Sept. 15, 1959 W. R. OPIE ET AL **2,904,477**

ELECTROLYTIC METHOD FOR PRODUCTION OF REFRACTORY METAL

Filed April 25, 1956

Fig. 1.

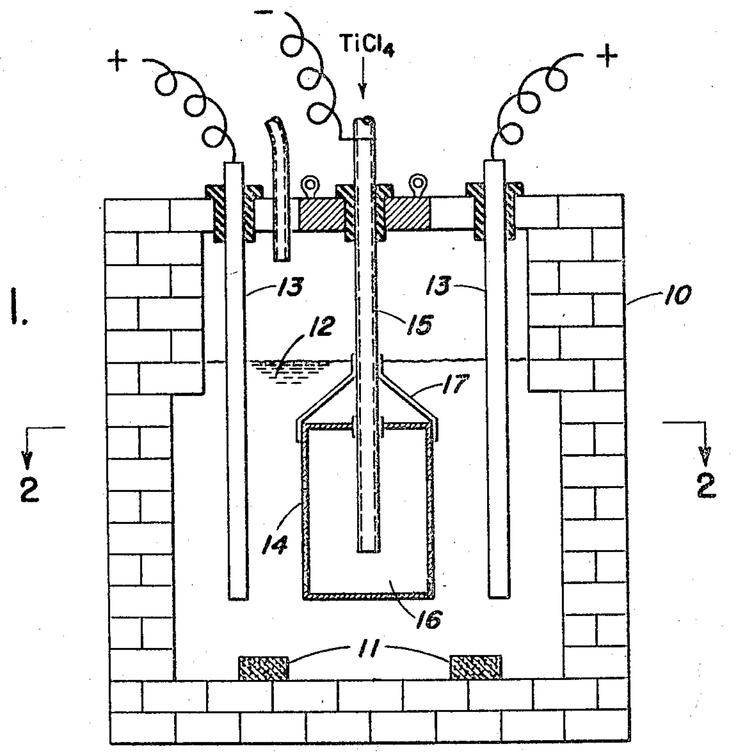
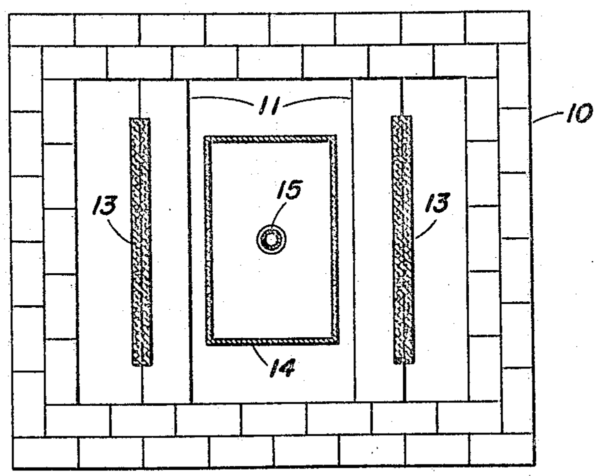


Fig. 2.



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United States Patent Office

2,904,477
Patented Sept. 15, 1959

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ELECTROLYTIC METHOD FOR PRODUCTION OF REFRACTORY METAL

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Application April 25, 1956, Serial No. 580,534

3 Claims. (Cl. 204—64)

This invention relates to the electrolytic production of refractory metals. More particularly, it relates to the production of high purity titanium metal by an electrolytic process adapted specifically to the production of titanium metal on a commercial scale, the instant application being a continuation-in-part of copending applications Serial No. 251,901, filed October 18, 1951, entitled "Electrolytic Production of Refractory Metal," now Patent No. 2,749,295, and Serial No. 325,819, filed December 13, 1952, entitled "Electrolytic Method and Means for Production of Refractory Metals," now abandoned.

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 the halides of the refractory metals by halogenation processes but 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, tungsten, thorium and uranium.

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 by direct chemical reduction of the halide employing metallic sodium or metallic magnesium as reducing agents. Such methods for producing titanium metal are described in the literature, for example 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.

The production of refractory metals, and in particular titanium metal by a direct electrolytic process, has now been accomplished, as is described and claimed in our above-identified copending applications. The instant application is concerned with novel operational features which have been discovered and which now make it possible to produce titanium metal of high purity on a commercial scale.

