Aluminium and its alloys

Subjects of interest

- Why aluminium alloys?
- Production of aluminium
- Physical metallurgy of aluminium alloys
- Heat treatments of aluminium alloys
- Corrosion in aluminium alloys
- Mechanical properties of aluminium alloys
- Corrosion resistance of aluminium alloys
- Classification of aluminium alloys
- Wrought aluminium alloys
- Cast aluminium alloys
Objectives

• This chapter provides fundamental knowledge of different methods of productions / heat treatments of aluminium alloys and the use of various types of cast and wrought aluminium alloys.

• The influences of alloy composition, microstructure and heat treatment on chemical and mechanical properties of aluminium alloys will be discussed in relation to its applications.
Introduction - Why aluminium alloys?

• Abundant element of 8% on earth crust and normally found in oxide forms \((\text{Al}_2\text{O}_3)\), i.e., bauxite, kaolinite, nepheline and alunite.
• Found in United states, Italy, France.
• Have not been found in Thailand but in Malaysia, Vietnam.

Bauxite with penny  
Bauxite-pebbly  
Kaolinite

http://www.galleries.com
Introduction - Why aluminium alloys?

- High corrosion resistance
- Excellent machining properties
- Light weight
- High thermal/electrical conductivity
- High ductility/easily deformable

Comparison of Al and steel

Attractive properties

http://ngdir.ir/minemineral
Applications for aluminium alloys

Construction & Equipment

Containers & Packaging

Automotives

Aerospace

Suranaree University of Technology

Tapany Udomphol

May-Aug 2007
Production of Aluminium

**France 1855:** • H. Sainte-Claire Deville first reduced aluminium chloride with sodium.

**Austria 1888:** • Karl Josef Bayer first patented the **Bayer process** (digesting crushed bauxite in strong sodium hydroxide solution at temperatures up to 240°C).

**Germany:** • Hall-Héroult introduced **Hall-Héroult process** by dissolving the alumina in molten cryolite \( \text{Na}_3\text{AlF}_6 \).

**United States 1976:** • Alcoa commenced a **chloride-based smelting process** using alumina combined with chloride.
Extraction of aluminium

Aluminium can be extracted from bauxite, Kaolinite or nepheline.

**Bauxite:**
- 30-50% Alumina ($\text{Al}_2\text{O}_3$)
- 3-13% Silica ($\text{SiO}_2$)
- 10-18% Titanium oxide ($\text{TiO}_2$)
- Balanced water ($\text{H}_2\text{O}$)

**Kaolinite**
- 30-32% Alumina ($\text{Al}_2\text{O}_3$)
- Balanced Silica ($\text{SiO}_2$) and water ($\text{H}_2\text{O}$)

**Nepheline**
- 30% Alumina ($\text{Al}_2\text{O}_3$)
- 40% Silica ($\text{SiO}_2$)
- 20% $\text{Na}_2\text{O} + \text{K}_2\text{O}$

**Note:** extraction processes of aluminium require high electricity consumption. → suitable for countries where cheap electricity is supplied.
Bayer process

Alumina \((\text{Al}_2\text{O}_3)\) is extracted by digesting crushed bauxite in strong sodium hydroxide \((\text{NaOH})\) solution at Temp upto 240°C.

First step

• Most of alumina is dissolved to give sodium aluminate \((\text{NaAlO}_2)\) which is soluble in water.

• Insoluble residues or ‘Red mud’, mainly composed of oxide of Fe and Si, are removed by filtration.

\[
\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O} + 2\text{NaOH} \rightarrow 2\text{NaAlO}_2 + (x+1)\text{H}_2\text{O}
\]  

…Eq. 1

Note: Optimisation of the process with the aid of temperature and pressure, depending on the nature of bauxite ores, (to obtain different forms of alumina \(\alpha\), \(\beta\) or \(\gamma\)).
Bayer process

Second step

• The next step is to decompose NaAlO$_2$ to give alumina (Al$_2$O$_3$), at temp ~ 50°C.

• This reverse reaction is achieved by adding crystals of trihydrate Al$_2$O$_3$.3H$_2$O (seeding agent) to promote fine precipitates of this compound.

\[ 2NaAlO_2 + 2H_2O \rightarrow 2NaOH + Al_2O_3.3H_2O \]

• The water is then removed by calcining at high temperatures.
  At Temp ~ 400-600°C → $\gamma$ alumina (chemically active).
  At Temp ~ 1200°C → $\alpha$ alumina (inert)

\[ Al_2O_3.3H_2O \xrightarrow[\Delta]{\text{calcining}} Al_2O_3 \]
**Bayer process**

- In the case of **bauxite** containing high **silica**, **alumina loss** during the process is increased.

- Silica reacts with **NaOH** at the first step to give **sodium silicate** $\text{Na}_2\text{SiO}_3$.

\[
\text{SiO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} \quad \text{...Eq. 4}
\]

- **Sodium silicate** then reacts with **sodium aluminate** to give nonsoluble **sodium alumosilicate**.

\[
2\text{NaAlO}_2 + 2\text{Na}_2\text{SiO}_3 \rightarrow \text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot 2\text{H}_2\text{O} + 4\text{NaOH} \quad \text{...Eq. 5}
\]

**Solution:** 1) **Using bauxite with high alumina, low silica.**
2) **Adding lime or lime stone to react with bauxite to give calcium silicate** $\text{Ca}_2\text{SiO}_4$. 
• **Bauxite** is washed ground and dissolved in *caustic soda (NaOH)* at high pressure and temperature.

• Sodium aluminate solution containing nonsoluble bauxite residues sink to the bottom → *red mud*.

• **Seeding agent** is added to the clear sodium aluminate solution to give *alumina precipitates* which sink to the bottom of the tank.

• Precipitates are passed through a rotary kiln for *calcination* at ~1100°C to give white powder of *pure alumina*. 
Fusion process or dry process

• Utilise $\text{Na}_2\text{CO}_3$ instead of $\text{NaOH}$ in Bayer process.

• The reaction of ground bauxite and $\text{Na}_2\text{O}_3$ takes place at 800-1200°C and give sodium aluminate and $\text{CO}_2$.

\[
\text{Al}_2\text{O}_3 + \text{Na}_2\text{CO}_3 \rightarrow \text{Al}_2\text{O}_3\cdot\text{Na}_2\text{O} \text{ or } 2\text{NaAlO}_2 + \text{CO}_2
\] ...Eq. 6

• The $\text{Al}_2\text{O}_3\cdot\text{Na}_2\text{O}$ product is further ground and dissolved in water at 90-95°C to give a solution called leaching.

**Carbonization**

\[
\text{Al}_2\text{O}_3\cdot\text{Na}_2\text{O} + \text{CO}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 + \text{Na}_2\text{CO}_3
\] ...Eq. 7

• $\text{Al(OH)}_3$ is insoluble and present as red precipitates, which will be dewatered using heat to give alumina $\text{Al}_2\text{O}_3$ powder.
**Hall-Héroult process**

- **Aluminium** is produced by electrolytic reduction of its molten oxide with cryolite (Na₃AlF₆) as an electrolyte.
- **Cryolite** is added to lower electrolytic temperature to ~ 950°C ($T_m$ of alumina ~ 2030°C)

The electrolytic cell consists of:
1) Carbon as anode → consumed
2) Molten cryolite-alumina electrolyte
3) Liquid aluminium pool.

**Condition:**
- Temp : 950°C
- Current : 250 kA
- Voltage : 4.5 V

**Capacity:** 1800 Kg/day

**Total reaction:**

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$$

...Eq. 8

**Hall-Héroult electrolytic cell.**

$CO_2$ is formed at the anodes, and $Al$ at the cathode.
Hall-Hérroult electrolytic cell

**Anode:** two types
1) baked petroleum coke or and coal-tar or petroleum pitch.
2) self-baking known as Soderberg type.

**Electrolyte** contains 80-90% $\text{NaAlF}_6$, 2-8% **alumina** with additives such as $\text{AlF}_3$ and $\text{CaF}_3$.

- A typical cell house contains about 200 cells and is arranged in series on two lines.
- Alumina is added to the cell periodically because its concentration drops during the electrolysis.

*Under Al feeding* → anode affect (sudden operational failure)
*Over Al feeding* → sick pot (formation of sludge → lower conductivity)
**Mechanism of electrolytic reaction**

**Cathode:**

Floroaluminate anions are discharged at the cathode interface to produce NaF.

**Anode:**

Al$_2$O$_3$ dissolved in electrolyte will produce AlO$_3^{3-}$ at anode and will later be discharged to give Al metal and liberated oxygen, which will combine with C to form CO$_2$.

\[
\begin{align*}
\text{Cathode:} & \\
Na_3AlF_6 & \rightarrow 3Na^+ + AlF_6^{3-} \\
AlF_6^{3-} & \rightarrow AlF_4 + 2F^- \\
AlF_4 & \rightarrow AlF_3 + F^- \\
\text{and} & \\
Na^+ + F^- & \rightarrow NaF \\

\text{Anode:} & \\
2Al_2O_3 & \rightarrow 2Al^{3+} + 2AlO_3^{3-} \\
2Al^{3+} + 6e^- & \rightarrow 2Al \\
2AlO_3^{3-} & \rightarrow Al_2O_3 + \frac{3}{2}O_2 + 6e^- \\
\Rightarrow & \\
Al_2O_3 & \rightarrow 2Al + \frac{3}{2}O_2 \\
3C & \rightarrow 3CO_2 \\
2Al_2O_3 + 3C & \rightarrow 4Al + 3CO_2
\end{align*}
\]

Overall reaction...

