Magnesium and its alloys

Subjects of interest

- *Introduction/Objectives*
- *Melting and casting of magnesium alloys*
- *Classification of magnesium alloys*
- *Commercial magnesium alloys*
- *Engineering designing with magnesium alloys*
- *Joining of magnesium alloys*

Objectives

- This chapter provides fundamental knowledge of different methods of productions / heat treatments of magnesium alloys and the use of various types of cast and wrought magnesium alloys.
- The influences of alloy composition, microstructure and heat treatment on chemical and mechanical properties of magnesium alloys will be discussed in relation to its applications.

Introduction

- Found 2.8% in sea water and other forms, i.e., ***dolomite*** (***$CaMg(CO_3)_2$***), ***magnesite*** (***$MgCO_3$***) and ***Carnallite*** (***$KMgCl_3.6H_2O$***).
- Found in USA, England, Australia, Germany, Russia, Italy.
- In ***Thailand***: Dolomite → Kanchanaburi, Chonburi.
  Magnesite → Chanthaburi,
- Magnesium with ***99.8% purity*** are readily available but rarely used in this stage for engineering applications.

Dolomite

Magnesite

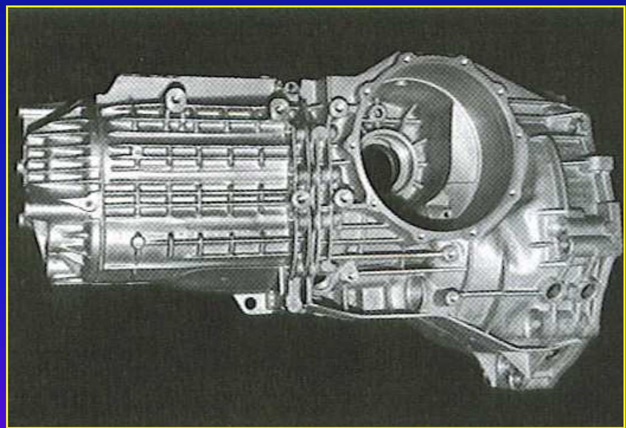
Carnallite

Introduction – *Applications*

Cam and mobile phone bodies.

Magnesium side panels

Alloyed wheel



Gearbox housing in the VW-Passat

Aerospace applications

Main application is for cast parts in automotive industry.

Physical properties of magnesium

Crystal structure	**HCP**	**a = 0.3202, c = 0.5199, c/a = 1.624**
Atomic diameter	**0.320**	**easily alloyed with Al, Zn, Ag, Zr**
Density ($g.cm^{-3}$)	**1.74**	
Melting point (^{o}C)	**650**	

- Alloyed with ***Al, Zn, Mn, rare earth metals*** to produce alloys with high-strength-to weight ratios.
- Tends to form compounds with negative valence ion (due to strong electropositive) rather than solid solution.
- Not readily plastically deformed at ***RT*** due to ***HCP structure***.
- ***Cast magnesium alloys*** dominate 85-90% of all magnesium alloy products, with ***Mg-Al-Zn*** system being the most widely used.

- Low strength and toughness and corrosion resistance.
- Easily flammable with oxygen.

⇨ **Limit applications of magnesium alloy**

Classification of magnesium alloys

• No international code, but can use ***ASTM system*** designated by two capital letters followed by two or three numbers.

• ***The letters stand for the two major alloying elements***
- ***first letter*** → the highest amount
- ***second letter*** → the second highest amount

• ***The numbers stand for the amount of the two major alloying elements***
- ***first number*** following the letters stands for the wt% of the first letter element.
- ***second number*** stands for the wt% of the second letter element.

A – Aluminium	*F – Iron*	*M - Manganese*	*S – Silicon*
B – Bismuth	*G – Magnesium*	*N – Nickel*	*T – Tin*
C – Copper	*H – Thorium*	*P – Lead*	*W –Yttrium*
D – Cadmium	*K – Zirconium*	*Q - Silver*	*Z - zinc*
E – Rare earths	*L – Lithium*	*R - Chromium*	

Example:

AZ91D:	The magnesium alloy contains 9 wt% ***aluminium***, 1 wt% ***zinc*** and the alloy is the ***D*** modification.
QE22A-T6	The magnesium alloy contains 2 wt% ***silver***, 2% ***rare earths*** and in the ***A*** modification. ***T6*** – solution heat-treated, quenched and artificially aged.

Note: *heat-treatment conditions are specified similar to those of Al alloys.*

Commercial magnesium alloys

- *Mg-Al casting alloys*
- *Mg-Al-Zn casting alloys*
- *Mg-Zn and Mg-Zn-Cu casting alloys*
- *Mg-Zn-Zr and Mg-RE-Zn-Zr casting alloy*
- *High temperature Mg casting alloys*
- *Wrought Mg alloys*

Mg-Al casting alloy

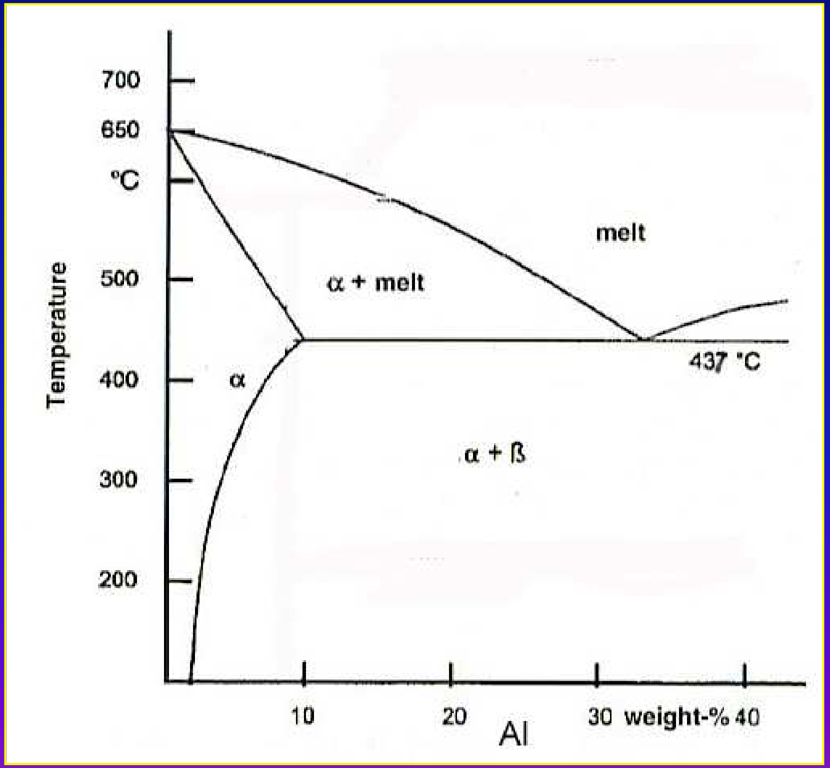
• ***Al*** is alloyed to increase strength, castability and corrosion resistance.

