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ELECTROLYTIC PRODUCTION OF MULTIVALENT METALS FROM REFRACTORY OXIDES

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Fig. 2

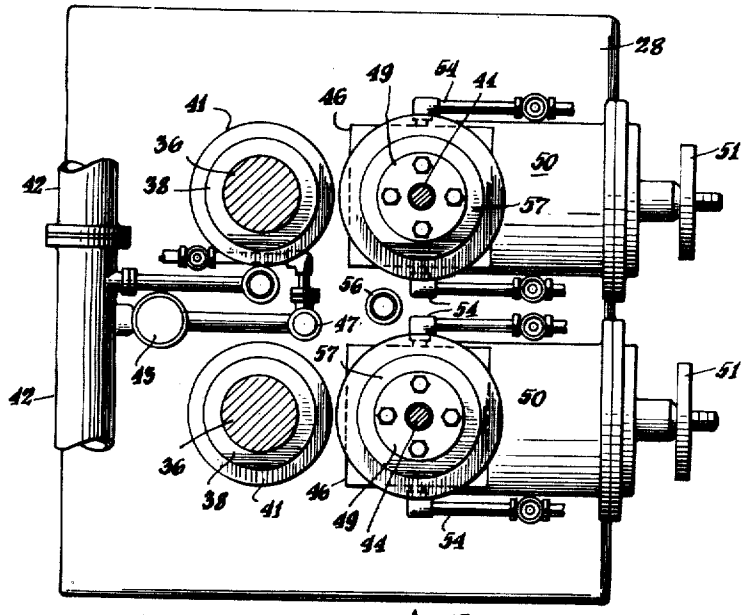
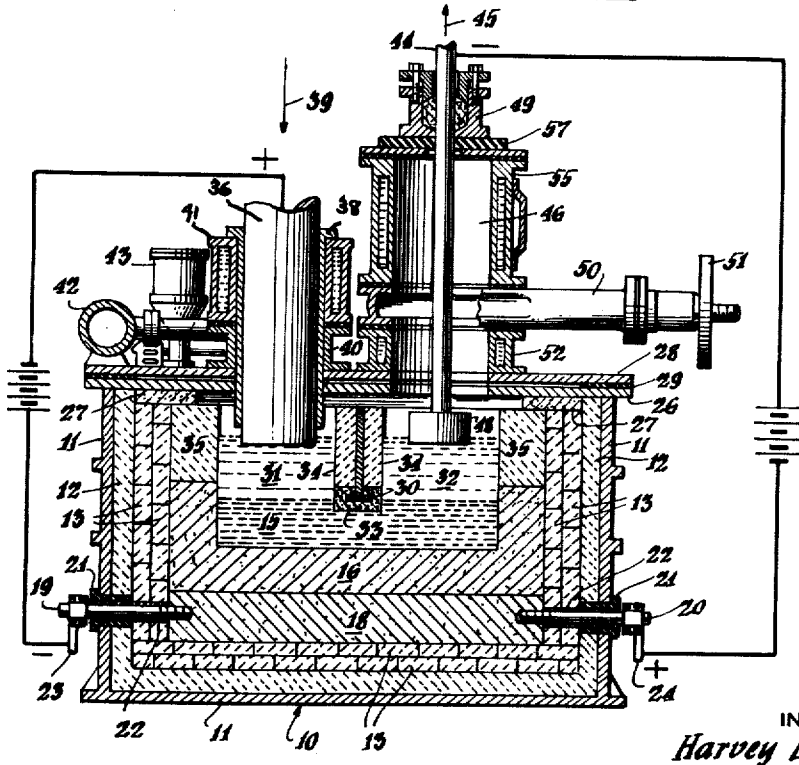


Fig. 1



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ELECTROLYTIC PRODUCTION OF MULTIVALENT METALS FROM REFRACTORY OXIDES

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The present invention relates to the process for the production of pure and ductile metal in large crystalline form by continuous fusion electrolysis of multivalent metals from the refractory oxides thereof and including the electrolytic production of titanium, zirconium, hafnium, thorium and uranium from their oxides and ores.

The present invention is a continuation-in-part and improvement of my copending application on the continuous process for production of titanium from its common ores, compounds and oxides by fusion electrolysis with a bipolar liquid electrode, Serial No. 383,762, filed October 2, 1953. It is also a continuation-in-part of my copending application Serial No. 542,837, filed October 26, 1955.

It is a primary object of this invention to provide a process that is practical, simple, and continuous for the production of these metals in pure and cold ductile form and the process will first be considered in connection with the production of titanium, comparable in quality to iodide-grade titanium, by the electrolysis of titanium oxides and compounds using a liquid alloy bipolar electrode containing metallic elements denser and nobler than titanium with respect to the electrolyte composition used, depositing titanium on said electrode wherein the deposited metal is dissolved and dispersed throughout the mass of the liquid electrode, and at the same time in an adjoining compartment of the electrolytic cell by means of another direct current source causing the selective solution of titanium metal from the same liquid bipolar alloy electrode into another fused salt electrolyte and depositing titanium metal in massive crystalline form on a solid cathode suspended in the same compartment of a single cell.

A further object of this invention is to provide a system for producing pure titanium metal at lowered cost continuously, with a minimum of skilled labor, from cheap raw materials and with long-lived equipment.

Still another object of this invention is to provide a new system for the production of pure titanium directly from its oxides wherein the power efficiency is very high, the recovery efficiency is excellent, and the crystal size of the deposited metal is large.

Another object of this invention is to provide a process for the recovery and refining of scrap, contaminated, or impure titanium metal by a continuous electrolytic process.

Other objects and advantages will become apparent to one skilled in the art from the following specification taken in connection with the accompanying drawing showing a diagrammatic sectional elevation and plan of one form of apparatus operating in accordance with this invention.

The process hereinafter described is advantageous in (1) using the cheapest compounds available—the oxides, (2) providing a system wherein no material loss can take place through oxidation and volatilization, (3) providing a method for triple purification and refining within one piece of equipment, (4) providing automatic common mechanical means for maintaining and recovering the pure metal product in a continuous operation, and (5)

providing the composition of the "anolyte," the "catholyte," and the common liquid alloy electrode thus insuring continuous carefree production of pure titanium with a minimum of supervision or cell shutdown and replacement.

Referring to the drawing, Fig. 1 shows an elevation of an electrolytic cell generally suitable for the practice of this invention (indicated as **10**) and Fig. 2 is a plan view of the top of the electrolytic cell. The cell has an iron shell **11** which is lined with a good thermal insulating brick **12** made of silica and one or more inner linings of high-fired magnesia brick **13** separated from the liquid common (bipolar) electrode **15**. The metal shell is welded and airtight, and may be cooled in any desired manner. The liquid electrode **15** is contained in a graphite chamber or cavity **16** made of "AGR" or similar grade of graphite manufactured by the National Carbon Company. The chamber or cavity is integrally supported by a block of carbon **18** to control the heat loss and into which the electrical leads **19** and **20** are screwed and cemented. These leads are made of iron, but copper or other suitable materials may be used. The number of leads in each side of the cell will depend on the capacity of the cell and the nature and size of the lead. The leads are electrically insulated from the shell by standard ceramic offset spacers **21**, and packed with blue asbestos rope and cement **22** to insure an airtight seal of the contents of the shell from the atmosphere. The electrical leads may be water cooled if desired. The standard means for connecting bus lines to the leads are provided by electrical connectors **23** and **24**. The interior of the cell is tightly sealed against the influx of the atmosphere by flange **26** and cover **28** and gasketed with a suitable material such as nickel asbestos, as indicated at **29**. The cover is preferably made of nickel or "Inconel" and has a protective refractory bottom facing **27**. The cover may be water cooled if desired. The cell is divided internally into two compartments (or more, if desired) by an iron baffle strip **30** welded across the cover and along the cell wall sides. The partition strip **30** is protected from the alloy electrode by suitable graphite sheath blocks **33** completing the seal in the liquid alloy. The sides of the iron baffle strip are protected from the "anolyte" or reductor electrolyte **31** on one side and the "catholyte" or refiner electrolyte **32** on the other by special fitted high-fired magnesia brick **34** which tends to seal the cracks on expansion by heat during operation. The two compartments are lined with this special magnesia brick **35**.

