CONTROL OF YTTRIUM DIFFUSION OUT OF YTTRIA STABILIZED ZIRCONIA DURING SOM ELECTROLYSIS FOR MAGNESIUM PRODUCTION

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Abstract

The solid oxide membrane (SOM) process has been used to produce magnesium by direct electrolysis of its oxide. In this process MgO is dissolved in a molten CaF_2-MgF_2 flux and an yttria-stabilized zirconia (YSZ) SOM membrane separates the cathode and the flux from the anode. YSZ membrane stability limits the operating life of the SOM electrolyzer. The YSZ membrane is known to degrade due to diffusion of yttrium into the flux. Yttrium diffusion can however be decreased by adding YF_3 to the flux. This study investigates the long-term stability of the YSZ membrane. Yttrium composition profiles in the YSZ membrane were determined using WDS as a function of immersion time and YF_3 content in the flux. An analytic solution to the diffusion equation was used to model the diffusion process. This study allows the determination of the optimum YF_3 content needed in the flux to minimize yttrium diffusion and increase membrane stability.

Introduction

Magnesium is the third most abundant metal in the earth's crust. Since magnesium is the lightest of all metals used for construction alloys, magnesium is the leading candidate to replace steel and aluminum in automobiles. Automobile manufacturers would like to increase magnesium content from 4-5kg per vehicle to 40-100kg per vehicle [1]. However, in order for automobile manufacturers to replace steel, it is generally believed the magnesium to galvanized steel price ratio must be 4.33:1. For magnesium to replace aluminum in automobiles, the magnesium to aluminum price ratio must be 1.8:1 [2]. In 2008 this ratio was 8:1 for magnesium/steel and 2.5:1 for magnesium/aluminum.

The solid oxide membrane (SOM) process for magnesium production has been successfully employed for relatively short periods of time in a laboratory setting [3]. These results have been extrapolated and the SOM process has been proposed as a method to meet the demand for low cost primary magnesium [2].

In the SOM process the metal oxide is dissolved in an ionic molten fluoride flux, and a potential is applied to separate the oxygen anion from the metal cation. The metal cation is reduced at the cathode, and an oxygen-ion-conducting yttria stabilized zirconia (YSZ) tubular membrane allows vacancy diffusion of the oxygen anions to the anode where they lose electrons to produce oxygen gas. It is believed that the YSZ membrane stability limits the operating life of the SOM process.

Previous work has shown the YSZ membrane to be stable in the molten ionic MgF_2-CaF_2 based flux for short times, less than 50 hours. Additionally, it was proposed that one mechanism of membrane degradation is yttrium diffusion from the membrane into the flux [4]. However, no previous work has been reported investigating the long term stability of YSZ in molten fluoride flux, nor has the yttrium diffusion out of the YSZ been modeled in any detail.

This paper deals with the primary mechanism of YSZ membrane degradation in ionic based fluoride fluxes, which is believed to be yttrium diffusion from the membrane to the flux. It is also shown that the yttrium diffusion from the membrane is not dependent on the applied potential during magnesium electrolysis. Furthermore, it is believed that diffusion of yttrium from the membrane into the flux can be prevented by adding yttrium fluoride to the flux. The YF_3 increases the activity of yttrium in the flux and decreases [or reverses] the chemical potential gradient of yttrium at the flux-YSZ membrane interface. Therefore with appropriate additions of yttrium fluoride in the flux, it is possible to decrease or eliminate yttrium diffusion from the YSZ membrane into the flux and by reversing the chemical potential gradient with higher amounts of YF_3 in the flux it is possible for yttrium to diffuse into the membrane from the flux.

The diffusion process is modeled based on the semi-infinite solution to Fick's second law. The model correlates YSZ membrane stability to the concentration of yttrium fluoride in the flux and shows that the YSZ membrane is stable in the flux across a range of flux compositions without undergoing a phase transition or large changes in ionic conductivity. The range of flux compositions provides a basis for determining the parameters with which a large scale SOM process for magnesium production can run for long times, thousands of hours.

