# 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** Friction wear resistance

Interactions between articulating surfaces results in release of wear particles





During the lifetime of the implant wear debris is produced, which can induce osteolysis (active resorption of bone matrix by osteoclasts), a major cause of orthopaedic-implant aseptic loosening

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

Decreased wear with increased femoral head diameter 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 oxide layer on surface of the implant that protects the underlying materials (subject to fretting corrosion)

This is also achieved by coating the metal implant with oxides



## **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,

 Stainless steel
 189-205 GPa
 170-310 MPa

 Ti alloys
 110-117 GPa
 758-1117 MPa

 Co-Cr alloys
 230 GPa
 450-1000 MPa

K<sub>1C</sub>= 3-6 MPa/m<sup>2</sup> 50-200 MPa/m<sup>2</sup> 55-115 MPa/m<sup>2</sup>





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

The reaction of the metallic ions that leaches away from the implant due to corrosion in the human body affects several biological parameters

- As a material starts to corrode, the dissolution of metal will lead to erosion which in turn will eventually lead to brittleness and fracture of the implant
- Once the material fractures, corrosion gets accelerated due to increase in the amount of exposed surface area and loss of protective oxide layer
- If the metal fragments are not surgically extracted, further dissolution and fragmentation can occur, which may result in inflammation of the surrounding tissues

The release of corrosion products will obviously lead to adverse biological reactions in the body

Increased concentrations of corroded particles in the tissue near the implants and other parts of the human body such as kidney, liver etc. have been reported

<b>Biomaterial Metals</b>	Effect of Corrosion
Nickel	Affects skin - such as dermatitis
Cobalt	Anemia B inhibiting iron from being absorbed into the blood stream
Chromium	Ulcers and Central nervous system disturbances
Aluminum	Epileptic effects and Alzheimer's disease
Vanadium	Toxic in the elementary state

#### Effects of Corrosion in Human Body Due to Various Biomaterial

[Ref: Aksakal B, Yildirim ÖS, Gul H. Metallurgical failure analysis of various implant materials used in orthopedic applications. J Fail Anal Prevent 2004; 4(3): p. 17].

Corrosion is of great concern when a metallic implant is placed in the hostile electrolytic environment of the human body

The implants face severe corrosive environment which includes blood and other constituents of the body fluid containing several constituents like water, sodium, chloride, proteins, plasma, amino acids The aqueous medium in the human body consists of various anions such as chloride, phosphate, and bicarbonate ions, cations like Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> etc., organic substances of low-molecular-weight species as well as relatively highmolecular-weight polymeric components, and dissolved oxygen

The biological molecules upset the equilibrium of the corrosion reactions of the implant by consuming the products due to anodic or cathodic reaction.

e.g. Proteins can bind themselves to metal ions and transport them away from the implant surface. Adsorbed proteins absorbed also reduce the diffusion of oxygen at certain regions of the surface and cause preferential corrosion at those sites

In addition, the presence of bacteria enhances corrosion by absorbing the hydrogen present in the vicinity of the implant because hydrogen formed by cathodic reactions normally acts as a corrosion inhibitor

Although the pH value of the human body is normally maintained at 7.0, this value changes from 3 to 9 due to several causes such as accidents, imbalance in the biological system due to diseases, infections and other factors and after surgery the pH value near the implant varies typically from 5.3 to 5.6.

It has been well accepted that the tolerable corrosion rate for metallic implant systems should be about  $2.5 \times 10^{-4}$  mm/yr

The two physical characteristics which determine implant corrosion are 1) thermodynamic forces which cause corrosion either by oxidation or reduction reaction

2) the kinetic barrier such as surface oxide layer

Surface oxide film formed on metallic material plays an important role as an inhibitor for the release of metallic ions and the behavior of the surface oxide changes with the release of ions.

Further, the composition of the surface oxide film changes according to reactions between the surfaces of metallic materials and living tissues. Even low concentration of dissolved oxygen, inorganic ions, proteins, and cells may accelerate the metal ion release.

