A ceria based conversion coating on squeeze cast Mg- 4wt. %Y alloy for improved corrosion resistance in 0.1 M NaCl solution

Presented by
Partha Saha *, Meeta Kamde and Yogendra Mahton

Department of Ceramic Engineering
National Institute of Technology Rourkela
Odisha-769008, India
Why magnesium...???

- **Magnesium (Mg)** is the 6th most abundant element and the **lightest structural material** present on the Earth’s surface.

- It has **high specific strength, excellent damping capabilities, good castability, excellent machinability, good electromagnetic shielding**, and **recyclability**.

- However, Mg has poor **high temperature mechanical properties (creep)** and limited **salt-water corrosion resistance**, which decreases its widespread application in engineering materials.

**Applications**

- Aerospace application
- Magnesium side panel
- Phone bodies
- Gearbox housing
- Alloyed wheel

Mg alloys are extremely susceptible to galvanic corrosion, which can cause severe pitting in the metal resulting in decreased mechanical stability.

Thermodynamically Mg is very active and prone to oxidation, standard Gibbs free energy ($\Delta G^0$) for the following oxidation reactions are negative.

\[
\begin{align*}
\text{Mg}^{2+} + 2\text{OH}^- & = \text{Mg(OH)}_2, \quad (\Delta G^0) = -833 \text{ kJ/mol} \quad \text{(1)} \\
\text{Mg} + \frac{1}{2} \text{O}_2 & = \text{MgO}, \quad (\Delta G^0) = -569 \text{ kJ/mol} \quad \text{(2)} \\
\text{Mg} + 2\text{H}_2\text{O} & = \text{Mg(OH)}_2 + \text{H}_2, \quad (\Delta G^0) = -359 \text{ kJ/mol} \quad \text{(3)}
\end{align*}
\]

Prevention of corrosion in magnesium

- Alloying additions
- Keeping the impurities below tolerance level
- Electrodeposition methods
- Conversion and/or electrophoretic coatings
- Anodization of Mg alloys

E–pH diagram with possible stable substances in a Mg–H$_2$O electrochemical system.

Objectives

- Development of Mg based alloys using Y as alloying addition within their permissible maximum solid solubility limits by squeeze casting.

- Determine the microstructures and mechanical properties.

- Perform Cerium conversion coating (CeCC) on Mg-4wt.%Y samples for different time periods.

- Examine the influence of surface films formed on Mg alloys by open-circuit corrosion in 0.1 molar NaCl solution by electrochemical and immersion corrosion methods.

- Perform XRD, SEM/EDS on the samples to determine mechanical properties before and after salt-water corrosion to monitor the growth processes of surface films during open-circuit corrosion and the subsequent polarization experiment in 0.1 molar NaCl solutions.
Experimental procedure

Mg-4.0 wt.% alloy was developed using a bottom pouring type stir casting furnace with squeeze casting setup (Swamequip, Chennai, India)

Materials used

99.99% Pure Magnesium ingot (Minex Metallurgical Ltd. Pune)
Mg-30 wt.% Y master alloy (China Human High Board Materials)

- Preheating of furnace to 750°C
- Addition of Pure Magnesium ingot and Mg-30 wt.% Yttrium master alloy
- Complete melting of both the ingots
- Flow of Ar and SF₆ gas mixture
- Melt stirring at 750°C
- Pouring of melt in the mould
- Application of squeeze pressure

- Squeeze casting set-up combines the advantages of casting and forging process.
- Prevention of gas and shrinkage due to rapid solidification by pressure applied.
- Offers fine microstructures with higher strength components.
Flow chart of CeCC on Magnesium specimen

Samples were cut into 10 mm x 10 mm x 2 mm dimension and polished with 320 and 1200 grit SiC paper

Polished samples were cleaned ultrasonically with propanol & rinsed with DI water & dried at room temperature

Cleaned samples were coated with 0.05 M Ce(NO₃)₃.6H₂O and 0.254 M H₂O₂ at room temperature with pH=2.9 (For time- 30, 60, 120 and 1800 s)

Coated samples were then post-treated in 2.5 wt.% NaH₂PO₄ aqueous solution for 5 minutes at 85 °C

CeCC on Mg-4Y samples for 30, 60, 120 and 1800s
XRD analysis of CeCC on Mg-4Y samples

The base metal peaks appeared at high intensity along with the low intensity peaks of CeO$_2$ and Mg(OH)$_2$ confirming the presence of CeO$_2$ deposition on the base metal.
ATR-FTIR plots of CeCC on Mg-4Y samples

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Functional groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>617</td>
<td>Stretching vibration of Ce-O band</td>
</tr>
<tr>
<td>1034</td>
<td>Stretching band of C-O</td>
</tr>
<tr>
<td>1500</td>
<td>Mg-O</td>
</tr>
<tr>
<td>2340</td>
<td>C-H stretching vibration</td>
</tr>
<tr>
<td>3357</td>
<td>OH stretching vibration peak</td>
</tr>
<tr>
<td>3738</td>
<td>Stretching vibration of hydroxyl group</td>
</tr>
</tbody>
</table>

Presence of CeO₂ and Mg(OH)₂ has been validated with functional groups
Microstructure and morphology of CeCC on Mg-4Y alloy

CeCC for 30 s

CeCC for 60 s

CeCC for 120 s

CeCC for 1800 s
Surface chemical composition of CeCC on Mg-4 wt.% Y alloy

The amount of nitrogen was negligible with marginal lowering of Yttrium content throughout the coating duration. In addition, the amounts of Oxygen and Cerium were increasing with the increasing coating duration.

