

Department of Materials Science and Engineering



# Non-ferrous metals Balázs Varbai, PhD, EWE/IWE

Materials Engineering BMEGEMTBGF1 2022 Fall semester



Торіс



- Light metals
  - Aluminium and its alloys
  - Magnesium and its alloys
  - Titanium and its alloys
- Heavy metals
  - Copper and its alloys
- Other metals with technical importance

## Light and heavy metals

- Light metals according to the density lighter than 4.5 gcm<sup>-3</sup> Al, Mg (Be, Li...)
- Borderline case...
   Ti, ρ≈4.5 gcm<sup>-3</sup>

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 Heavy metals heavier than 4.5 gcm<sup>-3</sup> Cu, Zn, Sn, Pb, Ni, W precious metals











	ρ (gcm <sup>-3</sup> )	R <sub>eH</sub> (MPa)	R <sub>eH</sub> /ρ	T <sub>creep</sub> (°C)
Al and alloys	2.70	25-650	9-240	150-250
Mg and alloys	1.70	70-270	40-160	150-250
Ti and alloys	4.50	170-1300	38-300	400-600
Be	1.82	100-700	50-380	~250
Cu and alloys	8.94	60-1400	7-150	
Structural steels	7.90	180-1600	25-200	400-600

### **att** Physical and mechanical character

M Ű E G Y E T E M 1 7 8 2

	R <sub>m</sub>	Ε	ρ	R <sub>m</sub> /p	Ε/ρ	\$/t
Cast iron	200	110	7150	280	154	900
Steel						
-soft	450	210	7860	573	267	600
-hard	1500	210	7800	1923	269	800
-corr. Res.	500	210	7930	631	265	2700
Aluminium						
-soft	70	70	2710	258	258	2000
-hard	450	70	2800	1601	250	2500
Copper						
-soft	140	120	8930	156	134	2000
-hard	400	120	8500	471	141	2000
Magnesium	250	42	1740	1436	241	6000
Titanium	1200	120	4580	2620	262	20000





- Light, low density (p=2.7 gcm<sup>-3</sup>)
- Low melting temperature (660°C)
- Good electric conductor (~2/3 of that of Cu)
- Good heat conductor
- FCC lattice
  - Good formability, Z~90%, cold and hot forming
- Good corrosion resistance (surface oxide layer)
- Low strength
  - R<sub>m</sub>=40...120 MPa, R<sub>p0.2</sub>=20...60 MPa
- Low Young's modulus
- E=70 GPa





### Strengthening



- Increasing the strength
  - Alloying
  - Cold plastic deformation
  - Heat treatment precipitation hardening
  - Dispersion hardening
  - (Composites)



http://www.world-aluminium.org/





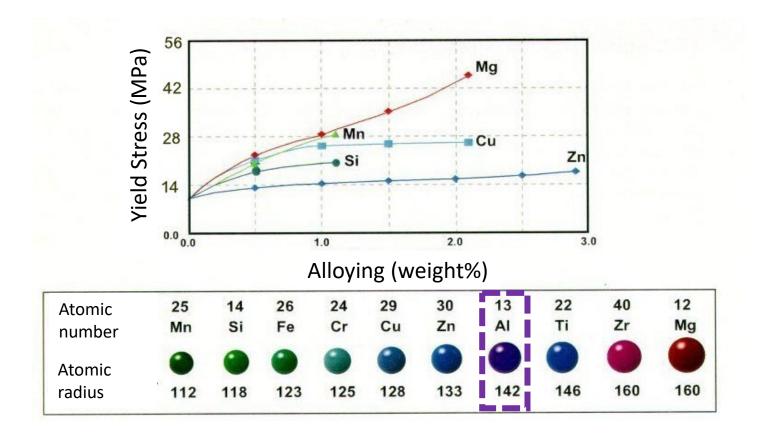
- Produced in "pure" (99.5%) state. Even small amount of alloying elements has a significant effect.
  - Strengthen: Cu, Mg, Zn, Mn, Si
  - Decreases the grain size: Ti, Cr
  - Enhance the corrosion resistance: Mn, Sb
  - Enhanced the strength at high temperatures: Ni
  - Enhanced the machinability: Co, Fe, Bi
- Most important impurities: Fe, Si, H, etc.



### Solid solution

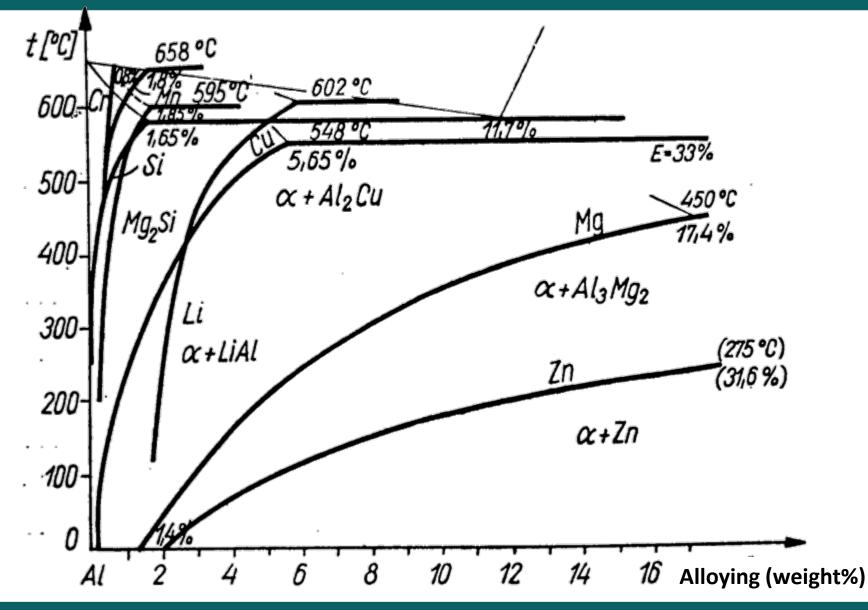


- Alloying element as substitutional atoms in the lattice
  - Even H has place only in octahedral lattice sites
  - Different effect on strength



