Zinc and its alloys

Subjects of interest

- *Objectives/Introduction*
- *Extraction of zinc*
- *Physical properties of zinc*
- *Zinc casting alloys*
- *Wrought zinc alloys*
- *Engineering design with zinc alloys*

Objectives

• This chapter provides fundamental knowledge of different methods of productions of zinc alloys and the use of various types of cast and wrought zinc alloys.

• The influences of alloy composition and microstructure on chemical and mechanical properties of zinc alloys will be discussed in relation to its applications.

Introduction

Advantages:

- Fast rate of die casting
- Excellent atmospheric corrosion resistance.
- Ability to form a well-adhering coating on steel.

Applications

- Used for galvanic protection in steel and decorative finish.
- Used in die casting.

Steel coated with pure zinc

Zinc roof protection

Zinc diecast

Extraction of zinc

• ***Zinc*** can be extracted from zinc sulphide (***ZnS***) or ***zinc blende*** or ***sphalerite***.

• Found in many countries such as USA, Mexico, Peru, etc., and also in Thailand.

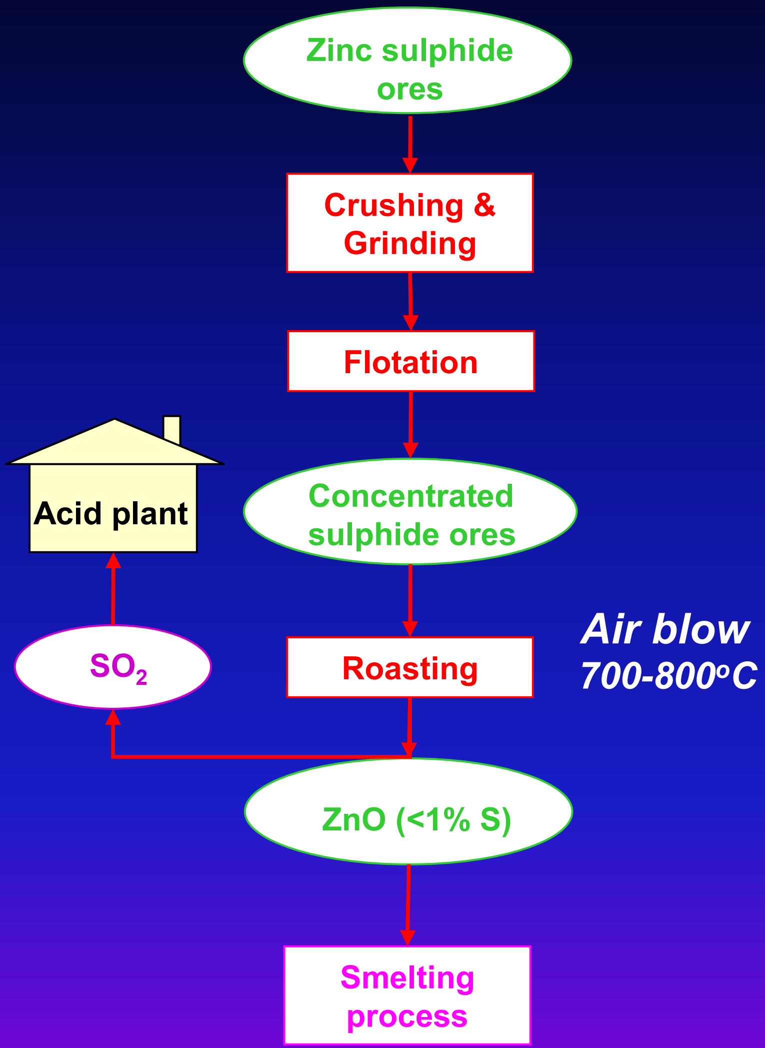
Ores are found in the forms of

1) Smithsonite ($ZnCO_3$) – 67% Zn
2) Hemimorphite or ($Zn_4Si_2O_7(OH)_2.H_2O$). – 54.2% Zn
3) Zincite (ZnO)
4) Willemite (Zn_2SiO_4) – 58.5%.

