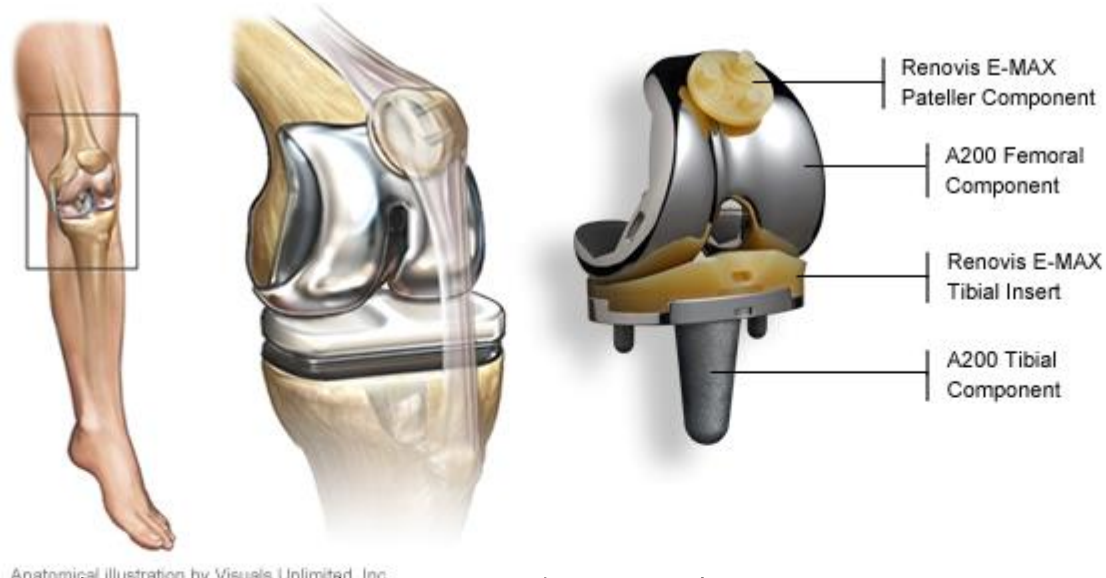
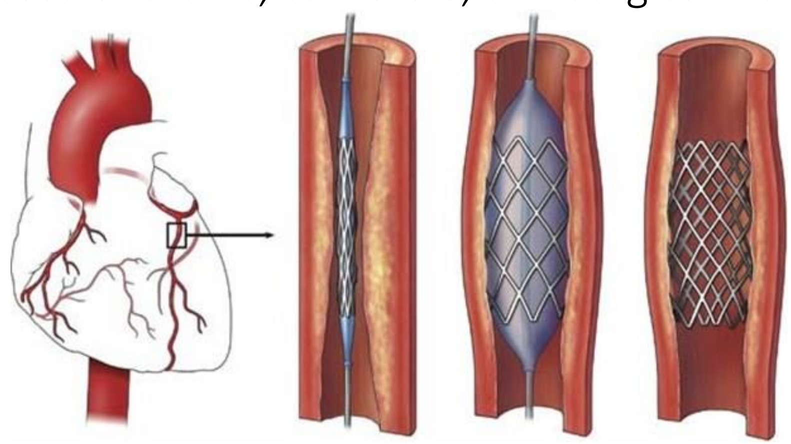
MME 4506 Biomaterials