• Maximum solid solubility is ~ 12.7% at 473°C.

• ***Light weight and superior ductility***.

• ***Solid solution treatment*** of these alloys however produce non-coherent, coarse precipitates of equilibrium $Mg_{17}Al_{12}$ (lying on the basal plane of the matrix) without the formation of the ***GP zone***. → ***no solid solution strengthening***.

Zn addition



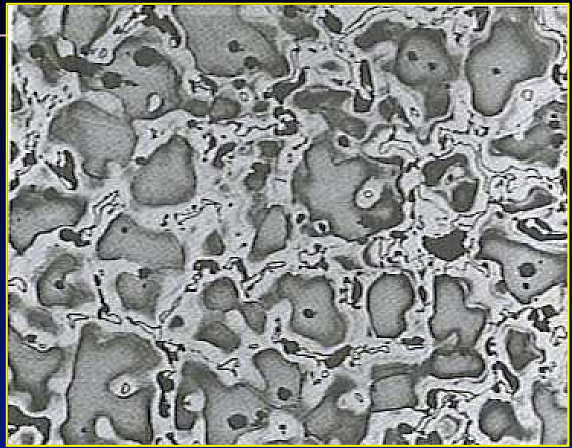
Mg-Al phase diagram

Mg-Al-Zn casting alloys

• Light weight, strength and relatively good corrosion resistance and easily cast.

• ***Zn addition*** increases strength by ***solid solution strengthening*** and ***precipitation hardening***.

• σ_{TS} ~ 214-241 MPa with 1-8% elongation.



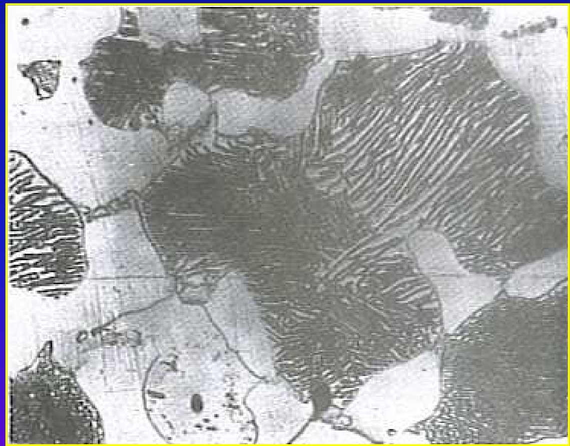
(a) Chill cast alloy with the β phase ($Mg_{17}Al_{12}$) at grain boundaries.

• A network of $Mg_{17}Al_{12}$ or β phase is formed around ***GBs*** in the as-cast condition, *fig (a).* → reduce σ_{TS}, ***%E***.

• More slowly cooled alloy appears discontinuous β phase at ***GBs*** with a cellular or ***pearlitic structure***, *fig (b).*

T6 temper

$Mg_{17}Al_{12}$ is refined and uniformly distributed. → improved properties.



(b) Discontinuous precipitation in more slowly cooled alloy.

Cast structures of AZ80 alloy

Note: AZ91 is the most widely used (die cast) due to fine and uniform as-cast structure.

Chemical compositions and applications for Mg-Al and Mg-Al-Zn casting alloys

Die castings

Alloy	% Al	% Mn	% Zn	Other	Applications
AM60B	6.0	0.13*			Automobile wheels
AS41A	4.2	0.35†		1.0 Si	Automobile engines and housings; good creep resistance
AZ91D	9.0	0.15*	0.7	0.001 Ni max 0.005 Fe max	Die castings; parts for cars, lawnmowers, business machines, chain saws, hand tools, sporting goods; good corrosion resistance

Sand and permanent-mold castings

Alloy	% Al	% Mn	% Zn	Other	Applications
AM100A	10.0	0.1*			Pressure-tight sand and permanent-mold castings
AZ63A	6.0	0.15*	3.0		Sand castings requiring good room-temperature strength and ductility
AZ81A	7.6	0.13*	0.7		Tough leak-proof sand castings
AZ91E	8.7	0.26†	0.7	0.001 Ni max 0.005 Fe max	Sand and permanent-mold castings requiring room-temperature strength and ductility
AZ92A	9.0	0.10*	2.0		Pressure-tight sand and permanent-mold castings; room-temperature strength and ductility

Mechanical properties of Mg-Al and Mg-Al-Zn casting alloys

Alloy	Tensile strength		0.2% yield strength		% elongation (in 50 mm)
	ksi	MPa	ksi	MPa	
Die castings					
AM60A-F	32	220	19	131	8
AS41A-F	31	214	20	138	6
AZ91D-F	34	234	23	158	3
Sand and permanent-mold castings					
AM100A-T6	35	241	17	117	2
AZ63-A-T6	34	234	16	110	3
AZ81A-T4	34	234	10	69	7
AZ91E-T6	34	234	16	110	3
AZ92A-T6	34	234	18	124	1

Mg-Zn and Mg-Zn-Cu casting alloys

Mg-Zn alloy

- Response to age hardening ($MgZn_2$ forms from GP zones)
- not amendable to grain refining
- susceptible for microporosity.

→ Not used for commercial castings.

Mg-Zn-Cu alloy

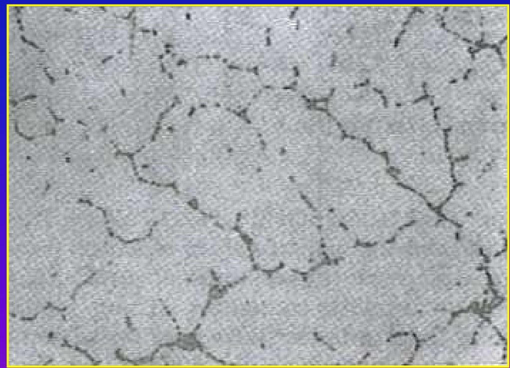
- Cu addition notably improves ductility and large response to age hardening.
- σ_y ~130-160 MPa, σ_{TS} ~215-260 MPa
- Ductility 3-8%.
- Cu addition also raises eutectic temp. → give maximum solution of Zn and Cu.