There are two methods of zinc extraction;

1) Pyrometallurgy
2) Hydrometallurgy → ***Electrochemical treatment***

Pyrometallurgical treatment

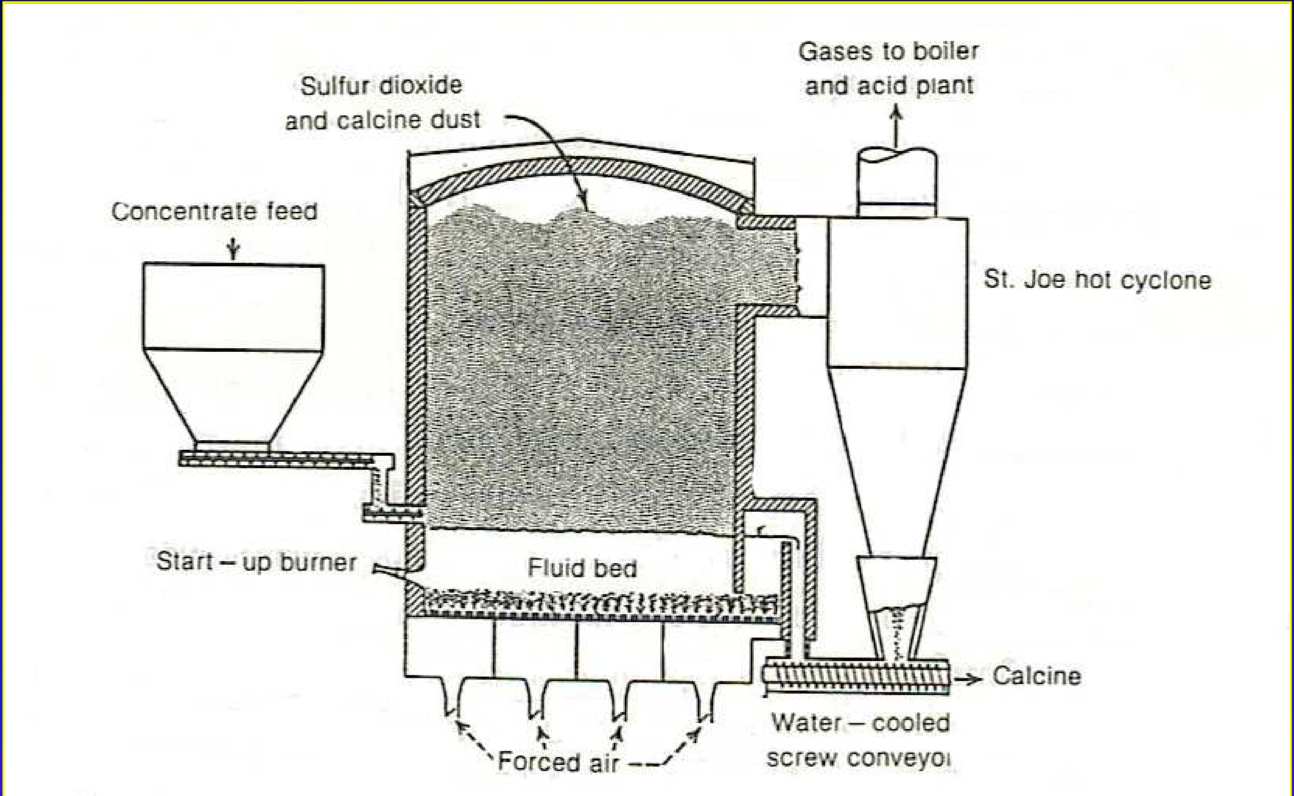


Roasting Process

- The ***zinc sulphide ores*** are concentrated by crushing down the size → wet grinding and then flotation.
- ***Concentrated zinc sulphide*** ores are roasted at ***T***~700-800°C with ***air blow*** to produce ***ZnO***.
- The reaction is exothermic, which increases the temp upto 1000°C.

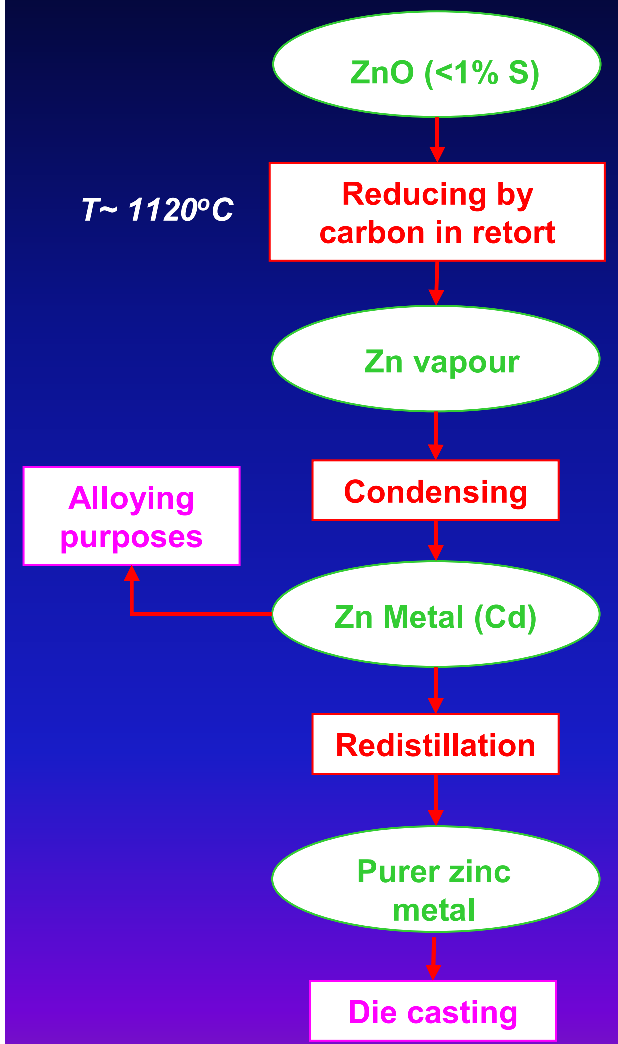
$$ZnS + \tfrac{3}{2}O_2 \rightarrow ZnO + SO_2$$

