Department of Materials Science and Engineering
MŰEGYETEM 1782

Non-ferrous metals

Imre Norbert ORBULOV, PhD

Materials Engineering
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Topic

- 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 metals according to the density
  - lighter than 4.5 gcm^{-3}
    - Al, Mg (Be, Li…)

- Borderline case…
  - Ti, $\rho \approx 4.5\ gcm^{-3}$

- Heavy metals
  - heavier than 4.5 gcm^{-3}
    - Cu, Zn, Sn, Pb, Ni, W

  precious metals

Physical and mechanical character

	ρ (gcm^{-3})	R_{eH} (MPa)	R_{eH}/ρ	T_{creep} (°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

Physical and mechanical character

	R_m	E	ρ	R_m/ρ	E/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

Aluminum

- Light, low density (ρ=2.7 gcm^{-3})
- 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_m=40…120 MPa, $R_{p0.2}$=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/

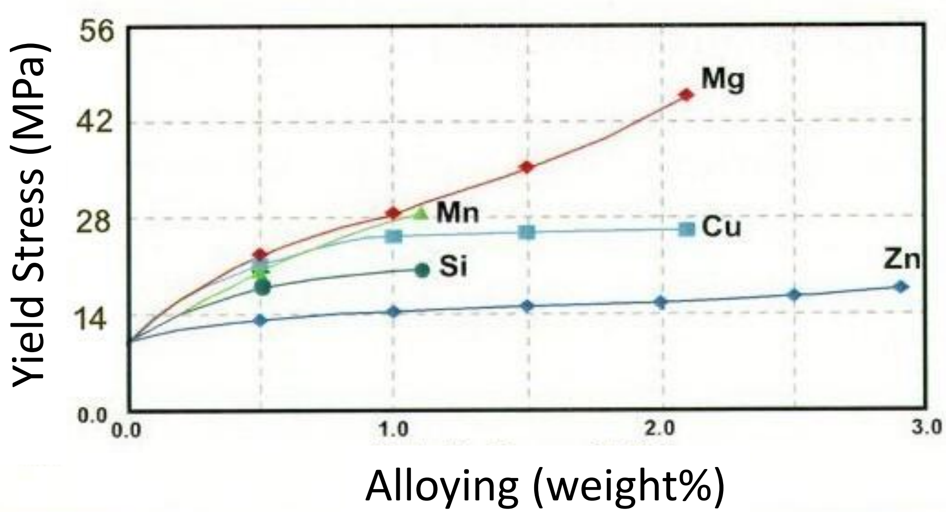
Alloying

- 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.

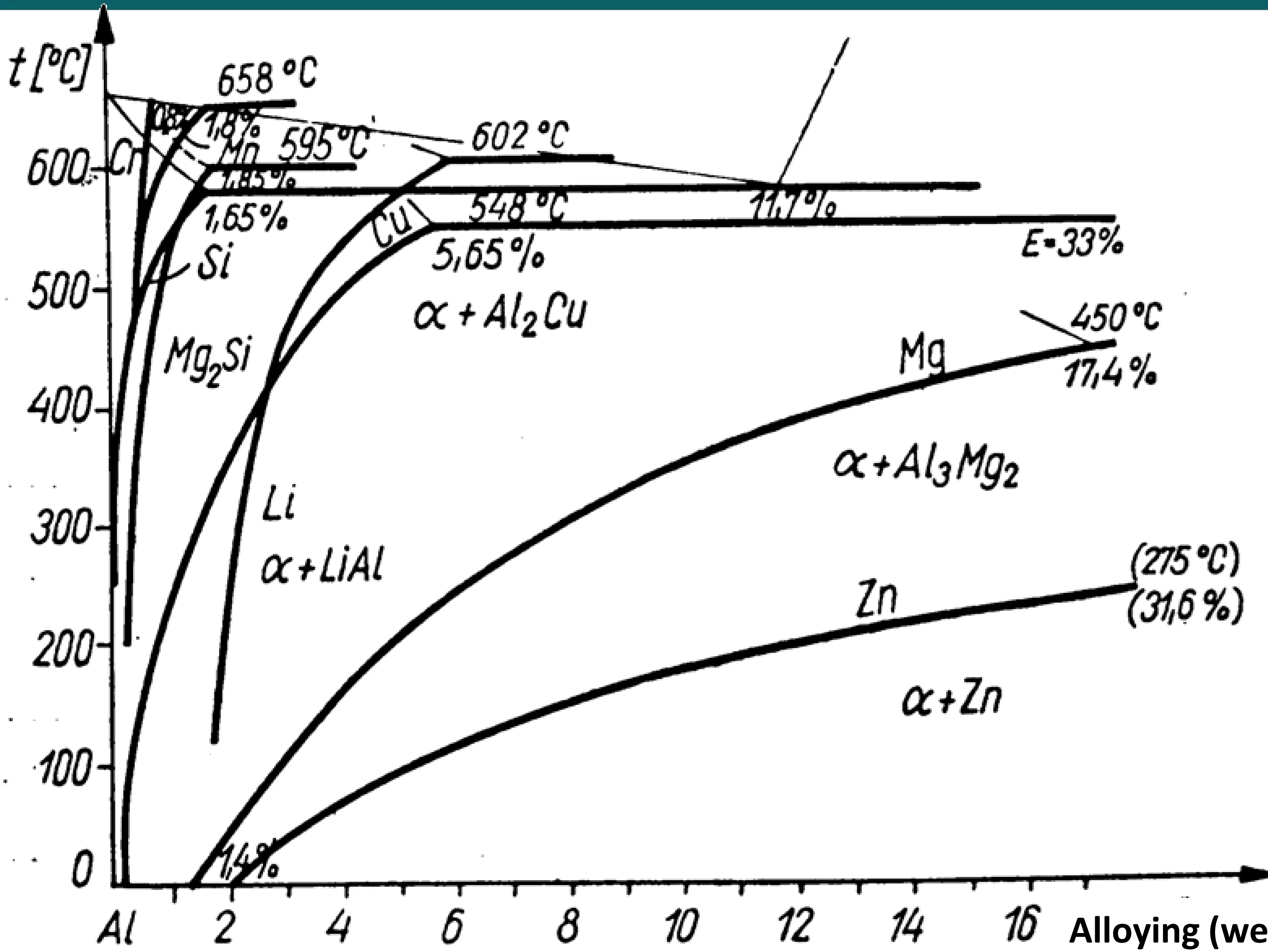
Solid solution

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



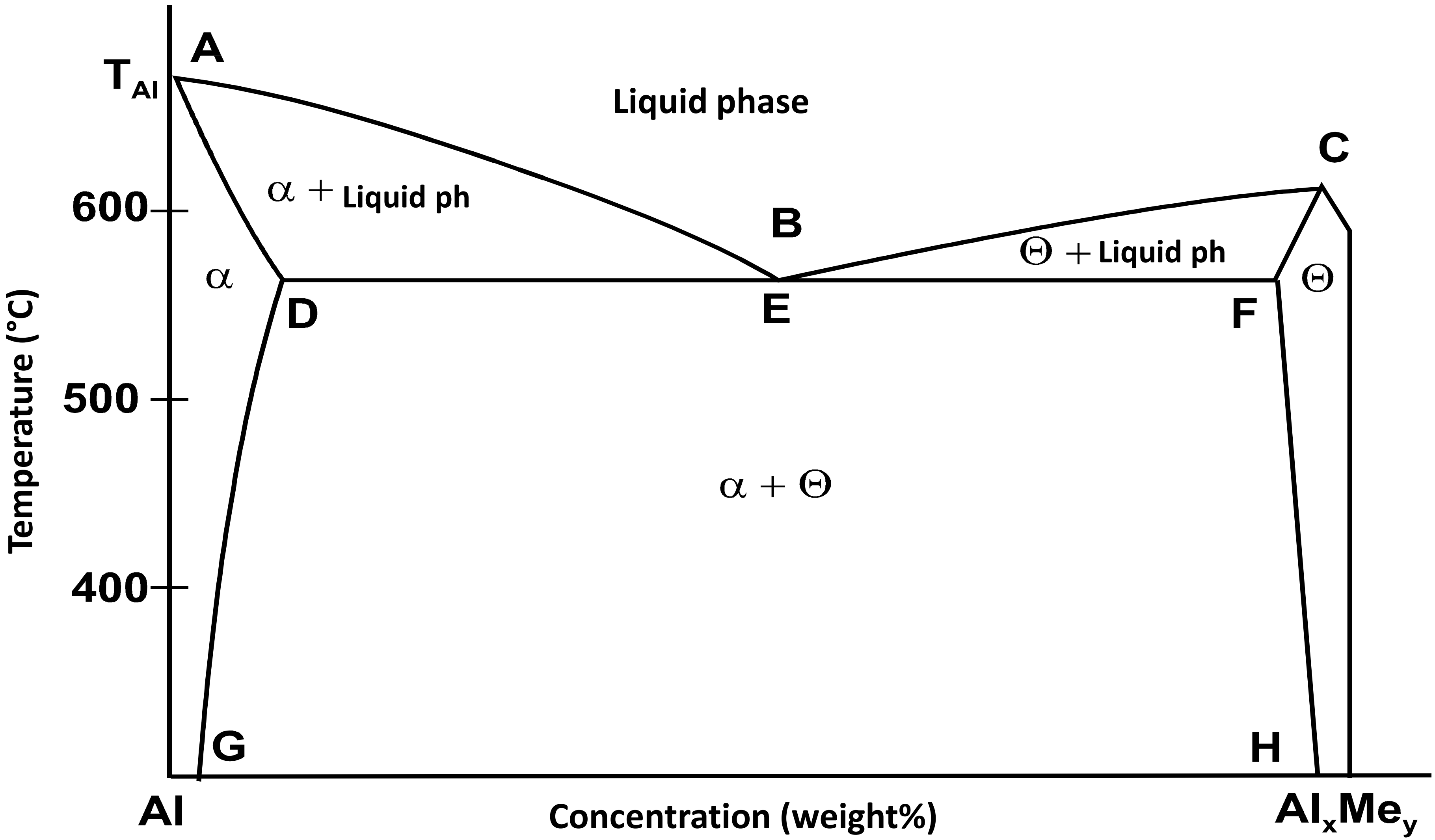
Atomic number	25 Mn	14 Si	26 Fe	24 Cr	29 Cu	30 Zn	13 Al	22 Ti	40 Zr	12 Mg
Atomic radius	112	118	123	125	128	133	142	146	160	160

