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Materials in cryogenics

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Properties of Solids in Low Temperature

Specific heat

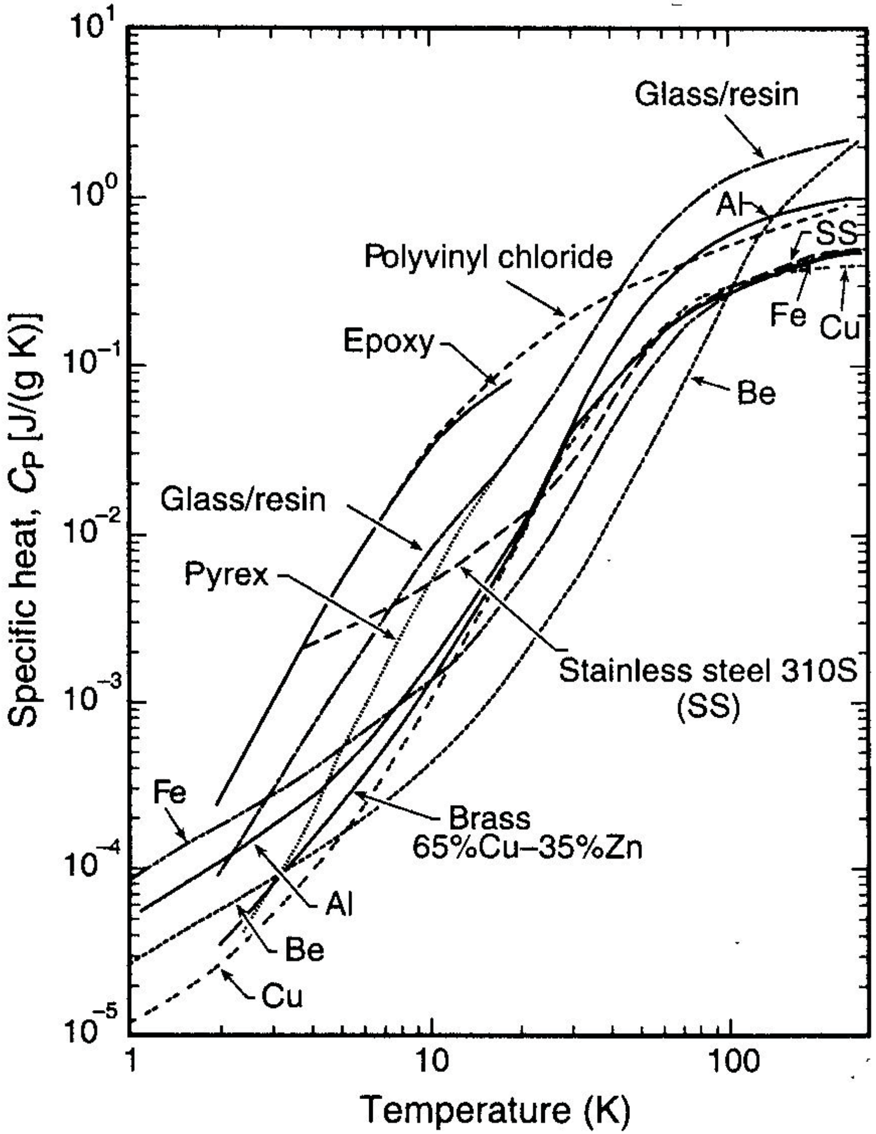
Specific heat (Heat capacity) defines amount of heat that has to be introduced /extracted to/from 1kg of material to increase/decrease material temperature by 1K

$$c = \frac{dU}{dT} = \frac{Q}{m \cdot \Delta T}$$

c – specific heat, J/(kg·K)
U – internal energy J/kg
Q – Heat, J
m – material mass, kg
T – temperature, K

In cryogenic the specific heat determines an apparatus cool – down time and cost

Specific heat [1]



Specific heat

- For T>77K – *c* decreases slowly while below 77K $c \sim T^3$
  - Systems cool down faster as they get colder
  - At cryogenic temperatures, small heat leaks may cause large temperature rises, what can cause sample temperature oscillation
  - Helium systems are often pre-cooldown with LN2 to 77K

Thermal expansion/contraction

Thermal constriction defines amount of length change due to temperature change

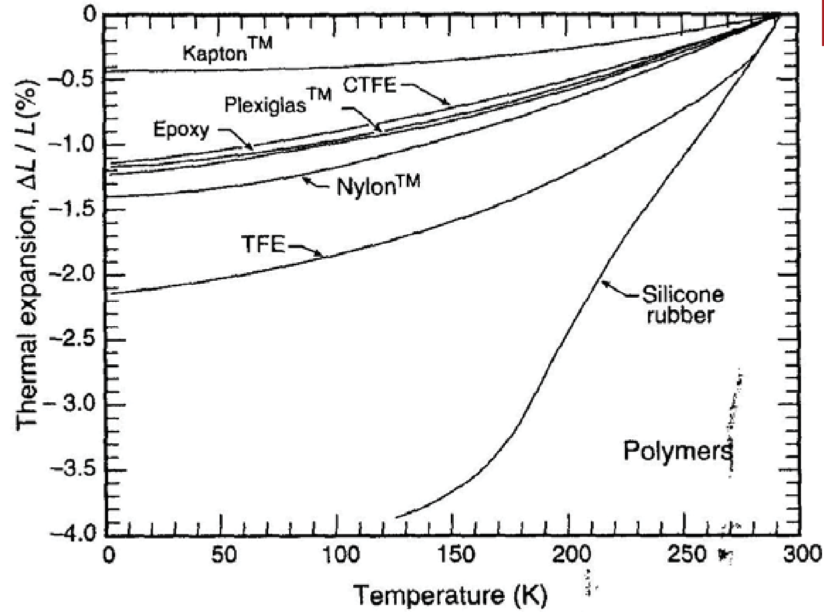
$$\alpha \equiv \frac{1}{L}\frac{dL}{dT}$$

