July 29, 1958 C. M. OLSON 2,845,386

PRODUCTION OF METALS

Filed March 16, 1954

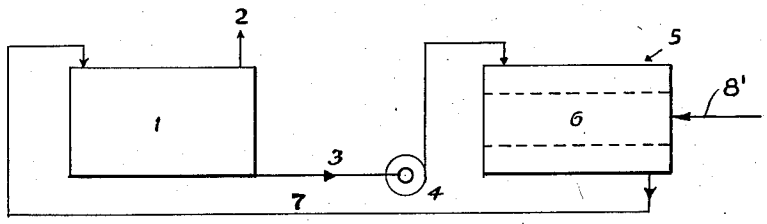

FIG. 1

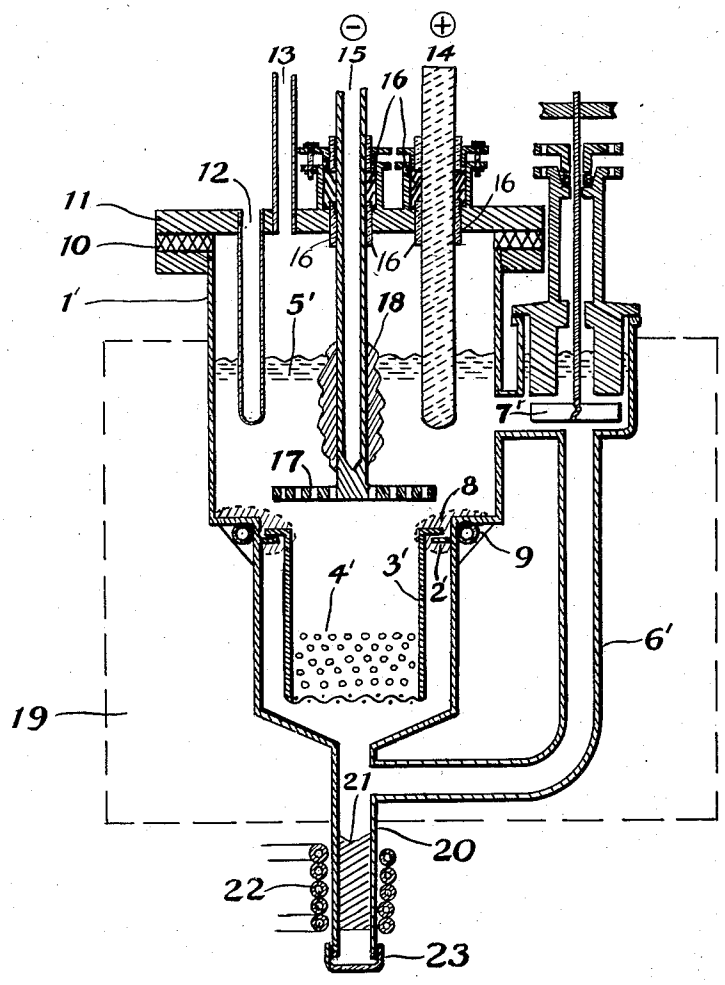

FIG. 2

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AGENT

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PRODUCTION OF METALS

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9 Claims. (Cl. 204—64)

This invention relates to the production and purification of metals whose oxides are unsuited for ordinary pyrometallurgical reduction processes. More particularly, it relates to the production of such metals by reduction of the metal oxide by a molten salt reducing agent.

In order to describe clearly the novelty and benefits of my invention the problems attending the production of pure metals will be analyzed using titanium metal as representative of the metals alluded to above and which are not obtained in satisfactory high purity by the usual pyrometallurgical furnacing methods. Pure titanium metal has become increasingly important because of its strength, low density, and superior resistance to corrosion. The large scale commercial exploitation of this metal is gravely hindered by the multiplicity of unit steps required in the existing commercial processes. One present process employs the reaction between titanium tetrachloride and magnesium. Both of these reactants require many process steps for their separate preparation and purification. The additional reduction steps involved in the preparation of titanium thus puts titanium in the class of expensive metals exploited only for very special uses. The many favorable properties possessed by titanium will be utilized only when the metal is produced at lower cost by a more economical process.

