MAGNESIOTHERMIC SOM PROCESS FOR PRODUCTION OF METALS

Inventor: Uday B. Pal, Dover, MA (US)

Correspondence Address:
WILMERHALE/BOston
60 STATE STREET
BOSTON, MA 02109 (US)

Appl. No.: 12/445,375
PCT Filed: Oct. 11, 2007
PCT No.: PCT/US2007/081144
§ 371 (c)(1), (2), (4) Date: Jun. 10, 2010

Publication Classification
Int. Cl.
C22B 5/12 (2006.01)
C25B 15/08 (2006.01)
C22B 5/18 (2006.01)

U.S. Cl. 205/763; 204/233

ABSTRACT
A process and apparatus are provided that allow metals including metals having stable oxide phases and metals with variable valencies to be extracted from their respective ores via an electrolytic process that is environmentally sound and economically viable. The process for lowering the oxidation state of a metal in a metal oxide comprises providing an electrolysis chamber housing a flux containing a highly reactive metal (e.g., Mg) and having a cathode, an anode, and a solid oxide membrane. A reducing chamber housing the metal oxide having a higher oxidation state to be reduced is provided. A solid oxide membrane (SOM) process is used to generate vapor of the highly reactive metal in the electrolysis chamber. The vapor of the highly reactive metal is directed to the reducing chamber, where the vapor of the highly reactive metal reacts with the metal oxide to be reduced to provide a metal or metal oxide having a lowest oxidation state and an oxide of the highly reactive metal (e.g., MgO). In certain embodiments, the oxide of the highly reactive metal is recycled back to the flux in the electrolysis chamber.
MAGNESIOthermic SOM Process for Production of Metals

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority under 35 U.S.C. §119(e) to U.S. Provisional Patent Application No. 60/850, 907, filed on Oct. 11, 2006, entitled Magnesiothermic SOM Process for Production of Metals, which is incorporated herein by reference in its entirety.

BACKGROUND

[0002] 1. Technical Field

[0003] This invention relates generally to the production of metals from metal compounds.

[0004] 2. Discussion of Related Art

[0005] Electrolysis is a common form of electrochemical refining. In an electrolysis process, the ore is dissolved in an aqueous or non-aqueous solution or melted in an electrolytic furnace. Once dissolved or melted, the ore dissociates into ionic species, forming an electrolyte. The metallic components of the ore to be extracted become positively charged cations. The remaining components, typically oxygen, carbonate, sulfate, chloride, or fluoride become negatively charged anions. To extract the metal from the ore, an electric potential is applied across two electrodes which are immersed in the electrolyte. The metallic ions are thereby attracted to the negatively charged cathode, where they combine with electrons and are deposited as metal. The oxygen, sulfate, carbonate, chloride or fluoride ions are driven to the positively charged anode and evolve as waste gases.

[0006] The formation of metals and oxygen from molten metal salts containing a metal oxide of interest has been described, in which a cathode is immersed in a molten-salt electrolyte (containing the metal oxide of interest) separated from an anode by a solid oxygen-ion-conducting yttria-stabilized zirconia (YSZ) solid electrolyte. High-energy-content metals such as magnesium, tantalum and titanium can be synthesized directly from their respective oxides (dissolved in fluoride-based molten salts). The electrolysis process is referred to as the solid-oxide-membrane (SOM) process because the electrolyte is a solid ceramic oxide.

[0007] In the SOM process, the YSZ electrolyte separates a chemically inert cathode and the molten salt electrolyte from the anode. The molten salt electrolyte has high ionic conductivity, high oxide solubility and low viscosity. When the applied electrical potential between the electrodes exceeds the dissociation potential of the oxide, oxygen ions are pumped out of the flux and through the YSZ membrane to the anode where they are oxidized. The process can be enhanced by the presence of forming gases at the anode to reduce the oxygen formed at the anode to carbon dioxide and water or by the use of a carbon-containing liquid metal anode (such as copper, tin, and silver). The molten salt electrolyte is referred to, interchangeably, as the flux or flux containing the metal oxide of interest.

[0008] While electrochemical processes are usually preferred compared to pyrometallurgical processes for quick energy efficient extraction and refining of metals, material selection for the electrolyte and process apparatus prevents broad application. They are usually restricted to the extraction of metals whose ores form very stable compounds. Driven by the ever-rising demand for metals and the increasing scarcity of available mineral resources, there exists a need for an energy efficient, environmentally benign process for the refining of ores.

SUMMARY

[0009] A process and apparatus is provided that allow metals including metals having stable oxide phases and metals with variable valencies, i.e., metals having more than one oxidation state, to be extracted from their respective ores via an electrolytic process that is environmentally sound and economically viable. The process employs a SOM process to reduce a first metal oxide source into a highly reactive metal; the highly reactive metal is then combined with a second metal oxide to reduce the oxidation state of the second metal oxide and regenerate the first metal oxide.

