Ceramics for Molten Materials Transfer

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Concepts for this paper were developed under the Lunar Oxygen Production by Electrowinning project led by KSC under the Management of William Larson.

The support of many program management leaders was essential especially Joe Howell, Carole Mclemore, John Fikes and Chuck Owens who managed the MSFC In Situ Resource Utilization effort.

The efforts of Jerry Sanders, JSC, as the NASA In Situ Resource Utilization lead have been particularly essential for continued progress in the study of lunar resource utilization.
Outline

- Introduction
- Electrowinning cell feeding
- Material removal from the electrowinning cell
  - Removal of gasses
  - Removal of solids
  - Removal of liquids
High Temperature Metal Oxide Electrolytic Cell

- Liquid oxide bath from regolith
- Inert Anode
- Conductive Cathode in contact with liquid metal
- Selective extraction of elements
- Oxygen production

Electrolysis is one method to selectively extract metals and silicon

(Donald Sadoway, Massachusetts Institute of Technology, 2004)
Introduction

Gas: inert gas
Solid: charging materials

Gas: oxygen, others?
Liquid: electrolyte, metal
Solid: metal

Electrowinning cell

Working hypothesis:

Anticipated processes and characteristics

<table>
<thead>
<tr>
<th>Process</th>
<th>Products</th>
<th>Temperature</th>
<th>Process duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>High temp. (HTEW)</td>
<td>Molten metal &amp; alloys, molten oxides, gases</td>
<td>&gt;1400°C</td>
<td>4 - 24hrs</td>
</tr>
<tr>
<td>Low temp. (LTEW)</td>
<td>Solid metal &amp; alloys, molten mix of fluorides, chlorides &amp; oxides</td>
<td>~1000°C</td>
<td>?</td>
</tr>
</tbody>
</table>
- Introduction
- Electrowinning cell feeding
- Material removal from the electrowinning cell
  - Removal of gasses
  - Removal of solids
  - Removal of liquids
Feed device for metal compound

- Description of technology
  - delivery duct delivers metal compound to circulating electrolyte, enhancing dissolution
  - metal compound can be delivered above or under the surface of the electrolyte

- History – 2006 patent

- Application of technology – electrowinning processes with metal-based anodes below 940 °C

- Limitations for application to lunar missions – none apparent

Feed device for hygroscopic metal compounds

Description of technology
- allows the use of hydrated or oxygen containing feed-stock for cells that require freedom from oxygen containing compounds
- furnace adjacent to cell (see fig.) used to melt and chlorinate feed-stock
- pumps used to maintain melt circulation in furnace
- melt pumped through channels to the electrolytic cell; excess electrolyte returned to furnace

History – 2001 patent

Application of technology – described for production of Li and Mg

Limitations for application to lunar missions – irrelevant unless the lunar environment contains free water or oxygen

Siviloti O., Method and apparatus for feeding electrolytic cells, Canadian Patent, CA 2,340,528 (2001)
Outline

- Introduction
- Electrowinning cell feeding
- Material removal from the electrowinning cell
  - Removal of gasses
  - Removal of solids
  - Removal of liquids
Removal of Gasses

Oxygen removal from containers

- Description of technology
  - Flooding of the environment with nitrogen or argon gas
  - Oxygen residual ~ 1%

- History – described in patent by Maget et al.

- Application of technology – used in the pharmaceutical industry

- Limitations for application to lunar missions
  - Large capital expenditure
  - Requires large quantities of nitrogen or argon

- Description of technology
  - Limitation of free volume in the cell
  - Evolved oxygen pressure use for self-removal

- History – to design

- Application of technology – none known

- Limitations for application to lunar missions – none apparent
Removal of Gasses

Gas Extraction from Closed Cells

Description of technology

- removal of gasses particularly oxygen from closed containers
- apparatus senses the oxygen

FIG. 1 is a schematic side elevation view, partially in section, showing the principal components of the electrochemical oxygen extractor.

FIG. 2 illustrates the configuration for a prior art zinc-air battery operated with oxygen from air, where the air is supplied simultaneously to the battery and the electrochemical cell.

FIG. 2 illustrates the configuration of the present invention for a zinc-air battery extracting oxygen from a container, wherein the oxygen flows solely toward the air intake port of the zinc-air battery.

FIG. 3a is a schematic diagram showing the electrochemical oxygen extractor in a closed system configuration.

FIG. 3b is an equivalent diagram showing the electrochemical oxygen extractor in an open system configuration.

