

Emerging SOM Technology for the Green Synthesis of Metals from Oxides

Uday B. Pal, David E. Woolley, and George B. Kenney

This article is intended to demonstrate that the environmentally sound solid-oxide-membrane (SOM) technology is an emerging process that can efficiently synthesize metals and alloys directly from their oxide ores with minimum feed-material preparation and produce oxygen gas or water vapor as the major byproduct. To demonstrate the proof-of-concept and economic viability, this article will focus on the synthesis of magnesium metal. The current production methods for magnesium are either metallothermic reduction (magnetherm process) at high temperatures (1,600°C) involving expensive metal reductant (FeSi) or electrolysis from a halide electrolyte bath that requires extensive and expensive feed-material preparation. Both these techniques are also energy intensive, have low yield and generate large quantities of waste reaction products harmful to the environment. In the SOM process, the oxide reduction is electrochemical and has efficiencies close to 100%. It will be shown that unlike the current metallothermic and the electrolytic processes, the SOM process has the potential to be more economic and less energy intensive, and its process products are environmentally benign. The results reported in this article for magnesium synthesis are also applicable for environmentally sound production of other high-energy-content metals that are produced by less-efficient techniques that result in environmentally harmful reaction products. To date, in addition to magnesium, the SOM process has been used to produce silicon, chromium, and iron, along with alloys from their respective oxides dissolved in appropriate solvents.

INTRODUCTION

The solid-oxide membrane (SOM) process is a generic environmentally sound, energy-efficient alternative for oxide electrolysis utilizing an inert-oxygen-ion-conducting membrane-based anode. The process can be an attractive alternative process for synthesizing high-energy-content metals such as aluminum, magnesium, titanium, high-purity silicon, chromium, and value-added ferroalloys. To demonstrate the proof-of-concept and economic viability of the SOM process, this article will mainly focus on the synthesis of magnesium metal.

The fundamental configuration of the SOM process, as shown in Figure 1, consists of a solid-oxygen-ion-conducting stabilized-zirconia electrolyte (membrane) that separates the anode from the melt containing the oxide of the metal to

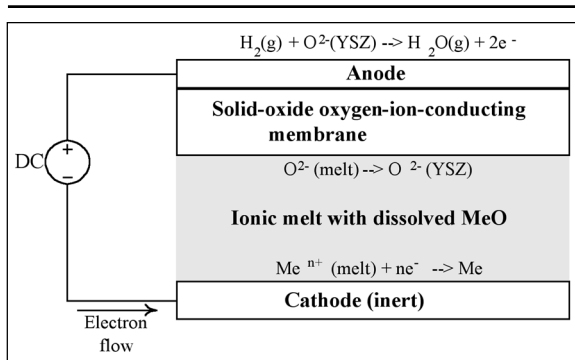


Figure 1. The SOM process for metal (Me) production by direction reduction of its oxide.

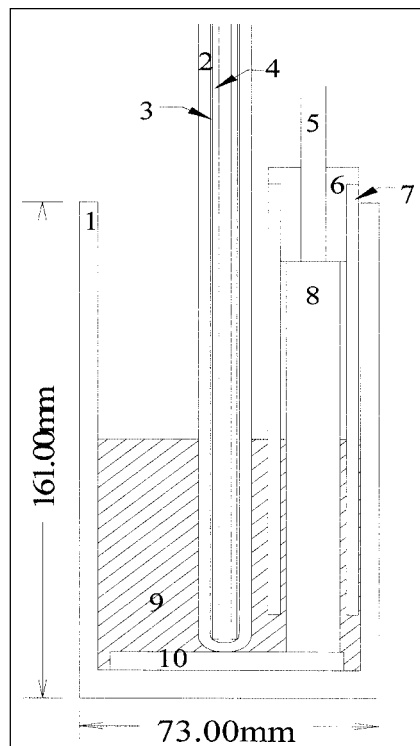


Figure 2. The apparatus used in proof-of-concept experiments with SOM technology for magnesium production: 1—graphite crucible, 2—YSZ tube, 3—Ni-YSZ anode, 4—stainless-steel tube, 5—steel rod, 6—graphite plug, 7—MgO tube, 8—graphite cathode, 9—MgCl₂-NdCl₃-MgO melt, 10—MgO disc.