Solid solution – Alloys solubility

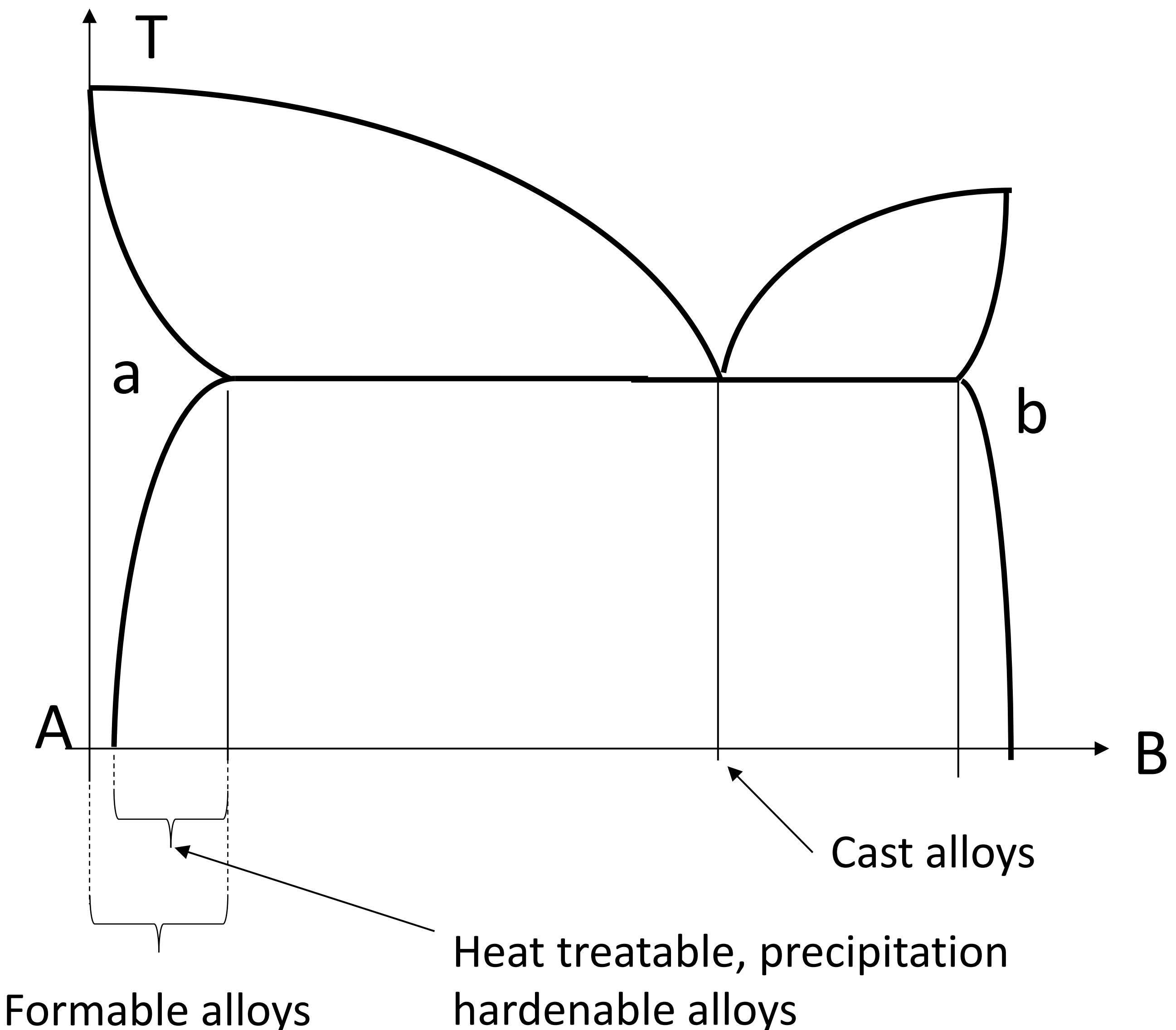


Alloying (weight%)

General phase diagram



Classes according to processing



Designation system

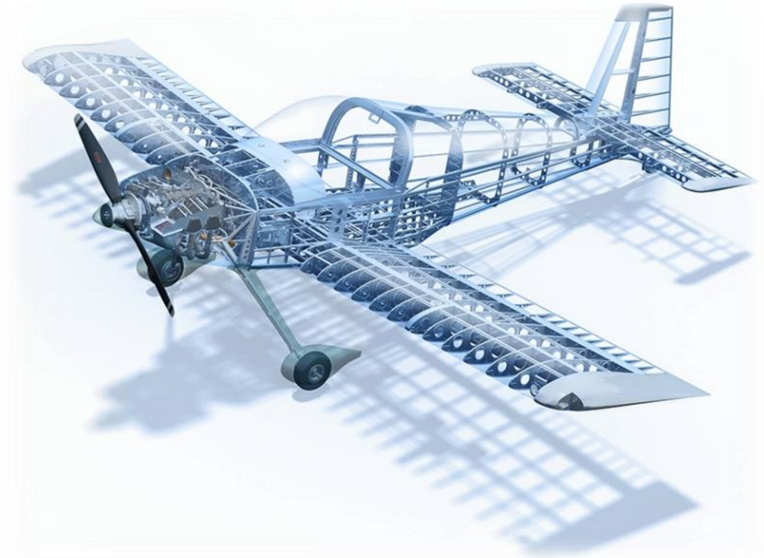
	Formable	Castable
Al	1xxx	1xx.x
Al-Cu	2xxx	2xx.x
Al-Mn	3xxx	
Al-Si	4xxx	4xx.x
Al-Si(-Cu/Mg)		3xx.x
Al-Mg	5xxx	5xx.x
Al-Mg-Si	6xxx	
Al-Zn(-Mg)	7xxx	7xx.x
Al-Li	8xxx	
Other elements	9xxx	9xx.x
Al-Sn		8xx.x
Not used		6xx.x

1xxx

- >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



3xxx

- <2% Mn alloying
  - 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

4xxx

- 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
  - Low melting point, low shrinkage, good fluidity
- Adding Mg → heat treatable alloy(6xxx) strength increasing
- Engines, castings for modest loads and sizes, pistons

5xxx

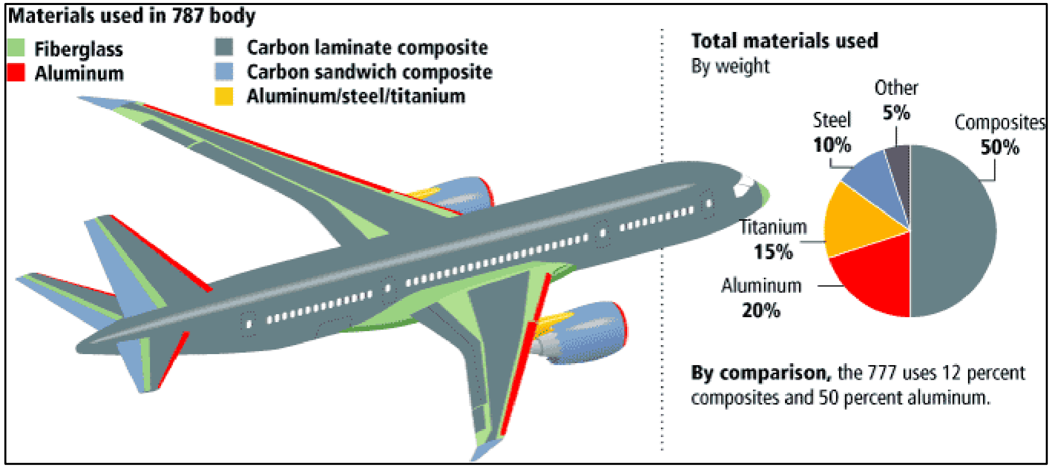
- 0.5-0.7% Mg alloying
- Strengthening cased by Mg can be enhanced by cold working
- Good formability
- Good weldability
- Good anodizability
- Good corrosion resistance
- Automotive industry, architecture, shipbuilding, chemical industry
- With >3% Mg alloying the corrosion resistance decreases
  can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