Experimental

Experimental details: Yttrium diffusion profiles in the YSZ membranes were determined after performing static membrane stability tests. A static membrane stability test involved immersing a section of a YSZ tube in the MgF_2-CaF_2 based flux at 1190°C for a given time interval, with no applied potential. The YSZ tube was then raised out of the flux. After cooling, a section of the YSZ membrane was mounted and polished. The composition profile in the membrane was then determined by wavelength dispersive x-ray spectroscopy (WDS). All YSZ tubes were 0.75" outer diameter and contained 10.5w% yttria.

The compositions of flux tested in the static membrane stability tests are shown in Table 1. Magnesium fluoride hydrate was purchased from Alfa-Aesar and dried at 250°C for 12 hours. 96% pure magnesium oxide, 99.5% pure calcium fluoride and 99.99% pure yttrium fluoride were also purchased from Alfa-Aesar and dried for 12 hours at 250°C. After drying, the powders were mixed for 2 hours on a ball mill, at 200 rpm. Once mixed the powders were poured into a one end closed stainless steel tube.

The powders were then melted by heating to 1190°C in 95% argon, 5% hydrogen atmosphere. After equilibrating at

1190°C for 1 hour a 2 inch section of as received YSZ tube was lowered into the flux. The YSZ tubes were immersed in the flux for 16, 24, 32, or 100 hours before being raised out of the flux and then cooled to room temperature at 4°C/min.

The YSZ tubes were then cut with a diamond saw and mounted in Buehler Epothin Epoxy Resin (20-8140-032) with Epothin Epoxy Hardener (20-8142-016). Once mounted the samples were initially ground with a 45 micron diamond wheel, and polished (0.25 micron diamond polishing). A carbon coating was applied to the surface via sputtering and WDS spectroscopy was performed in order to determine the yttria concentration in the membranes. Compositional analysis was done every 5 microns for the first 40 microns from the membrane flux interface and every 10 microns thereafter.

%YF3	%CaF2	%MgF2	%MgO
0	40.5	49.5	10.0
1.6	39.8	48.6	10.0
2.0	39.6	48.4	10.0
5.0	38.3	46.8	10.0

Table 1: Flux compositions tested in static membrane stability tests

Electrolysis experiment: SOM electrolysis was performed with flux containing no YF_3 in order to evaluate the effect of applied electric potential on yttrium diffusion out of the YSZ tube. Figure 1 shows the schematic of the SOM electrolyzer used in the electrolysis experiment. It consists of an upper electrolysis chamber, heated to 1190°C and a lower condensation chamber kept at a temperature range of 1050°C-300°C. The set-up is fabricated using SS-304 (Grade 304 stainless steel). It was heated to the aforementioned temperatures in a reducing atmosphere (5%H_2-Ar). The crucible wall of the electrolysis chamber served as the cathode. Silver inside the YSZ tube served as the anode. An alumina spacer was used to insulate the YSZ membrane from the steel which acted as the cathode. A 0.25" molybdenum tube served as the anode current collector. Before electrolysis was performed, the cell was purged with Ultra High Purity Argon at 300cc/min into the cathodic chamber through the annulus between the inner diameter of the stainless steel tube and the outer diameter of the YSZ tube to lower the magnesium partial pressure. The argon gas is required to keep the magnesium vapor produced from reducing the YSZ, as well as act as a carrier gas to transport the magnesium vapor to the condenser. The magnesium vapor produced on the cathodic side is transported to the condensation chamber through the two stainless steel tubes. These two tubes extend above the flux to prevent any molten flux from entering the condenser. On the anodic side, hydrogen was bubbled in the silver through the molybdenum tube at rate of 60cc/min to prevent oxidation of the molybdenum current collector.
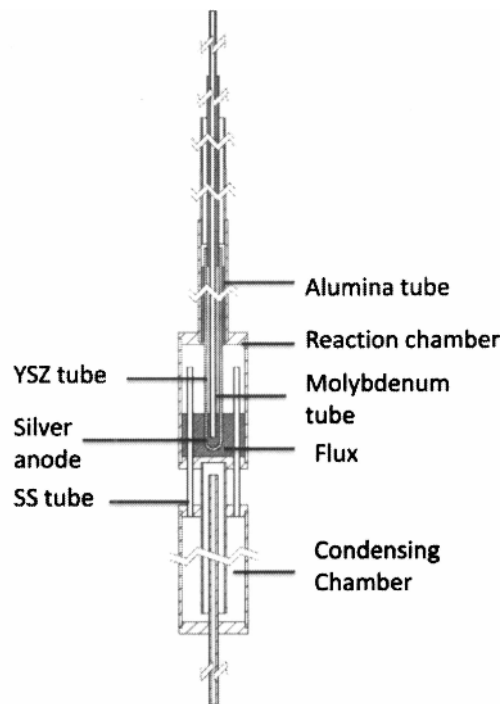