The reductor compartment (anolyte **31**) has two or more graphite anodes **36** dipping into its electrolyte. The anodes are electrically insulated from the shell and partly protected from the hot cell gases by cylindrical sleeves of alumina **38** or other suitable material. The anodes are continuously fed to the electrolyte **31** as they are consumed through these sleeves by a standard feed mechanism known in the art as indicated by arrow **39** and not shown. The feed rate is coupled to the rate of electrolysis and is affected by the cell characteristics. The insulating sleeves are supported by packed adaptors **40** which may be water cooled. The anodes are cooled by circulating water in jackets **41**. The anodes are suitably connected to a source of direct current and made positive to the cathode leads **19**. This anolyte circuit is complete and independent of the refining circuit through "catholyte" **32**. Between each pair of anodes in the cover is located a vent line (Fig. 2) that connects to a gas manifold line **42**. Also between each pair of anode assemblies in the cover is located a material feed port in the form of a pipe T **47**, that is sealed from the atmosphere by an enclosed wormfeeder **43**. The top of the feed port T is fitted with a cap and designed so that the operator may observe the interior of the compartment

through a quartz window sealed in the cap without exposing the contents of the cell to the atmosphere. The cap and the transparent window may be removed for the purposes of sampling the cell contents. All joints are either properly gasketed or welded gas-tight. There are also located in one arm of the T and in the screw feeder **43** a valve and means for introducing an inert gas into the anolyte or reductor compartment of the cell.

The refining compartment (catholyte **32**) has two or more cathodes **44**. The refining compartment is kept continuously flooded with pure dry inert gas such as argon by maintaining the pressure in the compartment slightly above atmospheric. The cathodes are continuously withdrawn from the electrolyte **32** during deposition by a withdrawal mechanism (not shown) indicated by arrow **45**. Each cathode is provided with a water jacketed cooling chamber **46** into which the cathode tip **48** and the electrodeposit adhering thereto may be separately withdrawn and cooled in the inert gas. The cathode cooling chambers are effectively sealed from the atmosphere by airtight packed glands **49**, and are sealed from the interior of the cell by gate valve mechanisms **50** operated by handles **51**. The valves are supported on the cover of the cell by adapters **52** which are cooled by water circulating in the adapters. The water inlets and outlets on all the cooling jackets are not shown. In each valve body **50** are provided bosses into which are tapped suitable inlets and outlets **54** for the supply and exhaust of inert gas above the valve seat. The individual outlets are provided for connections to a suitable vacuum system. The cathode cooling chambers are equipped with sealable doors **55** that permit access to the interior of the cathode cooler. Between each pair of cathode housings in the cover is located a sealable view and feed port **56** that communicates with the interior of the refining compartment. The port is provided with a suitable means for purging and introducing pure dry inert gas. Each cathode is electrically insulated from the shell by a "transite" or similar insulating plate **57**. The cathodes **44** are connected through their own separate direct current source to the anode connectors **24** and leads **20**. All joints are suitably gasketed and where possible welded gastight. The cell is supported by I-beams and electrically insulated from ground. The cathode withdrawal mechanisms and the anode lowering mechanisms are also electrically insulated from ground. Finally, the mechanisms are electrically insulated from their respective electrodes as well.

The cell is operated in the following manner:

A low voltage A.-C. arc is struck across the graphite anodes **36** and the graphite hearth **16**. The normal cathode tips **48** are temporarily replaced by graphite and the electrodes are lowered so that a low voltage A.-C. arc may be struck between these electrodes and the graphite hearth **16**. A catholyte solvent, which has been carefully purified and prepared in an auxiliary vessel by fusion in a strong current of dry HCl gas and rendered anhydrous and oxide-free, is poured into the cell via the feed port **56** until the bottom of the graphite cavity **16** is covered and the salt depth is about one to two inches. The interior of the cell should be free from moisture and dry. Argon gas, previously purified and dried, is pumped through the cell to purge it of air. The temperature in the cell is allowed to rise slowly until the fused salts are above the liquidus temperature of the alloy electrode. The requisite quantity of alloy is added via the reductor feed ports **43**, preferably as dry solid lumps, in small increments, allowing each batch to fuse before adding the next. As the alloys are denser or heavier than the electrolyte solvents, they sink and are protected by the salt layer from attack by any residual atmospheric gases and moisture in the cell. The molten alloys may be fused outside the cell and poured into the cell under an argon or fused salt blanket. Such a procedure is hazardous and extreme caution should be taken as the alloys are inflammable and even explosive. In the cell, the fused salts are ample protection and the alloys are safe and easy to handle. The alloy is added until the level of the liquid alloy electrode **15** reaches the graphite baffle **33**. Additional alloy is added to bring the level up above the bottom of the baffle **33** about three inches to complete the compartmentalization. The height of the graphite sheath **33** extends about two to three inches above this level. From time to time during the addition of alloy, it will be necessary to add electrolyte to the cell in order to maintain a salt depth above the alloy of at least one to two inches as some of the salt desirably will soak into the graphite chamber. Care must be exercised to avoid contacting the refractory walls **34** or **35** with the fused alloy as in this state the liquid alloy is extremely reactive and would attack the refractory lining. During the melting of the alloy, the electrodes (anodes and cathodes) are slowly withdrawn in order to maintain an adequate arc in the well-known manner. The final level of alloy may be six to eight inches and with a passage or channel depth of about four inches plus, i. e., distance from the bottom of the baffle **33** to the top of the graphite cavity **16**.

The flow of pure dry argon gas or similar inert gas is maintained in the cathode compartment continuously at **54**. The reductor compartment may be similarly protected through manifold line **47**. The purified refining electrolyte solvent is fed into the refining compartment until the liquid level is about six inches above the level of the alloy. The reductor solvent is also added to the anode compartment at the same time. The molten electrolytes slightly penetrate into the refractory linings and fill all the remaining pores and crevices in the refractory and by freezing therein provide a tight container for the electrolysis. As the density of the reductor electrolyte usually is greater than that of the refiner electrolyte, the electrolyte depth in the reductor compartment may be somewhat less than six inches. In order to complete the preparation of the electrolytes, the desired weight of oxide solute is added and dissolved in the reductor electrolyte, and the requisite quantity of halide solute is added and dissolved in the refining electrolyte. The feed-view port caps are closed and the cell buttoned up. The A.–C. power is shut off and disconnected. The cathodes **44** are withdrawn one by one into cooling chamber **46** and the gate valve **50** is closed thereby sealing the interior of the cooling chamber from the refining compartment. The door **55** is opened and the cool temporary tip is removed and replaced by the regularly used tip, preferably made of titanium. The tip **48** can be made of molybdenum if desired. The door **55** is resealed and the cooling chamber **46** is carefully purged of air and moisture by alternately evacuating the chamber through gas outlet **54** in valve **50** body and refilling the chamber with argon through an inlet located in the valve body as described. The gate valve **50** is opened and the cathode leads **44** and their attached tips **48** are lowered into the electrolyte **32**. A source of D.–C. power is connected across the cathode leads **19** and the anode leads **20**. A sufficient voltage is imposed across these electrodes to insure the attainment of proper current densities as explained below. The temperature in the refining compartment is controlled by a submerged thermocouple (not shown) located in the brickwork that activates a relay to bring additional D.–C. power or superimpose a low voltage A.–C. source to these electrodes if the temperature should fall. Usually the cell is designed to run "too hot" and the temperature in the cell is controlled by cooling or reducing the power input at each cathode **44**.

At the same time, a source of D.–C. power is connected across the anodes **36** and the cathode lead **19** at **23**. A sufficient voltage is applied to cause metal deposition at **15** and to maintain adequate current densities there at the cathode. The temperature of the reductor electro-

lyte is usually higher than that in the refining compartment and its temperature is regulated in part by a submerged thermocouple (not shown) located in the brickwork, activating suitable relays that increase or decrease the voltage across the electrodes or which superimpose an added low voltage A.–C. power across the electrodes. Ordinarily, the capacity of the cell is designed to run "hotter" than desired and the temperature in the reductor compartment is controlled by cooling or reducing the power input at each anode **36**. The reductor chamber need not be the same size as the refining chamber. There is some advantage in making it smaller than the refining chamber in order that it run hotter and thereby afford better current density regulation.