[0010] According to one embodiment, a method of lowering the oxidation state of a metal in a metal oxide comprises providing an electrolysis chamber housing a magnesium-oxide containing flux. The electrolysis chamber includes a cathode, an anode, and a solid oxide membrane. A reducing chamber housing the metal oxide to be reduced is provided. The metal oxide to be reduced has a first higher oxidation state. A solid oxide membrane (SOM) process is used to generate Mg vapor in the electrolysis chamber. Mg vapor is directed to the reducing chamber, where the Mg vapor reacts with the metal oxide to be reduced to provide a metal or metal oxide having a lowest oxidation state and magnesium oxide (MgO).

[0011] In another aspect of the invention, the metal or metal oxide having the lowest oxidation state is isolated from the MgO.

[0012] In another aspect of the invention, the MgO is returned to the electrolysis chamber via a conduit in communication with the electrolysis chamber and the reducing chamber.

[0013] In another aspect of the invention, the metal oxide having the lowest oxidation state is subjected to a further reducing step comprising a second SOM process to generate a metal.

[0014] In another aspect of the invention, the metal generated in the second SOM process is isolated.

[0015] In another aspect of the invention, the metal provided in the reducing chamber comprises dissolved oxygen and the metal provided in the reducing chamber is subjected to a second SOM process in which the dissolved oxygen is substantially removed.

[0016] In another aspect of the invention, the metal produced in the reducing chamber is used to provide a cathode in the second SOM process.

[0017] In another aspect of the invention, the metal oxide to be reduced comprises tantalum.

[0018] In another aspect of the invention, the metal oxide to be reduced comprises aluminum.

[0019] In another aspect of the invention, the metal oxide to be reduced comprises titanium.

[0020] In another aspect of the invention, a solid oxide membrane (SOM) process is used to generate Mg gas in the electrolysis chamber. The SOM process includes providing an anode encased in an oxygen-ion-conducting solid electrolyte.
[0021] In another aspect of the invention, the oxygen-ion-conducting solid electrolyte includes yttria-stabilized zirconia (YSZ).

[0022] In another aspect of the invention, the oxygen-ion-conducting solid electrolyte is substantially electrochemically stable when the SOM process is used to generate Mg vapor.

[0023] In another aspect of the invention, isolating the metal or metal oxide having the lowest oxidation state from the MgO includes a separation technique selected from the group consisting of gravimetric sedimentation and selective isolation using a process comprising dissolution of MgO.

[0024] According to another embodiment, a system for use in reducing the oxidation state of a metal in a metal oxide includes an electrolysis chamber. The electrolysis chamber includes a vessel for housing a flux having magnesium oxide (MgO) and an electrode having a solid oxide membrane (SOM). The electrolysis chamber is constructed and arranged to reduce MgO in the flux having MgO to produce magnesium vapor. The system includes a reduction chamber housing the metal oxide to be reduced where the metal oxide has a higher oxidation state. The reduction chamber is constructed and arranged to oxidize magnesium vapor to produce MgO and to reduce the metal oxide having the higher oxidation state to produce a metal or metal oxide having a lowest oxidation state. The system includes at least one conduit between the electrolysis chamber and the reduction chamber for delivering MgO produced in the reduction chamber to the electrolysis chamber.

[0025] In another aspect of the invention, the electrode having the SOM includes an anode encased in an oxygen-ion-conducting solid electrolyte.

[0026] In another aspect of the invention, the vessel for housing the flux comprises a steel cathode.

[0027] In another aspect of the invention, the oxygen-ion-conducting solid electrolyte comprises a yttria-stabilized zirconia (YSZ).

[0028] In another aspect of the invention, the oxygen-ion-conducting solid electrolyte is substantially electrochemically stable when the electrolysis chamber is used to reduce MgO in the flux having MgO to produce magnesium vapor.

[0029] In another aspect of the invention, separation apparatus for isolating the metal or metal oxide having the lowest oxidation state is provided where the separation apparatus selected from the group consisting of gravimetric sedimentation apparatus and MgO dissolution apparatus.

[0030] In another aspect of the invention, a second electrolysis chamber housing the metal oxide having the lowest oxidation state and having a SOM is provided where the second electrolysis chamber constructed and arranged to reduce at least a portion of the metal oxide having the lowest oxidation state to produce a metal.

[0031] In another aspect of the invention, a second electrolysis chamber housing the metal produced in the reduction chamber and having a SOM is provided where the metal produced in the reduction chamber comprises dissolved oxygen and wherein the second electrolysis chamber constructed and arranged to substantially remove the dissolved oxygen.

[0032] In another aspect of the invention, the second electrolysis chamber includes a cathode comprising the metal produced in the reduction chamber.

