

U Metals and Alloys for Implants & Medical Devices B

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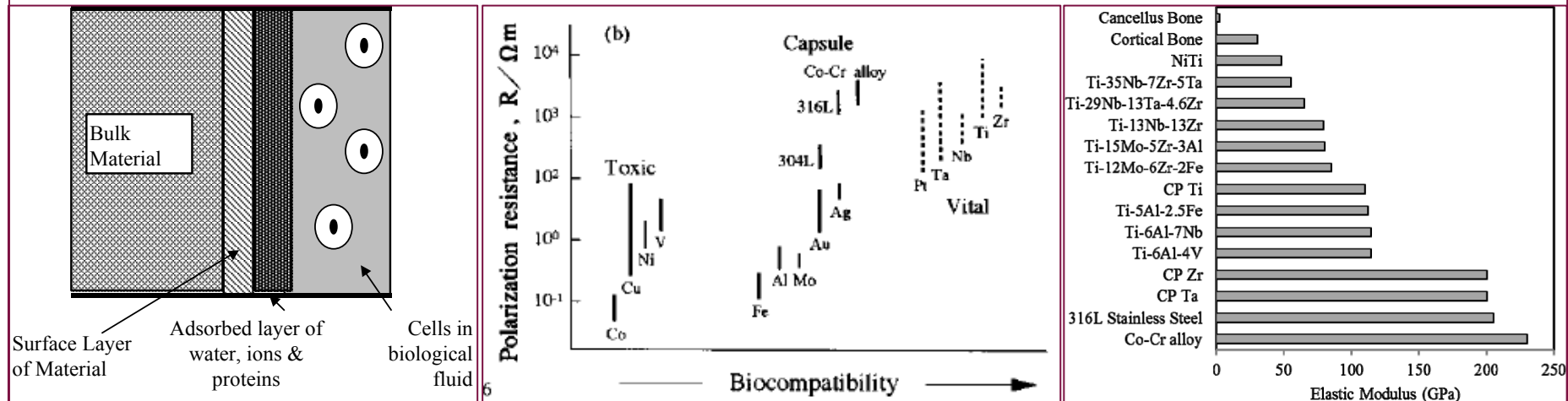
Outline

- **Introduction:** Metallic biomaterials
- **Material types:**
 - $\alpha+\beta$ and β -Ti alloys
 - NiTi (nitinol)
 - CoCr alloys
 - Stainless steels
 - Other metals: gold, tantalum, etc...
- **Processing:**
 - Investment casting
 - Forging
 - Machining
 - Advanced processing: metal 3D Printing
- **Conclusions**

Metallic Biomaterials

Introduction

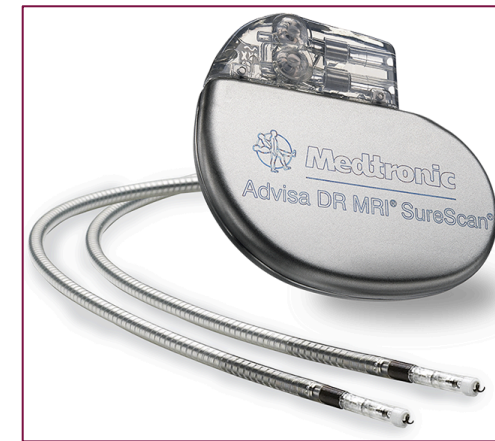
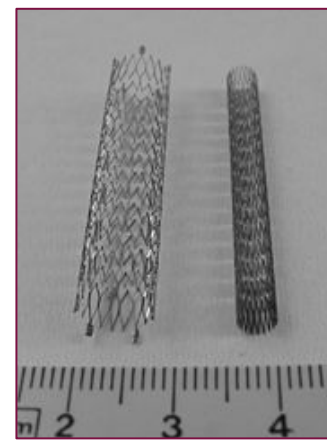
- For a metal to be used as a **biomaterial**, it needs to be
 - **Bioinert/Biotolerant**: having minimal interaction with the surrounding body fluids, soft/hard tissues.
 - **Mechanically biocompatible**: especially for orthopaedic implants, having a similar modulus to the hard tissues.
 - **Strong**: expressed in the form of mechanical strength, fatigue resistance (if cyclic loading is required), wear, etc...



Metallic Biomaterials

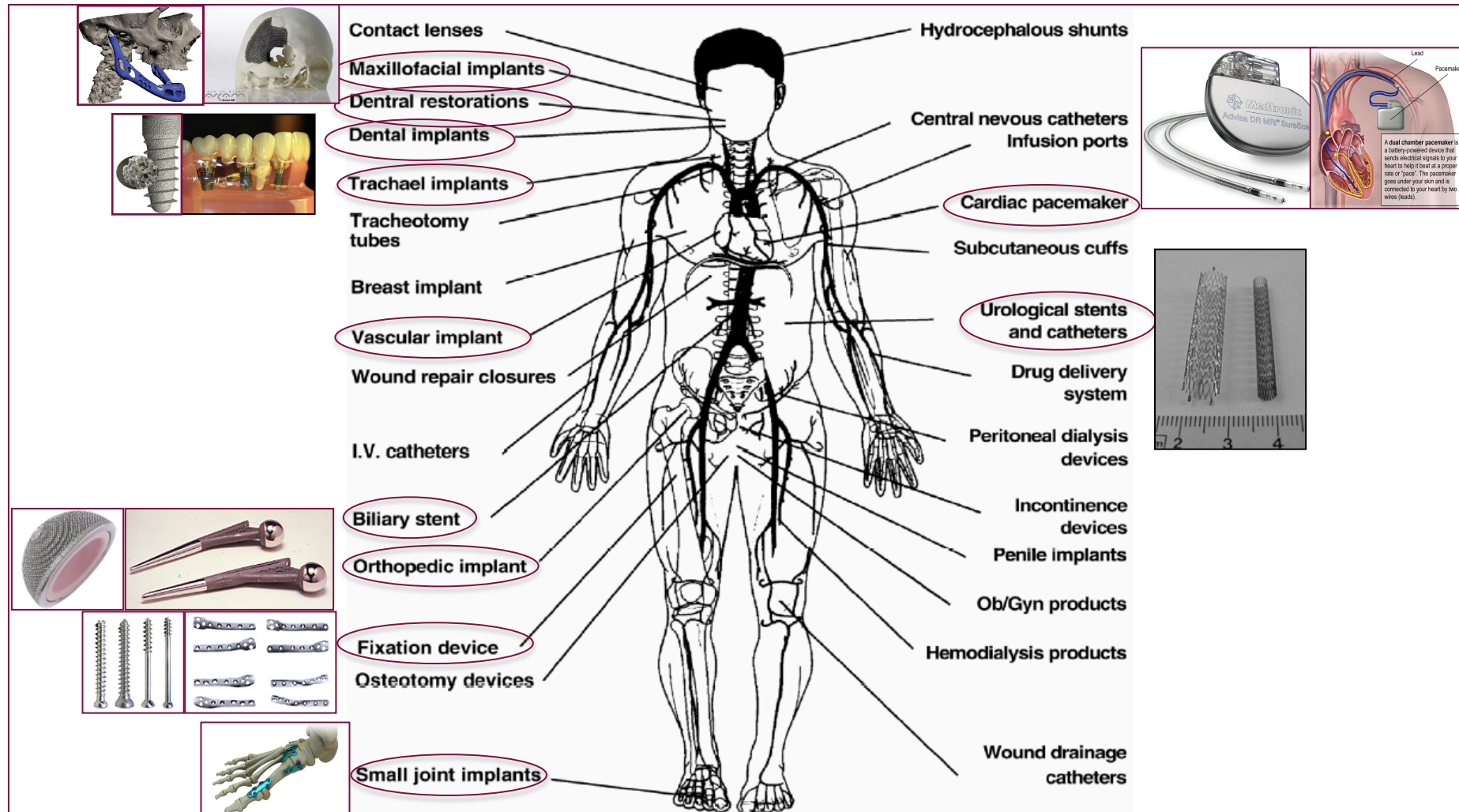
Introduction: Definitions

- ❑ **Prosthesis:** to replace a portion of the body (e.g. joints).
- ❑ **Fixation devices:** to stabilise broken bones during healing or permanently (e.g. plates, screws, spinal devices, wires).
- ❑ **Vascular & urological systems devices:** stents
- ❑ **Functional devices:** pacemakers or cochlear implants.
- ❑ **Requirements:** no irritation to tissues, an excessive inflammatory response, allergic and immunologic reactions, and cancer.



Metallic Biomaterials

Introduction*



Metallic Biomaterials

Typical Materials & Applications of Metallic Implants

□ Typical devices/annual use:

Device	Annual # of Devices in USA
**Heart Valves (<i>rings, cages</i>)	100,000 (some)
**Pacemakers	400,000
*Coronary Stents	1,500,000
*Hip Prostheses (2002)	250,000
*Knee Prostheses (2002)	250,000
*Dental Implants	910,000

Ratner *et al.* "Biomaterials Science: An Introduction to Materials in Medicine, 2nd Edition, Elsevier Academic Press, San Diego, CA, 2004.

*all or predominantly metal

**metal-containing

NHS	2015
Total completed ops	137,784
Hip procedures	65,062
Knee procedures	66,585
Ankle procedures	585
Elbow procedures	614
Shoulder procedures	4,938
NJR consent rate	93%
Independent	2015
Total completed ops	70,810
Hip procedures	32,291
Knee procedures	37,211
Ankle procedures	135
Elbow procedures	36
Shoulder procedures	1,137
NJR consent rate	95%

UK National Joint Registry, Statistics 2015.

