Flame-resistant Magnesium Alloys with High Strength

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13:30 to 14:00 (30 min.), December 3, 2013.
Contents of My Talk

1. Magnesium Alloys and their Major Problems

2. *KUMADA/I*Mg Alloys

3. *KUMADA/RS P/M* Mg Alloys

4. FAA-Flammability Tests of *KUMADA/Mg Alloys*

5. Spreading Effects and Future Challenges
What is Magnesium?

Magnesium is a promising sustainable metal in the 21st century.

Advantages of Magnesium

**Lightweight**
- Mg
- Al
- Fe

**Resourceful**
- Practical metals in the earth’s crust
  1. Si
  2. Al
  3. Fe
  4. Mg

**Green**
- Metals in human body
  1. Ca
  2. K
  3. Na
  4. Mg

**Recyclability**
- Low melting temperature

Kumamoto University
Advantage of Magnesium Alloys as Structural Materials

- Magnesium alloys have the highest specific stiffness among metallic materials.

**Weight of bar with the same stiffness**

The elastic deflection of a beam loaded at its center:

\[
\delta = \frac{FL^3}{48EI}
\]

\[
I = \frac{BH^3}{12}
\]

- **Normalized weight of bar with the same stiffness**
  - Mg alloys
  - Al alloys
  - Ti alloys
  - Steel

![Graph showing normalized weight comparison between Mg alloys, Al alloys, Ti alloys, and Steel.](image)
Major Problems to Solve in Magnesium Alloys

- Mechanical strength of magnesium alloys is inferior as compared with aluminum alloys.

Low mechanical strength
Low ignition temperature
Low corrosion resistance

Diagram showing tensile yield strength, $\sigma_{0.2}$/MPa, for different commercial alloys: 2017-T4, 2024-T6, 7075-T6, AZ31B, AZ61A-F, ZK60A-T5.
Major Problems to Solve in Magnesium Alloys

- The ignition temperature of magnesium alloys is low, resulting in flammable material.

Low mechanical strength

Low ignition temperature

Low corrosion resistance

Fire and Its Spread at Mg-recycling Factory
(Japan, May 22nd, 2012)

Fire fighting was restricted because the discharge of water or extinguisher brings out hydrogen explosion. It took one week to die down the fire of 200 tons Mg scraps.
The corrosion resistance of magnesium alloys is much lower than that of aluminum alloys.

Major Problems to Solve in Magnesium Alloys

- Low mechanical strength
- Low ignition temperature
- Low corrosion resistance
Contents of My Talk

1. Magnesium Alloys and their Major Problems
2. KUMADA\textregistered I/M Mg Alloys
3. KUMADA\textregistered RS P/M Mg Alloys
4. FAA-Flammability Tests of KUMADA\textregistered Mg Alloys
5. Spreading Effects and Future Challenges
Two kinds of KUMADAI Mg alloys have solved the major problems in Mg alloys, resulting in an innovation.

Solve the Major Problems in Magnesium Alloys

We have developed new magnesium alloys with high ignition temperature, high strength, good corrosion resistance.

(1) KUMADAI Heat-resistant Mg Alloy
(2) KUMADAI Non-flammable Mg Alloy
**Alloy Compositions of KUMADAI Heat-resistant Alloys**

- **KUMADAI** heat-resistant Mg alloys are Mg-TM-RE system, in which TM is Co, Ni, Cu or Zn, and RE is Y, Gd, Tb, Dy, Ho, Er or Tm.
- The combination of TM and RE has some roles in crystal structure, atomic radius, mixing enthalpy and solid solubility limit.