...Eq. 8
Purifying aluminium by Cl$_2$

- **Aluminium** produced by electrolytic process normally contains impurity such as powder of coal or electrolyte and hydrogen gas.

- Cl$_2$ is blown through a graphite tube to purify aluminium. This reaction produces bubbles of **aluminium chloride** AlCl$_3$ which floats away and helps carrying impurity out from aluminium.

\[2Al + 3Cl_2 \rightarrow 2AlCl_3\]  \[\text{...Eq. 9}\]

- In the case of **ultra-pure aluminium**, i.e., for use as conductors, the electrolytic process is again used to purify aluminium.

- **Aluminium** obtained from the first process is now anode and the electrolyte used is 60% BaCl$_2$, 17% NaF, 23% AlF$_3$ and 5% NaCl. (\(T \sim 760-800^\circ\text{C.}\))
Physical metallurgy of aluminium

Density / Specific Gravity (g.cm\(^{-3}\) at 20 °C)  2.70
Melting Point (°C)  660
Specific heat at 100 °C, cal.g\(^{-1}\)K\(^{-1}\) (Jkg\(^{-1}\)K\(^{-1}\))  0.2241 (938)
Latent heat of fusion, cal.g\(^{-1}\) (kJ.kg\(^{-1}\))  94.7 (397.0)
Electrical conductivity at 20°C (% of international annealed copper standard)  64.94
Thermal conductivity (cal.sec\(^{-1}\)cm\(^{-1}\)K\(^{-1}\))  0.5
Thermal emmisivity at 100°F (%)  3.0
Reflectivity for light, tungsten filament (%)  90.0
Solubility of elements in aluminium

- **Mg, Cu, Zn** and **Si** are the most commonly used alloying elements in aluminium, which have sufficient solid solubility.
- **Cr, Mn** and **Zr** are used primarily to form compounds which control grain structure.

<table>
<thead>
<tr>
<th>Element</th>
<th>Temperature (°C)</th>
<th>Maximum solid solubility (wt%)</th>
<th>(at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>649</td>
<td>0.4</td>
<td>0.09</td>
</tr>
<tr>
<td>Cobalt</td>
<td>657</td>
<td>&lt;0.02</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Copper</td>
<td>548</td>
<td>5.65</td>
<td>2.40</td>
</tr>
<tr>
<td>Chromium</td>
<td>661</td>
<td>0.77</td>
<td>0.40</td>
</tr>
<tr>
<td>Germanium</td>
<td>424</td>
<td>7.2</td>
<td>2.7</td>
</tr>
<tr>
<td>Iron</td>
<td>655</td>
<td>0.05</td>
<td>0.025</td>
</tr>
<tr>
<td>Lithium</td>
<td>600</td>
<td>4.2</td>
<td>16.3</td>
</tr>
<tr>
<td>Magnesium</td>
<td>450</td>
<td>17.4</td>
<td>18.5</td>
</tr>
<tr>
<td>Manganese</td>
<td>658</td>
<td>1.82</td>
<td>0.90</td>
</tr>
<tr>
<td>Nickel</td>
<td>640</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>Silicon</td>
<td>577</td>
<td>1.65</td>
<td>1.59</td>
</tr>
<tr>
<td>Silver</td>
<td>566</td>
<td>55.6</td>
<td>23.8</td>
</tr>
<tr>
<td>Tin</td>
<td>228</td>
<td>~0.06</td>
<td>~0.01</td>
</tr>
<tr>
<td>Titanium</td>
<td>665</td>
<td>~1.3</td>
<td>~0.74</td>
</tr>
<tr>
<td>Vanadium</td>
<td>661</td>
<td>~0.4</td>
<td>~0.21</td>
</tr>
<tr>
<td>Zinc</td>
<td>443</td>
<td>82.8</td>
<td>66.4</td>
</tr>
<tr>
<td>Zirconium</td>
<td>660.5</td>
<td>0.28</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Note:
(i) Maximum solid solubility occurs at eutectic temperatures for all elements except chromium, titanium, vanadium, zinc and zirconium for which it occurs at peritectic temperatures.
(ii) Solid solubility at 20°C is estimated to be approximately 2 wt% for magnesium and zinc, 0.1–0.2 wt% for germanium, lithium and silver and below 0.1% for all other elements.
Phase diagrams of aluminium with various alloying elements

Maximum solid solubility in binary aluminium alloys occurs at eutectic and peritectic temperatures.

Section of Al-Ti peritectic phase diagram

Section of Al-Cu eutectic phase diagram
Solid solution strengthening of high purity binary aluminium alloys

- **Annealed high-purity aluminium** has very low yield strength (7-11 MPa), but can be strengthened by **solid solution hardening**.

- **Mn** and **Cu** are the most effective strengtheners at 0.5%, but tend to form **Al₆Mn precipitates** and insoluble **Al-Cu-Fe constituents** respectively.

- **Mg** is the most effective strengthener on the weight basis due to its **high solubility**.

Note: Zinc has high solubility but contributes to only mall solid solution strengthening.
Heat treatments in aluminium alloys

Principles of age-hardening

- Age hardening requires a decrease in solid solubility of the alloying elements with decreasing temperature.

Heat treatment usually involves the three following stages:

1. Solution treatment at relatively high temperature to dissolve the alloying elements.

2. Rapid cooling or quenching usually to room temperature to obtain supersaturated solid solution (SSSS) of these elements in aluminium.

3. Controlled decomposition of the SSSS to form a finely dispersed precipitates, normally accompanied with ageing at appropriate temperatures.
**Decomposition of supersaturated solid solutions**

*Decomposition of SSSS* is complex and normally involves several stages:

- Equilibrium phase
- Guinier-Preston (GP) zones
- Intermediate precipitates

The presence of a critical dispersion of GP zones or an intermediate precipitates, or both contributes to the maximum hardening in commercial alloys.

*Variation of yield stress with ageing time*
1) The GP zone

- The **GP zones** are **ordered**, solute-rich clusters of atoms, and **coherent** with the matrix, *fig (a)*. The **GP zones** are normally finely distributed in the matrix, which contribute to **hardening**.

- The **GP zone solvus** shown as a metastable line in the equilibrium diagram (*fig b*) which defines the **upper temperature limit of stability** of the **GP zones**. The GP zone size distribution varies with ageing time, *fig (c)*.

(a) Schematic of the distortion of matrix lattice plane near the coherent GP zone.

(b) Section of Al-Cu eutectic phase diagram

(c) Schematic of the variation of GP zone size distribution with ageing time.
2) Intermediate precipitates

• *Intermediate precipitates* have a definite composition and crystal structure and are of *much a larger size* than that of *GP zones*.

• Intermediate precipitates are partly *coherent* with the matrix and can nucleate at the sites of stable *GP zones* or *dislocations*.

3) Equilibrium precipitates

• The final *equilibrium precipitates* occur when *the intermediate precipitates loss its coherency with the matrix*.

• They are formed only at relatively high ageing temperatures and appear as coarsely dispersed precipitates → *little hardening effect*. 

*TEM of rods of S-phase (Al2-Cu-Mg) precipitates heterogeneously distributed on dislocation lines.*
**Precipitate free zones (PFZ) at grain boundaries**

**PFZs** appear as depleted zones from precipitates, due to

1) *Depletion of solute atom* (~50 nm) by ready diffusion to the boundary where large precipitates are formed.

2) *Depletion of vacancies* to nucleate precipitates at particular ageing temperature.

The width of the PFZ can be altered by heat treatment conditions:

- Higher solution heat treatment temperature
- Faster quenching rate

Wide PFZs in Al-4Zn-3Mg aged at 24 h at 150°C.

Narrower PFZ
**Trace element effects**

- The presence of *trace elements* may greatly affect the nucleation and growth of precipitates, due to:

  1) Preferential interaction with vacancies
  2) Raising the GP zone solvus
  3) Stimulating nucleation of existing precipitates
  4) Promoting formation of different precipitates
  5) Providing heterogeneous sites for nucleation
  6) Increasing supersaturation.

---

**TEM showing Sn particles promote precipitation of semi coherent \( \theta' \) (Al\(_2\)Cu) by lowering the interfacial energy.**

Ag of 0.3% modifies PFZ width and distribution in Al-4Zn-3Mg, aged at 24h at 150\(^\circ\)C.
**Hardening mechanisms**

- **Hardening mechanism** in aged-harden alloys is based on the concept of precipitation hardening, where the strength is controlled by the *interaction of moving dislocations with precipitates*.