Roasting Process



Zinc sulphide concentrate fluid bed roaster

Smelting process



- ***Zinc oxide*** is reduced using ***carbon*** to obtain ***Zn metal.*** (T~1120°C) , T_b ~ 906°C

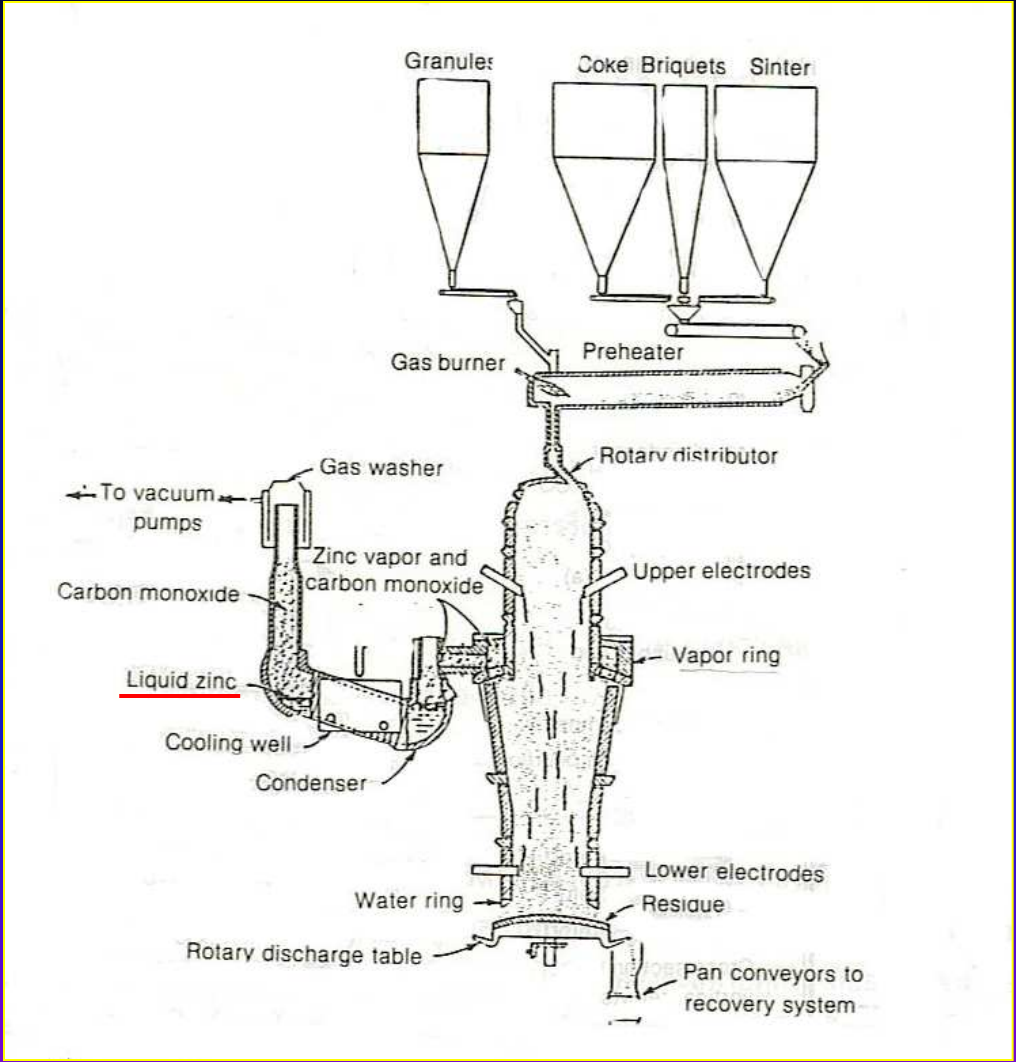
$$ZnO + CO \rightarrow Zn + CO_2$$
$$CO_2 + C \rightarrow 2CO$$
$$\Rightarrow ZnO + C \rightarrow Zn + CO + \Delta H$$

- ***Zn vapour*** is produced due to high reducing temp and ***CO*** is released for the use of ***preheating*** the starting materials.

