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CATHODE ASSEMBLY FOR ELECTROLYTIC CELLS

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Fig. 1.

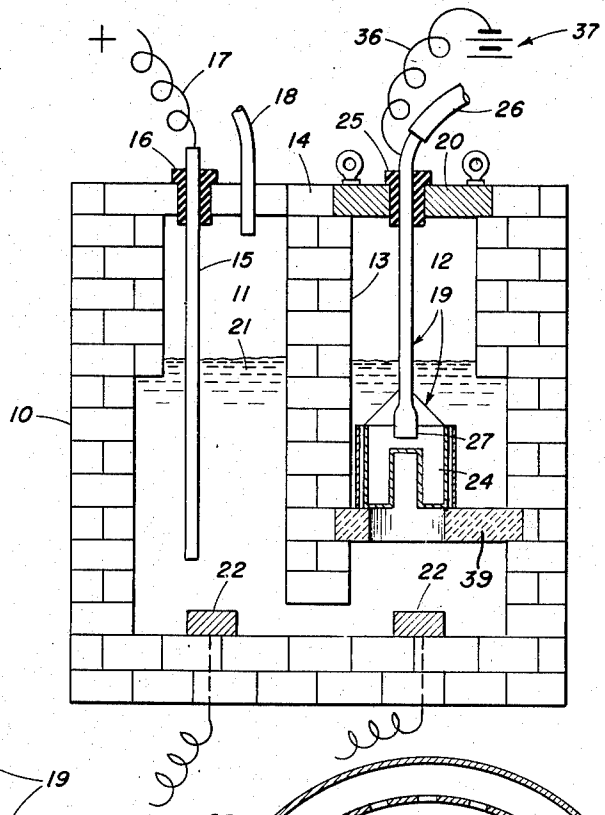
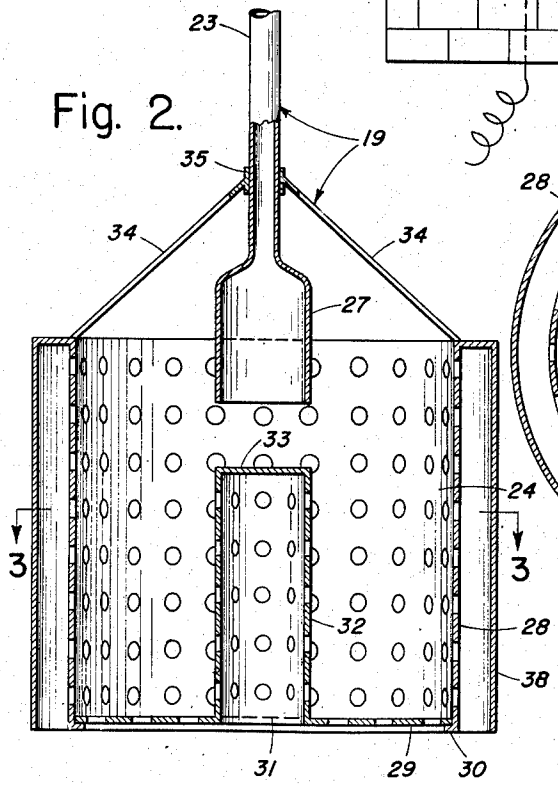


Fig. 2.



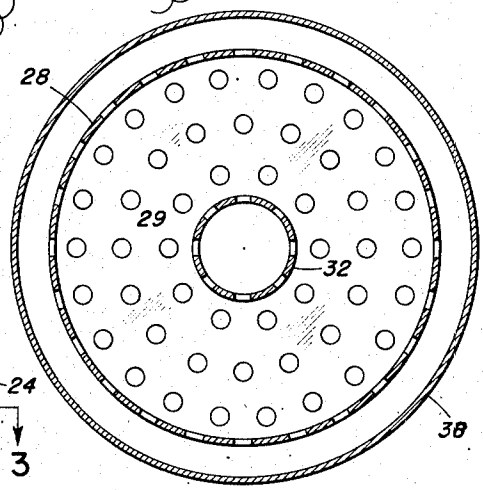


Fig. 3.

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CATHODE ASSEMBLY FOR ELECTROLYTIC CELLS

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The present invention relates in general to the production of refractory metals by an electrolytic process and more particularly to an electrolytic cell of the fused salt bath type having a cathode assembly for achieving high current efficiencies together with high yields of refractory metals of superior quality, the instant application being a continuation-in-part of a copending application Serial No. 325,819 filed December 13, 1952, now abandoned re Electrolytic Method and Means for Production of Refractory Metal.