Figure 1: Design of experimental setup for SOM process.

An alumina tube attached to the YSZ tube (with Aremco 552 paste) was used to carry the $H_2O_{(g)}$ out of the anodic chamber and also prevent the $H_2O_{(g)}$ from reacting with the magnesium vapor produced on the cathodic side.

After the experiment the YSZ tube was sectioned and polished. The yttrium concentration profile in the YSZ tube was measured using Energy-dispersive X-ray spectroscopy (EDAX) and compared with the results of the static experiments with no YF_3 in the flux.

Results and Discussion

A static membrane stability test was preformed with no yttrium fluoride in the flux for 32 hours. The first 50 microns from the membrane flux interface contained no yttria and high porosity, 50-70 microns from the membrane flux interface the yttria concentration gradually increased and after 70 microns yttria concentration was uniform and matched the bulk concentration, Figure 2.

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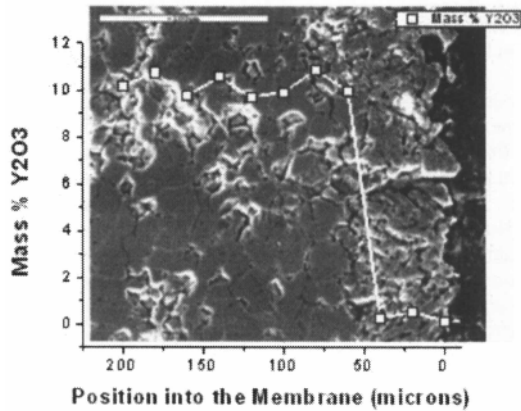
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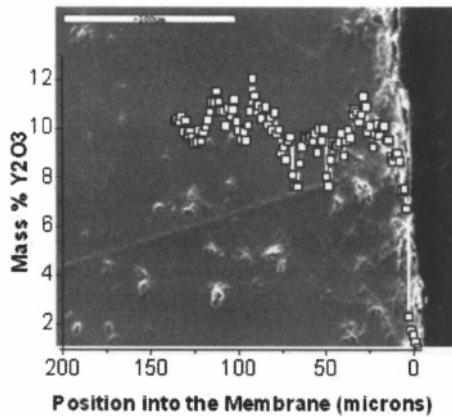
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Figure 2: A. Yttria concentration profile overlaid on top of SEM image of YSZ exposed to the flux for 32hrs. B. As received YSZ.

It is believed that the decrease in yttria concentration at the membrane flux interface is due to yttrium diffusing from the membrane into the flux. If the mechanism for yttrium depletion in the membrane is chemical diffusion, then by controlling the activity of yttrium in the flux it should be possible to control the yttrium diffusion out of the membrane. It was found when the activity of yttrium in the flux is higher than that of the yttrium in the membrane, yttrium diffused from the flux into the membrane, increasing the yttria concentration in the membrane; this happened when 5w% YF₃ was added to the flux, Figure 3.
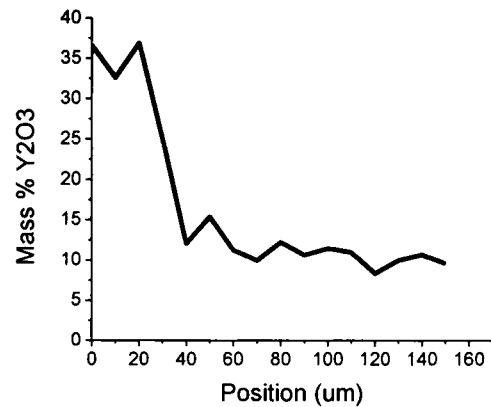

Figure 3. Yttria profile in the YSZ membrane exposed to flux with 5 w% YF$_3$ for 32hrs.