**Mg–TM–RE**

<table>
<thead>
<tr>
<th>TM:</th>
<th>Co, Ni, Cu, Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>RE:</td>
<td>Y, Gd, Tb, Dy, Ho, Er, Tm</td>
</tr>
</tbody>
</table>

**periodic table of elements**

- $-22\% \leq 100(r_{TM}r_{Mg})/r_{Mg} \leq -17\%$
- $11\% \leq 100(r_{RE}-r_{Mg})/r_{Mg} \leq 12\%$
- $-31\text{kJ/mol} \leq \Delta H_{\text{mix}}^{\text{TM-RE}} \leq -22\text{kJ/mol}$

*Y. Kawanura et al.: Mater. Trans., 2007*
Microstructure of KUMADAI Heat-resistant Alloys

- KUMADAI heat-resistant Mg alloys are duplex of $\alpha$-Mg phase and LPSO phase, and are strengthened by LPSO phase.
- LPSO phase has a novel LPSO structure, where stacking and chemical modulations are synchronized.

Microstructure of as-cast $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ (at%) alloy

Synchronized LPSO Structure

Stacking and chemical modulations are synchronized in LPSO structure
Mechanical strength of *KUMADAI* heat-resistant Mg alloys is improved drastically by plastic deformation with keeping the elongation. The improvement of mechanical properties is due to kind-band formation of LPSO phase and grain refinement of $\alpha$-Mg matrix.

![Graph showing stress-strain behavior of extruded and as-cast Mg alloys](image-url)

**Extruded**
- $R=10$, $T_e=623K$
- $\sigma_{0.2}=375$ MPa
- $\delta=4.0\%$

**As-cast**
- $\sigma_{0.2}=120$ MPa
- $\delta=4.0\%$

![LPSO Phase](image-url)

![Kink band](image-url)

![$\alpha$-Mg Phase](image-url)
KUMADAI non-flammable Mg alloys are Mg-Al-Ca system with high Al and Ca contents.

**Mg-Al-Ca**

- Al: 8.0~11.0 at%
- Ca: 4.0~6.5 at%

KUMADAI Non-flammable alloys

Ordinary Mg-Al-Ca alloys
KUMADA|I non-flammable Mg alloys are duplex of $\alpha$-Mg phase and C36-type intermetallic compound (IMC).

Microstructure of As-cast KUMADA|I Non-flammable Alloys

Microstructure of Mg$_{85}$Al$_{10}$Ca$_{5}$ (at%) alloy

Eutectic Structure of C36-type IMC/$\alpha$-Mg

C36 structure

$(\text{Mg, Al})_2\text{Ca}$

Hexagonal laves phase
Microstructure of Extruded KUMADAI Non-flammable Alloys

C36-type intermetallic compound (IMC) is finely dispersed by extrusion, resulting in high strength and reasonable ductility.

Microstructure of Extruded Mg\textsubscript{85}Al\textsubscript{10}Ca\textsubscript{5} (at\%\%) alloy

SEM

TEM

C36-type IMC-dispersed band

fine C36-type IMC

Extrusion direction

20 µm

500 nm
KUMADA/M Mg alloys have superior yield strength to high strength Al alloys.
KUMADA I/M Mg alloys have similar corrosion resistance to commercial Mg alloy (AZ31).
**High Ignition Temperature of KUMADAI I/M Mg Alloys**

**KUMADAI I/M Mg alloys have higher ignition temperature than flame-resistant Mg alloys containing Ca, CaO, or Ca+Y.**

**Chip Heating Method**

- 470 ~ 550°C
- 620 ~ 810°C
- 780 ~ 940°C
- 1,050 ~ 1,100°C

※ obtained by B. S. You (KIMS)

**Ignition Temperature**

- **T_i**, in °C

**Furnace temp.: 1000°C**

0.1g chip (as-cast)

**T_i (pure Mg)**

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**Commercial alloys**

- Ca-added alloys
- CaO-added alloys
- (Y + Ca)-added alloys

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**flame-resistant Mg alloys**
KUMADAI non-flammable I/M Mg alloy did not burn up to 1,117°C that is higher than its boiling point (1,065°C).