- ***Sulphur*** must be excluded from the process which can cause the reverse process giving ***ZnO*** instead.

- ***Zn vapour*** is then condensed to give a liquid form of ***Zn***. (contains small amounts of ***Cd***). If used as alloying elements for ***Cu*** and ***Ni*** alloys is ok but if used for die casting → redistillation at T~ 765°C to vaporise ***Cd*** off.

Smelting process



Electrothermic zinc furnace

Hydrometallurgical treatment

For low grade ores *(using non-sulphide form and processed without roasting)*

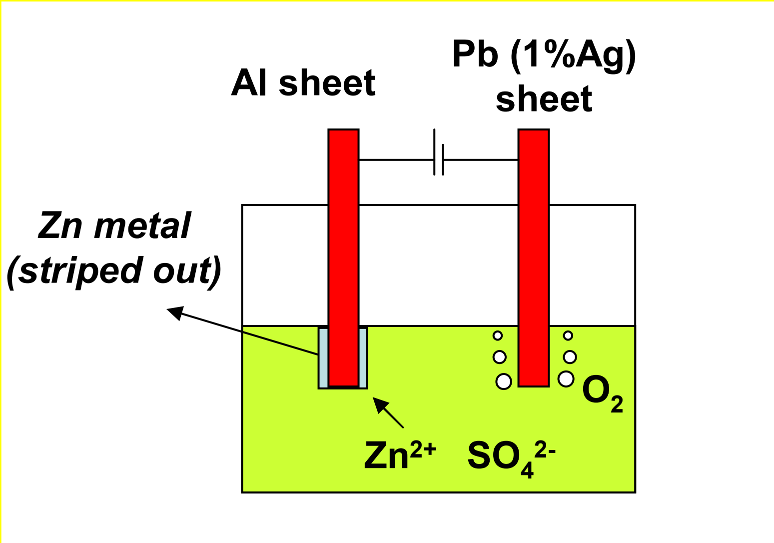
- ***ZnO*** is dissolved in dilute ***H_2SO_4*** ***(leaching)*** to give ***$ZnSO_4$***. (***Pb*** - impurity)

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$$

- ***$ZnSO_4$*** is then undergone electrolysis process to give ***Zn***.

Note: *In Thailand,* ***Phadang industry*** *utilises the same process sequence but using* ***Hemimorphite*** *(****$Zn_4Si_2O(OH).H_2O$****) as the starting ore. The obtained* ***$ZnSO_4$*** *is then gone through electrolysis process.*

Electrolysis of $ZnSO_4$



Cathode	: Al sheet
Anode	: Pb (1%Ag) sheet
Electrolyte	: $ZnSO_4$ solution at pH 5
Voltage	: 3.5-3.7 volts
Current density	: 700-1000 A/m^2

- ***O_2*** is released at ***anode***.
- ***Zn^{2+}*** goes to ***cathode*** and is then removed or striped out. → dried and further melt to form ingot.
- The ***electrolyte*** will become ***H_2SO_4*** which then can be used in the beginning process.

$$ZnSO_4 \rightarrow Zn^{2+} + SO_4^{2-}$$
$$2H_2O \rightarrow 2H_2 + O_2$$

Physical properties of zinc

Crystal structure	HCP
c/a ratio	1.856
Density ($g.cm^{-3}$)	7.14
Atomic weight	65.39
Atomic number	30
Melting point (°C)	419.6
Boiling point (°C)	906

30 HCP
Zn
Zinc
65.39

- ***Zinc*** recrystallises and creeps near room temperature so it ***cannot be strain-hardened*** significantly.
- Most structural ***zinc*** is used in the form of die casting (has advantage of a low melting point).
- Good strength but low toughness and low creep strength. Cannot be used for high temperature applications.
- Anisotropic properties due to ***HCP*** structure.