Furthermore, the amount of Mg gradually decreased as the coating duration was increased from 30s to 300s confirms the progressive growth of CeCC.
Surface roughness and coating thickness of CeCC

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Surface roughness (μm)</th>
<th>CeCC thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-4Y_30s</td>
<td>0.13 ± 0.01</td>
<td>1.30 ± 0.001</td>
</tr>
<tr>
<td>Mg-4Y_60s</td>
<td>0.32 ± 0.09</td>
<td>0.73 ± 0.06</td>
</tr>
<tr>
<td>Mg-4Y_120s</td>
<td>0.34 ± 0.18</td>
<td>1.03 ± 0.15</td>
</tr>
<tr>
<td>Mg-4Y_1800s</td>
<td>1.22 ± 0.03</td>
<td>4.20 ± 0.54</td>
</tr>
</tbody>
</table>

The coating thickness was found minimum in Mg-4Y_60s and maximum for Mg-4Y_1800s sample.
Corrosion Testing

**Immersion test**
The immersion corrosion test were performed on both the bare and CeCC Mg-4Y samples, taking specimens of $10 \times 10 \times 2 \text{ mm}^3$, and immersed in a 0.1 M NaCl solution at 25°C for 8h. The change of pH was recorded after each hour with a standard pH-meter. The samples after immersion were cleaned using a solution having (20% Cr$_2$O$_3$ + 1% AgNO$_3$) to remove the corrosion products. From the weight difference of the samples before and after corrosion, the corrosion rate was calculated.
pH and corrosion rate obtained after static immersion in 0.1 M NaCl for 8 h

- The corrosion rate was calculated according to ASTM G 31-72. Mg-4Y_bare samples showed maximum corrosion rate whereas Mg-4Y_30 s samples showed the minimum corrosion rates implying that the CeCC helped in reducing corrosion in Mg alloys.

- With increasing immersion time, the pH increased towards the basic nature, and Mg-4Y_1800s sample showed highest increase in pH and Mg-4Y_bare and Mg-4Y_30s samples showed minimum increase in pH values.
The XRD patterns showed high intensity base metal peaks along with the low intensity peaks of CeO$_2$ confirming the presence of CeO$_2$ deposition on the base metal surface with the formation of oxides (MgO and Mg(OH)$_2$) on Mg after corrosion.
Morphology of the corroded samples after post immersion test in 0.1 M NaCl

For the bare Mg-4Y sample, corrosion pits were formed with adjoining boundaries on the surface. For the CeCC samples some sunken places appeared and tiny crevices in the film.

For the Mg-4Y_30s samples, crevices appeared but as the CeCC duration increased the crevices aggressively started penetrating in the alloy underneath and started forming deep corrosion pits.

Note: Samples were cleaned with the solution containing 20% CrO$_3$ and 1% AgNO$_3$ after the immersion test.
Ce$^{3+}$ + 2H$_2$O = Ce(OH)$_2^{2-}$ + 2H$^+$ + e$^-$  

..........(1)

H$_2$O$_2$ + 2e$^-$ = 2(OH)$^-$  

..........(2)

Reaction (1) and (2) combines to give the following reaction as

2Ce$^{3+}$ + 2H$_2$O + H$_2$O$_2$ = 2Ce(OH)$_2^{2+}$ + 2H$^+$  

..........(3)

In the solution comprising Ce/H$_2$O$_2$, the alloys when immersed in the ~2.9 pH solution, accompanying the dissolution, there also occurs reduction of protons in the acidic solution. Once the interfacial pH is high enough, the 2Ce(OH)$_2^{2+}$ species precipitates as CeO$_2$ as given in the following reaction

2Ce(OH)$_2^{2+}$ = CeO$_2$ + 2H$^+$  

..........(4)
Conclusions

Mg-4 wt.% Y alloy was developed using the bottom pouring squeeze casting set-up.

XRD pattern and EDX confirmed the presence of $\alpha$-Mg and $\text{Mg}_{24}\text{Y}_5$ phases in the casted alloy.

The samples of the ingots were coated using the CeCC for different time periods of 30s, 60s, 120s and 1800s.

FESEM-EDX revealed that the Cerium concentration increased with the coating duration and also the coating had been locally damaged with several dry-mud like crisscrossed cracks.

CeCC for 30s demonstrated improved corrosion resistance than the bare and other CeCC coated samples for longer duration during immersion and electrochemical corrosion test.
Reference

Thank you