Included in the group of metals which fall within the class known as refractory metals are titanium, zirconium, vanadium, niobium, tantalum, molybdenum and tungsten, and while many compounds of these refractory metals are found in nature, it is extremely difficult to reduce these compounds to a metallic state.

Heretofore these refractory metals have been recovered from their compounds by thermal reduction methods employing pressure and a reducing metal or by chemical reduction of a refractory metal halide in the presence of a reducing agent. Considerable success in the production of refractory metals has been achieved also by electrolytic methods embodying the use of a fused salt electrolyte and introducing a halide of the refractory metal to be produced into the electrolyte while concurrently passing electric current therethrough at a rate such that the amount of current being added to the cell is sufficient to reduce the metal halide substantially directly to metal.

Theoretically, the amount of current required per mol of refractory metal halide is determined by the valence of the halide. Thus, when titanium tetrachloride is used in the production of titanium metal, 4 faradays of electricity passed concurrently into the electrolyte per mol of titanium tetrachloride should be sufficient to reduce the halide to metal. Similarly, for the production of molybdenum, the theoretical current requirement would be five faradays of current per mol of molybdenum pentachloride.

However, in actual practice it has been found that due to the inefficiencies, side reactions and similar inherent operational characteristics of electrolytic cells of the fused salt bath type, the theoretical amount of current required for reducing a halide to metal is insufficient and that, in fact, a considerable excess of current over the theoretical amount is required. Specifically, it has been found necessary to increase the current by as much as 50% over the theoretical amount in order to insure efficient cell operation and high yields.

When operating a single electrolytic cell, such excess current requirements are not prohibitive. However, when employing large number of cells for the production of refractory metals on a commercial scale, excess current requirements seriously jeopardize the economy and commercial feasibility of such enterprises.

An object, therefore, of the present invention is to provide an improved electrolytic cell of the fused salt bath type for the production of refractory metals in an efficient and economical manner.

A further object of the invention is to provide an electrolytic cell of the fused salt bath type for producing a refractory metal with a cathode assembly which is so constructed as to effect maximum yields of high quality metal at high current efficiencies.

A further object of the invention is to provide an electrolytic cell of the fused salt bath type for producing a refractory metal with a cathode assembly so constructed as to provide a cathodic surface in substantially immediate proximity to the point of introduction of a refractory metal halide into the salt bath.

A still further object of the invention is to provide an electrolytic cell of the fused salt bath type for producing titanium metal having a cathode assembly, the cathodic surfaces of which are so arranged that a high concentration of reduced halides of the refractory metal are maintained in the fused salt bath, thereby insuring the deposition of a highly ductile metal of fine quality.

These and other objects, features and advantages of the present invention will be described and illustrated in more detail by the description which follows and the accompanying drawings in which:

Figure 1 is a vertical section of an electrolytic cell of the fused salt bath type including one of the cathode assemblies of this invention.

Figure 2 is an enlarged fragmentary vertical elevation in section of the cathode assembly shown in the cell of Figure 1, and

Figure 3 is a transverse sectional view of the cathode assembly shown in the cell of Figure 1 on line 3—3 of Figure 2.

By way of introduction to the operation of an electrolytic cell of the fused salt bath type for producing a refractory metal, in general, these cells are equipped with an anode and a cathode which is preferably a hollow tube, through which the refractory metal halide is introduced into the fused salt electrolyte. The latter comprises preferably a molten halide salt of an alkali or alkaline earth metal including magnesium, particularly the chlorides of these metals employed singly or in combination. Mixtures of these halides which form low melting point eutectics are most convenient, such as for example mixtures of sodium chloride and strontium chloride, sodium chloride and lithium chloride, sodium chloride and barium chloride, or mixtures thereof. Both the anode and cathode of the cell are connected to a source of direct current whereby an electric potential is set up in the electrolyte to effect movement of ions from the anode to the cathode. Thus, electrolysis of the fused salt bath, concurrently with the introduction of the refractory metal halide into the fused salt bath solubilizes the metal halide to produce lower valent halides which are further reduced to the refractory metal in the form of a crystalline deposit on the cathodic surfaces of the cathode.

Theoretically, if less than one mol of a refractory metal halide, such as for example titanium tetrachloride, is introduced into the cell for each four faradays of electricity which passes through the cell, other metals than titanium may be deposited on the cathode from the fused salt electrolyte. On the other hand, when the titanium tetrachloride is added in a quantity in excess of one mol for each four faradays of current, the reduced halides of titanium i. e. titanium dichloride and titanium trichloride, will be formed in the electrolyte and will diffuse and be transferred through the bath to the anode where the reduced chlorides will combine with the chlorine released at the anode and be rechlorinated to form titanium tetrachloride which will escape from the cell by way of the chlorine exhaust pipe. In fact, the efficiency of the cell will be noticeably decreased when the amount of titanium tetrachloride being added exceeds about 1.2 mols for each four faradays of electricity.