An object, therefore, of the present invention is to provide a superior electrolytic process for producing titanium metal of high purity from titanium metal halides.

A further object is to provide an improved method for operating an electrolytic cell whereby titanium metal of high purity may be produced economically in relatively large quantities and in a semi-continuous commercially feasible manner.

Another object of the invention is to operate an electrolytic cell of the fused salt bath type in such a manner as to deposit out titanium metal from said bath onto a porous cathodic surface, meanwhile maintaining the titanium metal deposit perforative so as to recover substantially all of the titanium metal in the form of relatively large coarse particles.

A still further object of the invention is to provide a superior electrolytic cell for producing highly ductile titanium metal on a commercial scale.

These and other objects of this invention will become apparent from the following more complete description thereof and the accompanying drawings in which:

Figure 1 is a vertical cross section of an electrolytic cell embodying a perforated cathodic surface in the form of a cathodic basket-like member; and

Figure 2 is a plan view of the cell on section line 2—2 of Fig. 1.

In its broadest aspects, the instant invention contemplates a semicontinuous method for producing a refractory metal, and in particular titanium metal in an electrolytic cell having a cathode, an anode and a fused salt bath by introducing a perforated cathodic basket-like member beneath the surface of the fused salt bath, introducing vaporous $TiCl_4$, below the surface of said bath and into the interior of the cathodic member while simultaneously passing direct current between the anode and cathodic member at a rate synchronized with the $TiCl_4$ addition so that the amount of current is sufficient to reduce the $TiCl_4$ being added to metal; and depositing the titanium metal as an adherent mass of crystalline titanium metal on the interior surfaces of the cathodic member while maintaining said adherent mass of titanium metal and the cathodic member in perforative form, the electrolyte exteriorly of the cathodic basket-like member being maintained substantially free from reduced titanium values.

As has been disclosed in our above-identified copending applications, the halides of the refractory metals, and in particular the chlorides and bromides of titanium, can be electrolytically reduced to titanium metal by passing direct current through the cell at a rate synchronized with the rate of titanium metal halide addition to the fused salt bath so that the amount of current is sufficient to reduce a substantial portion, if not all of the titanium metal halide, substantially directly to titanium metal. This technique is hereinafter referred to as substantially direct electrolysis of titanium metal halides in a fused salt bath.

According to the present invention it has been discovered that in general the production of titanium metal by direct electrolysis may be considerably improved not only by confining the titanium metal halide in the fused salt bath to the immediate vicinity of a cathodic surface such that the titanium metal will be deposited substantially in toti thereon but that by controlling the operating conditions of a particular cell and the type and orientation of the cathodic surface relative to the anode and the point of introduction of the titanium halide into the fused salt bath, the titanium metal deposit may be maintained perforative for a period of time sufficient to insure the practical commercial operation of the cell and the economical production of titanium metal in the form of a highly ductile commercially acceptable product.

The phrase "confined to the immediate vicinity of the cathode," as used herein, will be understood to mean that the titanium halide introduced into the fused salt bath is not permitted to diffuse throughout the molten salt electrolyte but is directed toward and maintained substantially in intimate contact with a cathodic surface whereby the titanium halide values are reduced to metal in the form of a titanium metal deposit on the cathodic surface. The preferred method and means by which the titanium halide may be confined to the immediate vicinity of a cathodic surface and the metal deposit formed thereon forms the subject matter of the instant invention and is described hereinafter in detail.

The phrase "operating conditions," as used herein, has reference to the control which must be maintained over variables such as time, temperature of the fused salt bath, the cathode current density, current-to-$TiCl_4$ feed ratio, basket cathode design, and titanium content of the electrolyte within the basket in order to carry out the step of maintaining the deposit of titanium metal in perforative form.