Metallic Biomaterials

Most common orthopedic materials: 4/10 of all implant materials



Also used in cardiovascular stents, catheters, and surgical instruments

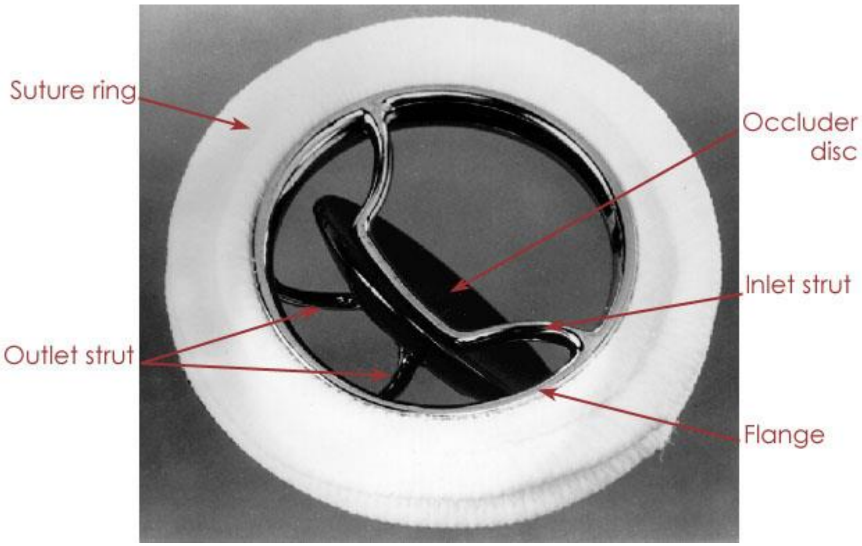


High tensile and fatigue strength, ease of processing

The market for metallic implants is estimated around 30 Billion $US

Critical properties in metallic biomaterials

Fatigue



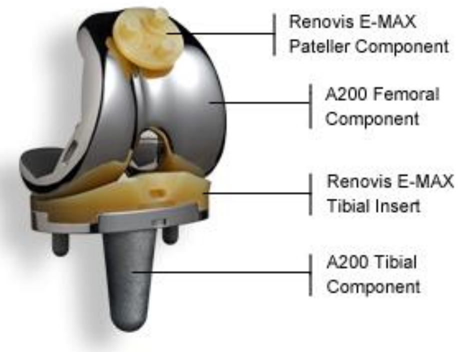
Cobalt alloy

Failed by fatigue fracture of the welds on the struts

Critical properties

Friction wear resistance

Interactions between articulating surfaces results in release of wear particles



Elevated Co and Cr concentrations in blood and urine are found for contacting metals in hip replacement cup

Decreased wear with increased femoral head because of increased fluid lubrication

Metals can be coated with ceramics, nitrided or diamond coated to improve wear resistance

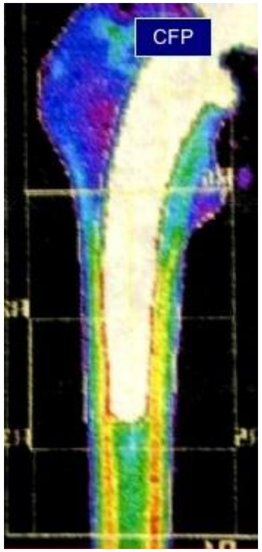
Highly reactive metals like titanium, aluminum and chromium form an impervious oxide layer on surface of the implant that protects the underlying materials (subject to fretting corrosion)

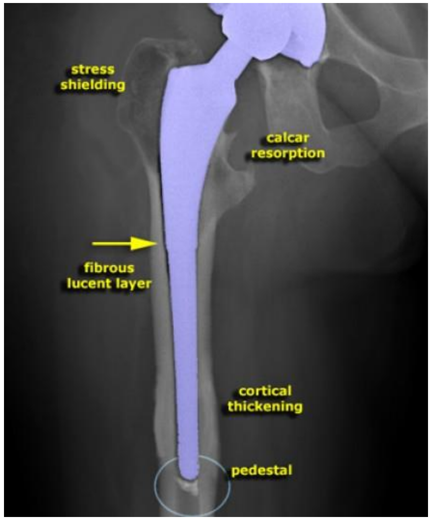
Critical properties

Elastic modulus

Stress shielding may occur in orthopedic applications if the modulus of the metal is much higher than that of bone

Cortical bone properties:	E= 5-23 GPa,	Strength= 164-240 MPa,	K_{1C}= 3-6 MPa/m^2
Stainless steel	189-205 GPa	170-310 MPa	50-200 MPa/m^2
Ti alloys	110-117 GPa	758-1117 MPa	55-115 MPa/m^2
Co-Cr alloys	230 GPa	450-1000 MPa	



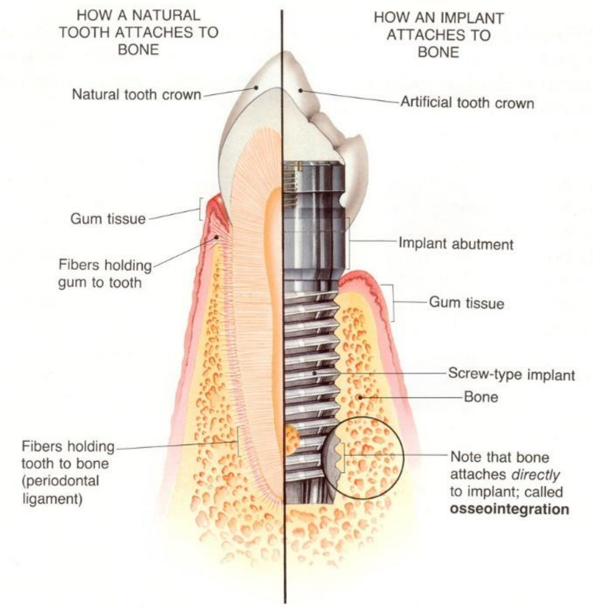


The more rigid the stem, the less load it transfers to the bone

Bone tissue resorbs as a result of remodeling due to lack of mechanical loading, leading to implant loosening

