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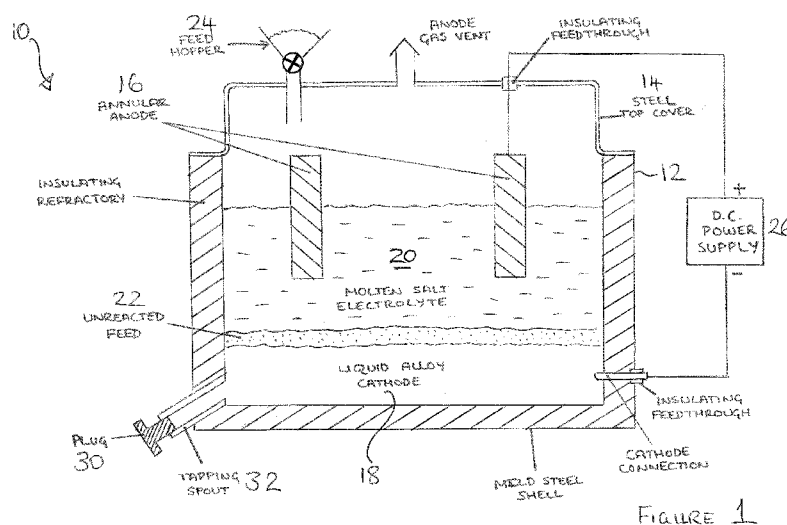


FIGURE 1

(57) Abstract: An electro-chemical metal winning process comprises: providing an electrolytic cell (10) comprising an anode (16), a cathode (18) and a salt electrolyte (20) which is molten at an operating temperature of the electrolytic cell (10); heating the electrolytic cell (10) to the operating temperature; adding a feed (22) to the molten salt electrolyte (20), the feed (22) comprising an oxide of a first metal (e.g. titanium dioxide) and a substance comprising a second metal (e.g. iron), with the first and second metals at least in part being capable of forming an alloy which has a melting point below the operating temperature of the electrolytic cell (10); applying a potential difference between the anode (16) and the cathode (18) of the electrolytic cell (10) to reduce the oxide of the first metal; and removing a molten alloy comprising the first and second metals from the electrolytic cell (10).



5 TITLE: METHODS AND APPARATUS FOR THE PRODUCTION OF METAL10 DESCRIPTION15 Field of Invention

The present application relates to an electro-chemical metal winning process, and particularly but not exclusively such a process for reducing an oxide of a Group IV metal, such as titanium.

20 Technical Background and Prior Art

Reactive metals such as titanium, zirconium and hafnium occur naturally as simple oxides, such as rutile, titanium oxide, TiO_2 for titanium and baddeleyite, Zr(Hf)O_2 for zirconium and hafnium or as more complex oxides such as ilmenite, FeTiO_3 for titanium and zircon, Zr(Hf)SiO_4 for zirconium and hafnium. These materials often occur in certain beach sands, from which they are recovered by taking advantage of their high density and individual electrical and magnetic properties. Once isolated, they are subjected to chemical processing to convert them into pure compounds of the respective metals. If the objective is preparation of the metals in pure form, or alloys of the metals, the usual intermediate compound is a halide or mixture of halides, usually chlorides, but in some processes, the intermediate compound is an oxide or mixture of oxides.

The metals are usually produced in individual batches by the Kroll process or by similar processes. In such processes the tetrachloride of the desired metal is introduced over a period of time to a steel retort provided with a liner of stainless steel and
5 containing molten magnesium to serve as reductant. The magnesium reacts with the tetrachloride of the desired metal to form its own chloride and the desired metal, which collects in the bottom part of the retort as a porous mass known as sponge. The halide magnesium chloride collects as a liquid layer above the sponge. The process is stopped by stopping the flow of the tetrachloride of the desired metal into the retort before all
10 of the reductant metal is consumed. The retort and its contents are then allowed to cool, whereupon the retort is cut open and the contents removed. The liner is peeled away from the reacted mass, and the upper layer of solidified magnesium chloride is parted from the lower layer, known as a "doughnut", comprising the sponge of the desired metal and the unreacted magnesium, along with some magnesium chloride.

15 The doughnuts from several batches are then placed in an apparatus called a still, which is welded closed and from which essentially all the air is removed. The part of the still containing the doughnuts is then heated, raising their temperature to a level at which the magnesium chloride and the residual magnesium evaporate, to condense in a
20 separate part of the still which is kept cool. When removal of the reductant metal and its halide from the doughnuts is complete, the still is allowed to cool and a mixture of argon with a little oxygen cautiously admitted, so that a thin, protective layer of oxide will form on the surface of the desired metal, in order to prevent its further oxidation when exposed to air.

25 The still is then cut open, and the doughnuts crushed so that the bulk of the sponge comprising them falls within a desired size range. Under-size material is rejected and the remainder subjected to examination for pieces of sponge showing evidence of contamination, which are also rejected.

