the fused salt electrolyte was heated to a temperature of 700° C. Titanium tetrachloride vapors were added at the rate of 2.9 grams per minute through the introductory conduit adjacent to the cathode. Concurrently an electrical current equivalent to 5.0 faradays per mol of tita-

nium tetrachloride was passed through the cell. This amount of current was in effect sufficient to immediately and completely reduce the titanium tetrachloride to titanium metal. In order to obtain substantially 5.0 faradays per mol of titanium tetrachloride introduced 125 amperes with an impressed voltage of approximately 6.5 volts was required. The cathode current density was 3 amperes per square centimeter and the anode current density was 0.5 ampere per square centimeter. The cell resistance was 0.03 ohm. The process was continued for a period of 2 hours at which time the introduction of titanium tetrachloride vapor was halted, and no further current was passed through the electrolytic cell. Titanium metal was deposited on the cathode in the form of an irregular tenacious mass composed of very fine crystals of powder-like characteristics. The titanium metal formed was removed from the cell and cooled in a chamber having an inert atmosphere. After cooling, the titanium metal was leached with dilute hydrochloric acid until the occluded salts were dissolved and the solubilized salts were removed by decantation and washing. The titanium metal was then washed in acetone and dried at room temperature. The final product weighed 50 grams and analyzed 98.0% titanium. After melting the sample to form a solid metal mass the metal possessed a Brinell hardness value of 490. The yield comprised 60% of the original titanium values added initially as titanium tetrachloride.

Example 2

Using the electrolytic cell shown in Fig. 1 but substituting the hollow cathode shown in Fig. 2 for the solid cathode shown in Fig. 1, 50 pounds of sodium chloride were introduced into the cell and heated to a temperature of 875° C. 2.95 grams per minute of titanium tetrachloride vapor were introduced into the electrolyte through the hollow cathode. Concurrently an electric current of 112 amperes at an impressed voltage of approximately 6 volts was passed through the cell.

This current was equivalent to 4.5 faradays per mol of titanium tetrachloride introduced into the cell. The cathode current density averaged 2 amperes per square centimeter and the anode current density was approximately 0.5 ampere per square centimeter. The cell resistance was 0.03 ohm. The hollow cathode was inserted into the electrolyte so that the open end was 2 inches below the surface of the salt bath. The titanium metal deposited initially as coarse crystals at the open end of the hollow cathode, and these crystals rapidly bridged across the end of the cathode to form a porous titanium metal mass. As the reaction progressed and the deposit grew, the center area of the metal deposit in contact with the incoming titanium tetrachloride was redissolved, thus leaving a hollow portion as illustrated in Fig. 3. The reduced titanium values passed through the porous spongy metal mass and in so doing were restricted to the vicinity of the cathode where they were readily further reduced to the metallic state, and the metal deposited on the outer surface of the cathodic deposit. The process was continued for a period of 2 hours. The metallic deposit was removed from the fused salt electrolyte and cooled in a chamber having an inert atmosphere. The cooled deposit was leached as described in Example 1. The dried leached titanium metal was recovered as coarse crystals having a definite metallic luster and being quite ductile. A sample prepared by arc melting these crystals analyzed 99.9% titanium and possessed a Brinell hardness of 133. About 80% of the titanium values introduced as titanium tetrachloride were recovered as titanium metal.

Example 3

Using the same operating conditions as described in Example 2, tianium metal was produced in the electrolytic cell shown in Fig. 4. The cathode consisted of a porous mass of titanium metal powder into which the titanium tetrachloride was directly introduced. Titanium metal of a quality substantially equal to that described in Example 2 was obtained.

As stated previously, the detailed description of the process including the examples for purposes of clarity have been illustrated using titanium tetrachloride, particularly titanium tetrachloride. It should be understood however that the other refractory metals may be produced by the process of the instant invention.

It has clearly been shown by the description of the instant invention and by the examples presented that refractory metals may be continuously and directly produced by passing electric current through an electrolytic cell at a rate synchronized with the metal halide addition so that the amount of electricity added per mol of refractory metal halide measured in faradays is numerically substantially equal to the number of halide atoms present in the said refractory metal halide molecule. Furthermore, it has been found that although most metal halides are in themselves either insoluble or slightly soluble in the fused salt electrolyte, by using a process of the instant invention refractory metals may be produced by a direct electrolytic method. The process of the instant invention employs simple and inexpensive apparatus and by such a process it is possible to produce economically refractory metals continuously by an electrolytic process.

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. The method for producing titanium metal by electrolysis of titanium tetrachloride in an electrolytic cell having a cathode, an insoluble anode and a fused bath consisting essentially of salt selected from the group consisting ol alkali metal halides, alkaline earth metal halides and mixtures thereof, comprising the steps of: introducing titanium tetrachloride into said cell below the surface of said electrolyte in juxtaposition to said cathode to contact the surfaces thereof; simultaneously, with the introduction of said titanium tetrachloride, passing electric current between said anode and said cathode at a rate synchronized with the titanium tetrachloride addition so that the amount of current is at all times sufficient to reduce the titanium tetrachloride being added to metal; depositing the titanium values of the titanium tetrachloride as a tenaciously adhering coarse crystalline deposit of titanium metal on the cathodic surface; and maintaining the electrolyte in a condition substantially free from dissolved titanium values except in the immediate vicinity of the cathode.

2. The method for producing titanium metal by electrolysis of titanium tetrachloride in an electrolytic cell having a cathode provided with a bore extending therethrough, an insoluble anode and a fused bath consisting essentially of salt selected from the group consisting of alkali metal halides, alkaline earth metal halides and mixtures thereof, comprising the steps of: introducing titanium tetrachloride into said cell through the bore of said cathode and below the surface of said electrolyte to contact the surfaces of said cathode; simultaneously, with the introduction of said titanium tetrachloride, passing electric current between said anode and said cathode at a rate synchronized with the titanium tetrachloride addition so that the amount of current is at all times sufficient to reduce the titanium tetrachloride being added to metal; depositing the titanium values of the titanium tetrachloride as a tenaciously adhering coarse crystalline deposit of titanium metal on the cathodic surface; and maintaining the electrolyte in a condition substantially free from dissolved titanium values except in the immediate vicinity of the cathode.

3. The method for producing titanium metal by electrolysis of titanium tetrachloride in an electrolytic cell having a porous titanium metal cathode, an insoluble

anode and a fused bath consisting essentially of salt selected from the group consisting of alkali metal halides, alkaline earth metal halides and mixtures thereof, comprising the steps of: introducing titanium tetrachloride into said cell below the surface of said electrolyte in juxtaposition to said cathode to contact the surfaces thereof; simultaneously, with the introduction of said titanium tetrachloride, passing electric current between said anode and said cathode at a rate synchronized with the titanium tetrachloride addition so that the amount of current is at all times sufficient to reduce the titanium tetrachloride being added to metal; confining, by said porous titanium metal cathode, said reduction to the immediate vicinity of said cathode, thereby depositing the titanium values of the titanium tetrachloride as a tenaciously adhering coarse crystalline deposit of titanium metal on the cathodic surface; and maintaining the electrolyte in a condition

substantially free from dissolved titanium values except in the immediate vicinity of the cathode.

4. Method according to claim 1 in which the cathode current density is from 1 to 6 amperes per square centimeter.

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