Classification of zinc alloys

Zinc alloys can be mainly classified into to

1) Zinc casting alloys

- *Conventional zinc casting alloys (4% Al)*
- *Zn-Al (ZA) casting alloys*

2) Wrought zinc alloys

- *Zn-Pb alloys*
- *Zn-Cd alloys*
- *Zn-Cu alloys*

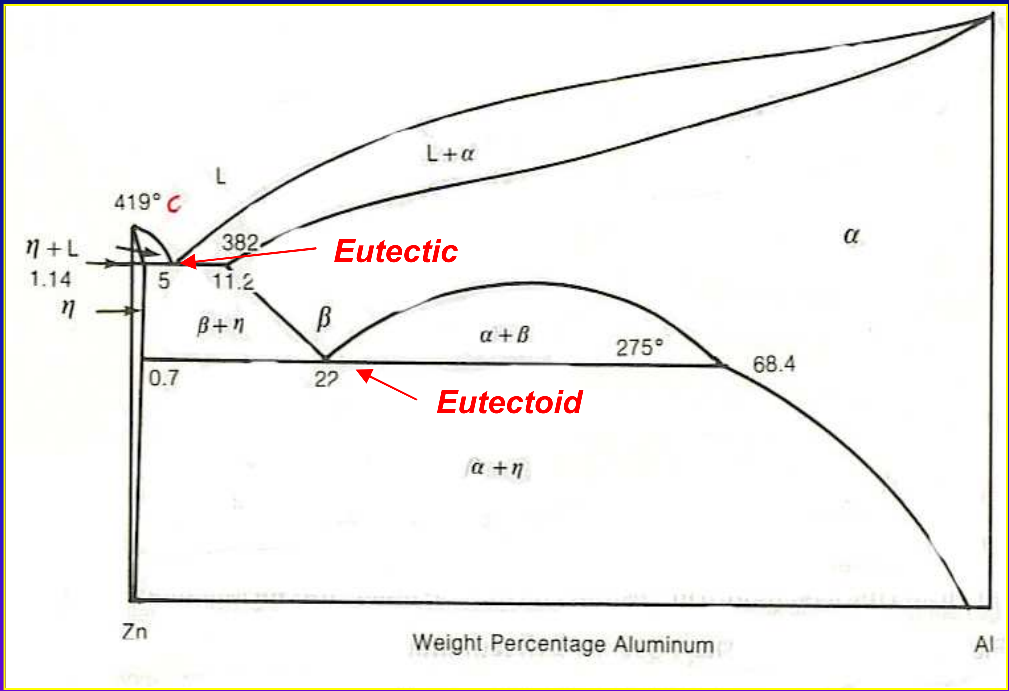
Zinc casting alloys

- ***Al*** can form solid solution with ***Zn*** at low quantity (max at 1.14%) at 382^{o}C and gives ***eutectic reaction*** at 5%***Al***.

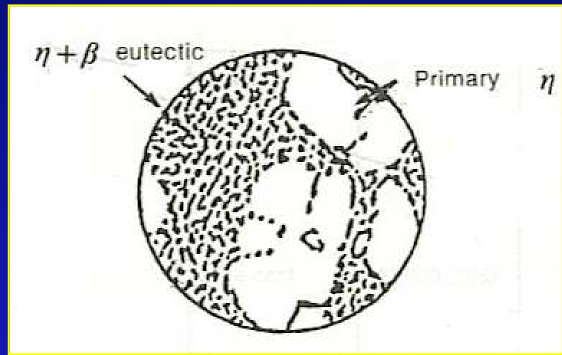
$$L \leftrightarrow \beta + \eta$$

- ***Eutectoid reaction*** occurs at 275^{o}C.