The above situation emphasizes the desirability of obtaining a more direct production process. One method to achieve this goal is the reduction of titanium oxide directly to the metal. Processes for the production of pure titanium oxide in terms of hundreds of tons per day are operating commercially. Prior methods for the reduction of titanium oxide by an active metal, i. e. alkali metals, alkaline earth metals and aluminum have not realized the goal of low cost metal. Of the above group of reductants, calcium is technologically preferable but strontium and barium are also operable by the methods of my invention. Calcium, strontium and barium have sufficient affinity for oxygen to permit the reduction to go to completion with the production of elemental titanium. Unfortunately in prior methods, it has been necessary to employ at least twice the stoichiometric quantity of calcium in order to obtain metal of sufficient purity for practical utility. The prior methods contemplated reaction vessels of the bomb type which utilized heavy structural design and difficult closure means. The use of metallic calcium as a reactant also leads to serious disadvantages because calcium metal (also barium and strontium) unlike sodium and magnesium is very expensive to prepare. It is not produced in the common type of electrolytic cell and even in the special equipment now used the efficiency is very poor with the result that the price of calcium is about ten times that of magnesium. In prior methods impurities, of which nitrogen is most deleterious, were introduced with the calcium in spite of attempts to scrape or otherwise mechanically remove the contaminants. The products obtained from these methods were mixed with the by-products of the

reaction. Hence a separation entailing the removal of calcium oxide by lixivation of the reaction mass in an acid was utilized.

One object of my invention is to overcome the disadvantages of present processes for the production of metals such as titanium, zirconium, vanadium, and chromium by utilizing a more easily obtainable raw material. A further object is to eliminate the many difficulties encountered in prior methods using calcium, strontium and/or barium as the reducing metal. A still further object is to provide a more economical process for the production of said metals having a minimum oxygen content. Further objects will become apparent from the following description of my invention.

These and other objects are accomplished by my invention relative to the production of metals selected from the group consisting of titanium, zirconium, vanadium and chromium by reduction of an oxide of said metals with a compound of an alkaline earth metal of the group calcium, barium, strontium, which comprises commingling said oxide with a molten salt reducing agent comprised of a halide of said alkaline earth having a deficiency of halogen from the normal dihalide, causing relative movement between the reactants to achieve intimate contact and dissolve the by-product alkaline earth oxide, and subsequently recovering the reduced metal from residual reaction components. A particular embodiment of my invention relates to a process for the preparation of titanium metal by reduction of an oxide of titanium with a separately prepared reducing agent involving calcium which comprises partially reducing molten calcium chloride, commingling the molten active calcium compound with said oxide, causing relative movement between the reacting phases, continuing the reduction until the oxygen is substantially all removed from said oxide and subsequently recovering titanium metal from residual reaction components.

The molten salt reducing agent mentioned above as an essential part of my process may be suitably prepared in an electrolytic cell which may be operated as an integral part of the reduction apparatus. The alkaline earth metal halides when subjected to electrolysis yield a halogen gas and the alkaline earth metal is collected around the cathode. This metal tends to dissolve into the molten salt up to about 15% of the salt composition and the nature of this solution has been discussed in a publication of the United States Atomic Energy Commission in 1950 entitled, "A Chemistry and Metallurgy of Miscellaneous Materials." Edited by L. L. Quill (McGraw-Hill Book Company, Inc.). While it is not definitely proven that a compound such as Ca_2Cl_2 exists, it seems absolutely certain that the metal dissolves in the salt phase on a molecular scale. These authors (see pages 11 and 12) lean to the view that a strong interaction between the metal ions of the salt and the metal molecules exist. In view of these considerations I am referring to the metallic reducing agent as a subhalide of an alkaline earth metal.

In the preferred embodiment of my invention wherein titanium metal is produced from oxide of titanium while employing calcium chloride as the molten salt, the molten salt is passed through an electrolytic cell prior to its contact with the titanium oxide being reduced. The flow through the cell should be from the anode zone to the cathode zone and thence to the zone wherein the oxygen is to be removed from the titanium. At the anode, oxygen is removed from the calcium chloride melt, while at the cathode free calcium is generated which becomes dissolved in the calcium chloride to give my reducing agent. The latter is passed on to contact with the metal oxide for removal of its oxygen and calcium oxide is

formed at this point. The latter while in solution in the calcium chloride is passed on to the cell and while surrounding the anode of the cell the oxygen content is removed as carbon monoxide accompanied by consumption of the carbon anode and thus the oxygen is removed from the system. The cyclic flow of the calcium chloride is continued until the oxygen has been removed from the metal oxide. It is thus seen that the reaction is carried out in an apparatus employing several zones wherein specific changes of the system are taking place as the removal of oxygen from the salt at the anode, the production of subchloride at the cathode and the removal of oxygen from the metal oxide in the reduction chamber proper. The molten salt as it leaves the latter contains calcium oxide, while the salt entering this zone is substantially free of oxygen and is laden with calcium which is molecularly dispersed in the molten salt.