In this connection it should be explained that by perforative is meant a porous crystalline type of deposit as distinguished from a dense solid deposit. While there is some doubt as to the exact nature of the electrolytic chemistry involved, it has been found that direct electrolytic reduction of titanium halide values to titanium metal as large deposits of ductile crystalline metal can be accomplished on a commercial scale by the use of a perforated cathodic surface, preferably in the form of a basket, into which the $TiCl_4$ is introduced below the surface of the electrolyte. It may be postulated that ionic currents proceed from the anode through the perforations in the walls of the basket and through the voids in the perforative deposit of titanium metal to the inside of the basket where titanium ions may be found and reduced to titanium metal on the inner walls thereof. Contrary to what one might expect, a major portion of the ionic current does not stop at the exterior surfaces of the cathodic basket but apparently continues on through the perforations of the basket wall and through the relatively infinite number of substantially parallel paths in the perforative deposit of titanium metal to the interior of the basket.

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.

Referring to Fig. 1, the apparatus shown consists of a cell container **10** heated by graphite electrodes **11—11.** The cell container is filled or partially filled with an electrolyte **12** in which is suspended a pair of graphite anodes **13—13** between which is supported a cathode-member indicated generally at **14.** The fused salt electrolyte, sometimes referred to hereinafter as a fused salt bath, used in this and other cells hereinafter described comprises preferably a molten halide salt of an alkali or alkaline earth metal, including magnesium, particularly the chlorides of said metals 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, for example, mixtures of sodium chloride and strontium chloride, sodium chloride and lithium chloride, sodium chloride and barium chloride, sodium chloride and magnesium chloride or mixtures thereof. In general, the temperature of the fused salt bath may vary within the range of from 375° C. to 950° C. depending upon the particular salts used, the type of metal being deposited and the construction of the cell itself. For the production of titanium metal using a sodium chloride bath, operating temperatures within the range of from 825°–950° C. have been found suitable.

Referring again to the cathode-member **14,** the latter comprises a metal feed pipe **15** for introducing the tetrachloride into the electrolyte; and a substantially rectangular cathodic enlargement adjacent its lower end comprising preferably a metal basket-like member **16** having perforated side walls and an imperforate top and bottom. The basket is formed of titanium metal although sheet iron or steel may be used, and inasmuch as it is integral with or connected electrically to the cathodic feed pipe **15** by metal straps **17** or the like, it itself is cathodic. An important control in the operation of the cell is that of introducing the incoming titanium chlorides into the fused salt bath at a point in the basket-like member **14** below its mid-section and to this end the feed pipe **15** extends into the basket far enough so that the lower extremity of the pipe terminates close to the bottom of the basket. As a consequence, the titanium chlorides are brought into intimate contact with its cathodic surfaces which confine and restrict the dispersion of the titanium chlorides to that portion of the electrolyte within the interior of the basket **14** such that titanium metal is deposited on the perforated walls thereof in the form of a relatively large particles of ductile metal. Although the cathodic basket shown is highly satisfactory, it will be understood that it is within the purview of the invention to provide a basket having other configurations than that shown.

Other variables which must be controlled in the operation of any given cell so as to insure the formation of a perforative deposit of titanium metal are the size and arrangement of the holes in the walls of the basket and the basket thickness. Although holes varying from 1/8" in diameter spaced 1/4" on centers (16 holes to the square inch), to holes 1/2" in diameter spaced 1" on centers (1 hole per square inch) have been used, the preferred arrangement is 1/4" holes spaced 1/2" on centers (4 holes to the square inch). Moreover, baskets having two or four perforated sides are satisfactory but since a rectangular basket with two perforated sides used in conjunction with two anodes provides relatively constant plating area, this construction is preferred.

For reduction to take place on the inside or inner surfaces of the titanium deposit it is necessary that the ionic current pass through the perforative deposit of titanium metal to the interior of the basket where the titanium ions are found. As the deposit increases in thickness it offers increased resistance to the passage of the ionic current which for constant rate of reduction requires higher voltage and amperage. This in turn results in lower current efficiencies. In brief, the nature of the basket operation is such that it will cut itself off. However if operated under proper conditions a deposit of practical thickness and porosity will be formed on the inner walls of the basket.

In carrying out the process of the instant invention, the metal halide is added, preferably in vapor form, to the fused salt bath concurrently with the addition of current and in order that the halide may be added at a substantially constant rate, it is within the purview of the invention to meter the halide while it is in either a liquid or solid state. When using $TiCl_4$ it is convenient to meter the same in the liquid state.