A cell of this type is operated at a relatively high cu-

rent density, a typical cathode current density being about 3 amperes/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 one-half and six amperes/square centimeter has been found satisfactory. Within this current density range titanium metal will be deposited on and adhere to the cathodic surfaces of the cathode.

The instant invention relates to an improved cell structure and more particularly to an improved cathode assembly, the construction of which is based on the discovery that when electrolyzing titanium tetrachloride in a fused salt bath, a superior titanium metal deposit characterized by large crystals of high purity and ductility will form on the cathodic surfaces of the cathode basket when a relatively high concentration differential of the reduced halides, i. e. titanium trichloride and titanium dichloride, is maintained in the electrolytic bath within the basket cathode, and that this condition exists provided the cathodic surfaces of the basket are so arranged as to provide regions within the basket cathode wherein electrolytic reduction of the metal is rapid and substantially unimpeded, alternating with regions wherein the reduction of the metal halide to metal is less rapid.

In its broadest aspects, therefore, the invention relates to an improved electrolytic cell of the fused salt bath type comprising an anode, a cathode assembly, including a cathodic basket, and a source of direct current connected to the anode and to the cathode assembly respectively, the cathode assembly being constructed and arranged so that the refractory metal halide introduced into the fused salt bath will be reduced electrolytically to the low valent halide, i. e., titanium dichloride, and from thence to metal relatively rapidly in the peripheral regions and in the center region respectively of the cathodic basket; and less rapidly in the regions of the cathodic basket intermediate its periphery and center portion.

Referring to Figure 1, the apparatus shown consists of a substantially rectangular cell housing **10** formed of refractory brick or an equivalent material and divided into an anode and cathode compartment **11** and **12** respectively by means of a vertical barrier **13** which is joined at its upper end to the top wall **14** of the cell, its lower end being spaced above the bottom of the cell to provide a passage connecting the anode compartment with the cathode compartment. The aforesaid top wall **14** of the cell seals the respective compartments from the atmosphere and is adapted to support the anode and cathode assembly of the respective compartments. The anode **15** comprises a metal rod, the upper end of which is supported in a bushing **16** which, in turn, is secured with a gas tight seal in an aperture in the top wall **14** of the cell. A conductor **17** is secured to the upper end of the anode for connecting the latter to a source of electric current. During the operation of the cell, chlorine gas is released at the anode, and consequently the top wall of the anode chamber is provided with a vent **18** by which the chlorine may escape from the cell.

The cathode assembly **19**, which forms the subject matter of the instant invention, is supported in the cathode compartment of the cell in a manner to facilitate removal of the cathode assembly therefrom for the purpose of recovering the refractory metal, and to this end is supported from a cover member **20** which is removably mounted in a suitable aperture in the top wall **14** of the cell.

As has been pointed out above, the cell is adapted to be filled or partially filled with an electrolyte, as indicated at **21**, in which the anode **15** and the cathode assembly **19** are suspended, the electrolyte comprising a molten halide salt of an alkali or alkaline earth metal including magnesium which is maintained in the molten condition by means of graphite electrodes **22** located at the bottom of the cell.

As shown in Figures 1 and 2, the cathode assembly

19 comprises, in general, a cathode tube **23** and a cathode basket **24**. The cathode tube **23**, which serves to introduce a vaporous refractory metal halide, as for example titanium tetrachloride, into the electrolyte, may be formed of nickel, stainless steel, iron or other suitable metal and is supported at its upper end from the cover member **20** of the cathode compartment of the cell by an electrically insulating bushing **25**. A flexible feed tube **26** is connected at one end to the upper end of the cathode tube **23**, its other end being connected to a source of refractory metal halide (not shown). The lower end of the cathode tube **23** is shown with an enlargement comprising essentially a bell shaped mouth **27** which is adapted normally to extend into the electrolyte **21** beneath the surface thereof. Although the bell shaped mouth is preferred, it will be understood that this construction is not critical to the successful operation of the cathode assembly; and that the lower end of the cathode tube may have a straight wall or wall of other configuration.