The 127m *Benchijigua Express*, built by Austal Ships, is the world's largest aluminum ship

6xxx

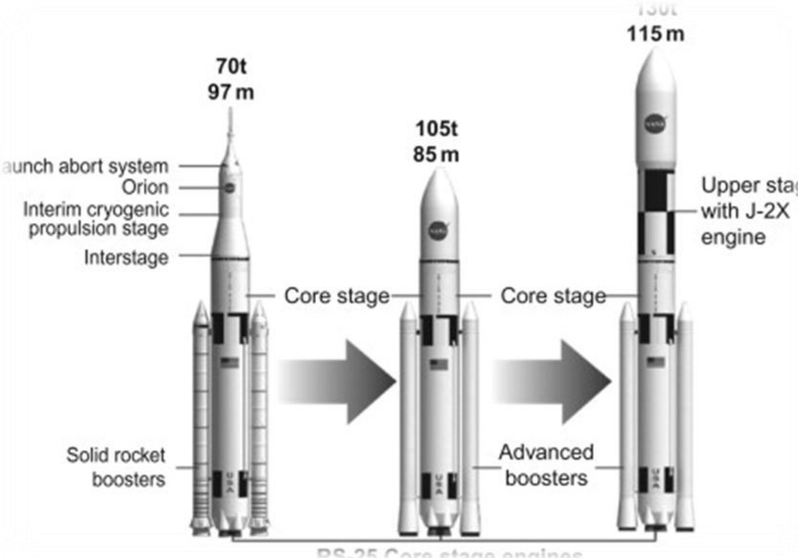
- 0.3-1.5% Mg and Si
- Precipitation hardenable alloys (Mg_2Si)
- Moderate to high strength
- Good formability
- Good weldability
- Good anodizability
- Good corrosion resistance
- One of the most common Al alloy:
  electric industry, Automotive industry, architecture, machine industry, commodity
- Mn and Cr addition: grain refinement, increased strength and toughness, decreased stress-corrosion resistance

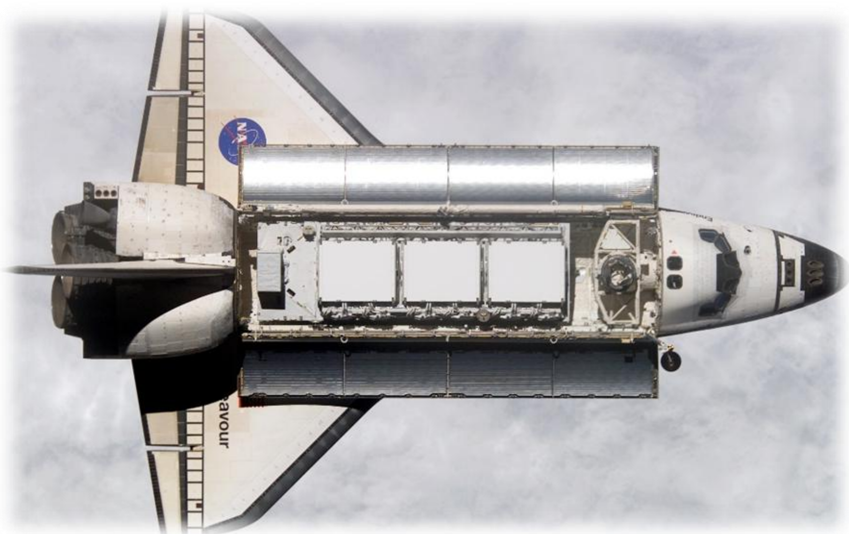
- 4-6% Zn (and 1-3% Mg), „hard” alloys
- Precipitation hardenable
  At 443°C ~70% Zn solubility
  ⇔ at 20°C 0.1% (!)
- Up to $R_{p0.2}$=600 MPa
- Outstanding strength and appropriate formability
- Automotive industry, architecture, sporting goods



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

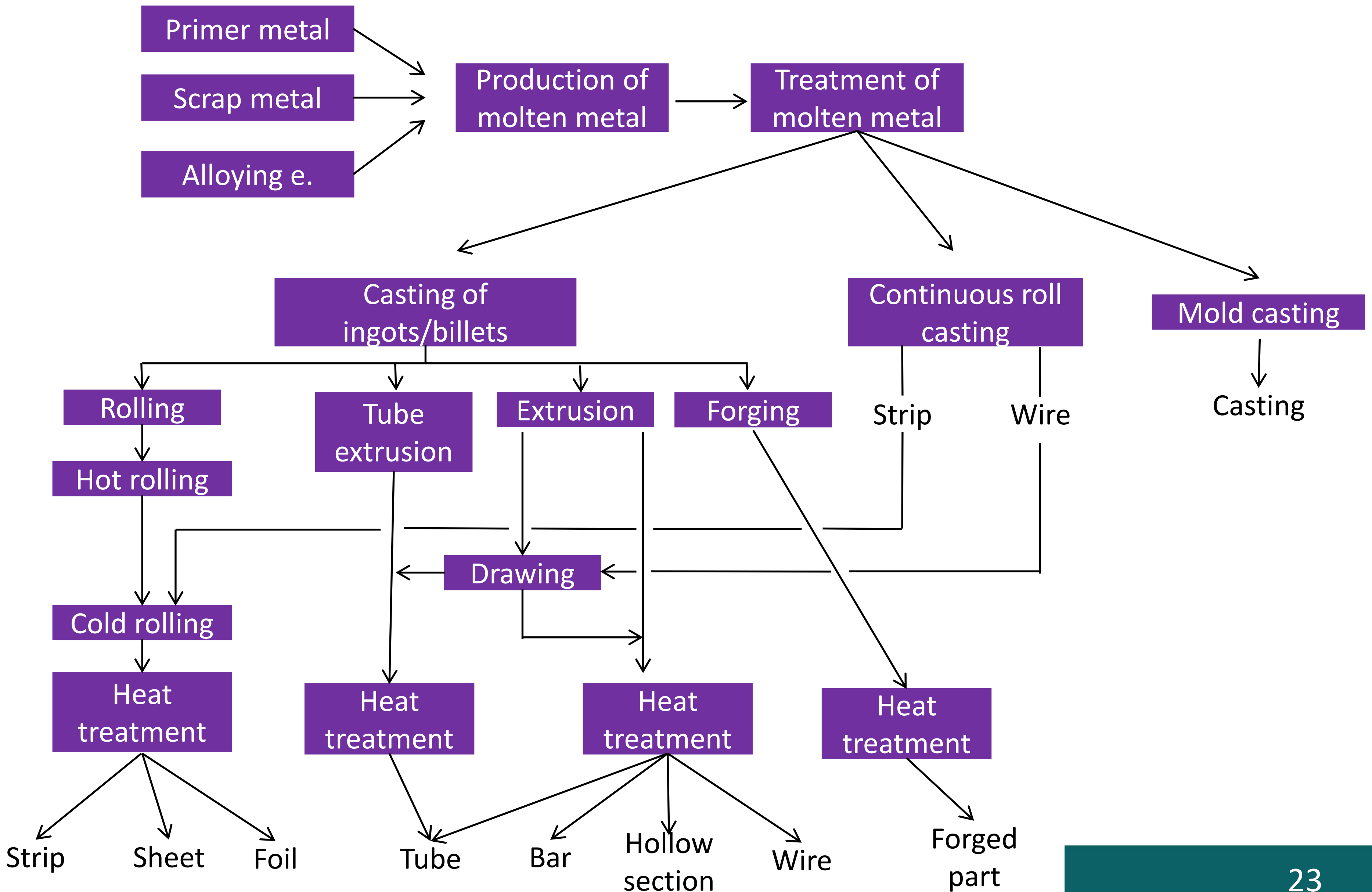




Overview

Formable alloys		Cast alloys	
Non-heat treateble (weldable) Good corrosion resistance Good electric condictivity Good formability	heat treateble - high-strength alloys	Non-heat treateble	heat treateble
Al-Mn Al-Mg Al-Mg-Si $Al-Mg_{0.5}-Si_{0,5}$ Al-Mg-Zn Al-Mg-Li	Al-Mg-Si Al-Mg-Li Al-Li-Mg Al-Cu-Mg Al-Cu-Li Al-Cu-Li-Mg Al-Zn-Mg Al-Li-Cu-Mg Al-Zn-Cu-Mg	Al-Si Al-Mg	Al-Si-Mg Al-Si-Cu Al-Mg-Si Al-Cu Al-Cu-Ni Al-Zn-Si Al-Zn-Mg

