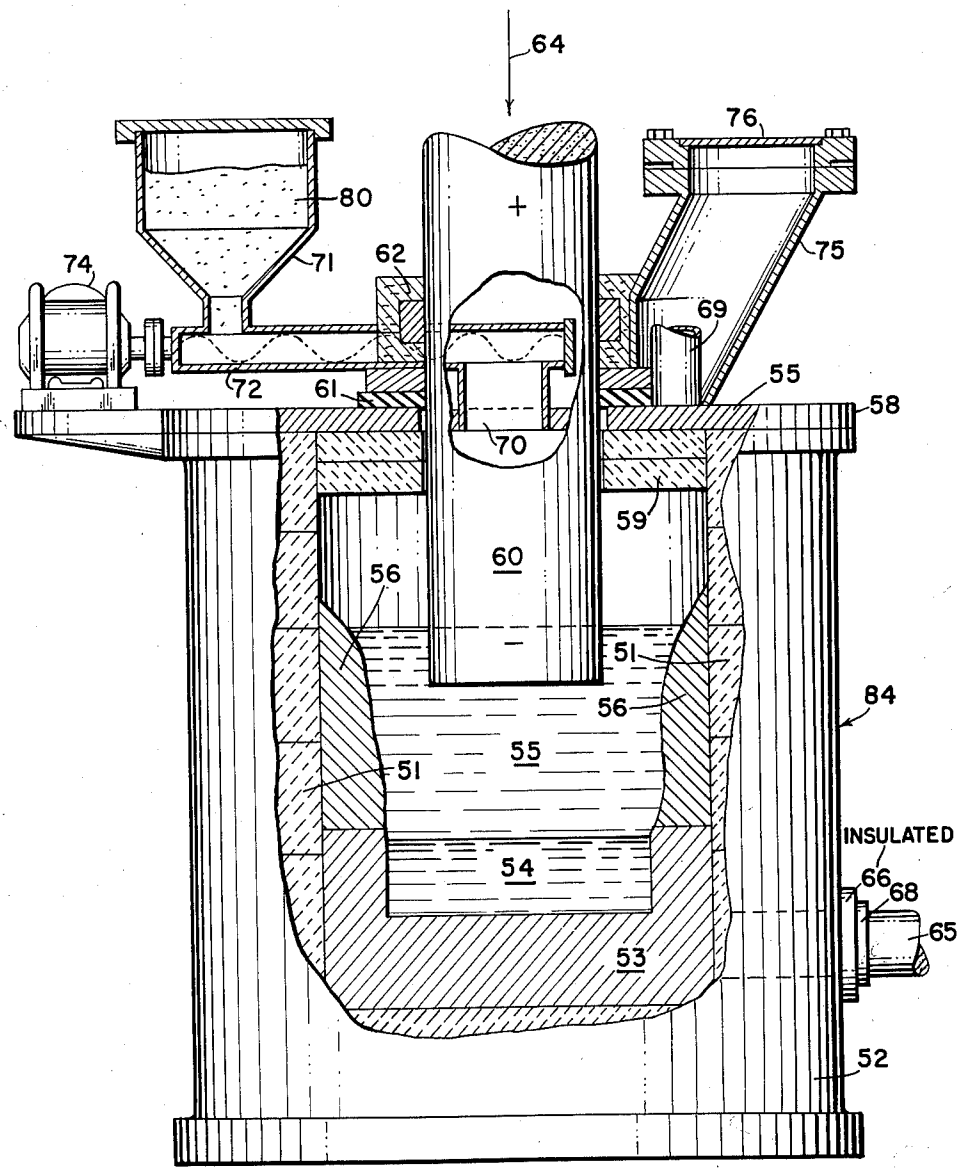
April 30, 1963 H. L. SLATIN 3,087,873

ELECTROLYTIC PRODUCTION OF METAL ALLOYS

Filed June 15, 1960



INVENTOR

HARVEY L. SLATIN

BY George C. Bower

ATTORNEY

United States Patent Office 3,087,873 Patented Apr. 30, 1963

3,087,873

ELECTROLYTIC PRODUCTION OF METAL ALLOYS

Harvey L. Slatin, New York, N.Y., assignor to Timax Associates, New York, N.Y., a New York partnership

Filed June 15, 1960, Ser. No. 36,294
12 Claims. (Cl. 204—71)

This invention relates to the production of alloys of the metals in group IV, titanium, zirconium and hafnium, from their oxides and oxygen compounds by fusion electrolysis, and particularly relates to those metallic alloys suitable for use in the production of these elementary metals in pure and ductile form by electrorefining.