The cathode basket **24**, as shown in Figure 3, is substantially circular in cross section comprising substantially cylindrical side walls **28** formed of perforated sheet metal preferably titanium metal although iron or steel may be used; and a perforated sheet metal bottom **29** supported at its outer edge on a circumferential flange **30** which projects inwardly from the bottom edge of the cylindrical side walls **28** of the basket. While circular baskets are preferred inasmuch as refractory metal deposits of superior crystalline structure are obtained therefrom, it will be understood that the disclosure of a circular basket does not preclude the use of baskets of rectangular or other cross section. The bottom **29** of the cylindrical basket is provided with a relatively large substantially centrally located aperture **31** from which a perforated metal tube **32** projects upwardly into the basket, the lower end of the perforated metal tube **32** being open while the upper end is closed by an imperforate end wall **33**.

The cathode basket **24** is supported from the tubular cathode **23** in substantially concentric relationship thereto by means of metal straps **34**, preferably four in number, which are secured to the upper edge of the perforated basket at four circumferentially spaced points thereabout and are attached at their upper ends to a metal collar **25**, or equivalent device, secured on the lower end of the tubular cathode **23** immediately above its bell mouth **27**. The bottom of the cathode basket rests on a transverse shelf **39** directly over a circular opening therein which, as shown in Figure 1, is only slightly smaller in diameter than the diameter of the basket by which arrangement ions in the electrolyte below the shelf **39** are precluded from passing upwardly in the electrolyte except through the perforated bottom of the basket.

As shown, the tubular cathode **23** is connected by a lead **36** to a current source **37**, and since the cathode basket **24** is, in turn, connected to the tubular cathode by the metallic straps **34**, which constitute electrical conductors, both the tubular cathode **23** and the perforated basket cathode **24** are cathodic.

The present invention is based on the discovery that by this construction and in particular provision of the perforated tube **32** which projects upwardly from the bottom of the basket cathode adjacent the bell mouth of the cathode tube **23**, the halide of the refractory metal being introduced into the bath by the cathode tube is reduced to metal especially rapidly at the peripheral portions of the basket as well as that central portion therof defined by its perforated tube **32**; and relatively slowly in that annular portion of the basket between its walls and the concentric walls of its perforated tube **32**. On the basis of this fact it has bene postulated that in accordance with the construction of the improved basket of this invention, the distribution of current to the cathodic surfaces is such that the low valent halide, i. e. titanium

dichloride is formed and reduced substantially immediately to metal not only in proximity to the peripheral walls of the cathode basket but also in proximity to the peripheral walls of the perforated center tube of the basket whereas the higher valent halide, i. e. titanium trichloride, is formed intermediate the aforesaid regions of divalent chloride, but is reduced less rapidly to metal and that, therefore, a high concentration differential of reduced halides is maintained in the bath, as a consequence of which the metal crystals which form on the cathodic surfaces of the basket are characterized by relatively large size and high ductility.

It has also been observed that by providing the perforated tube **32** in the center of the basket, considerable less electrical energy is utilized in maintaining the required current density on these cathodic surfaces of the basket than that required for the type of basket cathode shown and described in the above-identified copending application with which as high as 5 or 6 faradays of current have been required to maintain the necessary current density on all areas of the basket. By providing the improved basket cathode construction of this invention, substantially the theoretical current requirement of from about four to four and one-half faradays of current will suffice to maintain the required current density over the cathodic surfaces of the basket on which the refractory metal is deposited.

Although the cathodic basket shown in Figures 1, 2 and 3 embodies a substantially flat perforated bottom characterized by a single upwardly extending perforated tube **32**, it will be appreciated that it is within the purview of the invention to provide the cathode basket with more than one perforated tube in the bottom thereof, as well as obvious modifications thereof, such as for example baskets having bottoms of conical or concave configuration.

The cell is operated by heating the fused salt bath to a predetermined temperature and then energizing the anode **15** and basket cathode assembly **19** respectively, the electric current being regulated so that about four to four and one-half faradays of current are introduced into the electrolyte for each mol of refractory metal halide fed into the molten salt bath by way of the hollow cathode. While the exact manner in which the crystals of metal grow within the basket is not known and would be extremely difficult to determine due to the constant circulation of reduced chlorides in the bath, it has been postulated that crystal growth is from the peripheral and center regions of the bath within the basket corresponding to the regions of low concentrations of titanium dichloride.

In this connection it has been noted that some metal may grow outwardly from the periphery of the basket and form a so-called "bustle" around the bottom edge thereof; and that after prolonged periods of operation the metal bustle has sometimes grown to such proportions as to engage the surrounding walls of the cathode chamber, thereby inhibiting removal of the basket from the cell.

To circumvent this contiguency a metal hood, such as indicated at **38** in Figures 1, 2 and 3, may be supported from the basket cathode so as to extend thereover in a manner to form an annular barrier between the wall of the basket and the adjacent wall of the cathode chamber **12**. Hence, any outward growth of metal from the basket will be prevented by the hood **38** for engaging the wall of the cell and consequently, following the completion of each run, the basket may be removed from the cell with ease and dispatch.