	Type of Corrosion	Material	Implant Location	Shape of the Implant
	Pitting	304 SS, Cobalt based alloy	Orthopedic/ Dental alloy	
	Crevice	316 L stainless steel	Bone plates and serews	
	Stress Corrosion cracking	C0CrMo, 316 LSS	Only in in vitro	
	Corrosion fatigue	316 SS, CoCrNiFe	Bone cement	
	Fretting	Ti6Al4V, CoCrSS	Ball Joints	Ball inserted
,	Galvanie	304SS/316SS, CoCr+Ti6Al4V, 316SS/Ti6Al4V Or CoCrMo	Oral Implants Skrews and nuts	
-	Selective Leaching	Mercury from gold	Oral implants	

Types of Corrosion in the Conventional Materials Used for Biomaterial Implants

[Ref: Blackwood DJ. Biomaterials: past successes and future problems. Corrosion Rev 2003; 21(2-3): pp. 97-124.]

## The oxide film which inhibits the dissolution of metal ions is not always stable in the human body

It can easily be destroyed and takes time to regenerate on the surface

Metallic BiomaterialSurface OxidesSurface Analysis		Surface Analysis			
Titanium(Ti)	Ti <sup>0+</sup> , Ti <sup>2+</sup> , Ti <sup>3+</sup> , Ti <sup>4+</sup>	<ul> <li>Ti<sup>2+</sup> oxide thermodynamically less favorable than Ti<sup>3+</sup> formation at the surface.</li> <li>Ti<sup>2+</sup> and Ti<sup>3+</sup> oxidation process proceeds to the uppermost part of the surface film and Ti<sup>4+</sup>observed on the surface outer most layer.</li> </ul>			
Titanium alloys Short	regeneration time (10	hrs)			
Ti-6Al-4V	TiO <sub>2</sub>	Surface consists of small amount of Al <sub>2</sub> O <sub>3</sub> , hydroxyl groups, and bound water and the alloying element Vanadium was not detected			
Ni-Ti	TiO <sub>2</sub> -based oxide	Minimal amounts of nickel in both oxide and metal states			
Ti-56Ni	TiO <sub>2</sub>	Very low concentrations of metallic nickel, NiO, hydroxyl groups and bound water on the surface were detected.			
Ti-Zr Titanium and Zirco oxides		Titanium and zirconium are uniformly distributed along the depth direction. The thickness of the oxide film increases with increase in zirconium content.			
Stainless steel Long	regeneration time (35	hrs)			
Austenitic stainless steel	Iron and chromium	Only very less amount of molybdenum was observed on the surface and nickel was absent when tested in both the air and in chloride solutions.			
316L	Oxides of Iron, chromium, nickel, molybdenum and manganese(thickness about 3.6 nm)	The surface film contains a large amount of OH, that is, the oxide is hydrated or oxyhydroxide. Iron is enriched in the surface oxide film and nickel, molybdenum, and manganese are enriched in the alloy substrate just under the surface oxide film.			
Co-Cr-Mo alloy Co-36.7Cr-4.6Mo	Oxides of cobalt and chromium without molybdenum(thickness 2.5 nm)	Surface contains large amount of OH <sup>-</sup> , that is the oxide is hydrated or oxyhydroxidized. Chromium and molybdenum distributed more at the inner layer of the film.			

#### Analysis of the Surface Oxide Film on Various Metallic Biomaterials

*In vitro* corrosion studies on orthopaedic biomaterials are carried out either in Hank's solution or Ringer's solution whose constituents are given in tables whereas the corrosion resistance for dental materials is evaluated using synthetic saliva

Composition	of Hank's	Solution
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Substance	Composition (g L <sup>-1</sup> )	
NaCl	8.0	
KCl	0.4	
NaHCO <sub>3</sub>	0.35	
NaH <sub>2</sub> PO <sub>4</sub> .H <sub>2</sub> O	0.25	
Na <sub>2</sub> HPO <sub>4</sub> .2H <sub>2</sub> O	0.06	
CaCl <sub>2</sub> .2H2O	0.19	
MgCl2	0.19	
MgSO <sub>4</sub> .7H2O	0.06	
glucose	1.0	
рН	6.9	

[Ref: Bundy KJ. Corrosion and other electrochemical aspects of biomaterials. Crit Rev Biomed Eng 1994; 22: pp. 139-251].