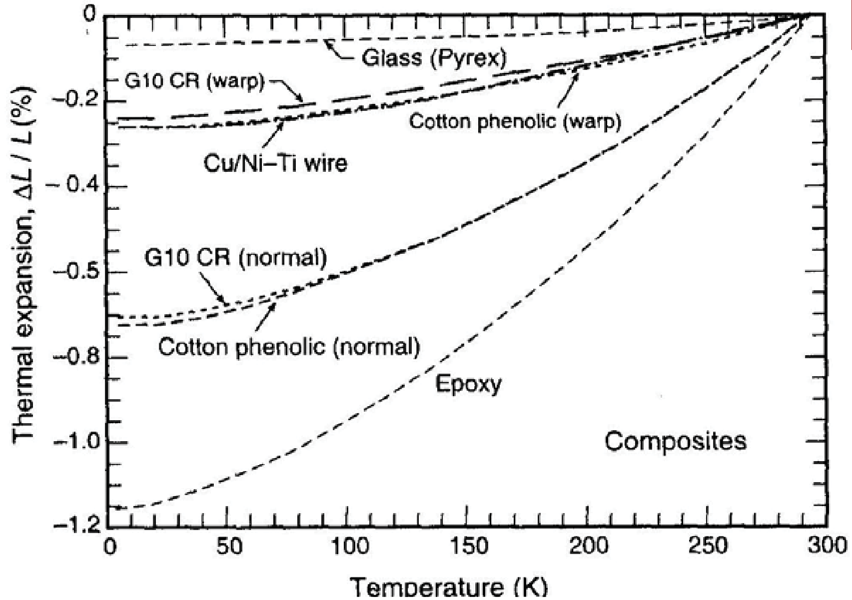
α – Thermal expansion coeeficient, 1/K
L – Lenght, m
T – Temperature, K

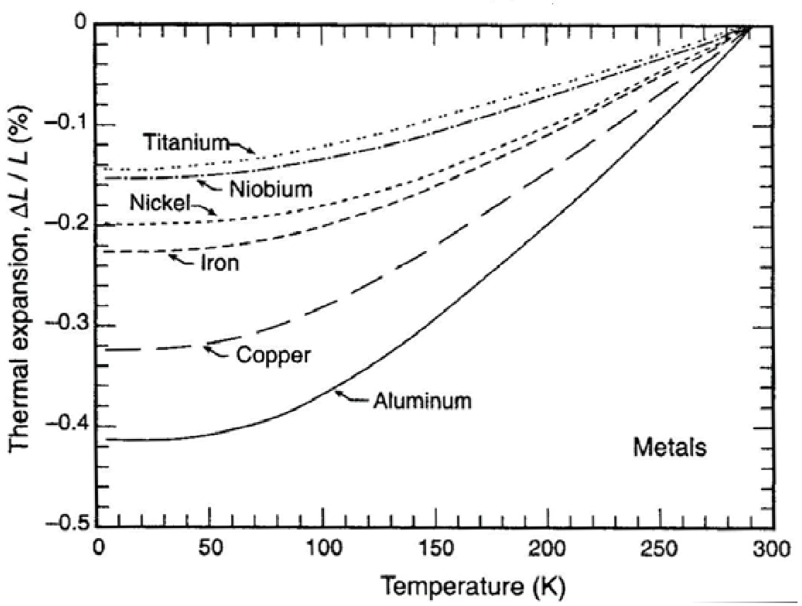
Due to thermal expansion coefficient in low temperatures is strong temperature depended a *total thermal linear expansion* $\Delta L/L$ become very useful for calculation purpose:

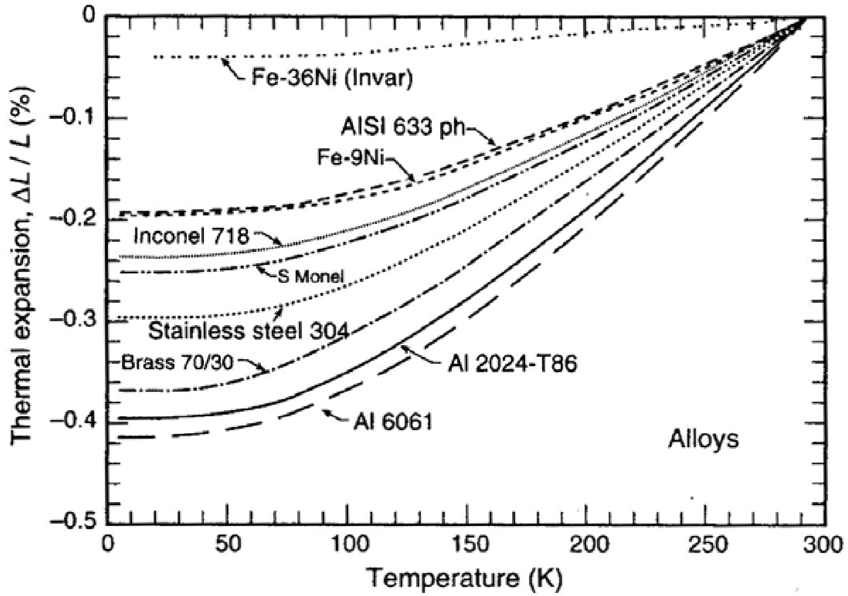
$$\frac{\Delta L}{L} \equiv \frac{L_T - L_{293}}{L_{293}}$$

Thermal expansion [1]









Thermal expansion/contraction

- When cryogenic apparatus elements are made of different material, after cool down the apparatus components can be strongly stressed. Therefore expansion elements, as compensation bellows, and special material shapes (U, Z) should be considered in apparatus design.

- Thermal expansion coefficient is strongly changed down to 50 K and after is almost temperature independent. Therefore if cryogenic apparatus survive LN2 cool-down process lower temperatures should be dangerous

- Direct tight connection of material with high and low thermal expansion, for example Stainless Steel and Pyrex Glass, should be avoided.

Electrical resistivity

- Electric charge is transported through metals by so call „free” electrons
- Parameters determine an electrical resistivity of metals are:
  - *N* – number of conduction electron per unit volume
  - *e* – charge carried by an electron
  - *m* – mass of an electron
  - *v* – av. velocity of the conduction electrons
  - *l* – av. distance (the mean free path) the electron travels before being scattered by atomic-lattice perturbation
- Only electron free path *l* is temperature depended

Electrical resistivity

- At high T electron free path *l* is dominated by electron scattering from thermal vibrations (photons) of the crystal lattice, so is strongly temperature-dependent
- At low T electron free path *l* is limited mainly by electron scattering off chemical and physical crystal lattice imperfections (impurities, vacancies, interstitials), so scattering at low T is temperature independent
- An indication of metal purity is realize by determination of a Residual Resistance Ratio: RRR = ρ(300 K)/ ρ(4.2K)