30 The sponge is then compacted into cylindrical cakes; if the desired final product is an alloy, rather than the pure reactive metal, the alloy constituents are added in appropriate amounts to each cake of compacted sponge. The cakes are then assembled into an electrode by tack-welding them together in an electron-beam welder. The

electrodes, the diameter of which is determined by the diameter of the sponge cakes and length by the number of cakes welded together, are then converted to ingots by vacuum arc-melting in a suitable furnace. It is customary to repeat the arc-melting process at least three times, with the diameter of the resulting ingot increasing with
5 each repetition. This not only results in an ingot of desired diameter but also facilitates homogeneous distribution of the alloy constituents.

The ingots are now ready for fabrication. This usually starts with a forging step, in which the ingots are heated to redness and converted to billets in a hydraulic forge-
10 press. Subsequent fabrication may involve hot-and cold-rolling if plate and sheet are the desired product or extrusion and drawing if tubing, rod or wire are required. Cleaning, surface conditioning and pickling are required between the fabrication steps.

It will be seen from the preceding description that production of fabricated forms of
15 reactive metals, starting with the ore of the particular metal, is a complicated process comprising many steps. The overall process is both expensive and subject to considerable loss of material, since there is some production of waste at each step. Thus, if a way could be found to reduce the overall number of steps, it is likely that production costs would be reduced.

20 It is well known that continuous processes are usually less costly and more efficient than batch processes, and that among the least costly of reduction processes, other than those that use carbon as a reductant, are those that use electrolytic reduction. As carbon is an unsuitable reductant for production of pure reactive metals, interest has
25 focused on electrolysis as a possible replacement for the Kroll process in particular for the production of reactive metals.

It is also well known that certain metals, such as copper and nickel, are produced by electrolysis of aqueous solutions of their salts. This process is not applicable to
30 reactive metals, however, because attempts to electrolyse aqueous solutions of their compounds invariably result instead in electrolysis of the water of these solutions. It is thus usual to resort to electrolysis of molten salts of metals that cannot be electrowon from aqueous solutions of their compounds. Examples of metals that are produced in large quantities by electrolysis of molten salts include aluminium, magnesium and

sodium. In all of these examples, the electrolytic process is operated continuously, and the metal is formed in the molten state, and thus can be removed conveniently from the electrolysis cells, by tapping it in the molten state. It can then be cast into ingots, or, in the case of aluminium, continuously cast into slab or billet, which can be used as
5 feed for rolling-mills and other fabrication equipment. The ability to operate such processes contributes materially to the comparatively low cost of aluminium articles.

There have been several attempts to produce the reactive Group IV metals titanium, zirconium and hafnium by electrolysis of molten salts. In the proceedings of the
10 Second International Conference on the Peaceful Uses of Atomic Energy 4 (1958), 280-285, Ogarev et al disclosed a process for production of zirconium by electrolysis of a melt consisting of 25 to 30 % potassium hexafluorozirconate and 75 to 70 % of potassium chloride. The zirconium was deposited as solid dendrites on an inert electrode, from which it was periodically removed by scraping. It is known, however,
15 that emitted anode gases contain a considerable amount of chlorofluorocarbons, which now preclude its continuing use.

In addition, there have been numerous attempts to devise commercial processes for electro-winning of titanium and other Group IV metals (IUPAAC nomenclature 1985)
20 in the molten state, thereby affording the operation of a continuous or semi-continuous process. With the exception of the Ogarev process, all large-scale commercial processes for electrowinning of metals prepare the desired metal in the molten state, and it is therefore unsurprising that recent attempts to commercialise the electro-winning of titanium and similar metals have sought to do likewise

25 The high melting-point of titanium (near 1670°C) requires, however, that the process be operated above this temperature, which places very severe demands on the structural materials of the process equipment, and complicates the problem of preventing contamination of the newly prepared metal through reaction with
30 atmospheric gases and with containment materials.

There is therefore a need to provide a process for the electro-winning of Group IV metals that obviates operation of the process at such high temperature and, separately, to take advantage of the availability of a molten product to operate the process

continuously or semi-continuously. Fulfilling this need would also allow the desired metal to be prepared in its substantially pure state or in a desired intermediate state from the continuously produced molten product.

Statement of Invention

5

In accordance with one aspect of the present invention, there is provided an electro-chemical metal winning process, comprising: providing an electrolytic cell comprising an anode, a cathode and a salt electrolyte which is molten at an operating temperature of the electrolytic cell; heating the electrolytic cell to the operating temperature; adding
10 a feed to the molten salt electrolyte, the feed comprising an oxide of a first metal and a substance comprising a second metal, with the first and second metals being capable at least in part of forming an alloy which has a melting point below the operating temperature of the electrolytic cell; applying a potential difference between the anode and the cathode of the electrolytic cell to reduce the oxide of the first metal; and
15 removing a molten alloy comprising the first and second metals from the electrolytic cell.

The first metal may have a melting point in excess of the operating temperature of the electrolytic cell. Thus, forming the alloy with a melting point below the operating
20 temperature of the electrolytic cell allows for extraction of the first metal from the electrolytic cell in a molten state. The alloy may be a binary alloy, consisting of the first and second metals. Alternatively, alloy may comprise at least one other metal in addition to the first and second metals. Thus, the feed may comprise at least one other metal in addition to the first and second metals. The second metal and the at least one
25 other metal may be regarded as alloying elements.