The current density at the cathode **44** and the distance from cathode to alloy liquid anode may be maintained fairly constant by regulating the rate of withdrawal by mechanism indicated by arrow **45** to synchronize with the rate of electrodeposition. Similarly, the anode current densities in the reductor chamber and the anode to cathode liquid alloy distance are maintained fairly constant by mechanisms indicated by arrow **39** which synchronize the rate of lowering of the graphite anodes with the rate of anode consumption in electrolysis.

The reductor electrolyte is kept replenished with oxide raw material properly dried and prepared, by means of screw feeder **43**. The rate of feed is regulated so as not to exceed the desired solute concentration in the electrolyte **31**. After some simple and routine testing, the speed of the screw and the quantity of feed can be adjusted to keep pace with the rate of depletion of the solute electrolyte. From time to time, the solvent in the electrolyte may require replenishment or replacement. These corrections can be made through the feed-view ports **47**. If required, a portion or all of the electrolyte may be syphoned out of the cell and replaced. The refining electrolyte is a more sensitive electrolyte and hence is kept under a pure dry inert gas blanket. The electrolyte will require replenishment or adjustment from time to time. The electrolyte for replacement or replenishment must be prepurified, anhydrous and oxide-free. The additions are made to the cell via the cooling chambers at the time of introducing a fresh tip to the bath as explained below.

From time to time it may become necessary to adjust the separate D.–C. power inputs into the cell in order to keep the alloy electrode composition **15** fairly constant or balanced. A "thief" made of iron is plunged into the reductor section of the cell via feed-view **T** until it strikes the bottom of the cavity **16** and quickly withdrawn. A layer of electrolyte **31** will be found frozen to the cold rod as well as a layer of frozen alloy. The electrolyte and the sample of alloy **15** are analyzed separately. As a result of the analysis, appropriate correction in the composition of the electrolyte can be made easily. The composition of the alloy electrode **15** can be adjusted by increasing the D.–C. power input at the anodes **36** and decreasing the D.–C. power input at the cathodes **44**, or vice versa depending on whether the liquid alloy is leaner or richer in the solute metal than desired. The refining electrolyte can be checked each time the titanium cathode is withdrawn. The anodes **36** are consumed in the process and are replenished by screwing new electrodes to the old butts in the known manner. The rate of consumption of the anodes is dependent upon the nature and valency of the feed, the efficiency and non-productive losses due to oxidation.

The argon gas may be recycled after purification, if desired. The anode gases issue through the vent in the cover to the gas exhaust manifold line **42** and are conducted to a stack or absorber in any known manner. The reductor compartment may be kept swept clear of discharging gases by means of an inert gas. If it should become necessary to purify or reclaim the alloy electrode, it may be syphoned out into another cell under an inert gas and salt blanket. Usually it is purified in situ by replacing the D.-C. source on the reductor section of the cell temporarily with low voltage A.-C. and stripping the solvent alloy of solute and accumulated impurities by deposition in the refining sections. If the oxide feed is of a good grade, frequent alloy purification is normally unnecessary as the concentration of metallic impurities that can be retained by the liquid alloy without impairing the high purity of the cathode product is quite high.

The metal product gleaned on the cathode tips **48** is recovered at regular intervals in turn in the following manner: a single cathode, after accumulating a sufficient crop of metal, is rapidly raised by the withdrawal mechanism indicated at **45** until the tip and its adherent electro-deposit are lodged in its cooling chamber **46**. The valve **50** is closed. In a few minutes, the cathode has cooled to room temperature in the argon atmosphere and the tip, with its deposit, is removed from the cathode lead **44**. A fresh dry tip is inserted in its place and the cooling chamber is purged in the manner described above. The gate valve **50** is opened and the cathode is quickly lowered until the tip is immersed in the electrolyte **32** where a new crop of metal is grown. Each cathode is processed separately and usually in turn. The cathode tip may be handled in a dry-box, if desired. The deposited metal may be stripped from the cathode tip in a strip press and the metal recovered from the small amount of adhering salts by washing, fusions, vacuum distillation, or other known means for separation. The tips are cleaned by washing, dried and prepared for reuse in the refining section. It may take some time to clean up the electrolytic bath, etc. before superpure metal is obtained. There are other ways of starting up a cell as explained in my pending applications, but this is the most trouble free. The term "pure" metal is defined to be metal that is at least as pure as that obtained by the Von Arkel thermal dissociation of the iodide process. Once the cell has been started up, the operation is obviously a continuous one. The cathode product, deposited below its melting point, will be found to consist of adherent large bright silvery crystals in a tight compact matrix. There will be little salt inclusions and adhering salt, as most of the salt will run off the hot cathodes as they are raised. The metal will be massive in crystal size and very pure and malleable, provided that the conditions set forth below are observed in practicing my invention.

Reactions of the invention

The reductor compartment houses the raw material feed and the primary electrolysis. The overall reaction appears to be the electrolysis of the metal oxide to discharge oxygen at the graphite anode and metal at the metal cathode in the refining section. The oxygen discharged may be the result of secondary reaction, nevertheless it reacts with the carbon to form the monoxide which may be further oxidized to carbon dioxide. An inert gas may be blown into the anode-reductor chamber to more rapidly purge the free space above the bath of reactant gases and product gases. The anode gases that issue from the cell have been analyzed during normal operation. No halogen gas or halide compound has been detected in the gas stream. The effluent gas consists mostly of CO_2, and some CO and a little O_2. The anodic current density may be varied over a wide range from a fraction of an ampere per square inch to about 85 amperes per square inch depending primarily on the cationic valency of the oxide feed and the concentration in the electrolyte. The current density at the anode is preferably kept below about 10 amperes per square inch, and sometimes can be kept below about 30 amperes per square inch without deleterious effects as anode effect, etc.

The electrolyte solute may be any of the oxides of

titanium but the lower valent monoxide is preferred. The concentrations of the solute in the electrolytic bath are never as high as one would like. The lower oxides seem to be more soluble than the higher valent oxides probably due to their greater ionic nature. In the processing herein described, the lower valent oxides appear to be most stable and at the same time give better results in the electrolysis than the higher valent oxides. Nevertheless, if desired, the cheaper dioxide may be used. The process can be operated with low concentrations of dissolved solute. An excess of oxides in the bath, beyond the limit of solubility, is to be assiduously avoided. An excess of oxide causes the bath to become pasty and mushy and may even become inoperable. The undissolved oxides are usually heavier than the solvent and sink to the bottom of the electrolyte coming to rest on the surface of the liquid alloy electrode where they tend to objectionably shield the electrode. Persistent excesses of oxide feed material will, in time, result in the formation of an impenetrable crust over the surface of the electrode which must be broken mechanically if the electrolysis is to continue. It is better to make frequent small additions to the bath than to dump in a mass of oxide at longer intervals. Anode effect sets in when the oxide is depleted and the feeder can be adjusted to supply the oxide feed at a rate equivalent to the rate of consumption of the oxide by the electrolytic current. I prefer to have the feeder lag behind the electrolytic requirement to maintain a constant solution that is not oversaturated. TiO or TiO_2 concentrations of 0.3 to 3.0% are adequate. The feed material should be anhydrous and may be pelleted or nodulized to reduce its apparent density. By this means, the oxide particles will have a longer opportunity to dissolve in the electrolyte as they slowly settle through the bath. The electromagnetic field that is set up in accordance with the positioning of the electrode tends to stir the bath. The sight-glass in the feed T can be used to observe the solution process in the early stages to determine the feed rate. The oxide solute concentration may vary from a few tenths of a percent by weight to over five percent by weight. Naturally the higher solute concentrations are preferred. Finally, in some instances, the solubility limit of the respective oxides may be improved somewhat by adding a fluoride salt.