  1) **Coherent and finely distributed particles**

- **Coherent particles or GP zones** are readily cut by dislocations, leading to localised deformation on only a few active slip planes on which dislocations moves. → **high yield strength** but only **small hardening**.

- This might causes **planar slips** and **dislocation pile-up** at grain boundary.

---

**Suranaree University of Technology**

Tapany Udomphol

May-Aug 2007
2) Large and widely-spaced particles

• Dislocations can easily bypass widely spaced particles, leaving dislocation loops around the particles.

• In this case, the yield stress is low but the rate of work hardening is improved and plastic deformation tends to spread uniformly throughout the grains.

Note: This is the situation in over-aged alloys.
Relationship between strength and particle size in age-hardened alloy

- In age-hardened alloys, **strength will increase and drop with ageing time** (increasing particle size).
- Intersection $P$ represents the **maximum strength** that can be developed in that particular alloy.

$V_f \uparrow \sigma_y \uparrow$ Lift the curve up

Increase the number of small particles which still resist shearing by dislocation.

Relationship between strength and particle size for age-hardened alloy
Heat treatment strategies

There are a number of heat treatment strategies, which stimulate the formation of dispersed precipitates that resist cutting by dislocation.

1) Duplex ageing first below and then above the GP zone solvus temperature, enabling the formation of finer dispersion of intermediate precipitates.

2) Co-precipitation of two phases, fine and coarse particles in which the former contributes to yield strength and the latter result in uniform plastic deformation.

3) Co-precipitation of two or more intermediate phases, having different crystallographic plane, influencing dislocation mobility.

4) Nucleation of uniform dispersions of intermediate precipitates by adding some particular trace elements.

Note: Suitable heat-treatment scheme can increase strength up to 40 times.
Corrosion in aluminium alloys

**Surface oxide film**

• Aluminium is active and readily oxidised. → form thick natural protective *oxide layers/films of alumina* on the surface which protect reactions in the bulk material.

• These *protective films* are stable in aqueous solutions of *pH ~ 4.5-8.5*, but not stable in strong acid and alkali solutions.

• In aqueous solution, the *corrosion product* is aluminium hydroxide and then change to → *hydrated aluminium oxide*, which is *less adherent* and *less protective* than ones form in air.

• The *natural oxide films* are of typically *2-3 nm* thick and mainly composed of *Al₂O₃*.

• The films will grow thicker with time and depending on conditions.
Coating of oxide films

Conversion coating

- Film is ~ 1-2 μm thick.
- $\text{Al}_2\text{O}_3$ film is produced by immersion of component in hot acid or alkaline solutions.
- The film is composed of mainly $\text{Al}_2\text{O}_3$ with Chromate → increase corrosion resistance.
- Used in aircraft structures.
- $\text{Cr}$ is toxic.

Anodizing

- Film is ~10-20 μm thick.
- $\text{Al}_2\text{O}_3$ film is produced by making the component as the anode in an electrolyte such as 15% $\text{H}_2\text{SO}_4$.
- The film is first porous, later sealed.
- The film can be dyed to give attractive colours. → architectural products.

Decoration of anodized aluminium at Bullring, Birmingham, UK
Contact with dissimilar metals

• The **electrode potential** of **Al** is **-0.85 V** whereas **Al alloys** range from **-0.69 to -0.99 V**.

• **Mg** is anodic (more active) to **Al** whereas **mild steel** is cathodic to **Al**.

However, the magnitude of galvanic corrosion depends not only on electrode potential but also the total electrical resistance, polalization.

• The **nature of oxide firm** at the metal-liquid interface affects polalization, which alters the corrosive condition.

---

<table>
<thead>
<tr>
<th>Metal or alloy</th>
<th>Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium</td>
<td>-1.73</td>
</tr>
<tr>
<td>Zinc</td>
<td>-1.10</td>
</tr>
<tr>
<td>Alclad 6061, Alclad 7075</td>
<td>-0.99</td>
</tr>
<tr>
<td>5456, 5083</td>
<td>-0.87</td>
</tr>
<tr>
<td>Aluminium (99.95%), 5052, 5086</td>
<td>-0.85</td>
</tr>
<tr>
<td>3004, 1060, 5080</td>
<td>-0.84</td>
</tr>
<tr>
<td>1100, 3003, 6063, 6061, Alclad 2024</td>
<td>-0.83</td>
</tr>
<tr>
<td>2014-T4</td>
<td>-0.69</td>
</tr>
<tr>
<td>Cadmium</td>
<td>-0.82</td>
</tr>
<tr>
<td>Mild steel</td>
<td>-0.58</td>
</tr>
<tr>
<td>Lead</td>
<td>-0.55</td>
</tr>
<tr>
<td>Tin</td>
<td>-0.49</td>
</tr>
<tr>
<td>Copper</td>
<td>-0.29</td>
</tr>
<tr>
<td>Stainless steel (3xx series)</td>
<td>-0.69</td>
</tr>
<tr>
<td>Nickel</td>
<td>-0.07</td>
</tr>
<tr>
<td>Chromium</td>
<td>-0.49 to +0.18</td>
</tr>
</tbody>
</table>

*Compositions corresponding to the numbers are given in Tables 3.2 and 3.4.*

Note: In contact with steels are less corrosive in comparison to electrode potential whereas in contact with copper causes worse effect.
**Influence of alloying elements and impurities**

- Aluminium solid solution, micro-constituents and compounds such as silicon, $\text{Al}_2\text{CuMg}$, $\text{Mg}_2\text{Si}$ have different electrode potentials → forming their own minute **corrosive cells** within the alloy.

- In general, solid solution is the most corrosive resistant.

- **Al-Mg alloys** retain a relatively high corrosion resistance.

- **Al-Zn alloys** are used as cladding for certain **Al alloys** and as galvanic anodes for cathodic protection of **steel structures** in sea water.

---

**Table 2.4 Electrode potentials of aluminum solid solutions and micro-constituents with respect to the 0.1 M calomel electrode in aqueous solutions of 53 g l$^{-1}$ NaCl and 3 g l$^{-1}$ H$_2$O$_2$ at 25°C (from Metals Handbook, Volume 1, American Society for Metals, Cleveland, Ohio, 1961)**

<table>
<thead>
<tr>
<th>Solid solution or micro-constituent</th>
<th>Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$_5$Al$_3$</td>
<td>- 1.24</td>
</tr>
<tr>
<td>Al–Zn–Mg solid solution (4% MgZn$_2$)</td>
<td>- 1.07</td>
</tr>
<tr>
<td>MgZn$_2$</td>
<td>- 1.05</td>
</tr>
<tr>
<td>Al$_2$CuMg</td>
<td>- 1.00</td>
</tr>
<tr>
<td>Al–5% Mg solid solution</td>
<td>- 0.88</td>
</tr>
<tr>
<td>MnAl$_3$</td>
<td>- 0.85</td>
</tr>
<tr>
<td>Aluminium (99.95%)</td>
<td>- 0.85</td>
</tr>
<tr>
<td>Al–Mg–Si solid solution (1% Mg$_2$Si)</td>
<td>- 0.83</td>
</tr>
<tr>
<td>Al–1% Si solid solution</td>
<td>- 0.81</td>
</tr>
<tr>
<td>Al–2% Cu supersaturated solid solution</td>
<td>- 0.75</td>
</tr>
<tr>
<td>Al–4% Cu supersaturated solid solution</td>
<td>- 0.69</td>
</tr>
<tr>
<td>FeAl$_3$</td>
<td>- 0.56</td>
</tr>
<tr>
<td>CuAl$_2$</td>
<td>- 0.53</td>
</tr>
<tr>
<td>NiAl$_3$</td>
<td>- 0.52</td>
</tr>
<tr>
<td>Si</td>
<td>- 0.26</td>
</tr>
</tbody>
</table>
Surface pitting and exfoliation corrosion in aluminium alloys.

- **Micro-constituents** are the source of electrochemical corrosion, leading to *non-uniform attack* in specific areas.
- Pitting and intergranular corrosion are examples of localized attacks.
- **Fe** and **Si** as impurities (**Al₃Fe**) are cathodic to aluminium, promoting electrochemical attack in the surface oxide film.
- **Al₆Mn**, **Mg₂Si** have similar electrode potential to aluminium.
Metallurgical and thermal treatments

- **Ageing and tempering treatments** alter quantity and distribution of micro-constituents, affecting corrosion resistance.

- **Thermo-mechanical treatments** can introduce residual stresses into components → stress corrosion cracking.

- **Temperature gradient due to thermal treatment** such as in welding introduces potential difference between weld beads, heat-affected zone, and the parent alloy.

- **A mixture of unrecrystallised and recrystallised grain structures** in forged or extruded components or **elongated grain structure** along the three principal directions in rolling might provide potential difference.
Mechanical behaviour of aluminium alloys

Mechanical properties of aluminium alloys are controlled by a number of principal microstructural features;

1) Coarse intermetallic compounds (or constituent particles)

Formed interdendritically by eutectic decomposition during ingot solidification.