This application is a continuation-in-part of my pending patent applications Serial Nos. 383,762; 493,442; and 499,343; filed October 2, 1953; March 10, 1955, and April 5, 1955, respectively, all of which have been abandoned.

It should be noted that although this application makes specific reference to titanium, it applies equally well to the sister metals zirconium and hafnium.

The chief object of this invention is to provide a commercially practicable process for the production of alloys of titanium from its ores, oxides or other compounds (stage one), said alloys being, among other things, suitable for use in the electrorefining of titanium as described and claimed in my co-pending applications Serial Nos. 496,286 and 498,361 and 499,343, filed on March 23, 1955, and March 31, 1955, and April 5, 1955, respectively (stage two), all of which have been abandoned.

Another object of the invention is to provide a process not only for the production of titanium alloys, but adaptable also to the enrichment of existing alloys with titanium.

A further object of the invention is to provide a suitable electrolyte for the production of multivalent metallic alloys of the more electropositive elements.

Other objects of the invention are:

(*a*) To provide a method for producing titanium alloys that are liquid and mobile below about 1100° C., with metallic elements more electronegative than titanium;

(*b*) To provide a process for the production of alloys of titanium from its oxides and oxygen compounds, which are substantially free of iron, silicon, carbon, aluminum and other similar elements that impair the mobility of the molten alloy produced;

(*c*) To provide a process for the production of alloys of titanium from its oxides and oxygen compounds by simple and direct electrolytic means that lends itself to continuous and large scale production; and

(*d*) To provide a process for the production of liquid alloys of titanium wherein the titanium may be a major constituent.

Other objects and advantages will be apparent from or will appear in the course of the following description.

The process of the invention comprises the electrolytic reduction of titanium oxides and other oxygen compounds dissolved in an electrolyte comprising cations more electropositive than titanium with respect to halogens and oxygen and depositing the titanium therefrom in a liquid cathode metal heavier than the electrolyte consisting of selected metallic elements more electronegative than titanium with respect to halogens, said alloy being so compounded as to be fluid and mobile when molten and at a temperature below about 1100° C. The cations more electropositive than titanium with respect to halogens and oxygen are calcium and strontium. At lower temperatures, magnesium may be suitable.

The accompanying drawing shows, somewhat diagrammatically, an electrolytic cell designated generally as **84** suitable for practicing the invention. The cell is lined with a heat and chemically resistant refractory material **51** made of high fired alumina, magnesia or titania brick enclosed in a steel shell **52**. The heat and electrical insulating refractory supports a carbon cavity or chamber **53** made of graphite. The electrolyte **55** floats on top of a liquid metal cathode which lies in this graphite cavity and forms a frozen crust **56** which protects the fused electrolyte from possible contamination by the refractory. Alternatively, the carbon or graphite cavity may be extended the height of the cell. The frozen crust may be maintained by water cooling, if necessary. The cell is fitted with a cover **58**, preferably made of nickel or Inconel, insulated thermally and electrically by suitable refractory brick **59** and other known means. If the cover is water cooled, the refractory brick **59** is unnecessary. The cover has two or more apertures centrally located for admission of carbon anodes **60**, made preferably of AGR grade graphite (a product of the National Carbon Company). These anodes are electrically insulated from the cover and the cell by suitable means, such as a plate of dielectric material **61** properly cooled. The anodes are supported and fed through a packing or similar gland **62**. The direct current leads and a mechanism (not shown) for automatically and continuously lowering these electrodes are indicated generally by arrow **64**. The anodes and the cathode leads **65** may be water cooled if desired. The cathode lead is insulated electrically from the cell by an appropriate spacer **66** and a mechanical adapter **68** suitably cooled.

Between each set of anodes **60**, cell vents **69** are located in the cover for the disposal of electrode gases. Also between the anodes are feed ports **70** (seen in the drawing through a broken section of one of the anodes) that admit raw material **80**, such as dried ground titanium dioxide, to the cell electrolyte. The oxides are stored in hoppers **71** and are automatically fed to the cell by a screw conveyor **72** that is powered by motor **74**. The rate of feed is determined by the current passing through the cell, and the feed mechanisms are controlled in accordance with the amount of direct current passed through the cell.

In the cover **58** is a withdrawal port **75** having a sealable door **76** which affords access to the cell contents for withdrawal of the alloy **54** from the cell and the introduction of alloy materials to the cell.