# Solid solution – Alloys solubility

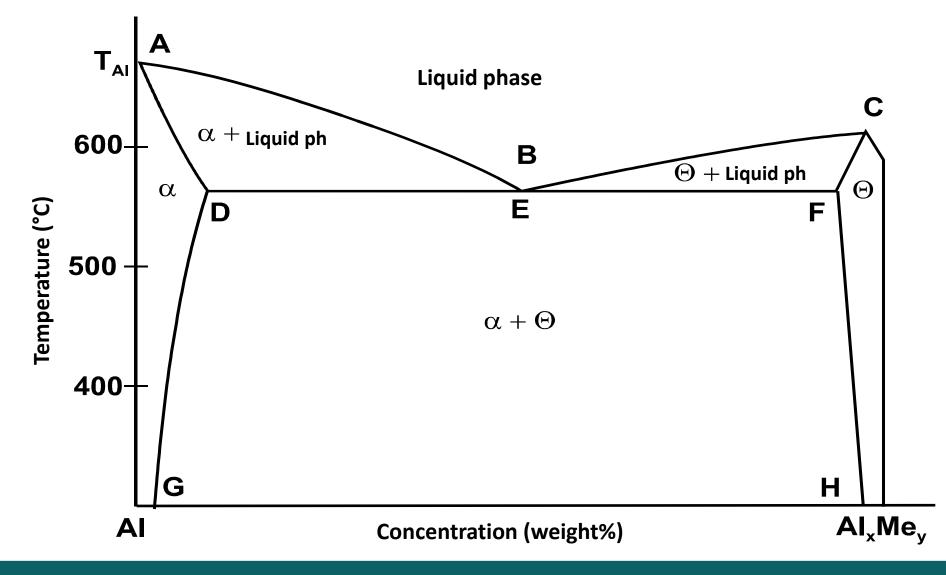




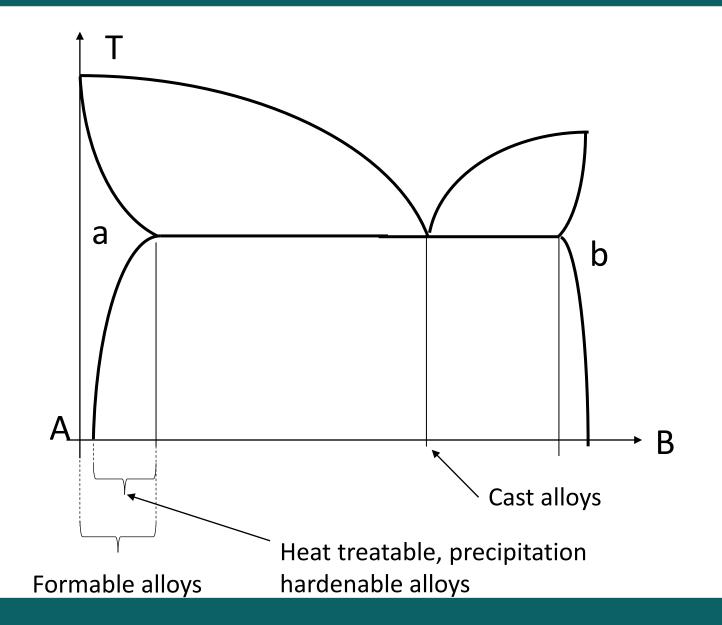


### General phase diagram





# **Catt** Classes according to processing





#### Designation system

M Ű E G Y E T E M 1 7 8 2

	Formable	Castable
Al	1xxx	1xx.x
Al-Cu	2xxx	2xx.x
Al-Mn	Зххх	
Al-Si	4xxx	4xx.x
Al-Si(-Cu/Mg)		3xx.x
Al-Mg	5xxx	5xx.x
Al-Mg-Si	6xxx	
Al-Zn(-Mg)	7xxx	7xx.x
Al-Li	8xxx	
Other elements	9xxx	9xx.x
Al-Sn		8xx.x
Not used		6xx.x



- >99% purity
- E.g. Al1050 99.5% Al
- Can contain Fe and Si impurities

- Good formability
- Good corrosion resistance
- Good conductivity
- Sheet for deep drawing, foil, electric cables
- Fe/Si influences the formability,
  - - Fe/Si>2.5 advantageous





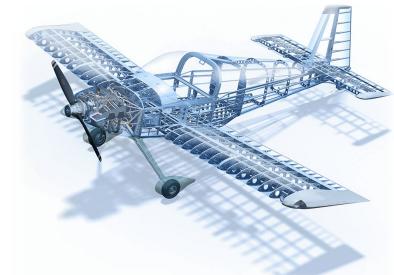




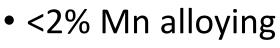
- Duralumin
- 3-6% Cu alloying
  - 0.4-2.5% Mg 0.3-1.0% Mn 0.2-1.3% Fe 0.2-1.2% Si 1.0-2.0% Ni



- Heat treatable alloys
  - 4% Cu + 2% Mg --- 440 MPa  $\,R_{m}^{}_{}$  and 320 MPa  $R_{p0.2}^{}$
  - Military technology, automotive and aircraft industry







 Above compounds which spoils the properties

- Non-heat treatable, can be strengthened by cold forming
- Modest strength
- Good formability
- Good weldability
- Good anodizability
- Packaging, kitchenware, architecture





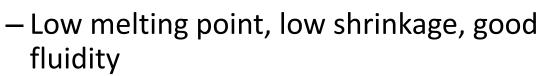








- Up to 17% Si alloying
  - Si as intermetallic phase, or as elemental Si brittle, non-formable
- Low Si% : for cladding filler material for welding
- Higher Si %: alloys for casting



- Adding Mg → heat treatable alloy(6xxx) strength increasing
- Engines, castings for modest loads and sizes, pistons