□ Typical metallic systems/classification:

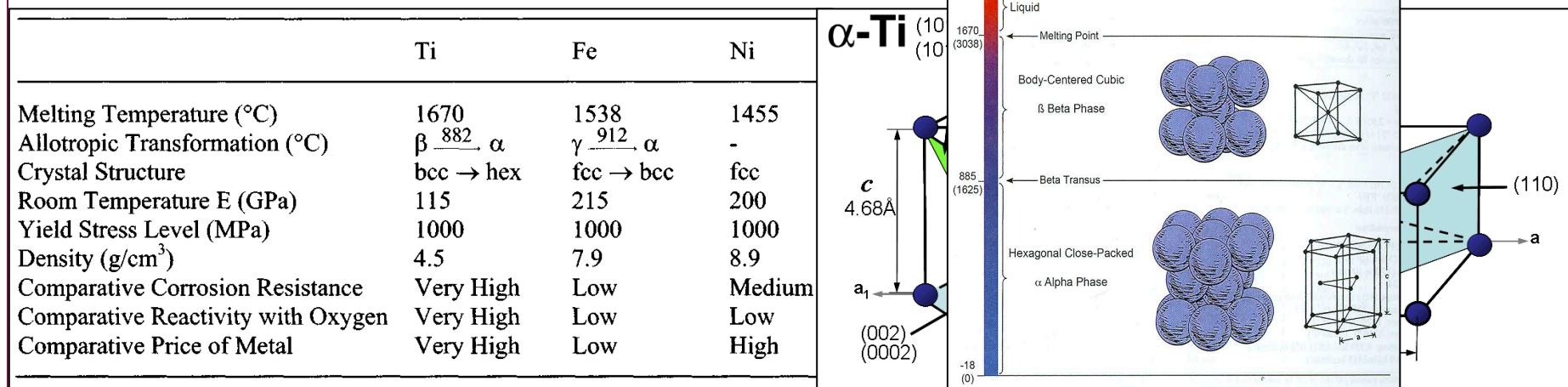
Metal type	Example	Characteristics
Bio-tolerant	Au, CoCr, Zr, Nb, Ta, Stainless steels	Creates thin fibrous tissue interface as a capsule.
Bio-inert	Ti and Ti-alloys,	Minimal interaction, leading to contact osteogenesis.

U **Titanium and Its Alloys** B

Titanium & Its Alloys

Physics Metallurgy*

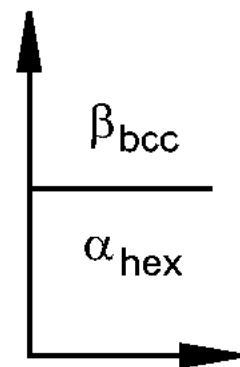
- Compared to Fe & Ni, Ti has the highest melting point, corrosion resistance, oxygen reactivity, & price.
- Commercial Ti-alloys contain two phases: α (HCP) & β (BCC).
- On heating to above the β -transus, only the β -phase exists.
- Alloying, as well as thermal & thermo-mechanical treatments can create alloys with tailored the mechanical properties.
- Components can be cast, forged, rolled, or machined.



Titanium & Its Alloys

Physics Metallurgy*

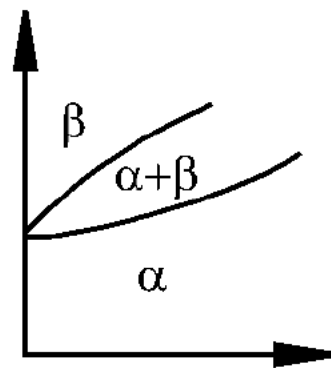
- Certain alloying elements (e.g. Mo, V, Nb) stabilise the β phase at low temperatures, while others (e.g. Al, Sn, Zr) stabilise α .
- Other elements have a neutral effect or cause the formation of intermetallics.



Ti

neutral

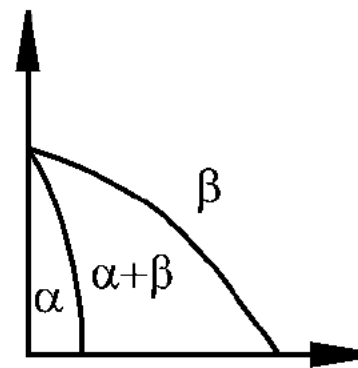
(Sn,Zr)



Ti

 α -stabilizing

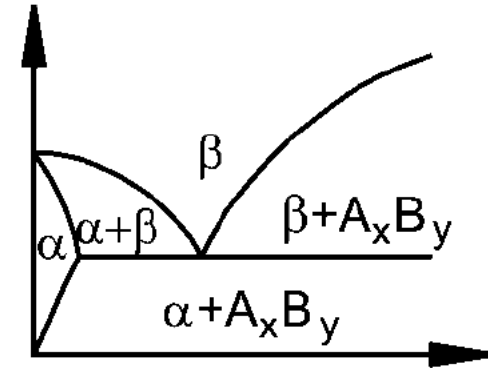
(Al,O,N,C)



Ti

 β -stabilizing β -isomorphous

(Mo,V,Ta,Nb)



Ti

 β -eutectoid

(Fe,Mn,Cr,Co,Ni,Cu,Si,H)

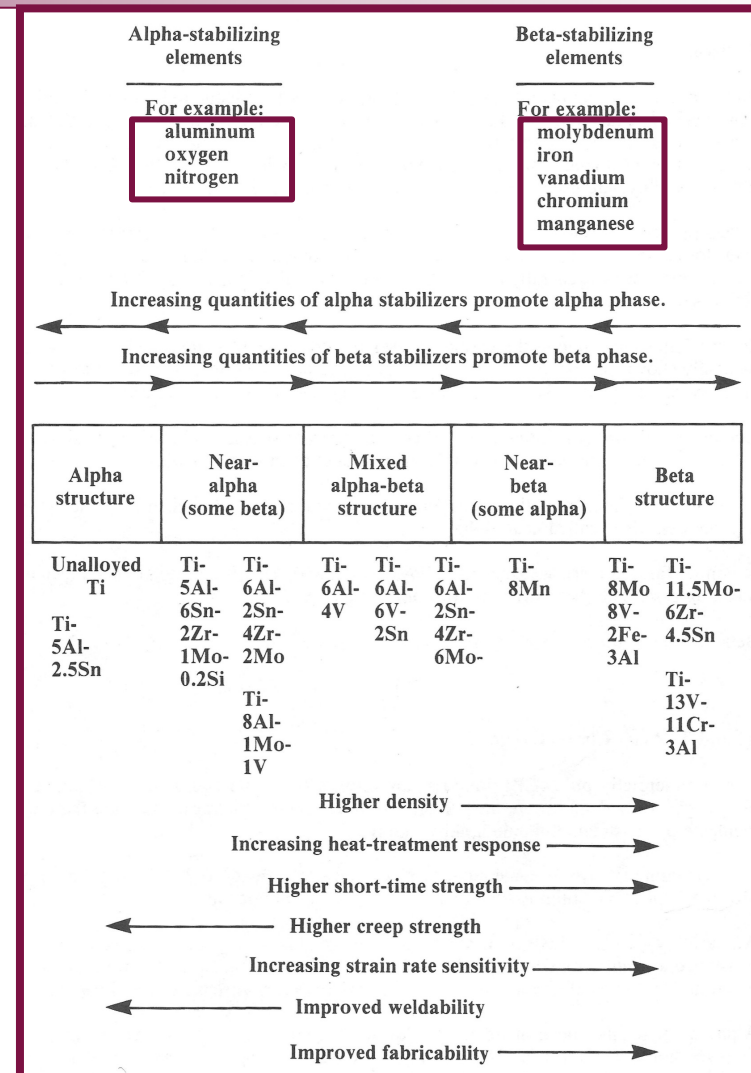
Titanium & Its Alloys

Alloy Classes*

□ Donachie's Classification:

- CP + α
- near α
- $\alpha+\beta$
- near β
- β .


□ Correlating the change in the alloying elements with the variation in properties.



Titanium & Its Alloys

Key Characteristics Versus Other Implant Materials*

- Titanium outshines other metals in its corrosion resistance, specific properties (e.g. strength-to-weight), and low modulus.
- **Limitations:** cost and oxygen reactivity (during processing).



Material	Tissue tolerance	Corrosion resistance	Tensile strength (MPa)	Fatigue strength (MPa)	Elastic modulus (GPa)	Toughness	Wear resistance	Specific gravity	Relative total cost ^c
<i>Stainless steels</i>									
316 (annealed)	10	7	517	350	200	8	8	8.0	1.0
317 (annealed)	9	7	630	415	200	10	8.5	8.0	1.1
321 (annealed)	9	7	610	410	200	10	8	7.9	1.1
347 (annealed)	9	7	650	430	200	10	8.4	8.0	1.2
<i>Co-Cr alloys</i>									
Cast alloy ^a	10	9	655	425	238	2	10	8.3	3.7
Wrought alloy ^b	10	9	896	600	242	10	10	9.13	4.0
<i>Titanium alloys</i>									
Unalloyed Ti	8	10	550	315	110	7	8	4.5	1.7
Ti-6Al-4V	8	10	985	490	124	7	8.3	4.43	1.9
<i>Composites (fabric reinforced)</i>									
Epoxy-70% glass	7	7	680	200	22	3	7	2.1	3
Epoxy-63% carbon	7	7	560	170	56	3	7.5	1.61	10
Epoxy-62% aramid	7	7	430	130	29	5	7.5	1.38	5

^aComposition: 27–30 Cr, 2.5 Ni, 5–7 Mo, 0.75 Fe, 0.36 C, 1 max Mn and Si, Rem Co.

^bComposition: 20 Cr, 10 Ni, 15 W, 0.13 Mo, 3 max Fe, 0.1 C, 2 max Mn, 0.48 Si, Rem Co.

^cTotal cost includes cost of material per unit volume, processing cost, and finishing cost.