The first metal may be selected from the group consisting of Group IV, V and VI metals. For example, the first metal may be a Group IV metal selected from the group consisting of titanium, zirconium and hafnium. In one particular embodiment, the first
30 metal may be titanium.

The second metal and/or the at least one other metal may be selected from the group consisting of iron, manganese, copper and zinc. The substance may comprise an oxide of the second metal, either alone (e.g. iron oxide) or in combination with another metal

such as the first metal (e.g. iron titanium oxide FeTiO_3). Alternatively or in addition,, the substance may comprise the second metal in elemental form (e.g. iron). Adding the second metal in elemental form (i.e. as a metal rather than as a compound comprising the metal, such as an oxide) avoids the need for it to be reduced before it is
5 incorporated into the alloy, thereby reducing the overall energy expended in the process.

If the first metal is titanium and the second metal is iron, the alloy may be ferrotitanium (e.g. approximately 70% titanium). Thus, the oxide of the first metal
10 may comprise titanium dioxide (e.g. rutile TiO_2), and the substance may comprise iron titanium oxide (e.g. ilmenite FeTiO_3).

The alloy may have a eutectic composition. In this way, the composition of the alloy may remain constant as the process proceeds.

15 The anode may be substantially inert. For example, the substantially inert anode may be non-carbon based, and may comprise a material selected from the group consisting of iridium and calcium ruthenate.

20 In the electrolytic cell, at least a part of the cathode may be molten at the operating temperature. The cathode, or molten part thereof, may have a composition substantially equivalent to the alloy. The cathode may be positioned in the electrolytic cell so that it remains in electrical contact with the molten alloy formed following reduction of the oxide of the first metal. The molten salt, together with any unreacted
25 feed in the electrolytic cell may float on the molten alloy. Thus, the cathode may be positioned at a lower depth in the electrolytic cell than the anode.

In the electrolytic cell, the salt electrolyte may comprise calcium chloride. The salt electrolyte may further comprise at least one of calcium fluoride and calcium oxide.

30 The process may further comprising controlling molar quantities of the first metal and second metal in the feed in proportion to a molar ratio of the first metal to the second metal in the alloy.

35 In the process, molten alloy may be removed from the electrolytic cell via a tap.

The process may further comprise separating the first metal from the second metal in the alloy once removed from the electrolytic cell. The first metal may be separated from the second metal by relying on a difference in vapour pressure between the first
5 metal and the second metal at a temperature in excess of the melting point of the first metal. The first metal may be separated from the second metal by electron-beam refining.

In accordance with another aspect of the present invention, there is provided a process
10 for the electro-winning of a reactive metal, such as a Group IV metal, which comprises preparing an alloy of the metal and causing it to be employed in the process as a cathode in conjunction with a molten salt electrolyte and an anode, wherein the alloy is present in the molten state, whereby the process may be operated on a continuous basis.

15 The metal to be electro-won is preferably one of titanium, zirconium and hafnium.

The anode is preferably inert or at least substantially inert. This does not, however, preclude the possibility of using a consumable graphite anode.

20 The basis of the invention is that the metal of alloy to be electro-won should be in a liquid state. Thus, in the process of the present invention, an alloying element(s) is used to reduce the liquidus temperature of the alloy below that of the reactive metal. This affords the possibility - with a carefully selected alloy composition - of its melting
25 point being substantially reduced so that the process can be operated in practice in the molten state.

From a practical point of view, the melting point (or liquidus point) of the selected alloy should ideally be substantially below that of the metal per se, for example at least
30 50°C, more preferably at least 250°C or even at least 500°C below that of the metal.

In general, selection of the alloy of the metal to be electro-won is based on achieving the lowest melting point of the alloy because the lower the operating temperature of the process, the better it is in terms of apparatus life and durability and lower energy
35 costs.

The alloy of the metal to be electro-won may advantageously have a eutectic (or near eutectic) alloy composition.

5 In the process, the metal may be electrowon continuously or semi-continuously. Continuously electro-won all may be cast into ingots. The alloy may be formed from a mixture of the oxide of the metal and the oxide of the alloying element(s). Alternatively or additionally, the alloy may be formed from a mixture of a complex oxide of the metal and of the alloying element(s). The alloy may contain additional
10 oxide of the metal.

The feed to the electro-winning process may be a mixture of the oxide of the reactive metal and the alloying element in its elemental form. Alternatively or additionally, the feed to the electro-winning process may be a mixture of the oxide of the reactive metal and an alloy of the reactive metal with the alloying element.

15 The reactive metal may be selected from elements of Group IV, V and VI of the Periodic Table, separately or in combinations. For example, the reactive metal may be titanium. The alloying element may be selected from the iron, copper, manganese and zinc. The alloying elements may be used in combination. The feed may comprise
20 titanium oxide, natural rutile, ilmenite, and mixtures thereof.

Electro-won alloy may be transferred, for example continuously or batch-wise, to a process for separating the reactive metal from the alloying element(s). The alloying element may be separated from the reactive metal by electron beam hearth-melting and
25 refining. The alloying element may be separated from the reactive metal in an electron-beam hearth-melting furnace in one or a succession of hearths.