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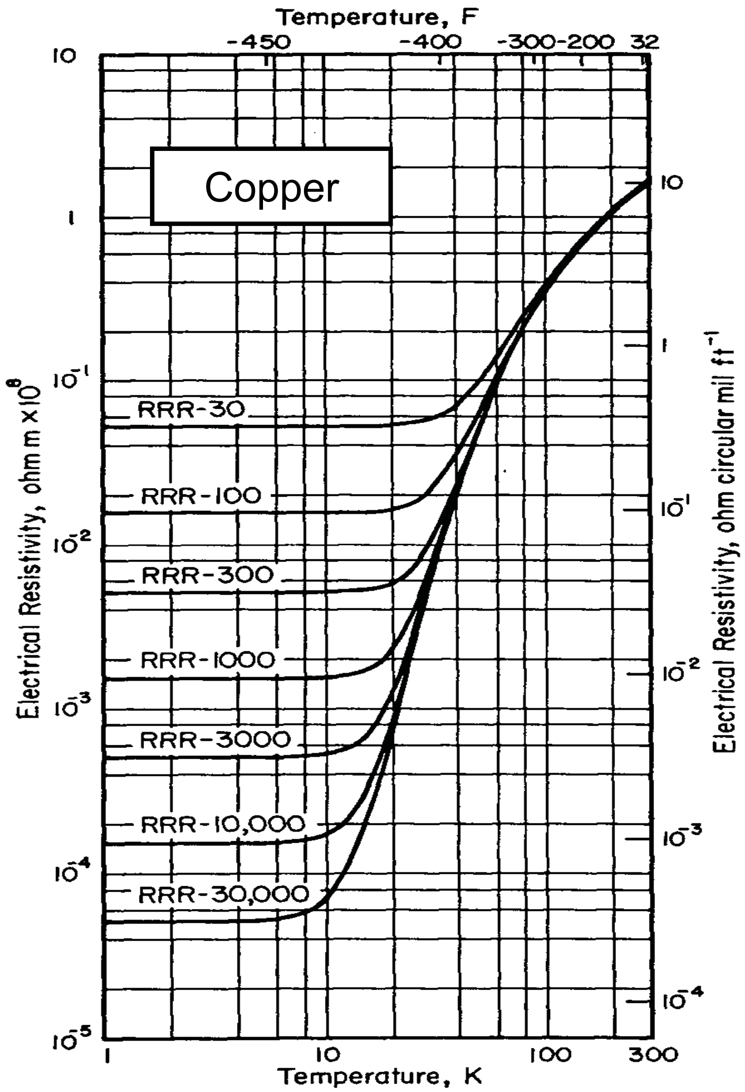
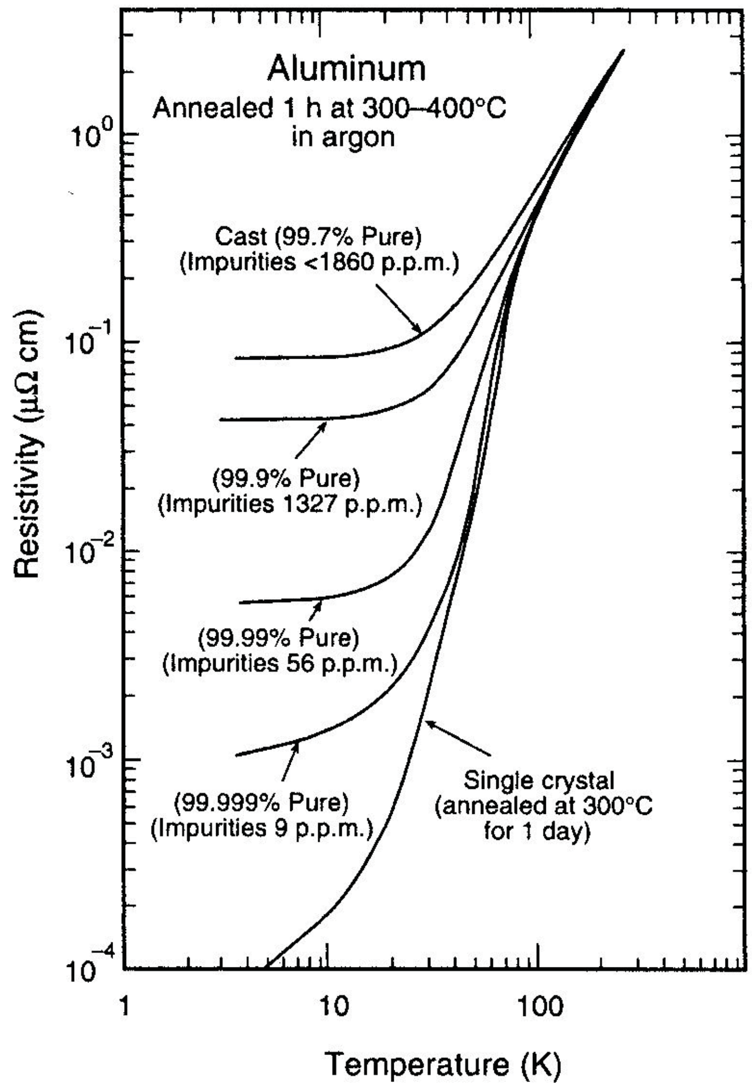
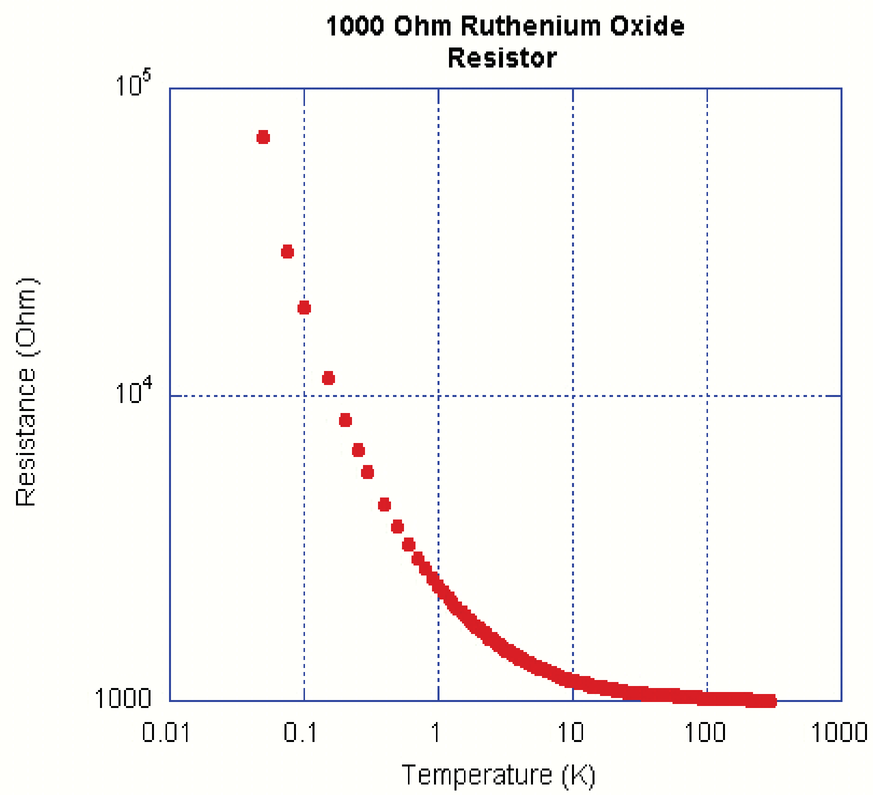
Electrical resistivity [1,2]