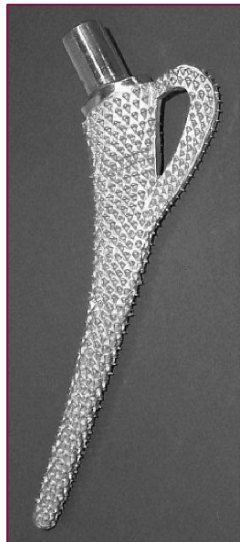
Titanium & Its Alloys

Typical Applications

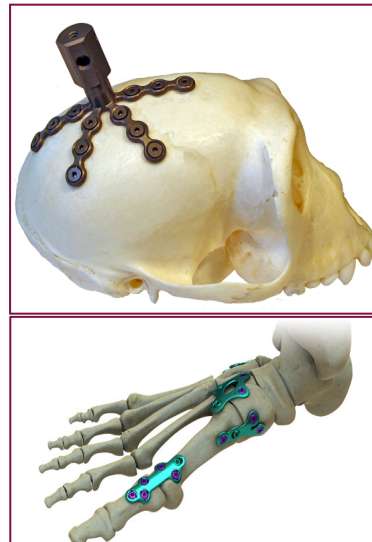
Material	Hip replacement				Knee replacement	
	Hip stem (uncemented)	Femoral head	Cup/ insert	Metal back shell	Femoral component	Tibial plate
CP Ti	–	–	–	X	–	–
Ti alloys	X	–	–	X	X	X

CP Ti: commercially pure titanium; X: clinically used. –: clinically not used or not successful;etal bearing;

C Yao TJ Webster. Titanium and CoCr alloys for hips and knees. Woodhead Publishing, 2011.



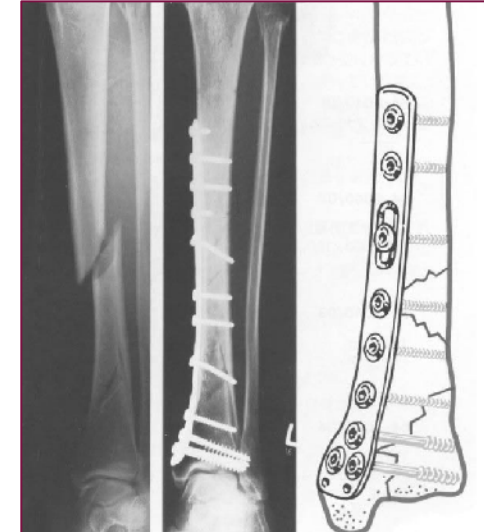
Hip stem*



Plates/fixtures



Cardiac valve prostheses
Artificial Hearts/

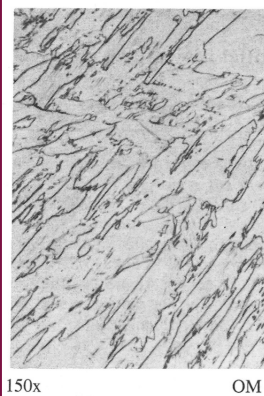


CP Ti bone plate implant*

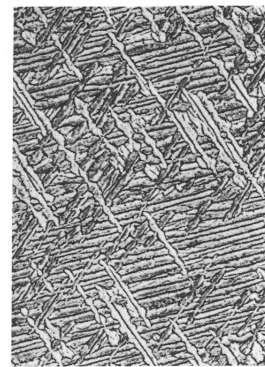
Titanium & Its Alloys

Alloy Classes Used as Biometals: CP/ α -Titanium

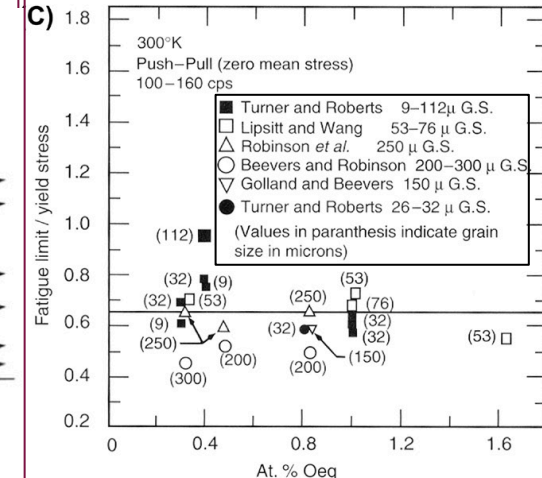
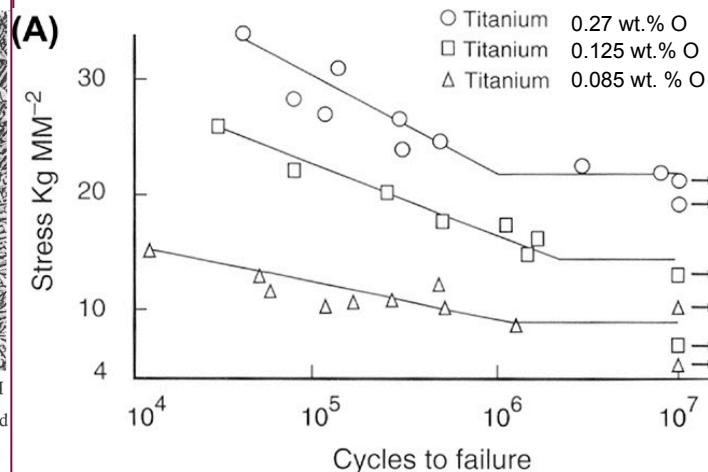
- Unalloyed Ti, limited amounts of Fe, and interstitial elements (O,N).
 - Highly corrosion resistant (bio-inert, bio-compatible).
 - Relatively good fabricability.
 - Relatively low mech. properties (170-480 MPa).
 - O-content affects the microstructure & properties; higher strength with O-content increase.



(a) Relatively pure titanium



(b) a Ti 0.3 wt % O alloy obtained after annealing in the β region and then cooling to 25°C (77°F)



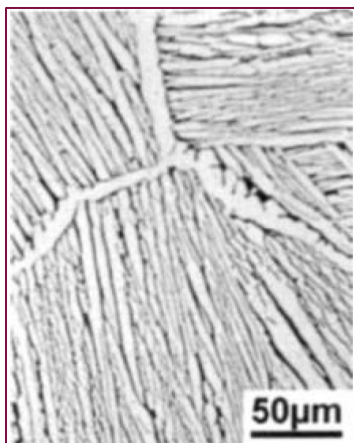
MJ Donachie-Jr. Titanium: A Technical Guide. Metals Park, OH: ASM International, 1998.

JB Brunsk. Chapter I.2.3 Metals: Basic Principles. In Biomaterials Science: Introduction to Materials in Medicine. BD Ratner, AS Hoffman, JF Schoen, JE Lemons (Ed.s), Elsevier, 3rd Ed., 2013.

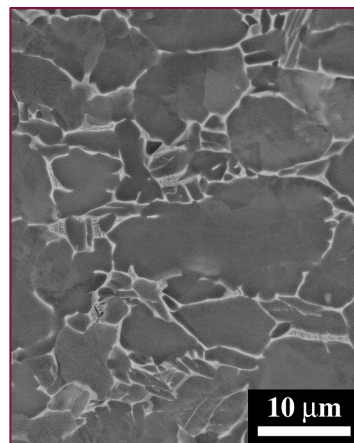
Titanium & Its Alloys

Alloy Classes Used as Biometals: $\alpha+\beta$ -Titanium

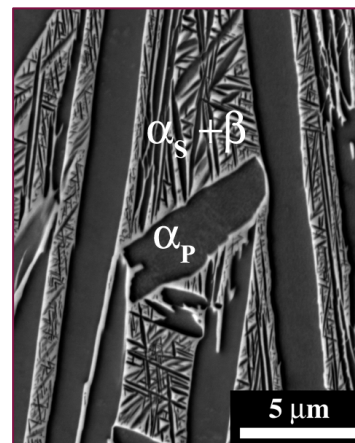
- Ti-6Al-4V, the most common Ti alloy, or Ti-6Al-7Nb (reduced toxicity from V & Al) using non-toxic elements (e.g. Zr, Ta, Nb).
- Good balance of all mechanical properties, yet dependent on the microstructure (outcome of the processing route and thermomechanical history).
- Castings have coarse grains and lamellar microstructure.
- Most common application: hip stem, bone plates.



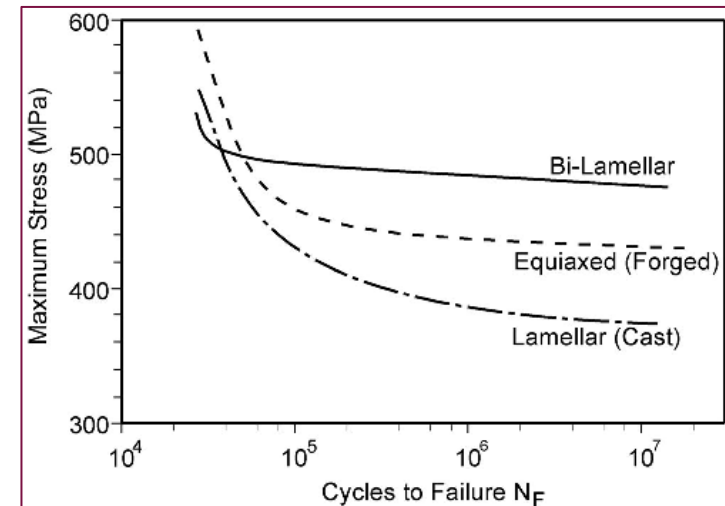
Lamellar



Equiaxed



Bi-lamellar



Titanium & Its Alloys

Alloy Classes Used as Biometals: β -Titanium

- A growing new generation of β -Ti-alloys, using biocompatible alloying elements (Nb, Ta, Zr, Mo), with the following key characteristics:
 - lower modulus of elasticity (60-85 GPa), compared to $\alpha + \beta$ alloys.
 - Investment castings of heavily stabilised β -alloys have nearly identical properties compared to β -annealed wrought products.
 - Examples: The Japanese alloys Ti-29Nb-13Ta-4.6Zr (TNTZ) and Ti-29Nb-13Ta-4Mo, Ti-12Mo-6Zr-2Fe (TMZF), modified Beta 21S alloy (Beta 21SRx).