[0033] According to another embodiment, a method of lowering the oxidation state of a metal of a first metal oxide includes providing a first metal oxide and a second metal oxide, where the oxidation potential of the metal of the second metal oxide is higher than the oxidation potential of the metal of the first metal oxide. An electrolysis chamber housing a flux comprising the second metal oxide is provided. The electrolysis chamber includes a cathode, an anode, and a solid oxide membrane. A reducing chamber housing the first metal oxide to be reduced is provided, where the first metal oxide to be reduced has a high oxidation state. A solid oxide membrane (SOM) process is used at a temperature sufficient to generate a vapor of the metal of the second metal oxide in the electrolysis chamber. The vapor of the metal of the second metal oxide is directed to the reducing chamber, where the vapor react with the first metal oxide to provide the metal of the first metal oxide or a metal oxide of the first metal oxide having a low oxidation state. The second metal oxide is regenerated.

[0034] In another aspect of the invention, the second metal oxide comprises lithium.

[0035] In another aspect of the invention, the second metal oxide comprises calcium.

BRIEF DESCRIPTION OF THE DRAWING

[0036] The subject matter is described with reference to the figures that are described herein, which are presented for the purpose of illustration only and are not intended to be limiting of the invention.

[0037] FIG. 1 is a schematic representation of the solid oxide membrane cell with carbon-consuming liquid metal anodes used for electrolyzing metal oxides (MeO).

[0038] FIG. 2 is a schematic representation of a solid oxide membrane system for the production of tantalum using a magnesiothermic process according to one or more embodiments.

[0039] FIG. 3 is a schematic representation of a solid oxide membrane system for the production of titanium or lowering the oxidation state of titanium using a magnesiothermic process according to one or more embodiments.

[0040] FIG. 4 is a schematic representation of an experimental SOM setup for synthesizing titanium from TiO-containing flux, according to one or more embodiments.

DETAILED DESCRIPTION

[0041] In one or more embodiments, the SOM process is employed to generate magnesium (or other highly reactive metals such as lithium and calcium) from magnesium oxide (MgO) (or other respective oxides) and use the generated magnesium (or other highly reactive metal) to reduce the oxidation state of a metal or metal oxide. The process is environmentally friendly and energy efficient. By employing a multi-step process to synthesize metals electrical energy may be efficiently used to form metal compounds while significantly reducing environmentally degrading waste products that would otherwise be produced in alternate processes for the synthesis of metals from their oxides.

[0042] The energy efficiency of the present process is attributed, in part, to the combination of two steps, one in which a metal oxide is reduced to form highly reactive metal and another in which a metal compound of interest is reduced while the highly reactive metal is oxidized. In one or more embodiments, it takes significantly less electrical energy to reduce the highly reactive metal and use it to produce the desired metal (or metal compound) from the metal compound of interest than it does to reduce the metal compound of
interest to produce the desired metal (or metal compound) in an alternate, single-step process. This is because in the first step of the proposed multi-step process, the energy used to reduce the metal oxide to form the highly reactive metal is less than energy that would otherwise be used to directly reduce the metal of interest in a comparable single-step electrolysis process (such as a direct SOM electrolysis which is energy intensive). And, in the second step of the proposed multi-step process, no substantial amount of energy is needed to reduce the metal of interest because the highly reactive metal facili-
tates a chemical reaction. In sum, less energy is used to reduce a selected amount of the metal of interest than would be used in a comparable single-step electrolysis process. The multi-
step process is also environmentally friendly in that the present multi-step process generates environmentally benign waste products—whereas a comparable single-step elec-
trysis process for the production of the same amount of metal typically generates environmentally degrading prod-
ucts. In addition, the oxidized form of the highly reactive metal, generated in the second step of the process, is a reus-
able reagent and is recycled back into the first step of the process. In one or more embodiments, recycling MgO gen-
erated in the second step to produce Mg in the first phase significantly minimizes the generation of waste Mg. By mini-
mizing waste and energy consumption, the multi-step process has significant cost benefits.

[0043] The SOM process has been successfully employed to produce gaseous magnesium from its oxides. When the dissolved oxide in the flux is MgO, Mg(g) evolves at the inert cathode (steel) and is condensed in a separate chamber yielding a high-purity Mg metal. The SOM process is run at a temperature that forms magnesium vapor, which is then trans-
ferred to another chamber wherein oxides of a second metal (such as tantalum, titanium, aluminum, etc.) are reduced by the magnesium vapor. The reactive metals produced by the SOM process react with the oxides of the second metal to form a second metal species in a reduced oxidation state. Magnesium reverts back to its oxide by reducing the oxides of the second metal. The magnesium oxide that forms as a result of the chemical reduction of the oxides of tantalum, titanium, aluminum, etc., can be reused or recycled back into the SOM reactor to continue the process of magnesiothermic reduction of a new metal. The process of magnesiothermic reduction of metals from its oxide refers to the process by which an SOM process is employed to reduce magnesium oxide into a magnesium vapor which is then combined with a selected metal oxide to reduce the oxidation state of that selected metal oxide and regenerate the magnesium oxide.