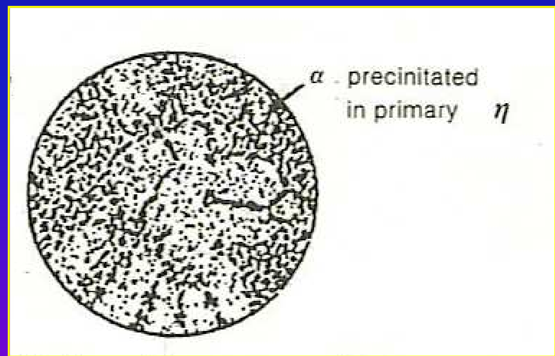
$$\beta \leftrightarrow \alpha + \eta$$



Zn-Al phase diagram



Freshly cast



Aged at RT

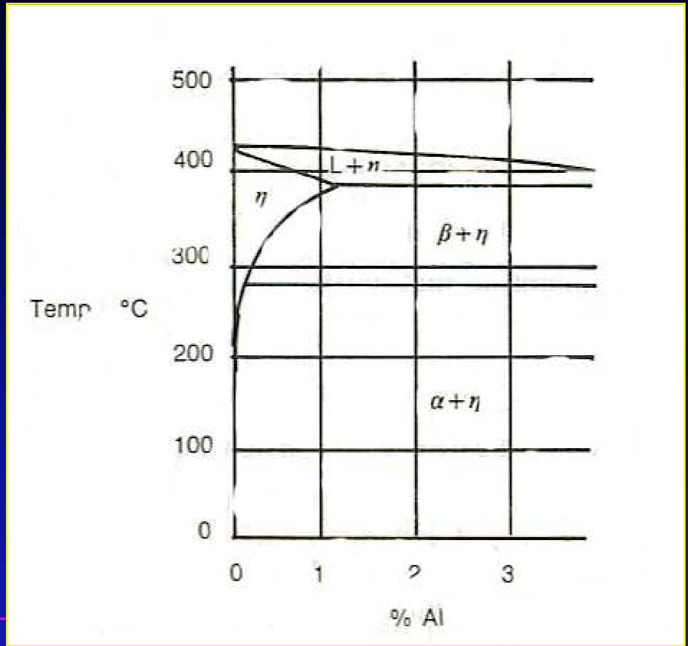
Microstructure of Zn-4%Al

Conventional zinc casting alloys

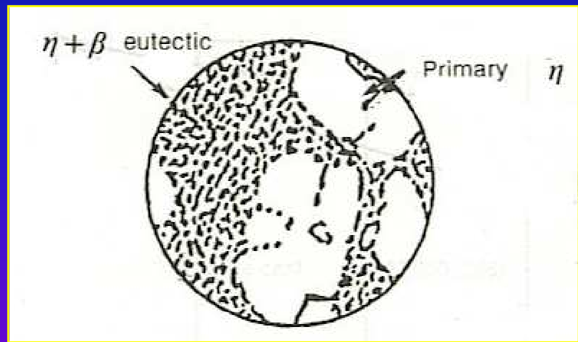
- *Conventional zinc casting alloys* are based on ***Zn-4%Al*** composition due to
  - High castability
  - Easy finishing
  - Good mechanical properties
  - Free from intergranular corrosion.

Microstructure

- Microstructure of as die cast ***Alloy 3*** (4.1%***Al*** 0.1%***Cu*** 0.04%***Mg***) consists of primary ***Zn-Al solid solution regions*** (primary phase η) surrounded by ***eutectic structure*** ($\beta+\eta$).
- ***All eutectic structure of Zn-Al*** (at 5%Al) is avoided due to its extremely brittle nature.