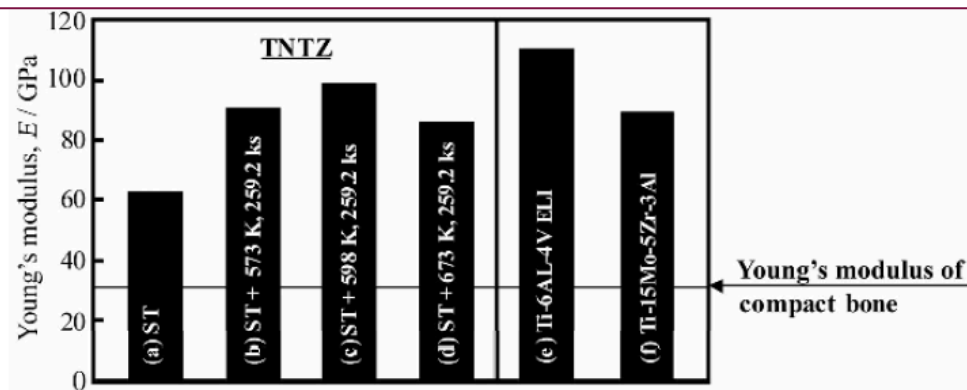
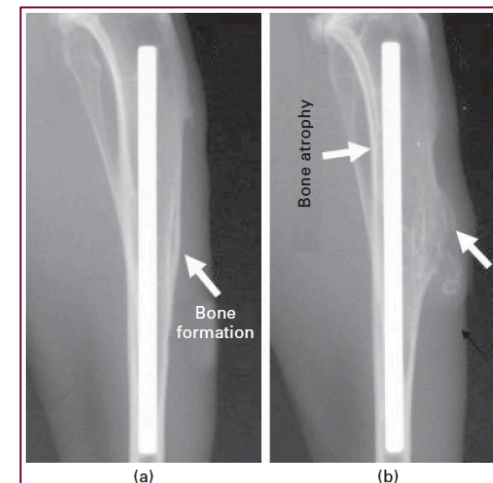


Fig. 10.28. Modulus of elasticity E of TNTZ (Ti-29Nb-13Ta-4.6Zr) in unaged condition (a) and after aging for 72 h at 300°C (b), 325°C (c), and 400°C (d), Ti-6Al-4V (e) and Ti-15Mo-5Zr-3Al (f) [10.41]



15.22 X-ray photographs of intramedullary rods made of (a) TNTZ and (b) SUS 316L stainless steel at 24 weeks after implantation into tibiae of rabbits (Niinomi and Hattori, 2010).

*G Lujering, JC Williams. Titanium. Springer, 2007

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Titanium & Its Alloys

Alloy Classes Used as Biometals: β -Titanium

- The modulus and strength can be controlled by increasing the ageing (α -phase precipitation)
- The unaged condition has low modulus (60 GPa), but shows low fatigue and yield strengths.

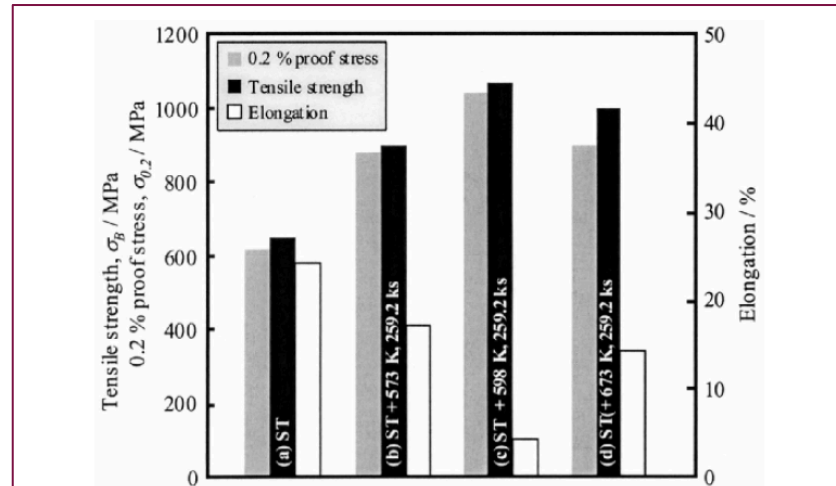


Fig. 10.29. Tensile properties of TNTZ (Ti-29Nb-13Ta-4.6Zr) in unaged condition (a) and after aging for 72 h at 300°C (b), 325°C (c), and 400°C (d) [10.41]

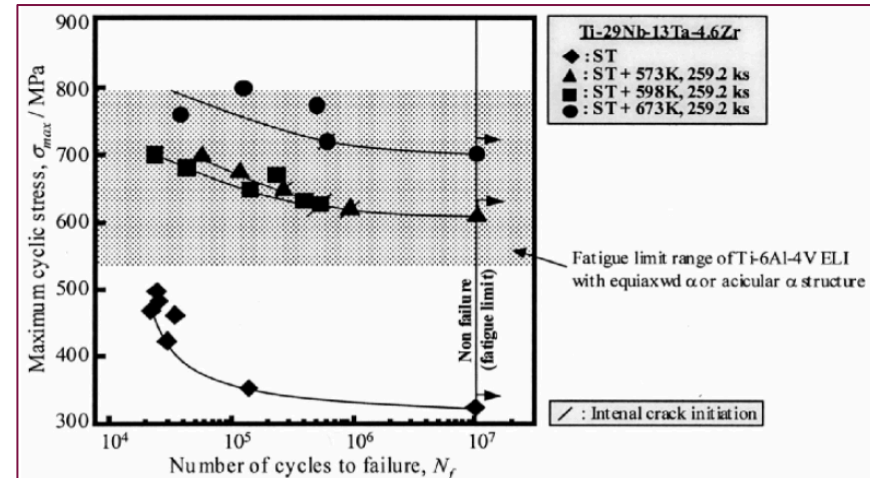


Fig. 10.30. S-N curves ($R = 0.1$, 10 Hz) of TNTZ (Ti-29Nb-13Ta-4.6Zr) in the unaged condition and after aging for 72 h at 300°C, 325°C, and 400°C [10.41]

U **NiTi-based** B Superplastic & Shape Memory Alloys

NiTi-based Alloys

Different Types of Performance

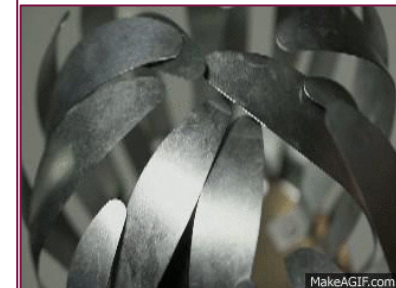
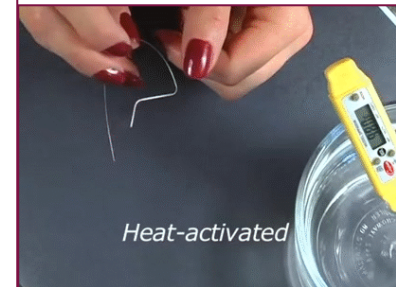
□ Superelasticity (SE)

- Reversible deformation
- Strain-induced martensitic transformation
- 20% recoverable strain



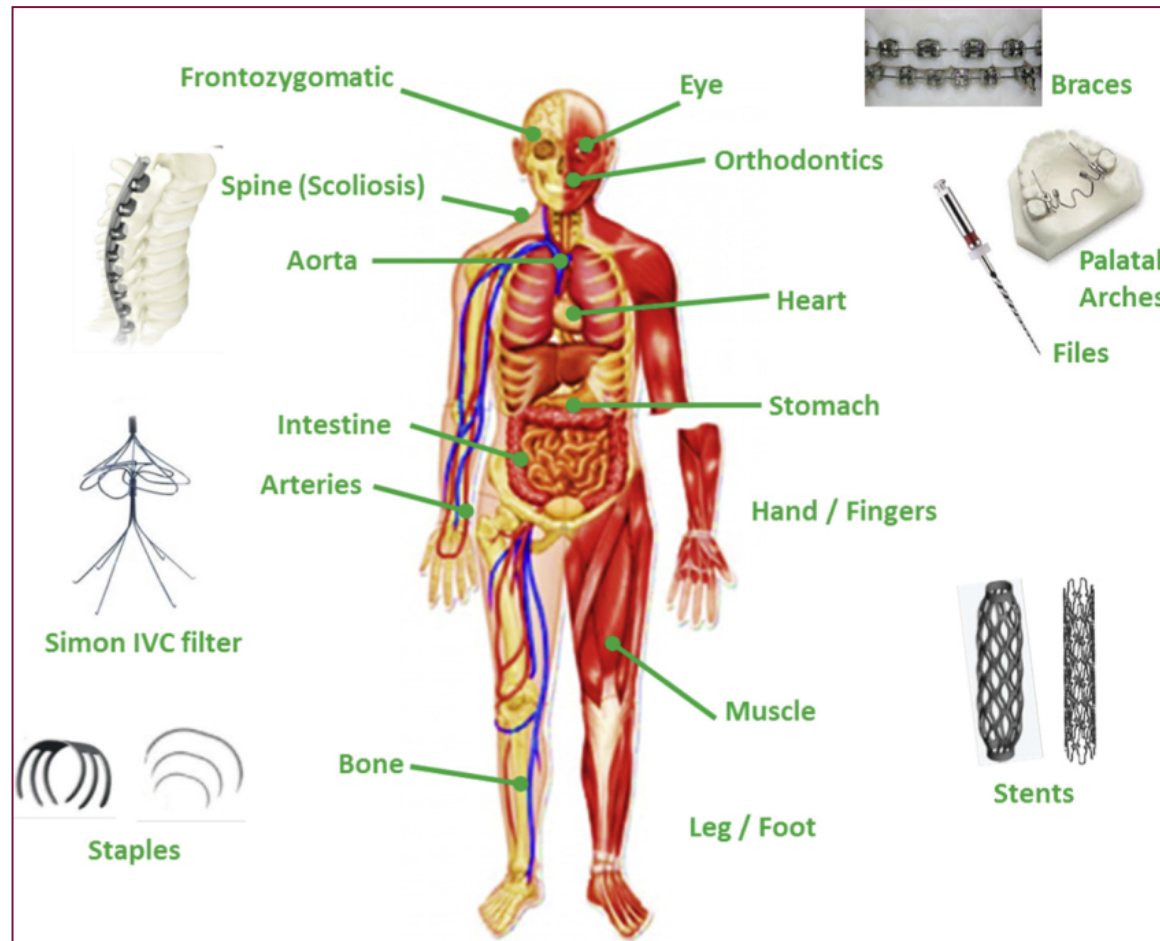
□ Shape Memory Effect (SME)

- **1-Way SME:** Deform in low temperature in the martensitic field, recovers initial shape upon heating to the austenitic field.
- **2-Way SME:** Change between a low temperature shape and a high temperature shape according temperature after training.