- Divided into soluble constituents (Al$_2$Cu, Al$_2$CuMg, Mg$_2$Si) and non-soluble compounds (Al$_6$(Fe,Mn), Al$_3$Fe, $\alpha$Al(Fe,Mn,Si), Al$_7$Cu$_2$Fe).
- These particles are non-useful in high strength wrought alloys and appear as aligned stringers in the working direction.
- Removal of these particles necessitate a significant cost.

Aligned stringers of coarse intermetallic compounds in a rolled Al-alloy
2) **Smaller submicron particles or dispersoids (0.05-0.5 μm)**

*Formed during homogenization of the ingots by solid state precipitation.*

- The compounds contain one of transition metals, i.e., \( \text{Al}_{20}\text{Mn}_3\text{Cu}_2 \), \( \text{Al}_{12}\text{Mg}_2\text{Cr} \) and \( \text{Al}_3\text{Zr} \).
- They retard recrystallization and grain growth during processing and heat treatments.
- Influencing dislocation movements, which affect some mechanical properties.

3) **Fine precipitates (upto 0.1 μm)**

*Formed during age-hardening.*

- Contribute to the most significant effect on strengthening.
4) **Grain size and shape**

- Aluminium *dynamically recovers* during hot deformation producing a network of subgrains.
- Less deformation occurs in thick sections → *do not undergo* bulk recrystallization. → elongated grain structure is remained.

5) **Dislocation structure**

- Caused by cold working and do not respond to age-hardening.

6) **Crystallographic textures**

- Formed in rolled products, giving a marked effect on formability and anisotropic mechanical properties.

*Earing in drawn can*
Tensile properties

- **Tensile properties of aluminium alloys** can be divided into two groups depending on how they respond to precipitation hardening.

1) **Responed to precipitation hardening**: dominant effect in raising $\sigma_y$ and $\sigma_{TS}$ depends on finely dispersed precipitates.

2) **Not responded to precipitate hardening**: obtained $\sigma_y$ and $\sigma_{TS}$ depend on dislocation structures by cold working.

| Table 2.5 Variation in tensile properties with direction in 76 mm thick aluminium alloy plates (from Forsyth, P.J.E. and Stubbington, A., *Metals Technology, 2, 158, 1975*) |
|----------------------------------|----------------|----------------|--------|
| Alloy direction                  | 0.2% proof stress (MPa) | Tensile strength (MPa) | Elongation (%) |
| Al-Zn-Mg-Cu (7075)              | 523            | 570            | 15.5 |
| Longitudinal (L)                 | 482            | 552            | 12.0 |
| Long transverse (LT)             | 445            | 527            | 7.5   |
| Short transverse (ST)            | 0.85           | 0.93           | 0.48  |
| ST/L ratio                       |                |                |       |
| Al-Cu-Mg (2014)                  | 441            | 477            | 14.0  |
| Longitudinal (L)                 | 423            | 471            | 10.5  |
| Long transverse (LT)             | 404            | 449            | 4.0   |
| Short transverse (ST)            | 0.91           | 0.94           | 0.29  |

- **Coarse intermetallic compounds** reduce tensile ductility.
- **Mechanical fibering and crystallographic texture** influence tensile properties in each direction. Greatest in the longitudinal direction and smallest in the short transverse direction.
**Toughness**

- **Toughness** is resistance of material to fracture (in the presence of cracks).

- **Toughness**  ■  **yield strength**  ■
  Depends greatly on microstructures.

- **Crack extension** is due to nucleation of crack by decohesion at second phase particle-matrix interface.

- Toughness is greatest in **underaged condition** and decrease as ageing proceeds to peak strength.

**Note:** Reducing **Fe** and **Si** (impurities) greatly improves the toughness.
Fatigue

• The improvement in **tensile strength** is not always accompanied with increased **fatigue strength** in non-ferrous alloys.

• The more an alloy is dependent upon precipitation-hardening for its tensile strength, the lower its **fatigue ratio** (endurance limit : tensile strength) becomes.

• **Age-hardened aluminium alloys** possess disappointing fatigue properties due to **localised straining of precipitates** under cyclic stressing. → Improved by **more uniformly dispersed precipitates** to prevent **coarse slips formation**.

• An increase in **dislocation density** by themomechanical processing helps to improve fatigue performance, **fig**.

*Note: duplex structure is required where fine particles to yield high tensile strength and coarse particles (producing dispersed dislocations) to improve fatigue strength.*
**Metallurgical factors influencing fatigue properties**

Precipitate depleted zone in a persistent slip band formed by fatigue stressing a high purity Al-Zn-Mg alloy.

Coarse slip bands containing high density of dislocations, leading to localisation of strain (lower fatigue performance).

Dispersed dislocation around coarse second precipitates, produced during fatigue cycling, help to improve fatigue performance.
Stress-corrosion cracking

• **Stress-corrosion cracking (SCC)** develops when the alloy is exposed to simultaneous *tensile stress* in a *corrosive environment*, i.e., water vapour (with trace halide iron).

• The **failure stress** is well below the level of the yield strength.

• **Electrochemistry** between metallurgical structures and corrosive environment dominates the SCC.

• *Cu, Mg, Zn, Si* and *Li* as solute elements have the adverse effects.

*Note:* Should avoid stressing in direction normal to the short transverse direction (susceptible to corrosion due to mechanical fibering).
**Metallurgical features influencing stress-corrosion cracking**

1) **PFZs** or **grain boundaries** are considered to be anodic to the grain centres and also causing localised straining.

2) **The nature of the matrix-precipitate** – maximum susceptibility occurs when the **GP zones** are present.

3) **Dispersion of precipitate particles** in GBs.– Closely spaced particles at GBs promote SCC.

4) **Solute concentration** at GBs – modifying electrochemical potentials.

5) **Hydrogen embrittlement** at GBs due to rapid diffusion.

6) **Chemisorption of atom species** at the crack surface.- lowering the cohesive strength.

*Development of hydrogen bubble at precipitate particles at grain boundary in artificially aged Al-Zn-Mg alloy exposed to laboratory air for three months*
Corrosion fatigue

- Simultaneous **cyclic stressing in a corrosive condition** leads to a significant reduction in strength, which is much greater than in individual cases.

- **Protective films** provided on the metallic parts are normally broken during cyclic stressing.

- Sites such as **corrosion pits** are the origin of the fatigue crack propagation.

Note: the reduction of the fatigue strength under corrosive condition is related to the corrosion resistance of that material to the medium.

Corrosion pits as the cause of corrosion fatigue failure
Creep

• **Creep fracture** (at high temperature) normally initiates at **grain boundaries** especially in aluminium alloys.

• Continued exposure to high temperature leads to **over-ageing and softening**. → the operating temperature must be lower than the ageing temperature to avoid a loss of strength.

• **Submicron intermetallic compounds** such as $\text{Al}_9\text{FeNi}$ or **particles** introduced during processing which are stable at service temperature help to improve creep resistance in aluminium alloys.

• Aluminium alloys reinforced by **short fibres** also provide enhanced creep resistance.
Melting of aluminium

Direct-chill casting process

- Uniform ingot structure is obtained by **direct-chill (DC) casting** most common in vertical than horizontal process.
- Molten alloy is poured into water-cooled moulds having retractable bases.
- During the **solidification process**, metal solidifies at the **bottom block** with subsequent solidification of the rest occurs rapidly by means of chill water.

Note: the ingot obtained may be rectangular or round depending on further working processes: rolling, forging or extrusion.
Continuous casting process

• The process produces *continuous thin slabs* and sheets with sizes to those required in final products. → reducing great amount of *investment cost* required to reduce in sizes from large ingot.

• **Continuous casting of aluminium alloys** involves complex surface cooling patterns, due to the alternation of rolls and spray zones.

• Sets of *water-cooled rolls* are rotated continuously to produce slab.

*Thermal field (a) and solid fraction (b)*
Metallurgical factors affecting melting of aluminium

Molten aluminium is susceptible to:

1) **Excess absorption of hydrogen gas** (embrittlement)

2) **Oxidation** of the melt to form complex oxides of **Mg, Na, Ca, Sr** (affecting mechanical properties) as films or particles

3) **Inclusions** in forms of borides, oxides, carbides and non-metallic particle, i.e., **Al₂C₃** (found in all **Al alloys**). → stress concentration.
Primary factors are:
1) Dendritic cell size or dendrite arm spacing,
2) Form and distribution of microstructural phase,
3) Grain size.

Fine grain size or structures are desirable, leading to improvements of:

- feeding characteristics
- tear resistance
- mechanical properties
- pressure tightness
- response to thermal treatment
- chemical, electrochemical and mechanical finishing.