Zn-Al phase diagram



Freshly cast

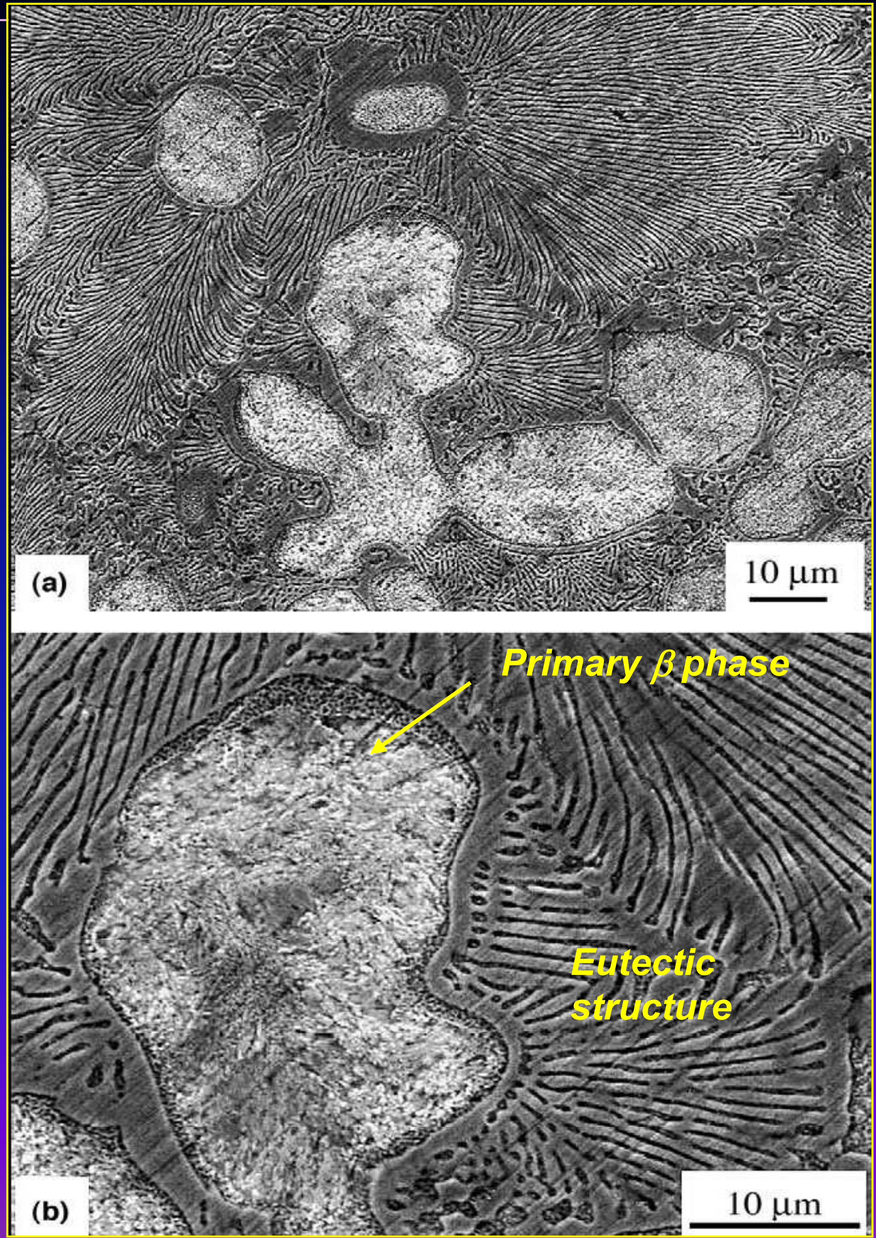
Microstructure of Zn-4%Al

Conventional zinc casting alloys

- ***Hypereutectic zinc casting alloys*** ex; ***Zn-8%Al*** composition.
- Primary phase is β set in a eutectic matrix of β and η.
- On cooling passing eutectoid temperature, β decompose to α and η.

Al contents ↑ ***Tensile strength*** ↑

Fatigue strength ↑



Microstructure of squeeze cast ZA-8 alloy (SEM)

The role of alloying elements in conventional zinc casting alloys and mechanical properties

The role of alloying elements

- ***Al*** is added for ***strengthening***, reducing ***grain size***, improving ***fluidity*** (castability) and minimising the attack of the molten zinc alloy on the iron and steel in the casting equipment.
- ***Mg*** is added in small amount (0.01-0.3%) to prevent ***intergranular corrosion*** due to the presence of ***Pb, Cd*** and ***Sn*** impurities. But excessive amount lowers fluidity and promotes hot cracking → reduce elongation. (***Pb*** < 0.003% and ***Sn*** <0.001%).
- ***Cu*** minimises effects of ***impurities***, improve strength and hardness. (Cu < 1% → higher amounts lead to reduced toughness, embrittlement).

Mechanical properties

• Tensile strength	: 220-440 MPa
• Yield strength	: 210-380 MPa
• Elongation	: 1-10%

Zinc (ZA) casting alloys

- ***ZA*** casting alloys are ***ZA-8, ZA-12 and ZA-27***.
- ***Z*** and ***A*** letters refer to ***Zn*** and ***Al*** respectively and numbers refer to wt% of ***Al*** in each alloy.
- Small additions of ***Cu*** and ***Mg*** give a good strength, stability and castibility.

Mechanical properties

Property	No. 3 AG-40A	No. 5 AC-41A	ZA-8		ZA-12			ZA-27		
	Die cast	Die cast	Permanent mold cast	Die cast	Sand cast	Permanent mold cast	Die cast	Sand cast	Sand cast HT	Die cast
Tensile strength, lb in$^{-2}\times10^3$ (MPa)	41 (283)	48 (331)	32–37 (221–255)	53–56 (365–386)	40–46 (276–317)	45–50 (310–345)	57–60 (393–414)	58–64 (400–441)	45–47 (310–324)	59–65 (407–441)
Yield strength, 0.2% offset, lb in$^2\times10^3$ (MPa)			30 (207)	41–43 (283–296)	30 (207)	36–40 (248–276)	45–48 (310–331)	53 (365)	37 (255)	52–55 (359–379)
Young's modulus, lb in$^{-2}\times10^6$ (GPa)			12.4 (85.5)	—	12.0 (83)	12.0 (83)	—	10.9 (75)	11.5 (79)	
Elongation, % in 2 in, (51 mm)	10	7	1–2	6–10	1–3	1.5–2.5	4–7	3–6	8–11	2.0–3.5

***Note:** the alloys have excellent machinability, good surface finish for decorative parts. Normally is first choice of replacing cast iron, brass and aluminium alloys.*