#### **Composition of Ringer's Solution**

Substance	Composition (g L <sup>-1</sup> )
NaCl	8.69
KCl	0.30
CaCl <sub>2</sub>	0.48
рН	6.4

[Ref: Gonzalez EG, Mirza-Rosca JC. Study of the corrosion behavior of titanium and some of its alloys for biomedical and dental implant applications. J Electroanal Chem 1999; 47. 1997

#### Blood plasma Ringer's

Na <sup>+</sup>	140 mM	130 mM
K+	4 mM	4 mM
CI-	103 mM	109 mM
Ca <sup>+</sup>	2 mM	2 mM
lactate	5 mM	28 mM

<b>Composition of Different A</b>	rtificial Saliva
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	Artificial Saliva			
Components	Xialine1 (g L <sup>-1</sup> )	Xialine2 (g L <sup>-1</sup> )	Saliveze (gL <sup>-1</sup> )	
Xanthan gum	0.92	0.18	-	
Sodium carboxymethylcellulose	-	-	10	
Potassium chloride	1.2	1.2	0.62	
Sodium chloride	0.85	0.85	0.87	
Magnesium chloride	0.05	0.05	0.06	
Calcium chloride	0.13	0.13	0.17	
Di-potassium hydrogen orthophosphate	0.13	0.13	0.80	
Potassium di-hydrogen orthophosphate		-	0.30	
Sodium fluoride	-	-	0.0044	
Sorbitol	Ξ.	-	29.95	
Methyl p-hydroxybenzoate	0.35	0.35	1.00	
pH	Neutral	Neutral	Neutral	

[Ref: Preetha A, Banerjee R. Comparison of artificial saliva substitutes. Trends Biomater Artif Organs 2005; 18(2): pp. 178-186].

When the surface oxide film of a metallic material is disrupted, corrosion proceeds and metal ions are released continuously unless the film is regenerated The interactions between the physiological medium and the material play a decisive role on the reformation of the oxide layer and the time taken

Calcium and phosphate ions are preferentially filled up during regeneration of surface oxide film on pure titanium and the film consists of titanium oxide, titanium oxyhydroxide, titanium phosphate and calcium phosphate

Calcium phosphate was also observed on the surface of Ti-6Al-4V oxide film regenerated in Hanks' solution Only titanium phosphate without calcium is formed on Ti-56Ni, Ti-Zr and Zr based biomaterials

The stability of the surface oxide layer in 316L SS as well as in Ni-Ti is not very high and the possibility of metal ions being released is greater when compared to conventional alloys such as Co-Cr and Ti-6Al-4V

Hence, in general a coating on the implants is preferable as it will reduce the corrosion rate and also improve bioactivity by providing adsorption sites for calcium and phosphates

## **Critical properties in metallic biomaterials** Fatigue



Cobalt alloy Failed by fatigue fracture of the welds on the struts

## 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 Presence of less carbon decreases the chance of forming chromium carbide that generally results in intergranular corrosion 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, %	<b>TABLE 40.2</b> Mechanical Properties of 316L Stainless Steel for Implants				
Carbon Manganese	0.03 max 2.00 max	Condition	Ultimate Tensile Strength, min (MPa)	Yield Strength (0.2% offset), min (MPa)	Elongation 2-in (50.8 mm) min%	Rockwell Hard
Phosphorus* Sulfur	0.03 max 0.03 max	Annealed	485	172	40	95 HRB
Silicon	0.75 max	Cold-worked	860	690	12	
Chromium	17.00-20.00					
Nickel	12.00-14.00					
Molybdenum	2.00 - 4.00					

Molybdenum improves resistance to pitting corrosion in salt water

Nickel and chromium 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 oxygendepleted 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

	CoCrMo (F75)		CoCrWNi (F90)		CoNiCrMo (F562)		CoNiCrMoWFe (F563)	
Element	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximun
Cr	27.0	30.0	19.0	21.0	19.0	21.0	18.00	22.00
Мо	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	<u> </u>	0.75	h	3.0	_	1.0	4.00	6.00
С		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
N			14.0	16.0			3.00	4.00
)						0.015		
						0.010		0.010
ï						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
- Large implants such as hip joint stems can only be made by hot-forging Disadvantages
- 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 220-240 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