Grain refiners:
- master alloys of Ti
- Al-3-5%Ti refiners
- Al-Ti-0.2-1%B refiners (Ti:B ~ 5:50)
Grain refinement by inoculation

Grain refiners used are:

- master alloys of Ti
- Al-3-5%Ti refiners
- Al-Ti-0.2-1%B refiners
  \((Ti:B \sim 5:50)\)

\[ Al_{(liq)} + TiAl_{3(crys)} \rightarrow \alpha - Al\ alloy\ solid\ solution \]

- \(TiAl_3\) crystals act as nuclei for grains to grow.
- Multiple nucleation of averagely eight sites may occur on each particle.
- \(TiB_2\) also offers grain refinement effect.

Petal-like \(TiAl_3\) particles in \(\alpha\)-Al solid solution
Homogenisation of DC ingots

Homogenisation of DC ingots at temperatures 450-600°C prior to working processes is common in aluminium alloys in order to:

1) Reducing micro-segregation
2) Removing non-equilibrium, low melting point eutectics that may cause cracking during subsequent working.
3) Controlling excess amount of precipitates that are dissolved during solidification.

- During homogenisation, alloying elements will diffuse from GBs and other solute-rich regions to grain centres.
- Diffusion time depends on diffusion distance (grain size, dendrite arm spacing) and the diffusion rate of alloying elements.

\[ x = \sqrt{Dt} \]  
where

- \( x \) = mean distance
- \( D \) = diffusion coefficient
- \( t \) = time

Note: homogenisation time varies from 6-24 hrs, depending on conditions and alloy systems.
Fabrication of DC ingots

• After homogenisation, the ingot is **hot-worked** to **break down the cast structure** (coarse grain structure), giving **uniform grain size** as well as constituent size and distribution.

• **Cold working** is followed especially to **strengthen** alloys which do not response to precipitate hardening. This might be followed by **immediate annealing** at $T \sim 345-415^\circ C$. 

![X-section of extruded bar having coarse recrystallised grains around the periphery](image1)

![X-section of a high-strength alloy sheet roll-clad with pure aluminium](image2)
**Thermal treatment**

Thermal treatment is performed to develop desirable mechanical properties required for service performance.

**Solution treatment**

- Solution treatment should be ideally carried out at temperatures within the single phase to obtain complete solution of most of the alloying elements.
- However, this temperature should not be over the solidus temperature to avoid overheating, i.e., liquation of compounds and at GBs, as well as grain growth affecting mechanical properties.
- Absorbed hydrogen atoms can recombine at internal cavities to form pockets of gas or blistering. Should minimise water vapour in the furnace or cladding.
Quenching

The alloy is quenched after solution treatment normally to room temperature to achieve maximum supersaturated alloying elements for subsequent ageing.

1) Cold-water quenching: for high cooling rate especially in thick sections, but gives distortions (residual or quenching stresses) in thin sections. → can be relaxed (20-40%) during ageing.

The effect of minor additions of Cr and Zr on the quench sensitivity

Tensile strength as a function of quenching rate in $T_{\text{crit}} \sim 290-400^\circ C$
Quenching

2) **Hot or boiling water quenching as well as air-cooled quenching**: slower rates of cooling and quenching stresses, showing acceptable response to subsequent ageing – also depending on quench sensitivity of each alloy systems. However this might cause heterogeneous nucleation of coarse particles.

3) **Salt-bath quenching**: (at 180°C and holding for a time before cooling to room temperature.) for **high-strength Al-Zn-Mg-Cu alloys**. Provides rapid cooling rate but reduced residual stresses.
Age-hardening is the final stage to optimise properties in the heat-treatable aluminium alloys.

- Natural ageing – at room temperature
- Artificial ageing – at elevated temperatures (100-190°C)

Ageing temperature and time depend upon alloy systems and the final required properties.

- **Single-step ageing**: to develop high strength ~ 8-24 hrs.
- **Multiple ageing**: to give specific properties such as stress-corrosion resistance, toughness.

**Note**: RT ageing provide incubation or nuclei for the growth of GP zone in the subsequent elevated temperature ageing.
**Thermo-mechanical processing**

**Thermo-mechanical treatment (TMT)** is the combination of plastic deformation and heat treatment to provide high strength properties.

There are two types of TMT for high strength aluminium alloys.

1) **Intermediate TMT**: The deformation is applied to give very fine recrystallised grains prior to solution treatment.

2) **Final TMT**: the deformation is applied after solution treatment and may involve cold or warm working before, during or after ageing.
Wrought aluminium alloys

The composition of aluminium alloys are regulated by internationally agreed classifications system for each wrought and cast alloys.

Classification for wrought aluminium alloys;

1XXX Al of 99% minimum purity
2XXX Al - Cu alloys
3XXX Al - Mn alloys
4XXX Al - Si alloys
5XXX Al - Mg alloys
6XXX Al - Mg - Si alloys
7XXX Al - Zn - Mg alloys
8XXX Miscellaneous alloys, e.g. aluminium-lithium alloys

Each registered alloy is described by a four digit number, with a further letter and number indicating the temper, or condition of the alloy.
### Aluminium alloy and temper designation systems (IADS system)

<table>
<thead>
<tr>
<th>4-digit series</th>
<th>Aluminium content or main alloying elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 xxx</td>
<td>99.00% minimum</td>
</tr>
<tr>
<td>2 xxx</td>
<td>Copper</td>
</tr>
<tr>
<td>3 xxx</td>
<td>Manganese</td>
</tr>
<tr>
<td>4 xxx</td>
<td>Silicon</td>
</tr>
<tr>
<td>5 xxx</td>
<td>Magnesium</td>
</tr>
<tr>
<td>6 xxx</td>
<td>Magnesium and silicon</td>
</tr>
<tr>
<td>7 xxx</td>
<td>Zinc</td>
</tr>
<tr>
<td>8 xxx</td>
<td>Others</td>
</tr>
</tbody>
</table>

- The first digit indicates the alloy group.
- The second indicates modifications to alloy or impurity limit.
- The last two identify the aluminium alloy or indicates the aluminium purity.

#### Temper designations

<table>
<thead>
<tr>
<th>First suffix digit</th>
<th>Second suffix digit</th>
<th>Condition H only</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Indicating residual hardening*</td>
</tr>
</tbody>
</table>

- *Where a second digit is used for T tempers, or a third is used for condition H, this indicates a specific treatment, e.g. amount of cold work to secure specific properties.

#### Examples of alloy and temper descriptions

1) 5152 H36 = Aluminium-magnesium alloy, cold worked and stabilised to develop a ¾ hard condition

2) 6061 T6 = Aluminium – magnesium – silicon alloy, solution heat treated followed by artificial ageing.
Designation system in Britain

1) **BS (British standard) specifications** for general engineering use.
2) **BS Specifications** for aeronautical use (designated as the L series).
3) **DTD (Directorate of Technical Development) specifications** issued by the Ministry of Technology for specialized aeronautical applications.
Work-hardening of aluminium and its alloys

During **plastic deformation**: Dislocation generation and multiplication occur faster than annihilation by dynamic recovery → dislocation tangles, cells and subgrain walls → increased strength.

**Solid solution elements** have significant effects on **work hardening** in several ways;

1) Enhancing the rate of **dislocation multiplication**
2) Reducing the rate of **recovery**
3) Increasing the effectiveness of dislocations as **barrier** to metal flow.
Work-hardening curves

For non-heat treatable alloys

Strain hardening provide strength to the alloys via dislocation interaction.

For heat treatable alloys

Strain hardening may supplement the strength developed by precipitation hardening.

Strength ▲ Ductility ▼

No good for application that ductility is critical.

Note: Cold working causes an initial rapid increase in yield stress.
Work-hardening characteristics

During **tensile testing**, the alloy exhibits work hardening after yielding.

**Work hardening curves** of annealed, recrystallised aluminium alloys can be expressed as follows

\[
\sigma = k\varepsilon^n
\]

Where
- \( \sigma \): true stress
- \( \varepsilon \): true strain
- \( n \): work hardening exponent

...Eq. 11

**Work hardening curves** of cold-work tempers (non-heat-treatable alloy after cold working to the initial strain \( \varepsilon_0 \)) can be expressed as follows

\[
\sigma = k(\varepsilon_0 + \varepsilon)^n
\]

Where
- \( \varepsilon_0 \): true strain
- \( n \): work hardening exponent

...Eq. 12

Note: work-hardening of **aluminium alloys** decreases with increasing temperature.
Deformation and texture of aluminium alloys

• Aluminium has a high stacking fault energy $\rightarrow$ cellular substructure is formed during deformation, which imparts work-hardening.

• Deformation of aluminium and its alloys proceeds by slip on the $\{111\}$ planes in the $<110>$ directions.

• Aluminium wire, rod and bar normally possess a fibre texture in which the $<110>$ direction is parallel to the working direction.

• This crystallographic texture developed by cold working causes directionality not only in certain mechanical properties but also in metal forming processes.

• Earing on the top of the drawn cup is due to preferred orientations in the plane of the sheet.