As mentioned above, in order to reduce titanium tetrachloride to metal, a predetermined amount of current must be passed concurrently through said cell at a rate synchronized with the rate of titanium tetrachloride addition. A theoretically sufficient current will comprise about four faradays of electricity passed concurrently through the cell while approximately one mole of titanium tetrachloride is being introduced into the cell. In actual practice, however, it has been found desirable to add a quantity of electricity somewhat in excess of the theoretical amount in order to make up the current loss caused by side reactions in the cell. This extra quality of electricity will vary depending upon the cell design. With the types of cell shown in Fig. 1, it has been found desirable to add from about 4.5 to 6.0 faradays of electricity per mole of titanium tetrachloride introduced in order to maintain efficient cell operation.

Theoretically, if less than one mole of titanium tetrachloride is introduced into the cell for each four faradays of electricity which pass through the cell, other metals from the fused salt electrolyte may be deposited at the cathode. When titanium tetrachloride is added in a quantity in excess of one mole for each four 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 be noticeably decreased when the amount of titanium tetrachloride exceeds about 0.9 mole of titanium tetrachloride introduced for each four faradays of electricity.

An additional factor in the operation of the cell is the cathode current density which has been defined as current per unit area of perforated cathodic surface, the "area" being the multiple of the linear dimensions of the surface. In general, a cell of the type shown is operated at a relatively high current density, a typical cathode current density being about 400 amperes per square foot. Good results may be obtained within a broad range depending upon the cell characteristics and operating conditions. Generally, a cathode current density between 200 and 550 amperes per square foot has been found satisfactory. Within this current density range the metals and particularly titanium metal are deposited on and adhere to the cathode.

Yet another factor to be considered in operating any given cell to produce a perforative deposit of titanium metal is the interdependency of time, current-to-feed ratio and current density. As seen in the table below, runs of 24 hours duration can be made successfully using current-to-feed ratios of from 5.0 to 7.0 faradays per mole and current densities of from 200 to 500 amperes per square foot. However, with increasing time, the permissible range of current density and current-to-feed ratio narrows. Generally at constant current-to-feed ratio the deposit becomes denser with increasing current density while with constant current density the deposit decreases in density with increasing current-to-feed ratio. The table below shows approximate ranges of conditions determined by actual runs as being satisfactory for the deposition of perforative deposits of titanium metal on a perforated cathodic surface.

TABLE

Maximum time (hours) for operating under varying conditions of cathode current density and varying current-to-feed ratio

Current-to-feed ratio in faradays/mole $TiCl_4$	Cathode current density in amperes/square foot			
	200	300	400	500
	Hours	*Hours*	*Hours*	*Hours*
5.0	24	--------	--------	--------
5.5	36	48	--------	--------
6.0	48	60	60	--------
6.5	36	60	72	48
7.0	24	60	72	60

Time is also a factor to be considered in connection with the concentration of titanium values within the cathodic basket. Deposition of a perforative deposit of titanium metal occurs with titanium concentrations of well under one percent. This will be recognized as significantly below the concentration range employed in previously known methods. Satisfactory operations have been conducted with titanium concentrations not exceeding 1.0% and preferably not more than 0.1 or 0.2%. Concentrations above one or more percent are indicative of the formation of a solid relatively non perforative deposit of metal and in practice measurements of this magnitude or greater are used to alert the operator that the operation should be shut down since the metal deposit is tending toward the non perforative form.