[0044] The overall current needed for the multi-step magnesiothermic reduction is approximately that which is mea-
sured during the SOM electrolysis process whereby the mag-
nesium oxide is reduced to magnesium. The magnesium is then directed at chemically producing the less reactive metals (such as tantalum, titanium, aluminum, etc.) from their oxides while the more reactive magnesium metal is oxidized, without necessitating an additional current input. Magnesium metal is essentially cycled between its metallic and oxide states. Thus, the amount of energy used to generate the less reactive metal is less than would be required to generate it directly in a SOM process.

[0045] In the case of certain metal combinations, e.g., alu-
minum, it may be possible to directly obtain alloys, e.g., aluminum-magnesium alloy since magnesium and aluminum are mutually soluble.

[0046] The process employs the well proven SOM process for magnesium production. No new flux is needed. The metal produced can be easily separated from magnesium oxide by-product from many industrial processes. The magnesium oxide by-product can be fed back into the SOM reactor to continue the process. Constant supply of new magnesium oxide is not needed for the process. The overall process is energy efficient and environmentally sound.

[0047] Any conventional SOM process suitable for generating metallic Mg may be used. In one embodiment, the anode is a reactive anode. One type of anode that has been success-
fully used in SOM production of metallic Mg is a liquid metal anode having a high oxygen solubility, such as liquid copper, tin or silver. The liquid anode may contain a carbon source. At the liquid anode, the oxygen ions oxidize, dissolve in the liquid anode and react with the carbon forming CO(g)/CO2 (g). As an example, the experimental cell with liquid copper anode can be described as:

C/Cu(l)/Yttria Stabilized Zirconia (YSZ)/ionic flux with dis-
solved MgO/Steel.

[0048] The liquid copper (Cu(l)) electrode serves as a medium to transport oxygen from the YSZ/copper interface to graphite where it is oxidized. All three liquid metal anodes used (copper, tin and silver) have low vapor pressure, high oxygen solubility and high oxygen diffusivity in the tempera-
ture range of interest. An exemplary system for electrolyzing metals such as magnesium is shown in FIG. 1. When the dissolved oxide in the flux is MgO, Mg(g) evolves at the inert cathode (steel) and is condensed in a separate chamber yielding a high-purity Mg metal.

[0049] The anodic and cathodic reactions and the transport of various species are as shown in FIG. 1. FIG. 1 shows cell 100 having an inert cathode 135, YSZ electrolyte 120, liquid metal anode 110 and graphite layer 180. The rate of the slowest step determines the overall metal production rate in the cell. In order to increase the overall rate, the rate of the slowest step may be enhanced. The flux 130 is an electron blocker and ionic resistance of the flux 130 is typically much smaller than that of the YSZ membrane 120. Adequate stirring of the flux 130 and having sufficient MgO in the flux 130 ensures that transport in the flux is rapid and the magnesium is formed in the vapor state. The temperature is sufficiently high (≥1000°C.) so charge transfer reactions are rapid. Since the oxygen solubility and diffusivity are high in the liquid anode 110 and the anode is well stirred by the evolving CO(g)/CO2(g), oxygen transport in the liquid anode 110 is also rapid. The free energy change of carbon oxidation at these temperatures indicates that the carbon oxidation will occur readily and the product gas will mostly be CO(g). Quantitative analysis of all these steps is provided in a published article of the process, A. Roina, “HSC Thermodynamic Software”, Outokumpu Research Oy, Pori, Finland, fifth edition. 2003, the entirety of which is herein incorporated by reference. Other aspects of magnesium extraction from mag-
nesium oxide by the SOM process are described in a pub-
[0050] The individual half-cell reactions can be written as follows:
At the cathode: Mg²⁺ + 2e⁻ → Mg(g)
At the anode interface: C + O²⁻ → CO(g)
Overall cell reaction can be given as: Mg²⁺ + C + O²⁻ → Mg(g) + CO(g) or MgO + C → Mg(g) + CO(g)

[0051] Other electrolysis systems can be used, such as, for example, systems that employ inert anodes, such as cerments. Exemplary anodes include Ni—YSZ. A reforming gas can flow over the anode to improve the efficiency of the SOM process. See, e.g., “Emerging SOM Technology for the Green Synthesis of Metals from Oxides,” JOM, October 2001, which is incorporated by reference in its entirety.

