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ULTRA HIGH TEMPERATURE RARE EARTH METAL EXTRACTION BY ELECTROLYSIS

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Abstract

Current industrial methods used for rare earth element (REE) extraction involve: 1) ore enrichment, 2) separation of rare earth oxides (REOs), 3) chlorination or hydrofluorination, and 4) individual electrowining of REEs from a molten halide electrolyte. The complexity of REE extraction is inherited from their electronic configuration. Recently, molten oxide electrolysis (MOE) has been used to produce reactive metals directly from their oxides, e.g. titanium. As a single-step alternative to processes 3) and 4), or laboratory has investigated rare earth extraction by MOE. A key challenge is to find a molten electrolyte more stable than REOs. One possibility is to use binaries of REOs directly as a solvent. We have, therefore, developed two experimental approaches for studying molten REOs at temperatures exceeding 2200°C. The present work reports the most recent experimental results obtained with $\text{La}_2\text{O}_3\text{-Y}_2\text{O}_3$. Those promising results demonstrate potential for operating with molten REOs and refine the underlying materials challenge for electrodes to enable metal recovery.

Introduction

The rare earth elements (REEs), e.g. dysprosium or praseodymium, possess unique properties that are critical to a diversified energy portfolio [1]. Additionally, REEs are increasingly used in applications ranging from consumer (cellphones) to defense (lasers). Current consumption rates stand at a meager 130 kt annually, but are expected to increase substantially in the next decade with expansion of high growth markets for REEs, i.e. high technology sectors [2]. The similar chemistry of the 17 rare earth oxides (REOs) means that they occur together in the Earth's crust, and the extraction of a single REE requires separation from the 16 others via a complex series of processes [3]. We propose investigating molten oxide electrolysis (MOE) as a simplifying and efficient alternative to current methods of rare earth metal extraction and recovery.

During MOE, metal cations are reduced to metal directly from a molten oxide electrolyte at the cathode using electricity. If an inert anode is used [4], oxygen gas is the lone byproduct of the anodic reaction. A schematic of a MOE cell is shown in Figure 1. This technique has been studied at the laboratory scale for producing reactive metals, e.g. titanium [5].

Figure 1: Simplified schematic of an MOE cell illustrating important features

A key challenge for rare earth MOE is determining a suitable oxide supporting electrolyte which is more stable than the rare earth oxides (REOs). Figure 2 is a diagram à la Ellingham-Richardson-Jeffes showing the minimum cell potentials for decomposition and relative stability of the REOs in comparison with a selection of other reactive metal. Certainly, choices of a supporting electrolyte for rare earth MOE are limited to the most stable oxides, obviating silicates or borates. The approach presented here studied the use of an electrolyte composed of the REOs themselves. Given their ultra high melting points [6], operation with a REO-based supporting electrolyte necessitates cell operation at temperature above 2200°C. Operation at such temperatures would enable additional features for separation including exploitation of differences in vapor pressures of the products. Figure 3 is a modified version of Figure 2, which focuses on decomposition potential of only the rare earth oxides in the temperature range of interest to this study.

Figure 2: Minimum cell decomposition potential vs. temperature of a selection of the oxides of the reactive metals including the REOs, assuming unit activity for reactants and products [7].

Figure 3: Minimum cell decomposition potential vs. temperature of the REOs in the vicinity of their melting temperatures, assuming unit activity for reactants and products [7].

Experimental Methods

Given the lack of information on the electrolytic nature of molten rare earth oxides in the literature [8] and the challenging nature of high temperature experiments, the development of a setup supporting electrochemical experimentation at temperatures above 2200°C is an important feature of this work. We have developed two laboratory-scale approaches for studying molten rare earth oxides using electrochemistry techniques using i) graphite furnace and ii) floating zone furnace (FZF) methods.

Graphite Furnace Approach

A CG26-6x12-1Z graphite crucible furnace (Mellen Company, Inc.) equipped with 3/8 in. graphite rod heating elements and capable of temperatures up to 2600°C was used (see Figure 4). The graphite furnace is equipped with a pyrometer that is focused on a block of graphite positioned at the center of the hot zone. The electrolyte was prepared by weighing and mixing by hand 99.9% purity powders of La_2O_3 and Y_2O_3 (Alfa Aesar) followed by sintering in a furnace (Lindberg/Blue M) at 1600°C for 48 hours to obtain maximal densification prior to experiment. Chunks of the sintered electrolyte were weighed and placed in a tungsten crucible (Sage Industrial Sales, Inc.) and the assembly was loaded into the graphite furnace with an EDM graphite (GraphiteStore.com) secondary crucible. The furnace was evacuated and purged with ultra high purity argon gas (Airgas) and ramped to 700 °C under vacuum to remove volatiles followed by refilling and ramping to the desired process temperature. In the preliminary stages of this approach, the crucible was used also as the cathode by running a tantalum cathode lead wire to the crucible base from a port in the cap (see Figure 4). Iridium (Furuya Metals Co. Ltd.), tungsten (Midwest Tungsten Service Inc.), and EDM graphite (MWI Inc.) rods have been tested as anodes. Subsequent testing used a three electrode setup in an effort to increase the cathodic current density. A Reference 3000 Potentiostat (Gamry Instruments) was used for electrochemical measurements.