The cell is operated as follows: The anodes **60** are lowered into the cell until they contact the graphite cavity **53**. A low voltage A.C. arc is struck and solvent salts are simultaneously fed to the cell via port **75**. As the salts melt, the anodes are raised and more salt is added until the desired electrolyte level is obtained. Anhydrous salts are used. After fusion, one or more of the alloying elements hereinafter described are added and sink into the cathode cavity where they melt. Sufficient alloy solvent is added to provide a cathode depth of a few inches, but this is kept shallow enough to keep the more voluminous titanium-rich alloy from contacting the ceramic lining. The level of the electrolyte may be, for example, 8 to 12 inches above the cathode surface level. The fused salts initially penetrate into the lining and fill the holes and crevices in the brick and the carbon chamber, freezing therein. It is advisable to cause a layer **56** of the electrolyte to freeze on the inner lining of the cell **51** by cooling the cell wall **52**.

The anodes, which are continuously raised during the melting operation, are established in proper depth in the electrolyte for electrolysis. The A.C. power is discontinued when the required temperature is reached and direct current is connected across the cell. The requisite amount of titanium solute, for example, titanium oxides

or oxygen compounds, is added to the solvent to form the electrolyte, and the electrolysis is started. During the course of the electrolysis, the titanium oxides are consumed and are replaced by worm feeder **72** which is operated in accordance with the current flow, as hereinafter described. The anodes **60** are slowly consumed during electrolysis and are continuously lowered by the mechanism **64** so as to maintain substantially constant current density at the anodes. The bins **71** can be kept full of dried titanium compounds in any desired way.

In carrying out the present invention in the preferred manner, it is advisable to abide by the following considerations in order to produce a liquid titanium alloy with the requisite properties demanded in electrorefining.

A. *The Anode and Feed Material*

Anodes made of carbon, AGR grade of graphite (a product of the National Carbon Company) are preferred. The reaction at the anode is the liberation of oxygen from the electrolyte. The oxygen almost immediately reacts with the graphite to form CO and CO_2. Analysis of the cell gases shows a preponderance of CO_2 and very little, if any, CO and O_2. The consumption of the anode is dependent on the oxygen content of the feed and the protection of the hot anode from the atmosphere.

The feed material **80** should be ground to facilitate solution in the electrolyte. Particle sizes of the order of 100–200 mesh are satisfactory. The feed material should be calcined to eliminate water. Usually the particles will dissolve slowly in the bath as they gradually sink to the bottom of the electrolyte and may come to rest on top of the fluid alloy. As a result of this action, the cathode deposition surface will enjoy the richest concentration of titanium ions in the bath. The rate of feed should be regulated carefully so that the amount of undissolved titanium compounds is never appreciable. An excess of undissolved titanium oxides in the electrolyte causes objectionable increase in the viscosity of the bath, produces anode effect and loss of titanium. Under such conditions, the cell may become wholly inoperative. By carefully feeding the dried powdered compound in synchronization with the rate of titnaium deposition in the alloy, such operating difficulties are avoided. The preferred concentration of titanium oxides (calculated as TiO_2) in the bath is below 5% by weight.

The feed material should be substantially free of iron, silicon and aluminum impurities as these elements, under the conditions of the electrolysis, will deposit in the alloy and cause a reduction in the mobility thereof. Although lower valent oxides may be used, the preferred feed material is the dioxide.

B. *The Electrolyte*

The purity and composition of the electrolyte will determine the purity and usefulness of the final alloy. In order that high purity and ductile titanium may conveniently be made from the alloy, the solvent electrolyte should have the following properties:

(1) It must comprise metal cations that are more electropositive than titanium in its lowest valent state at the temperature of operation. I have found that although only the calcium compounds can fullfill this condition at about 1100° C., at lower temperatures strontium and magnesium compounds may be added in varying amounts to increase the solubility of titanium oxides and oxygen compounds in the electrolyte and improve bath fluidity.

(2) The solvent should be chemically and physically stable in the course of electrolysis, i.e. it should have low vapor pressure at operating temperatures to prevent excessive salt loss by evaporation.