be reduced. If the membrane is inert in contact with the melt, then it can be viewed as part of an inert-anode structure. An inert cathode is placed in the melt. When the applied electric potential between the anode and the cathode exceeds the dissociation potential of the oxide to be reduced, the desired metal cations are reduced at the cathode, and the oxygen ions migrate through the membrane and are oxidized at the anode. The applied electric potential between the electrodes can be increased as long as the potential at the melt-zirconia interface does not exceed the dissociation potential of the solid zirconia and undesired oxides are not reduced at the cathode. This allows for larger potentials to be applied between the electrodes in order to increase the

rate of production of the desired metal. The full benefit of the SOM process can be realized if the process is conducted at temperatures between 1,200–1,400°C.^{1,2} This is done to minimize the ohmic resistance drop across the stabilized zirconia membrane and the mass transfer resistance in the melt, and to obtain high current density of 1 A/cm² or greater. At these temperatures, the process efficiency can be further increased by directly reforming hydrocarbon fuel over the anode. It may be noted that several attempts have been made at employing the solid-oxygen-ion-conducting membrane as part of an inert anode at temperatures below 1,000°C. However, these efforts have not been successful in developing a commercial process^{3–6} mainly because sufficiently high current densities could not be obtained through the membrane.

The SOM process is continuous and easily amenable to scaleup. This article will highlight the important research issues involved in this process: the purity of the metal produced, the stability of the zirconia membrane in the selected flux, volatility of the selected flux, and the Faradaic efficiency of the process.

PROOF-OF-CONCEPT RESULTS

For the proof-of-concept experiments with magnesium, the solvent selected to dissolve the magnesium oxide was based

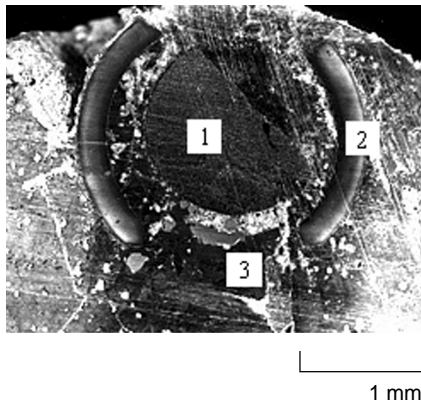
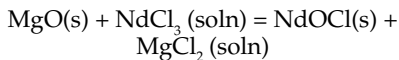


Figure 3. A cross-section of cathode near contact with MgO disc: 1—graphite cathode, 2—MgO tube, 3—magnesium globules. Magnesium globules are found on the side of the cathode nearest the anode.

on the $\text{MgCl}_2\text{-NdCl}_3\text{-MgO}$ system reported earlier by Sharma.^{7,8} However, in the experiments conducted by Sharma, a solid-oxide oxygen-ion-conducting membrane was not used and, as a result, oxygen as well as chlorine gases were generated at the anode when current density exceeded 100 mA cm^{-2} . Furthermore, molten tin was used as a cathode and primarily Sn-Nd alloys were produced instead of pure magnesium.

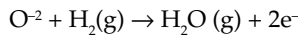
A series of experiments have been conducted with this melt system to confirm the proof-of-concept for magnesium production. The composition of the selected melt was 80 wt.% MgCl_2 – 20 wt.% NdOCl . It is well established that NdOCl is created by the following reaction:⁸



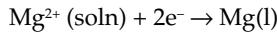
Details on making the 80 wt.% MgCl_2 – 20 wt.% NdOCl have been described in an earlier publication.⁹