Figure 1 is a flow diagram of my preferred process. Vessel **1** represents an electrolytic cell wherein the reduced alkaline earth metal salt is produced by electrolysis. This molten salt flows from vessel **1** to the reactor **5** through line **3** impelled by well known means **4**. The metal oxide, e. g., titanium oxide charged to the reactor via line **8'** is represented by **6**. The molten salt flows into intimate contact with the titanium oxide charged into reactor **5** and after reaction exits through line **7** to return to vessel **1**. In vessel **1** the oxygen, removed from the titanium oxide by the molten reducing agent and present therein as an oxide of the alkaline earth metal, is stripped from the said molten agent by electrolysis. This step produces the reduced calcium compound i. e., calcium molecularly dispersed in normal calcium chloride and carbon monoxide by the interaction of the oxygen with the carbon anode of the cell during electrolysis. As the electrolysis proceeds to complete removal of oxygen from the anolyte, chlorine in admixture with the oxide of carbon may be evolved along with the increase in the amount of the molecularly dispersed calcium within the molten salt.

Figure 2 is a section view of an apparatus whereby my invention may be carried into effect. The cylindrical iron reaction vessel **1'** is provided with a shelf **2'** upon which rests a cylindrical iron container **3'** provided with a perforated bottom. The charge of titanium oxide material to be reduced **4'** is contained in this basket. The charge of molten salt **5'** is contained in vessel **1'** and is circulated from the bottom up through line **6'** back into the upper portion of vessel **1'** by impeller **7'**.

Impeller **7'** is driven through a belt and pulley arrangement by a motor situated apart from the heated area; these are not shown in drawing. A seal of solidified salt **8** between vessel **1'** and container **3'** is obtained and maintained by cooling element **9**.

The lid **11** is bolted to vessel **1'** and has a gasket **10** of heat resistant material. Thermowell **12** of metal pipe, for temperature measurement in cell, extends through lid into the molten salt. Product gases leave the reaction vessel through vent pipe **13**. Carbon anodes **14** and iron cathode **15** are insulated from the apparatus by sleeves **16**. Electric power is supplied to these electrodes by well known means not shown in drawing. The iron cathode **15** consists of a water cooled upper section terminating in a perforated flat circular plate **17**. The cooled tube provides and maintains a frozen salt mass **18** which insulates this portion of the cathode from the anode region of the cell. The vessel **1'** is surrounded by a furnace **19**, extending slightly above the level of the molten salt. The molten salt may be drained from the apparatus by removing cap **23** from line **20**, turning off cooling water to coils **22**, and melting frozen salt seal **21**.

In practicing the method of my invention, a charge of titanium oxide to be reduced or crude metal to be refined is placed in the basket **3'**. This charge is preferably in the form of small particles generally not exceeding ⅜ of an inch in size. The charged basket **3'** is then placed in vessel **1'**. A charge of molten salt, preferably calcium chloride is heated to about 900° C. and then poured into vessel **1'** up to a level slightly above the impeller discharge pipe. Immediately after charging the vessel the furnace **19** is heated and brought up as rapidly as possible until the molten salt mass is about 850° C. as measured by a thermocouple in thermowell **12**. During this heating-up period, lid **11** is installed with the electrodes retracted above the salt level. As soon as the temperature indicates a molten state, the cooling water into **9** and **22** is turned on, the impeller **7'** is tested for freedom of movement, the electrodes **14** and **15** are immersed to the correct level and outlet **13** is connected to a noxious gas vent system. Then the impeller motor is turned on and electrolytic power supplied to the electrodes. Direct current having a voltage of from 25–35 volts is suitable for the process and optimum value will depend on apparatus design. The temperature of the molten salt is kept at about 850° C. by regulating the amount of heat supplied from the furnace. Electrolysis is continued until oxides of carbon are not detected in the gases given off from the cell. On completion of the run the electric power is turned off from the electrodes and stirring motor, the electrodes are retracted, the furnace heating source turned off and cooling water into **9** turned off. When the temperature of the molten salt decreases to about 800° C., the salt is drained from the vessel into an iron pot as described above. The titanium metal is protected by a coating of salt and the atmosphere which is maintained inert until the mass has cooled somewhat.