It was seen that when YSZ is exposed to a flux containing 2w% YF$_3$ for 100 hours the membrane has limited porosity, Figure 4, and concentration at the membrane flux interface increases to 15w%, Figure 5. MgF$_2$-CaF$_2$ flux containing 2 w% YF$_3$ appears to be a composition in which YSZ is stable for long time periods.
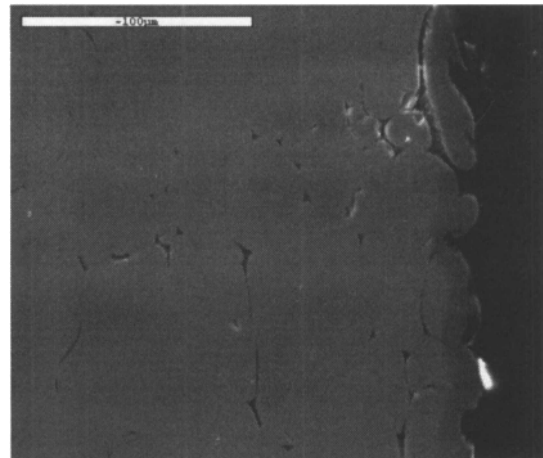

Figure 4. YSZ exposed to flux containing 2w% YF$_3$ for 100hrs.

The yttria concentration profile in YSZ exposed to flux containing yttrium fluoride can be modeled using the semi-infinite solution to Fick's second law, equation 1.

$$C = C_O + (C_\infty - C_O) * \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \qquad (1)$$

In equation 1 C_0 is the steady state concentration of yttria at the membrane flux interface, and C_∞ is the bulk concentration in the membrane. The experimental results from the static membrane tests were used to fit for the diffusivity, using the least squares approximation. The results of this model are overlaid on top of the experimentally determined results from the static membrane stability tests in Figure 5.
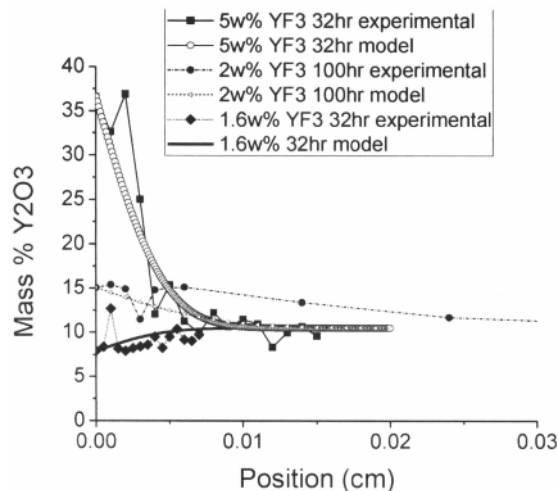
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Figure 5: Experimental yttrium diffusion profiles and modeled results.

From the model, the diffusivity of yttrium in the membrane was determined to be $5.6 \times 10^{-11} cm^2/sec$. According to the model the yttria concentration throughout the membrane will never reach the C_0 value during the operation of the SOM process, because the diffusivity is very low. However, it is important to determine the C_0 value because the corresponding change in Y_2O_3 concentration in the diffusion zone of the YSZ membrane may lead to changes in ionic conductivity or crystal structure.

A key factor in modeling the diffusion of yttrium in the membrane is knowing the C_0 value for a specific flux composition. Static membrane stability tests with 2w% YF_3 in the flux where performed for 32 and 100 hours. The C_0 value was measured to be 15.4 w% Y_2O_3 for the 100hr case and 16.1 w% Y_2O_3 for the 32 hour case. The difference in C_0 values for 32 and 100 hour studies falls within the experimental error for compositional analysis using WDS. It is therefore believed that the 32 hour static membrane stability tests are sufficiently long to determine the C_0 value for a given flux composition.