Although the melting point of titanium is near 1670°C, and the melting points of other reactive metals such as zirconium and hafnium are still higher, the melting point of
30 these elements is often lowered when other elements or compounds are added to them. Thus, the melting point of ferrotitanium, the eutectic alloy of titanium containing about 68 % titanium by weight, is near 1078°C. Similarly, the system manganese-titanium exhibits a eutectic at 57.5 % titanium by weight, melting at 1175°C. In the system copper-titanium, alloys ranging from about 10 % to 58 % titanium by weight are

completely molten above about 1000°C and in the system zinc-titanium, alloys ranging up to near 60 % titanium by weight are molten above about 1012°C. The minimum liquidus temperature of some ternary alloys of titanium with pairs of elements, including those mentioned above, may be even lower than those liquidus temperatures
5 cited above.

Examples of the difference between the melting point of the metal and the eutectic temperature of the alloy quoted are as follows:

10 Ti-Fe 575°C; Ti-Mn 495°C; Zr-Fe 713°C; Zr-Mn 525°C; Hf-Fe 360°C; Hf-Mn 460°C.

Thus, an aspect of the invention is the ability to electro-win titanium in the form of an alloy that has a liquidus temperature below the melting point of pure titanium or other Group IV metal.

15

The invention is generally applicable to processes for the electrowinning of metals in the molten state, especially the metals of Group IV of the Periodic Table of Elements, comprising titanium, zirconium and hafnium and more particularly to titanium itself.

20 In particular, it has the potential to be used as a modification of the FFC - Cambridge process for electrolytic production of Group IV metals and alloys from their solid oxides, mixtures of oxides or complex oxide compounds without or with the admixture of simple oxides. The FFC process is described in Patent Publication WO 99/64638 in the name of Cambridge University Technical Services Limited. An example of the
25 process is production of the commercially useful product ferrotitanium from a mixture of rutile (TiO₂) and ilmenite, (FeTiO₃) and other precursors. To date, the FFC process has been designed to produce metals and alloys only in the solid state and on a batch (non-continuous) basis.

30 If the FFC process is modified in accordance with the invention, however, it could be operated at a temperature above the melting point of the desired product, thereby affording the product to be in a liquid or molten state and the process to be operated on a continuous basis.

The process of the invention will hereafter be described in relation to the electro-winning of titanium alloys without, however, implying that application of the process is restricted to those alloys alone.

5 The electrolyte originally proposed to operate the FFC was calcium chloride, an essential property of which is the accommodation in solution oxide ions, O^{2-} , which during electrolysis dissolved in the electrolyte at the cathode, accompanying the formation of the desired metal, and which diffused throughout the electrolyte, and were discharged at the anode as oxides of carbon in the case of a carbon anode or as
10 elemental oxygen in the case of an inert anode. Thus any electrolyte which is a liquid at the contemplated operating temperature and which will accommodate oxide ions in solution is a candidate for operation of the FFC process. Examples of suitable electrolytes besides calcium chloride, which melts near $772^{\circ}C$ but which exhibits an inconveniently high vapour-pressure as the melting-point of pure titanium is
15 approached, are calcium fluoride, which melts near $1425^{\circ}C$, and mixtures of calcium fluoride with calcium chloride, which may be used from the eutectic temperature near $645^{\circ}C$ at a composition near 15 weight % calcium fluoride, to temperatures approaching the melting-point of calcium fluoride, if the calcium chloride content must be decreased to avoid its higher vapour-pressure should operation at higher
20 temperatures be found desirable. Likewise, mixtures of calcium fluoride with calcium oxide are suitable for operation at temperatures ranging from the eutectic temperature near $1360^{\circ}C$ at a composition near 84.8 % calcium fluoride by weight to considerably higher temperatures, the optimal composition depending on the operating temperature chosen and on the desired oxide ion concentration, among other considerations. In the
25 molten state, both calcium chloride and calcium fluoride, and their mixtures, dissolve substantial amounts of calcium oxide, so that dissolution and conduction of oxide ions and their anodic discharge is assured in any molten mixture of the two halides.

The melting-point of titanium, near $1670^{\circ}C$, makes electrowinning of pure liquid
30 titanium a matter of some difficulty; but as stated above, there are numerous alloys that contain a high proportion of titanium and which are completely molten at temperatures considerably below $1670^{\circ}C$ and thus are candidates for the electrowinning of titanium in the molten state. Further, appropriate mixtures of calcium fluoride and calcium

chloride with small calcium oxide additions make available electrolytes capable of dissolving and conducting oxide ions at temperatures ranging from about 625°C to well above the melting-point of titanium near 1670°C. In practice, however, other considerations, such as durability of available structural materials, make operation at
5 temperatures approaching the melting-point of pure titanium rather difficult.