Semiproducts



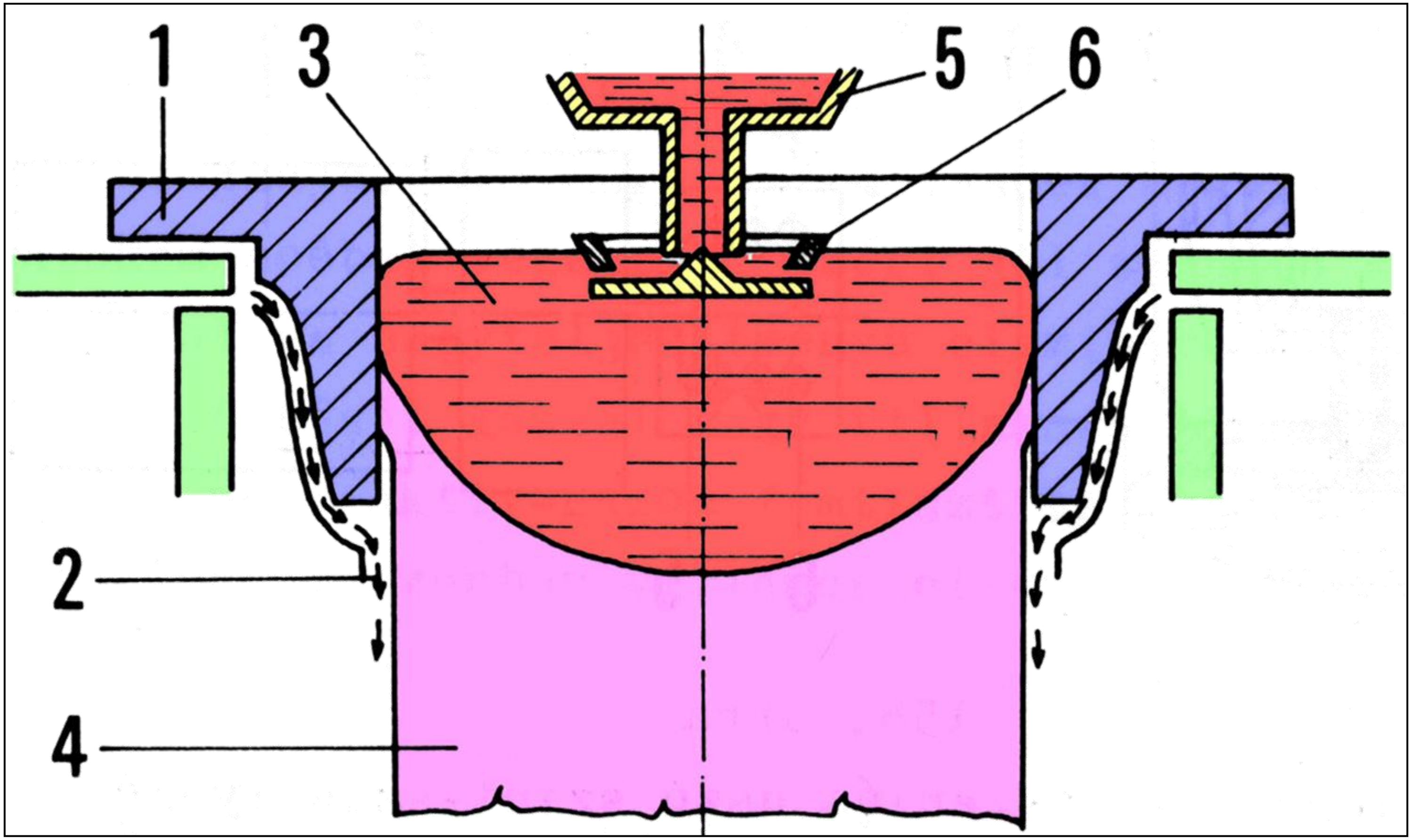
Casting of ingots and billets

- 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

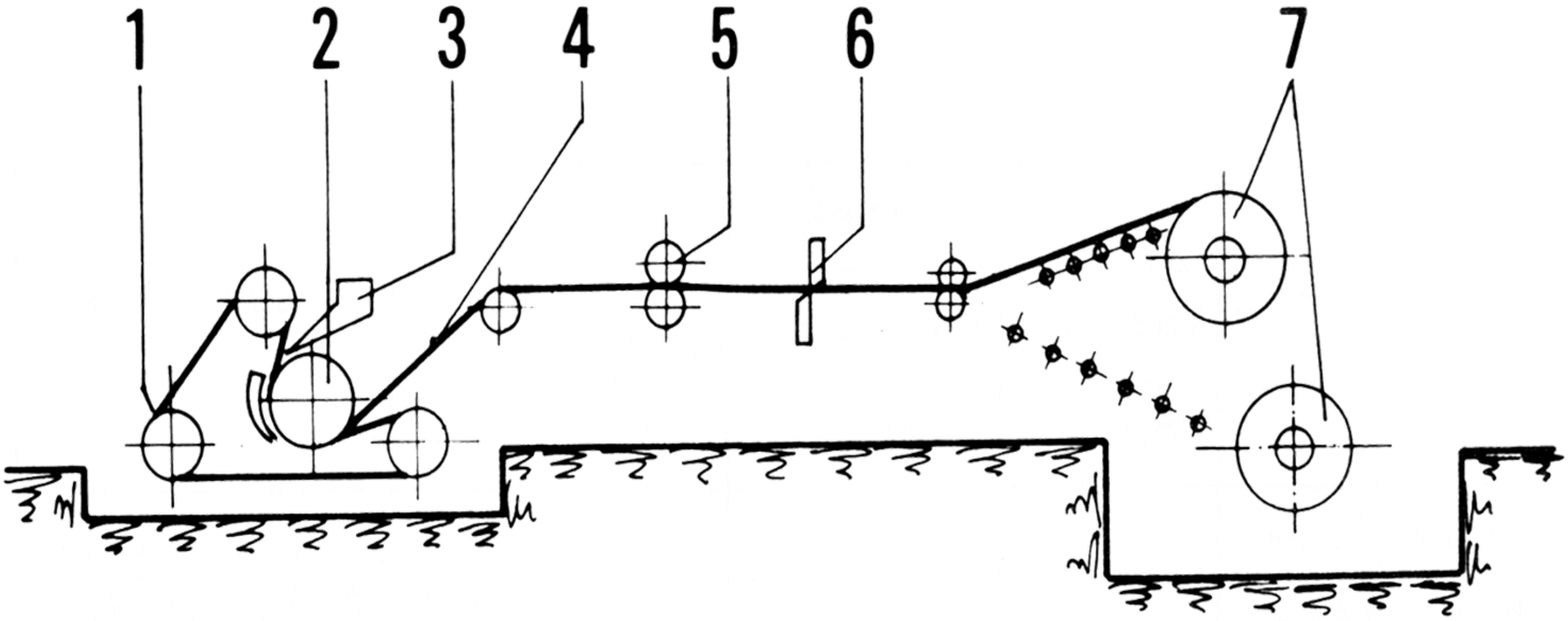


Pouring liquid metal continuously into a short mold (7.5–15 cm deep) that is open at the bottom. Only an outer layer of metal solidifies within the water-cooled mold. After leaving the closed mold at its bottom (e.g. with 5–15 cm/min), water is directly sprayed on the new ingot, continuing the solidification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

Vertical direct chill casting

VDC aluminum billet vertical casting video

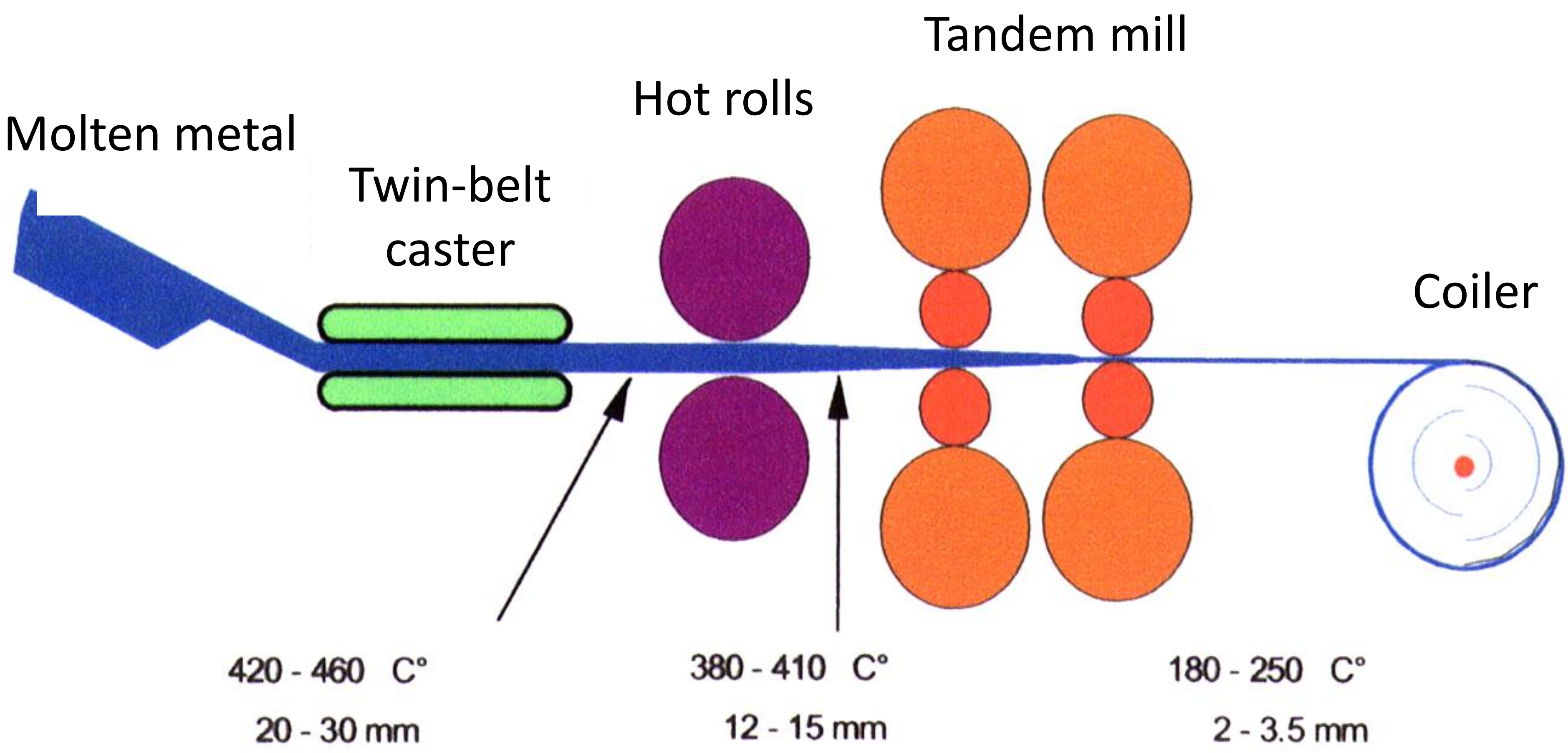
- Wires and strips
- It is followed by rolling generally