The basket is then removed from the vessel and the titanium metal product is then washed substantially free of calcium chloride by lixivation with water. The metal product is then discharged from the basket into a tray and dried in an oven to remove adherent water. The particulate metal product then can be treated by prior art means to obtain massive shapes or utilized as is for suitable applications.

Specific results using the above manner for the application of my invention are given in the following examples.

Example I

A quantity of pressed pellets, about ¼ inch in size, of pure TiO_2 were prepared in a pellet press and 1800 g. were charged to the basket of an apparatus as shown in Figure 2. The molten calcium chloride was added to the vessel until about 25 kg. was charged. The treatment proceeded as hereinabove described using a bath temperature of about 850° C. The electrolysis was run for approximately 8 hours until the evolution of oxides of carbon ceased. The apparatus was cooled as described above and the titanium metal extracted free of calcium chloride with water and dried at 120° C. The metal product analyzed 99.5+% Ti and .10% O_2. The metal after melting in a vacuum arc furnace was found to have a Vickers hardness number of 187.

Example II

The application of my invention to the removal of small amounts of oxygen from contaminated titanium metal is herein described. A charge of 3360 grams of titanium metal contaminated with 4% oxygen was placed in the basket of the apparatus as described, Figure 2. The titanium metal was in the form of small lumps, approximately ⅛ to ¼ of an inch in size. The charge of calcium chloride was prepared as before and the electrolysis operation carried out. After 3 hours the reaction was complete and the current was stopped. The product was washed and dried as before with a final weight of 3200 grams of titanium metal being obtained. This was analyzed to be 99.5+% Ti and .14% O_2. After melting a sample in a vacuum arc furnace the metal had a Vickers hardness number of 210.

The above examples serve to illustrate modes of ap-

plication of my invention and are not meant to limit the application of my invention thereby. Equivalent methods of operation of my invention may be more suitable on a larger scale. In this manner a separation of the electrolysis cell from the titanium oxide reduction section would allow one cell to serve a number of reduction units. The reduced calcium molten salt product being impelled from the electrolysis cell through a mass of titanium oxide held in a reduction unit and then the used molten salt returned back to the electrolysis cell for renewal of the reduced calcium content. My invention treats titanium oxygen compounds of varying ratios from titanium dioxide to low oxygen content titanium metal. A titanium alloy may be produced by the use of a titanium raw material such as metal titanates (example iron titanate). As a molten salt electrolyte, I prefer to use anhydrous calcium chloride, although other salt mixtures may be utilized, said mixture comprising a halide of calcium, barium and strontium either alone or admixed. The preferable temperature range for operation of my invention is from about 800 to 1000° C. depending upon the electrolyte used although the process may be carried out at a higher temperature, the limit depending upon equipment considerations and the volatility of reaction components. Many modifications in the electrolysis apparatus are possible to one skilled in this art but it suffices to say it is preferable to arrange the cell so that cathode products are held apart from the gases being evolved at the anodes in order that secondary reactions which defeat the purpose of electrolysis are prevented. Many modifications for the reduction vessel are also possible but herein also some principles are observed, in that it is necessary that adequate commingling of the titanium oxide and the reduced calcium molten salt take place. Also the calcium oxide which is produced must be removed from the metal product and this is achieved by relative movement of the two phases, the one solid and the other molten. The molten salt stream as it leaves the cathode compartment of the cell may be suitably forced downwardly through a bed of titanium oxide to be reduced in a continuous manner and passed through the bottom of the support for the titanium oxide at its trip back toward the anode compartment of the cell. Such a mode of operation provides that the metal oxide to be reduced is continually contacted with a flowing stream of the reducing salt and as the calcium oxide content increases it moves on toward the anode compartment of the cell for the release of the oxygen while the calcium content of the salt is increased simultaneously in the cathode compartment. It is thus seen that this method of operation provides a highly effective reducing agent which is substantially free of oxygen and that this high temperature reducing agent may be continuously replenished in a closed cyclic system.