The electrolyte solvent consists preferably of the more electropositive metal halide salts. The fluorides are preferred, and the chlorides may be used to increase the conductivity and for other reasons. The bromides and iodides are not recommended. The alkaline earth halides, with or without additions of the alkali metal halides have been used. The calcium halides with or without additions of strontium halides are preferred. I have also found that calcium oxide (and sometimes strontium oxide) may be added to the solvent with advantageous results. The following solvent baths are utilized in order of increasing preference:

(a) MgF_2—NaF—KF, (b) BaF_2—MgF_2—$CaCl_2$
(c) BaF_2—$BaCl_2$—CaF_2, (d) CaF_2—LiF
(e) $CaCl_2$—$SrCl_2$, (f) $CaCl_2$, (g) $CaCl_2$—CaO
(h) CaF_2—$BaCl_2$, (i) CaF_2—$SrCl_2$, (j) CaF_2—$CaCl_2$
(k) CaO—$CaCl_2$—CaF_2

After considerable testing of many electrolyte solvents, I have found that for the oxides being considered in this invention the last four baths or mixtures thereof have proved to be the best electrolytes for the purpose. With such an electropositive element as titanium, the alkaline earth fluorides are more satisfactory. The solvent electrolyte has only cations more electropositive than those of titanium with respect to oxygen and halogens.

The liquid cathode must have the following characteristics: (1) it must be more electronegative than titanium with respect to halogen so that it will not undergo electrolytic solution in the simultaneous refining process going on in the refining section of the cell; (2) it must be a reasonably good solvent for the depositing titanium, and the concentration of the titanium solute should be high enough to permit subsequent electrolysis at fairly high current densities without permitting either co-solution of the impurities accumulating in the solvent or the solvent metal itself; (3) the solvent metal or metals of the liquid cathode should have as low a liquidus temperature as is practical in order that at the operating temperature the liquid alloy electrode will be freely mobile; (4) the solvent metal should be stable physically and chemically in the process; and (5) the liquid alloy should have a higher specific gravity than both the electrolytes.

The alloying metals or constituents that can be used are in general copper, silver, tin, antimony, zinc, lead, bismuth, iron, nickel, cadmium, silicon, and cobalt and mixtures of these.

In the ordinary practice, it is extremely difficult if not impossible to electrolyze the oxides under consideration and obtain a desired metallic product on a solid cathode. If metal is obtained it is contaminated with oxides and oxygen that are not easy to remove. The oxides are very stable compounds requiring high potentials for decomposition on a solid cathode. On the liquid cathode that is composed of metal or metals more electronegative than the depositing titanium and is a solvent for the depositing metal the electrodeposition, on the contrary, is relatively easily accomplished at lower potentials than required for the solid cathode. Whatever the reason the presence of a high concentration of alkaline earth fluoride, like calcium fluoride for instance, improves the operating characteristics at the surface of the liquid cathode. Titanium is electrodeposited on the cathode surface where it is absorbed, dissolved, and dispersed in the alloy electrode. The rate of solution of the deposited metal is increased by the "stirring effect" of the electromagnetic field generated. The metal liquid is thereby vigorously stirred and agitated causing rapid circulation of the metal in the cavity. Inasmuch as the direction of the field generated in the refining compartment is in an opposite direction, there is indeed a good mixing of the metal in the bath compartments which tends to maintain a uniform composition of the electrode throughout. A mechanical means for stirring the electrode has yet to be devised.

The liquid cathode current density can be varied over a considerable range, i. e., from a few amperes per square inch up to about 265 amperes per square inch. The higher current densities reflect higher efficiencies and better yields as long as adequate solute concentrations are maintained. The cathode current density is limited mostly by the cell design. Generally the voltage across the terminals at the cell electrodes is kept sufficiently above the decomposition potential of the specific oxides to insure a cathode current density of at least 50 amperes per square inch.

The temperature of electrolysis in the reductor section of the cell will usually be higher than that in the refining section. The temperature of electrolysis must be high enough to insure mobility and fluidity of the liquid electrode. The electrode temperatures will run somewhat higher than the bath temperature. High temperatures improve the solute solubility, improve the liquid alloy mobility and increase the overall efficiency, and facilitate both deposition and diffusion of the deposited metal in the cathode. However, the cell life is curtailed by high temperatures and practically temperatures below about 1100° C. are preferred. Nevertheless, temperatures in the electrolyte above 1250° C. have been used for a short period. In practice, the fusion temperatures of the electrolytes can be adjusted by proper compounding to be lower than that of the alloy electrode. The limitation lies in the formulation of an alloy that will be mobile and of the proper composition to satisfy the physics and chemistry of the processing. A controlling factor in determining the reductor temperature of operation then is the liquidus temperature of the alloy electrode. A tempera-

ture of about 50–100° centigrade above the selected alloy liquid temperature is usually adequate to insure the proper mobility and physical characteristics of the electrode.

In the reductor compartment, the first purification of the metal takes place, in that titanium and those metals less electropositive than titanium will deposit in preference to the solvent cation-metal. If the oxide feed is reasonably pure and free of metallic element oxides or compounds less electropositive than the metal desired (an easy and inexpensive condition to accomplish in the oxides preparation), the alloy electrode will not accumulate any large quantity of impurities in a short time. The impurities that are normally encountered and deposited in the electrode in the deposition of titanium will not affect the further processing of the metal in refining.

The refining compartment accommodates the selective solution of the desired metal from the liquid alloy electrode and the deposition of the metal at a solid cathode under more favorable conditions than exist in the reductor section of the cell.

The liquid anode in the refining compartment, under the influence of the electrolyzing current, selectively and preferentially dissolves the more active electropositive metal titanium forming thereby the metal ion and leaving the solvent metal or metals and such metal impurities as may have accumulated in the alloy behind. No gases are discharged at this electrode as the energy required for halogen liberation is considerably greater than that required for solution of the metal ion. There is no oxidation to higher valencies either under the conditions set forth in the invention as for some reason high valent compounds are never detected. In the use of a chloride electrolyte, for example, no chlorine or gaseous chloride product have ever been detected. The anode and cathode reactions in this compartment are always in balance.

The anode current density at the electrolyte interface can be varied from a fraction of an ampere per square inch up to about ten amperes per square inch without causing solution of the less electropositive elements and thereby affecting the purity of the product. The current density for cathode deposit is determined by the particular liquid alloy in question, the concentration of the solute metal, and the mobility of the alloy electrode. Low solute concentrations require lower anode current densities. The range cited is a fair approximation of the usual requirement.

The electrolyte solvent is composed of the halides of the alkali and alkaline earth metals as their cations are more electropositive than those of titanium with respect to halogen. Although the fluorides, iodides, and bromides, or mixtures of these and the chlorides may be used as an electrolyte solvent, the chlorides alone are preferred. Eutectic mixtures of the alkali and alkaline earth chlorides have special advantages. Generally, $CaCl_2$, $CaCl_2$—NaCl, $CaCl_2$—$SrCl_2$, and similar combinations are preferred. The solvent salts must be carefully purified, dehydrated and deoxygenated before use.

The electrolyte solute in the refining bath is chosen from the reduced or lower valent halides of the metal to be refined. The halide may be the simple halide or the complex salt. The fluorides are not preferred because of poor solubility in the subsequent washing operation. The bromides and iodides are generally too expensive. Nevertheless, the reactions in the refining compartment do permit their use without engendering excessive recovery or equipment costs. The lower valent chlorides are preferred. In practice it does not matter what chloride is added to the bath to seed, as the tetrachloride, trichloride, dichloride, etc., will quickly be reduced by the liquid alloy solute to the lower stable valency. The electrolyte behaves as if there were merely a transfer of electrons through the titanium and titanium ions present and the nature of the anion seems to have little bearing on the process. The concentration of the dihalide or trihalide, etc., in the electrolyte may be varied over a wide range without affecting the purity of the metal deposited, viz., from a few tenths of a percent by weight to over 43 percent by weight. However, I have found that in this continuous process in order to minimize dragout recovery problems and in order to improve the nature of the deposit, and for other reasons, the lower concentrations of dichloride, below about 15 percent by weight, are preferred.