Aluminum rod continuous casting and rolling mill

[Aluminum rod continuous casting and rolling mill]

Twin-belt casting



Hazelett twin-belt casting

Further processing

<u>Billet for rolling</u>

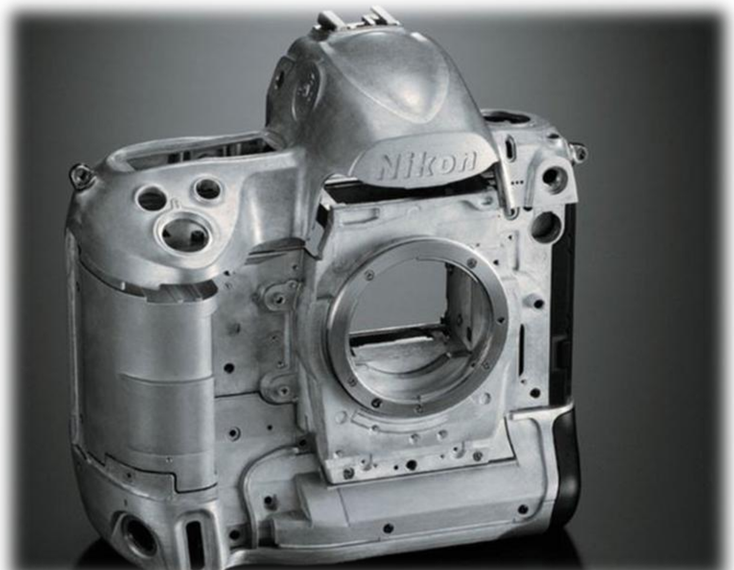
- Hot rolling
- Cold rolling
- Heat treatment
- Foil production

<u>Billet for extrusion</u>

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

Magnesium

- Lowest density metal for mass production for structural purposes, $\rho=1.8\ gcm^{-3}$
- 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

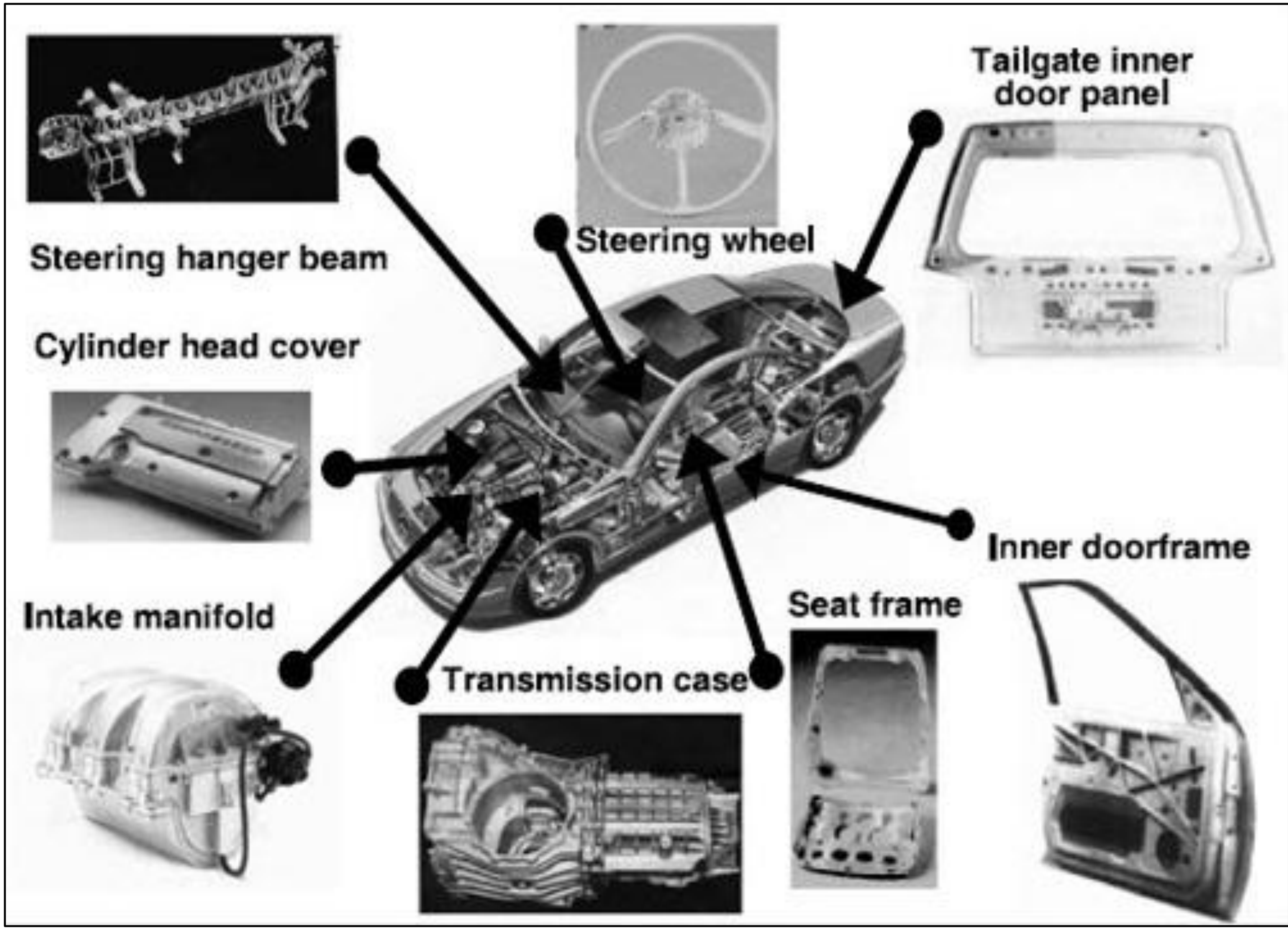


Technological properties

- 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



https://www.totalmateria.com/page.aspx?ID=CheckArticle&site=ktn&LN=TR&NM=246

Alloys with good castability

Zn, Zr, Th, Y → PH
Mn → Corrosion res.
Sn → 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

e.g..: AZ91

A	Aluminium
B	Bismuth
C	Copper
D	Cadmium
E	Rare earths
F	Iron
H	Thorium
J	Strontium
K	Zirconium
L	Lithium
M	Manganese
N	Nickel
P	Lead
Q	Silver
R	Chromium
S	Silicon
T	Tin
V	Gadolinium
W	Yttrium
X	Calcium
Y	Antimony
Z	Zinc

Mg-Al-Zn cast alloys

- 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_2Si precipitations, enhanced creep resistance
- Mg-Al-Zn-RE alloys
  - Ce, La, Nd, Pr, precipitation, better creep resistance
- Mg-Al-Zn-Cu alloys
  - Engine houses