(3) The solvent should be able to dissolve titanium oxides, be an electrolytic conductor, and have a lower specific gravity than the alloy. Contrary to the prior art, I have found that TiO_2 is not dissolved in $CaCl_2$ or other alkali and/or alkaline earth chlorides. Also, the presence of fluorides does not help the solubility much. Under such conditions, titanium dioxide appears not to be reduced by primary electrolysis. However, this situation is radically changed by the presence of calcium oxide in the electrolyte. Although the precise nature of the action of CaO in the electrolyte solvent is not exactly known, in the presence of a substantial amount of CaO the solubility of TiO_2 is facilitated and the titanium appears to be directly electrolyzed.

(4) The electrolyte should not be a solvent for the liquid alloy.

The electrolyte that is used consists preferably of a eutectic mixture of CaF_2—$CaCl_2$—CaO with or without additions of MgF_2, MgO, SrF_2, SrO and the like. This electrolyte solvent with reduced amounts of $CaCl_2$ can be used at the higher temperatures described below. The permissible electrolytes that can be used are, in part, also determined by the alloy selected. The solubility of titanium oxides in the electrolyte is not high, but is vastly improved by the addition of calcium oxide as shown in a typical electrolyte composition:

CaO	8–18%	solvent.
CaF_2	10–22%	
$CaCl_2$	60–80%	
TiO_2	½–8%	solute.

with less than 25% additions of MgF_2, SrF_2, BaF_2 and a corresponding reduction in the $CaCl_2$ content.

Baths composed solely of oxides with some fluoride additions are required by high temperature electrolysis. A eutectic of CaO—CaF_2, for example, may be operated under some circumstances up to about 1500° C.–1800° C. as a solvent. The fluorides, and to a more limited extent the oxides, are not good electrolytic conductors and may require some calcium chloride additions to improve the electrolytic conductivity.

C. *The Liquid Cathode*

The liquid electrode must comply with the following conditions if a suitable alloy is to be produced for electrorefining:

(*a*) The alloying element or elements must be less electropositive than titanium in order that they may be retained in solution in the alloy during subsequent refining.

(*b*) The alloying element or elements must be reasonably good solvents for titanium below about 1100° C. and such liquid alloys of titanium must be freely mobile throughout the course of electrolysis.

(*c*) The alloying element or elements should not have high vapor pressures and thereby cause loss of metal solvent during the processing.

(*d*) The concentration of titanium in the liquid alloy must be adequate to prevent codeposition of impurities or solvent metals, particularly at high current densities during electrorefining.

(*e*) The liquid alloy should not be a solvent for the electrolyte.

(*f*) The alloy should have a higher specific gravity than the electrolyte.

Although many alloys can be made via this invention, if the alloy is to be used in electrorefining, the alloy solvent constituents are limited to the elements Cu, Ag, Sn, Zn, Cd, Sb, Bi, Pb. At temperatures above about 1000° C. copper is the preferred solvent. The eutectic composition of 72 copper–28 titanium has special advantages in electrorefining and compositions containing 15 to 60% titanium (balance copper) have been prepared and used.

Adequate mobility of the liquid alloy is necessary for ease in handling and for aiding in maintaining the purity of the liquid titanium alloy. At high cathode current densities, high temperatures, and low titanium concentration in the alloy or in the electrolyte, calcium may be co-

deposited in the alloy. A fluid mobile alloy will permit the calcium metal so deposited to chemically reduce any titanium ions with which it comes in contact, thereby precipitating titanium and redissolving the calcium in the electrolyte. A thin liquid alloy of titanium will slosh about in the bottom of the cell under the influence of the magnetic fields induced in the cell. This desirable action should not be impeded.

D. *The Temperature*

The temperature of the electrolyte should be kept above the temperature at which the body of the titanium alloy would solidify and sufficiently above to insure good mobility. The available materials of construction, the restrictions on alloy compounding where used in electrorefining, and practical design considerations limit the practical temperature of operation to below about 1100° C. The preferred temperature used in the electrolysis is between about 700° C. and 1150° C. and 900–1000° C. has been used most frequently.

E. *The Current Density*

The anode current density should be kept low enough to prevent chlorine liberation and loss of electrolyte solute by the formation of titanium tetrachloride. The anodes and their holders will require cooling in order to reduce useless deterioration of the graphite at high temperatures. This phenomenon is more apparent with electrolytes that are less mobile and more viscous. Generally, anode current densities below about 10 amperes per square inch are used and anode current densities below 6 amperes per square inch are preferred.

The cathode current density may be varied widely. There are advantages to high cathode current densities. Cathode current densities up to about 100 amperes per square inch have been used. The preferred range of current densities is from about 5 to 50 amperes per square inch.