EXAMPLE I

Using a cell similar to that shown in Figure 1 a basket type cathode having two perforated sides provided with ¼" apertures spaced ½" on centers and having a ⅜" feed pipe for the introduction of titanium tetrachloride vapors into the interior of the cathodic basket adjacent the bottom thereof was lowered into a fused salt electrolyte consisting of 700 pounds of sodium chloride maintained at a temperature of about 840° C. Titanium tetrachloride vapors were then introduced at the rate of 900 grams per hour into the feed pipe of the basket cathode, the perforated walls of which were arranged opposite the anodes and served to confine the titanium values within the cathodic basket. Concurrently, an electric current equivalent to 6.15 faradays per mole of titanium tetrachloride was passed through the cell. This amount of current was in effect sufficient to completely reduce the titanium tetrachloride to titanium metal substantially all of which was deposited on the walls of the basket as relatively large coarse particles of metal. In order to obtain substantially 6.15 faradays per mole of titanium tetrachloride introduced, 780 amperes with an impressed voltage of approximately 6.9–7.5 volts was required. The cathode current density was about 400 amperes per square foot. The run was made for a period of 46 hours during which time the deposit of titanium metal remained perforative and the apertures in the basket open. At the end of this period the introduction of titanium tetrachloride vapor was stopped and no further current was passed through the electrolyte. The basket cathode was withdrawn from the cell and titanium metal was found deposited on the perforated walls of the basket cathode in the form of an irregular perforative tenacious mass composed of relatively large crystals. The titanium metal was removed from the cell and cooled in a chamber having an inert atmosphere. The cooled deposit was leached and the dried leached titanium metal was recovered as coarse crystals weighing 9000 grams having a definite metallic luster and being quite ductile. A sample prepared by arc melting these crystals possessed a Brinell hardness of 146. About 90% of the titanium values introduced as titanium tetrachloride were recovered as titanium metal.

EXAMPLE II

Using a cell similar to that shown in Figure 1, a basket type cathode provided with two perforated sides having ¼" apertures spaced ½" on centers and having a ⅜" feed pipe for introducing $TiCl_4$ vapors into the basket was lowered into a fused salt electrolyte consisting of 700 lbs. of sodium chloride maintained at a temperature of about 850° C. $TiCl_4$ vapors were introduced into the interior of the basket below the surface of the electrolyte at the rate of 835 grams per hour and titanium metal was deposited on the walls of the basket as relatively large coarse particles of metal. Concurrently an electric current equivalent to 6.35 faradays per mole of $TiCl_4$ was passed through the cell. This amount of current was in effect sufficient to completely reduce the $TiCl_4$ to titanium metal. In order to obtain substantially 6.35 faradays per mole of $TiCl_4$ introduced 750 amperes with an impressed voltage of approximately 6.8–7.2 volts was required. The cathode current density was about 400 amperes per square foot. The run was made for a period of 83 hours during which time the deposit of titanium metal remained perforative and the apertures in the basket open. The basket cathode was withdrawn from the cell and titanium metal was found deposited on the interior perforated walls of the basket cathode in the form of an irregular perforative tenacious mass composed of relatively large crystals. The leached titanium metal recovered, as described in the preceding example, weighed 16,000 grams which analyzed substantially 100% titanium and possessed a Brinell hardness of about 115.

EXAMPLE III

Using the same operation described in Examples I and II but a cathode basket having ¼" perforations spaced 8 to the square inch and a ⅜" feed pipe, $TiCl_4$ was fed into the electrolyte at the rate of 860 grams per hour, the temperature of the sodium chloride bath being 860° C. Electric current equivalent to 6.2 faradays per mole of $TiCl_4$ was passed through the cell, the amount of current required being 750 amperes at an impressed voltage of from 6.6 to 6.7 volts. The cathode current density was about 550 amperes per square foot and the run was continued uninterruptedly for 54 hours. The coarse titanium metal produced by this run weighed approximately 7,800 grams, the Brinell hardness of which was about 114.

EXAMPLE IV

Using the cell shown in Figure 1 and a basket cathode having four perforated sides each with apertures ⅛" in diameter and ¼" on centers and ¼" feed pipe, $TiCl_4$ was fed into the electrolyte within the basket at the rate of 670 grams per hour and the bath was maintained at a temperature of about 900° C. An electric current equivalent to 4.2 faradays per mole of $TiCl_4$ was passed through the cell, the amount of current required being 400 amperes at an impressed voltage of from 5.2 to 5.6 volts. The cathode current density was about 180 amperes per square foot and the run was continued for 24 hours. The titanium metal produced by this run comprised 2,300 grams of coarse material which represented a 66% yield of titanium and had a Brinell hardness of 137, the quality of the metal being very dense.

EXAMPLE V

Using the cell shown in Figure 1 and a basket cathode having 1 perforated side with apertures ¼" in diameter and ½" on centers and a ¼" feed pipe, $TiCl_4$ was fed into the electrolyte within the basket at the rate of 608 grams per hour and the bath was maintained at a temperature of about 825° C. An electric current equivalent to 7 faradays per mole of $TiCl_4$ was passed through the cell, the amount of current required being 600 amperes at an impressed voltage of from 8.7 to 10 volts. The cathode current density was about 1,070 amperes per square foot and the run was continued for 24 hours. The titanium metal produced by this run comprised 2,200 grams of coarse material which represented a 62% yield of titanium and had a Brinell hardness of 163, the quality of the metal being extremely dense.