Mg-Zn compounds around GBs and dendrite arms

Binary Mg-Zn alloy treated at 330°C/8h

Cu addition ↓

Lamella structure



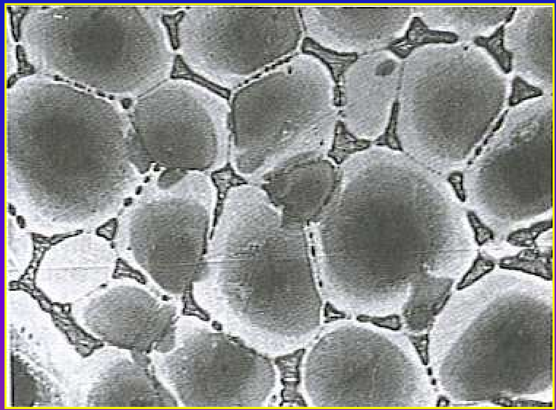
Mg-6Zn-1.5Cu solution treated 430°C/8h

Mg-Zn-Zr and Mg-RE-Zn-Zr casting alloys

Mg-Zn-Zr alloys

• ***ZK51*** and ***ZK61*** are sand cast
5-6% ***Zn*** addition → ***SS*** strengthening
1% ***Zr*** addition → grain refinement.

• The alloys have ***limited use*** due to their susceptibility to ***microporosity*** during casting and ***not weldable*** due to ***high Zn content***.



Mg-RE-Zn-Zr alloy as cast and heated at 400°C 48 h

Mg-RE-Zn-Zr alloys

• ***RE (Ce, Nd)*** is added to produce ***EZ33*** and ***ZE41*** (sand cast), giving ***good castability*** due to ***low-melting point eutectics*** formed as networks in ***GBs*** during solidification. → microporosity ↓ .

• Lower strength due to removal of ***Zn*** from ***SS*** to form the stable ***Mg-Zn-RE phase*** in ***GBs***.

Precipitation sequence

$$Mg_{ssss} \rightarrow GP\ \ zones \rightarrow \beta^{''} \rightarrow \beta^{'} \rightarrow \beta(Mg_{12}Nd)$$

__Note:__ β'' phase is the main strengthening precipitates

Chemical compositions and applications and mechanical properties of Mg-Zn-Zr and Mg-RE-Zn-Zr casting alloys

Alloy	% Zn	% RE	% Zr	Applications
ZK51A	4.6		0.7	Sand castings; good strength at room temperature
ZK61A	6.0		0.8	Sand castings; good strength at room temperature
EZ33A	2.6	3.2	0.7	Pressure-tight sand and permanent-mold castings for applications at 175–260°C
ZE41A	4.2		0.7	Sand castings; good strength at room temperature;
ZE63A	5.7	2.5	0.7	improved castability over ZK alloys

Alloy	Temper	Tensile strength		0.2% yield strength		% elongation in 50 mm
		ksi	MPa	ksi	MPa	
ZK51A	T5	34	234	20	138	5
ZK61A	T6	40	275	26	179	5
EZ33A	T5	20	138	14	96	2
ZE41A	T5	29	200	19.5	134	2–5
ZE63A	T6	40	275	27	186	5

High-temperature magnesium casting alloys

- *Primarily used for aerospace applications due to light weight (major consideration).*
- *Application range 200-250^{o}C with tensile strength ~240 MPa.*

• *Mg-Ag-RE alloys*

QE22 has been used for aerospace applications, i.e., landing wheels, gear box housings.

• *Mg-Y-RE alloys*

WE43 has been developed for improved elevated temperature tensile properties.

• *Mg-Ag-Th-RE-Zr alloys*

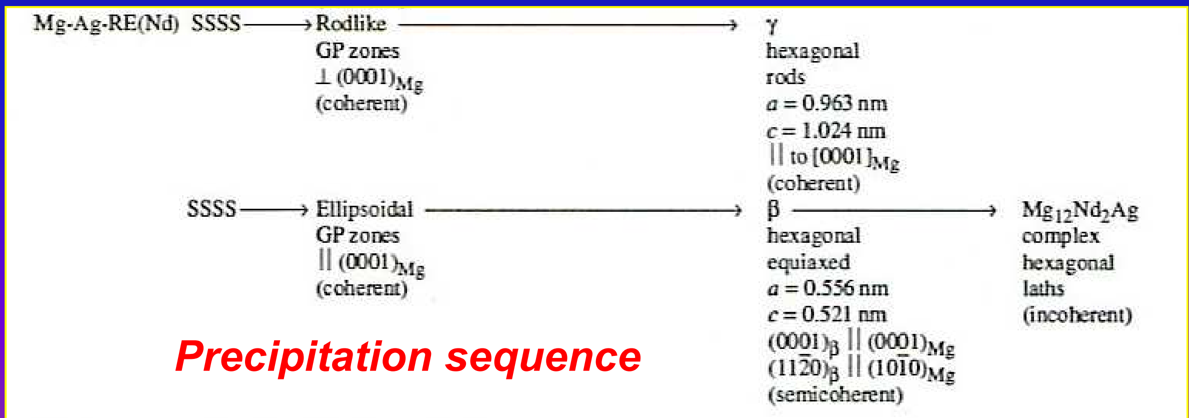
Thorium is best known to improve high temperature properties, due to age hardening and refined grain but slightly radioactive → not commercially available.

Mg-Ag-RE alloys

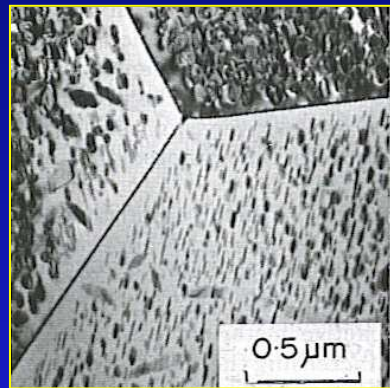
- ***Ag*** was found to have a positive effect on precipitation behaviour of ***Mg-RE*** alloys. → development of ***QE series*** to improve ***elevated temperature strength*** and ***creep resistance***.
- ***Mg_9R*** compound is produced at ***GBs*** of ***Mg*** solids solution embedded with a fine precipitate of ***$Mg_{12}Nd_2Ag$*** precipitates.