The chemical principle involved in the series of reactions are not clearly understood but the following theory leads to a reasonable explanation. In the electrolysis of molten calcium chloride at a temperature near the melting point of calcium a cathode product is obtained which does not separate out elemental calcium but instead a dark colored substance appears to form immediately in the vicinity of the cathode. In a recent publication by Cubicotti, J. A. C. S. 71, 2149 (1949), he postulates that a compound Ca_2Cl_2 is formed with probably an ion of the Ca_2^{++} type i. e. one Ca^{++} ion bonded to or combined with each calcium atom. Thus he observed solutions having the equivalent of about 15% calcium dissolved in calcium chloride at 900° C. A molten-salt alkaline earth halide is thus obtained in which the alkaline earth metal ion is in a reduced state or in other words in which the salt has a deficiency of halogen from the normal dihalide. I have found that this reduced calcium will react with titanium oxide to produce titanium metal and calcium oxide. Calcium oxide is soluble to the extent of several percent in molten calcium chloride and when this molten solution is passed through an electrolytic cell fitted a carbon or graphite anode at the usual calcium cell conditions of temperature and voltage the anode is consumed and the oxygen content of the anolyte is reduced substantially to zero. The results with barium and strontium are substantially equivalent to that achieved with calcium.

The process which I have outlined by example depends on the removal of oxygen from titanium by reaction with a molten chloride of calcium which has often been referred to as the subchloride of calcium as well as solution of calcium in calcium chloride. This calcium compound is extremely high in its reducing action and is able to break the bond between titanium and oxygen. Calcium oxide and the normal calcium chloride are thereby formed simultaneously with the production of substantially oxygen-free titanium metal. The oxide of calcium is soluble in calcium chloride and when the titanium oxygen compound or the resulting titanium metal product is continuously treated with the molten calcium chloride, the calcium oxide is dissolved and withdrawn from the desired metal product, leaving the latter in substantially pure condition. The calcium oxide containing salt melt is recirculated to the cell for regeneration of the Ca_2Cl_2, or the subchloride if one chooses to use this nomenclature. The cell effluent comprising a mixture of Ca_2Cl_2 and $CaCl_2$ may be passed continuously through the cell and into contact with the titanium product undergoing reduction. The reaction is in reality the use of electric current in the removal of oxygen from titanium, using calcium chloride as a vehicle for carrying out the operation with transfer of the oxygen to the electrolytic cell as calcium oxide dissolved in calcium chloride. Further chemical reaction takes place at the carbon anode by the formation of carbon monoxide and the overall chemical reaction may be considered to be the removal of oxygen from metal oxide by carbon in a two step operation.

The use of pressed titanium oxide pellets was mentioned in Example I, but it is understood that one may produce substantially pure titanium metal by reducing an artificially prepared titanium oxide product such as is commercially produced in titanium pigment plants and generally referred to as calciner discharge. Such a product may consist of coarse lumps which work well in the herein-described process. Other commercial products may be substituted. Other metal oxides or mixtures of oxides will give the corresponding metals and alloys.

The subhalides of calcium, strontium, and barium have been designated as useful in the process for the removal of oxygen from titanium oxide or other oxygen containing compositions of titanium, zirconium, vanadium and chromium. It is desirable that the reduction be carried to the point where the product contains not more than .2% oxygen and preferably to less than 0.1% oxygen. It is known that the ductility varies with the oxygen content and the most desirable products have been found to analyze not more than .05% which can be reached by my novel process by continuing the contact of the titanium or other starting oxide material with the molten reducing agent or cell effluent until the oxygen content is thus depleted.

In the examples outlined above, I have shown an operation in which calcium chloride is circulated to a reactor containing a static bed of oxygen containing titanium composition and continuously displacing the chloride as its reducing power is spent by fresh cell effluent in a cyclic manner through the regenerating cell and the reduction zone. It is essential to the invention that there be relative movement between the molten salt reducing agent and the titanium oxide in order to remove the calcium oxide reaction product and to constantly expose the product undergoing reduction to the molten salt possessing the required reducing power. It is obvious that this relative movement between the titanium undergoing treatment and the molten salt may be carried out in other ways and

accordingly, the invention should be considered as covering such equivalent operations.