Applications

- some infrequent maintenance may be required
- need appropriate sensors for high temperature processes

Removal of Gasses

- Description of technology
  - Metal based anode with electrically conductive structure parallel to the cathode
  - Parallel electrically active anode members (see fig.) on which oxygen is evolved during electrolysis
  - Electrolyte is circulated through the gaps driven by the escape of the oxygen

- History – 2003 patent
- Application of technology – described for aluminum electrowinning cell
- Limitations for application to lunar missions – none apparent

Oxygen Extracting Anodes

Material Removal from the Electrowinning Cell

Removal methods for solids and liquids

- removal of solids
  - freezing of the electrolytic cell and removal of solids
  - removal of solid metal sheet from the liquid electrolyte

- removal of liquids
  - molten liquid pumping systems
  - gravity separation systems
  - pressurized removal systems
Freezing of the Electrolytic Cell and Removal of Solids

- **Description of technology**
  - used in experiments of electrowinning of molten titanium from titanium dioxide
  - at the end of each run the cell temperature was reduced below 1600°C, the anode was lifted above the electrolyte surface and the system cooled to room temperature
  - once cooled, the contents of the cell were removed
  - internal dimensions of the cell: diameter-80 mm, height -120 mm.

- **Application of technology** – High and low temperature electrowinning

- **Limitations for application to lunar missions**
  - Potential use for an initial lander mission to return sample to earth and analyze them
Removal of Solids

Removal of Solid Metal Sheet from the Liquid Electrolyte

- Description of technology – 2 steps:
  - remove cathode from electrolysis cell after specified time (thickness of metal deposit)
  - remove solid metal sheet from cathode

- Limitations for application to lunar missions - cathode removal
  - for an initial lander mission - cathode returned to earth for analysis of metal deposit
  - for a pilot plant where metal deposit is used on lunar surface
    - to minimize crew intervention use an automated cathode exchange mechanism (see next slide)
    - metal deposit stripped from cathode using a patented stripping mechanism (see subsequent slide)
    - cathode exchange mechanism and the cathode stripping mechanism needs to be coupled
  - may require some crew intervention working with hot electrode to exchange electrodes and moving electrodes from the electrolysis cell to a stripping chamber unless they are coupled
Description of technology:

- Cathode carousel is computer driven and can be commanded to place a specific cathode at the engagement position.
- Cathode injection arm can rotate about vertical axis and translate in vertical direction.
- Injector arm rotates to cathode engagement position and translates down to engage an electrode.
- After engagement, it translates up with electrode and rotates to electrode insertion position.
- It then translates down to insert electrode into electrolysis cell.
- Reverse motions are applicable to eject the electrode from the cell and place it back on the carousel.
- Electrical connections for electrolysis is on injector arm - each electrode does not need a separate electrical connection.
Cathode Exchange Mechanism

History

- The sample exchange mechanism has been successfully flown on the shuttle as part of the Crystal Growth Furnace (CGF) and Advanced Automated Directional Solidification Furnace (AADSF).
- CGF could accommodate 6 samples and AADSF could accommodate 3 samples.
- Total weight of sample exchange mechanism was approximately 15 lbs.
- Weight of each sample assembly is approximately 4 lbs.
Description of technology
- In modern production plants for Cu, Ni or Zn the cathode is usually made of a different metal than the metal to be produce.
- Metal to be produced is removed in plate-like sheets (typically over 5 mm thick) from surface of permanent cathodes.
- Permanent cathodes are continuously circulated between the electrolytic tanks and removal station.
- Interval between removals is typically from one to seven days.

History – 2003 patent

Stripping Mechanism 2

Description of technology

- Metal to be produced is removed in plate-like sheets (typically over 5 mm thick) from surface of permanent cathodes.
- Grooves are produced in the metal plates to facilitate breaking and removal.

History — 2003 patent

Removal of Liquids

Molten Liquid Pumping Systems

Description of technology

- Pump pushes liquid reactants upward and out of the cell
- Submerged intake allows separation of two different fluids by adjusting device height
- Advantages: large volume transfer per unit time, less superheat required
- Types of pumping systems
  - Positive-displacement pressure pump
  - Centrifugal pump
  - Electromagnetic pump

Arrangement for two centrifugal pumps for transfer of electrolyte and molten metal

Removal of Liquids

Molten Liquid Pumping Systems
-electromagnetic pumps-

Arrangement for electromagnetic pump used in casting

Industrial electromagnetic pumps
(CMI Novacast Inc.)
Removal of Liquids

Molten Liquid Pumping Systems

- Technology application, scale and results
  - commonly used with Al, Mg, Zn and Pb molten alloys
  - size scaling is not a problem; e.g., one foundry has poured a 9,000 kg casting using a transfer pump
  - temperature scaling: centrifugal pump used to pump 72,600 kg molten Cu for 55 min

- Application of technology – high temperature electrowinning

- Limitations for application to lunar missions
  - for mechanical pumps - spare parts to be procured from earth
  - electromagnetic pumps have no moving parts but only good for metals
Removal of Liquids

Gravity Separation Systems

Description of technology

- pipes submerged in the reactants at levels appropriate for the two products
- removal of materials controlled by plugging the extraction pipes, or by translating the pipes vertically above the surface of the electrolyte
- acts as a level control mechanism
- filters could be used on metal extraction pipe to insure complete separation from electrolyte or oxide inclusions

History - technology will be specially designed for the current project

Limitations for application to lunar missions

- high viscosity of materials and low lunar gravity
Removal of Liquids

Pressurized Removal Systems

- Description of technology
  - Pressure is applied on top of the liquids in the cell to remove electrolyte and molten metal.
  - Pressure can be exercised either by the residual oxygen that is produced in the electrolytic cell, or by an inert gas to be pumped from outside.