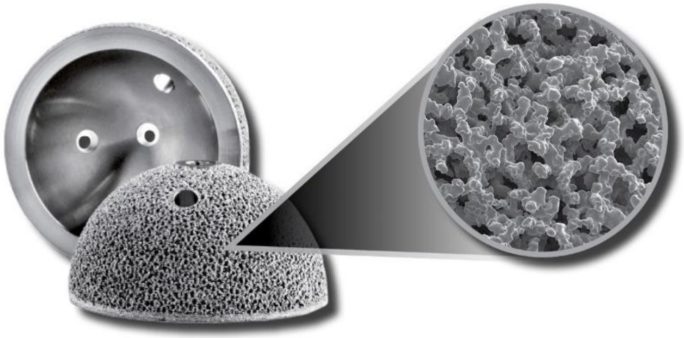
Critical properties
Surface roughness and porosity

Increase in surface roughness or addition of porosity increases osseointegration



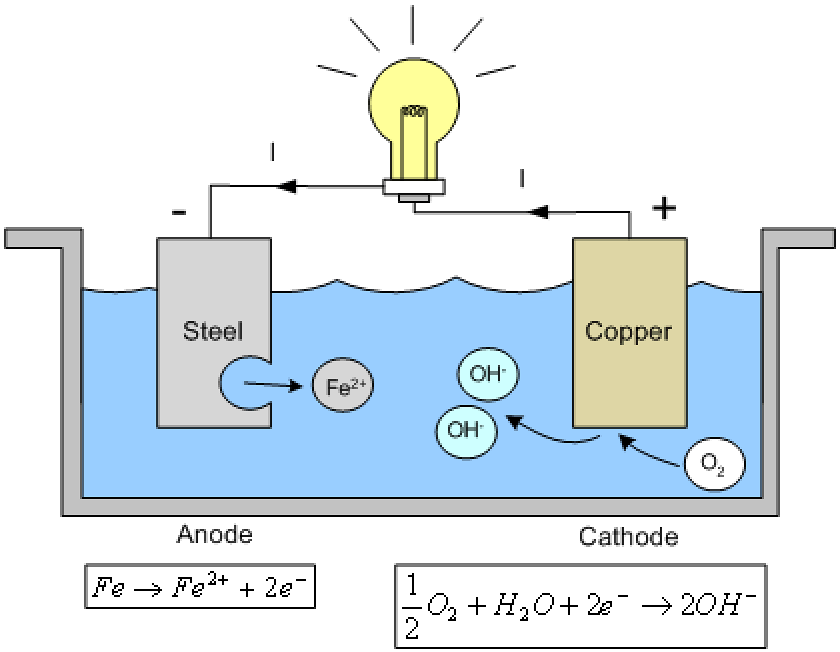
Surface roughness techniques for metals: High temperature sintering of alloy particles, plasma or flame spraying of metal powder onto the surface

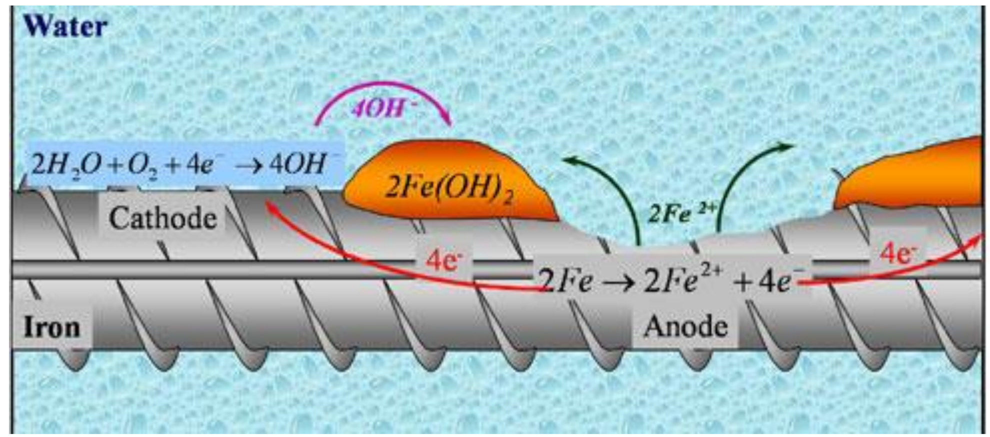
Metal fibers or porous ceramics can be used for porous layers