Electrical resistivity [3]

- Amorphous materials and semiconductors have very different resistivity characteristics than metals
- The resistivity of semiconductors is very non linear and typically **increases** with decreasing T due to fewer electrons in the conduction band
- Superconductivity – another lecture title



Thermal conduction

- Heat is transported through solid by electrons λ_e and phonons (lattice vibration) λ_p – $\lambda = \lambda_e + \lambda_p$
- In metals and alloys the electrons heat conduction is dominated - $\lambda_M = \lambda_e$
- In thermal insulator the photons heat conduction λ_p is dominated - $\lambda_I = \lambda_p$
- In semiconductors heat conduction is a mixture of photon and electron conduction - $\lambda_{SC} = \lambda_e + \lambda_p$

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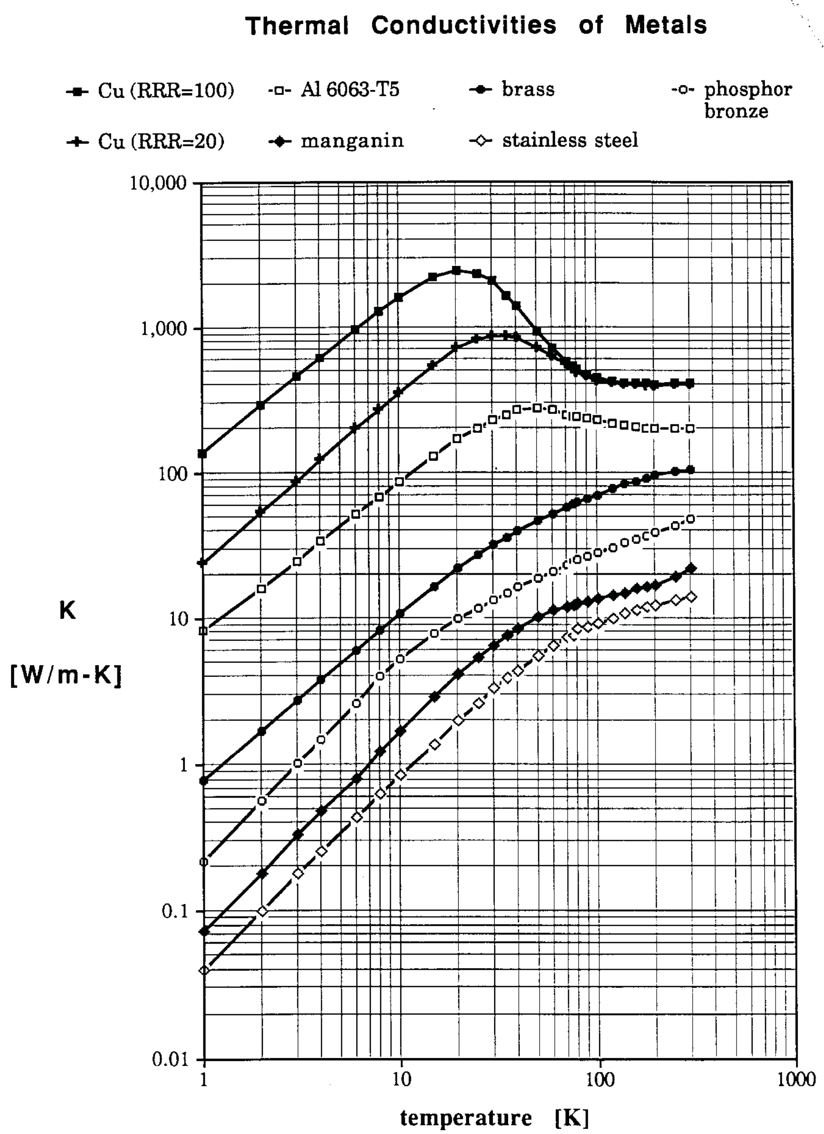
Thermal conduction [4]