As shown in Figure 2, the solid-oxide oxygen-ion-conducting membrane used was a bottom-closed yttria-stabilized zirconia tube (YSZ) with an inner diameter of 1 cm and a wall thickness of 1.5 mm. A graphite crucible contained the melt and a graphite rod dipped in the melt served as the cathode. The anode was a thin layer of porous Ni-YSZ cermet coated⁹ along the inner wall of the YSZ tube. A reducing gas was passed through the YSZ tube to prevent oxidation of the nickel in the cermet, and the tube was immersed in the melt to begin the electrolysis process. A magnesia-refractory separator controlled the solvent flow between the cathode and the anode (Figure 2) and prevented the magnesium metal deposited at the cathode from reaching and reacting with the YSZ tube. This arrangement helped to isolate and collect the magnesium produced at the cathode. When the applied electric potential exceeded the dissociation potential of the oxide in the melt, magnesium was reduced at the cathode while the

oxygen ions passed through the YSZ tube and were oxidized at the Ni-YSZ anode. The anode reaction is



and the cathode reaction is



In the experiments conducted at 700–900°C, MgO dissociation was observed above 1.0V and the current density (100–760 mA/ cm^2) increased with the applied potential. The current passed was generally in the range of 0.1–2.5 A. At around 700°C, pure liquid magnesium (>99 wt.%) was obtained at the cathode (Figures 3 and 4). The total charge passed through the cell as a function of time in one of these experiments is shown in Figure 5.

These experiments measured the dissociation potential of the MgO in the melt, and also determined the current-potential profile and current density, the latter of which is equivalent to the metal production rate. Figure 6 illustrates data from one of the experiments at 900°C in which the applied potential was slowly increased as the current was measured. Since the melt is not stirred, over time the current decreases as a result of polarization (Figure 6). The current observed prior to MgO dissociation is probably due to nonstoichiometry of the zirconium membrane.

At temperatures greater than 700°C, magnesium vapor was produced but significant volatilization of the chloride melt also occurred.⁹ Therefore, due to the high volatility of the chloride bath, temperatures greater than 900°C could not be employed to obtain higher current density essential for scale-up and commercialization. For this technology to be industrially viable, the SOM process must be performed at 1,200–1,400°C to exploit the high O^{2-} -diffusivity of the zirconia membrane at higher temperatures and obtain the larger current density required for industrial scale operation. This will involve researching alternate solvent/melt systems with low volatility and required transport properties

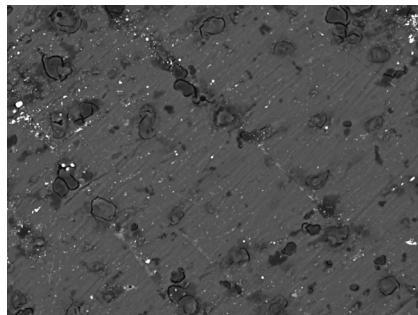


Figure 4. A backscattered electron image of the magnesium metal globule (99.98 wt.% pure) deposited at the cathode.

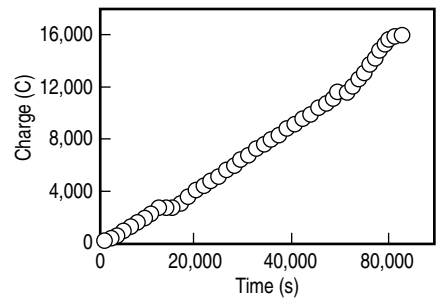


Figure 5. A charge passed through SOM cell during the experiment at 700°C.

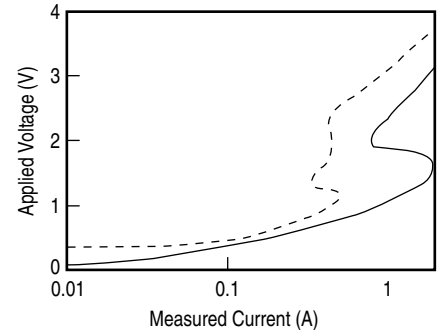


Figure 6. The results of potentiodynamic experiments conducted at 900°C: solid line—initial behavior, dashed line—behavior during the second and after the first potentiodynamic experiment.

that can both dissolve magnesium oxide and remain chemically stable in contact with the zirconia membrane.