The temperature in the refining cell will run lower than that in the reductor compartment. The determining factor as to temperature has been discussed above and holds true for the refining compartment, i. e., a temperature about 100° C. above the temperature at which the alloy is completely liquid usually provides for adequate mobility.

The cathode current density may be varied over a wide range and current densities from a few amperes per square inch to over 1000 amperes per square inch have been used. Generally, current densities of the order of about 50 to 250 amperes per square inch give the largest crystals and are preferred. The behavior of this electrode is not at all like the common cathode encountered in fusion electrolysis on a solid cathode below the fusion point of the metal deposited. For one thing, the metal grows in a different fashion. In fact, at times, there is the appearance on the cathode of a deposit that is like that obtained by the iodide dissociation process. In this refining process, deposition probably takes place from the simple ion. The fairly high current densities deposit the metal rapidly on old nuclei rather than on new so that masses of large thick "single" crystals are grown. The crystals are packed one on top of the other in a tight matrix, but without the production of powdery material. Whether or not the metal undergoes incipient fusion or sintering is not known. If one presumes that the deposition in the Von Arkel-De Boer process takes place by means of a gaseous metallic ion, then the two processes may be said to only have a different medium for ion transfer. The metal purity of the present processing is of the same order of magnitude, and occasionally is purer and more ductile than the reported iodide material.

The optimum cathode current density is influenced greatly by the cell design, but one skilled in the art can make a few simple tests that will pin-point the current density that will assure the continued production of the desired metal product in large crystalline size.

The cathode lift mechanism has the following functions: (A) by adjusting the rate of cathode withdrawal, the initial current density at the cathode deposition surface can be maintained a bit more constant; (B) by removing the deposited metal from the sphere of catholyte action, resolution by secondary reactions is obviated; (C) by withdrawing the cathode and its adherent deposit slowly out of the bath, the electrolyte salts have an opportunity to drain off the hot electrode and thereby the dragout losses are reduced to a minimum; in addition, the subsequent removal of salt from the deposited metal becomes an easier chore, and economical by even the most elaborate methods due to the small amount of salts retained; (D) by removing the product from the electrolyte during deposition and coupling that act with the high current density at the cathode deposition-surface-interface and with the preferred low solute concentration, the presence of included lower valent halide or chloride salts with the metal is substantially precluded.

The following example is given for additional illustrative purposes.

Into a laboratory cell built generally along the lines of that described above except that because of the small size auxiliary external heating was required, dry purified argon was pumped to purge the cell of air. Calcium chloride ($CaCl_2$) was fused in a closed nickel pot under a dry HCl atmosphere and purified by bubbling the hydrochloric acid gas through the melt and electrolyzing the latter at low voltage to remove impurities. This was

poured into the cell under an argon blanket until the level of pure white transparent salt stood a few inches above the baffle opening in both compartments of the cell. An alloy of Ti—Cu in solid form was added in increments, a little at a time, to the melt and allowed to fuse. Enough alloy was added to fill the bottom of the cell and raise the liquid level above the opening in the baffles sufficiently to isolate each compartment. The cell needed about 16.5 pounds. The temperature was maintained at 950° C. +25°.

To one compartment of the cell, the anolyte section, sufficient anhydrous and prepurified CaF_2 and $CaCl_2$ were added to make a 14.2 CaF_2–85.8 $CaCl_2$ melt. At the same time, to the second compartment, the catholyte section, sufficient NaCl and $CaCl_2$, anhydrous and prepurified, were added to make a 66.8 $CaCl_2$–33.2 NaCl melt. The salt level in each compartment was about 4 and 4½ inches respectively above the liquid alloy level. Dry purified argon was continuously fed into the catholyte chamber and allowed to empty into the anolyte atmosphere. The anode was made of 1½" diameter graphite and the cathode tip was made of a titanium rod about 1" in diameter.

About 30 grams of TiO (—200 mesh) was added to the anolyte side of the cell to make a 3 to 5% solution and about 150 grams of $TiCl_2$ was generated in the catholyte chamber by bubbling $TiCl_4$ below the surface of the liquid Ti—Cu alloy to make a 3 to 5% $TiCl_2$ (calculated) solution. A source of D. C. current was impressed across the electrodes and manually controlled to pass about 150 amperes through the cell. During the course of electrolysis, TiO was slowly and continuously fed to the anolyte at a rate of about 165 grams per hour. The cathode was slowly removed from the bath during electrolysis. The cathode, its tip and the adherent deposit, was periodically withdrawn from the bath and cooled to room temperature in an isolable compartment filled with inert gas. The adherent salts were white and showed no discoloration. The cathode tips and their metallic deposits were washed free of salts in cold water. After vacuum drying the product without heat, 84.4% was retained to a No. 10 U. S. sieve screen. The larger silvery crystals were found to be 99.97% titanium, whereas the batch was 99.91%. The operating details were:

Duration of run	5½ hours.
Alloy at start	27.7% Ti.
Anode current density	13.4 amps/in.^{2}.
Cathode current density, initial	30.3 amps/in.^{2}.
Liquid cathode current density	21.2 amps/in.^{2}.
Liquid anode current density	7.4 amps/in.^{2}.
Alloy at end	26.8% Ti.
Brinell hardness of product	40–60.

The electrolysis was continued unchanged except that TiO_2 (—200 mesh dried) feed was substituted for the TiO feed above, and separate sources of supply of D. C. were connected across the graphite anode and the liquid alloy cathode in the anolyte compartment as one circuit, and across the titanium cathode and the liquid alloy anode in the catholyte compartment as the other circuit. The dried TiO_2 was fed to the anolyte at the rate of 112 grams per hour. The temperature was 950° C.+25°. The current flowing through the anode compartment was manually controlled at 150 amperes, while the current flowing independently through the cathode compartment was kept at about 75 amperes.

The cathode deposit obtained was treated in the same way as described above. It was found to be relatively free of included salts, and such salts as still adhered to the deposit on removal from the electrolyte were white. The larger pieces analyzed 99.98% titanium, while the batch was found to be 99.91%. Although the grade of TiO_2 was of commercial pigment grade, substantially all of the metallic impurities were retained by the liquid alloy and not transferred to the cathode product. The operating details were:

Duration of run	2½ hours.
Anode current density	13.4 amps/in.^{2}.
Liquid cathode current density	21.2 amps/in.^{2}.
Cathode current density, initial	17.9 amps/in.^{2}.
Alloy at end	26.6% Ti.
Brinell hardness of product	40–60.
Iodide titanium composition	99.96% Ti.

The process herein described for the continuous production of titanium is always under control by the very nature of the invention. The valency of the solute electrolyte is uncontaminated, kept low, and the depositing cation is continually replenished only as fast as it is consumed. The power required for the refining step is theoretically zero, and the only power needed is substantially that used to replace heat loss. The third purification step takes place at the cathode where the more electronegative metal deposits preferentially to the electrolyte solvent metal. It can be seen that by this liquid electrode "filtering" process only the metal ions of the element desired have been allowed to come through for deposition at the solid cathode. No special weirs, dams, or diaphragms are needed and there are no problems of reaction-product separation.

The reactions which take place in this electrolytic cell are new and not well known, and I do not wish to be committed to any theory. The physical and chemical conditions prevailing during the electrolysis insure the production of pure and ductile titanium from its oxides. In summary, in the first section of the compartmentalized cell, the titanium oxide is dissolved and forms some kind of ions. At the carbon anode, either by primary oxidation or secondary reaction or both, oxygen is discharged with the formation of CO and CO_2 gases. At the alloy liquid cathode, either by primary reduction or secondary reaction or both, titanium is deposited in the liquid alloy. The energy or potential required for this deposition is lower than that required to decompose the oxide alone with inert solid electrodes. The liquid alloy electrode renders the process a feasible one. The titanium is inherently absorbed into the alloy and dispersed throughout the liquid electrode by the swirling and sloshing of the liquid alloy caused by the strong electromagnetic fields generated within the cell. In the refining section of the divided cell, the titanium atoms in the liquid electrode are preferentially and selectively "pulled" into solution and ionized by the potential across the electrodes. The resulting cations are repelled by the liquid alloy anode and attracted to the solid cathode where deposition of titanium metal occurs. The energy required for this step in the process is relatively small, and the potential is insufficient to cause the deposition of more basic elements or halogen. With each of the three steps of the invention, there is a further purification of titanium.