Critical properties

Corrosion resistance





The first metal alloy developed specifically for human use was vanadium steel for bone fracture plates and screws

It is no longer used in implants since its corrosion resistance is inadequate in vivo.

Most metals in the implants such as iron, chromium, cobalt, nickel, titanium, tantalum, molybdenum, and tungsten can be tolerated by the body in very small amounts

These implants can corrode in an in vivo environment so they are not biocompatible

The consequences of corrosion are the disintegration of the implant material and the harmful effect of corrosion products on the surrounding tissue

Stainless steels

The first stainless steel utilized for implant fabrication was 18-8 or type 302, which is stronger and more corrosion resistant than the vanadium steel

It was modified with a small percentage of molybdenum as 18-8sMo, to improve corrosion resistance in salt water. It is also known as 316 stainless steel

Later in the 1950s, the carbon content of 316 stainless steel was reduced from 0.08% to 0.03 for better corrosion resistance to chloride solution. Its classification number is 316L

ASTM recommends type 316L rather than 316 for implant fabrication

All types of stainless steels contain at least 11% chromium for effective corrosion resistance. They also contain significant amounts of Ni and Mo

TABLE 40.1 Compositions of 316L Stainless Steel

Element	Composition, %
Carbon	0.03 max
Manganese	2.00 max
Phosphorus[a]	0.03 max
Sulfur	0.03 max
Silicon	0.75 max
Chromium	17.00–20.00
Nickel	12.00–14.00
Molybdenum	2.00–4.00

TABLE 40.2 Mechanical Properties of 316L Stainless Steel for Implants

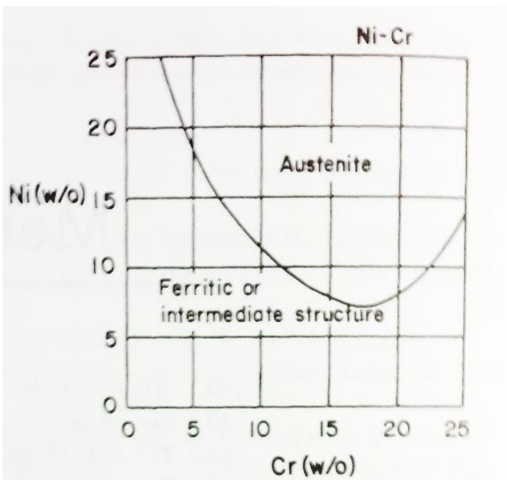
Condition	Ultimate Tensile Strength, min (MPa)	Yield Strength (0.2% offset), min (MPa)	Elongation 2-in (50.8 mm) min%	Rockwell Hard
Annealed	485	172	40	95 HRB
Cold-worked	860	690	12	—

Molybdenum improves resistance to pitting corrosion in salt water

Nickel stabilizes the austenite phase at room temperature and enhances corrosion resistance

The austenitic stainless steels are most widely used for implant fabrication. They offer better corrosion resistance than other types. They can only be hardened by cold working

The austenitic phase stability can be influenced by both the Ni and Cr contents



Even the 316L stainless steels may corrode in the body at highly stressed and oxygen-depleted regions such as the contacts under the screws of a fracture plate

Thus they are suitable to use only in temporary implants such as fracture plates and hip nails

CoCr alloys

There are two basic types:

- CoCrMo which is usually used for casting. Has been used for many decades in dentistry and recently for artificial joints
- CoNiCrMo alloy which is usually wrought by hot forging. It is used for making stems of prosthesis for heavily loaded joints such as knee and hip

There are also CoCrWNi and CoNiCrMoWFe wrought alloys that are less commonly used as implants