Brief Description of the Drawings

An embodiment of the invention, together with examples illustrating the principle of
10 the present invention, will now be described with reference to the accompanying Figures, in which:

Figure 1 is a schematic illustration of an electrolytic cell used in a process embodying the present invention; and

15 Figure 2 is a graph plotting Log (Vapour Pressure, mm) versus temperature for several metallic elements.

Detailed Description of the Drawings

20 Figure 1 is a schematic illustration of an electrolytic cell 10 used in an electro-chemical metal winning process embodying the present invention. The electrolytic cell 10 comprises a vessel 12 with a cover 14 which are made of steel and insulating refractory. The electrolytic cell 10 is heated to an operating temperature, which may be over 1000°. The electrolytic cell 10 further comprises an inert annular anode 16
25 (for example made of iridium), a cathode 18 (for example made of ferrotitanium) and a salt electrolyte 20 (for example comprising calcium chloride). The cathode 18 and the salt electrolyte 20 are both molten at the operating temperature of the electrolytic cell 10, with the molten salt 20 floating on the molten cathode 18. A feed 22 is added to the vessel 12 via a hopper 24. The feed 22 comprises an oxide of a first metal (for
30 example, titanium dioxide) and a substance comprising a second metal (for example, iron in elemental form). The first and second metals are selected to form (possibly in combination with at least one other metal present in the feed 22) an alloy with the same composition as the cathode 18. A potential difference is applied between the anode 16 and the cathode 18 using the D.C. supply 26. The oxide of the first metal is

reduced and, with the second metal, forms the alloy in the vessel 12 which, like the cathode 18, is molten at the operating temperature of the electrolytic cell 10. The newly formed alloy combines with the cathode 18, with excess product being removed from the vessel 12 by removing a plug 30 from tapping spout 32.

5

Example 1

Continuous electrowinning of molten alloys of titanium may be accomplished using the FFC process in a variety of ways. The first step is to choose the alloy desired, then to
10 prepare a sufficient amount of this alloy to serve as a liquid cathode with which to start the process. Thus, for example, appropriate amounts of titanium-42 % manganese by weight, or titanium-43 % copper by weight, or titanium-36 % zinc by weight are prepared. These alloys are completely liquid above about 1180°C, 1005°C and 1020°C respectively. They can be prepared from the pure metals, which are available
15 commercially, by any of a number of methods familiar to those of normal skill in the art.

The second step is to prepare the electrolyte, either calcium chloride or a mixture of calcium chloride and calcium fluoride, depending on the operating temperature chosen,
20 and with the optional addition of a small proportion, about 3 % by weight, of calcium oxide. Again, preparation of the appropriate electrolyte may be done using pure, dry calcium chloride, calcium fluoride and calcium oxide as starting materials, by means familiar to those of normal skill in the art. Again, the choice of calcium salts is not to be taken as implying that the invention described is restricted to the use of calcium
25 salts; in practice, the salts of other elements may be used, particularly those of magnesium, strontium and barium.

The third step is to charge the cathode alloy to the electrochemical cell, to add the electrolyte and to bring the cell and its contents to operating temperature.

30

The fourth step is to start adding the feed to the cell and to commence electrowinning of the chosen alloy, by application of an appropriate potential difference between the anode and cathode of the cell. In order for the cell to produce alloy of the chosen composition, the feed must be of the corresponding appropriate composition. It may

comprise either a mixture of titanium oxide with the oxide of the other metal of the chosen alloy, or a mixture of titanium oxide with the other metal of the chosen alloy already in the metallic state. In the latter case, less energy expenditure will be required, as there will be no requirement to reduce the oxide of the alloying element.

- 5 If the desired alloy is titanium-zinc, however, it would be necessary to add the zinc as the oxide, in admixture with titanium oxide, or as metal in an alloy with titanium, because the operating temperature would necessarily be above about 1020°C, the liquidus temperature of the titanium-zinc alloy in the composition range of interest, and this exceeds the boiling-point of elemental zinc at atmospheric pressure. Otherwise, the
- 10 feed to the cell may be made up of a compound oxide containing titanium oxide and the oxide of the other metal in the desired alloy. In such a case, the available compound oxide may not contain titanium oxide and the other oxide in the desired proportion; such would be the case if the objective were to produce ferrotitanium from ilmenite, FeTiO_3 , which contains a lower proportion of titanium than present in
- 15 commercial ferrotitanium. In such a case, the feed would comprise a mixture of ilmenite and rutile, or other form of titanium oxide, in amount sufficient to raise the proportion of titanium in the product to that desirable in ferrotitanium.

As the electrowinning of the chosen alloy proceeds, the amount of alloy in the cell will

20 increase and must be removed at intervals or continuously, by tapping or other means. It then may be cast into ingots if, as in the case of ferro-titanium for example, the alloy so produced is the required product. Otherwise, it is transferred in the molten state directly to the next stage of the process, in which the alloying element is separated from the titanium and recovered for reuse.

- 25 Alternatively, the alloy could be transferred to the next stage of the process as solid chunks obtained by break-up of the ingots produced by casting.

The fifth step of the process, when required, is the separation of the alloying element

30 from titanium.

This may usefully be accomplished by electron-beam refining. This process comprises melting of the alloy in a sequence of hearths connected in series, in which the alloy is maintained in the molten state by means of beams of electrons directed onto the surface

of the metal in the hearths. Separation of the alloy's components relies on the difference in vapour-pressure of titanium and the alloying element at temperatures above the melting-point of pure titanium. The alloying element is thus chosen with two properties in mind: the first is that it should form an alloy with titanium that melts at a
5 convenient temperature and contains a high proportion of titanium, and the second is that it should have a vapour-pressure considerably greater than that of titanium at temperatures above the melting-point of pure titanium.