Advantages of zinc alloys

1) *Ability of zinc to **die cast at high productivity** rates due to zinc's relatively low melting point (419^{o}C).*
2) *Ability to produce **near-net shapes of intricate designs** with close dimensional tolerance and good surface finishes.*
3) *Zinc die castings can be machined, bent, swaged or coined for finishing.*
4) *Zinc die castings can be riveted, welded, and soldered in assembly operations.*
5) *Relatively **good atmospheric corrosion resistance**, especially in **Cr** solution (forming surface passive film).*
6) ***Sufficient strength** for some applications.*
7) ***Cost of Zn** is competitive with **Al** and **Cu** alloys for many applications.*

Wrought zinc alloys

Limitation of wrought zinc alloys

1) *Pure zinc is ductile at RT and do not have a definite yield point because it creeps at RT.*
2) *Rolled zinc has anisotropic deformation properties due to HCP structure.*

Despite its limitations, wrought zinc alloys can find its applications as shown in table.

Typical tensile mechanical properties and characteristics of selected wrought zinc alloys

Alloy composition	Cold-rolled Orientation	Tensile strength MPa	Tensile strength ksi	Elongation, %	Typical uses
Zn–0.08 Pb	Longitudinal	145	21.0	50	Drawn battery cans, eyelets, fuse links, and a variety of articles drawn, formed and spun
	Transverse	186	27.0	40	
Zn–0.06 Pb–0.06 Cd	Longitudinal	150	22.0	40	Drawn battery cans, eyelets and grommets; extruded battery cans; address plates, laundry tags
	Transverse	200	29.0	30	
Zn–1.0 Cu	Longitudinal	170	25.0	45	Weatherstrips and drawn and formed articles requiring stiffness
	Transverse	210	31.0	28	
Zn–0.8 Cu–0.15 Ti	Longitudinal	210	31	40	Corrugated roofing, leaders and gutters, and other uses requiring maximum creep resistance
	Transverse	280	40	25	
Superplastic Zn alloy					
Zn–22 Al–0.5 Cu–0.01 Mg	As rolled	310	45	27	Electronic enclosures, cabinets and panels, business machine parts
	Annealed	400	58	11	

Engineering design with zinc alloys

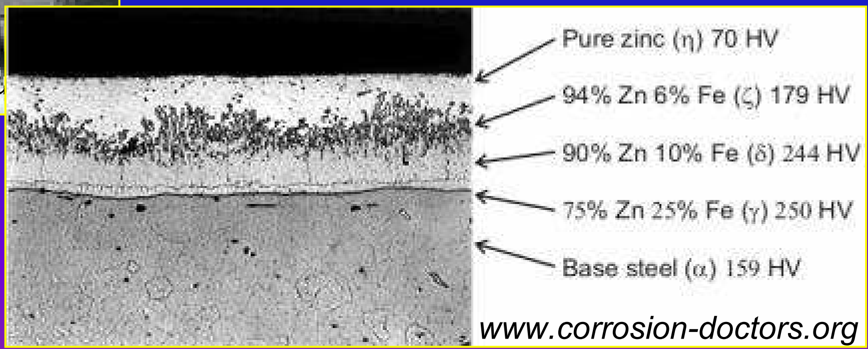
The alloys are die cast, permanent mould cast and sand cast.

Applications

- Used for ***automobile parts*** such as handles, locks mechanical and electrical components.
- Body hardware, light fittings, instruments.
- Galvanic coating on steels.

Zn-Al alloy products for automobile rear view mirror

Steel coated with pure zinc



ZA-27 products

Disadvantages of zinc alloys

1) **Cannot be used at T > 95°C** *due to loss of strength and hardness (creep at RT).*

2) **Relatively high density** *(7.1 $g.cm^{-3}$) in comparison to* **Al** *(2.7 $g.cm^{-3}$) and magnesium (1.74 $g.cm^{-3}$). → not suitable for applications where weight is critical.*

3) **HCP structure** *limits plastic deformation of zinc.*

References

- มนัส สถิรจินดา, โลหะนอกกลุ่มเหล็ก, 2536, สำนักพิมพ์จุฬาลงกรณ์มหาวิทยาลัย, ISBN 974-582-155-1.
- Smith, W.F., ***Structure and properties of engineering alloys***, second edition, 1993, McGraw-Hill, ISB 0-07-59172-5.
- Fatih Çay and S. Can Kurnaz, ***Hot tensile and fatigue behaviour of zinc–aluminum alloys produced by gravity and squeeze casting***, Materials & Design, Vol. 26, Issue 6, 2005, p. 479-485.