TABLE 40.3 Chemical Compositions of CoCr Alloys

	CoCrMo (F75)		CoCrWNi (F90)		CoNiCrMo (F562)		CoNiCrMoWFe (F563)	
Element	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
Cr	27.0	30.0	19.0	21.0	19.0	21.0	18.00	22.00
Mo	5.0	7.0	—	—	9.0	10.5	3.00	4.00
Ni	—	2.5	9.0	11.0	33.0	37.0	15.00	25.00
Fe	—	0.75	—	3.0	—	1.0	4.00	6.00
C	—	0.35	0.05	0.15	—	0.025	—	0.05
Si	—	1.00	—	1.00	—	0.15	—	0.50
Mn	—	1.00	—	2.00	—	0.15	—	1.00
W	—	—	14.0	16.0	—	—	3.00	4.00
P	—	—	—	—	—	0.015	—	—
S	—	—	—	—	—	0.010	—	0.010
Ti	—	—	—	—	—	1.0	0.50	3.50
Co			Balance					

The two basic elements of the CoCr alloys form a solid solution of up to 65% Co

Mo is added to produce finer grains which result in higher strength after casting or forging

Advantages of CoNiCrMo

- Highly corrosion resistant to seawater under stress
- Cold working can increase the strength considerably but requires high stresses
- Superior fatigue and tensile strength

Disadvantages

- Large implants such as hip joint stems can only be made by hot-forging
- Poor frictional properties with itself and other metals

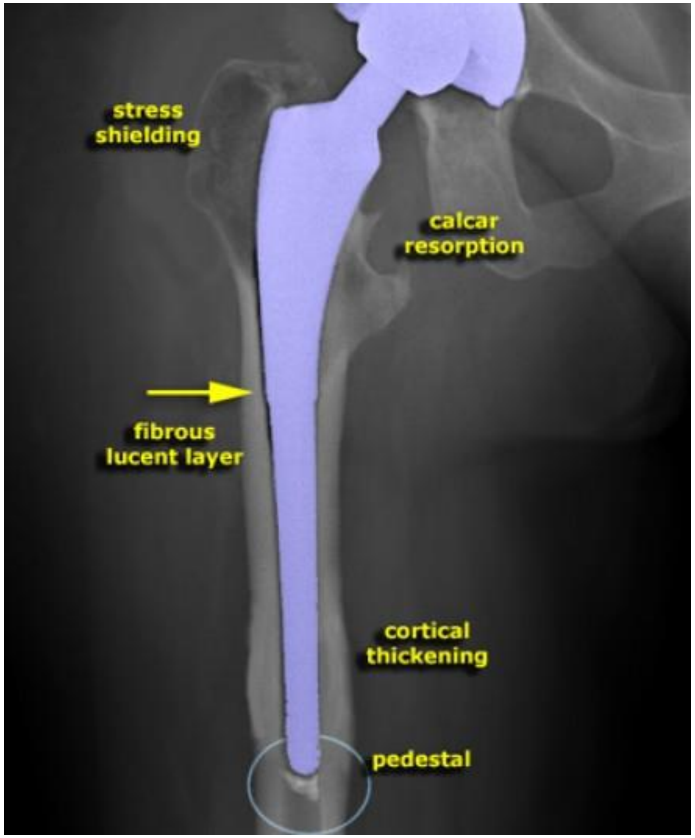
Overall the wrought CoNiCrMo alloy is suitable for applications that require long service life without fracture or stress fatigue such as stems of hip joint prosthesis

The modulus of elasticity for the CoCr alloys do not change much with the composition. It is between 220-234 GPa which is higher than other metals such as stainless steels

This may result in different load transfer modes to the bone in artificial joint replacements due to the stress shielding effect

TABLE 40.4 Mechanical Property Requirements of CoCr Alloys

Property	Cast CoCrMo (F75)	Wrought CoCrWNi (F90)	Wrought CoNiCrMo (F562) Solution Annealed	Wrought CoNiCrMo (F562) Cold Worked and Aged
Tensile strength, MPa	655	860	793–1000	1793 min
Yield strength (0.2% offset), MPa	450	310	240–655	1585
Elongation, %	8	10	50.0	8.0
Reduction of area, %	8		65.0	35.0
Fatigue strength, MPa*	310			



Titainium and its alloys

The first titanium implant was used in cat femurs in late 1930s

Titanium's lightness and good mechanochemical properties make it suitable for implants

Metal	Density
Titanium	4.5
316 stainless steel	7.9
CoCrMo	8.3
CoNiCrMo	9.2

It derives its resistance to corrosion by the formation of a solid oxide layer. Under in vivo conditions TiO_2 layer forms a thin adherent film and passivates the material