[0052] In one or more embodiments, the SOM process is paired with a chemical reduction process for reducing the oxidation state of a second metal. In such embodiments, the magnesium vapor formed in the SOM process is directed from the SOM cell and into contact with a metal compound (e.g. a metal oxide to be reduced). The metal compound may be a metal oxide, metal ore, metal salt, or other form of metal-containing compound. The metal compound may be housed in a container or reaction chamber. In the second container, the metal compound is exposed to the magnesium vapor and undergoes a reduction reaction. Exemplary metal compounds include metal oxides. Most metal oxides that are less stable than MgO may be selected for reduction in this process. The metal oxide may be, for example, tantalum oxide, aluminum oxide, titanium oxide, or any other suitable transition metals. Comparatively reactive metals such as magnesium, once produced by the SOM process detailed above, can spontaneously chemically revert back to their corresponding oxide by reducing the oxides of comparatively less reactive metal compounds. Thus, for the present reduction step, the oxidation potential of the metal to be reduced will be lower than the oxidation potential of magnesium, since the magnesium will oxidize comparatively readily and contribute to the reduction of the metal compound to be reduced.

[0053] The reduction process performed in the second container may employ a metal oxide in a form that promotes chemical reaction with the magnesium. In some embodiments, the metal compound may be a powder. The powder may be processed to provide high surface area thereby ensuring that the Mg is able to penetrate the compound. By way of example the particle size should be sufficiently small to not interfere with the diffusion process. In one or more embodiments, the powder is stirred or agitated by introducing Mg vapor from a lower portion of the container so the Mg vapor permeates through the powder. The magnesium reduction may take place at any appropriate temperature. The temperature range for the reduction reaction stage is selected in accordance with the requirements for the particular metal oxide chosen, and higher than the vaporization temperature of Mg. Whereas the SOM electrolysis process is generally conducted in the temperature range 1050 C-1300 C in order to optimize energy consumption and exploit the high oxygen-ion conductivity of the SOM membrane, a lower temperature range will be typically used for the reduction process performed in the second container. For example, temperature ranges selected for performing the reduction process to reduce tantalum oxide Ta₂O₅ are described in Okabe, T. H. et al., Production of Tantalum Powder by Magnesiothermic Reduction of Feed Preform, Materials Transactions, Vol. 44, No. 12 (2003), which is herein incorporated by reference in its entirety. For other metals oxides such as titanium oxide and aluminum oxide, the reduction process will be performed at a suitable temperature as determined by the thermal balance for the reaction.

[0054] The process performed in the second container reduces the selected metal compound from a first higher valence-state to a second lower valence-state and oxidizes the magnesium vapor to form MgO. Separation of the metal oxide having a lower valence state from the MgO is then performed using any number of conventional separation techniques known in the art and detailed below. Then, the MgO is redirected to electrolysis chamber. The MgO is thus recycled back to the SOM process to supply the MgO in the flux that is used to create the Mg vapor.

[0055] In one or more embodiments, the second container is constructed of a material inert to the selected metal being produced (e.g. stainless steel). Conduits connect the electrolysis chamber (e.g. first container) and the reduction chamber (e.g. second container). A first conduit transports magnesium vapor from the electrolysis chamber to the reduction chamber. A second conduit transports MgO from the reduction chamber back to the electrolysis chamber. Details concerning the transport of Mg vapor are provided below.

[0056] A schematic of an exemplary system for tantalum production from its oxide is shown in FIG. 2. A SOM cell 200 was designed to form magnesium gas and direct the gaseous magnesium from the SOM cell into a second chamber 250 housing the metal oxide to be reduced 260.

[0057] The electrolytic cell 200 can utilize up to 33 cm² of the liquid anode area 210 and operate at anode current densities as high as 1 A/cm². The YSZ solid electrolyte 220 is in the form of a one-end-closed tube (1.9 cm OD, 1.42 cm ID, 20 cm long) and contains the liquid anode 210. A high-density graphite rod (0.6 cm OD) 215 is used as a consumable feed in the liquid anode 210. Liquid copper, tin or silver or other suitable materials can be used as anodes. The YSZ electrolyte tube is chemically stable when in contact with the liquid metal anodes, and the flux composition 230 is selected to be inert to the YSZ electrolyte. A steel crucible 235 holds the MgO-containing ionic flux 230. The steel crucible 235 also serves as the cathode. In order to protect the YSZ tube above the flux from the Mg vapor that is produced along the wall of the stainless steel container (cathode), an inert gas such as argon gas may be introduced into the chamber via input 290 as a carrier and diluent. The resultant argon-magnesium gas mixture passes out of the electrolysis chamber 200 at an exit port 240 to the lower condensation chamber 250 where a metal oxide 260 to be reduced is located. Nearly any metal oxide that is less stable than MgO may be reduced by this process. The exemplary embodiment shows Ta₂O₅ as the metal oxide 260 to be reduced. As noted above, the metal oxide may be, for example, tantalum oxide, aluminum oxide, titanium oxide, or any number of other compounds. Other embodiments are contemplated, for example, the cell may include a YSZ membrane and the anode and flux may be located on opposing sides of the membrane.