It has been clearly shown by the description of the instant invention and by the examples presented that refractory metals may be obtained by passing a refractory metal halide into an electrolytic cell by means of a hollow basket-type cathode at a rate synchronized with the electric current addition such that the amount of electricity added per mole of refractory metal halide measured in faradays is numerically substantially greater than the number of halide atoms present in the said refractory metal halide molecule; and that by confining the reduced halides to the immediate vicinity of the cathode while concurrently retaining the titanium metal deposit on the cathodic surfaces, high recoveries of highly ductile relatively coarse titanium metal may be obtained. Thus the electrolytic process of the instant invention employs simple and inexpensive apparatus whereby it is possible to produce refractory metals economically and continuously.

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. In a method for producing titanium metal in an electrolytic cell having an anode and a fused bath consisting essentially of salt selected from the group consisting of alkali metal halides, alkaline earth metal halides, magnesium halides and mixtures thereof, the steps comprising introducing a perforated cathodic basket-like member beneath the surface of said fused bath, introducing $TiCl_4$ below the surface of said bath into the interior of said cathodic member, passing electric current between the anode and cathodic member at a rate synchronized with the $TiCl_4$ addition so that the amount of current is sufficient to reduce the $TiCl_4$ being added to metal, maintaining the cathode current density of the cell within the range of from 200 to 500 amperes per square foot and maintaining the current to $TiCl_4$ feed ratio within the range of from 5.0 to 7 faradays per mol at said cathode current density thereby depositing an adherent mass of perforative titanium metal on the interior surfaces of the cathodic member, and maintaining the electrolyte exteriorly of the cathodic basket-like member substantially free from reduced titanium values.

2. In a method for producing titanium metal in an electrolytic cell having an anode and a fused bath consisting essentially of salt selected from the group consisting of alkali metal halides, alkaline earth metal halides, magnesium halides and mixtures thereof, the steps comprising introducing a perforated cathodic basket-like member beneath the surface of said fused bath, maintaining the temperature of the bath at from 375° C. to 950° C. introducing $TiCl_4$ below the surface of said bath into the interior of said cathodic member, passing electric current between the anode and cathode at a rate synchronized with the $TiCl_4$ addition so that the amount of current is sufficient to reduce the $TiCl_4$ being added to metal, maintaining the cathode current density at about 400 amperes per square foot, maintaining the current to $TiCl_4$ feed ratio at about 6 faradays per mol at said cathode current density, and maintaining the concentration of reduced titanium chlorides in the electrolyte within said basket within the range of from 0.1 to 0.2% thereby depositing an adherent mass of perforative titanium metal on the interior surfaces of the cathodic member, and maintaining the electrolyte exteriorly of the cathodic basket-like member substantially free from reduced titanium values.

3. In a method for producing titanium metal in an electrolytic cell having an anode and a fused bath consisting essentially of salt selected from the group consisting of alkali metal halides, alkaine earth metal halides, magnesium halides and mixtures thereof, the steps comprising introducing a perforated cathodic basket-like member beneath the surface of said fused bath, maintaining the temperature of the bath at from 375° C. to 950° C. introducing $TiCl_4$ into the interior of said cathodic member at a point adjacent the bottom thereof, passing electric current between the anode and cathode at a rate synchronized with the $TiCl_4$ addition so that the amount of current is at all times sufficient to reduce the $TiCl_4$ being added to metal, maintaining the cathode current density of the cell at about 400 amperes per square foot, maintaining the current to $TiCl_4$ feed ratio at about 6 faradays per mol at said cathode current density, controlling the concentration of reduced titanium chlorides in the electrolyte within said cathodic member so as not to exceed 1.0% based on the amount of the titanium, thereby depositing an adherent mass of perforative titanium metal on the interior surfaces of the cathodic member, and maintaining the electrolyte exteriorly of the cathodic basket-like member substantially free from reduced titanium values.

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