Deep drawn aluminium cups showing earing
Designations of wrought aluminium alloys

Non-heat-treatable alloys

• 1xxx series (Super-purity and commercial-purity aluminium)
• 3xxx series (Al-Mn and Al-Mn-Mg alloys)
• 5xxx series (Al-Mg alloys)
• 8xxx series (Miscellaneous alloys)

Heat-treatable alloys

• 2xxx series (Al-Cu and Al-Cu-Mg alloys)
• 6xxx series (Al-Mg-Si alloys)
• 7xxx series (Al-Zn-Mg and Al-Zn-Mg-Cu alloys)
Roles of alloying elements

- Zn, Mg, Cu, Mn, Si are mainly used for principal commercial aluminium alloys.

- Most elements have a very low solid solubility in Al and are segregated to the dendrite cell boundaries during casting.

- Second-phase particles (~10 mm) are formed if high amount of these elements is added and remain as particles after processing.

- These particles contribute to little improvement in strength but lower toughness and corrosion resistance.
Super-purity and commercial-purity aluminium (1xxx series)

- Super-purity (SP) aluminium (99.99%)
- Commercial-purity (CP) aluminium (upto 1% impurities or minor additions)

Properties:
- Low tensile strength (90 MPa in CP 1100)
- Yield stress of only 7-11 MPa.

Applications:
- Electrical conductors
- Chemical process equipment
- Foils
- Decorative finishes.

Fe and Si are always present as impurity and form refined FeAl₃, Fe₃SiAl₁₂ or Fe₂Si₂Al₉ constituents.
**Al-Mn and Al-Mn-Mg alloys (3xxx series)**

- **Al-Mn alloys (up to 1.25% Mn)**
  Greater amount leads to large primary Al₆Mn particles → deleterious local ductility.

  **Properties:**
  - Moderate strength, i.e., $\sigma_{TS} \sim 110$ MPa in annealed 3003.
  - High ductility
  - Excellent corrosion resistance

  **Applications:**
  - Foil
  - Roofing sheet

- **Al-Mn-Mg alloys**
  (provide solid solution strengthening) and widely used in a variety of strain-hardened tempers.

  **Properties:**
  - Moderate strength, i.e., $\sigma_{TS} \sim 180$ MPa in annealed 3004.
  - Readily fabricated
  - Excellent corrosion resistance

  **Applications:**
  - Manufacturing beverage cans

---

Suranaree University of Technology
Tapany Udomphol
aluminium.matter.org.uk
May-Aug 2007
**Al-Mg alloys (5xxx series)**

- **Mg** \( T_m = 651^\circ C, \) **HCP** structure
- **Small solubility** of 3% at RT and 15.35 at 451\(^\circ\)C (eutectic).
- Eutectic reaction gives **K phase** (**FCC**) and **\( \beta \) phase** (**\( Al_3Mg_2 \)**)

---

Phase equilibrium diagram of Al-Mg

5086-H34 sheet showing the constituent distribution and discontinuous \( Mg_2Al_3 \) grain boundary particles

---

Suranaree University of Technology
Tapany Udomphol
May-Aug 2007
Al-Mg alloys (5xxx series)

- Mg additions (0.8-5%) provide solid solutions and give a wide range of alloy compositions → strength properties

Properties:
- Al-0.8Mg (5005): $\sigma_y$ 40 MPa, $\sigma_{TS}$ 125 MPa
- Al-(4.7-5.5)Mg (5456): $\sigma_y$ 160, $\sigma_{TS}$ 310 MPa
- High rate of work hardening
- High corrosion resistance
- Bright surface finish

Applications:
- Transportation structural plates
- Large tanks for petrol, milk, grain
- Pressure vessel
- Architectural components
Miscellaneous alloys (8xxx series)

• This series contains several dilute alloys

Properties:
• High corrosion resistance at high temp & pressure
• Deep drawing

Applications:
• Al-1.1Ni-0.6Fr (8001) - nuclear energy installations.
• Al-0.75Fe-0.7Si (8011) - bottle caps.
• Al-Sn (up to 7%) soft bearings
Al-Cu alloys (2xxx series)

- **Cu** ($T_m = 1085^\circ$C, **FCC** structure)
- Good solubility upto 5.65% at 548$^\circ$C (eutectic).
- Eutectic reaction gives $\alpha$ phase (5.65%Cu) - **ductile** and $\theta$ phase (CuAl$_2$-52.75%Cu) – **brittle**.

- Eutectic phase consists of alternate lamella structure of $\alpha$ and $\theta$ phases, resembling **pearlite** in carbon steels, which give high strength but brittle.

**Hypoeutectic**

- $> 5\%$ Cu, cooling is in equilibrium, grain boundaries of $\alpha$ phase surrounded by ($\alpha + \theta$) eutectic phase – reduced toughness.
- $< 5\%$ Cu, $\alpha$ phase in some cases surrounded by $\theta$ phase.

**Hypereutectic**

- Cu $\to$ 33%, too brittle due to high amount of $\theta$ phase.

*Equilibrium phase diagram of Cu-Al*
Al-Cu alloys (2xxx series)

Properties:
• High strength (2119: $\sigma_{TS}$ 505 MPa).
• Good creep strength at high temp.
• High toughness at cryogenic temp.
• Good machinability.

Applications:
• Fuel tanks

Precipitation hardening – by forming $\theta$ phase in $\alpha$ matrix, gives high strength and toughness.
Al-Cu-Mg alloys (2xxx series)

- Miner amount of Mg (0.2%) modifies the precipitation process, resulting in greater age-hardening.

Properties:
- High strength (2024: $\sigma_{TS} = 520$ MPa).
- High toughness.

Applications:
- Pistons, rivets for aircraft constructions.

- 2024 heated ingot showing soluble $\text{Al}_2\text{CuMg}$.
- 2024-T4 (solution heat treated) plate showing redistribution of constituents due to mechanical working.
- Aluminium pistons and devices for thermal shock used in airplane.
Al-Mg-Si alloys (6xxx series)

- Mg and Si are added in balanced amount to form \( \text{Mg}_2\text{Si} \).
- Excess amount of Si \( \rightarrow \) brittle.
- Congruent \( \text{Mg}_2\text{Si} \) has properties similar to pure metal can dissolve in \( \alpha \) phase upto 1.85% at 595\(^\circ\)C (eutectic) and reduces to 0.2% at 200\(^\circ\)C.

\[
L \leftrightarrow \alpha + \text{Mg}_2\text{Si} + (\text{Si})
\]

---

Pseudo-binary Al-Mg\(_2\)Si diagram

6061-T6 sheet showing excess soluble \( \text{Mg}_2\text{Si} \) particles as redistributed by mechanical working (dark phase)

Suranaree University of Technology

Tapany Udomphol

May-Aug 2007
**Al-Mg-Si alloys (6xxx series)**

*Mg + Si (0.8-1.2%)*

**Properties:**
- Medium-strength structural alloys (most widely used 6063-T6, $\sigma_y$ 215 MPa, $\sigma_{TS}$ 245).
- Readily extruded
- Colour anodized.

**Applications:**
- Architectural & decorative finishes.
- Automotive trim.
Al-Mg-Si alloys (6xxx series)

Mg + Si (> 1.4%)

- Some alloys contain excess amount of Si (to form Mg$_2$Si), which promotes additional response to age-hardening by
  1) Refining the size of Mg$_2$Si particles
  2) Precipitating as silicon.

Properties:

- Higher strength on ageing, 6013 - Al-Mg-Si-Cu, $\sigma_y$ 330 MPa(T6) and 415 (MPa) T8.

Applications:

- Aircraft, automotive
- Recreation applications
- Extruded sections
Age-hardening for Al-Cu and Al-Mg alloys

- Alloys with < 0.5% Cu or < 1.4% Mg in Al-Cu and Al-Mg alloys respectively cannot be aged-hardened.

- Aged hardening of alloys with > 5.7% Cu or < 17.4% Mg in Al-Cu and Al-Mg alloys respectively are less effective (less hardness).
Example: Age-hardening in Al-Cu alloys

- **Equilibrium cooling** of 4% Cu down to RT gives $\alpha + \theta (\text{CuAl}_2)$ which are non-coherent precipitates with the matrix (starting at A).

- **Quenching** from just above point A down to RT will give **supersaturated solid solution** ($\alpha'$ phase) where higher amount of Cu can be dissolved in the matrix. \(\rightarrow\) non-equilibrium.

- **CuAl\(_2\)** will precipitates from the $\alpha'$ phase if leave it for \(~6\) days (trying to get back to equilibrium) and this leads to **higher strength**.
Age-hardening mechanism in Al-Cu alloys

Coherent precipitates or $\theta'$ provide distortion within the atom lattice which affect dislocation movement. $\rightarrow$ improved mechanical properties.

Coherent $\theta'$ changes to non-coherent precipitates $\theta$ with increasing ageing time (try to get back to equilibrium) $\rightarrow$ less strength due to no distortion within the lattice. (Over aging)
Effects of time and temperature of precipitates – treatment on the structure and tensile strength of a suitable alloy

• *Ageing* at $T = 165^\circ C$ provides the optimum strength due to homogeneous distribution of high amount of $\theta'$. 
**Al-Zn-Mg and Al-Zn-Mg-Cu alloys (7xxx series)**

- High response to age-hardening especially with Cu addition (0.3%) to also give stress corrosion cracking resistance.