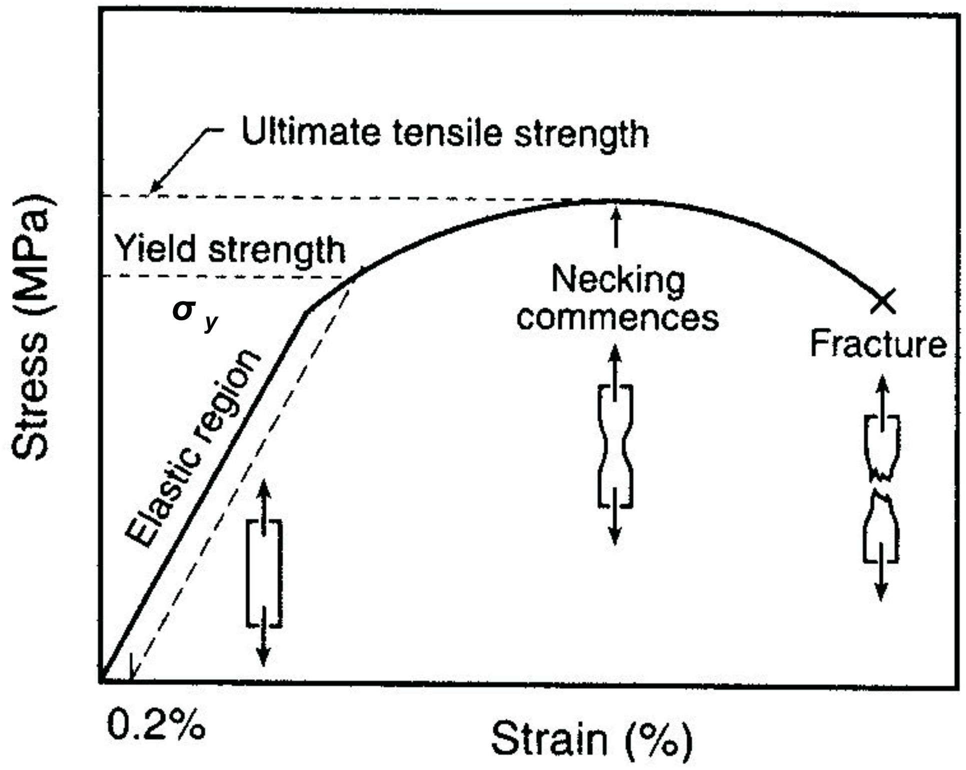


Mechanical properties

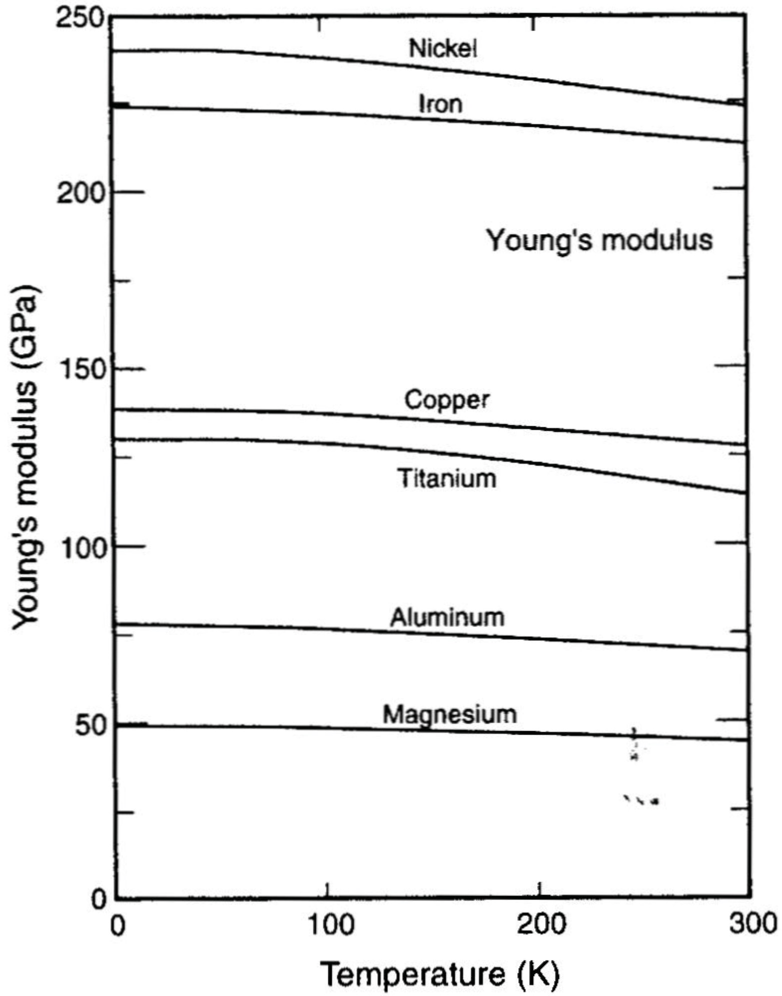
- Face-centered-cubic (f.c.c) crystal structure metals, such as: Stainless Steel (304, 310, 316); copper, aluminum, noble materials (Ag, Au) and alloys (brass), characterize very good mechanical properties at low and cryogenic temperatures
- Body-centered-cubic (b.c.c) metals, such as: chromium, iron, molybdenum and nickel steels, are strong at room temperature, but become brittle at low temperatures (below -50^{o}C)
- Hexagonal-close-packed (h.c.p.) metals, such as: beryllium, titanium and zinc, have mechanical properties between those of f.c.c. and b.c.c

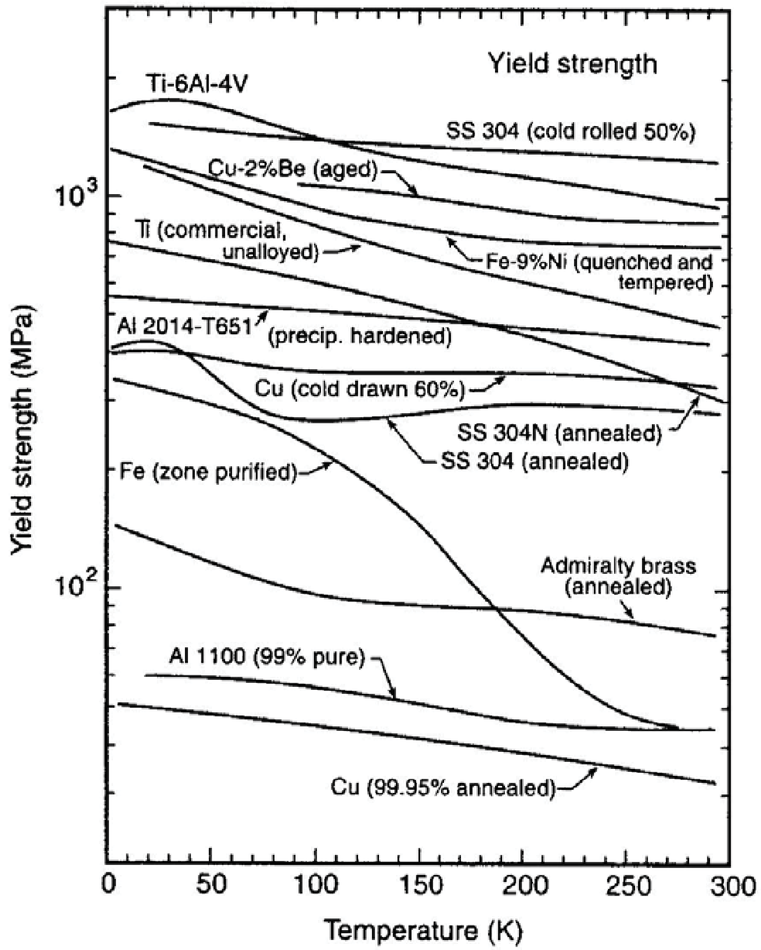
Mechanical properties [1]

- Stress $\sigma = F/A$
- Strain $\varepsilon = \Delta L/L$
- Young's (elastic) modulus $E = \sigma/\varepsilon$
- Yield strength σ_y – start of plastic deformation
- Ultimate tensile strength – commence of necking
- Fracture toughness – material break