TECHNOLOGY DRIVERS

The success of any primary magnesium production technology focused on the structural and automotive components marketplace will always be governed by its ability to compete directly with aluminum's Hall-Heroult process. Given the maturity of the aluminum industry, magnesium's first challenge is the economies of scale. The capital cost, ore to metal, for a modern 500,000 tonne per year aluminum plant—with total production capacity roughly equivalent to the global magnesium industry—is between \$6,500–\$7,200/tonne. The corresponding capital cost (ore to metal) for a 50,000 tonne per year modern magnesium plant is \$8,000–10,000/tonne. An additional competitive advantage of the aluminum process is its reliance on an oxide-based raw material, bauxite, which is converted via the Bayer process to alumina at roughly \$100 per tonne, followed by direct electrolysis to aluminum. The electrolytic magnesium process is based on an anhydrous chloride feed material that is recovered from brines via an elaborate and expensive front-end dehydration process, which can represent 80% of the plant footprint and 30% of its capital cost. Typically, the capital costs for aluminum production are divided as follows: front end process, 22%, electrolysis process, 28%, cast-

ing process, 10%, buildings, utilities and services, 21%, and indirect costs, 19%. For magnesium production, those capital costs are: front end process, 30%, electrolysis process, 20%, casting process, 7%, buildings, utilities and services, 15%, and indirect costs, 28%. The electrolytic magnesium process also generates a chlorine by-product at the graphite anode that can represent an environmental concern that requires additional capital and operating resources.

The alternative metallothermic process for producing magnesium is based on the thermal reduction of calcined dolomite or magnesite with ferrosilicon to form a magnesium vapor that is collected in an attached condenser. The ferrosilicon reductant represents 12 KWh/Kg, or roughly 40%, of the total energy required to produce magnesium, equal to roughly a third of its total production cost. Furthermore, this batch process generates about 4-5 tonnes of slag per ton of magnesium that has to be properly disposed.

To be competitive, technology for magnesium production must move to the direct electrolytic reduction of magnesium oxide and thereby eliminate the need for expensive front-end feed material preparation and reductants. Also, eliminating environmentally undesir-

able waste products in manufacturing will significantly reduce the disposal costs and the environmental impact.

THE SOM PROCESS

The proposed SOM process dramatically alters the existing electrolytic magnesium process flowsheet, Figure 7. It replaces the magnesium-chloride dehydration process with a simple magnesium-oxide calcining operation, thereby eliminating its front-end capital and operating cost disadvantage relative to aluminum. This also reduces the overall energy consumption of magnesium production by roughly 50%. The energy per tonne of metal consumed in magnesium production breaks down to ore preparation, 0.3 MWh, cell feed preparation, 10-19 MWh, and electrolysis 13-20 MWh, for a total of 26-34 MWh. For aluminum, the energy consumption is broken down as follows: ore preparation, 0.3 MWh, caustic soda, 1.2 MWh, cell feed preparation, 3.3 MWh, anode production, 0.4 MWh, and electrolysis, 14.5 MWh, for a total of 19.7 MWh.

Eliminating the magnesium-chloride cell feed also eliminates the production of chlorine and chlorinated hydrocarbons. Other waste products associated with magnesium production are solid wastes, HCL, and shielding gas (SF₆).

Table I. Maximum Current Density Estimates Through YSZ Membrane (1.5 mm thick)

Temperature (°C)	Current Density (mA/cm ²)
700	150
900	750
1,000	1,500
1,100	2,900
1,200	4,200
1,300	5,600

Wastes generated in aluminum processing include solid wastes, fluoride gases, perfluorocarbon gases including off-gases and polycyclic aromatic hydrocarbons, and particulate emissions including Al₂O₃ dust and fluorides.