Examples of elements that may be used to produce alloys from which titanium can be
10 produced by electron-beam refining may include iron, copper, manganese and zinc. Other elements may form suitable alloys with titanium and it is not the intention of this disclosure to exclude such elements. The vapour-pressures of iron, copper, manganese, zinc and titanium, in Torr or millimeters (mm) of mercury, taken from the compilation of Smithells, are plotted against temperature in Figure 2. It is clear from
15 this plot that titanium has the lowest vapour pressure at all temperatures, indicating that in alloys of titanium with the other elements, the other elements would tend to evaporate preferentially, leaving titanium behind. If the object is to separate titanium from a second element, the larger the difference in vapour pressure, the easier this will be. Thus iron is a less desirable alloying element if the object is to produce pure
20 titanium, and copper, manganese and zinc more desirable.

Approximate numerical values for the vapour pressure of titanium, iron, manganese, copper and zinc are given in Table 1 for temperatures ranging from 1675°C, just above the melting-point of titanium, to 2500°C. Table 2 gives the ratio of the vapour
25 pressure of the alloying metal to that of titanium at the same sequence of temperatures. Since the ease with which the alloying element can be separated from titanium is related to the ratio of the alloying element's vapour-pressure to that of titanium, and since the rate of removal will be proportional to the absolute value of the alloying element's vapour-pressure, it can be seen from the data of Table 1 and Table 2 that,
30 for all alloying elements, the efficiency of removal is likely to decrease with increasing temperature, because the values of the vapour-pressures differ less at higher temperatures, while the rate of removal will increase, as the absolute value of the alloying elements' vapour-pressures rise with temperature. It would further appear that

production of pure titanium from ferrotitanium would be the most difficult, and that the ease of production increases with the progression copper, manganese, zinc as alloying elements. It would appear the zinc offers the best prospects when all properties are considered: titanium-zinc alloys containing up to around 64 % by weight
5 titanium can be prepared with liquidus temperatures near 1020°C, and zinc appears to be the alloying element most easily removed, requiring also the lowest temperatures to accomplish removal. Addition of zinc to the electrowinning process must be done as either zinc oxide or as a titanium-zinc alloy, since the boiling-point of pure metallic zinc is below the liquidus temperature of the alloy. Next is manganese, which can be
10 used in alloys containing about 58 % titanium by weight, and from which it can be removed with apparent ease. It can be added to the electrowinning process as manganese oxide or as metallic manganese along with the titanium dioxide feed. The titanium-manganese alloy melts near 1180°C, and its preparation by electrowinning will entail use of higher temperatures than alloys of the other elements considered, and
15 may require an electrolyte with a fairly high proportion of calcium fluoride to accommodate the higher temperature. This is not expected to pose any special problem, however. Last is copper, used as an alloy containing about 57 % by weight titanium with a liquidus temperature near 1005°C. The copper would be the most difficult alloying element to remove, but its comparatively low electrowinning
20 temperature and the fact that it can be added with the titanium oxide feed, as either metal or oxide, like manganese, are attractive features.

The above disclosure has described how the process of electrowinning reactive metals, particularly titanium, for example by the FCC Cambridge process, can be made
25 continuous by providing that the reactive metal is formed as the major component of a liquid alloy, which can be removed from the electrolysis cell by tapping. It has also described how the reactive metal may be recovered from the alloy by electron-beam hearth-melting and refining, taking advantage of the different volatility of the reactive metal and the alloying element.

Table 1

Vapour Pressure, mm, for some Liquid Metals at Temperatures above the Melting-Point of Titanium

5 (Data from Smithells)

T, °C	Ti	Fe	Cu	Mn	Zn
1675	0.006	0.094	1.39	70.0	74500
1700	0.009	0.13	1.78	83.5	81100
1900	0.091	0.92	10.5	291	149000
2100	0.66	4.76	45.3	807	275000
2300	3.49	19.0	155	1878	370000
2500	14.53	61.7	439	3814	522000

Table 2

10 **Ratios of the Vapour Pressure of some Liquid Metals to that of Titanium at the same Temperature**

T, °C	P_{Fe}/P_{Ti}	P_{Cu}/P_{Ti}	P_{Mn}/P_{Ti}	$P_{Zn}/P_{Ti} \times 10^{-3}$
1675	15.5	227	11470	12200
1700	14.7	209	9820	9540
1900	10.0	115	3190	1630
2100	7.2	68.8	1230	372
2300	5.5	44.3	539	106
2500	4.2	30.2	263	36

(Only the values for zinc are to be multiplied by 1,000; those for Fe, Cu and Mn are as stated.)