Although the details and principles set forth above are specifically related to the continuous production of pure and ductile titanium, they may be adapted, in general, to the continuous production of other multivalent metals such as zirconium, hafnium, thorium and uranium.

These metals have the following in common with titanium: (1) They all form multivalent compounds; (2) their halides are not stable physically or chemically at high temperature in the presence of moisture or oxygen; (3) they are difficult to produce in a pure state by commercially practical means; (4) their oxides are refractory, are not easily decomposed, and are not used to make pure ductile metal; (5) impurities, such as oxygen, carbon, nitrogen, hydrogen, and halogen, tend to reduce the ductility of the metals.

In applying the principles of this invention to the production of other multivalent metals in large crystalline form, the lower valent oxide or dioxide of the multivalent metal is dissolved, as described above, in a molten elec-

trolyte containing metallic cations more electropositive than the desired multivalent metal with respect to oxygen and halogens. The quantity of oxide dissolved is not critical to the success of the process as long as some oxide is in solution. The precautions against fouling the electrolyte with excesses of oxide must be observed. The solubility limit of the respective multivalent metal oxide in the electrolyte frequently may be extended by the addition of a fluoride salt of the multivalent metal to the solvent electrolyte. The temperature of the electrolysis will be determined by the composition of the alloy liquid electrode as cited. As the other elements chosen for the metal liquid alloy are less electropositive than the multivalent metal with respect to the halogen of the reductor section too, it does not make too much difference in the results if the higher valent compounds are used initially. The process in operation will adjust itself automatically to the proper valence state of the particular multivalent metal. For example, it is not necessary to seed the refining electrolyte with the dichloride or the trichloride of zirconium. By adding the tetrachloride to the electrolyte, it will be automatically reduced to the stable valency by the zirconium in the liquid alloy. In this case, it appears to be the di-valent specie that is stable and dominant. In the reductor section, the problem of solubility is as important as valency of the metallic cation. If the higher valent specie is fed to the cell, it too may be reduced to the lower valent specie by the liquid electrode, but the action is not critical as, for example, thorium dioxide works well in the process.

The use of an inert gas in each compartment, the rate of oxide feed to the electrolyte, the rate of anode feed, and the rate of cathode deposit withdrawal, are matters influenced mostly by cell design, and can be determined for the production of pure large crystalline metal by simple routine tests during operation. As far as the process variables are concerned, a guide for the use of the electrometallurgist for the continuous production of pure multivalent metallic elements of the group titanium, zirconium, hafnium, thorium and uranium, in accordance with the invention hereinbefore described is given in the tables below.

Exam.	Element	Reductor Section			Alloy (3)
		Solvent (1)	Solute (2)	Temperature	
(I)	Titanium	CaF_2—$CaCl_2$, 14.2—85.8	1-3% TiO	950-1,000	28Ti—72Cu.
(II)	Titanium	CaF_2—$CaCl_2$, 14.2—85.8	1-3% TiO	ca. 800	5Ti—95Sb.
(III)	Titanium	CaF_2—$CaCl_2$, 14.2—85.8	.3-3% TiO_2	950-1,000	28Ti—72Cu.
(IV)	Uranium (6)	CaF_2—$CaCl_2$ (7)	2-3% UO_2	950-1,000	5U—95Bi.
(V)	Uranium (6)	CaF_2—$CaCl_2$ (7)	2-3% UO_2	800-850	89U—11Fe or 88U—12Ni.
(VI)	Zirconium	CaF_2—$CaCl_2$ (9)	2-5% ZrO	850-950	10Zr—90Sn.
(VII)	Zirconium	CaF_2—$CaCl_2$ (9)	1-2% ZrO_2	950-1,000	47Zr—53Cu.
(VIII)	Thorium	CaF_2—$CaCl_2$ (12)	1-3% ThO_2	950-1,000	15.2Th—84.8Ag.
(IX)	Hafnium	CaF_2—$CaCl_2$ (13)	1-3% HfO_2	950-1,000	5Hf—95Sn.

Exam.	Element	Alloy (3)	Refining Section		
			Solvent (4)	Solute (2)	Temperature (5)
(I)	Titanium	28Ti—72Cu	$CaCl_2$—$SrCl_2$, 56.5—43.5	3-5% $TiCl_2$	950-1,000
(II)	Titanium	5Ti—95Sb	$CaCl_2$—NaCl, 66.8—33.2	3-5% $TiCl_2$	ca. 800
(III)	Titanium	28Ti—72Cu	$CaCl_2$—NaCl, 66.8—33.2	3-5% $TiCl_2$	950-1,000
(IV)	Uranium (6)	5U-95Bi	$BaCl_2$—$SrCl_2$, 36—64 (8)	5-15% UCl_3	950-1,000
(V)	Uranium (6)	89U—11Fe or 88U—12Ni	$BaCl_2$—KCl, 46.2—53.8 (8)	5-15% UCl_3	800-850
(VI)	Zirconium	10Zr—90Sn	KCl—KF (10), 57.5—42.5	3-10% $ZrCl_4$ (11)	850-950
(VII)	Zirconium	47Zr—53Cu	$BaCl_2$—$SrCl_2$, 36—64	3-10% $ZrCl_4$ (11)	950-1,000
(VIII)	Thorium	15.2Th—84.8Ag	$BaCl_2$—$SrCl_2$, 36—64 (8)	3-10% $ThCl_4$	950-1,000
(IX)	Hafnium	5Hf—95Sn	$BaCl_2$—$SrCl_2$, 36—64	3-10% $HfCl_4$	950-1,000

Explanations (1) to (13):
(1) Fluoride additives may be added as disclosed, such as BaF_2, SrF_2, $BaCl_2$, $SrCl_2$, etc. also the use of CaO additions for titanium solvent is noted.
(2) The lower valent compounds are always preferred. The percentages are all in weight percent.
(3) Other alloys may be used, but caution must be observed in adding diluent metals.
(4) The salts must be thoroughly dehydrated in accordance with instructions given. Other salts may be used as disclosed.
(5) All temperatures are in degrees centigrade.
(6) A cathode tip made of iron, molybdenum, or tungsten is recommended, as cathode.
(7) The solvent power of the uranium oxide electrolyte may be improved by additions of UF_4; alkali fluorides may also be added.
(8) The process prevents carbon contamination from the anode. This bath is recommended in order to avoid light metal impurities in the deposited metal.
(9) The solvent power of the electrolyte may be improved by the addition of ZrF_4, simple or complexed.
(10) The KF solvent must be absolutely anhydrous.
(11) The zirconium salt will be reduced to a stable valency and complex in the bath as explained. The $ZrCl_4$ is used only as it is convenient.
(12) The solvent power of the electrolyte may be improved by additions of ThF_4 to the electrolyte, also by alkali fluorides.
(13) The solvent power of the electrolyte for the HfO_2 may be improved by the addition of fluorohafniates or HfF_4.

fining electrolyte, only the multivalent element will be preferentially and selectively dissolved in the electrolyte. The electrolyte in the refining section is selected from the halides of the more electropositive metallic elements than the desired multivalent metal with respect to the halogen in order to prevent contamination of the product or co-deposition. The solute used in the refining section usually is the lower valent halide of the multivalent metal desired. However, as in the case with the oxide solute in the re-

The range of current desnsities given for titanium production from its oxides are generally applicable to the multivalent metals under consideration here. Where the concentration of oxide solute is low, the anode current density should be in the lower range. Where a higher valent oxide solute is used, usually the lower limits of current density at the anode are invoked. Generally, higher temperatures permit the use of the higher current density at the anode.

The current density at the liquid alloy cathode should be as high as attainable within the range disclosed and is influenced in part by the cell design and by the oxide concentration in the electrolyte, but not as rigorously as the anode. The presence of calcium fluoride in the bath tends to keep this alloy cathode liquid surface "clean" and allows the use of the current density in the upper part of the range, above 100 amperes per square inch.