[0058] A constant potential is applied to the cell 200 during electrolysis. The applied electrical potential can be in the range of about 1-10V, or about 3-5V, and the cell can be operated at temperatures above the vaporization temperature of magnesium, e.g., over 1090 °C. In one or more embodiments, the cell is operated between 1100-1300 °C by running the cell at an applied electric potential of 3-4 V for an
extended period (5-10 hours) with continuous MgO and C feed and collecting a mixture of tantalum metal and metal oxide in the second chamber 250. The overall reaction occurring in the second chamber, whereby tantalum oxide is reduced and magnesium vapor is oxidized, can be written as follows:

$5\text{Mg(g)} + 2\text{Ta}_2\text{O}_5 = 5\text{MgO} + 2\text{Ta(g)}$.

[0059] The resulting reduced metal and MgO can be separated using conventional separations techniques, such as gravimetric sedimentation or selective dissolution of MgO. The resulting MgO byproduct is recycled back into the SOM reactor to be dissolved into the flux 230 to from which magnesium vapor is generated. The resulting tantalum metal is isolated and the argon gas is outputted 295. According to one or more embodiments, constant supply of new magnesium oxide is not needed to continue the process of magnesiothermic reduction of tantalum from its oxide. Magnesium metal may therefore be cycled between its metallic and oxide states.

[0060] As noted above, any number of metals compound having a lower oxidation potential than that of magnesium may be produced in the present process. In one embodiment, Ta$^5+$ is reduced to Ta$^5-$ in a single step, however the reduction product is always or necessarily a zero-valence metal. Reduction of multi-valence metal compounds poses unique challenges. Titanium compounds provide one such example. In one aspect, titanium is not an ideal candidate for the magnesiothermic SOM process for reduction of metals because certain titanium compounds will not be completely reduced to titanium metal. In another aspect, titanium is not an ideal candidate for a single-step SOM process due the presence of multi-valence oxides of titanium (Ti$^{2+}$, Ti$^{3+}$, and Ti$^{4+}$) in the flux that imparts electronic conductivity, leading to lower current efficiency and SOM degradation. More particularly, it has been found that during electrolysis the higher valence titanium ions undergo valence reductions at the cathode, causing intermediate valence states of titanium to exist, which imparts the electronic conductivity to the MgO-containing flux. These challenges may be overcome, and effective reduction of multi-valence metal compounds (such as titanium oxide) may be achieved, by a two-step process that combines a magnesiothermic SOM process with an additional SOM process. It is advantageous to isolate a single titanium oxide from a mixture of different valence oxides of titanium before producing the titanium metal though an additional process. By reducing the titanium oxide start up feed to its lowest oxidation state via reduction by Mg(g) generated from SOM electrolysis of magnesium oxide in the magnesiothermic SOM process, the problems of current efficiency and membrane degradation otherwise found in the single-step SOM process may be overcome.

[0061] By way of example, titanium (Ti$^{4+}$) in the form of Ti$O_2$ is reduced to yield a titanium having titanium of a lower valence state Ti$_2$O. In an exemplary process for the production of lower-oxidation state of titanium from its higher-oxidation state, an electrolytic cell and magnesium generation apparatus may be desired to form magnesium vapor. The magnesium vapor may be directed from the SOM cell into a second container housing the titanium oxide (Ti$O_2$) to be reduced. In the present embodiment, the magnesiothermic SOM process may be used to isolate titanium in its lowest oxidation state (Ti$O$) from one or more of its oxides. Then an additional SOM process may be used to isolate titanium metal from the titanium in its lowest oxide state (Ti$_2$O).

[0062] FIG. 3 illustrates apparatus for lowering the oxidation state of titanium in Ti$_2$O through SOM MgO electrolysis and then employing the product for continuous production of titanium metal. An electrolysis chamber 300 is used to generate magnesium vapor from MgO in a MgO-containing flux 330 through the SOM process described above. The apparatus for this electrolytic cell 300 is substantially the same as that described in the previous examples. A steel crucible 335 houses the MgO-containing flux 330 and provides a cathode. A liquid anode 310 is contained in a one-end closed tube comprising YSZ solid electrolyte 320. In one or more embodiments, the reduction chamber 350 is used to lower the oxidation state of titanium in TiO$_2$ 360 to create titanium oxide having the lowest oxidation state (TiO) according to the following reaction:

$5\text{Mg(g)} + \text{TiO}_2 = 5\text{MgO} + \text{Ti(g)}$.