QE22 (2.5% ***Ag*** and 2% ***RE*** such as ***Nd***) and other heavy ***RE*** gives

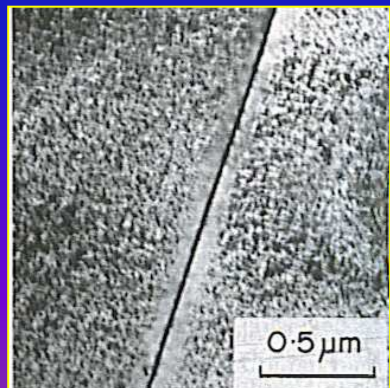
- Outstanding age-hardening response.
- Good tensile properties up to 200°C.



Precipitation sequence



Ag addition



Finer and higher V_f of precipitates

Mg-Y-RE alloys

Advantages:

- ***Mg-Y alloys*** are capable of age-hardening with solid solubility of ***Y*** up to 12.5 wt%.
- Good strength and creep resistance upto 300^{o}C.

Drawbacks:

- ***Y*** is expensive
- Difficult to alloy due to high T_m ~ 1500^{o}C.
- High affinity for oxygen.

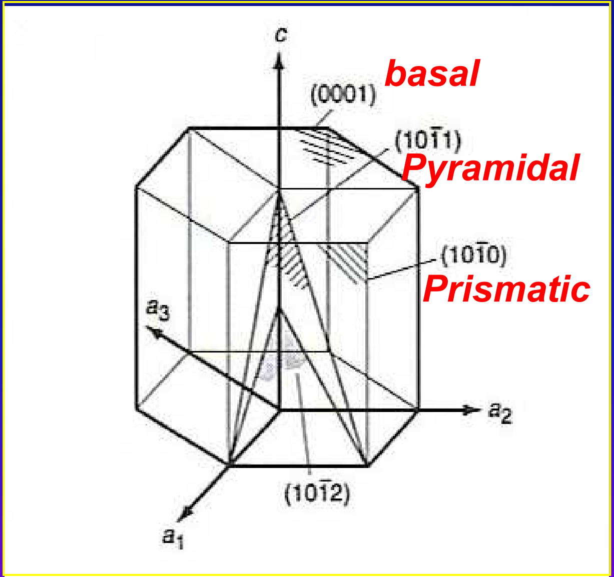
WE43 (4% Y, 2.25% Nd, 1% heavy rare earths, 0.3% Zr)

- Improved high temperature properties.
- Maintained RT tensile strength of 250 MPa after long-term exposure at 200^{o}C.
- For advanced aerospace applications.

Mg-Y containing alloy

Wrought magnesium alloys

- Deformation is limited due to ***HCP structure***, only occur on
  1) By slip on the **{1000}** ***basal*** planes in the **$\langle 11\bar{2}0\rangle$** direction.
  2) Twining on the **$\{10\bar{1}2\}$** ***pyramidal*** planes.
- At ***$T>250^oC$*** slip can occurs on ***pyramidal*** and ***prismatic*** planes.



- More workable at elevated temperatures (300-500^{o}C) rather than at ***RT***.
- ***Magnesium alloys*** are normally produced in ***sheets, plates, extruded bars, shapes , tubes, and forgings.***

Wrought magnesium alloy products

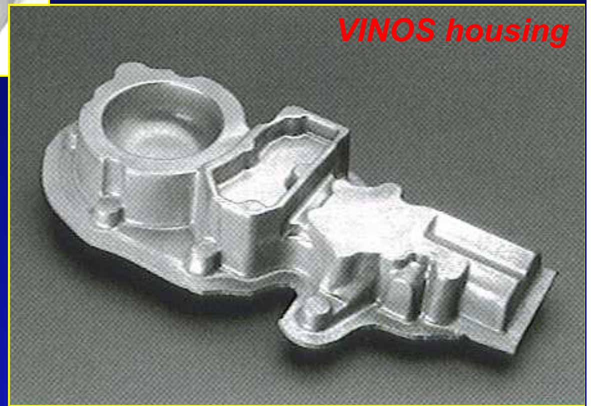
Extruded parts

Profiles of variable cross-section

A profile of large cross-section (6m long)

Anterior bars of vehicle

Extruded parts



Forged parts

Magnesium strips

Magnesium sheet (1500×1.8mm)

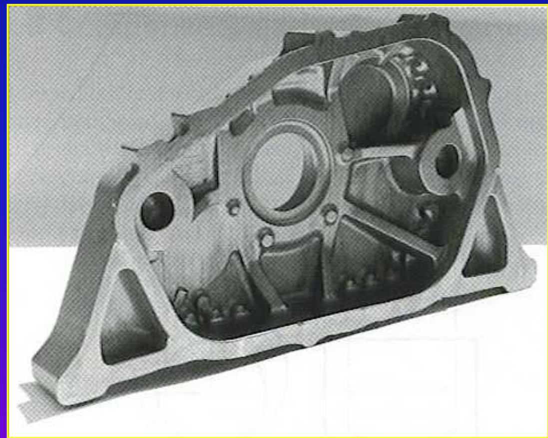
Sheet, strips

Forging of magnesium alloys

Advantages of forged magnesium components compared to commonly used die cast magnesium parts:

1) Excellent strength, especially with the fibres lying parallel to the main load direction.
2) Very good properties for pressure-sealed components because of a forging process in preventing a porous microstructure.

- *Grain size and multiphase microstructure are the main problems in magnesium forging. This can be overcome by additional extrusion process to give a sufficient grain size for forging.*
- *Complex component geometries are usually produced in several forging steps.*



Drop-forged gearbox cover for a helicopter

Forging of magnesium alloys

	forged magnesium wheel alloy: MgZn3Zr (ZK30)	forged aluminium wheel alloy: AlMgSi1 (AA6082-T6)
wheel weight	6,8 kg	10,5 kg
hardness	66,6 HRB	78 HRB
testing moment	3.000 Nm	3.000 Nm
load cycles	84.000	1.064.000

Prototype of a magnesium forged wheel(ZK30)

Produced on the basis of the corresponding aluminium part in series production for the Audi A8

Table 5: Strength properties of the magnesium wheel (ZK30)

Extraction point of the specimen	Orientation	Yield strength R_p 0.2 [MPa]	Tensile strength R_m [MPa]	Elongation at fracture, A [%]
rim	axial	248	302	13,7
	tangential	196	266	12,3
spoke/dish	axial	157	260	14,9
	tangential	203	265	12,3

Forging of magnesium alloys

Properties of forged magnesium wheels
compared to cast magnesium wheels
+ 5–10% weight saving (identical design assumed)
+ better abusing behaviour due to higher strength and toughness
+ pressure-tightness because of a non-porous microstructure without cavities
– higher costs
compared to aluminium forged wheels
+ 10–15% weight saving (identical design assumed)
– worse abusing behaviour due to lower strength and toughness
– marked tendency towards contact corrosion
– lower surface pressure and different friction coefficient
– much higher costs