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

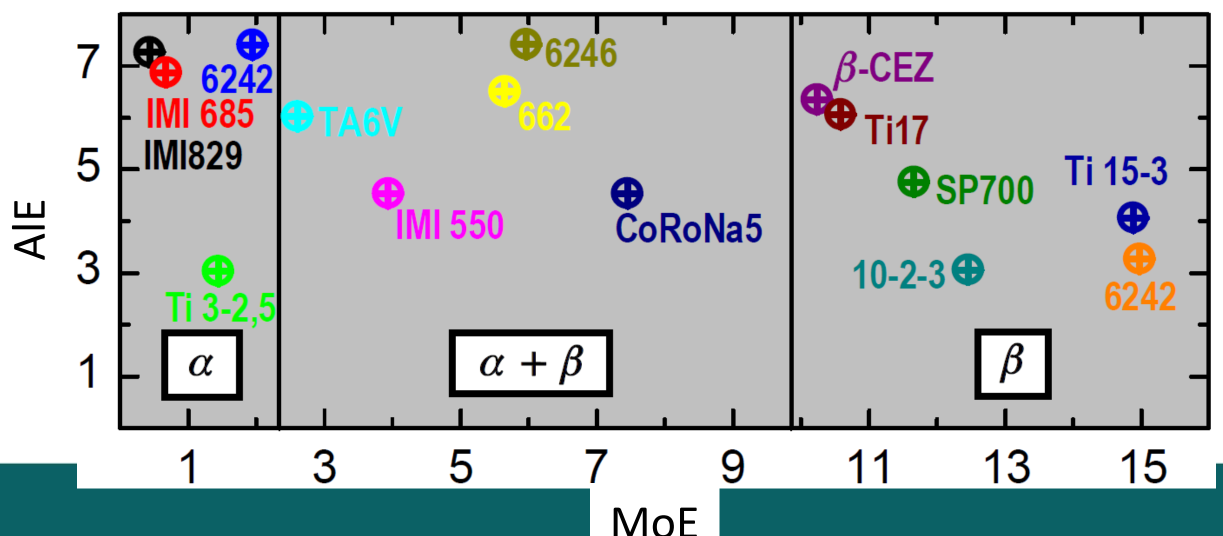
Titanium

- Not really light (4.5 gcm^{-3})
- Two allotropic forms
  - α-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
  - Grade1…4, according to the dissolved oxygen content
- α and near-α → Not heat treatable
- α + β
- β and near-β → Ductile
- Schäffler-diagram-like diagram: Mo and Al equivalent

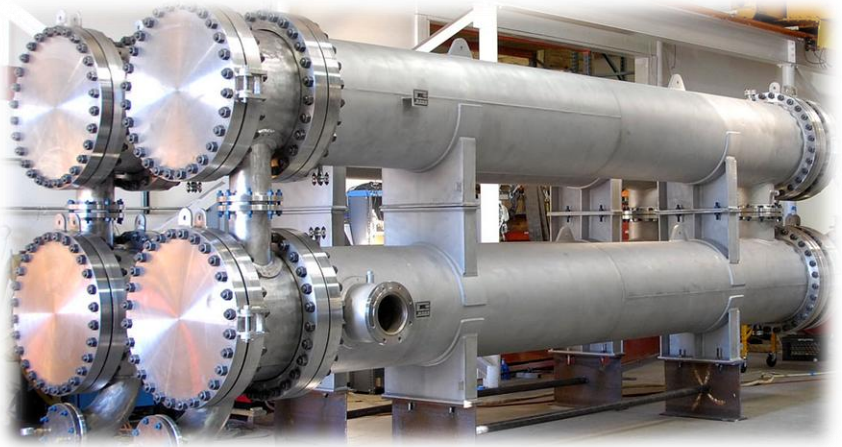
$$AlE = Al + \frac{Sn}{3} + \frac{Zr}{6} + 10 \cdot (O + C + 2 \cdot N) \quad MoE = Mo + \frac{2}{3}V + \frac{4}{9}W + \frac{8}{5}Cr + 3Fe + \frac{4}{3}Cu + \frac{2}{7}Nb - Al$$



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

- 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^{-3})
- 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_2O eutectic at grain boundaries – brittleness
- Corrosion resistant
- Bronze and brass
  - Tin bronze, lead bronze, aluminum bronze, chrome bronze

Industrial coppers

- 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.

- 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

Low alloyed copper alloys II.

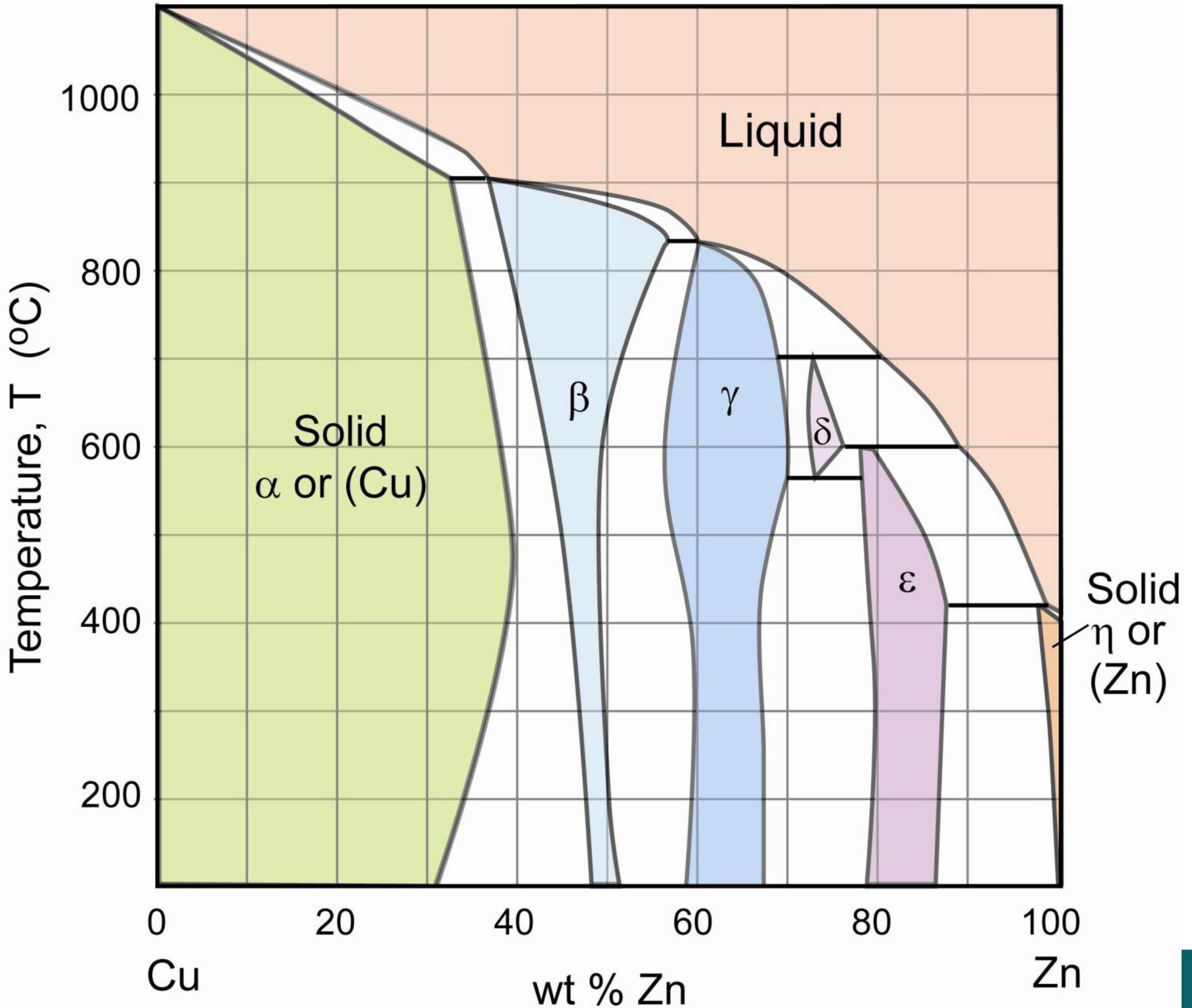
- Cu-Cr
  - 450 MPa strength by precipitation hardening
  - E.g.: spot welding electrode, brake, high-performance switches

- 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
  - α-alloy (Zn<33%) as above
  - α+β alloy (33%<Zn<45%), β enhances the strength and machinability, but causes brittleness

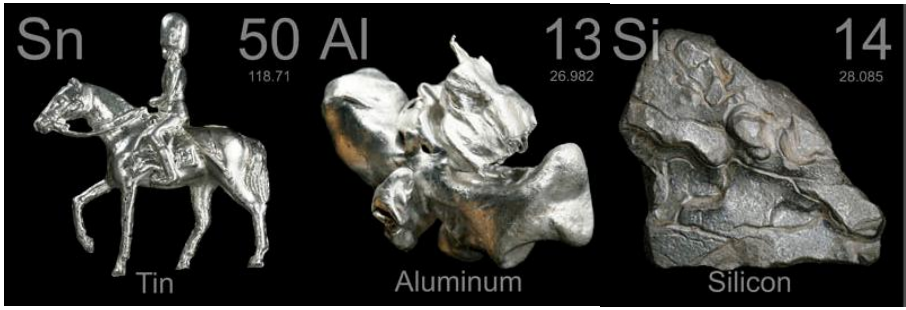
Cu-Zn phase diagram



Alloyed brass

- Pb:
  - spherical shaped grains
  - better machinability

- Sn, Al, Si:
  - β phase promoting elements
  - enhance the hot workability



- Ni, Mn, Fe:
  - α phase promoting elements
  - enhance the formability

High alloyed copper alloys – Brasses III.