The envisioned SOM process would operate at 1,300°C or above in order to take advantage of the higher possible current density through the yttria-stabilized zirconia membrane (Table I). This also means that the magnesium would be produced as a vapor and collected in condensers similar to those used in the metallothermic process. The advantage of operating above 1300°C is that the SOM process could potentially be operated at more than five times the current density (1 A/cm²) of existing aluminum electrolysis cells. This means that the SOM process could, theoretically, produce over 6.5 times more magnesium metal per unit surface area of membrane compared to aluminum production in a Hall-Heroult cell. This estimation is based on the fact that magnesium has a double valence compared to triple valence of aluminum and the atomic weights of magnesium and aluminum are 24 and 27, respectively. Also, although thicker membranes may be used if needed for structural integrity, the SOM process could still be operated at current density over 1 A/cm² because of the higher oxygen ion conductivity of the zirconia membrane above 1,300°C. This increased magnesium production per-unit-volume of SOM cell should more than compensate for the additional capital and operating cost associated with the required magnesium condensers. In addition, slag generation in the SOM cell would be reduced from the 4-5 tonnes per tonne of magnesium produced in the metallothermic process to less than 45 kg, which represents a 100-fold improvement. This means that the production cycle of the SOM cell could be two orders of magnitude greater than the metallothermic process. All these favorable factors related to the SOM process would have a substantial positive impact on the environment, production efficiency, yield per cell, plant production capacity, labor requirements, materials of construction due to reduced thermal cycling, and slag disposal.

The SOM cell may resemble the Hall-Heroult cell, where the zirconia mem-

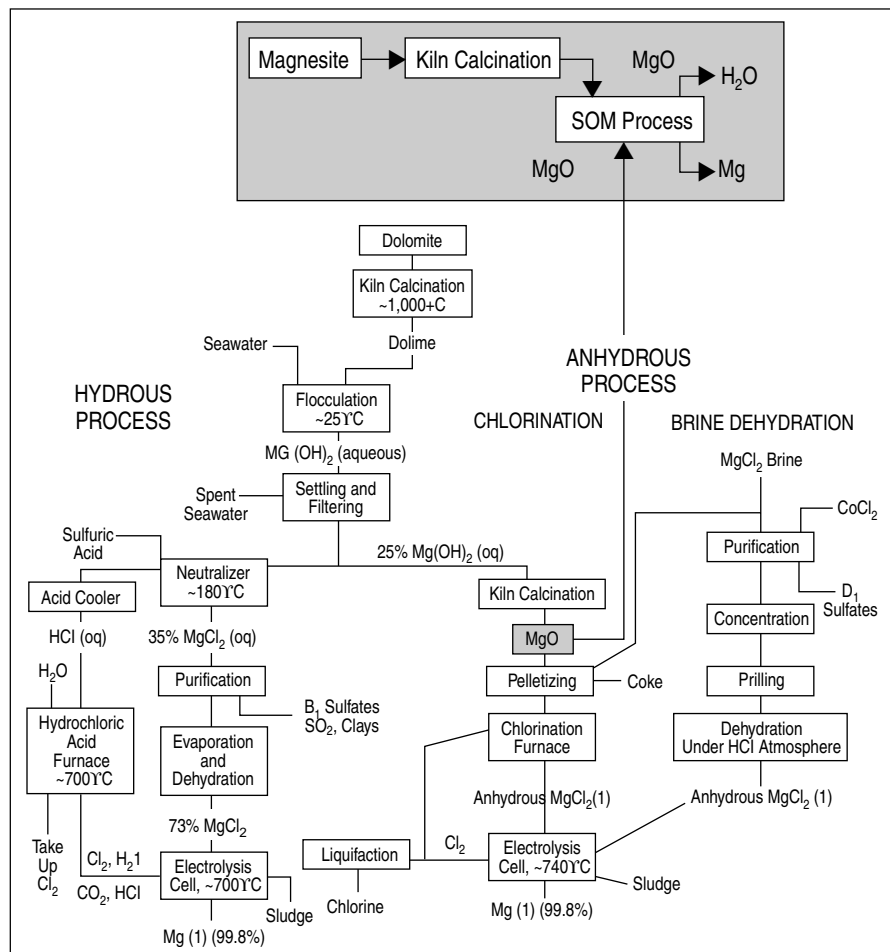


Figure 7. The electrolytic magnesium process flow sheet.

branes with the cermet (or its equivalent) serve as the anode in the SOM cell along with an arrangement of condensers for collecting the magnesium vapors generated at the cathode. However, at this time, a quantitative economic analysis of the SOM process and its design must await the confirmation of various projected processing parameters, several of which will flow from ongoing research. In the meantime, it is not unreasonable to expect that the accumulated capital and operating advantages of the SOM process could easily reduce the total production cost of magnesium by a factor of 2 or more when compared with existing magnesium process.