**Properties:**
- Strength is insensitive to cooling rate → suitable for welding.
- **Yield strength** might be double to Al-Mg and Al-Mg-Si alloys (~ up to 600 MPa).
- **Stress corrosion cracking resistance** in Al-Zn-Mg-Cu alloys.

**Applications:**
- Light weight military bridge
- Aircraft construction.

Al 7039 aircraft construction
Al 7075 Component in motorcycle
Al 7005 post box
Cast aluminium alloys

Properties required for good casting

• Low melting temperature
• Low solubility of gases except $\text{H}_2$
• Good fluidity
• Good surface finishes

Disadvantage

• High solidification shrinkage (3.5-8.5%)

Factors controlling properties

• Melting and pouring practices
• Impurity levels
• Grain size
• Solidification rate

Note: Innovations and development are mainly oriented to the automobile sector which is the most important market for castings.

Cast aluminium alloys are widely used for transport applications, Ex: Cast engine block
**Designations of cast aluminium alloys**

**United States Aluminium Association system**

- Using four-digit system.

<table>
<thead>
<tr>
<th>1xx.x</th>
<th>Al, 99.00% or greater</th>
</tr>
</thead>
<tbody>
<tr>
<td>2xx.x</td>
<td>Cu</td>
</tr>
<tr>
<td>3xx.x</td>
<td>Si with added Cu and/or Mg</td>
</tr>
<tr>
<td>4xx.x</td>
<td>Si</td>
</tr>
<tr>
<td>5xx.x</td>
<td>Mg</td>
</tr>
<tr>
<td>6xx.x</td>
<td>Unused series</td>
</tr>
<tr>
<td>7xx.x</td>
<td>Zn</td>
</tr>
<tr>
<td>8xx.x</td>
<td>Sn</td>
</tr>
<tr>
<td>9xx.x</td>
<td>Other elements</td>
</tr>
</tbody>
</table>

- **1xx.x series**
  - Second two digits indicate the minimum percentage of Al, Ex: 150.x → 99.50% Al.
  - Last digit (after decimal point) indicates product forms.
    - 1 = casting, 2 = ingot

- **2xx.x to 9xx.x series**
  - Second two digits identify the different aluminium alloys.
  - Last digit (after decimal point) indicates product forms.

*Note: The 6xx.x series is allocated to Al-Si-Mg alloys in Australia.*
British System

- Designation of cast Al alloy in British system is covered by the British Standard 1490.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>As-cast</td>
</tr>
<tr>
<td>TB</td>
<td>Solution treated and naturally aged</td>
</tr>
<tr>
<td>TB7</td>
<td>Solution treated and stabilised</td>
</tr>
<tr>
<td>TE</td>
<td>Artificially aged after casting</td>
</tr>
<tr>
<td>TF</td>
<td>Solution treated and artificial aged</td>
</tr>
<tr>
<td>TF7</td>
<td>Solution treated, artificially aged and stabilised</td>
</tr>
<tr>
<td>TS</td>
<td>Thermally stress-relieved</td>
</tr>
</tbody>
</table>
The most common aluminium casting techniques are:

1) Sand casting
2) Die casting - gravity casting
   - high pressure die casting
   - low pressure die casting
   - vacuum die casting
   - squeeze casting

**Selection of casting process** depends upon alloy composition which is related to controlled characteristics such as solidification range, fluidity, susceptibility to hot-cracking.

<table>
<thead>
<tr>
<th>Castability</th>
<th>3xx.x &gt; 4xx.x &gt; 5xx.x &gt; 2xx.x &gt; 7xx.x</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si, Cu, Mg</td>
<td>Si</td>
</tr>
<tr>
<td>Mg</td>
<td>Cu</td>
</tr>
<tr>
<td>Zn</td>
<td></td>
</tr>
</tbody>
</table>
Alloys based on the Al-Si system

The most important group and constitute for 85-90% of the total aluminium casting.

- **Eutectic (Al – 12.7%Si)** is formed just over 1% Si addition, which contains a coarse microstructure of large plates or needles of Si in a continuous Al matrix.

- Large Si plates → low ductility and brittleness.

Equilibrium binary Al-Si phase diagram

Hypoeutectic Al-Si

Eutectic Al-Si

Hypereutectic Al-Si

Require modification
## Composition of common Al-Si casting alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Method(b)</th>
<th>Si</th>
<th>Cu</th>
<th>Mg</th>
<th>Fe</th>
<th>Zn</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>319.0</td>
<td>S, P</td>
<td>6.0</td>
<td>3.5</td>
<td>&lt;0.10</td>
<td>1.0</td>
<td>1.0</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>332.0</td>
<td>P</td>
<td>9.5</td>
<td>3.0</td>
<td>1.0</td>
<td>1.2</td>
<td>1.0</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>355.0</td>
<td>S, P</td>
<td>5.0</td>
<td>1.25</td>
<td>0.5</td>
<td>&lt;0.06</td>
<td>0.35</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>A356.0</td>
<td>S, P</td>
<td>7.0</td>
<td>&lt;0.20</td>
<td>0.35</td>
<td>&lt;0.2</td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td>A357.0</td>
<td>S, P</td>
<td>7.0</td>
<td>&lt;0.20</td>
<td>0.55</td>
<td>&lt;0.2</td>
<td>&lt;0.1</td>
<td>0.05 Be</td>
</tr>
<tr>
<td>380.0</td>
<td>D</td>
<td>8.5</td>
<td>3.5</td>
<td>&lt;0.1</td>
<td>&lt;1.3</td>
<td>&lt;3.0</td>
<td>&lt;3.0</td>
</tr>
<tr>
<td>383.0</td>
<td>D</td>
<td>10.0</td>
<td>2.5</td>
<td>0.10</td>
<td>1.3</td>
<td>3.0</td>
<td>&lt;3.0</td>
</tr>
<tr>
<td>384.0</td>
<td>D</td>
<td>11.0</td>
<td>2.0</td>
<td>&lt;0.3</td>
<td>&lt;1.3</td>
<td>&lt;3.0</td>
<td>0.35 Sn</td>
</tr>
<tr>
<td>390.0</td>
<td>D</td>
<td>17.0</td>
<td>4.5</td>
<td>0.55</td>
<td>&lt;1.3</td>
<td>&lt;0.1</td>
<td>&lt;0.1 Mg</td>
</tr>
<tr>
<td>413.0</td>
<td>D</td>
<td>12.0</td>
<td>&lt;0.1</td>
<td>&lt;0.10</td>
<td>&lt;2.0</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>443.0</td>
<td>S, P</td>
<td>5.25</td>
<td>&lt;0.3</td>
<td>&lt;0.05</td>
<td>&lt;0.8</td>
<td>&lt;0.5</td>
<td></td>
</tr>
</tbody>
</table>

(a) Remainder: Aluminum and other impurities  
(b) S, Sand Casting; P, Permanent Mold Casting;  
D, High Pressure Die Casting

### Properties:
- Good castability and high fluidity due to Al-Si eutectic  
- High corrosion resistance  
- Good weldability.  
- Low solidification shrinkage.  
- Machining difficulty in hypereutectic compositions.

**Note:** Available with hypoeutectic and less commonly hypereutectic compositions.
Modification of microstructure

- Apart from fast cooling to refine the microstructure, *modification* can be carried out by adding certain *alkali fluorides* to the melt prior to pouring.
- Additions of *Sr* or *Na* change *eutectic microstructure* from needle-like or lamellar to *fibrous*.
- Higher concentration of 0.02% *Sr* fully modifies to fibrous structure.
- *Grain refinement* improves resistance to *hot tearing*, decreases *porosity* and increases *mass feeding*.

*Note:* Higher Si content requires more modifying agent.

Microstructures of 413 alloy (Al-Si eutectic alloy) and modified with Sr
Mechanical property improvement due to refined microstructure

<table>
<thead>
<tr>
<th>Condition</th>
<th>Tensile strength (MPa)</th>
<th>Elongation (%)</th>
<th>Hardness (Rockwell B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal sand cast</td>
<td>125</td>
<td>2</td>
<td>50</td>
</tr>
<tr>
<td>Modified sand cast</td>
<td>195</td>
<td>13</td>
<td>58</td>
</tr>
<tr>
<td>Normal chill cast</td>
<td>195</td>
<td>3.5</td>
<td>63</td>
</tr>
<tr>
<td>Modified chill cast</td>
<td>220</td>
<td>8</td>
<td>72</td>
</tr>
</tbody>
</table>

Note: Cast Al alloys normally have inferior mechanical properties to those of wrought Al-alloys.

Fracture toughness of alloy A357 (Al-7Si-0.5Mg) with and without Sr modification

Tensile strength
% Elongation
Hardness
Fracture toughness
Example: Modification with Na

- **Modification mechanism** by Na addition are still controversial.

- The effect of Na on the nucleation and growth of eutectic silicon during solidification.

- Na restricts growth of Si particles by segregation at periphery of Si plates and prohibiting growth.