The experimentally determined values of C_0 were obtained using 32 hour experimental holds. Once more data points are acquired, a polynomial fit using a least squares approximation will be used to determine the C_0 value for a given YF_3 flux concentration. As long as the steady state value at the membrane flux interface is known, the model will allow us to determine the yttrium concentration profile in the YSZ membrane from the YSZ/flux interface.

10.5 w% Y_2O_3 stabilized zirconia after aging at 1200°C has both tetragonal and cubic phases present and high ionic conductivity [5]. Both the tetragonal and cubic phases are metastable from 5-16.5 w% Y_2O_3 [6]. From a mechanical stand point the YSZ membrane is most stable when both the tetragonal and cubic phases are present. Thus the Y_2O_3 stabilization in zirconia plays an important role in determining the phase, conductivity and mechanical properties of the membrane. Therefore, it is necessary to determine the amount of yttria in the YSZ during the entire SOM process in a commercial scale operation.

The equation acquired from the polynomial fit, will be used to determine the yttria concentration at the flux-YSZ interface as a function of the YF_3 content in the flux. This equation will provide a range of flux compostions where the SOM

electrolyzer can successfully operate and will not undergo a phase change. Further analysis of the mechanical properties of the YSZ tubes is not a major concern for the SOM process since the tubes are suspended and stationary.

A YSZ tube was exposed to the flux for 23 hours and electrolysis of magnesium oxide was performed. A separate static membrane stability test was performed for 24hrs. In both cases no yttrium fluoride was present in the flux. The resulting yttrium composition profiles, measured with EDAX, are nearly identical, Figure 6. This shows that the diffusion process is not affected by the applied potential during electrolysis. Therefore it is believed the yttrium concentration in the YSZ membrane is dependent only on chemical diffusion and migration does not play a major role in determining the yttrium concentration profile. It is interesting to note earlier calculations on application of electrical potential across a YSZ membrane predicted no noticeable demixing of yttrium would be detected [7].
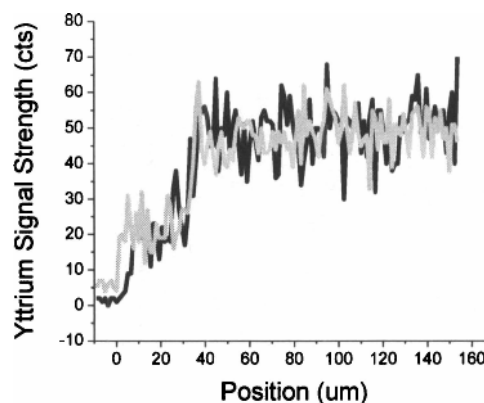

Figure 6: Yttrium concentration from the membrane flux interface. The red line is after 24 hours in the flux with no applied potential, black line is after a 23 hour electrolysis hold.

The diffusion model does not apply when there are trace amounts or no yttrium fluoride in the flux, because, it causes yttria concentration in the membrane to fall below 5 w% which leads to extensive porosity in the membrane. The porosity allows the flux to enter the membrane and increases the surface area of YSZ exposed to the flux; a complete diffusion profile is not observed and the yttrium concentration undergoes a step change. Figure 2(a).

Conclusion

Yttrium diffuses from the YSZ membrane into molten MgF_2-CaF_2 flux over relatively short time scales. The diffusion of yttrium is related to the activity difference between yttrium in the membrane and yttrium in the molten flux. By increasing the activity of yttrium in the molten flux it is possible to prevent yttrium from diffusing into the flux. It was also shown that yttrium will diffuse into the YSZ membrane from the flux when the activity of yttrium in the flux is sufficiently high. Experimentally, YSZ was shown to be stable in flux containing 2w% yttrium fluoride. The diffusion of yttrium in the membrane was modeled using a semi-infinite solution to flicks second law. More data points are needed to correlate the concentration of yttrium fluoride in the flux to the concentration of yttrium in the membrane during the SOM electrolysis.

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