PROCESS DEVELOPMENT AND COMMERCIAL VIABILITY

A high current density and energy efficiency are necessary to ensure commercial viability of the SOM process. The SOM technology R&D program for magnesium production is directed at obtaining high current density, confirming the stability of the materials of construction, and scaling up the process. Higher operating temperatures (1,300–1,400°C) must be employed in order to exploit the increasing O²⁻-diffusivity of stabilized zirconia with temperature so that current density greater than 1 A/cm² can be easily obtained. Since the ionic resistance of the zirconia membrane and the charge-transfer resistances are likely to be negligible compared to other resistances in the system at these higher operating temperatures, the production efficiency may be enhanced by decreasing the convective resistance of the melt through stirring, applying higher electric potentials between the electrodes, increasing the desired oxide concentration in the melt, increasing the area of the melt-electrode interface, decreasing the ionic resistance of the melt, and/or designing the melt-zirconia and the zirconia-gas-anode interfaces to limit local polarization effects. Furthermore, at these higher operating temperatures, natural gas can be very efficiently reformed at the anode for generating the required H₂ gas to react with the oxygen ions migrating through the membrane.

This will also increase the overall energy efficiency of the process since part of the electrical energy requirement will be directly obtained from the electrochemical anodic oxidation of the reformed natural gas. It may also be possible to use the heat in the by-product anode gas for on-site cogeneration or bottoming cycle.

WORK IN PROGRESS

Keeping commercial viability in mind, the ongoing research is aimed at producing and collecting magnesium with near 100% current efficiency by using the SOM process at steady-state current density on the order of 1 A/cm² or greater. This would result in a magnesium production rate that is at least 1.33 times the current aluminum mass production rate in Hall cells.

More specifically, the following tasks are being completed:

- The long-term stability of the zirconia membrane is being evaluated in a few relatively non-volatile melt systems, each with viscosity less than 10 poise, electrical conductivity greater than 1 ohm-cm⁻¹ and MgO solubility at least around 7 wt.%, at temperatures between 1,300–1,400°C. These requirements are expected to provide kinetically favorable conditions suitable for scale-up.^{9–11}
- An adherent-porous-stable cermet or its equivalent is being utilized as an anode for the SOM cell operating at temperatures between 1,300–1,400°C.
- Based on the results of the first task in this list, appropriate MgO-containing melt systems are selected to confirm the dissociation potential for MgO, and to determine the current-potential profile and current density as a function of temperature. The parameters that result in current density on the order of 1 A/cm² or greater are of interest. This information will help assess the electrical power requirements and the possible metal production rates for scaling up the process.^{10–12}
- A condenser design is being established to collect the magnesium vapors produced at the cathode for analysis.

Results obtained are being used to formulate a process model for scale-up and to conduct pilot-scale trials of this technology.^{10,11}

The results obtained are expected to verify the potential production, energy, environmental, and economic efficiency of magnesium production by the SOM process and will be used to model the process and propose scale-up to determine commercial viability.^{10,11}

ACKNOWLEDGEMENTS

The authors acknowledge the help of E. Chiang, T. Keenan, and H. Lingertat on melt preparation, cermet processing, and set-up for electrolysis. Financial support of the National Science Foundation, award DMI-9424069, is acknowledged for initiating the concept used in this research. Financial support from the Northwest Alliance for Transportation Technologies Program at the U.S. Department of Energy's Pacific Northwest Laboratory (Battelle) is also gratefully acknowledged.

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