From the foregoing description it will be evident that the invention provides, in its broadest aspects, an improved type of electrolytiic cell of the fused salt bath type characterized by a cathode assembly which is specifically designed both to maintain a high concentration differential of reduced halides in the fused salt bath within the confines of the cathode assembly but also to introduce

the halides of a refractory metal into the fused salt bath therein to be solubilized and reduced to a refractory metal within the cathode basket; and that the specific design of the cathode assembly for effecting these functions embodies, in its broadest sense, cathodic elements designed to effect substantially complete electrolytic reduction of the halides in regions of the bath defined by the periphery and central portions respectively of the basket cathode and less complete electrolytic reduction of the halides in regions intermediate these portions of the basket.

In accordance with these structural features of the invention, deposits of refractory metal of unusually large crystal structure are formed, the metal being of a high purity and ductility. Moreover, electrolysis of the fused salt bath is carried out at unexpectedly high current efficiencies.

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

We claim:

1. In an electrolytic cell for the production of a refractory metal, said cell having a chamber for containing a fused salt bath, anode and cathode compartments in said chamber, an anode in said anode compartment and a source of electric current connected to said anode; a cathode assembly in said cathode compartment, said cathode assembly comprising a tubular cathode having open ends and a cathodic basket attached thereto having perforated side walls and a bottom wall; feed means connected to the upper open end of said tubular cathode for feeding a refractory metal halide into said fused salt bath; said source of electric current connected to said cathode assembly for electrolyzing said fused salt bath, thereby to reduce said refractory metal halide to metal, said cathodic basket having a perforated tube projecting upwardly from the bottom thereof and terminated by an imperforate end wall below the bottom open end of said tubular cathode to maintain a concentration differential of reduced refractory metal halides in said fused salt bath within said cathodic basket during the reduction of said refractory metal halide to metal; and an imperforate cathodic metallic hood connected to and arranged to circumscribe the side walls of said cathodic basket, thereby to confine said metal to said cathodic basket.

2. In an electrolytic cell for producing a refractory metal, said cell having a chamber for containing a fused salt bath, anode and cathode compartments in said chamber, an anode in said anode compartment, and a source of electric current connected to said anode; a cathode assembly in said cathode compartment, said cathode assembly comprising a tubular cathode having open ends and a cathodic basket attached thereto having perforated side walls and a bottom wall; feed means connected to the upper open end of said tubular cathode for feeding a refractory metal halide into said fused salt bath; said source of electric current connected to said cathode assembly for electrolyzing said fused salt bath, thereby to reduce said refractory metal halide to metal, said cathodic basket having a perforated tube arranged to project upwardly from the bottom of said basket cathode said tube being open at its lower end and provided with an imperforate end-wall at its upper end below the open bottom end of said tubular cathode to control the distribution of current to the cathodic surfaces of said tubular cathode and said cathodic basket respectively and thereby maintains a concentration differential of reduced refractory metal halides in said fused salt bath within said cathodic basket during the reduction of said refractory metal halide to metal and an imperforate cathodic metallic hood connected to the upper edges of the side walls of said cathodic basket and arranged to circumscribe said side walls in spaced parallel relationship thereto thereby to confine said metal to said cathodic basket.

3. In an electrolytic cell for producing a refractory

metal, said cell having a chamber for containing a fused salt bath, anode and cathode compartments in said chamber, an anode in said anode compartment, and a source of electric current connected to said anode; a cathode assembly in said cathode compartment, said cathode assembly comprising a tubular cathode having open ends and a cathodic basket attached thereto having perforated side walls and a bottom wall having a central aperture; feed means connected to the upper open end of said tubular cathode for feeding a refractory metal halide in said fused salt bath; said source of electric current connected to said cathode assembly for electrolyzing said fused salt bath, thereby to reduce said refractory metal halide to metal, said cathodic basket having a perforated metal tube secured over the central aperture in the bottom of said basket and projecting upwardly from the bottom thereof said tube being open at its lower end and provided at its upper end with an imperforate end-wall opposite the bottom open end of said tubular cathode to control the distribution of current to the cathodic surfaces of said tubular cathode and said cathodic basket respectively and thereby maintain a concentration differential of reduced refractory metal halides in said fused salt bath within said cathodic basket during the reduction of said refractory metal halide to metal and an imperforate cathodic metallic hood connected to the upper edges of the side walls of said cathodic basket and arranged to circumscribe said side walls in parallel relationship thereto thereby to confine said metal in said cathodic basket.

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