- 0.5-0.7% Mg alloying
- Strengthening cased by Mg can be enhanced by cold working
- Good formability
- Good weldability
- Good anodizability
- Good corrosion resistance
- Automotive industry, architecture, shipbuilding, chemical industry
- With >3% Mg alloying the corrosion resistance decreases

can be balanced with Mn









- 0.3-1.5% Mg and Si
- Precipitation hardenable alloys (Mg<sub>2</sub>Si)
- Moderate to high strength
- Good formability
- Good weldability
- Good anodizability
- Good corrosion resistance
- One of the most common Al alloy: electric industry, Automotive industry, architecture, machine industry, commodity
- Mn and Cr addition: grain refinement, increased strength and toughness, decreased stress-corrosion resistance

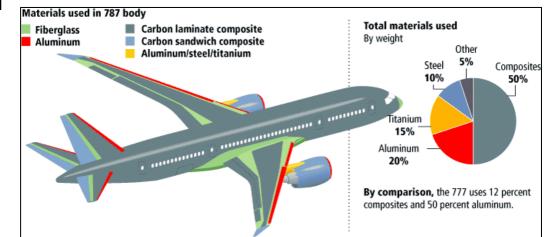






- 4-6% Zn (and 1-3% Mg), "hard" alloys
- Precipitation hardenable At 443°C ~70% Zn solubility
   ⇔ at 20°C 0.1% (!)
- Up to R<sub>p0.2</sub>=600 MPa
- Outstanding strength and appropriate formability
- Automotive industry, architecture, sporting goods



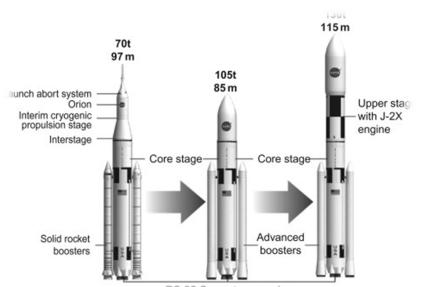


https://aviation.stackexchange.com/questions/35441/why-are-the-leading-edges-on-the-boeing-787-made-from-aluminum





- 1-5% Li alloying
- The lightest Al alloys
  - 1% Li alloying →
     ~3% decrease in density
- Precipitation hardenable alloys
- High strength
- The production is relative expensive
- Military industry, rocket and space technology







#### Overview

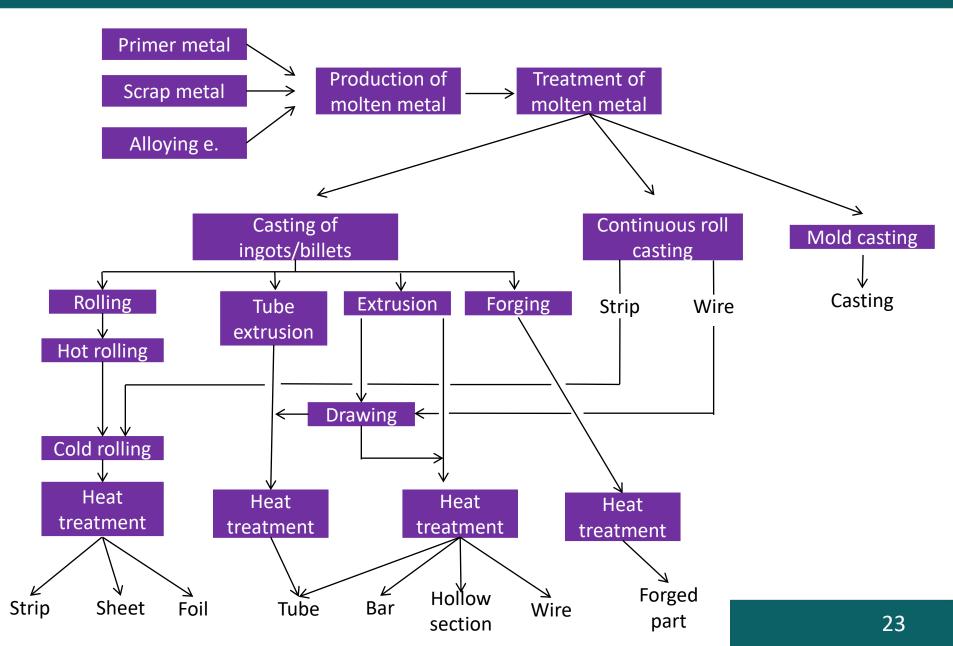


Formable alloys		Cast alloys	
Non-heat treateble (weldable)	heat treateble -		
Good corrosion resistance	high-strength	Non-heat treateble	heat treateble
Good electric condictivity	alloys		
Good formability			
Al-Mn		Al-Si	Al-Si-Mg
Al-Mg	Al-Mg-Si	Al-Mg	Al-Si-Cu
Al-Mg-Si Al-Mg <sub>0.5</sub> -Si <sub>0,5</sub>	Al-Mg-Li		Al-Mg-Si
Al-Mg-Zn	Al-Li-Mg		
Al-Mg-Li	Al-Cu-Mg		
	Al-Cu-Li		Al-Cu
	Al-Cu-Li-Mg		Al-Cu-Ni
	Al-Zn-Mg		
	Al-Li-Cu-Mg		Al-Zn-Si
	Al-Zn-Cu-Mg		Al-Zn-Mg



#### Semiproducts





# **Casting of ingots and billets**

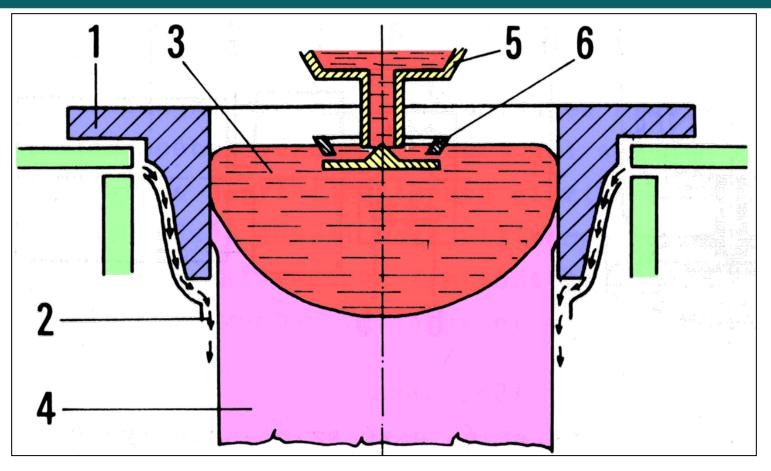


- For the purpose of rolling or extrusion
- Basic procedures
  - Mold casting
  - Direct chill (or semi continuous) casting
- Possibilities to increase quality
  - Direct chill casting in electromagnetic mold
  - Hot top mold direct chill casting
  - Descaling of ingots



### Direct chill casting





Pouring liquid metal continuously into a short mold (7.5–15 cm deep) that is open at the bottom. Only an outer layer of metal solidifies within the water-cooled mold. After leaving the closed mold at its bottom (e.g. with 5–15 cm/min), water is directly sprayed on the new ingot, continuing the solidification until complete (direct chill).