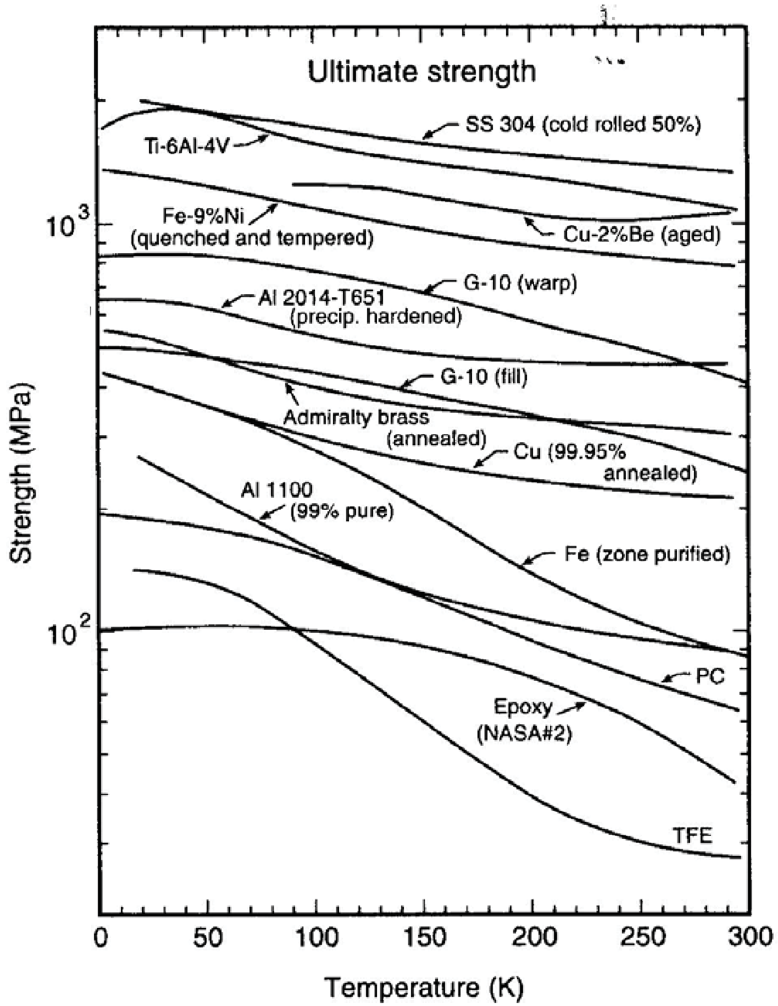


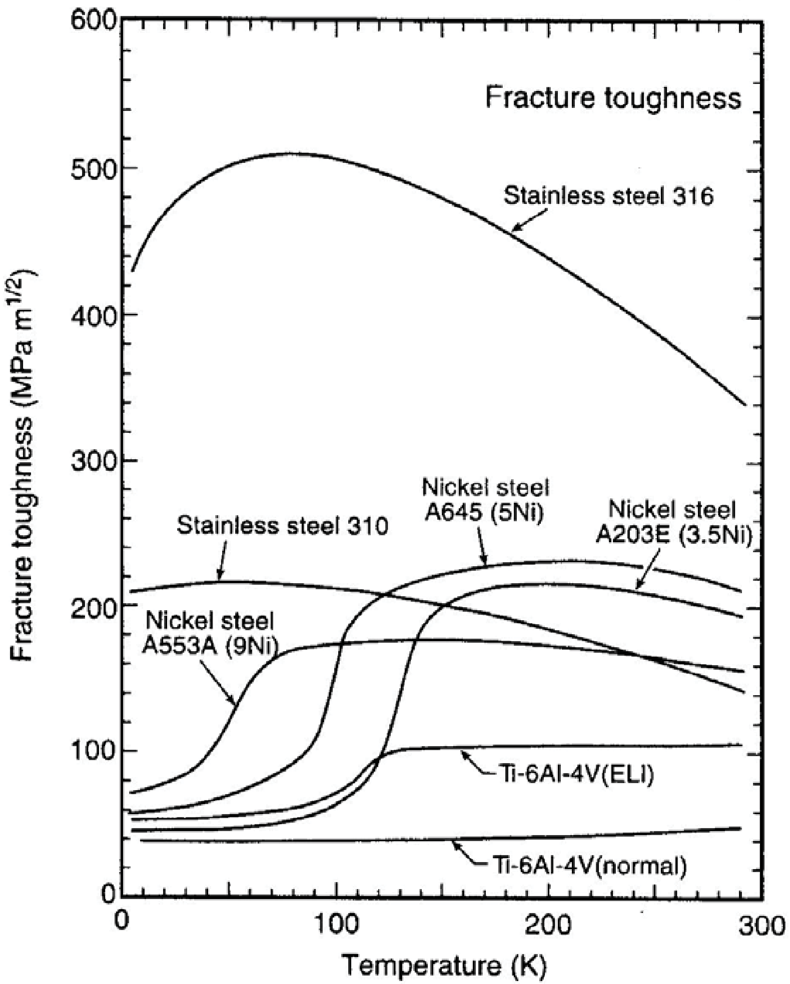
Mechanical properties [1]





Mechanical properties [1]