Characteristics of forged magnesium wheels (ZK30/ZK60) compared to other concepts

Prototype of a magnesium forged wheel(ZK30)

Engineering design with magnesium alloys

Advantages of magnesium alloys for engineering designs:

1. ***Ability to die cast at high productivity rate.***
2. ***Good creep resistance to 120^{o}C.***
3. ***High damping capacity due to ability to absorb energy elastically.***
4. ***High thermal conductivity permitting rapid heat dissipation.***
5. ***Good machinability.***
6. ***Easily gas-shield arc-welded.***

Disadvantages of magnesium alloys for engineering designs:

1. ***High tendency to galvanic corrosion when contact with dissimilar metals or electrolyte.***
2. ***Difficult to deform by cold working.***
3. ***High cost.***

Note: *Damping capacity : the ability of a material to absorb vibration and convert the mechanical energy into heat.*

Melting of magnesium alloys

• ***Magnesium*** is normally melt in ***mild steel crucibles*** for the alloying, refining or cleaning stage due to very slow reaction with the steels.

• Magnesium and its alloys are highly reactive with ***oxygen*** and can ***burn in air***. Oxide films accelerate the oxidation process.

Solution

• ***Melting stage:*** Using fluxes containing a mixture of chlorides such as ***$MgCl_2$, KCl or NaCl***. → Removal of chlorides is essential prior to pouring due to corrosive effect.

• ***Alloying and refining stage:*** Using flux containing a mixture of ***CaF_2***, ***MgF_2***, and ***MgO*** to form a coherent, viscous cake which excludes air.

• ***Sulphur hexafluoride SF_6*** protection is also used, which lowers ***oxidation melt losses*** and ***operating cost***.

Casting of magnesium alloys

- ***High pressure die casting***

  Most widely used for magnesium alloy components
  - hot chamber
  - cold chamber

- ***Squeeze casting***

  Vertical arrangement of casting unit and moulding direction
  - direct squeeze casting
  - indirect squeeze casting

- ***Thixocasting***

  Relatively new method based on the thixotropic properties of the semi-liquid alloys.

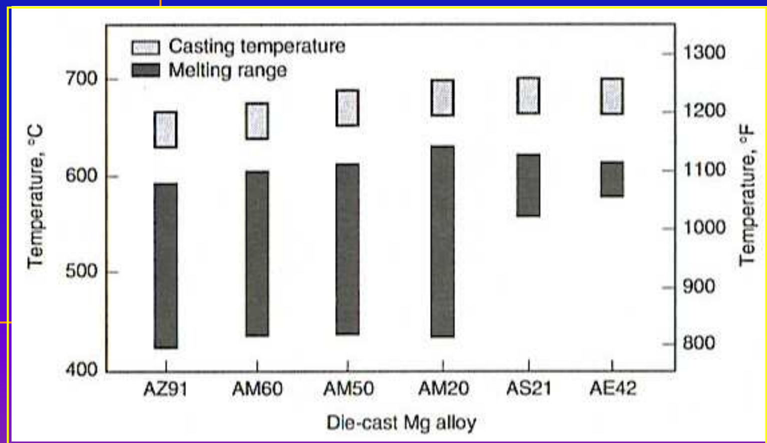
High-pressure die casting → **Hot chamber casting** **Cold chamber casting**

- Most widely used and most economic procedure for ***Mg*** processing (over ***Al*** and ***Zn***) due to
  - low casting temperature 650-680^{o}C.
  - Low thermal content → 50% faster than Al.
  - High precision and good surface finish.
  - Does not attack iron moulds → longer mould life
  - Good machine endurance.
  - High mould filling speed due to high pressure

- ***High productivity*** and ***rapid solidification***
  → can produce thin-walled and near-net-shaped components
  → fine-grained microstructure with good mechanical properties.

Mg die-casting parts

www.mfgsolutionsinnovation.com



Melting range and typical casting temperature of Mg die-casting alloys

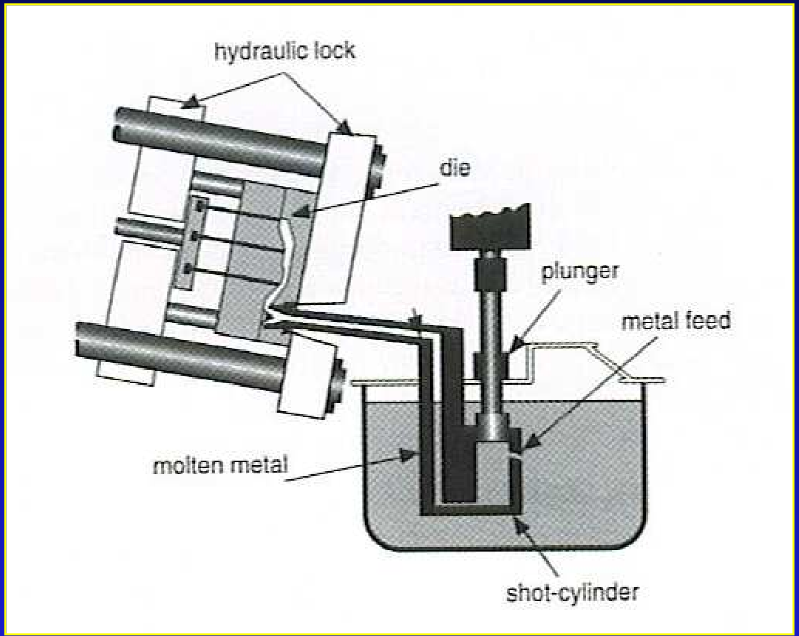
Hot-chamber die casting

• The hot chamber machine has a ***casting case*** with an integrated ***casting chamber*** that always stays within the ***casting furnace*** filled with molten metal.

• The molten metal is injected into the die by the downward motion of the plunger.

• Suitable for ***thin-walled parts***.

• ***High productivity*** (> 100 shots/hr) due to magnesium's excellent castability and rapid solidification.



Hot-chamber die casting

Capacity	Machine size ~ 900 ton Pressure of the melt ~150-120 bar Shot is limited to 5-6 kg Typical wall thickness 1 mm

Cold-chamber die casting

• The casting case is outside of the melt. The metal is pumped from a nearby furnace and put into the horizontal shot chamber.