### Vertical direct chill casting

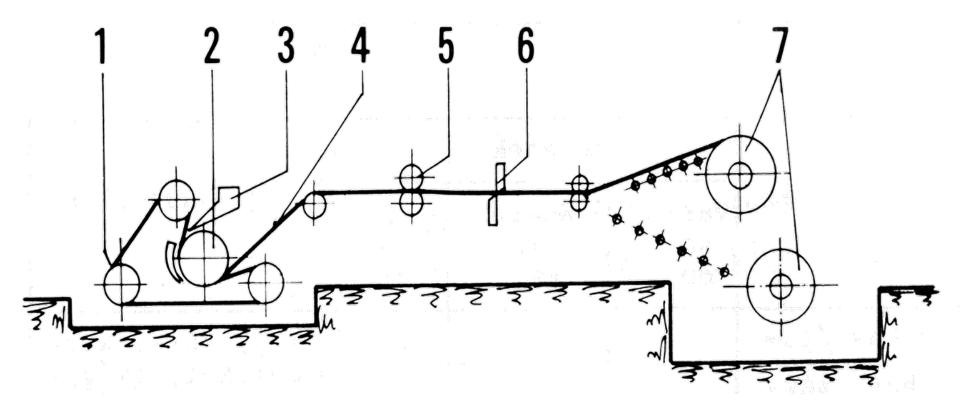


# VDC aluminum billet vertical casting video





- Wires and strips
- It is followed by rolling generally





#### Aluminum rod continuous casting and rolling mill



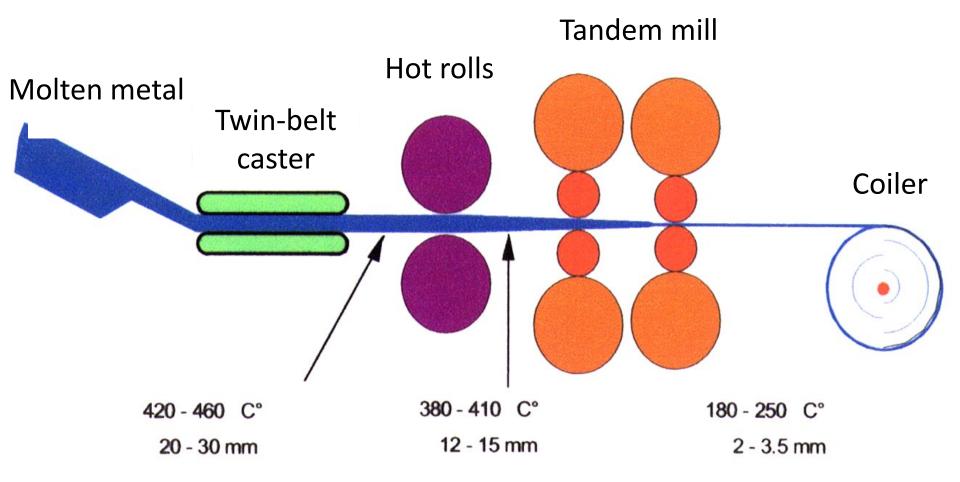
## Aluminum rod continuous casting and rolling

mill

### Twin-belt casting

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# Hazelett twin-belt casting







## Further processing



#### **Billet for rolling**

- Hot rolling
- Cold rolling
- Heat treatment
- Foil production

#### Billet for extrusion

- Extrusion
- Forging
- Tube production
- Drawing
- Heat treatment



## Magnesium



- Lowest density metal for mass production for structural purposes, ρ=1.8 gcm<sup>-3</sup>
- Low melting point, ~650°C
- Hexagonal lattice, low formability
- The "future's structural metal"
  - Low weight, automotive industry
- Presently ~35% as Mg-alloys, the rest as alloying for aluminum and steel





# **Technological properties**



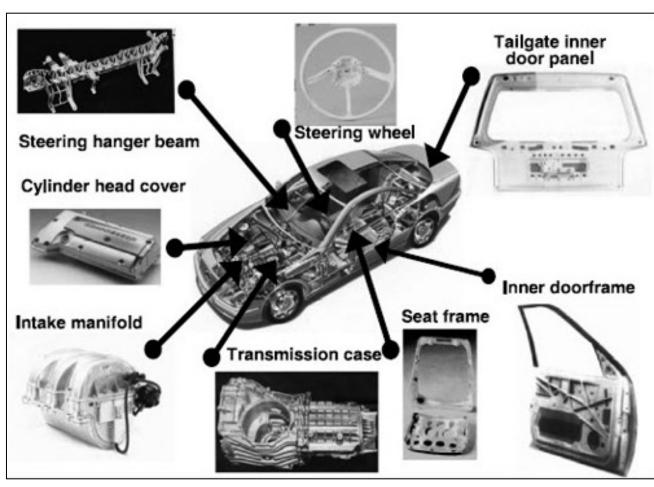
- Good machinability (less smearing than aluminum)
- Can be casted in faster cycles
- Longer lifetime for casting-dies
- High-end cameras, technical appliances, structural parts, airplane and rocket parts



## Magnesium alloys



- Cast alloys
  - Alloys with good castability
  - Mg-Al-Zn
     cast alloys
- Formable alloys
  - Al-Zn alloying
  - Mn alloying
  - Zr alloying
  - Zr-Th alloying
  - Rare earth element alloying
  - Li alloying