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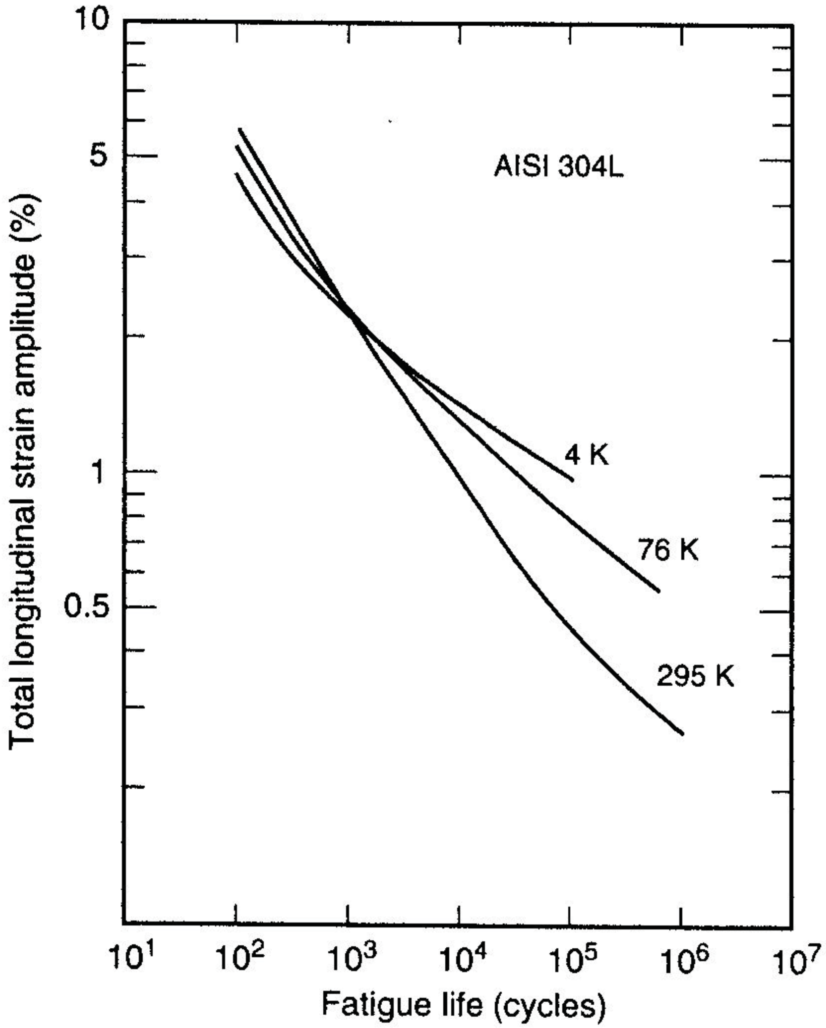
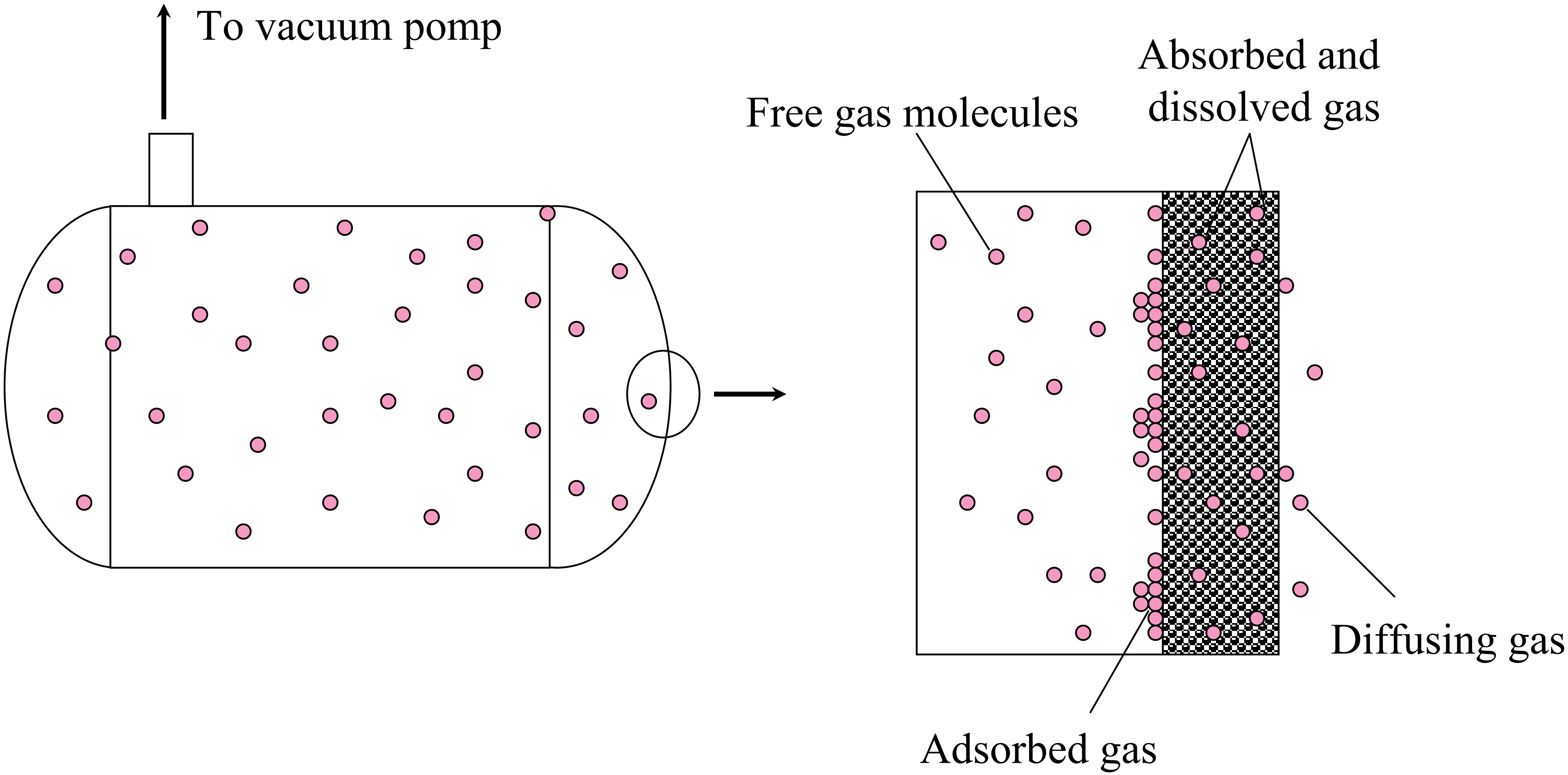
Mechanical properties [1]



Mechanical properties

- The most common construction materials are metals with face-centered-cubic (f.c.c) crystal structure
- Mechanical properties of f.c.c structure metals are improved with temperature decrease
- Usually mechanical calculation of low temperature elements are performed for room temperature values
- As the base of calculation the *Yield Strength* σ_y values are accounted

Vacuum properties



Vacuum properties - outgassing

Material	Condition	After 1 Hour ($x10^{-6}$)
Aluminum	degassed	0,17
Aluminum	none	1,3
Copper	_	2,3
Copper, 450 Deg,C	None	1,6
Copper, 450 Deg,C	degreased, pickled	0,26
Copper, 450 Deg,C	degreased	1,4
Silver	_	0,6
Steel, stainless	_	0,2
Steel, stainless	none	0,64
Steel, stainless	degreased	0,4
Steel, stainless	annealed	0,053
Mylar	outgassed	0,2
Silicone rubber	As received	30
Teflon	As received	5
Mylar	As received	3

Materials

Stainless Steel

- The most common used construction material in cryogenic engineering
- Good mechanical properties
- Relatively low thermal conductivity (the lowest form cryo metal construction materials)
- Low outgasing rate
- Relatively good welding properties
- Used for low therm conductivity parts (sample insulation, cryostat suports)

Stainless Steel

- 304
  - Good corrosion resistance
  - Good thermal resistance
  - Good low-temperature strength and mechanical properties
  - Good drawability such as Deep Drawing, Bending and does not harden during heat treatment
  - Non-magnetic
  - Can partially loss non-magnetic properties due to welding, heat treatment and cool down (austenite partially transforms to martensite ferromagnetic phase)
- 304L - low carbon 304 steel
  - Excellent resistance to inter-granular corrosion after welding and stress relieving
  - Corrosion resistant properties without heat treatment
- 304 LN
  - Strength and inter-granular corrosion resistance are improved by adding N (Nitrogen)
  - „more” non - magnetic

Stainless Steel

- 316
  - Excellent corrosion resistance
  - Good pitting corrosion resistance by adding Mo
  - Excellent drawing hardening (non-magnetic).
- 316 L – 316 Low carbon steel type
  - 316 steel properties plus excellent inter-granular corrosion resistance
- 321
  - By adding Ti, prevents intra-granular corrosion

Cooper

- Very high thermal conductivity
- High ductility
- High electrical conductivity
- High impact strength
- Diamagnetic
- Good creep resistance
- Ease of welding
- Difficult to connect with Stainless Steel (beam welding, brazing)