The current density at the liquid alloy anode in the refining section of the divided cell depends in part on the concentration of the multivalent metal in the liquid alloy electrode, and should be kept below 10 amperes per square inch.

The cathode current density in the refining cell can be

varied considerably for the other metals but within the range prescribed for titanium, and it is usually determined primarily by the cell design. For example, a cathode current density of about 165 amperes per square inch in a uranium refining cell gave crystals as large as a man's thumb in clusters three to four inches long whose purity was 99.99% uranium. The cathode current density is also affected by the solute concentration. Generally, the larger the metallic ion the higher the solute concentration should be at the same high cathode current density. Using the Cu—Ti alloy and the TiO feed, the Ti product obtained analyzed 99.97% Ti. With the TiO_2 feed of the third example, the purity was 99.98% Ti. The ductility in both instances was 40–60 Brinell.

The following examples are given for additional illustrative purposes.

A laboratory cell similar to that described in the titanium example, columns 2 and 3, was used for the electrolytic production of uranium. The cell was purged of air by dry purified argon gas and slowly brought to about 850° C. by external heating. An alloy of 88 U and 12 Ni, in solid form, was added and fused in the cell until the level of liquid metal in the cell had risen above the baffle opening, thereby isolating the two compartments.

The anolyte section was filled with a prepurified 14.2 CaF_2–85.8 $CaCl_2$ eutectic. The catholyte section was also filled with a prepurified eutectic of 46.2 $BaCl_2$–53.8 KCl. Sufficient pure dry UO_2 was added to the anolyte to make a 3% solution and sufficient anhydrous pure UCl_3 salt was added to the catholyte section to make a 15% UCl_3 (calculated) solution. The argon continued to flow through the cell throughout the run.

A graphite anode was inserted in the anolyte and a molybdenum tipped cathode was inserted into the catholyte. A D. C. current of about 200 amperes was passed through the anolyte section. During the course of the 7½ hour electrolysis, pure dried UO_2 was constantly shaken into the anolyte and about 8 pounds were added. The anolyte operating conditions were:

Duration of run	7½ hours.
Alloy at start	88 U–12 Ni.
Anode current density	12.7 amperes/in.².
Liquid cathode current density	28.5 amperes/in.².
Temperature	850° C.

At the same time, a D. C. current of about 150 amperes was passed through the catholyte section. During the course of the 7½ hour electrolysis the cathode and its deposit was slowly raised in the electrolyte. At the end of the run, the cathode and its deposit were withdrawn and allowed to cool to room temperature in the dry argon atmosphere in the cell. The crystals, after water washing, were silvery bright and substantially free of powder and entrapped electrolyte. The catholyte operating conditions were:

Duration of run	7½ hours.
Liquid anode current density	7.4 amperes/in.².
Cathode current density, initial	165 amperes/in.².
Purity of the U product	99.99% U.
Temperature of the run	850° C.

A cell identical in structure as that described above for titanium and uranium was used in the electrolytic production of pure and ductile thorium but with the bipolar liquid alloy a 15.2 Th–84.8 Ag mix. The anolyte was a 2.8% ThO_2 solution in a CaF_2—$CaCl_2$ eutectic mix to which about 5% pure anhydrous ThF_4 had been added. The temperature was maintained at about 1050° C.±50°. The catholyte was composed of 36 $BaCl_2$–64 $SrCl_2$ eutectic to which about 10% (calculated) $ThCl_4$ anhydrous chloride had been added. Again a pure dry argon gas was maintained in both compartments throughout the run. A graphite anode was immersed in the anolyte and a thorium tipped cathode was immersed in the catholyte. A D. C. current of about 100 amperes was passed through the cell. During the course of electrolysis pure dried ThO_2 was fed bit by bit to the anolyte electrolyte at a rate of about ½ pound per hour. The cathode was slowly withdrawn from the catholyte in an effort to maintain a high current density. After the completion of the run, the cathode and its adherent deposit were withdrawn from the electrolyte and allowed to cool to room temperature in the argon atmosphere. The deposit was found to be composed of massive silvery crystals bound together in a cluster. The adhering salt film was not discolored. The tip was removed and the crystals washed free of salts in cold water. The recovered metal was substantially free of powder and entrapped salt. A superior product is obtainable using a Th—Cu liquid bipolar alloy. The operating conditions were:

Duration of run	3 hours.
Alloy at start	15.2% Th.
Anode current density	8.9 amperes/in.².
Liquid cathode current density	13.4 amperes/in.².
Liquid anode current density	4.9 amperes/in.².
Cathode current density	30.1 amperes/in.².
Temperature of electrolysis	1050° C.±50°.
Purity of product Th	At least 99.9%.

Having broadly described the scope of the present invention and disclosed in detail the method of applying the invention, it is apparent that the invention is not limited to many of the details of equipment and procedure herein described, but can be carried out in other ways without departing from its spirit and scope as defined by the appended claims.

I claim:

1. A process for the electrolytic production of a pure and ductile multivalent metal of the group consisting of titanium, zirconium, hafnium, thorium and uranium, comprising passing an electrolyzing current through at least one compartment of an electrolytic cell between a liquid alloy electrode as cathode and a solid anode immersed in a molten electrolyte containing at least one oxide of said multivalent metal in a fused solvent having cations more electropositive than those of said multivalent metal with respect to oxygen and halogens, said liquid alloy electrode containing said multivalent metal and a solvent of at least one of the group of metals less electropositive than said multivalent metal with respect to halogens, thereby discharging oxygen at said anode and depositing said multivalent metal in said liquid alloy cathode, simultaneously passing an electrolyzing current through another compartment of said electrolytic cell between said common liquid alloy electrode as anode and a solid cathode immersed in a fused electrolyte containing at least one halide of said multivalent metal as a solute in a solvent halide having metallic cations more electropositive than those of said multivalent metal with respect to halogen, thereby selectively dissolving said multivalent metal in said electrolyte from said liquid alloy anode and depositing said pure and ductile multivalent metal on said solid cathode.

2. A process for the electrolytic production of a pure and ductile multivalent metal of the group consisting of titanium, zirconium, hafnium, thorium and uranium as set forth in claim 1, in which the atmosphere in each compartment of said electrolytic cell is a dry inert gas.

3. A process for the electrolytic production of a pure and ductile multivalent metal as set forth in claim 1 in which said liquid alloy electrode solvent has at least one element of the group copper, silver, tin, gold, lead, antimony, bismuth, zinc, cadmium, iron, nickel, cobalt and silicon.

4. A process for the electrolytic production of a pure and ductile multivalent metal of the group consisting of titanium, zirconium, hafnium, thorium and uranium as set forth in claim 1 in which said oxide solute of said

electrolyte of said first compartment of said electrolytic cell is the dioxide of said multivalent metal.

5. A process for the electrolytic production of a pure and ductile multivalent metal of the group consisting of titanium, zirconium, hafnium, thorium and uranium as set forth in claim 1 in which said solvent electrolyte in said first compartment of said electrolytic cell is of the group consisting of calcium fluoride, calcium chloride, said multivalent metal fluoride and mixtures thereof.

6. A process for the electrolytic production of a pure and ductile multivalent metal of the group consisting of titanium, zirconium, hafnium, thorium and uranium as set forth in claim 1, in which said multivalent metal is zirconium and in which said oxide solute in said first compartment of said electrolytic cell is at least one oxide of the group consisting of the dioxide and the lower oxide of zirconium, and in which said electrolyte soluble in said other compartment of said electrolytic cell is at least one halide of the group consisting of the di-, tri- and tetra-halides of zirconium.

7. A process for the electrolytic production of a pure and ductile multivalent metal of the group consisting of titanium, zirconium, hafnium, thorium and uranium as set forth in claim 1, in which said multivalent metal is hafnium and in which said oxide solute in said first compartment of said electrolytic cell is the dioxide of hafnium, and in which said electrolyte solute in said other compartment of said electrolytic cell is at least one halide of the group consisting of hafnium tetrachloride, hafnium tetrafluoride, and an alkali fluorohafniate.

