Lecture on

- Magnesium energy cycle driven by solar energy
- Elemental technologies constituting the cycle
  - Mg combustion
  - Solar pumped laser
  - MgO reduction with laser ablation

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- Given by
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OUTLINE

1. Introduction - The Mg based energy circle
2. Basic principles and facilities
3. Influencing parameters and their effects
4. Summary
Clean energy cycle using laser MgO reduction

**Solar pumped laser**

- MgO produced from sea water
- MgO + Laser → Mg + O₂
- Efficiency ~50%

**Solar Collector**
- Efficiency: ~40%

**Laser Reduction**
- 4000K Reduction

**Energy delivery to customers**
- Mg + H₂O → MgO + H₂ + Energy
- H₂ + 0.5O₂ → H₂O + Energy

**Safety & Easy**
- Power generation using Mg Engine and Fuel Cells
- Energy using and Mg recycling

**CO₂ free cycling**

**Our interesting**

- Solar energy conversion
- Storage in Mg
The reason to use Mg as energy medium

**Mg is**

1. Readily available
2. Safe to handle, transport & storage below 650 °C
3. Comparatively light metal
4. Compact energy storage

### Reasons

**Density of various metals**

<table>
<thead>
<tr>
<th>Metal</th>
<th>ρ, g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>1.78</td>
</tr>
<tr>
<td>Al</td>
<td>2.7</td>
</tr>
<tr>
<td>Zn</td>
<td>7.13</td>
</tr>
<tr>
<td>Fe</td>
<td>7.87</td>
</tr>
</tbody>
</table>

**Energy content of various fuels**

<table>
<thead>
<tr>
<th>Metal/fuel</th>
<th>Energy/volume (GJ/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>34.85</td>
</tr>
<tr>
<td>Ethanol</td>
<td>23.6</td>
</tr>
<tr>
<td>H₂ liquid</td>
<td>4.3 (70MPa)</td>
</tr>
<tr>
<td>Mg</td>
<td>43</td>
</tr>
</tbody>
</table>

So, how to produce Mg?
High-efficiency laser utilization for Mg production

Conventional methods
70% of world Mg production

- Thermal reduction
  - \(2(CaO \cdot MgO) + Si = 2Mg + Ca_2SiO_4\)
  - \(MgO + C = Mg + CO\)

- High energy consumption, Pidgeon method, efficiency 5.5 mg/kJ
- Greenhouse gas CO₂ (42 kg)

- Electrolysis process
  - \(MgCl_2 = Mg + Cl_2\)

- Applicable only for Sea Water

Laser –induced MgO reduction

- Directivity
- Monochromaticity

Laser characteristics

- High density
- Energy

Mg-O dissociation

Energy

Mg generation

- MgCl₂ = Mg + Cl₂

- Energy efficiently utilized
- No greenhouse gas CO₂
MgO reduction systems, “Conventional” vs. “Laser”

**Conventional refining process**

MgO reduction at relatively low temperature and recovering Mg by condensation

FeSi/CaO/MgO

- Low vacuum
- Arc discharge
- Mg

1500°C

Condense

**“Laser refining scheme”**

- No catalysis, localized heating ⇒ Simple and compact reaction facility
- Rapid temperature drop suppresses MgO back reaction

MgO

- Low vacuum or Atmospheric
- Mg

Residual MgO

Condense

- Exhaust

Experiment in atmosphere

30% reduction of MgO has been observed

⇒ 24 ton/GWh

Target efficiency for working plant:

68 ton / GWh

Laser irradiation

Atmospheric, cw laser ~1 kW
Vapor properties: Vapor spreading under laser irradiance

Preheating: 100W, 0.5 sec
Irradiation: 1000W, 1 sec
Pressure: 1 atm air

CO₂ laser
MgO powder

Vapor front cools when collides with ambient gas.
Outline of MgO reduction analysis

**About the research:**

- **MgO Reduction**
  - Optimize the reduction process for industry application
  - Factors: Laser selection, focusing condition, ambient gas effect and Mg collection method, etc.

**Tools to analyze the MgO reduction process**

- Two parts in MgO reduction process
  - Laser Spot: Reduction, Equilibrium between molten MgO and its vapor
    - Gibbs free energy (reaction direction), Langmuir Formula (vaporation)
  - Vapor Plume: Dynamical recombination
    - Arrhenius equation (re-oxidization rate)
Evaluation of the Amount of Mg Generated by Laser heating

1. Laser irradiation

- ZnSe lens
- CO₂ laser
- Cu collector
- MgO
- Vacuum pump

2. Detection

- Deposit
- Collector

- H₂ detector
- HCl, 1 mol/l

3. Calculations

- Reduction efficiency = [Mg mol]/[MgO mol]

- Energy efficiency = [Mg mass]/[laser energy]

- Mg+2HCl → MgCl₂+H₂
- MgO+2HCl → MgCl₂+H₂O
Improve Mg production by control the process

Aim: Improve and promote MgO dissociation in equilibrium.