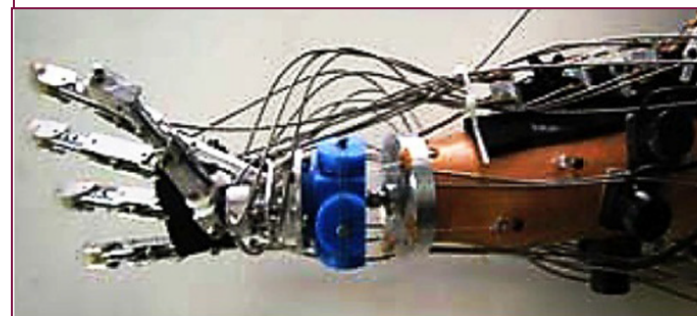
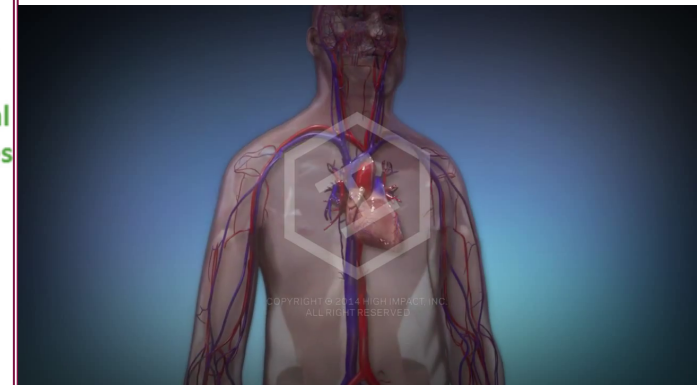


NiTi-based Alloys

Key Applications



Stent in Coronary Artery



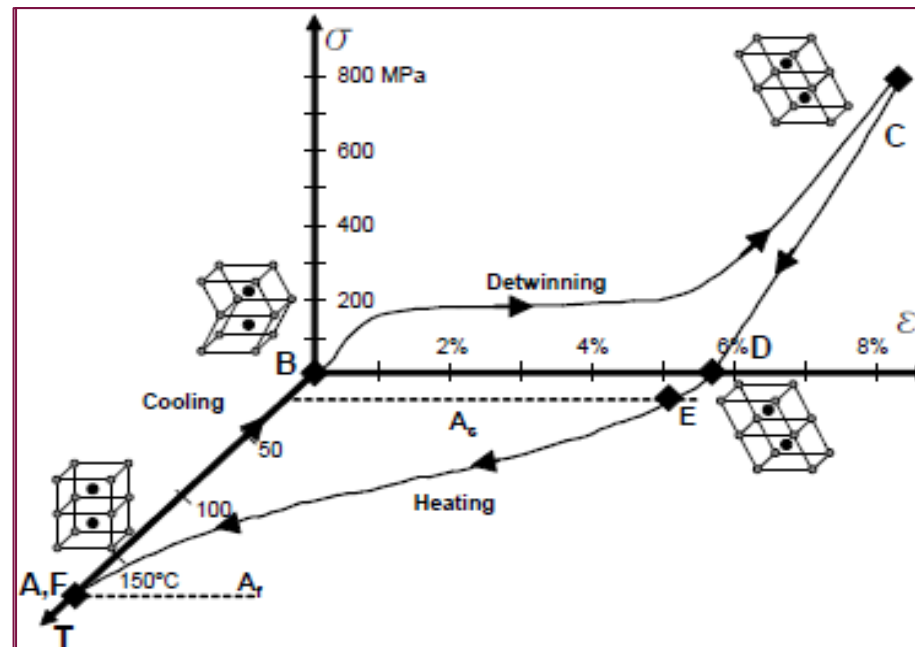
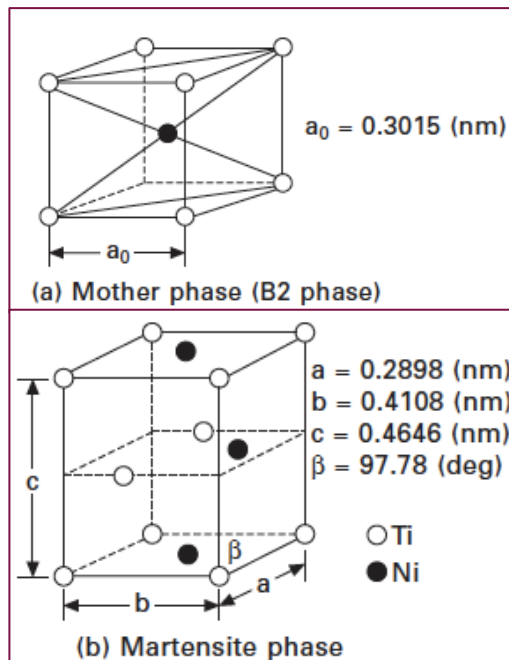
(a) Prosthetic hand prototype

Electrode

NiTi-based Alloys

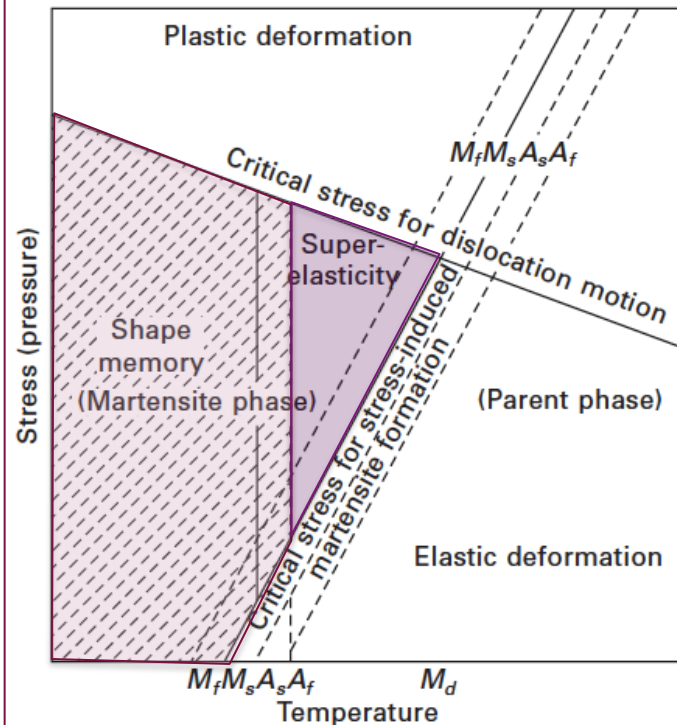
Phase Transformation Mechanisms

- **Key allotropes:** martensite (B2) and austenite (B19').
- **SME:** deformed martensite transforms into austenite upon heating, returning to parent shape upon cooling.
- **SE:** austenite transforms into martensite upon loading, then reverts to austenite on the removal of the load.



NiTi-based Alloys

Phase Transformation Mechanisms



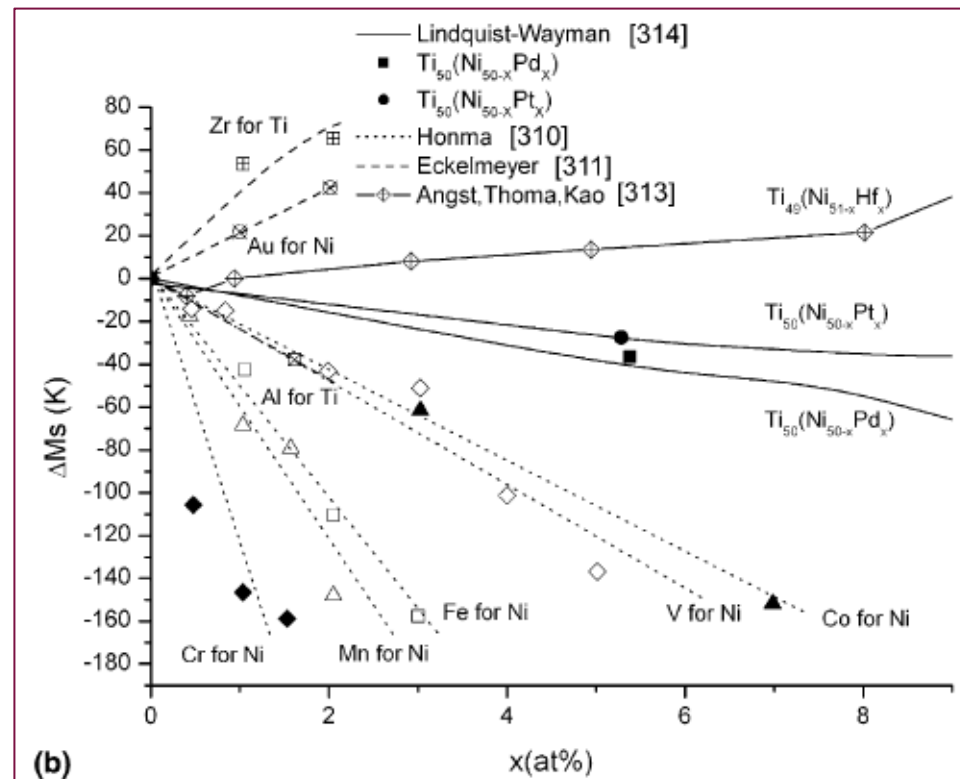
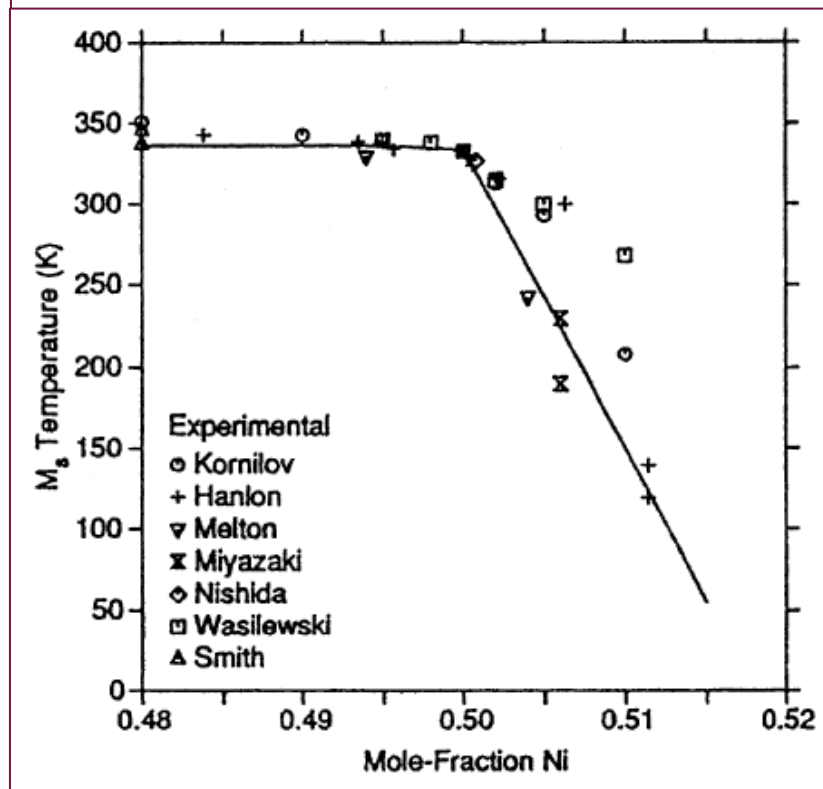
15.4 A schematic deformation map of shape memory alloy (SMA) showing phase stability, transformation temperatures, and critical stress for permanent deformation. M_s : martensite transformation start temperature; M_f : martensite transformation finish temperature, A_s : austenite transformation start temperature, A_f : austenite transformation finish temperature, and M_d : the highest temperature below which martensite transformation is induced by shear (Hosoda *et al.*, 1998).