8. A process for the electrolytic production of a pure and ductile multivalent metal of the group consisting of titanium, zirconium, hafnium, thorium and uranium as set forth in claim 1, in which said multivalent metal is thorium and in which said oxide solute of said multivalent metal in said first compartment of said electrolytic cell is thorium dioxide, and in which said electrolyte solute in said other compartment of said electrolytic cell is at least one halide of the group consisting of thorium tetrachloride, thorium tetrafluoride, and alkali fluorothorate.

9. A process for the electrolytic production of a pure and ductile multivalent metal of the group consisting of titanium, zirconium, hafnium, thorium and uranium as set forth in claim 1, in which said multivalent metal is uranium and in which said oxide solute in said first compartment of said electrolytic cell is uranium dioxide and in which said electrolyte solute of said other compartment of said electrolytic cell is at least one halide of the group consisting of uranium trihalide and uranium tetrahalide.

10. A process for the electrolytic production of a pure and ductile multivalent metal of the group consisting of titanium, zirconium, hafnium, thorium and uranium as set forth in claim 1, in which said solvent of said electrolyte in said anolyte compartment of said electrolytic cell is of the group comprising alkali and alkaline earth halides and said halide solvent electrolyte in said second compartment of said electrolytic cell is of the group consisting of the alkali and alkaline earth chlorides and mixtures thereof.

11. A process for the continuous electrolytic production of pure and ductile titanium in large crystalline form from its oxides comprising electrolyzing in one compartment of an electrolytic cell between a dependent anode immersed in a molten electrolyte and a liquid alloy electrode as cathode containing titanium as a solute and having as a solvent a metal of the group of metals less electropositive than titanium with respect to halogen and metal mixtures thereof, said molten electrolyte containing an oxide of titanium and having as a solvent fused salts whose cations are more electropositive with respect to oxygen and halogens than those of titanium, thereby discharging oxygen at said anode and depositing and dissolving and dispersing titanium in said liquid alloy cathode, simultaneously electrolyzing in another compartment of said electrolytic cell, between said common liquid alloy electrode as anode and a dependent cathode immersed in a molten electrolyte containing a lower valent halide of titanium as a solute and having as a solvent fused salts free of moisture and oxides of the group consisting of the alkali and alkaline earth halides and mixtures thereof, thereby selectively dissolving titanium from said liquid alloy anode and depositing titanium at said cathode in the form of large pure and ductile crystals.

12. A process for the continuous electrolytic production of pure and ductile titanium as set forth in claim 11 wherein said liquid alloy electrode containing titanium has copper as a solvent metal.

13. A process for the continuous electrolytic production of pure and ductile titanium as set forth in claim 11 wherein said halide electrolyte in said other compartment of said divided electrolytic cell contains titanium dichloride and said electrolyte solvent in said same compartment is of the group consisting of the alkali and alkaline earth chlorides and mixtures thereof.

14. A process for the continuous electrolytic production of pure and ductile titanium as set forth in claim 11 wherein the current density at said solid cathode in said other compartment of said divided electrolytic cell is in the range of 50 to 250 amperes per square inch and maintained within said range.

15. A process for the continuous electrolytic production of pure and ductile titanium as set forth in claim 11 wherein the current density at said liquid alloy anode in said other compartment of said divided electrolytic cell is kept below about 10 amperes per square inch.

16. A process for the continuous production of a pure multivalent titanium metal as set forth in claim 11 in which the concentration of the solute multivalent titanium metal in said mobile liquid bipolar electrode is maintained substantially constant during the course of electrolysis.

17. A process for the continuous production of a pure multivalent titanium metal as set forth in claim 11 in which said oxide solute of said electrolyte in said first compartment of said electrolytic cell is the di-oxide of said titanium.

18. A process for the continuous production of a pure titanium metal as set forth in claim 11 in which said solvent electrolyte in said first compartment of said electrolytic cell is of the group consisting of the alkali and alkaline earth halides and mixtures thereof.

19. A process for the continuous production of a pure multivalent titanium metal as set forth in claim 11 in which said solvent electrolyte in said first compartment of said electrolytic cell is of the group consisting of calcium fluoride, calcium chloride, and mixtures thereof.

20. A process for the continuous production of a pure multivalent titanium metal as set forth in claim 11 in which said solid cathode with its adherent metal deposit in said second compartment of said electrolytic cell is continuously withdrawn from the electrolyte during the electrolysis, thereby maintaining a relatively constant current density at said cathode deposition surface.

21. A process for the continuous production of a pure multivalent titanium metal as set forth in claim 11 in which the rate of oxide feed to said oxide electrolyte in said first compartment of said electrolytic cell is synchronized to the rate of electrolytic decomposition of said oxide solute, thereby avoiding an excess of said oxide in said electrolyte.

22. The process of electrolytically producing titanium metal at a cathode comprising passing current from an insoluble anode through a molten anolyte the solvent of which is liquid and stable at the temperature of operation, consists of salts of metals more electropositive than titanium and acts as a solvent for and contains at least one titanium oxide as a solute, passing said current to a liquid bi-polar electrode as cathode and simultaneously

passing current from said liquid bi-polar electrode as anode through a molten catholyte which is different from the anolyte and which is at least one of the group consisting of the halides of metals more electropositive than titanium and which is a solvent for and contains a solute halide selected from the group consisting of the di- and tri-halides of titanium, said catholyte being oxygen and oxygen compound free, and delivering the current through said catholyte to a cathode for deposit of titanium metal thereon, said bi-polar electrode being of molten metal denser than the anolyte and catholyte and of low solubility therein, less electropositive than titanium and acting as a solvent for and containing titanium.

23. A process of electrolytically producing titanium metal at a cathode as set forth in claim 22 in which the anolyte solvent is at least one of the group consisting of alkaline earth metal salts.

24. A process of electrolytically producing titanium metal at a cathode as set forth in claim 22 in which the catholyte solvent is at least one of the group consisting of the halides of the alkali and alkaline earth metals.

25. A process of electrolytically producing titanium metal at a cathode as set forth in claim 22 in which the catholyte solvent is at least one of the group consisting of the chlorides of the alkali and alkaline earth metals.

26. A process of electrolytically producing titanium metal at a cathode as set forth in claim 22 in which the catholyte solute is at least one of the group consisting of the di- and tri-chlorides of titanium.

27. A process of electrolytically producing titanium metal at a cathode as set forth in claim 22 in which the bi-polar electrode solvent is at least one of the group consisting of bismuth, antimony, tin, zinc, copper and lead.

28. A process of electrolytically producing titanium metal at a cathode as set forth in claim 22 in which the bi-polar electrode solvent is at least one of the group consisting of copper and tin.

29. A process of electrolytically producing titanium metal at a cathode as set forth in claim 22 in which the anode is at least one of the group consisting of carbon and graphite.

30. A process of electrolytically producing the titanium metal at a cathode as set forth in claim 22 in which the anode is impure titanium metal and supplies titanium ions to the bath.

31. A process of electrolytically producing titanium metal at a cathode as set forth in claim 22 in which the liquid bi-polar electrode material is renewed to attain corresponding purification of the titanium and avoidance of contamination thereof.

32. The process of electrolytically producing pure titanium metal at a solid cathode as set forth in claim 22 in which the anode comprises at least one of the group consisting of carbon, graphite and impure titanium and titanium carbide, and in which process the molten anolyte solvent is at least one of the group of inorganic salts liquid at the temperature of electrolysis, acting as a solvent for titanium oxides, conducting the electrolytic current from the anode to the bi-polar electrode, remaining stable at the temperature of electrolysis, and having only metal cations which are more electropositive than titanium.

No references cited.

UNITED STATES PATENT OFFICE

Certificate of Correction

Patent No. 2,861,030 November 18, 1958

Harvey L. Slatin

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 11, lines 10 and 63, for "950° C.+25°", each occurrence, read —950° C.±25°—; column 17, line 17, for "soluble" read —solute—.

Signed and sealed this 31st day of March 1959.

[SEAL]

Attest:
KARL H. AXLINE,
Attesting Officer.

ROBERT C. WATSON,
Commissioner of Patents.