- 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)

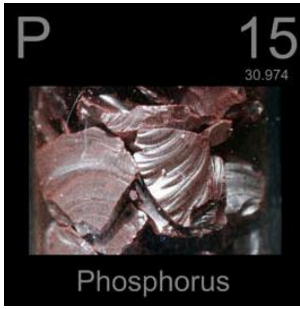
The section of a bronze propeller blade with distinctly dezincified areas, recognizable by their pinkish colour, can be noticed. Black areas are rests of antifouling paint. White residues are housings of tubular worms and barnacles.

High alloyed copper alloys – Bronzes I.

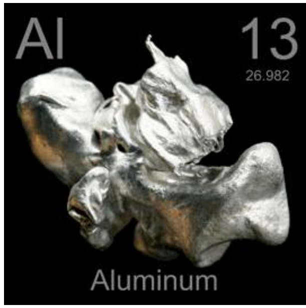
- Main alloying element is tin (Sn), 3-20%
- Unalloyed bronzes
  - 3-20% Sn, except:
    bell bronze (20-25%)
    speculum metal mirror (30-35%)
  - Industrial bronzes:
    - α bronzes: good formability, strength increases with increasing tin-content and cold forming
    - Cast α+δ bronzes, properties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

Additional alloying elements besides Sn

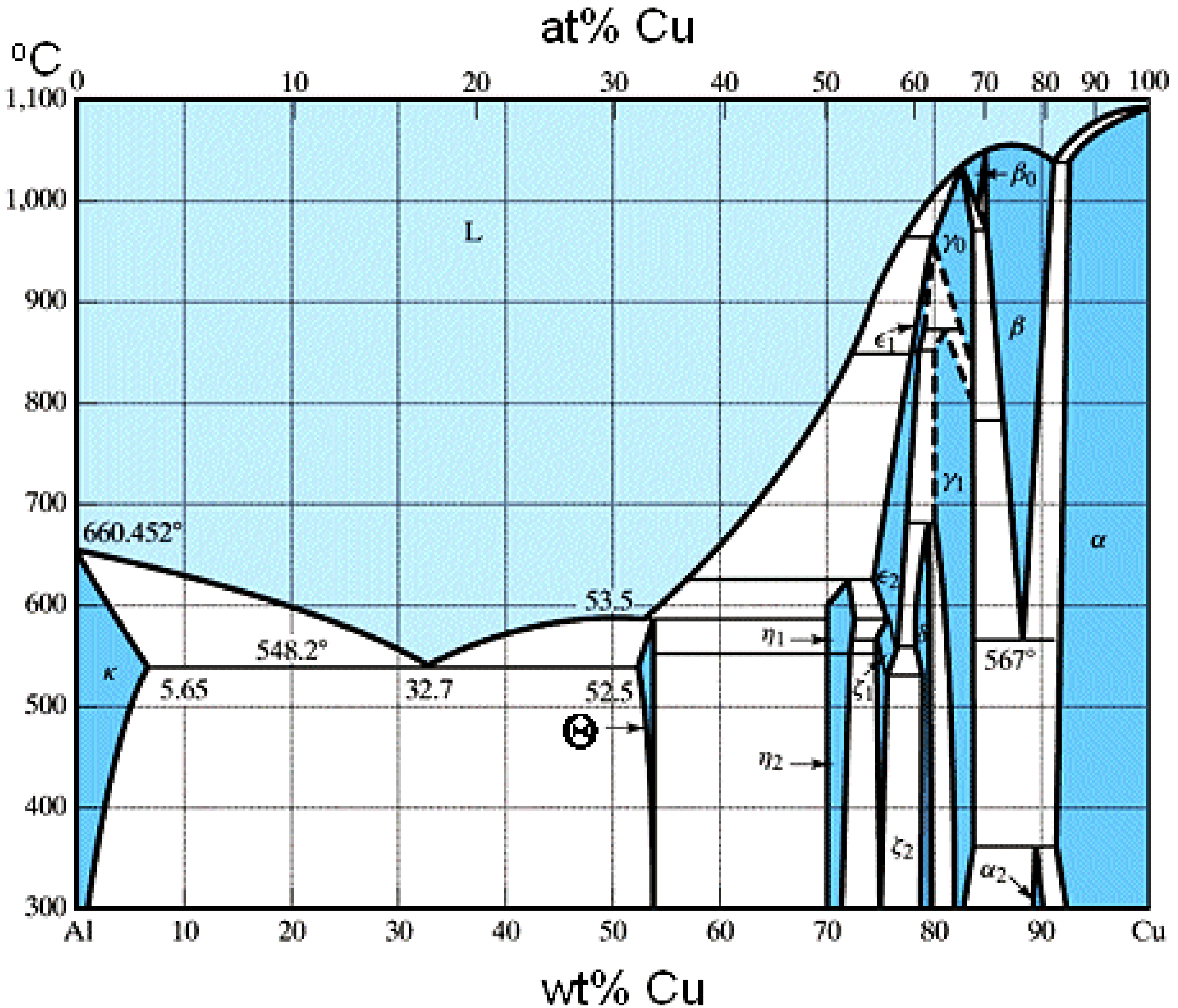
- Phosphorus bronzes ($CuSn_8P$)
  - Cu_3P precipitations increases the strength
- Leaded bronzes ($CuSn_8Pb_3Zn_6$)
  - Pb do not solve, good machinability, good gliding properties (up to 30% Pb)
- Zinc bronzes ($CuSn_5Zn_5Pb_5$)
  - Zn enhance the castability and formability water pipes and fittings



- Aluminum bronzes (cupro-aluminum)
  - 4-14% Al resist to seawater, stress corrosion and corrosion-fatigue, 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



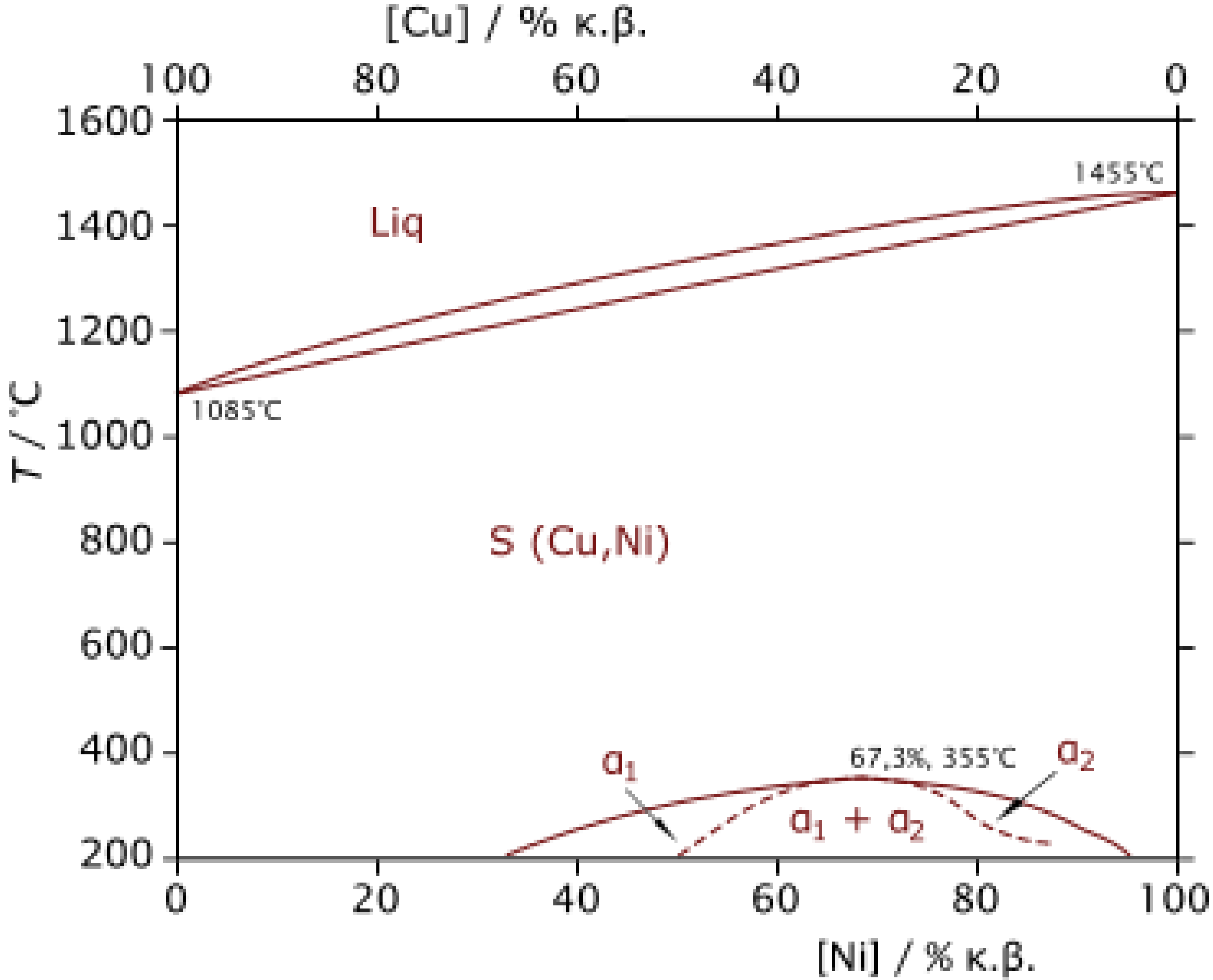
Al-Cu phase diagram



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

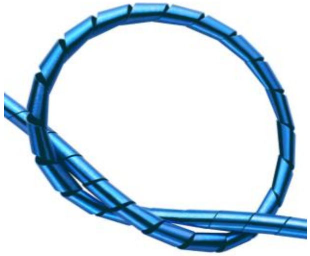


Other copper alloys

- Silicon bronzes (cupro-silicons)
  - Good friction properties, strength and corrosion resistance
  - $CuSi_3Mn$, $CuSi_2Al_{2,5}$