Cooper

- Oxygen-free high thermal conductivity (OFHC) – 99.99% Cu, RRR > 150
- Oxygen-Free Electronic (OFE) – 99.99%Cu, max 0.0005% O_2, RRR<80
- Oxygen-Free (OF) - 99.95% Cu, 0.001% O_2, RRR<40
- Electro Tough-Pitch (ETP) – minimum 99.9% Cu, 0.02% to 0.04% O_2, RRR<40

Cooper

- Used for high thermal conductivity parts
- Usually ETP copper is used
  - Readily available in different shapes (plates, rods, wire)
  - Relatively cheap (much cheaper then OF copper)
  - Easier to machine then OF
- If copper is subjected for hydrogen brazing OF copper should by used

Brass and Bronze

- Brass – mixture of copper and zinc
- Bronze – mixture of copper and tin

- Valve elements (bodies)
- Better mechanical properties than Cu
- Corrosion resist
- Low-friction properties
- Can be used in explosive environment (LH, LO)
- Large thermal conductivity
- Thermal contraction similar as Cu – used for fixing bolts in SS and Cu elements

Aluminum alloys

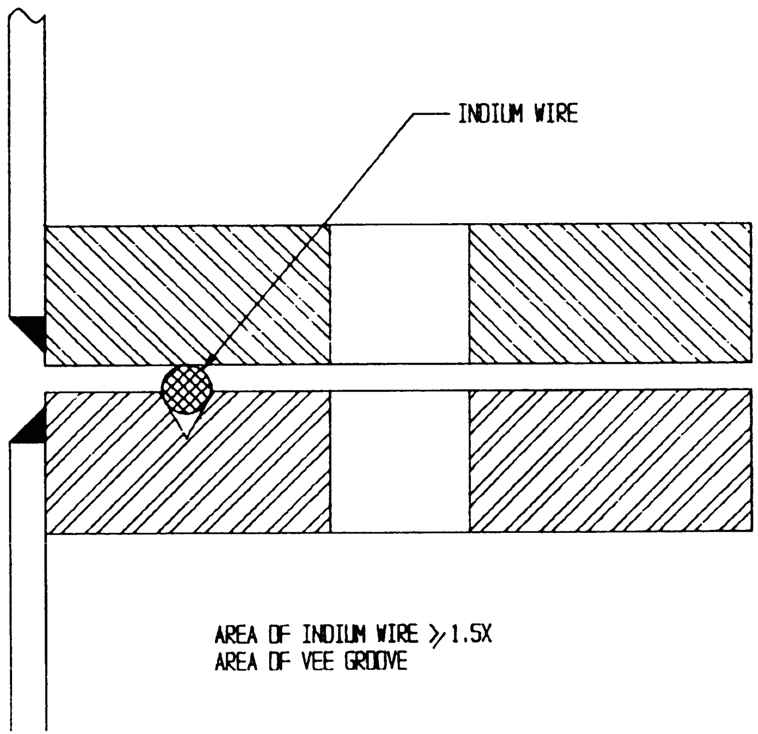
- Low density (one-third the weight of steel)
- The best mechanical strength to the mass ratio
- Relatively high thermal conductivity
- Low thermal emissivity (used to cover MLI reflective sheets)
- Used in many cryogenic applications :inner vessels, heat exchangers, thermal shields … (see next slide)

Aluminum alloys - cryogenic application [5]

- 1xxx (unalloyed) aluminum - Commercially pure aluminum (1100, with 99.00 percent minimum aluminum) and special versions of higher purity (e.g., 1350 conductor) are readily weldable, have high electrical conductivity, and exceptional corrosion/chemical resistance, but relatively low strength so are used for those applications where the former properties are paramount.
- 2xxx (Al-Cu) alloys - Certain members of the 2xxx series, notably 2219 and 2195, are readily welded and are stronger than the 1xxx, 3xxx, 5xxx, and 6xxx series, and so are used for critical applications like space tankage, and vehicles for transportation of cryogenic fluids.
- 3xxx (Al-Mn) alloys - Alloy 3003 has been quite widely used for heat exchangers in cryogenic service; it has higher strength than 1xxx varieties and is very readily brazed, welded, and soldered.
- 5xxx (Al-Mg) alloys - The 5xxx alloys offer an exceptional combination of strength, toughness, corrosion resistance, weldability, and economy of fabrication, and are the most widely used for critical arctic and cryogenic applications from tankage, bridges, chemical processing equipment. As a prime example, alloy 5083-O was the alloy selected for the 125-ft (45-m) spheres for shipboard transportation of liquified natural gas (LNG) around the world.
- 6xxx (Al-Mg-Si) alloys - Exceptional extrudibility combined with high strength, corrosion resistance, and weldability, has made the 6xxx alloys also among the favorites for arctic and cryogenic service, often in combination with 5xxx alloys. The ability to economically produce irregularly shaped extrusions with the metal placed where stresses are highest provides a major advantage of alloys like 6061 and 6063.
- 7xxx(Al-Zn) alloys - Familiar aircraft alloys like 7050, 7075, 7150, and 7475 have high strength, but are not weldable by commercial practices and generally exhibit a gradual decrease in toughness with decrease in temperature; the use of 7xxx alloys is generally discouraged, with weldable alloy 7005 being the principal exception.

Indium [4]

- Very soft
- Malleable
- Chemically similar to aluminum
- In cryogenic engineering used for solid materials sealing
  - After sealing disconnection indium have to be carefully removed form connected surface before reconnection



G10, G11

- Glass cloth laminate impregnated and cured with a non-brominated epoxy resin
- Thermal and electrical insulator
- High mechanical strength
- Easy to machine
- High helium diffusion coefficient
- Used for suspensions and supports. In superfluid helium systems is used for, so call, lambda plates

Example of lambda plate
NED cryostat

Special materials [6]

Vacuum greases

- Improve sealing with O-rings or other rubber seals at room temperature (over - 20°C)
- Relatively high thermal conductivity
- Low outgassing rate
- Low vapor pressure

- Some vacuum greases, as Apiezon N, are used to improve thermal contact between solid materials in vacuum
- Apiezon N , especially mixed with Cu powder, is very common used for temporary temperature sensor installation on solid surfaces in vacuum space

Special materials [7,8]

Stycast

- Versatile epoxy resin system for cryogenic use
- Electrically nonconductive
- Relatively high thermal conductivity
- Used for vacuum tight lead-throughs
- Alternative to Apiezon N grease when permanent sensor mounting is desired

Example of T sensor permanent attachment with Stycast

Special materials [9]

3M™ Scotch-Weld™ Epoxy Adhesive DP190

- Two components epoxy resin
- Relatively low thermal conductivity
- Used for vacuum tight lead-throughs
- Used for cold sealing where low heat transfer is desired

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