- Factors that control the reduction efficiency ($kg_{Mg}/J_{laser}$)
- Reduction Energy Efficiency, $\eta_{RE} = \text{Reduced Mg} / \text{Laser Energy Used}$

Control various parameters in following three steps:

3rd: Plume Deposition

2nd: Plume expansion

1st: Laser ablation

$\eta_{RE} = \text{Reduced Mg} / \text{Laser Energy Used}$
Controllable parameters in three steps

<table>
<thead>
<tr>
<th>Steps</th>
<th>Controllable parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser ablation</td>
<td>• Laser intensity, irradiation time, shot number, and incident beam angle.</td>
</tr>
<tr>
<td></td>
<td>• Target density, heat capacity, rotation speed, temperature.</td>
</tr>
<tr>
<td>Plume expansion</td>
<td>• Chamber ambient gas (species and pressure)</td>
</tr>
<tr>
<td></td>
<td>• Target to collector distance</td>
</tr>
<tr>
<td></td>
<td>• Plasma excitation</td>
</tr>
<tr>
<td></td>
<td>• Ejection of particulates</td>
</tr>
<tr>
<td>Plume deposition</td>
<td>• Collector (material, configuration, heat capacity, temperature, rotation, vertically-or-horizontal mounting, gas flow, and electrostatic filed.)</td>
</tr>
</tbody>
</table>

Aiming to industrial application
Elements of Reduction Efficiency, $\eta_{RE}$

- **Vaporization efficiency, $\eta_v$**
  - Vaporized MgO Rate / Laser Power
- **Stagnating Factor, $\eta_{Sg}$**
  - Actual Vap. Rate / Max Vap. Rate
- **Separation Efficiency, $\eta_{Sp}$**
  - Mg Density / Vapor Density
- **Deposition Efficiency, $\eta_D$**
  - Mg Deposition rate / Mg mass rate at the collector

$$\eta_{RE} = \eta_v \times \eta_{Sg} \times \eta_{Sp} \times \eta_D$$
Maximum Energy Storage Efficiency through MgO Reduction (Thermo Chemical Evaluation)

Exothermic

- $\text{MgO(s)}$
- $\text{Mg(g)(4000K)} + \text{O(g)(4000K)}$
- $-601.8 \text{ kJ/mol}$

Endothermic

- $\text{MgO(s)(273K), 1/2O_2(g)(273K)}$
- $1/2\text{O}_2(g)(4000K)$
- Heating
- Heating・Vaporization
- $\text{Mg(g)(923K)}$

Maximum Possible Energy Efficiency

$$\text{Energy Efficiency} = \frac{602}{602 + 478} = 56\%$$
Temperature for spontaneous MgO reduction

Change of Gibbs Free Energy of a Reaction

\[ \Delta G = \Delta H - T \Delta S \]

If the change is negative, the reaction is spontaneous

\( H \): Enthalpy
\( T \): Temperature
\( S \): Entropy

Equilibrium constant

\[ K = \exp\left(-\frac{\Delta G}{RT}\right) \]
Power Balance of MgO Vaporization

- $I_{\text{laser}} (10^4 \text{W/cm}^2) > I_{\text{vap}} (10^4 \text{W/cm}^2) + I_{\text{rad}} (2 \times 10^3 \text{W/cm}^2) + I_{\text{cond}} (10^3 \text{W/cm}^2)$
- $I_{\text{vap}}$ includes heat capacity ($0.9 \text{ J/K} \cdot \text{g}$), melting ($1.9 \text{ kJ/g}$), vaporization ($8.2 \text{ kJ/g}$), and dissociation ($9.2 \text{ kJ/g}$) energies of MgO. Heat conduction measured. Vaporization rate ($0.05 \text{ g/s}$) is measured.
- Solar radiation concentration limit, $10^3 \text{ W/cm}^2$
- Laser intensity will be required to maintain MgO reduction $> 100 \times$ Natural Sun Power
- Power Conversion rather than Beam Quality
Laser Intensity Dependence of Vaporization

- Laser intensity was changed by spot size while the total laser energy kept constant.
- This changes MgO temperature.
- Threshold laser intensity for MgO vaporization can be evaluated to be $1 \times 10^4$ W/cm$^2$.
- Because laser intensity balances with the vaporization intensity, the above intensity should equal to vaporizing intensity that corresponds to 3700 K.
Power Balance of Vaporizing MgO

- Over 3000 K, vaporizing intensity dominates the power balance and determines the temperature
- Only laser radiation can reach this high temperature and drive the MgO reduction
Why laser for MgO reduction?