- History – used for medium and large scale (tons/hr) molten metal transfer in foundries (see next slide).

- Limitations for application to lunar missions
  - Availability of a pressurizing gas (residual oxygen for production cells or external inert gas for small demonstration cells).
Removal of Liquids

Pressurized Removal System for Cast Iron

- operating temp. ~1450°C
- can operate for 24 hrs before stopping for stopper rod maintenance
- industrial records show operation times before relining of 10 to 24 months
- no technical size limitation
- pressure above molten iron establishes level of iron in furnace and discharge rate
Removal of Liquids

Pressurized Removal Systems for Cast Iron

25,000 lb pressure-pour furnace for cast iron

7,500 lb pressure-pour furnace for cast iron
(Waupaca foundry, WI)
Schematic Representation of the Demonstration Unit for Molten Materials Transfer and Handling from an Electrowinning cell.
CONCLUSIONS

The paper reviews the main issues associated with molten materials transfer and handling on the lunar surface during the operation of a high temperature electrowinning cell used to produce oxygen, with molten iron and silicon as byproducts.

A combination of existing technologies and purposely designed technologies show promise for lunar exploitation.

An important limitation that requires extensive investigation is the performance of refractory currently used for the purpose of molten metal containment and transfer in the lunar environment associated with electrolytic cells.

The principles of a laboratory scale unit at a scale equivalent to the production of 1 metric ton of oxygen per year are introduced. This implies a mass of molten materials to be transferred consistent with the equivalent of 1kg regolith/hr processed.
Back Up Slides
Production of \( \text{O}_2 \) from Lunar Regolith (1 kT \( \text{O}_2 \)/yr basis)

(From L.W. Mason, in Space 92, p.1139, ASCE (1992))
# Engineering with Lunar Elements

<table>
<thead>
<tr>
<th>Lunar Elements Only</th>
<th>Material Class</th>
<th>Lunar Elements Plus ~ 5% or Less Earth Imports</th>
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<tr>
<td><strong>High Capacity</strong></td>
<td><strong>Limited Capacity</strong></td>
<td><strong>High Capacity</strong></td>
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<tr>
<td><strong>Al</strong></td>
<td><strong>Mg</strong></td>
<td><strong>Fe</strong></td>
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<tr>
<td>Wt&amp;</td>
<td>1020</td>
<td>99.2</td>
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<tr>
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<td>1095</td>
<td>99</td>
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<tr>
<td>1060</td>
<td>1340</td>
<td>Ti-</td>
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<td>Mag</td>
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</table>

Waldin and Crisswell
# Engineering with Lunar Elements 2

<table>
<thead>
<tr>
<th>Material</th>
<th>Reinforced materials</th>
<th>Structural non metals</th>
<th>Electric / magnetic Materials</th>
<th>Conductors</th>
<th>Resistance alloys</th>
<th>Semi-conductors</th>
<th>Dielectrics / ins.</th>
<th>Magnetics</th>
<th>Electrodes</th>
<th>Abrasives</th>
<th>Fluid / Volatiles, Cryogenic ambient mp &lt; 500 CNaH</th>
<th>H2O (11%), H2O2 (6%), H2SO4, H2SO3, H3PO4</th>
<th>H2S (6%), H3P (9%), NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al2O3 in Al, Mg, Fe, Glass in Mg, Ti553 in Ti</td>
<td>Al2O3 in Ni SiO2 in Ni</td>
<td>Cr2O3, K2TiO3</td>
<td>Thermal materials, refractory, insulation, fibers</td>
<td>Fe, Al, Mg</td>
<td>Kanthal A-1</td>
<td>AlP, FeS2, NiO, CoO</td>
<td>Same as thermal except Ti553 (Ti5532) + titrates</td>
<td>Pemalloy</td>
<td>Pemendur Cr3</td>
<td>Fe3O4, TiO</td>
<td>Same as refractory except CaO + garnets</td>
<td>SO2, SO#, CrO3</td>
<td>Fluid / Volatiles, Cryogenic ambient mp &lt; 500 CNaH</td>
</tr>
<tr>
<td>Cast Basalt</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Si</td>
<td></td>
<td>Fe, Si—steels (M15, M5-8) Fe3O4, MgFe2O4, sendust</td>
<td></td>
<td></td>
<td>Fe3O4, TiO</td>
<td>Same as refractory except CaO + garnets</td>
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<tr>
<td>Dark Glass</td>
<td></td>
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<td>Fe3O4, TiO</td>
<td>Same as refractory except CaO + garnets</td>
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<td>H2O (11%), H2O2 (6%), H2SO4, H2SO3, H3PO4</td>
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<tr>
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<td>Fe3O4, TiO</td>
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<td>H2O (11%), H2O2 (6%), H2SO4, H2SO3, H3PO4</td>
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