			Wrought CoNiCrMo (F562)		
Property	Cast CoCrMo (F75)	Wrought CoCrWNi (F90)	Solution Annealed	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 (g/cc)
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

Element Grade 1 Grade 2 Grade 3 Grade 4 Ti6Al4	Grade 3	Grade 4	Ti6Al4V	$_{\sharp}$ Mechanical properties of Ti–6Al–4V alloy with different oxygen content [20].							
	110/11/	Oxygen content/microstructure	YS (MPa)	UTS (MPa)	EL (%)	RA (%)	K <sub>IC</sub> (MPa/m <sup>1/2</sup>				
Nitrogen	0.03	0.03	0.05	0.05	0.05	0.15–0.2%, equiaxed	951	1020	15	35	61
Carbon	0,10	0.10	0.10	0.10	0.08	0.15–0.2%, lamellar 0.13 Max equiaxed	884 830	903	13	23 44	78 91
Hydrogen	0.015	0.015	0.015	0.015	0.0125	0.18–0.2% equiaxed	1068	1096	15	40	54
Iron	0.20	0,30	0,30	0.50	0.25						
Oxygen	0.18	0.25	0.35	0.40	0.13						
Titanium			balance	*6%	6 AI. 4% \	/					

**TABLE 40.5** Chemical Compositions of Titanium and Its Alloy

Titanium is an allotropic material which exists as hcp  $\alpha$ -Ti up to 882 C and bcc  $\beta$ -Ti above that temperature

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

- Aluminum, O, N stabilize the  $\alpha$ -phase
- Vanadium, Mo, Nb, Fe, Cr stabilize the  $\beta$ -phase

The  $\alpha$ -alloys have single phase microstructure which promotes weldability but prevents hardening by heat treatment precipitation of a second phase High Al alloys of Ti also have high strength and oxidation resistance at high temperatures

The precipitates of the  $\beta$ -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 and strength generally increases with increasing  $\beta$  stabilizer content

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

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

Properties	Grade 1	Grade 2	Grade 3	Grade 4	Ti6AI4V	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

TABLE 40.6 Mechanical Properties of Ti and Its Alloys

The  $\alpha$  and  $\beta$  phases form the basis for normally accepted classification of titanium alloys

Alloys having only  $\alpha$  stabilizers and consisting entirely of  $\alpha$  phase are known as  $\alpha$  alloys.

Alloys containing 1–2% of  $\beta$  stabilizers and about 5–10% of  $\beta$  phase are termed as <u>near  $\alpha$  alloys</u>.

Alloys containing higher amounts of  $\beta$ stabilizers which results in 10–30% of  $\beta$  phase in the microstructure are known as  $\alpha + \beta$  alloys. Alloys with still higher  $\beta$  stabilizers where  $\beta$  phase can be retained by fast cooling are known as <u>metastable  $\beta$ </u> <u>alloys</u>. These alloys decompose to  $\alpha + \beta$  on aging.

Most of the biomedical titanium alloys (Ti–6Al–4V) belong to  $\alpha + \beta$  or metastable  $\beta$  class (Ti–35Nb–7Zr–5Ta)



higher strength, higher ductility and higher low cycle fatigue

Mechanical properties of biomedical titanium alloys.

Material	Standard	Modulus (GPa)	Tensile strength (Mpa)	Alloy type
First generation biomaterials (1950–1990)				
Commercially pure Ti (Cp grade 1-4)	ASTM 1341	100	240-550	α
Ti-6Al-4V ELI wrought	ASTM F136	110	860–965	$\alpha + \beta$
Ti–6Al–4V ELI Standard grade	ASTM F1472	112	895–930	α + β
Ti–6Al–7Nb Wrought	ASTM F1295	110	900-1050	α + β
Ti–5Al–2.5Fe	-	110	1020	$\alpha + \beta$
Second generation biomaterials (1990-till de	ite)			
Ti–13Nb–13Zr Wrought	ASTM F1713	79-84	973-1037	Metastabe β
Ti–12Mo–6Zr–2Fe (TMZF)	ASTM F1813	74-85	1060-1100	β
Ti-35Nb-7Zr-5Ta (TNZT)		55	596	β
Ti-29Nb-13Ta-4.6Zr	-	65	911	β
Ti-35Nb-5Ta-7Zr-0.40 (TNZTO)		66	1010	β
Ti-15Mo-5Zr-3Al		82		β
Ti–Mo	ASTM F2066			β