Ignition Test of Molten Alloys with 700°C

Burning Test by Acetylene Torch
1. Magnesium Alloys and their Major Problems

2. KUMADA\textregistered I/M Mg Alloys

3. KUMADA\textregistered RS P/M Mg Alloys

4. FAA–Flammability Tests of KUMADA\textregistered Mg Alloys

5. Spreading Effects and Future Challenges
Effects of Rapidly Solidified Powder Metallurgy Processing

RS P/M processing brings out 1.6-fold yield strength, 10-fold corrosion resistance and superplasticity of KUMADAII heat-resistant Mg alloys.
KUMADAi heat-resistant RS P/M Mg alloys have high yield strength above 530 MPa and reasonable elongation above 8 %. Its specific tensile yield strength is approximately 1.7 times as high as that of 7075-T6.

![Graph showing mechanical properties of KUMADAi alloys](image)

- **KUMADAi heat-resistant RS P/M Mg alloys (ϕ18 mm)**

  - **Mg$_{97}$Zn$_1$Y$_2$**
    - $\sigma_{0.2}=562$ MPa
    - $\delta=8.0\%$

  - **Mg$_{96.75}$Zn$_{0.75}$Y$_2$Al$_{0.5}$**
    - $\sigma_{0.2}=533$ MPa
    - $\delta=10.6\%$

- Ordinary RS P/M Mg Alloys

- Comparative graph showing specific yield strength of different alloys: KUMADAi, 7075-T6, ZK60A-T5, Ti-6Al-4V.
Corrosion resistance of *KUMADAI* heat-resistant RS P/M Mg alloys is approximately 1.8 times as high as that of 7075-T6.

**Corrosion Rate**

- Mg$_{97}$Zn$_1$Y$_2$ alloy: 0.230 mm/year
- Mg$_{96.75}$Zn$_{0.75}$Y$_2$Al$_{0.5}$ alloy: 0.160 mm/year
- Extra-super duralumin (7075-T6): 0.285 mm/year
Comparison of Performances with 7075-T6

*KUMADA* heat-resistant RS P/M Mg<sub>96.75</sub>Zn<sub>0.75</sub>Y<sub>2</sub>Al<sub>0.5</sub> alloy has superior mechanical and corrosion properties to 7075-T6.

<table>
<thead>
<tr>
<th></th>
<th>RS P/M KUMADA* Heat-resistant Mg Alloy (Mg&lt;sub&gt;96.75&lt;/sub&gt;Zn&lt;sub&gt;0.75&lt;/sub&gt;Y&lt;sub&gt;2&lt;/sub&gt;Al&lt;sub&gt;0.5&lt;/sub&gt;)</th>
<th>I/M Extra Super Duralumin (7075-T6)</th>
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<tbody>
<tr>
<td>Tensile Properties</td>
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<td></td>
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<tr>
<td>Yield Strength</td>
<td>533 MPa</td>
<td>505 MPa</td>
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<tr>
<td>Elongation</td>
<td>10.6 %</td>
<td>11 %</td>
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<tr>
<td>Fatigue Property</td>
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<tr>
<td>Fatigue Strength at 10&lt;sup&gt;7&lt;/sup&gt; cycles</td>
<td>325 MPa</td>
<td>275 MPa</td>
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<tr>
<td>Corrosion Property</td>
<td></td>
<td></td>
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<tr>
<td>Corrosion Rate</td>
<td>0.160 mm/year</td>
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2. *KUMADA*/ I/M Mg Alloys

3. *KUMADA*/ RS P/M Mg Alloys

4. FAA–Flammability Tests of *KUMADA*/ Mg Alloys

5. Spreading Effects and Future Challenges
FAA—Developing Flammability Test Method

FAA standard for flammability test is developing on the assumption that Mg alloys burn.