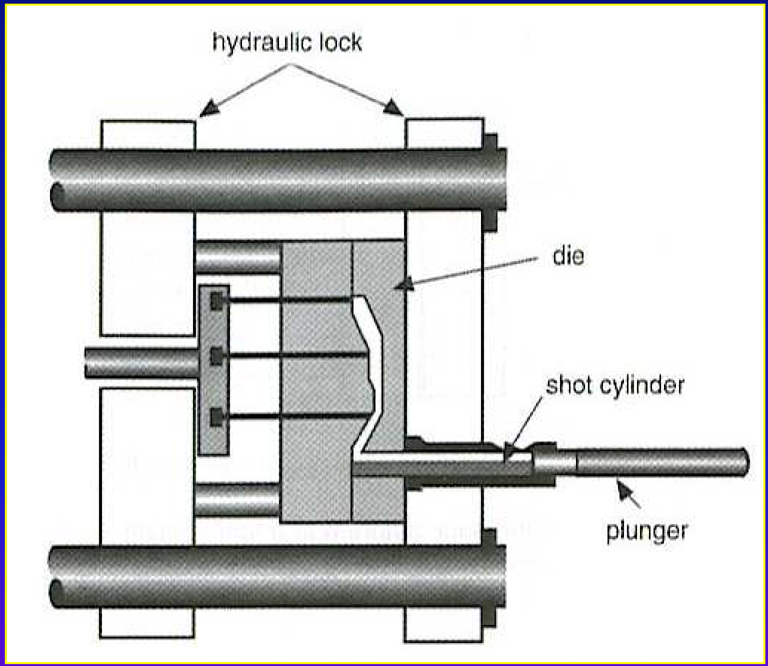
• The metal is then injected by the plunger into the die under high pressure.

• Used for ***large castings*** with ***heavy wall thickness***.

• ***Higher pressure*** is required to compensate high degree of shrinkage.

Capacity

Machine sizes upto 4,500 ton
Pressure of the melt ~300-900 bar
The shot is limited to 60 kg.
Wall thickness from 1.5-2.5 mm.



Cold-chamber die casting

Vacuum - die casting

Casting sequence:

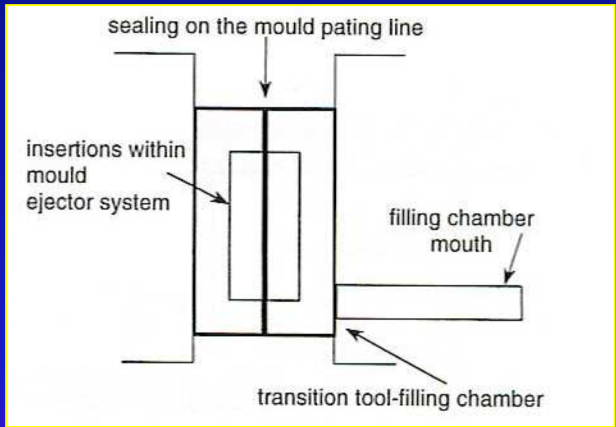
1) The liquid metal reaches the gate
2) Filling of the mould
3) The pressure is built up

Problems:

Air entrapment , air cushion during mould filling

Solution

Vacuum die casting

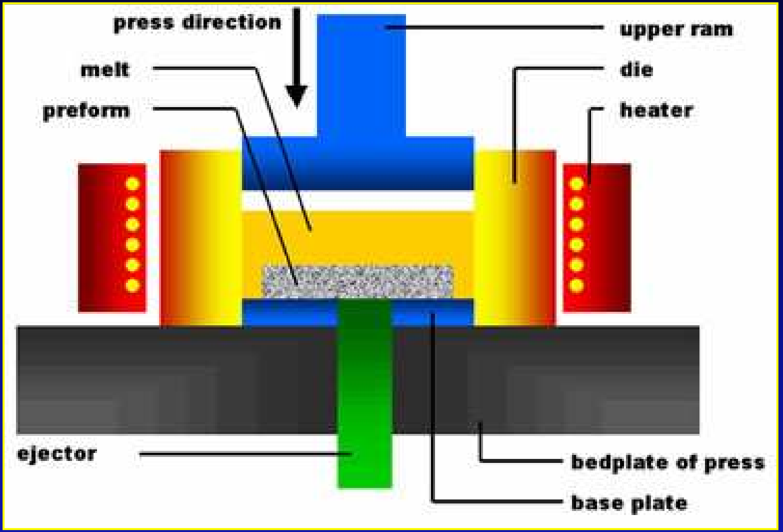


Tool-sealing during vacuum die-casting

- Casting chamber and mould are vacuumed to reduce entrapped gas or air cushion which disrupt the filling sequence.
- Higher costs of the parts.

Squeeze casting

- **Indirect squeeze casting**
- **Direct squeeze casting**

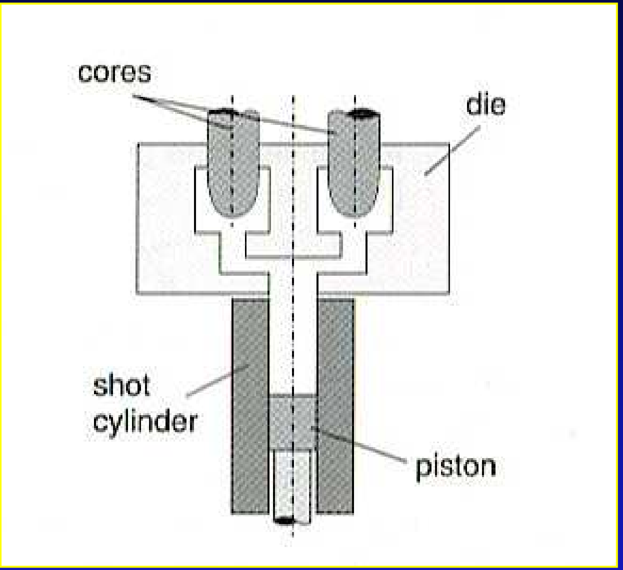


Advantages:

- Reduced porosity.
- Prevention of hot-cracking for alloys with wide freezing range.
- Increase in strength and ductility due to fine-grained and faultless structure.
- Possibility of heat treatment.
- Alloy difficult to cast can be processed.
- Alloy development.
- Production of magnesium composite.

Indirect squeeze - casting

- The ***liquid Mg*** is injected into the mould through a big ***injection canal*** with the flow rate of **0.5 m/s**. (compared with die casting ~30m/s)
- Low speed prevents ***turbulence flow***, which causes ***air entrapment***.
- ***Pressure*** and ***temperature*** are controlled during freezing, allowing the use of core or male mould.
- Offers opportunity of infiltrating so-called preforms (***porous fibres or particulates***) or producing ***composites***.