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 as implants 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

Low fatigue strength results from the formation of corrosion pits on the surface, which arise from the dissolution of Ti<sup>2+</sup> ions in the living body, wearing at sliding parts and fretting



## Applications









The defect area



The Implant on defect



The Implant



Perfect fitt





The Implant



Orbital P.S Implant

The Implant inserted on defect

## Nitinol (Titanium alloy)

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 martensite 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 arc-wires, 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









### Magnesium

Magnesium is the second most abundant (after Ca<sup>2+</sup>), intracellular, divalent cation

It has a structural role in the cell membrane and in chromosomes, and is involved in various mechanisms, e.g. as a cofactor for over 300 enzymes and in metabolic pathways

Bone contains approximately 67% of the body's magnesium, 30% of this being exchangeable due to its presence on the surface of bone, thus providing a magnesium reservoir

So magnesium and its corrosion products exhibit high biocompatibility

The first reported use of a magnesium -based material in medicine dates back to 1878 when magnesium wires were successfully employed to tie blood vessels

In the following years, several applications were tested including connectors or tubes to repair vessels and intestins, plates, sheets, and screws used in arthroplasty or fractures

The availability of ultra-high purity magnesium in recent times and the exceptional bioresorbability of the metal increased demand for its use as a base for alloys for cardiovascular and orthopaedic applications Magnesium-based implants are bioresorbable, and clinical evidence supports their osteoinductivity

The toxicity of magnesium is the lowest among metals as magnesium is essential to metabolism, and excess is generally very quickly by the kidney

The only problem associated with magnesium implants was extensive, post-operative subcutaneous gas cavities resulting from gaseous degradation product

Degradation rates as well as mechanical properties can be tailored by combining different factors such as magnesium purity, the choice of alloying elements, the metal microstructure, and the material processing route

e.g. rare earth elements (such as yttrium and gadolinium), zirconium, manganese, zinc, calcium, lithium, and strontium are commonly added to improve the stability of magnesium

Even though the biocompatibility of the rare earths remains questionable, their low concentrations do not pose health risks as the toxicity of any element is always a question of concentration

Atherosclerosis is defined by the accumulation of fatty substances, collagen, and elastin in areas of high shear stress in the artery. Such thickening of the vessel wall may lead to narrowing of the vessel



The common therapy is angioplasty, the mechanical widening of the narrowed or obstructed arteries by inflating a balloon, with or without placement of a permanent stent A permanent stent can provoke physical irritation, long-term endothelial/vascularisation dysfunction, chronic inflammatory reactions, thrombosis, etc.

These drawbacks have been partially reduced by the development of drug-releasing stents, which are usually coated with antiproliferative drugs Magnesium is the most suitable material for this application due its high mechanical properties, high degradation rate and high tolerability in the body (biocompatibility)

## Orthopedic applications

Other metals are more suitable for orthopedic implants considering their higher strengths However, their mechanical properties are generally poorly matched with those of bones. This can lead to aseptic loosening as a result of stress-shielding

Degradable magnesium based implants have similar mechanical and physical properties with bone which result in the following benefits during orthopedic applications:

(1) Avoidance of second or revision surgery,

Therefore decreased patient morbidity and health care costs,

(2) Temporary support during tissue recovery,

(3) Possible inherent repair due to osteoinduction



Magnesiumyttrium-rare earth-zirconium alloy screws as substitutes for titanium

Mechanical properties of different materials (n/a: not applicable).