# tt Alloys with good castability

Zn, Zr, Th, Y  $\rightarrow$  PH Mn  $\rightarrow$  Corrosion res. Sn  $\rightarrow$  Castability

- Main alloying: 0.6-0.7% Zr, weldable

  Never use as alloying: Al, Si, Fe, Mn, Co, Ni, Sb, Sn

  Mg-Zr-Zn-RE alloys (Ce)

  Complex parts, low eutectic temperature

  Mg-Zr-Ag-RE alloys (Nd)

  Thermal fatigue resistant up to 200°C
- Th bearing alloys (nowadays Y alloying)
  - Thermal fatigue and creep resistant
- Mg-Zr-Y-RE alloys (Nd)
  - Good corrosion resistant and mechanical properties

	Α	Aluminium	<u>Å</u> .
	В	Bismuth	M 1 7
	С	Copper	
	D	Cadmium	
	Е	Rare earths	
	F	Iron	
	Н	Thorium	
	J	Strontium	
	K	Zirconium	
	L	Lithium	
	М	Manganese	
	Ν	Nickel	
	Ρ	Lead	
	Q	Silver	
	R	Chromium	
	S	Silicon	
	Т	Tin	
	۷	Gadolinium	
	W	Yttrium	
	Х	Calcium	
	Y	Antimony	
	Z	Zinc	35





- Cheaper and widely used as the previous group
  - Susceptible to microporosity (wall thickness differences, die casting)
- Mg-Al dual phase alloys
  - Precipitation hardenable
- Mg-Zn dual phase alloys
  - Better toughness and corrosion resistance, precipitation hardenable
- Mg-Al-Zn-Mn alloys
  - Enhanced corrosion resistance
- Mg-Al-Zn-Si alloys
  - Mg<sub>2</sub>Si precipitations, enhanced creep resistance
- Mg-Al-Zn-RE alloys
  - Ce, La, Nd, Pr, precipitation, better creep resistance
- Mg-Al-Zn-Cu alloys
  - Engine houses

# 🗇 att 🛛 Formable magnesium alloys



• Mg-Al-Zn

- Most common, moderate strength, rollable, weldable

- Mg-Mn
  - For electrochemical purposes, cathodic protection of steels
- Mg-Zn-Zr
  - Grain refinement, rollable, forgeable
- Mg-Th
  - Increased heat resistance, radioactive
- Mg-RE
  - Hot formable
- Mg-Li
  - Good formability, excellent weldability



Titanium



- Not really light (4.5 gcm<sup>-3</sup>)
- Two allotropic forms
  - $\alpha$ -titanium (HCP), producing eg: Al, O, C, N
  - β-titanium (BCC), producing eg:
     Mo, V, Nb, Mn, Fe, Cr, Si, Ni, Cu
- Good strength/weight ratio
- Good corrosion resistance
- Biocompatible
- Good strength at elevated temperatures
- Bad formability and machinability
- High affinity to oxygen, deoxidizing and carbide forming element

On most aircraft, use of titanium was limited by the costs involved; it was generally used only in components exposed to the highest temperatures, such as exhaust fairings and the leading edges of wings. On the SR-71, titanium was used for 85% of the structure, with much of the rest polymer composite materials.



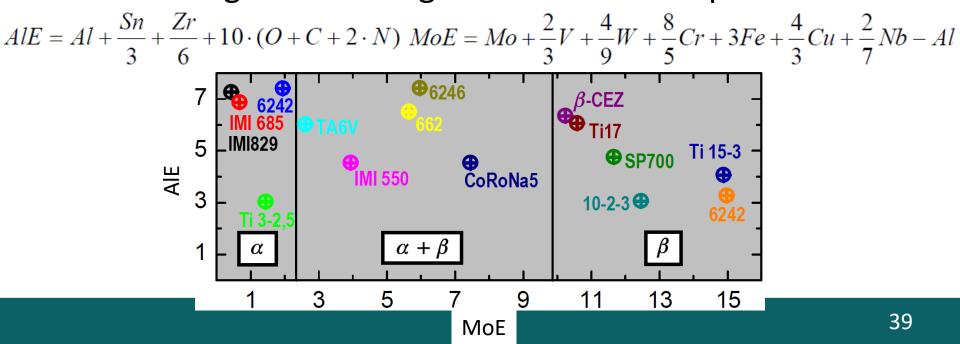




Pure titanium

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- Grade1...4, according to the dissolved oxygen content
- $\alpha$  and near- $\alpha \rightarrow$  Not heat treatable
- $\alpha + \beta$
- $\beta$  and near- $\beta \rightarrow$  Ductile
- Schäffler-diagram-like diagram: Mo and Al equivalent



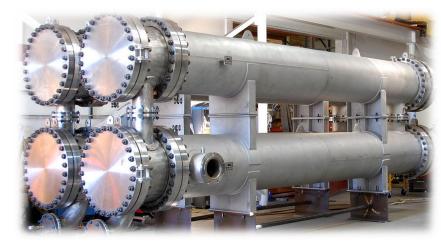
# **Titanium** alloys and utilization

- Corrosion resistant types
  - Unalloyed and low alloyed (Ti-0.2Pd), moderate strength
  - The small quantity of palladium added gives it enhanced crevice corrosion resistance at low temperatures and high pH
- High strength types
  - Solution treatment and aging (beta types)
  - Yield stress over 800 MPa, up to 25% alloying, many types, aviation- and cryogen-technique
- Creep- and heat resistant types
  - Much higher strength than Ni-alloys up to 700°C, excessively expensive

# **Titanium** alloys and utilization

- Turbo-jet engines, gas turbines
- Chemistry pumps, pipelines heat exchangers
- Parts for racing machines
- Armors, weapons
- Medical tools, implants, prosthesis
- Sporting goods
- Watch production, optical tools
- Architecture