CLAIMS:

1. An electro-chemical metal winning process, comprising:
providing an electrolytic cell comprising an anode, a cathode and a salt
5 electrolyte which is molten at an operating temperature of the electrolytic cell;
heating the electrolytic cell to the operating temperature;
adding a feed to the molten salt electrolyte, the feed comprising an oxide of a
first metal and a substance comprising a second metal, with the first and second metals
at least in part being capable of forming an alloy which has a melting point below the
10 operating temperature of the electrolytic cell;
applying a potential difference between the anode and the cathode of the
electrolytic cell to reduce the oxide of the first metal; and
removing a molten alloy comprising the first and second metals from the
electrolytic cell.
- 15 2. An electro-chemical metal winning process according to claim 1, wherein the
feed comprises at least one other metal in addition to the first and second metals, with
the molten alloy comprising the first and second metals and the at least one other
metal.
- 20 3. An electro-chemical metal winning process according to claim 1 or claim 2,
wherein the substance comprises an oxide of the second metal.
4. An electro-chemical metal winning process according to claim 1 or claim 2,
25 wherein the substance comprises the second metal in elemental form.
5. An electro-chemical metal winning process according to any one of the
preceding claims, wherein the first metal is selected from the group consisting of
Group IV, V and VI metals.
- 30 6. An electro-chemical metal winning process according to claim 5, wherein the
first metal is a Group IV metal selected from the group consisting of titanium,
zirconium and hafnium.

7. An electro-chemical metal winning process according to claim 6, wherein the first metal is titanium.
8. An electro-chemical metal winning process according to any one of the
5 preceding claims, wherein the second metal is selected from the group consisting of iron, manganese, copper and zinc.
9. An electro-chemical metal winning process according to claim 8 when dependent on claim 7, wherein the alloy is ferrotitanium.
- 10 10. An electro-chemical metal winning process according to claim 9, wherein the oxide of the first metal comprises titanium dioxide (e.g. rutile TiO_2).
11. An electro-chemical metal winning process according to claim 9 when
15 dependent on claim 3, wherein the substance comprises iron titanium oxide (e.g. ilmenite FeTiO_3).
12. An electro-chemical metal winning process according to any one of the preceding claims, in which the alloy has a eutectic composition.
- 20 13. An electro-chemical metal winning process according to any one of the preceding claims, wherein the anode is substantially inert.
14. An electro-chemical metal winning process according to claim 13, wherein the
25 substantially inert anode is non-carbon based.
15. An electro-chemical metal winning process according to claim 13 or claim 14, wherein the substantially inert anode comprises a material selected from the group consisting of iridium and calcium ruthenate.
- 30 16. An electro-chemical metal winning process according to any one of the preceding claims, wherein at least a part of the cathode is molten at the operating temperature.
- 35 17. An electro-chemical metal winning process according to claim 16, wherein the cathode, or molten part thereof, has a composition substantially equivalent to the

alloy.

18. An electro-chemical metal winning process according to any one of the preceding claims, wherein the salt electrolyte comprises calcium chloride.

5

19. An electro-chemical metal winning process according to claim 18, wherein the salt electrolyte further comprises at least one of calcium fluoride and calcium oxide.

20. An electro-chemical metal winning process according to any one of the
10 preceding claims, further comprising controlling molar quantities of the first metal and second metal in the feed in proportion to a molar ratio of the first metal to the second metal in the alloy.

21. An electro-chemical metal winning process according to any one of the
15 preceding claims, wherein molten alloy is removed from the electrolytic cell via a tap.

22. An electro-chemical metal winning process according to any one of the preceding claims, further comprising separating the first metal from the second metal in the alloy once removed from the electrolytic cell.

20

23. An electro-chemical metal winning process according to claim 22, wherein the first metal is separated from the second metal by relying on a difference in vapour pressure between the first metal and the second metal at a temperature in excess of the melting point of the first metal.

25

24. An electro-chemical metal winning process according to claim 22 or claim 23, wherein the first metal is separated from the second metal by electron-beam refining.