There are four grades of commercially pure titanium for implant applications
Oxygen has a great influence on the ductility and strength

TABLE 40.5 Chemical Compositions of Titanium and Its Alloy

Element	Grade 1	Grade 2	Grade 3	Grade 4	Ti6Al4V*
Nitrogen	0.03	0.03	0.05	0.05	0.05
Carbon	0.10	0.10	0.10	0.10	0.08
Hydrogen	0.015	0.015	0.015	0.015	0.0125
Iron	0.20	0.30	0.30	0.50	0.25
Oxygen	0.18	0.25	0.35	0.40	0.13
Titanium			balance		

Titanium is an allotropic material which exists as hcp α-Ti up to 882 C and bcc β-Ti above that temperature

Addition of alloying elements enables it to have a wide range of properties:

- Aluminum stabilizes the α -phase
- Vanadium stabilizes the β -phase

The α -alloys have single phase microstructure which promotes weldability
High Al alloys of Ti also have high strength and oxidation resistance at high temperatures

The precipitates of the β -phase are formed below the transformation temperature when vanadium is present. These alloys can be heat treated for strengthening and give the highest strength of Ti alloys

Higher V amount (13% in Ti13V11Cr3Al) results in a microstructure that consists of β only

Another Ti alloy (Ti13Nb13Zr) results in martensite structure which shows high corrosion resistance and low modulus

TABLE 40.6 Mechanical Properties of Ti and Its Alloys

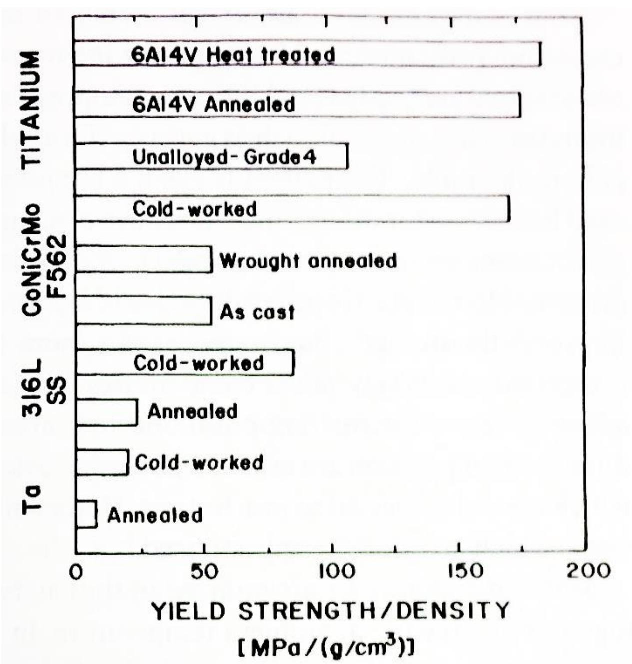
Properties	Grade 1	Grade 2	Grade 3	Grade 4	Ti6Al4V	Ti13Nb13Zr
Tensile strength, MPa	240	345	450	550	860	1030
Yield strength (0.2% offset), MPa	170	275	380	485	795	900
Elongation, %	24	20	18	15	10	15
Reduction of area, %	30	30	30	25	25	45

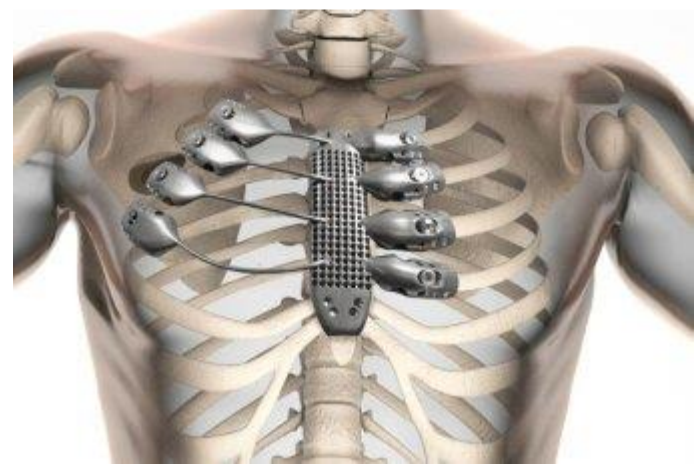
In general higher alloying content in Ti leads to higher strength and lower ductility