- Need reducing-agent free process for an energy and resource economy cycle
- Over 3700 K gives spontaneous MgO reduction
- Also need to overcome radiation and evaporating power loss
  - Only extremely high intense laser radiation can satisfy the criteria

Let’s see the MgO vaporization rate under high power laser ablation.
Theoretical Analysis of MgO vaporization

• Maximum vaporization rate estimated by the Langmuir formula with the Clausius-Clapeyron equation

\[ \dot{m} = \frac{p(T)}{4} \sqrt{\frac{3M}{RT}} \]

- A: laser spot size, m: evaporating mass rate, p: vapor pressure, M: atomic mass, T: vapor temperature
- \( E_{vap} \): the specific latent, \( R \): specific gas constant

• Temperature should be known, it is measured experimentally.

• Compare theoretical value and experimental result, to evaluate \( \eta_v \)
Spectroscopic Measurements of MgO Temperature

**Setup**

**CO₂ laser**

\[ \lambda = 10.6 \, \mu m \]

Intensity \( \approx 10^5 \text{W/cm}^2 \)

**MgO target**

**Spectrometer**

**Laser** \( P = 1 \text{ atm.} \)

**High speed camera**

**Pin hole** \( \Phi 1.5 \)

**V exp. = 0.3 \text{ [m/s]}**

**V vapor = 6.5 \text{ [m/s]}**

**\( 1 \sim 2 \text{ [mm]} \)**

**\( \Phi 7 \text{ mm} \)**

**\( \Phi 20 \text{ mm} \)**

**20 mm**
**Results**

**CO₂ Laser (cw), 1kW, ~10⁵ W/cm², MgO powder**

Wien’s law: \( T = \frac{b}{\lambda_{\text{max}}} \), \( b=\text{constant}=2.898 \times 10^{-3} \) [m K]

Spot temperature \( \approx 5000 \) K \( > \) MgO dissociation temperature = 3700 K
MgO is the dominant species that determine the density and temperature of the vapor near the hot spot.

At 5000K, MgO vaporization pressure will determine the pressure and density near the vaporization region.

Graph: Saturated (Maximum) density of Mg and MgO at high temperature.

- **Mg**
- **MgO**

1 atm pressure

4 atm equivalent
Theory and Measurements
~ The evaporation efficiency, $\eta_V$

- The evaporation efficiency, $\eta_V$, has been measured, $5000 \text{ K}$
- The corresponding MgO vaporization rate estimated with the Langmuir formula, vaporization rate is $0.14 \text{ g/s}$
- Average vaporization rate has been experimentally measured, $0.05 \text{ g/s}$
- Vaporization measured in experiments is $\sim 36\%$ of the maximum vaporization rate
- $\Rightarrow$ The measured temperature is too hot? Or this comes from the uneven temperature distribution at the ablation spot.
It is expected that all the vaporized MgO will be reduced at this high temperature.

However, the results obtained in experiments showed that Mg is less than 10 mol %

Reason?

Mg-Oxygen recombination in the plume
MgO production is reduced by “Mg-Oxygen recombination”?

- Dynamical image of the convecting Mg-O vapor

Deoxidization efficiency of MgO has been stayed at a few molar percent (5 mol%), which was attributed to Mg recombination with oxygen.
Direct Evidence: Use of Silicon as an Oxygen Absorber

- The influence of re-oxidization on the Mg production can be observed by adding Si as an “oxygen absorber”

**Si-based agents, Si or SiO**
1. Abundant resource in the crust, 27.7%
2. Lower oxidation activation energy (112 kJ/mole) than Mg (167 kJ/mole)
3. Easily collect after using, in solid form.
4. Sunny desert contains great mount of sand & magnesium ore.

After adding Si reducing agent, \( \Delta G = 0 \) at \( T < 2500 \text{ K} \) reducing agent lower \( T \)

More Mg stay in its elemental form (Mg reoxidization is reduced)

Oxygen capture by Si atom

MgO dissociating region

MgO and Si vaporizing region

12.1 mg/kJ has been achieved.
Are there enough Si to absorb O?