	Tensile strength [MPa]	Young's Modulus [GPa]	Density [g/cm <sup>3</sup> ]
Tissue [88]			0
Cortical bone	35 - 283	5 - 23	1.8 - 2.0
Cancellous bone	1.5 - 38	0.01 - 1.57	1.0 - 1.4
Polymers [89-92]			
Polyglocolide (PGA)	60 - 99.7	6 - 7	1.5 - 1.707
Polylactide (PLA)	32.2	0.35 - 3.5	1.21 - 1.25
Poly-L-lactide (PLLA)	45 - 70	2.7 - 4.14	1.24 - 1.30
Polycaprolactone (PCL)	23	0.21 - 0.44	1.11 - 1.146
Chitosan	34 - 44	1.1 - 1.4	n/a
Calcium Phosphates [88, 93]			
Beta-Tri-calcium phosphate (β-TCP)	18 - 130	23.4 - 84.8	3.14
Hydroxyapatite (HA)	40 - 200	70 - 120	3.05 - 3.15
Bulk metallic glasses [94]			
Bioglass (45S5)	42	35	2.2 - 2.8
Mg67Zn28Ca5	675 - 894	48	-
Metals			
Titanium alloys [95, 96]			
Ti6Al4V	895 - 930	110 - 114	4.43
Ti6Al7Nb	900 - 1050	114.00	4.51
Ti13Nb13Zr	973 - 1037	79 - 84	4.66
Iron alloys [97, 98]			
Pure Iron (electroformed)	160 - 435	211	7.86
Fe35Mn	235	-	-
Magnesium alloys [21, 88, 99-101]			
Pure Mg	90	44	1.74
AZ91E	165 - 457	45	1.81
WE43	250 - 277	44 - 46	1.84
Mg10Gd	69.1 - 85.4	-	1.88
Mg6Zn	277 - 281	42.3	1.84
Mg1Ca	75 - 240	-	1.73

## **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

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

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

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

Antibacterial activity is highest of implant metals (gold > titanium > cobalt > vanadium > aluminum > chromium > iron)

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 upon more than 4% Pt addition

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



Tantalum – Rare, hard, blue-gray, lustrous transition metal with high corrosion resistance Has an extremely high melting point of 3017 °C When exposed in air, a passivation layer of  $Ta_2O_5$  is formed on the surface, which accounts for its exceptional corrosion resistance Biocompatible and high mechanical properties (Tensile strength 207<>517 MPa, E Modulus = 190 GPa, Elongation < 30%) High density (16.6 g/cc)

Common applications are wire sutures, artificial joints, spinal fusion cages, dental implants and radioisotope nanoparticle markers for bladder tumors

Recently porous tantalum scaffolds have been developed by chemical vapor infiltration and deposition (CVI/CVP) and powder metallurgy to optimize the mechanical properties for orthopedic and dental applications. This porous tantalum bears an interconnected porous structure, which is similar to human cancellous bone

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Fig. 1. Scanning electron micrograph of human trabecular bone (left), porous tantalum fabricated by the CVD/CVI (middle) or PM (right) method.

Comparison of porous tantalum to typical materials associated with orthopedics.

Material properties	Porous tantalum (CVI/CVP)	Porous tantalum (PM)	Porous tantalum (NaCl)	Unalloyed tantalum (F560)	Ti-6Al-4V (F1472)	Co-28Cr-6Mo (F75)	UHMWPE (F648)
Modulus of elasticity (GPa)	2.5-3.5	2.05-2.37	1.7-2.3	186	106-115	210	12.6
Ultimate strength (MPa)	50-110	n/a	n/a	207-517	860	655-889	35
Yield strength (MPa)	35-51	n/a	n/a	138-345	758	445-517	21
Compressive strength (MPa)	50-70	57-66	48.8-51.8	n/a	n/a	n/a	n/a
Tensile strength (MPa)	63	n/a	n/a	n/a	n/a	n/a	n/a
Bending strength (MPa)	110	n/a	n/a	n/a	n/a	n/a	n/a
Elongation (%)	n/a	n/a	n/a	2-30	8	8	300
Reduction of area (%)	n/a	n/a	n/a	n/a	14	8	n/a

Other metals subjected to specialized implant applications are:

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