Their strengths vary from a value much lower than that of 316 SS or the CoCr to a value equal that of cast CoCrMo alloy

However titanium alloys are superior to other alloys used in implant production in terms of specific strength

The shear strength and friction wear resistance of Ti alloys are low which prevent its use in bone screws, plates and similar applications under shear stress



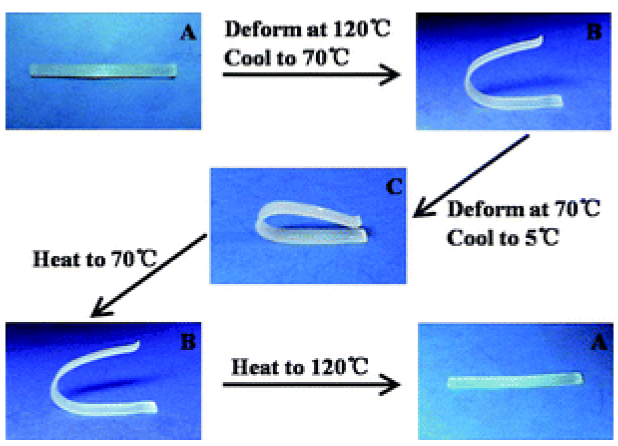


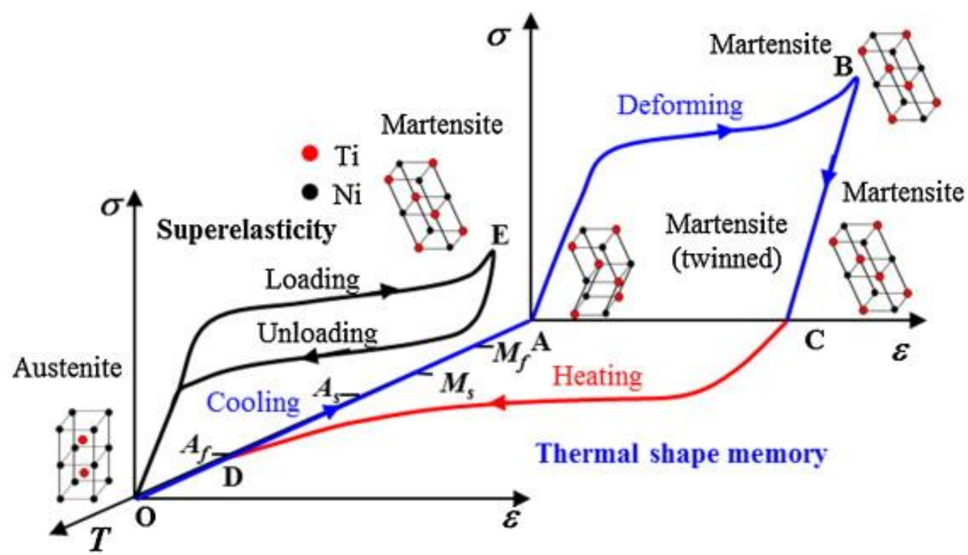
Exotic Titanium alloys

Ti-Ni alloy has shape memory effect which enables it to snap back to its previous shape when deformed prior to a heat treatment

Especially 1:1 atomic ratio Ti-Ni alloy reverts back to its original shape as the temperature is raised, if it is plastically deformed below the transformation temperature (480-510 C)

This shape memory effect is generally related to a diffusionless martensitic phase transformation which is thermoelastic in nature





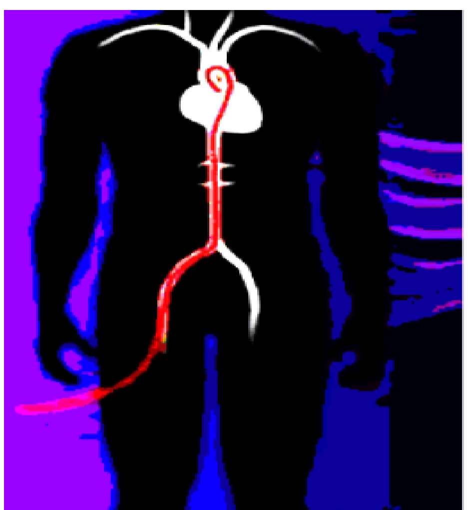
Applications of these alloys are orthodontic dental archwires, intercranial aunerysm clips, vascular filters, contractile artificial muscles and orthopedic implants