- The density (vapor pressure, $P_{\text{vapor}}$) of each species can be calculated using “Clausius-Clapeyron Equation”

$$P_{\text{vapor}}(T) = \exp \left( \frac{E_{\text{vap}}}{R} \left( \frac{1}{T_{\text{boil}}} - \frac{1}{T} \right) \right)$$

- $E_{\text{vap}}$: Heat of vaporization
- $T_{\text{boil}}$: Boiling temperature

- Note that the Mg density is determined by MgO vapor pressure(density)

Si is expected to vaporize with a several times larger pressure than that of Mg

(one Si atom can capture two oxygen atoms)
Verification of the effect of oxygen absorber

Experiment condition

- Mixed target: MgO:Si=1:0.5
- Mixed target: MgO:SiO=1:0.4
- Pure MgO target

Pressure: 7 Pa
Laser intensity: Parameter

【Results】

Without Si

Mg energy efficiency = 0.13 mg/kJ

With Si

SiO: Mg energy efficiency = 4.1 mg/kJ
Si: Mg energy efficiency = 9.4 mg/kJ

- 70 times!!

Without Si

- With Si

SiO: Mg energy efficiency = 4.1 mg/kJ
Si: Mg energy efficiency = 9.4 mg/kJ

• Si-based agents could also be produced with laser reduction tech.
Comparing total energy efficiency (Laser process v.s. Pidgeon process)

<table>
<thead>
<tr>
<th>Process</th>
<th>Laser</th>
<th>Laser</th>
<th>Laser</th>
<th>Pidgeon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reducing agents</td>
<td>No</td>
<td>Si</td>
<td>SiO</td>
<td>Si(Fe)</td>
</tr>
<tr>
<td>Molar ratio (MgO:R)</td>
<td>-</td>
<td>1:0.3</td>
<td>1:0.3</td>
<td>1:1</td>
</tr>
<tr>
<td>Energy consumed in MgO reduction step, kJ/ mg Mg</td>
<td>1</td>
<td>0.083</td>
<td>0.222</td>
<td>0.192</td>
</tr>
<tr>
<td>Energy consumed in agents production step, kJ/ Mg</td>
<td>0</td>
<td>0.113</td>
<td>0.064</td>
<td>0.165</td>
</tr>
<tr>
<td>Total Mg energy efficiency, mg/kJ</td>
<td>1</td>
<td>3.6</td>
<td>3.5</td>
<td>2.8</td>
</tr>
<tr>
<td>CO₂ emission, kg/kg-Mg</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>42</td>
</tr>
</tbody>
</table>

Laser process yields better total Mg energy efficiency
Mg energy cycle with Si-based agent (Theoretical value v.s. Current experimental value)

Sahara desert: Sunlight: 8 hours

8km²
8 billion-watt × 8h
Energy Con. Effi.
Theory: 40%
Experiment: 2%

2.4 billion-watt × 8h
Energy Conv. Effi.
Theory: 50%
Experiment: 13%

MgO + Si

Improvement (2% → 40%)
The development of solar pumped laser is in progress: Goal: 40%

Future improvement (12% → 50%)
Si-agents production step
MgO reduction step
Integrate to Single process

Goal:
Ecofreindly & High throughout

Goal:
Ecofreindly & High throughout

Goal:
Ecofreindly & High throughout

Mg
Goal: 40% × 50% ≈ 20% = 500 tons
Now: 2% × 13% ≈ 0.26% = 65 tons
Other ways to suppress Mg re-oxidation?

• Si is effective to improve Mg production efficiency, but...
  – Preparing Si require additional energy, cost and Si reduction technology.
• Are there other ways to resolve the problem?
• Take a look at the Arrhenius Equation for Mg recombination.

\[
Mg_{(g)} + O_{2(g)} \rightarrow MgO_{(s, l, g)}
\]

The reaction rate:
\[
R_{Mg} = k_0 \exp\left(-\frac{E_a}{RT}\right)P_{Mg}P_{O_2}
\]

- \(R_{Mg}\): recombination rate of Mg
- \(P_{O_2}\) and \(P_{Mg}\): pressure of O₂ and Mg
- \(T\): vapor temperature
- \(E_a\): activation energy
- \(K_o\): Arrhensius constant
- \(R\): gas constant

Temperature is a crucial factor of this reaction
Temperature control exhibits a strong influence over re-oxidation.

- Only a factor-of-two temperature control results in a many orders of magnitude reduction of recombination rate.

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Arrhenius Type (Re-oxidation) Reaction Rate

\[
\frac{dN_{\text{reco}}}{dt} = k \exp\left( -\frac{E_a}{RT}\right) N_{\text{reco}} N_{\text{O}_2}
\]

\[k=5 \times 10^5 \text{ [m}^3/(\text{s mol})]\]

\[E_a=167 \text{ [kJ/mol]}\]
Vapor properties: Effects of ambient gas molecular

Evidence of vapor cooling under ambient gas

- **Air ambient**
  - Vapor emits visible radiation
  - Expands like a jet.
  - More Collision

- **7 Pa**
  - No emission observed
  - Expand radically.
  - Less Collision
  - Hot gas emits radiation only when it cools down.