Copper



- Heavy metal (8.93 gcm<sup>-3</sup>)
- Melting point: 1083°C
- Good formability
- FCC lattice
- Soft, low strength Good electric and heat conductivity
  - Alloying spoils it
  - Most important impurity element: Oxygen, forms Cu<sub>2</sub>O eutectic at grain boundaries – brittleness
- Corrosion resistant
- Bronze and brass
  - Tin bronze, lead bronze, aluminum bronze, chrome bronze



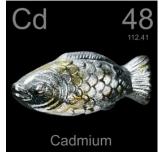




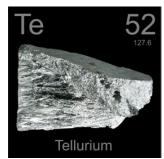
- Copper, containing oxygen(>99,9% Cu)
  - Good electric and heat conductivity
  - Produced by electrolysis (Cu-ETP) "Electrolytic Tough Pitch"
  - Formerly refined (Cu-FRHC and FRTP (casting)) "Fire-Refined Tough-Pitch High Conductivity"
- Oxygen-free (deoxidized) copper
  - Deoxidizing with phosphorous good weldability
  - Phosphorous spoils the electric conductivity
    - Cu-DHP: 0.013-0.5% P, Cu-DLP: 0.004-0.012% P
- Oxygen-free, high conductivity copper
  - Cu-OF: >99.95 Cu, Cu-OFE: >99.99% Cu (electronics)
  - Deoxidizing refinement

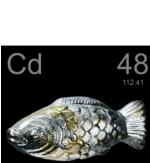
#### Low alloyed copper alloys I. att

- Cu-Ag
- Minimal silver alloying
- Recrystallization temperature increases from 200°C to 300°C
- E.g.: welding and soldering gun parts
- Cu-Cd
- Strength, fatigue limit, creep limit doubled by cold working
- E.g.: spot-welding
- Toxic, prohibited
- Cu-Te
- Enhanced machinability and strength, higher recrystallizations temperature,
- Conductivity decreases a little
- E.g.: laser-nozzle







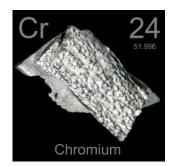




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# **Att** Low alloyed copper alloys II.

- Cu-Cr
- 450 MPa strength by precipitation hardening
- E.g.: spot welding electrode, brake, high-performance switches
- Cu-Be and Cu-Co-Be
- 500 MPa strength by precipitation hardening, keeps this strength up to 300°C
- ¼ conductivity
- E.g.: springs, wisher, membrane, nonsparking switches











### High alloyed copper alloys – Brasses I.

- Main alloy: Zn, 5-45%
- The color changes with Zn% from rosered to yellow





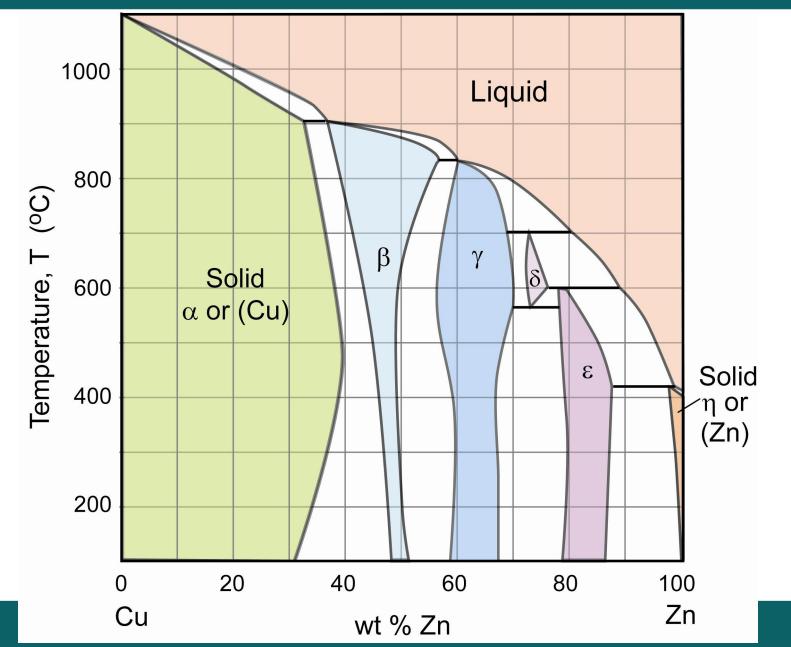
- Good castability, cold and hot formability
- Deep drawable, machinable
- Unalloyed Brass
  - $-\alpha$ -alloy (Zn<33%) as above
  - $-\alpha+\beta$  alloy (33%<Zn<45%),  $\beta$  enhances the strength and machinability, but causes brittleness





### Cu-Zn phase diagram







### High alloyed copper alloys – Brasses II.



### Alloyed brass

-Pb:

- spherical shaped grains
- better machinability
- Sn, Al, Si:
  - β phase promoting elements
  - enhance the hot workability

Pb 82 <sup>207.2</sup> Lead



#### – Ni, Mn, Fe:

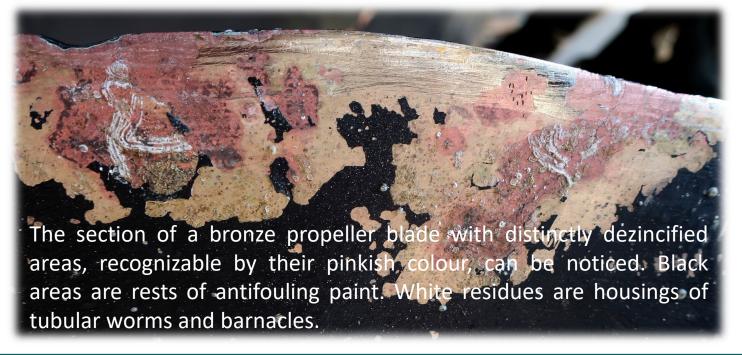
- $\alpha$  phase promoting elements
- enhance the formability







- The brasses have in general good corrosion resistance but over 15% of Zn two problems can appear:
  - Season cracking: residual stresses (welding), stress-corrosion, moist environment
  - Dezincification: the Zn is solved into the watery environment (primarily the high Zn-containing β-phase). Process can be slowed with arsenic (As) alloying: admiralty copper (71 Cu, 28 Zn, 1 Sn)

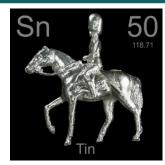




High alloyed copper alloys – Bronzes I.