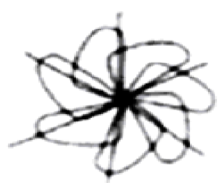
55-Nitinol (55 wt% or 50 at% Ni) has a single phase and mechanical memory, acoustic damping, thermomechanical conversion, good fatigue and ductility properties

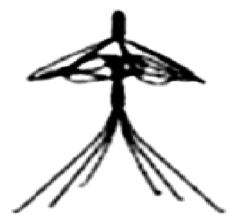
Shape recovery capability decreases and precipitation strengthening capability increases rapidly as the Ni content is increased to 60%

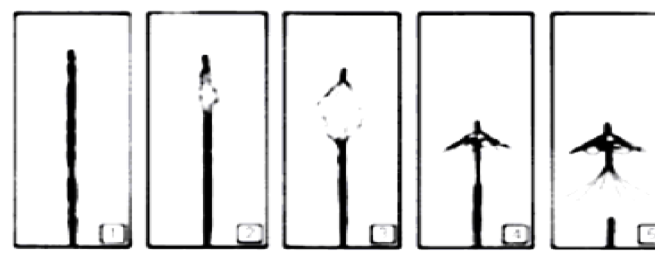
Both 55- and 60-Nitinol have low modulus of elasticity and are tougher than stainless steel, NiCr, or CoCr alloys

NiTi alloys also have good biocompatibility and corrosion resistance in vivo









Dental metals

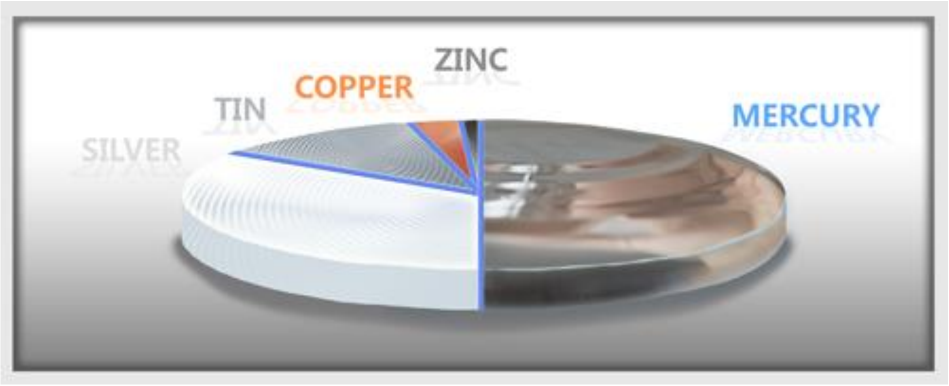
Amalgam is an alloy made of liquid mercury and other solid metal particulate alloy made of silver, tin, copper

The solid alloy is mixed with liquid mercury in a mechanical mixer and the resulting material is packed into the tooth cavity

A solid alloy composed of 65% Ag, 29% Sn, 6% Cu, 2% Zn, 3% Hg reacts with liquid Hg accordingly:

Alloy + Hg (l) = $Ag_3Sn + Ag_2Hg_3 + Sn_7Hg$

Fully set in about one day, the final composition of dental amalgam typically contains 45-55% Hg, 35-45% Ag, 15% Sn



Gold and its alloys are useful in dentistry because of their durability, stability and corrosion resistance

Gold alloys have superior mechanical properties than those of pure gold. They are used for cast restorations

Corrosion resistance of gold alloys are good if they contain >75% gold and other noble metals

Copper alloying significantly increases the strength of gold

Platinum alloying also improves strength but the melting temperature of the alloy increases excessively above 4% Pt

Small amount of Zinc is useful to lower the melting temperature and as a flux to remove oxides

Softer gold alloys containing >83% gold are used for inlays in tooth cavities which are not subjected to high stresses

Other metals subjected to specialized implant applications are:

Tantalum – Biocompatible but poor mechanical properties (Tensile strength 207<>517 MPa, E Modulus = 190 GPa, Elongation < 30%) and high density (16.6 g/cc)

Only applications are wire sutures and radioisotope for bladder tumors

Platinum – Pt and other noble metals in the platinum group are very resistant to corrosion but have poor mechanical properties

Only application is electrodes such as pacemaker tips

Ni-Cu alloys – 70-30% alloy has thermoseed property. They provide a continuous heat source through resistive heating of the material, upon application of an alternating magnetic field

Used in hyperthermia therapy