NiTi-based Alloys

Influence of Chemistry

- Transformation temperatures are affected by alloy chemistry.
- SE NiTi is austenitic at room temperature.



NiTi-based Alloys

Biocompatibility of NiTi Alloys

- Ni-sensitisation (allergy) has increased in the last 30 years.
- Increasing the Ti-content reduces Ni-ion release; equiatomic NiTi is safe, but Ni leakage can cause damage to patients.
- Excellent mechanical biocompatibility & properties.

	NiTi	
	Austenitic	Martensitic
Ultimate tensile strength (MPa)	800–1500	103–1100
Tensile yield strength (MPa)	100–800	50–300
Modulus of elasticity (GPa)	70–110	21–69
Elongation at failure (%)	1–20	up to 60

U

CoCr

B

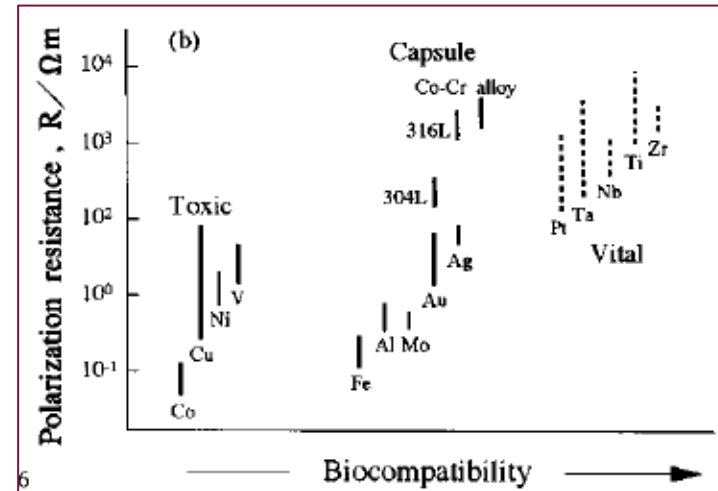
CoCr

Typical Applications

- More widely used in hip & knee replacements than SS and Ti.
- Highest wear resistance among metallic implant materials (**M**). Better corrosion resistance to SS.
- Used in the manufacture of stents and dental implants due to its excellent biocompatibility with blood and soft tissues.
- Processing:** casting and hot deformation (forging or wire drawing); cast products are used in dentistry and artificial joints, while wrought products are used for heavily loaded joints (e.g. femoral hip stems).

Material	Hip replacement				Knee replacement			
	Hip stem (uncemented)	Femoral head	Cup/ insert	Metal back shell	Femoral component	Tibial plate	Tibial cushion	Patella
CP Ti	–	–	–	X	–	–	–	–
Ti alloys	X	–	–	X	X	X	–	–
CoCr alloys	X	X	X(M)	X	X	X	–	–
Stainless steel	–	X	–	–	–	–	–	–

X: clinically used. –: clinically not used or not successful; M: metal-on-metal bearing;



CoCr

Alloy Design

- ❑ **Co**-base, with **Cr** (forming solid solution with Co, enhanced strength and corrosion resistance), plus **Mo** to produce fine grains which results in higher strength. Generally, a complex alloy system, with C, Mo, Ni, W, Fe.
- ❑ Elastic modulus varies from 185 to 250 GPa (**~equal to SS 316 and 2X Ti**)
- ❑ Introduced in the 1930s (vitallium: 30% Cr, 7% W, 0.5% C, Co-base)
 - Mostly for metallic dental castings
 - To replace the more expensive gold alloys
 - Larger partial denture castings

- ❑ ASTM recommends CoCr alloys for implants
 1. cast CoCrMo alloy (F75)
 2. wrought CoCrWNi alloy (F90)
 3. wrought CoNiCrMo alloy (F562)
 4. wrought CoNiCrMoWFe alloy (F563)

TABLE 1.3 Chemical Compositions of CoCr Alloys [American Society for Testing and Materials, F75–87, p.42; F90–87, p.47; F562–84, p.150, 1992]

Element	CoCrMo (F75)		CoCrWNi (F90)		CoNiCrMo (F562)		CoNiCrMoWFe (F563)	
	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
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							

CoCr

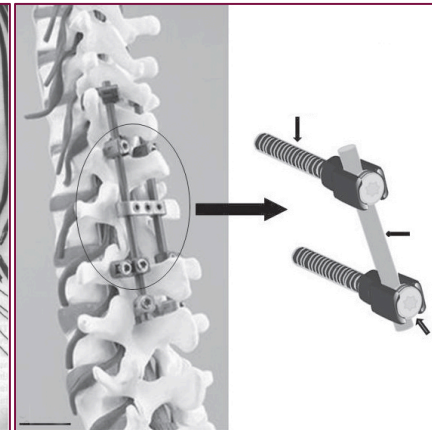
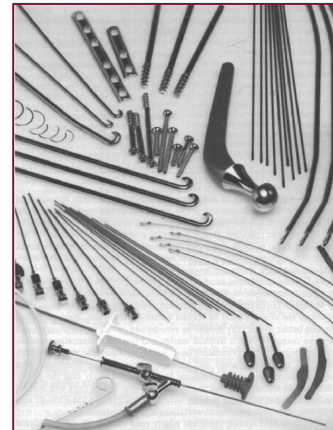
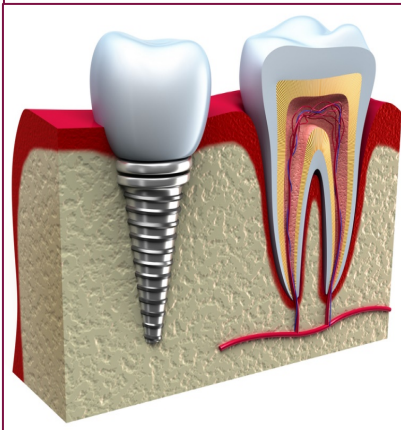
Processing-Properties Relationships

□ Cast CoCr:

- Flexible process for customisation (e.g. dental implants)
- Lower strength due to the slow cooling in casting (coarser grains).
- Carbide precipitation, reducing the ductility.
- A good balance of strength and toughness.

□ Forged CoCr:

- More uniform microstructure
- **Superior fatigue and strength**, making it suitable heavily loaded joints (e.g. femoral hip stems).
- **Expensive** – sophisticated press and tooling.



U **Stainless Steels** B

Stainless Steels

Chemistry

- A corrosion resistant steel alloy, with ~ 11 wt. % Cr.
- Common alloy: 316L (ASTM F138/139): 60-65 wt. % **Fe**, 17-20 wt. % **Cr**, 12-14 wt. % **Ni**, 2 wt. % **Mn**, 2 wt. % **Mo**, max 0.03 wt. % **C (L)**, plus minor amounts of Si, P.
- Non-magnetic, FCC (austenitic) structure.