- Excess amount of P → large particles of silicon resulting poor mechanical properties.

Ex: 0.005-0.01% Na or 0.02% Sr are required for modification for 7% Si.
# Variables determining microstructure

<table>
<thead>
<tr>
<th>Variable</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Type of modifier used</td>
<td>• Na is more powerful than Sr.</td>
</tr>
<tr>
<td>2) Amount of modifier used</td>
<td>• A critical level is required to obtain a full modification.</td>
</tr>
<tr>
<td></td>
<td>• Too high level → over modification.</td>
</tr>
<tr>
<td></td>
<td>• Modifier fading → need top up.</td>
</tr>
<tr>
<td>3) Impurities present in the melt</td>
<td>• P makes modification more difficult.</td>
</tr>
<tr>
<td></td>
<td>• Mg was found to make modification easier.</td>
</tr>
<tr>
<td>4) Freezing rate</td>
<td>• Higher solidification rates assist the modification process.</td>
</tr>
<tr>
<td>5) Si content of the alloy</td>
<td>• Higher amount of existing Si requires greater amount of modifier to obtain complete modification.</td>
</tr>
</tbody>
</table>
Over modification

• *Over modification* occurs when Na concentration exceeds 0.018 – 0.020%.

• *Coarsening of Si* takes place associated with bands of primary aluminium.

• *Na* is rejected in front of the solidifying interface and form AlSiNa which serves as nucleation sites for *coarse silicon particles*.

• Excess amount of *Sr* also cause over modification by *coarsening of the silicon structure*.

*Al₄SrSi₂ phase (1) caused by over modification of 356 alloy (x270)*
Al-Si-Cu, Al-Si-Mg alloys

Cu and Mg additions provide much greater strengthening effect.

Al-Si-Cu alloys

3 - 10.5% Si
1.5 - 4.5% Cu

Applications:

- Automative cylinder heads/blocks in place of cast iron.

Note: more complex compositions for special properties. i.e., elevated temperature properties.

EX: Al-12Si-1Cu-1Mg-2Si and Al-17Si-4Cu-0.55Mg).

Pistons and air compressor. 390.0 (Al-Si-Cu)
Pistons and connection rods. 319.0 (Al-Si-Mg)
Al-Cu alloy

- **Strength** and hardness at T up to 250°C is achieved from a combination of *precipitation hardening* together with *dispersion hardening* by intermetallic compounds.
- Strength is higher than other *cast Al alloys* and comparable to *wrought Al alloys*.

Properties:

- $\sigma_y$ 345-480 MPa and $\sigma_{TS}$ 415-550 MPa due to high response to *ageing*, with 5-10% elongation.

Applications:

- Elevated temperature applications. Ex: *Al-4Cu-2Ni-1.5Mg* for diesel engine pistons and air-cooled cylinder heads for aircraft.

*Note: Have casting problem with hot-tearing*

Suranaree University of Technology    Tapany Udomphol    May-Aug 2007
Al-Mg alloys

- **Al-Mg** alloys are less preferable than **Al-Si** in casting and require practice during melting and pouring due to **oxidation problem**.
- Mg content ~ 4 - 10%.
- Most are sand cast.

**Properties:**
- High resistance to corrosion
- Good machinability
- Attractive anodised surface.
- Little or no response to heat treatment.

**Applications:**
- Chemical and sewage
- Kitchen utensils.
- Watch body
- Kitchen utensils
**Al-Zn-Mg alloys**

• Binary **Al-Zn** alloys are obsolete except for use of *sacrificial anode for steel structure protection*.

• Normally **sand cast** because permanent moulds tends to cause hot-cracking.

**Properties:**
- $\sigma_y$ 115-260 MPa and $\sigma_{TS}$ 120-310 MPa.

**Applications:**
- High eutectic melting point.
- Good machinability.
- Dimensional stability.
- Corrosion resistance.
- Not suitable for high temperature applications due to rapid softening.
Casting processes

- Sand casting
- Die casting
- Semi-solid casting (Thixo-casting)
- Squeeze casting
- Cosworth casting
- Improved low pressure casting
Sand casting

- Versatile – complex designs, sizes, shapes
- Sand – silica sand, zirconia sand, olivine
- Sand mould is destroyed after each use and reusable
- Bonding of sand mould is a key step.
- Size and shape of sand also control the quality of the cast.

Half mould with cores and an example of a cast air intake for a turbocharger
Die casting processes

- Liquid metal is pushed into a die cavity either by ram, gas or a pump and either by means of high or low pressure.

*Low pressure die casting*

Liquid metal enters die at relatively low velocity.

*High pressure die casting*

Liquid metal enters die at high velocity. No sand cores are normally used.
Semi-solid processing (Thixo-casting)

- The use of *agitation* during solidification to break down *dendrites* can improve *fluidity* although the solid content has reached 60%.
- Broken down dendrites result in very fine grain size.
- Semi-solid slurry has thixotropy characteristics (agitating viscosity)

*Note: Use for the production of automotive components such as master brake cylinders, pistons, compressors*
Advantages of semi-solid casting

1) Reduced capital investment and operating cost due to
   • Contained process of melting.
   • Less energy required due to no complete melting.
   • Reduced cycle time and minimised scrap.

2) Reduced shrinkage and cracking
   • The alloy is partially solidified during casting.

3) Lower operating and pouring temperature
   • Improve the life of metal dies.

4) Readily produced composite materials (Compocasting)
   • Fibres or solid particles can be added into the feedstock.
Squeeze casting

- The process involves working or processing the liquid metal in a hydraulic press during solidification.
- The use of pressure (~200 MPa) which is higher than conventional casting helps to fill up pores by the flow of the melt.
- Promote intimate contact between casting and mould walls. → improve heat extraction → grain refinement.

Advantages:

- Improvement in ductility
- Provide isotropic properties where (wrought products suffer from directionality.
- Liquid metal can be infiltrated into a mesh or pad of fibres (or particulates) to produce composite materials. → used to manufacture pistons in for cars.
Direct squeeze casting

• Pour metered amount of liquid metal into a die and then pressurise to solidify the metal via the second moving half of the die.
• Runners and feeding systems are not required. → good cast yield.

Indirect squeeze casting

• Pour the liquid metal into a shot sleeve and inject vertically into the die by a piston, which sustains the pressure during solidification.
• Runners and feeding systems are not required. → good cast yield.
Cosworth Process

• The Cosworth Process allow quiescent transfer of metal from the stage of the ingots to the final filling of the mould.

• Minimising the undesirable effect of dispersing fine oxide particles and inclusions through the melt.

• Oxides/inclusions are separated by floating or sinking.

• No flux or chemicals additions. → atmosphere protection.

• The mould is permeable to allow air to escape. → improve tensile strength and ductility.

• Use reclaimable zircon sand rather than silicon sand for mould and core making. → stable mould volume → dimensional tolerance.

Cylinder head castings produced by Cosworth Process

Tapany Udomphol

May-Aug 2007
**Improved low pressure casting (ILP) process**

- **Automotive Precision casting process** developed in Australia.
- Molten metal transfer is *vertical* through a riser tube into the bottom of the mould cavity.
- Molten metal is *degassed* and *filtered* in the casting furnace due to a *pressurised atmosphere of nitrogen*. → quiescent, computer-controlled filling of the mould.
- The mould is sealed immediately after filling to allow *solidification* to occur remotely from the casting unit.
- **High productivity** → cycle time ~ 60 s.
- The *metal cores* are made from *resin-bonded silica* sand for mould which promotes rapid unidirectional solidification. → optimal properties.

*Reduced dendrite arm spacing and overall microshrinkage.*
Comparison of mechanical properties of 357 Al alloy produced by different casting process

<table>
<thead>
<tr>
<th>Process</th>
<th>0.2% proof stress MPa</th>
<th>Tensile strength MPa</th>
<th>Elongation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand cast</td>
<td>200</td>
<td>226</td>
<td>1.6</td>
</tr>
<tr>
<td>Chill cast</td>
<td>248</td>
<td>313</td>
<td>6.9</td>
</tr>
<tr>
<td>Squeeze cast</td>
<td>283</td>
<td>347</td>
<td>9.3</td>
</tr>
<tr>
<td>Cosworth</td>
<td>242</td>
<td>312</td>
<td>9.8</td>
</tr>
</tbody>
</table>
References

References

References

- www.boeing.com
- www.formigli.it
- www.hydro.com
- http://www.autointell-news.com
- www.light-alloy-wheels.com
- www.barrykeen.co.za
- www.packaging-technology.com
- virtualskies.arc.nasa.gov
- www.world-aluminium.org
- www.physchem.co.za
- www.scielo.br
- www.working-images.co.uk
- http://www.key-to-metals.com
- www.kamlit.ru
- www.wpi.edu
- www.mmate.ubc.ca
- www.sural.com
- www.aluvan.com
- 193.80.13.115/SAG/upload/images/Alutech/Druck...
- http://www.aluminiumlearning.com
- aluminium.matter.org.uk
- www.azom.com