Figure 4: Schematic representation of graphite furnace setup

FZF Approach

A Crystal Systems, Inc. type FZ-T-12000-X-S optical floating zone system equipped with four 25kW xenon lamps capable of heating samples to 3000°C was used (see Figure 5). The floating zone system is equipped with top and bottom rods that allowed for precise, automated control of the sample and electrode positioning within the furnace. Additionally, video feed is provided for direct monitoring of the experiment by a filtered camera. Sample rods of REOs with the dimensions 3-5mm diameter x 75-150mm length were prepared. First, 99.9% purity powders of La_2O_3 and Y_2O_3 (Alfa Aesar) were weighed and mixed to the desired composition by hand. Next, the mixture was ground to a finer powder and mixed by mortar and pestle. Then, the powder was hydrostatically pressed in a taught latex tube and removed in preparation of a green body ready for sintering. Sintered sample rods of greater than 90 percent densification were prepared by heating in a furnace (Lindberg/Blue M) at 1600°C for 48 hours. One end of the rod was wrapped in nickel wire for suspending in the FZF.

The sintered REO rods were loaded into the FZF. A custom quartz tube (Technical Glass Products, Inc.) sealed with rubber O-rings and fitted with four ports allowed for electrode connections (the three ports near the bottom), a thermocouple probe or light guide for optical pyrometer (one port near the top), and vacuum-purging with ultra high purity argon (Airgas). The electrodes, comprised of 99.95% purity tungsten (Rembar Company) and iridium (Furuya Metals Co. Ltd.), were threaded through a multi-bore alumina tube fixed to the bottom positioning rod in the FZF. Electrical connections were made by welding nickel wire to the base of the wires and threading the wires from the multi-bore tube through fittings (Swagelok) on the bottom three ports. A Reference 3000 Potentiostat (Gamry Instruments) was used for electrochemical measurements. Following measurements, samples were quenched by powering down the lamps.

Figure 5: (a) Image of inside the FZF; (b) Filtered image of molten La_2O_3 (60 at%)- Y_2O_3 (40 at%) droplet with iridium electrodes inserted during electrochemical measurements. The white and red dotted lines are present for clarification purposes.

Results and Discussion

With the graphite furnace, significant progress has been made with materials compatibility testing for crucible and electrode materials. Refinement of the electrochemical laboratory cell with this approach is still in progress. Tungsten has shown great promise as a crucible and cathode material. Figure 6 shows a polarized optical micrograph of the cross section of a premelt. Anode material tests demonstrate challenges with operating with carbon (graphite electrodes).

Figure 6: Polarized optical micrograph of a cross-section of La_2O_3 (60 at%)- Y_2O_3 (40 at%) premelted in a tungsten crucible in the graphite furnace at 2250°C .

For the first time, electrochemical measurements have been performed in molten rare earth oxides. The La_2O_3 (60 at%)- Y_2O_3 (40 at%) electrolyte used demonstrated relatively high electrical conductivity, with a bulk resistance between the wires located x mm apart of X ohms. (see Figure X, impedance data). Preliminary bulk electrolysis experiments with three iridium

wires, and observations of the electrolyte post-experiment show the formation of a quenched droplet (see Figure Y, BUT WITHOUT THE COMPOSITION), indicative of the production for metal during electrolysis. This results, which further analysis is ongoing, points to the key challenge of alloying/melting of the cathode material during electrolysis. Further developments are on the way to find more stable materials to work as a solid cathode in such conditions.

Conclusion

- ❖ REOs have been identified as potential candidate for a rare earth MOE supporting electrolyte
- ❖ Graphite furnace and floating zone furnace methods have been developed in an effort to probe molten REOs with pioneering in situ electrochemical measurements at ultra high temperatures
- ❖ Three iridium electrodes measurements in the FZF have been performed, offering promising results toward the development of t electrochemistry in molten REO supporting electrolyte at a temperature in excess of 2200°C.

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References

- [1] R. Jaffe, “Energy Critical Elements: Securing Materials for Emerging Technologies,” Washington D.C., 2011.
- [2] “Critical Materials Strategy,” 2011. U.S. Department of Energy.
- [3] C. K. Gupta and N. Krishnamurthy, *Extractive Metallurgy of Rare Earths*. New York: CRC Press, 2004, p. 504.
- [4] A. Allanore, L. Yin, and D. R. Sadoway, “A new anode material for oxygen evolution in molten oxide electrolysis.,” *Nature*, vol. 497, no. 7449, pp. 353–356, May 2013.
- [5] N. A. Fried and D. R. Sadoway, “Titanium Extraction by Molten Oxide Electrolysis,” *TMS Conf. (Charlotte, NC)*, 2004.
- [6] M. Zinkevich, “Thermodynamics of rare earth sesquioxides,” *Prog. Mater. Sci.*, vol. 52, no. 4, pp. 597–647, May 2007.
- [7] C. W. Bale, “FactSage 6.2.” Thermfact and GTT-Technologies, Montréal, 2013.
- [8] E. E. Shpil’rain, D. N. Kagan, L. S. Barkhatov, and L. I. Zhmakin, “Electrical conductivity of yttrium and scandium oxides,” *Rev. Int. Hautes Temper. Refract.*, vol. 16, pp. 233–236, 1979.