In one or more embodiments, the reduction chamber 350 is used to lower the oxidation state of titanium in TiO$_2$ 360 to create titanium metal, according to the following reaction:

$5\text{Mg(g)} + 3\text{TiO}_2 = 5\text{MgO} + 3\text{Ti(g)}$,

where Ti$_2$O is Titanium metal (Ti$^0$) having dissolved oxygen.

[0063] Magnesium vapor generated in the electrolysis chamber is transported to the reduction chamber via a conduit 340. As described above, in one aspect, argon gas is introduced as a carrier gas and diluent and thus a magnesium-argon gas mixture passes through the conduit 340 and into the reduction chamber 350. Sufficient amounts of argon gas are introduced to dilute the Mg vapor and ensure it does not damage the YSZ membrane. Sufficient dilution is particularly important at higher operating temperatures. Titanium oxide of a high-valence state (TiO$_2$) is housed in the reduction chamber 350 and exposed to the magnesium vapor. In one aspect, the titanium oxide (TiO$_2$) is initially in powder form to increase surface area and facilitate diffusion. The chemical process produces MgO and titanium oxide of the lowest oxidation state (TiO) or titanium metal with dissolved oxygen (Ti$_2$O).

[0064] The resultant mixture of titanium oxide having the lowest oxidation state or titanium metal and MgO collects in the reduction chamber 350. The reduced titanium oxide and MgO can be separated using conventional techniques such as gravimetric sedimentation or selective dissolution of MgO. The inert carrier gas—in the present embodiment, argon gas—is removed from the reduction chamber while the magnesium oxide is cycled back to the electrolysis chamber 300. As described above, the MgO is supplied to the flux 330 in the SOM reactor 300 to continue the process. The titanium oxide having the lowest oxidation state (TiO) or titanium metal having dissolved oxygen (Ti$_2$O) may then be supplied to additional apparatus for the synthesis of titanium.

[0065] One example of apparatus for the synthesis of titanium metal is shown in FIG. 4. In one or more embodiments, the apparatus may be a SOM reactor 400 for the synthesis of titanium metal from titanium oxide having the lowest oxidation state (TiO) using the SOM process. The SOM reactor 400 includes a steel crucible 435 housing a TiO-containing flux 430, a cathode (Ti) and a molybdenum/carbon anode having a YSZ membrane casing 420 and liquid tin 410 inside the YSZ membrane casing. The SOM apparatus 400 also includes a steel secondary cathode tube for the continuous addition of TiO 475 and an aluminum bismuth end cap 470. In this example, the TiO in the flux is reduced to provide titanium metal. In one or more embodiments, the additional apparatus may be a
SOM reactor for the synthesis of titanium metal from titanium metal having dissolved oxygen (TiO). In this example, the (TiO) serves as the cathode in the SOM electrolysis chamber (having a YSZ membrane). Through the SOM process, the soluble oxygen is removed to produce titanium metal. Other examples of apparatus for the synthesis of titanium from TiO-containing flux or from TiO are possible and may be envisioned.

[0066] While the present method for production of metals describes an SOM process using magnesium, other suitable metals (such as lithium, calcium, etc.) may be used. The electrolysis step, reduction step, and corresponding apparatus (e.g., solid oxide membrane) may be selected by a person of ordinary skill in the art, in accordance with the requirements for the alternate metal. Other examples of SOM processes for the production of metals that are consistent with the central aspects of the present disclosure may also be envisioned by a person of ordinary skill in the art.

[0067] As will be apparent to one of ordinary skill in the art from reading this disclosure, the present invention can be embodied in forms other than those specifically disclosed above. The particular embodiments described above are, therefore, to be considered as illustrative and not restrictive. In addition, the invention includes each individual feature, material and method described herein, and any combination of two or more such features, materials or methods that are not mutually inconsistent.