F. *Treatment of the Alloy*

The liquid titanium alloy produced in this process may sometimes require additional treatment before it is usable in electrorefining. This treatment may be a mere adjustment of the composition of the alloy or it may comprise further treatment. Usually, the need for such further treatment arises from the accumulation, in any given liquid alloy, of such elements as raise the melting point of the particular alloy or precipitate in the particular alloy, thereby impairing its mobility. For example, in making a copper-titanium alloy for use in subsequent refining, impurities such as iron, silicon, aluminum, and carbon tend to raise the temperature at which adequate mobility of the liquid alloy may be assured. In these copper-titanium alloys the bulk of iron, silicon and the like may be removed, if necessary, by the simple expedient of allowing the alloy to cool to a temperature where these impurities precipitate and may be removed mechanically. Occasionally it may be desirable to rid these liquid alloys of all impurities. In that event, the alloy is stripped of as much of its titanium content as is practical in the refining cell and the residual alloy is removed for cleansing. Air blown through the fluxed molten alloy at about 1200° C. will remove all the impurities. The clean alloy may then be returned to the electroreduction cell.

The titanium from electrolyte solution **55** is being deposited at the molten cathode **54** at a temperature at which titanium is normally a solid, and the content of deposit may be accumulated to any desired concentration in the molten cathode consistent with the fluid mobility at the then operating temperature. The essential mobility requires the alloy to be free flowing so that it promptly and freely pours and immediately takes the shape of the receiving vessel and has a level surface in a horizontal plane.

The following example illustrates the nature of the invention:

A eutectic mixture of $CaCl_2$—CaF_2 was dehydrated under vacuum at low temperature in a graphite-crucible-lined cell similar in construction to that shown in the drawing except that due to the small laboratory size no Al_2O_3 or frozen salt lining was used. The cell was heated externally by electricity. After dehydration the salts were rapidly fused under a dry argon atmosphere. Precalcined ground calcium oxide was added to the melt in the ratio of 1 part of CaO to 6 parts of $CaCl_2$. This solvent was electrolyzed at low voltage at 850° C. to remove impurities and residual water using an immersed graphite cathode. The temperature of the bath was allowed to rise to 950° C. and later an alloy of copper and titanium containing 72 parts of Cu to 28 parts of Ti was added to the bath and allowed to melt. This pool of molten alloy was made the cathode to an immersed graphite anode. Precalcined 200 mesh TiO_2 was added to the electrolyte as solute until about a 3% solution was obtained. The electrolysis was begun and continued for about eight hours. During the course of electrolysis, the electrode gases were swept from the cell by dry argon gas. Periodically as the TiO_2 was consumed in electrolysis, more TiO_2 was shaken into the electrolyte until about 200 grams had been added during the electrolysis. The alloy was stirred and sampled. The titanium content was found to be about 33.2%. The anode current density was calculated to be about 4.8 amperes per square inch and the cathode current density about 8.5 amperes per square inch.

Alloys of this type were subsequently electrorefined using an electrolyte composition as described and claimed in my copending application Serial No. 109,443, filed August 10, 1949, and using the process and method described and claimed in my copending application Serial No. 496,286, filed March 23, 1955, and now abandoned. The metal produced was in excess of 99.9% pure.

The foregoing shows how titanium alloys can be easily and cheaply made from oxides of titanium. The invention may be applied similarly to the production of alloys of other metals that are difficult to produce and which are characterized by the following:

(1) They are multivalent metals.

(2) They are high melting metals.

(3) They react with atmospheric gases at high temperature.

(4) They are strongly electropositive metals.

(5) They are normally found in nature as oxygen compounds.

The metals which readily can be made by the invention are zirconium, hafnium, thorium and uranium.

In a typical cell similar in consrtuction to that described above except that a graphite crucible was used as the inner lining, about 6 pounds of $CaCl_2$—CaF_2 eutectic was fused. Dry HCl gas was passed through the cell and melt during and after fusion to prevent hydrolysis. A clear melt was obtained. The HCl was discontinued and argon gas passed over the melt instead. About 200 grams of precalcined CaO were added to the melt and after solution an alloy of Zr—Cu was added. The alloy fused and formed a layer of about 2" in thickness. The concentration of Zr in the cathode alloy was 43.8% by weight. An anode of graphite was immersed in the electrolyte solvent from above and about 200 grams of precalcined ZrO_2 were added to the bath. The bath was electrolyzed at about 1000° C. with an estimated cathode and anode current density slightly below 10 amperes and 5 amperes per square inch respectively. Additions of ZrO_2 in 25 gram quantities were made at frequent intervals approximating the rate of consumption of the ZrO_2 by the electrolysis. The electrolysis was continued for 12 hours. At the end of that time a sample of Zr–Cu alloy was found to contain 48.1% Zr by weight. In another experiment similarly conducted but in the absence of CaO

in substantial quantity, ZrO_2 could not be electrolyzed efficiently if at all.