This series of reactions is utilized by my invention in a novel manner to produce titanium metal from easily obtainable and inexpensive raw materials. The extreme reactivity of calcium metal is obtained without the necessity of separately preparing and purifying the difficulty obtained reducing agent. The metal reduction reaction is carried out easily in a simple manner and results in a product having only water soluble material to be removed. This obviates the past disadvantages of calcium reduction wherein the calcium oxide was retained with the metal and extensive acid leaches were then required. Finally the product has the required low content of embrittling impurities and has desirable physical properties.

This application is a continuation-in-part of my copending application, Serial No. 193,813, filed November 3, 1950, now abandoned.

I claim as my invention:

1. A process for the production of a metal selected from the group consisting of titanium, zirconium and vanadium from an oxidic composition thereof which comprises circulating a molten halide salt composition of an alkaline earth metal selected from the group consisting of calcium, barium and strontium initially through an anode portion and a cathode portion of an electrolytic cell to partially reduce said salt and dissolve therein the free alkaline earth metal formed, thence passing the resulting molten salt mixture into a suitable chamber confining the oxidic composition, passing the molten salt effluent from the chamber to the anode portion of said cell where it is being subjected to electrolytic action with evolution of carbon monoxide by interaction of the oxygen content of the salt with a carbon anode, continuing the flow of salt composition into the cathode portion of the cell where the alkaline earth metal content of the salt composition is being restored, passing the cell effluent to the said chamber to complete the cyclic system, continuing the circulatory movement until carbon monoxide is no longer evolved at the anode and recovering the metal of high purity from the chamber.

2. A process for the production of titanium metal from an oxygen containing titanium composition which comprises circulating a molten halide compound of an alkaline earth metal selected from the group consisting of calcium, barium and strontium initially through an anode portion and a cathode portion of an electrolytic cell to partially reduce said salt and dissolve therein the free alkaline earth metal formed, thence passing the resulting molten salt mixture into a suitable chamber confining the said titanium composition, passing the molten salt effluent from the chamber to the anode portion of the cell where it is being subjected to electrolytic action with evolution of carbon monoxide by interaction of the oxygen content of the salt with a carbon anode, continuing the flow of salt composition into the cathode portion of the cell where the alkaline earth content of the salt composition is being restored, passing the cell effluent to the said chamber to complete the cyclic system, continuing the circulatory movement until carbon monoxide is no longer evolved at the anode and recovering the high purity titanium metal from the chamber.

3. A process for the production of titanium metal from an oxygen containing titanium composition which comprises circulating a molten calcium chloride salt composition initially through anode portion and a cathode portion of an electrolytic cell to partially reduce said chloride and dissolve therein the free calcium formed at the cathode thence passing the molten salt mixture into a suitable chamber confining the said titanium composition, passing the molten salt effluent from the chamber to the anode portion of said cell where it is being subjected to electrolytic action with evolution of carbon monoxide by interaction of the oxygen content of the salt and with a carbon anode, continuing the flow of salt composition into the cathode portion of the cell where the calcium content of the salt composition is being restored, passing the cell effluent to the said chamber to complete the cyclic system, continuing this circulatory movement until carbon monoxide is no longer evolved at the anode and recovering the titanium of high purity from the chamber.

4. A process for the removal of oxygen from titanium metal having oxygen intimately associated therewith which comprises circulating a molten halide salt composition of an alkaline earth metal selected from the group consisting of calcium, barium and strontium initially through an anode portion and a cathode portion of an electrolytic cell to partially reduce said salt and dissolve therein the free alkaline earth metal formed, thence passing the molten salt mixture into a suitable chamber confining the titanium metal from which oxygen is to be removed, passing the molten salt effluent from the chamber to the anode portion of the cell where it is being subjected to electrolytic action with evolution of carbon monoxide by interaction of the oxygen content of the salt with a carbon anode, continuing the flow of salt composition into the cathode portion of the cell where the alkaline earth content of the salt composition is being restored, passing the cell effluent to the said chamber to complete the cyclic system, continuing the circulatory movement until carbon monoxide is no longer evolved at the anode and recovering the titanium metal of high purity from the chamber.