Low [C] (<0.03 wt%):



Higher [C] (> 0.03 wt%):



Stainless Steels

Causes of Failure

- ❑ Deficiency of Mo (enhances corrosion resistance)
- ❑ Use of sensitised steel (high C)
- ❑ Topography and metallurgical finish
- ❑ Improper implant and implant material selection, misfit between the anatomical restrictions and implant geometry.
- ❑ 316L stainless steels may still corrode inside the body (stress-corrosion, contact/wear). Ideally, stainless steels are suitable for use only in *Temporary* implant devices such as fracture plates, screws, and hip nails.
- ❑ Surface modification methods are widely used in order to improve corrosion resistance, wear resistance, and fatigue strength of 316L SS
 - anodization, passivation
 - glow-discharge nitrogen implantation

U

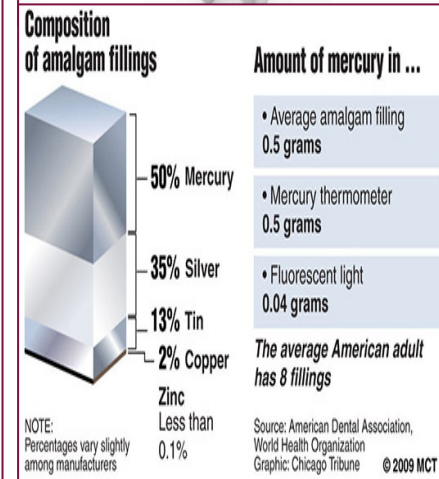
Other Systems

B

Dental Amalgams

Other Systems

- Dental filling material for treatment of cavities due to decay.
- **Composition:** elemental Hg (43-54 %), and an alloy powder composed of mainly Ag, Cu, Sn, and Zn.
- Hg (liquid) acts as a binder, creating a workable paste and a strong solid filling, giving it the unique silver grey colour.
- Elemental mercury can be toxic. Health risks associated with amalgam led to the development of new filling material.



Gold, PGM, and Tantalum

Other Systems

- **Key characteristics:** corrosion resistance and compatibility.
- **Typical alloys:** Ag+ noble metals (Pt) + Cu + Zn.
- Applications: dental implants (crowns, inlays, bridgework).
- **Pt-group metals** (Pt, Pd, Rh, Ir, Ru, Os) high corrosion resistance, electrical conductivity, but poor mech. properties.
- Electrode for pacemakers, stimulating onset of cardiac beats.
- **Tantalum:** limited applications due to cost, high T_m , poor mechanical properties, and high density.
 - Used for porous structures in bone implants.



Property	Type I	Type II	Type III	Type IV
Au content (%)	81–83	76–78	73–77	71–74
Pt content (%)	–	–	–	0–1
Pd content (%)	0.2–4.5	1–3	2–4	2–5
Characteristic	Soft	Medium	Hard	Very hard
Application	Occlusal inlays	Intracoronary inlays	Onlays, crowns, bridgework	Removable partials

[i] ^a Table adapted from 'Precious metal alloys', in "Dental Materials at a Glance", Chapter 10

U Manufacturing Methods B

Manufacturing Methods

Investment Casting

- ❑ Ideal method for Ti and CoCr orthopedic implants.
- ❑ Aluminium dies are used to create the wax shapes. Al-dies are cheap to manufacture and suitable for low melting point waxes.
- ❑ Assembly into a tree, ready for investment.



Manufacturing Methods

Investment Casting

- The tree is coated with a face-coat + stucco, and dried to a green state. The wax is removed by melting it out at 120°C.
- Firing the shells produces sintering of the stucco and a hard, rigid shell, capable of receiving very high temperature liquid metal.
- After taking up to 24 hours to make a shell the liquid metal is poured in.



Manufacturing Methods

Investment Casting



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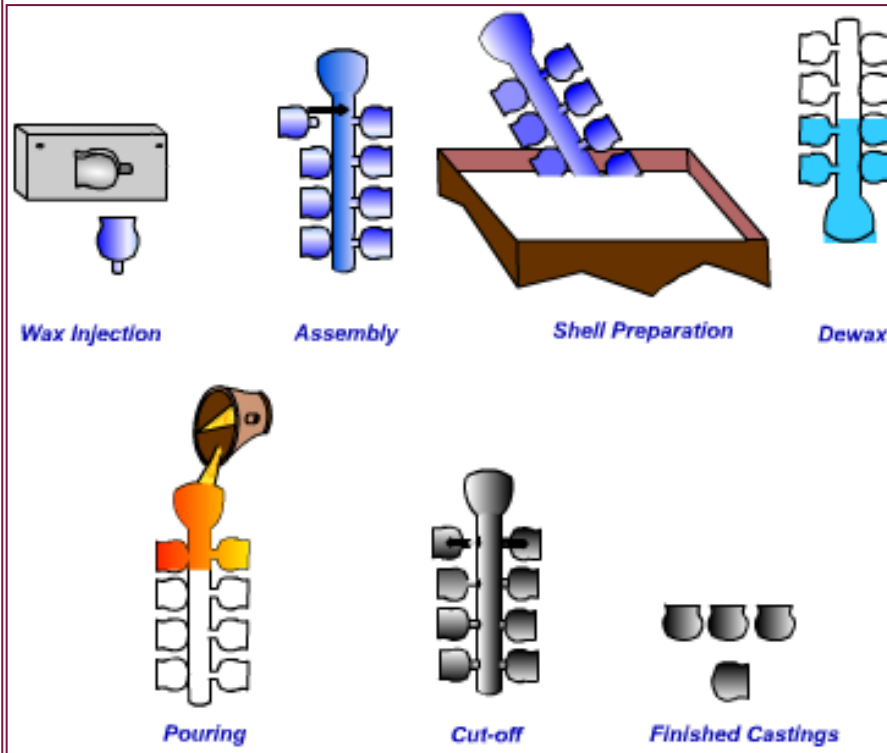
<http://www.youtube.com/watch?v=72017SJhZM>

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Manufacturing Methods

Investment Casting

1) Wax pattern injection, 2) Assembly of patterns into a tree, 3) Investment, firstly with a facecoat and then with backing stuccos, 4) Dewaxing, 5) Firing, 6) Casting, 7) knockout.

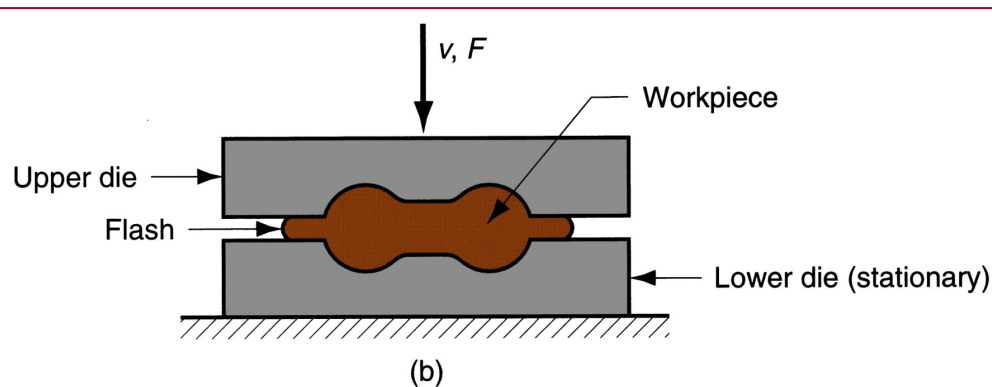


- An expensive process.
- Good surface finish.
- Good dimensional tolerance.
- Net-shape capability.
- Used for Ni-base alloys (turbine blades, and Co-base alloys (medical applications), artefacts, jewellery & surgical instrument, presently vanes & blades for gas turbines, wave guider for radar and triggers for fire arms.

Manufacturing Methods

Forging

- ❑ Forming a heated material by applying pressure with or w/out a shaped die (open die vs. cold die forging).
- ❑ Forging used for high strength fatigue-loaded components: e.g. hip stem.



Closed Die Forging



Manufacturing Methods

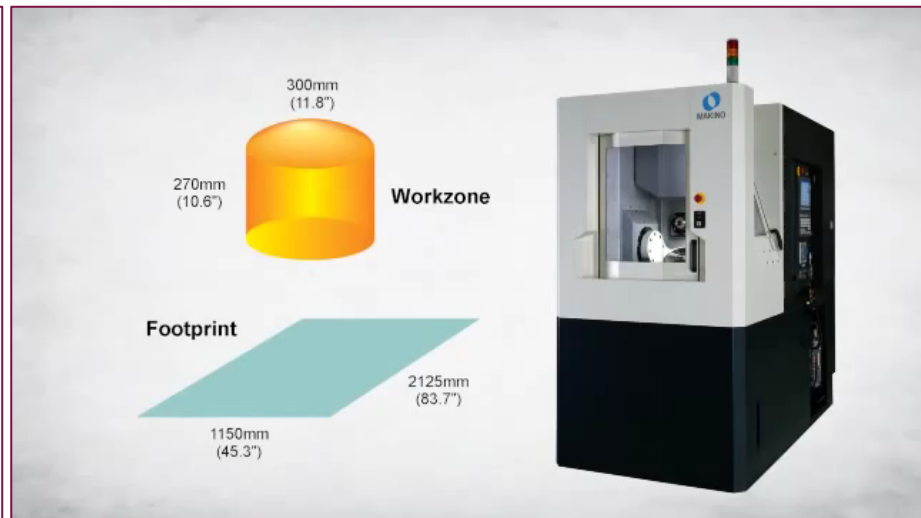
Machining

- Stents (laser micro-machining)
- Implants (CNC machining)



StarCut Tube

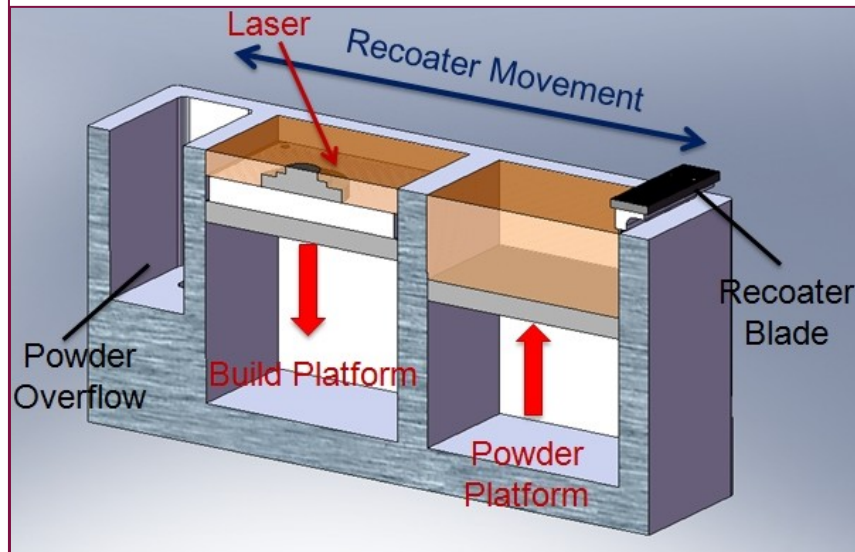
High-precision laser cutting system for tubes



Manufacturing Methods

Selective Laser Melting

- ❑ **Process:** Laser Powder Bed Fusion, Selective Laser Melting (SLM), metal 3D printing, or Additive Manufacture (AM).
- ❑ **Definition:** A process where thin layers of powders ($\sim 20\text{-}50\ \mu\text{m}$) are selectively melted and fused sequentially (usually on a substrate) to build 3D components from a CAD model.