A uranium-iron alloy was similarly deposited from UO_2 under an argon atmosphere. The solvent was composed of $CaCl_2$—CaF_2 eutectic, treated as above to which 5% by weight of CaO precalcined was added. The temperature was about 1000° C. The anode current density was estimated to be slightly below 5 amperes per square inch and the cathode current density somewhat below 20 amperes per square inch. The UO_2 was precalcined and added frequently at small intervals so as to maintain a 3 to 5% solute concentration. After electrolyzing for about 8 hours, the U concentration was raised from 86.6% by weight to 95.3% by weight.

Thorium was deposited in a similar fashion from precalcined ThO_2. The electrolyte solvent was

$$CaCl_2—CaF_2—CaO$$

The cathode at the start was molten copper at about 1150° C. The anode was graphite as above. Powdered ThO_2 was added to the bath periodically during the electrolysis so as to maintain a 2–3% ThO_2 concentration. The anode current density was estimated to be slightly below 5 amperes per square inch and the cathode current density somewhat below 20 amperes per square inch. The electrolysis was conducted under a dry purified argon atmosphere. The alloy was sampled after 4 hours of electrolysis and the Th content was found to be 3.8%. Subsequent samples were found to have 20.8% Th and 33.1% Th by weight.

It is understood that the invention is not limited to the details of procedure and equipment herein specifically 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 of producing a molten metallic alloy of a metal of the group titanium, zirconium and hafnium comprising providing a molten solvent consisting of cations more electropositive than said metal with respect to halogen and oxygen and at least one halogen of said cation and containing in addition to said halogen of said cation at least a few percent of the oxide of said cation to render the oxide of the metal soluble in the molten solvent, providing a solid anode and a liquid metallic cathode containing molten alloying metal, dissolving an effective amount of an oxide of the metal of said group in said solvent for reduction to the metal by the electrolytic action, electrolyzing said molten mixture between said solid anode and said liquid cathode and thereby depositing the metal of said group in said liquid cathode and forming said molten metallic alloy.

2. A process as set forth in claim 1 wherein said metal is titanium and said alloying metal is essentially nonvoltaile at about 1000° C. and at the temperature of electrolysis to produce a liquid alloy of titanium containing more than 5% of titanium.

3. A process as set forth in claim 1 wherein said metal is titanium and said molten metallic alloy containing titanium is cooled to a temperature above its melting point sufficiently to cause the precipitation of higher melting iron and silicon impurities and removing said impurities.

4. The process of claim 2 wherein said oxygen compounds are titanium oxides.

5. The process of claim 2 wherein said oxygen compounds are of the group consisting of titanium monoxide and titanium dioxide.

6. A process as set forth in claim 2 wherein the cathode solvent metal is of the group consisting of copper, zinc, tin, silver, iron and mixtures thereof.

7. A process as set forth in claim 2 wherein the temperature of the electrolyte is below about 1100° C.

8. A process as set forth in claim 2 wherein the anode current density is below about 10 amperes per square inch and the liquid cathode current density is between 5 and 50 amperes per square inch.

9. The process as set forth in claim 2 wherein the electrolyte composition comprises CaO 8–18 weight percent, CaF_2 10–22 weight percent, and the balance $CaCl_2$.

10. The process as set forth in claim 2, wherein the electrolyte composition comprises calcium oxide-calcium fluoride eutectic and up to 8% titanium oxides calculated as titanium dioxide.

11. The process of producing metallic alloys as set forth in claim 1 wherein the electrolyte solvent is calcium oxide and at least one of the group of calcium chloride and calcium fluoride.

12. The process as set forth in claim 11 wherein the calcium chloride is partially replaced by the fluorides of the group of magnesium fluoride, strontium fluoride and barium fluoride in an amount less than 25% by weight for operation of the electrolyte composition at temperatures in the range of 1500 to 1800° C.

References Cited in the file of this patent

UNITED STATES PATENTS

2,757,135	Gleave et al.	July 31, 1956
2,861,030	Slatin	Nov. 18, 1958