What is claimed is:
1. A method of lowering the oxidation state of a metal in an oxide comprising:
   - providing an electrolysis chamber housing a magnesia-oxide containing flux, the electrolysis chamber comprising a cathode, an anode, and a solid oxide membrane;
   - providing a reducing chamber housing the metal oxide to be reduced, the metal oxide to be reduced having a higher oxidation state;
   - using a solid oxide membrane (SOM) process to generate Mg vapor in the electrolysis chamber;
   - directing the Mg vapor to the reducing chamber, wherein the Mg vapor reacts with the metal oxide to be reduced to provide a metal or metal oxide having a lower oxidation state and magnesium oxide (MgO).
2. The method of claim 1, comprising isolating the metal or metal oxide having the lowest oxidation state from the MgO.
3. The method of claim 2, comprising returning the MgO to the electrolysis chamber via a conduit in communication with the electrolysis chamber and the reducing chamber.
4. The method of claim 1, comprising subjecting the metal oxide having the lowest oxidation state to a further reducing step comprising a second SOM process to generate a metal.
5. The method of claim 4, comprising isolating the metal generated in the second SOM process.
6. The method of claim 1, wherein the metal provided in the reducing chamber comprises dissolved oxygen and wherein the metal provided in the reducing chamber is subjected to a second SOM process wherein the dissolved oxygen is substantially removed.
7. The method of claim 6, comprising using the metal produced in the reducing chamber to provide a cathode in the second SOM process.
8. The method of claim 1, wherein the metal oxide to be reduced comprises tantalum.
9. The method of claim 1, wherein the metal oxide to be reduced comprises aluminum.
10. The method of claim 1, wherein the metal oxide to be reduced comprises titanium.
11. The method of claim 1, wherein using a solid oxide membrane (SOM) process to generate Mg gas in the electrolysis chamber includes providing an anode encased in an oxygen-ion-conducting solid electrolyte.
12. The method of claim 11, wherein the oxygen-ion-conducting solid electrolyte comprises ytria-stabilized zirconia (YSZ).
13. The method of claim 11, wherein the oxygen-ion-conducting solid electrolyte is substantially electrochemically stable when the SOM process is used to generate Mg vapor.
14. The method of claim 1, wherein isolating the metal or metal oxide having the lowest oxidation state from the MgO comprises a separation technique selected from the group consisting of gravimetric sedimentation and selective isolation using a process comprising dissolution of MgO.
15. A system for use in reducing the oxidation state of a metal in a metal oxide, comprising:
   - an electrolysis chamber including a vessel for housing a flux having magnesium oxide (MgO) and an electrode having a solid oxide membrane (SOM) in the flux having MgO to produce magnesium vapor;
   - a reduction chamber housing the metal oxide to be reduced, the metal oxide having a higher oxidation state, the reduction chamber constructed and arranged to oxidize magnesium vapor to produce MgO and to reduce the metal oxide having the higher oxidation state to produce a metal or metal oxide having a lowest oxidation state; and
   - at least one conduit between the electrolysis chamber and the reduction chamber for delivering MgO produced in the reduction chamber to the electrolysis chamber.
16. The system of claim 15, wherein the electrode having the SOM comprises an anode encased in an oxygen-ion-conducting solid electrolyte.
17. The system of claim 16, wherein the vessel for housing the flux comprises a steel cathode.
18. The system of claim 16, wherein the oxygen-ion-conducting solid electrolyte comprises ytria-stabilized zirconia (YSZ).
19. The system of claim 18, wherein the oxygen-ion-conducting solid electrolyte is substantially electrochemically stable when the electrolysis chamber is used to reduce MgO in the flux having MgO to produce magnesium vapor.
20. The system of claim 15, comprising separation apparatus for isolating the metal or metal oxide having the lowest oxidation state, the separation apparatus selected from the group consisting of gravimetric sedimentation apparatus and MgO dissolution apparatus.
21. The system of claim 20, comprising a second electrolysis chamber housing the metal oxide having the lowest oxidation state and having a SOM, the second electrolysis chamber constructed and arranged to reduce at least a portion of the metal oxide having the lowest oxidation state to produce a metal.
22. The system of claim 20, comprising a second electrolysis chamber housing the metal produced in the reduction chamber and having a SOM, wherein the metal produced in the reduction chamber comprises dissolved oxygen and wherein the second electrolysis chamber constructed and arranged to substantially remove the dissolved oxygen.
23. The system of claim 22, wherein the second electrolysis chamber includes a cathode comprising the metal produced in the reduction chamber.

24. The system of claim 15, wherein the metal oxide to be reduced comprises tantalum.

25. The system of claim 15, wherein the metal oxide to be reduced comprises aluminum.

26. The system of claim 15, wherein the metal oxide to be reduced comprises titanium.

27. A method of lowering the oxidation state of a metal of a first metal oxide comprising:

providing a first metal oxide and a second metal oxide, wherein the oxidation potential of the metal of the second metal oxide is higher than the oxidation potential of the metal of the first metal oxide;

providing an electrolysis chamber housing a flux comprising the second metal oxide, the electrolysis chamber comprising a cathode, an anode, and a solid oxide membrane;

providing a reducing chamber housing the first metal oxide to be reduced, the first metal oxide to be reduced having a high oxidation state;

using a solid oxide membrane (SOM) process at a temperature sufficient to generate a vapor of the metal of the second metal oxide in the electrolysis chamber;

directing the vapor of the metal of the second metal oxide to the reducing chamber, wherein said vapor reacts with the first metal oxide to provide the metal of the first metal oxide or a metal oxide of the first metal oxide having a low oxidation state; and

regenerating the second metal oxide.

28. The method of claim 27, wherein the second metal oxide comprises lithium.

29. The method of claim 27, wherein the second metal oxide comprises calcium.