- Main alloying element is tin (Sn), 3-20%
- Unalloyed bronzes
  - 3-20% Sn, except: bell bronze (20-25%) speculum metal mirror (30-35%)
  - Industrial bronzes:
    - $\alpha$  bronzes: good formability, strength increases with increasing tincontent and cold forming
    - Cast α+δ bronzes, properties depends on the hard δ phase (cooling rate!)









Additional alloying elements besides Sn

- Phosphorus bronzes (CuSn<sub>8</sub>P)
  - Cu<sub>3</sub>P precipitations increases the strength
- Leaded bronzes (CuSn<sub>8</sub>Pb<sub>3</sub>Zn<sub>6</sub>)
  - Pb do not solve, good machinability, good gliding properties (up to 30% Pb)
- Zinc bronzes (CuSn<sub>5</sub>Zn<sub>5</sub>Pb<sub>5</sub>)
  - Zn enhance the castability and formability water pipes and fittings



Phosphorus









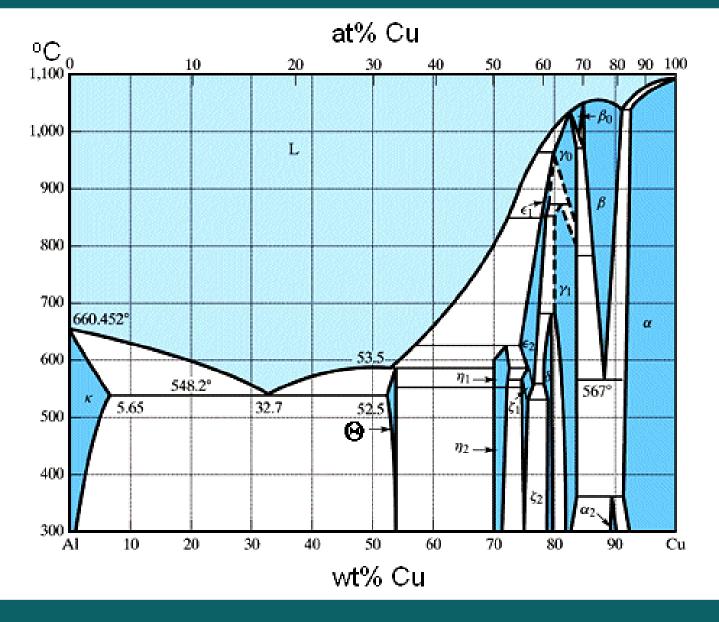
- Aluminum bronzes (cupro-aluminum)
  - 4-14% Al resist to seawater, stress corrosion and corrosionfatigue, high strength
  - Unalloyed: good formability, one or more phase (strength increases, toughness decreases)
  - Alloyed: Fe, Ni, Mn alloying
    - Enhanced corrosion resistance and strength
    - Ship propellers, turbine blades
    - Heat exchanger plates and tubes





### Al-Cu phase diagram

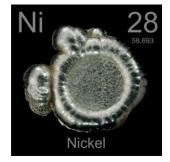








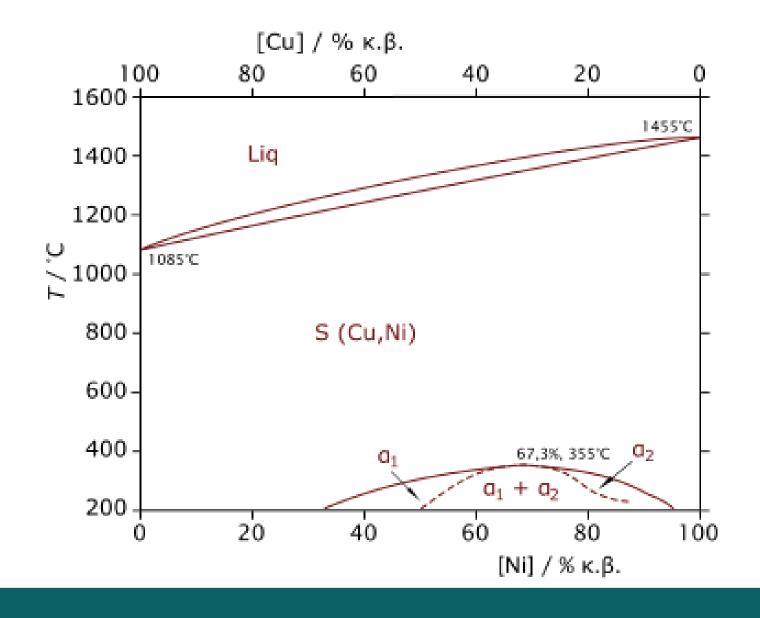
- Nickel bronzes (cupro-nickels)
  - Unlimited solubility between Cu and Ni
- Good resistance in high-speed-streaming seawater
- Few percent of Mn and Fe can be added
- Sheets, strips for general purpose, tubes for heat exchangers
- Constantan: 40-45% Ni content, conductivity does not change in wide range of temperature → strain gauges
- Nickel silver (alpacca): Cu-Ni-Zn alloy, between brass and cupro-nickels
  - One-phase alloys with good formability
  - Hot workable, two-phase alloy with good machinability





### Ni-Cu phase diagram

М ÚЕ G Y E T E M 1 7 8 2





## Other copper alloys



- Silicon bronzes (cupro-silicons)
  - Good friction properties, strength and corrosion resistance
  - CuSi<sub>3</sub>Mn, CuSi<sub>2</sub>Al<sub>2,5</sub>
- Lead bronzes
  - Good friction properties, plain bearings
  - CuPb<sub>8</sub>, CuPb<sub>15</sub>, CuPb<sub>20</sub>, CuPb<sub>30</sub>
- Shape memory copper alloys
  - Reversible martensitic transformation
  - Cu-Zn-Al, Cu-Zn-Ni alloys
  - Also NiTiNOL