- Lead bronzes
  - Good friction properties, plain bearings
  - $CuPb_8$, $CuPb_{15}$, $CuPb_{20}$, $CuPb_{30}$

- Shape memory copper alloys
  - Reversible martensitic transformation
  - Cu-Zn-Al, Cu-Zn-Ni alloys
  - Also NiTiNOL



Nickel

- Density 8.89 gcm^{-3}
- 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

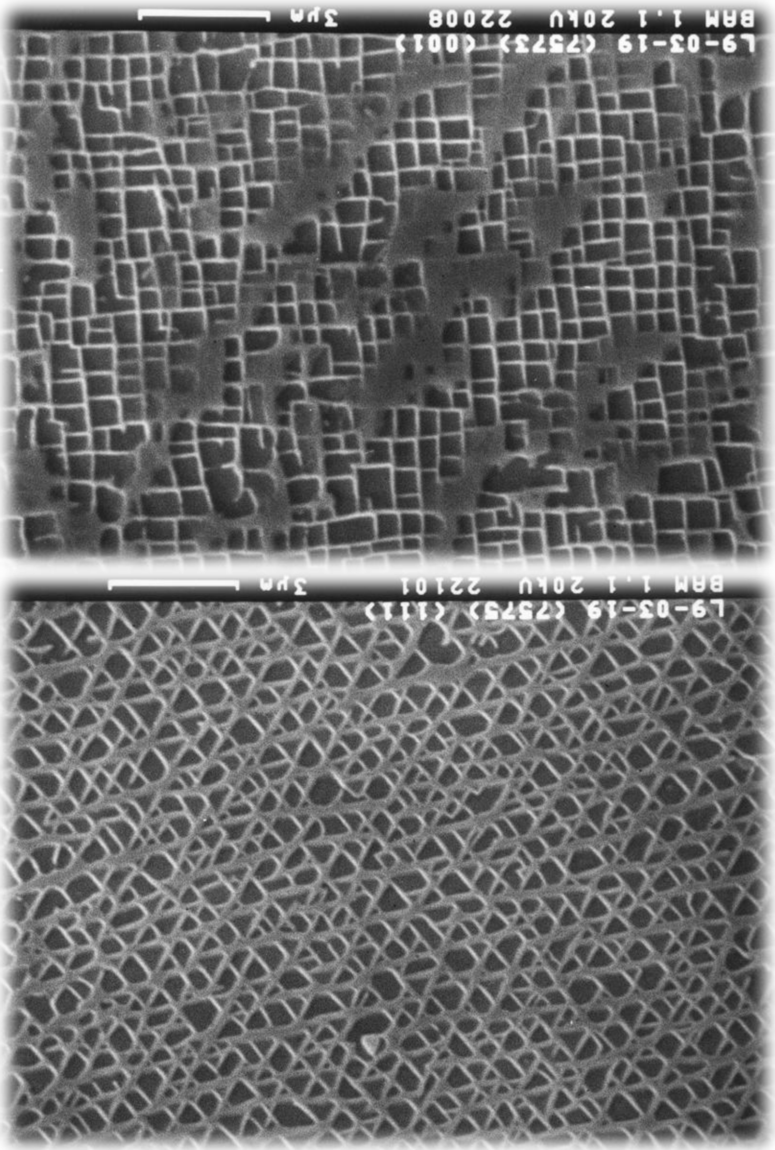
Heat resistant nickel alloys

- 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

Creep resistant nickel and cobalt alloys

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



https://www.phase-trans.msm.cam.ac.uk/2003/Superalloys/rafting.html

Special nickel alloys

- 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_3Al, YS 700 MPa at 800 °C!
- Maraging – X2NiCoMo18-9-5
  – Martensitic, precipitation hardenable
- Shape memory Ni-Ti alloys

Zinc

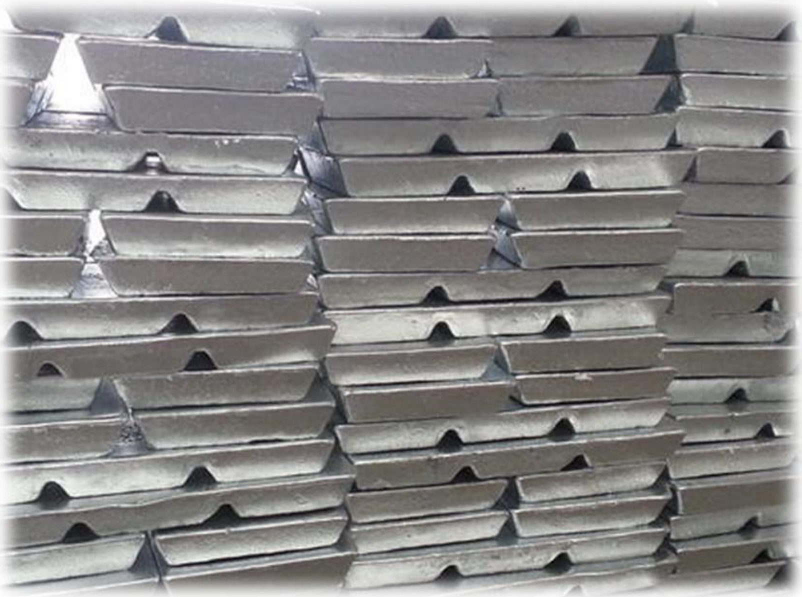
- Density 7.133 gcm^{-3}
- Melting point 419.5 °C
- Hexagonal lattice
- Base material for corrosion protection: coating
  - Zinc-carbonate surface layer
- 5 purity levels (Z1…Z5)
  - Z1: 99.995% Zn … Z5: 98.5% Zn
- Main impurity elements: Pb (Cd, Fe, Sn, Cu, Al)
- Anodic protection
- Cu, Ti increases 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

Zinc alloys

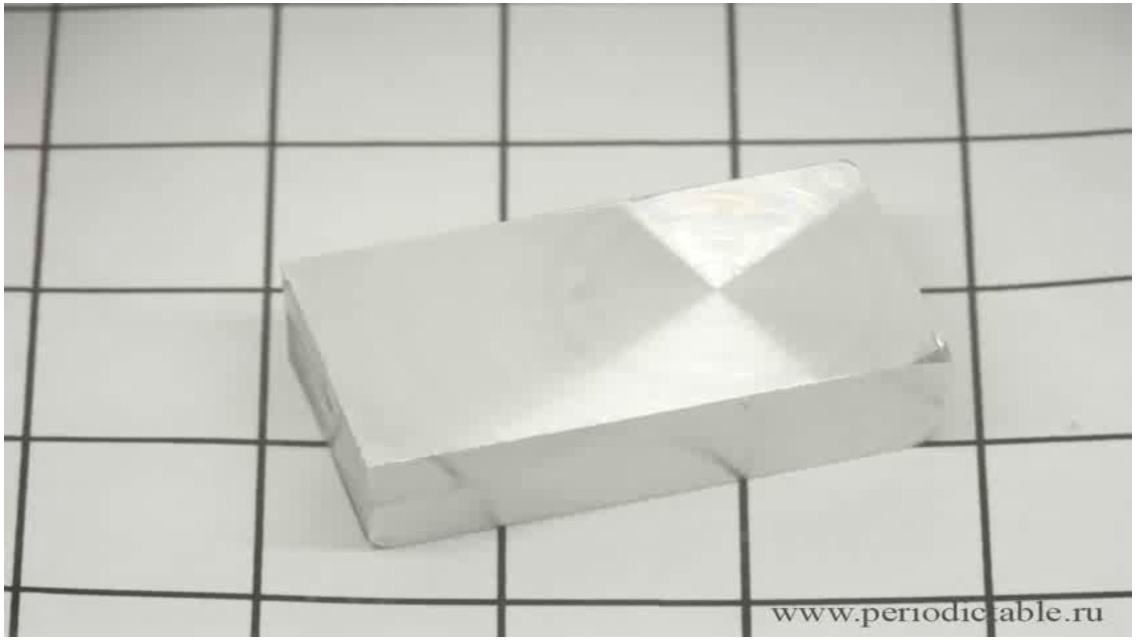
- Hypereutectoid alloys
  - 25-35% Al content
  - Good strength, up to 400 MPa yield stress
  - Porous surface – containing lubricant

- 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

Tin and its alloys

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

https://youtu.be/kzIsvbKHgfU



Thank you for your attention!