### Atmospheric pressure

- **t=1ms, 20 ms, 30 ms, 490 ms**
- Particle ejection
- Evaporation
- Particle ejection time $\approx 0.02$ s

### Effects of cooling gas

- More Collision
- Evaporation
Assist Gas Effects

• Removal of Mg and O atoms out of vaporizing region
• Cooling Mg atoms to form metal Mg before recombining with O
• Separation of Mg and O
Input inert gases, use valve to control gas flow rate.
EPMA experiment to get the elemental ratio, Mg fraction: about 5 wt%. The error of this estimation is majorly comes from the micro-sample selection.
Effects of Gas Flow on Vapor Removal

- Gas flow rate: $7 \times 10^{-5}$ to $2 \times 10^{-4}$ mol/s

Speed up vaporization rate
Inert Gases Effects comparison

Inlet of He gas leads to better energy efficiency
Cooling Rate: Effects of Collision Frequency

Calculation of the collision frequency between Mg, O, He & Ar atoms from

\[ f \left[ \frac{m^3}{s \cdot mol} \right]^* = N_A \sigma_{AB} \sqrt{\frac{8k_BT}{\pi \mu_{AB}}} \]

where

\( N_A \) is Avogadro's number,
\( \sigma_{AB} \) is the collision cross section \([= \pi d_{AB}^2, d_{AB} = r_A + r_B, r_A, r_B \) the radius of atoms A and B\],
\( k_B \) is Boltzmann’s constant \(1.38 \times 10^{-23} \) J/K,
\( \mu_{AB} \) is the reduced mass of reactants \([= m_A m_B / (m_A + m_B)]\), and
\( T \) is the temperature (measured = 1400 K at height 10 mm).

*One has to multiply this value by mole density

<table>
<thead>
<tr>
<th></th>
<th>Mg-O</th>
<th>Mg-He</th>
<th>Mg-Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f )</td>
<td>(3.4 \times 10^6)</td>
<td>(7.9 \times 10^6)</td>
<td>(4.1 \times 10^6)</td>
</tr>
</tbody>
</table>

Collision frequency for \((Mg-He)\) is higher than Ar’s

- Thermal conductivity
  - \(K_{He} = 0.14 \) W/m K
  - \(K_{Ar} = 0.016 \) W/m K

More collision  
Faster cooling

\(He\) gas is recommended as cooling/ carrying gas
Chamber Pressure: 7 Pa
CO\(_2\) laser: 1.28 \times 10^5 \text{ W/cm}^2
Irradiation time: 1 second
Shot number: 3 shots
Cu plate height: 4-20 mm

**Setup:**

- CO\(_2\) laser
- Lens
- Cu plate
- MgO
- Motor
- Vacuum
- 30°

**Results:**

- Max. Mg fraction = 3.1 mol%  
- Max. Energy efficiency = 0.5 mg/kJ  

**Graph:**

- Magnesium fraction
- Energy efficiency

**X-axis:** Copper plate height, mm

**Y-axis:** Magnesium fraction, mol%

**Energy efficiency, mg/kJ**

0.6
0.5
0.4
0.3
0.2
0.1
0
0
5
10
15
20
25

Max. Mg fraction = 3.1 mol%
Max. Energy efficiency = 0.5 mg/kJ
Summary of MgO Reduction

• Analysis of Laser heated MgO vaporization and resulting dissociation/recombination reactions needs both equilibrium and dynamical modeling
  – **Equilibrium**: Gibbs energy analysis
  – **Dynamics**: Arrhenius reaction rate analysis

• MgO can be reduced by focused laser radiation without reducing agents
• $>10^4$ W/cm$^2$ laser intensity vaporizes and dissociates MgO
• Assist gas is needed for cooling Mg vapor and separating them from O atoms
• Inert gases such as He and Ar are effective to improve reduction efficiency
Future research

Find a method on real-time detecting the Mg density profile in the vapor plume.

- Mg Re-oxidization is the dominant mechanism that result in low efficiency.
- A Mg density detection method is needed to get such information at different altitude in the plume.
- Laser absorption spectroscopy experiment is a promising solution.
- Detection of Mg laser absorption hasn’t been conducted mainly because of its deep ultraviolet absorption line.
- Besides, a heating pipe is firstly designed for calibrating the relation between laser absorption fraction and the absolute Mg density.
Thank you!