Nickel



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- Density 8.89 gcm<sup>-3</sup>
- Melting point 1440°C
- FCC lattice
- Excellent corrosion, heat and creep resistance
- Energy, chemical and oil industry, airplane engines





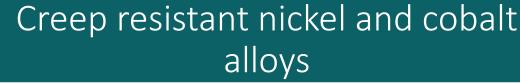
# Corrosion resistant nickel alloys

- Unalloyed chemical industry nickel two subtypes depending on C%
  - soft, can be strengthened by cold working, toughness decreases but, significant even at low temperatures
- Ni-Cu Alloys– Monel
  - 28-34% Cu, high pressure water, steam and seawater pipes, brass instrument, evaporators
- Ni-Cr-Fe and Ni-Mo alloys– Inconel, Hastalloy, Incoloy, Nimonic
  - Individual corrosion resistance
    - Ni-Cr-Fe: vitriolic, phosphoric acidic, seawater, chloric
    - Ni-Mo: hydrochloric, hydrogen fluoride environment
    - Ni-Cr-Mo: wide corrosion resistance, pitting and crevice corrosion resistance





- Ni-Cr and Ni-Cr-Fe alloys
  - Excellent strength at high temperatures, creep resistance
  - Resistance heaters, resist to hot air
- Fe-Ni-Cr alloys
  - Main component is Fe, not typical Ni alloys
  - Perform well even in oxidizing, carbonizing and sulfiding environment

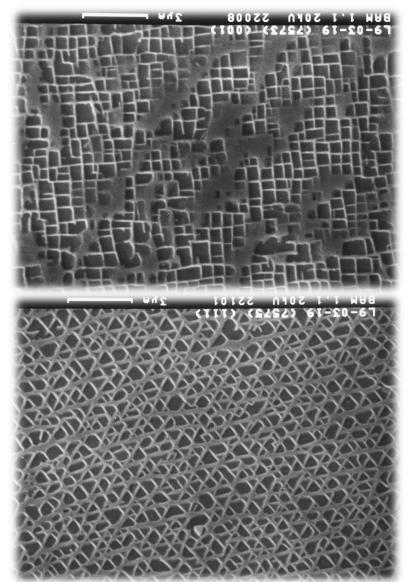




- High heat and creep resistant super alloys
- Developed for improving gas turbines' efficiency
- Up to 10-15 alloying components

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- C, Cr, Co, Ni, Mo, W, Ti, Al, Nb, Fe, B, Zr, Ta, V, Re, Hf, La, Y
- Single crystal turbine blades strengthened by precipitation hardening
- PH types: Al, Ti, Nb, YS 600 MPa





- Resistance heaters: Ni-20Cr-Si, CuNi45 (Constantan)
- Thermocouples: K type 90Ni-9Cr and 94Ni-AlMn-Fe-Si-Co
- Soft magnetic materials: Permalloy
- Alloys with low thermal expansion: Invar36, Kovar
  - Tooling for aerospace composites, standards of length, measuring devices, thermostat rods, laser components, etc.
- Intermetallic alloys, Ni<sub>3</sub>Al, YS 700 MPa at 800 °C!
- Maraging X2NiCoMo18-9-5
  - -Martensitic, precipitation hardenable
- Shape memory Ni-Ti alloys



- Density 7.133 gcm<sup>-3</sup>
- Melting point 419.5 °C
- Hexagonal lattice
- Base material for corrosion protection: coating

   Zinc-carbonate surface layer

Zinc

- 5 purity levels (Z1...Z5)
   Z1: 99.995% Zn ... Z5: 98.5% Zn
- Main impurity elements: Pb (Cd, Fe, Sn, Cu, Al)
- Anodic protection
- Cu, Ti increases the strength
- Soft (~100 MPa yield stress, creep starts form 100°C)





### Zinc alloys



- Excellent castability, numerous casting application
  - Rapid prototyping (sand mold + machining)
  - Small series production (die casting)
  - Large-scale production (pressure die casting)
  - Surface treating (Hot-dip galvanization)



 Keys, x-ray tube sockets, luxury goods, window lock mechanisms, pin, phone-case, locks, etc.



## Zinc alloys



- Zn-Al (eutectic at ~5% Al)
- Hypoeutectic, ~4% Al
  - End of 1930s, Zamak alloy (Zn-Al-Mg-Cu)
  - Investment casting



- Hypereutectic, 6-12% Al
  - 1950s: 6-8% Al, Zamak, heat and wear resistance
  - Tonsul alloy + Mg, jewelry alloys
  - Ilzro: 12% Al and 1% Cu, gravity casting, larger parts, e.g. office chair leg





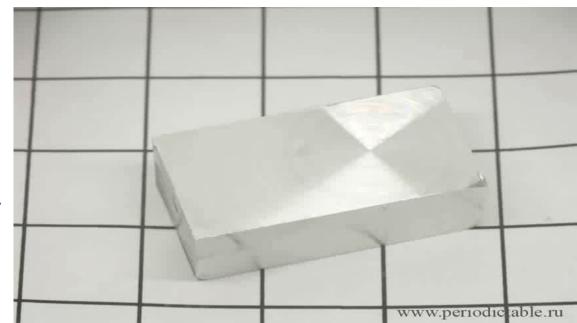
- Hypereutectoid alloys
  - -25-35% Al content
  - -Good strength, up to 400 MPa yield stress
  - -Porous surface containing lubricant
- Al free Zn-Cu-Ti alloys
  - –Zn-Cu: cast building industry parts, coins, deep draw tools
  - –Zn-Cu-Ti and Zn-Cu-Cr-Ti: large sand-mold cast parts, roof structures, 300 MPa yield stress
  - -Zn-Pb-Cd-Fe: batteries' case





- Corrosion and acid resistant
- Alloys for bearings and filler metals (Pb) for soldering
- Tin pest
  - Below 13.2°C tetragonal  $\rightarrow$  diamond lattice transformation
  - Allotropic transformation
  - Volume changes
  - Inner stresses
  - The part pulverizes
- Tin cry (twinning)

https://youtu.be/kzlsvbKHgfU







# Thank you for your attention!