5. A process for the removal of oxygen from titanium metal having oxygen intimately associated therewith which comprises circulating a molten calcium chloride salt composition initially through an anode portion and a cathode portion of an electrolytic cell to partially reduce said chloride and dissolve therein the free calcium formed, thence passing the molten salt mixture into a suitable chamber confining the titanium metal from which oxygen is to be removed, passing the molten salt effluent from the chamber to the anode portion of said cell where it is being subjected to electrolytic action with evolution of carbon monoxide by interaction of the oxygen content of the salt with a carbon anode, continuing the flow of salt composition into the cathode portion of the cell where the calcium content of the salt composition is being restored, passing the cell effluent to the said chamber to complete the cyclic system, continuing this circulatory movement until carbon monoxide is no longer evolved at the anode and recovering the titanium of high purity from the chamber.

6. A process for the production of zirconium metal from an oxygen containing zirconium composition which comprises circulating a molten halide compound of an alkaline earth metal selected from the group consisting of calcium, barium and strontium initially through an anode portion and a cathode portion of an electrolytic cell to partially reduce said salt and dissolve therein the free alkaline earth metal formed, thence passing the resulting molten salt mixture into a suitable chamber confining the said zirconium composition, passing the molten salt effluent from the chamber to the anode portion of the cell where it is being subjected to electrolytic action with evolution of carbon monoxide by interaction of the oxygen content of the salt with a carbon anode, continuing the flow of salt composition into the cathode portion of the cell where the alkaline earth content of the salt composition is being restored, passing the cell effluent to the said chamber to complete the cyclic system, continuing the circulatory movement until carbon monoxide is no longer evolved at the anode and recovering the high purity zirconium metal from the chamber.

7. A process for the production of vanadium metal from an oxygen containing vanadium composition which comprises circulating a molten halide compound of an alkaline earth metal selected from the group consisting of calcium, barium and strontium initially through an anode portion and a cathode portion of an electrolytic

cell to partially reduce said salt and dissolve therein the free alkaline earth metal formed, thence passing the resulting molten salt mixture into a suitable chamber confining the said vanadium composition, passing the molten salt effluent from the chamber to the anode portion of the cell where it is being subjected to electrolytic action with evolution of carbon monoxide by interaction of the oxygen content of the salt with a carbon anode, continuing the flow of salt composition into the cathode portion of the cell where the alkaline earth content of the salt composition is being restored, passing the cell effluent to the said chamber to complete the cyclic system, continuing the circulatory movement until carbon monoxide is no longer evolved at the anode and recovering the high purity vanadium metal from the chamber.

8. A process for the production of zirconium metal from an oxygen containing zirconium composition which comprises circulating a molten calcium chloride salt composition initially through anode portion and a cathode portion of an electrolytic cell to partially reduce said chloride and dissolve therein the free calcium formed at the cathode thence passing the molten salt mixture into a suitable chamber confining the said zirconium composition, passing the molten salt effluent from the chamber to the anode portion of said cell where it is being subjected to electrolytic action with evolution of carbon monoxide by interaction of the oxygen content of the salt and with a carbon anode, continuing the flow of salt composition into the cathode portion of the cell where the calcium content of the salt composition is being restored, passing the cell effluent to the said chamber to complete the cyclic system, continuing this circulatory movement until carbon monoxide is no longer evolved at the anode and recovering the zirconium of high purity from the chamber.

9. A process for the production of vanadium metal from an oxygen containing vanadium composition which comprises circulating a molten calcium chloride salt composition initially through anode portion and a cathode portion of an electrolytic cell to partially reduce said chloride and dissolve therein the free calcium formed at the cathode thence passing the molten salt mixture into a suitable chamber confining the said vanadium composition, passing the molten salt effluent from the chamber to the anode portion of said cell where it is being subjected to electrolytic action with evolution of carbon monoxide by interaction of the oxygen content of the salt and with a carbon anode, continuing the flow of salt composition into the cathode portion of the cell where the calcium content of the salt composition is being restored, passing the cell effluent to the said chamber to complete the cyclic system, continuing this circulatory movement until carbon monoxide is no longer evolved at the anode and recovering the vanadium of high purity from the chamber.

References Cited in the file of this patent

UNITED STATES PATENTS

808,066	Borchers et al.	Dec. 26, 1905
886,857	Price et al.	May 5, 1908
2,537,068	Lilliendahl et al.	Jan. 9, 1951

FOREIGN PATENTS

13,759	Great Britain	1904

OTHER REFERENCES

"Journal of the American Chemical Society," vol. 71 (1949), pages 2149 thru 2153, article by Cubicciotti et al.