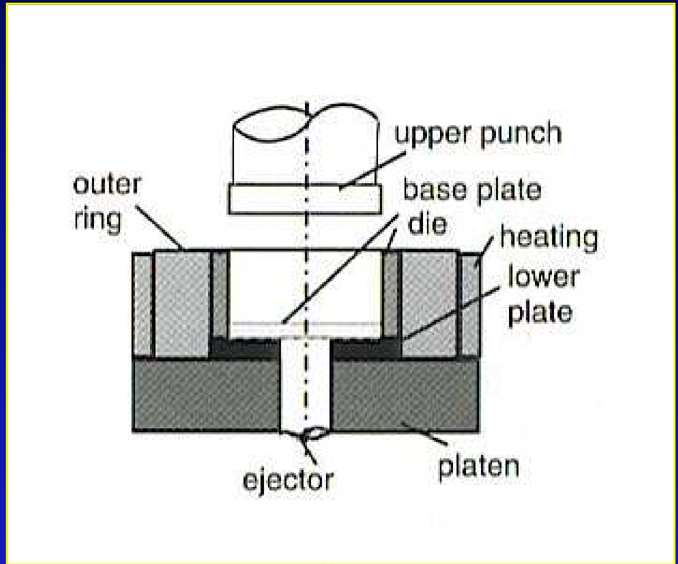


Indirect squeeze-casting

Disadvantage: *Big gate needed for separation from the actual part takes a lot of material. But this can also be used to host pores and micro-shrinkage when freezing is properly controlled.*

Direct squeeze - casting

- The ***pressure*** is applied by the ***upper punch***, with the lower one throwing out the cast part.
- ***Simple mould arrangement*** requires no clamping force → ***reduced cost***.
- Required ***exact amount of melt*** needed.
- Additional ***punches*** or ***cores*** can be used to produce more ***complex parts***.
- Capable of producing ***non-porous parts*** since freezing and pressure properties are not critical – due to no gate.



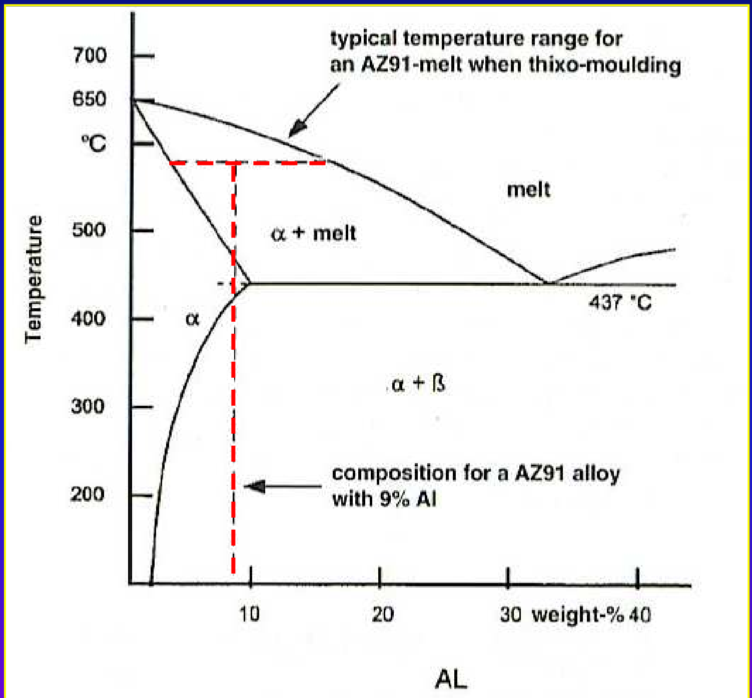
Direct squeeze-casting

Note: *freezing is influenced by temperature of the mould and the punch.*

Thixo-casting

- Relatively new method based on ***thixotropic properties*** of semi-liquid alloys.

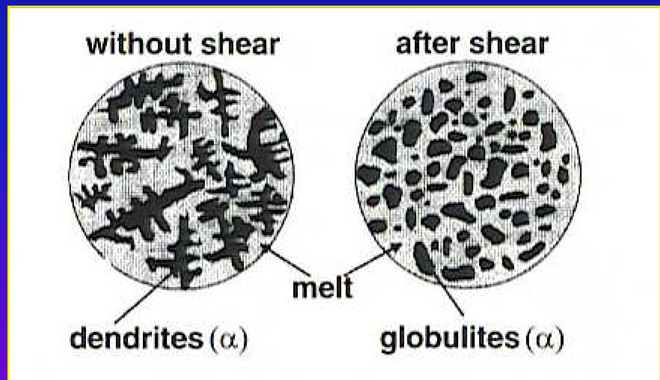
- Typical ***temperature range*** for ***thixo-casting*** is ~20°C below the ***liquidus temperature*** and contains a mixture of solid and liquid phases → ***semi-solid metal forming***.



Mg/Al phase diagram for the thixo-casting/moulding process

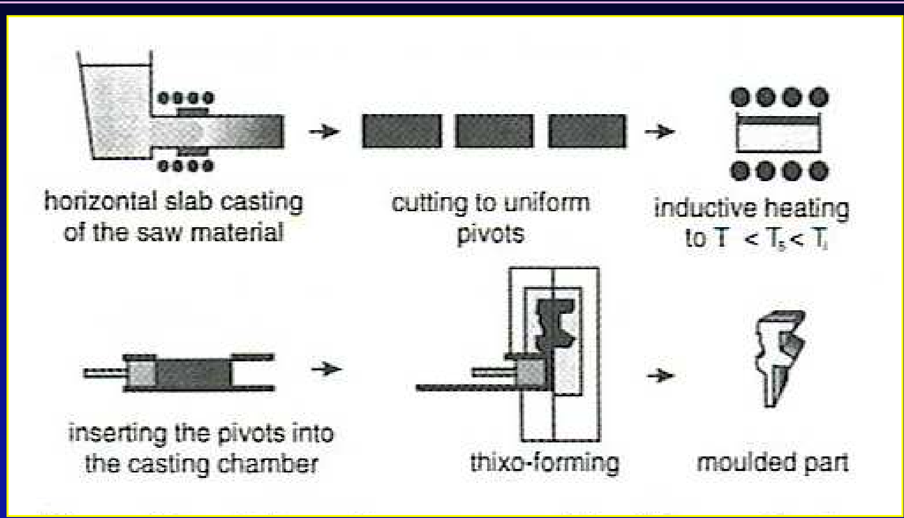
- Intense stirring changes ***dendrite*** → ***globular*** structure formation.