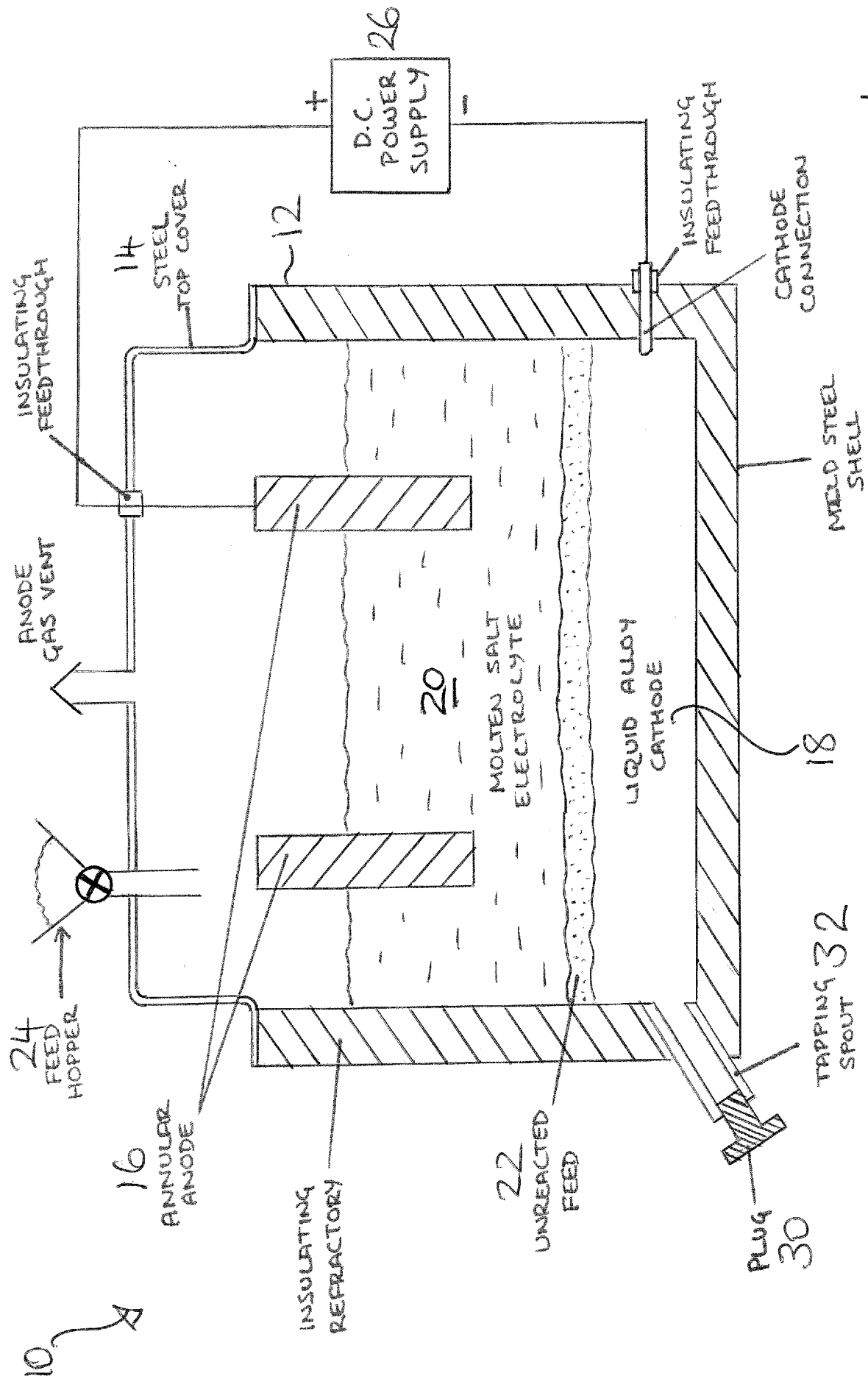


FIGURE 1

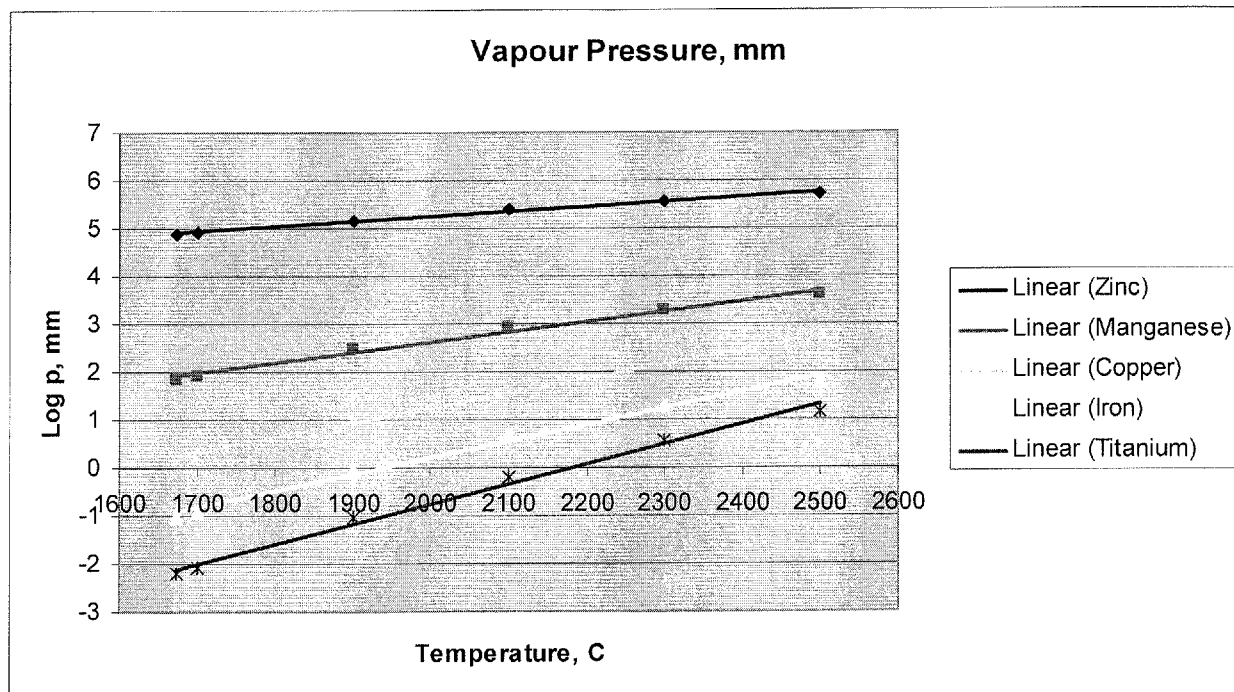


Figure 2 Log (Vapour Pressure, mm) versus temperature for several metallic elements