Results of FAA Flammability Test on **KUMADAi** Mg Alloys

KUMADAi heat-resistant alloy and KUMADAi non-flammable Mg alloy passed the test very easily, with essentially no burning at all.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Melt</th>
<th>Ignition</th>
<th>Bar Begins to Burn</th>
<th>Residence Begins to Burn</th>
<th>Burner Off</th>
<th>Bar Out</th>
<th>Residence Out</th>
<th>Total Bar Burn Duration (Sec)</th>
<th>Total Residence Burn Duration (Sec)</th>
<th>Sample Total Burn Duration (Sec)</th>
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</thead>
<tbody>
<tr>
<td>KUMADAi Non-Flammability Alloy-1</td>
<td>108</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>240</td>
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<td>—</td>
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<td>KUMADAi Non-Flammability Alloy-2</td>
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<tr>
<td>KUMADAi Non-Flammability Alloy-3</td>
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<tr>
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<tr>
<td>KUMADAi Heat-Resistant Alloy-1</td>
<td>113</td>
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<td>—</td>
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<td>240</td>
<td>—</td>
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<tr>
<td>KUMADAi Heat-Resistant Alloy-2</td>
<td>118</td>
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<td>—</td>
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<td>240</td>
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<tr>
<td>KUMADAi Heat-Resistant Alloy-3</td>
<td>116</td>
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<td>—</td>
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<td>240</td>
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<tr>
<td>KUMADAi Heat-Resistant Alloy-4</td>
<td>122</td>
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<td>—</td>
<td>—</td>
<td>240</td>
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<td>—</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>KUMADAi Heat-Resistant Alloy-5</td>
<td>120</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>240</td>
<td>—</td>
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</table>

**KUMADAi** non-flammable I/M alloy

**KUMADAi** heat-resistant I/M alloy
KUMADA heat-resistant alloy and KUMADA non-flammable Mg alloy passed the test very easily, with essentially no burning at all.

Photographs of Samples After FAA Flammability Tests

KUMADA heat-resistant I/M Mg alloy

KUMADA non-flammable I/M Mg alloy

residue
1. Magnesium Alloys and their Major Problems
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5. Spreading Effects and Future Challenges
Development Schedule of Large-scale KUMADAI Mg Alloys

Enlargement Technology of KUMADAI Mg alloys is steadily developed.
1) Expansion of application to the areas that cannot tolerate ignition of material

2) Large reduction in greenhouse gas emission

3) Enhancing safety of melting, casting, machining, and welding process

4) Cost reduction by non-use of cover gas and enhanced safety during operation
1) R&D for achieving increased performance of *KUMADAI* Mg alloys.

2) Development of manufacturing-base technology to enable producing large *KUMADAI* Mg alloys (plate, bar, tube, sheet).

3) Development of applications by provision of prototypes made by *KUMADAI* Mg alloys.
We have developed **KUMADA**/heat-resistant I/M Mg-TM-RE alloys, which are strengthened by LPSO phase.
- high mechanical strength ($\sigma_{0.2}$ of 350~400 MPa at RT)
- high heat-resistance ($\sigma_{0.2}$ of 300~350 MPa at 200°C)
- high ignition temperature (780~940°C)
- good corrosion resistance (AZ31 level)

We have developed **KUMADA**/non-flammable I/M Mg-Al-Ca alloys, which are strengthened by C36-type IMC.
- high mechanical strength ($\sigma_{0.2}$ of 410~460 MPa at RT)
- high ignition temperature ($1,050~1,100°C$)
- good corrosion resistance (AZ31 level)

We have developed **KUMADA**/heat-resistant RS P/M Mg-Zn-Y alloys, which are strengthened by LPSO phase.
- high mechanical strength ($\sigma_{0.2}$ of 530~610 MPa at RT)
- high heat-resistance ($\sigma_{0.2}$ of 380 MPa at 200°C)
- high ignition temperature (780~940°C)
- high corrosion resistance (twice of 7075-T6)
- high workability (high-strain-rate superplasticity)

**KUMADA**/heat-resistant Mg alloy and **KUMADA**/non-flammable Mg alloy have passed the FAA Flammability Test very easily, with essentially no burning at all.
Thank you for your attention