Viscosity ↑ ***Shearing strain*** ↓



Dendrite and globular formation of an Mg/Al alloy

Sequence of thixo-casting process



• The slab is cut to provide uniform pivots, which are then heated up close to the ***$T_{liquidus}$*** until the ***ratio of liq/sol*** (~30-40% melt) is reached.

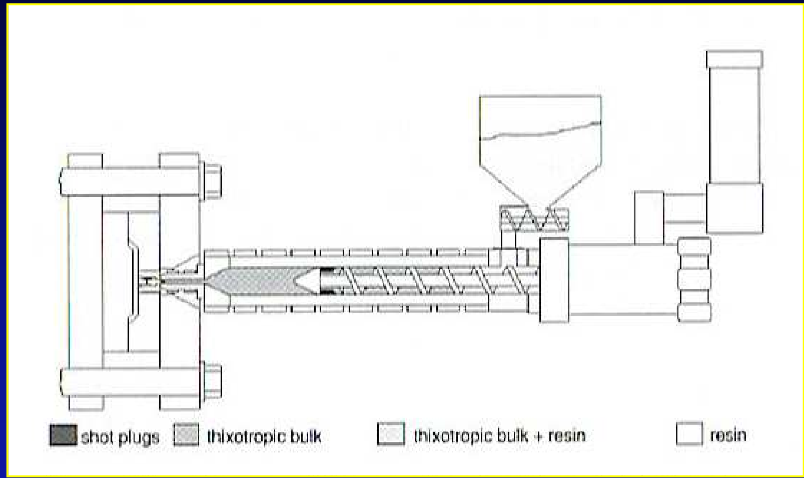
• This heated metal lump is then transferred to the ***thixo-forming machine***.

• The pressure is applied to develop ***shearing stress***, which decreases viscosity and the metal lump now behaves like a ***fluid.***

• ***Electromagnatic stirring*** might be applied for a short period of time to avoid ***dendritic growth***.

Thixo-moulding

- ***Thixo-moulding*** is a variation of thixo-casting but using an ***injection moulding machine*** instead of the die-casting machine. (similar to plastic moulding).

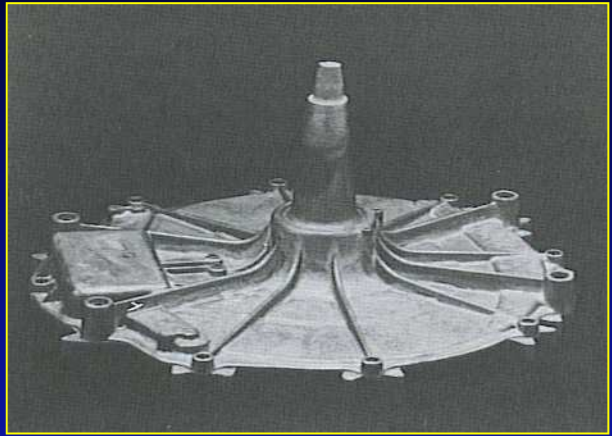


Thixo-moulding casting machine prior to the shot

- The process involves ***melting the thixo-moulding granulate*** in a ***screw conveyer***, which leads to the ***chamber***. (***T*** ~ 560-620^{o}C)
- The semi-solid melt is then pressed into the mould.
- The ***injection unit*** is protected with ***Ar*** during heating and cooling to ***prevent contact with air***.

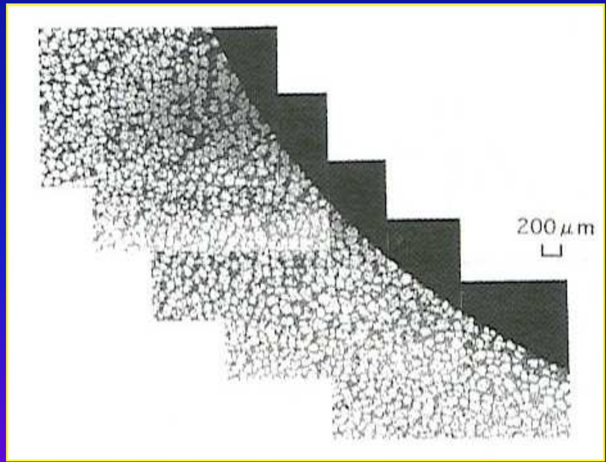
Advantages of thixo-casting

Thin-walled Mg alloy AZ91D casting produced by thixo-moulding



Advantages:

- Production can be fully automated.
- High productivity
- Cost saving due to low energy consumption
- Higher tool lifecycles
- Gas-inclusion-free parts → weldable
- Low cooling shrinkage and no blow holes
- Parts have excellent mechanical properties (fine grained)
- Produce thin-walled casting parts
- Near-net shape quality



Crack-free surface of a thixo-cast component (AZ91D)

Grain refinement

- ***Grain refinement*** is not necessary in high-pressure die casting, squeeze die casting or thixo-casting but for ***sand casting*** due to slow solidification rates.

- ***Al containing Mg alloys (Mg-Al, Mg-Al-Zn)***

  - ***Carbon inoculation*** with hexachloroethane or hexachlorobenzine compressed tablets to produce Al_4C_3 as heterogeneous nuclei.

  Notes: *Zr cant be used with Al since it forms intermetallic compound.*

- ***Non Al containing Mg alloy***

  - ***Zr*** is used as a ***grain refiner*** in ***non Al-containing Mg alloys***.
  - ***Zr*** could form ***heterogeneous nuclei*** for ***Mg*** alloy to solidify on.

References

- มนัส สถิรจินดา, โลหะนอกกลุ่มเหล็ก, 2536, สำนักพิมพ์จุฬาลงกรณ์มหาวิทยาลัย, ISBN 974-582-155-1.
- Polmear, I.J., ***Light alloys: metallurgy of the light metals***, Third edition, 1995, Arnold, London, ISBN 0-340-63207 (pb).
- Smith, W.F., ***Structure and properties of engineering alloys***, second edition, 1993, McGraw-Hill, ISBN 0-70-112829-8.
- Kainer, K.U. (editor), ***Magnesium alloys and technology***, DMG, 2003, WILEY-VCH, ISBN 3-527-30256-5.
- Avedesian, M.M., Baker, H., ***ASM specialty handbook, Magnesium and magnesium alloys***, 1999, ISBN 0-87170-657-1.
- webmineral.com
- http://www.galleries.com/minerals
- www.azom.com