Courtesy of EOS

Manufacturing Methods

Selective Laser Melting

□ Lower jaw



Manufacturing Methods

Electron Beam Selective Melting (ARCAM)

- ❑ **Process:** Selective melting using an electron beam source.
- ❑ **Description:** Similar to SLM, layers of powder are melted in a heated bed ($\sim 600\text{-}1000^{\circ}\text{C}$).
- ❑ **Advantages:** rapid, high throughput, resource efficient technology, multi-disciplinary technology.

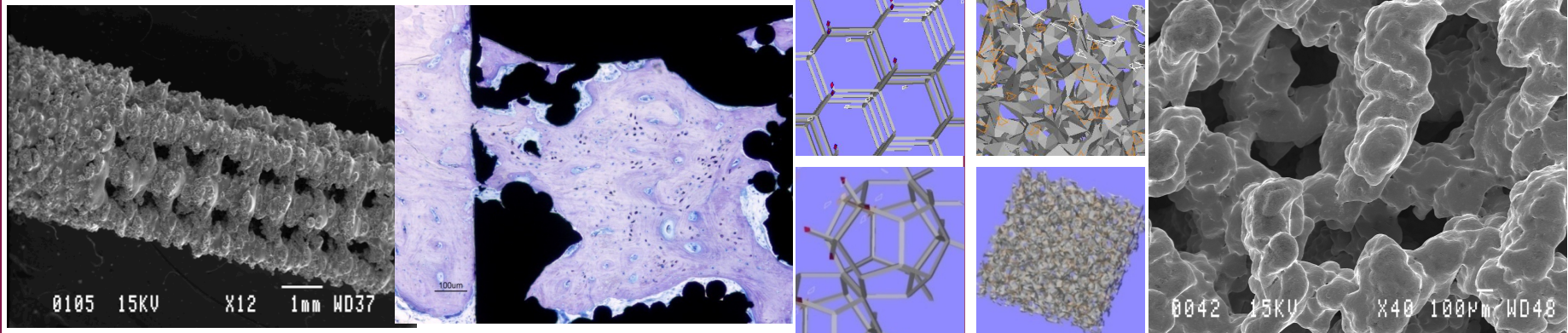
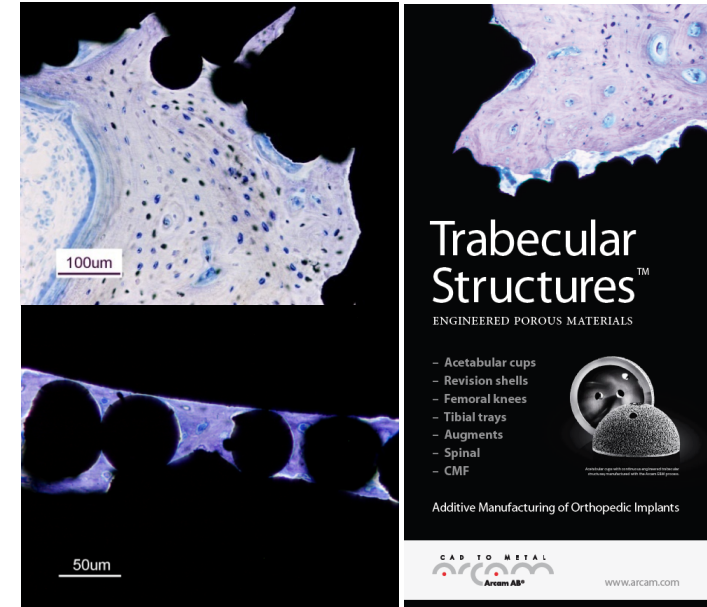


Courtesy of ARCAM

Trabecular Structures™

Created by EBSM (ARCAM) Technology

- Optimisation of the surface of medical implants for osteointegration (bio-compatibility)
 - Pore geometry (no limitation)
 - Pore size (down to $\sim 400 \mu\text{m}$)
 - Porosity (up to $\sim 85\%$)
- Competitive manufacturing costs
 - EBM® production cost, typical: $< 2 \text{ €/cm}^3$ trabecular structure



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Pictures of bone growing into EBM®-manufactured titanium implants with Trabecular Structures™. Courtesy of Professor Peter Thomsen, MD, Dept. of Biomaterials, University of Gothenburg.

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Trabecular Structures™

Created by EBSM (ARCAM) Technology

CE-certified since 2007

Material: Ti6Al4V
Build time: 16 cups in
10 hours



Courtesy of Adler Ortho s.p.a.

Fixa Ti-Por™ Acetabular Cup

Trabecular Structures™

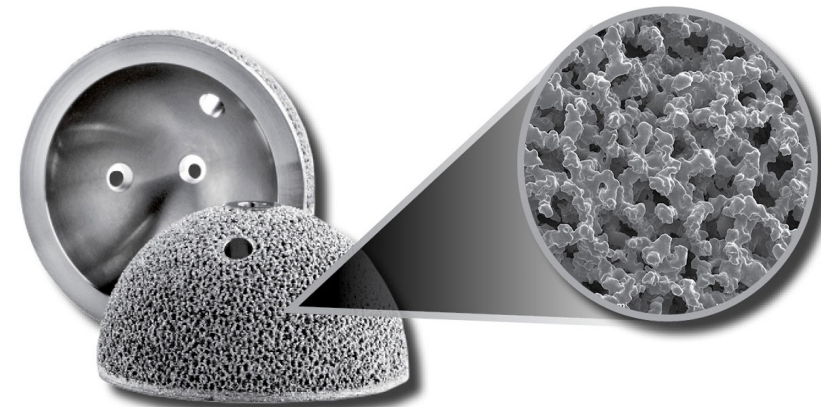
Created by EBSM (ARCAM) Technology

CE-certified since 2007

Material: Ti6Al4V
Build time: 16 cups in
10 hours



Courtesy of Lima-Lto s.p.a.

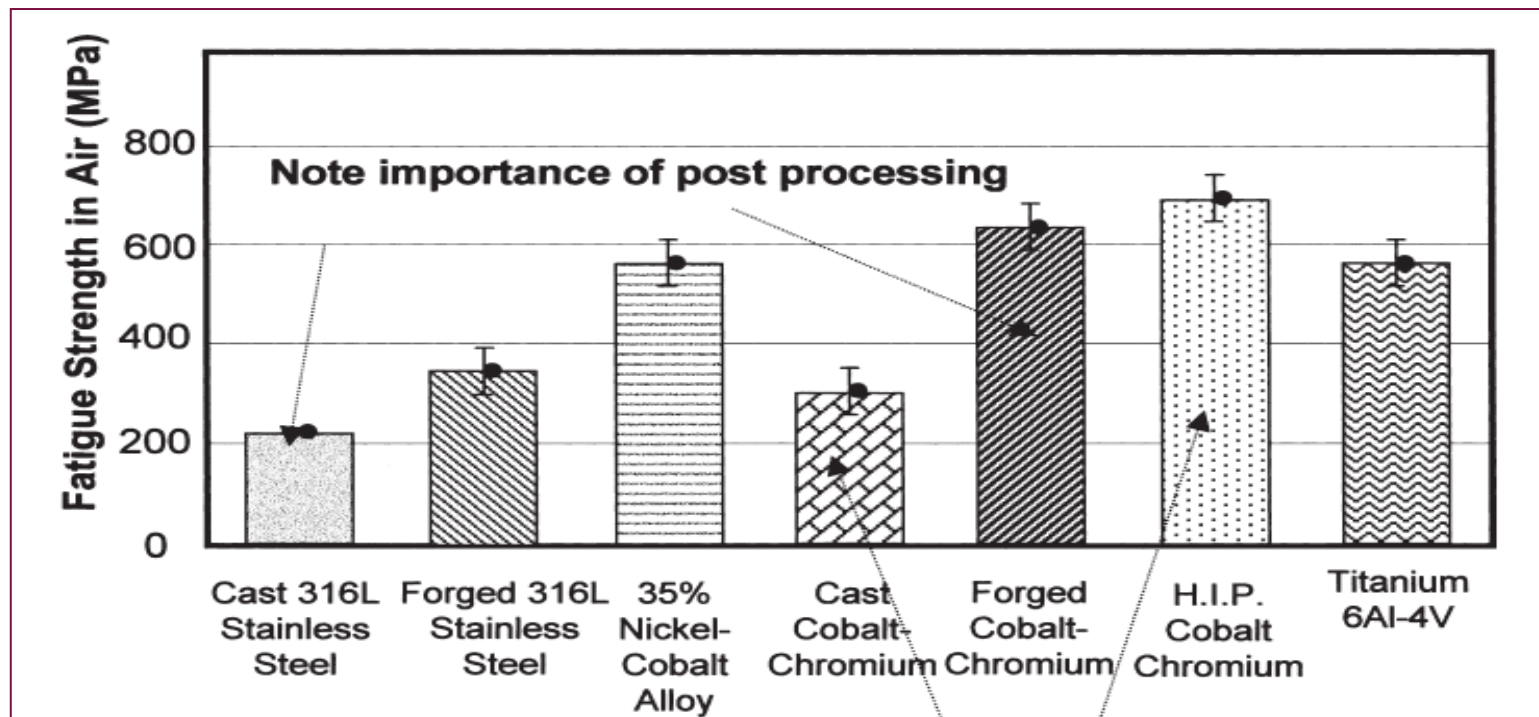


DELTA TT™ Acetabular Cup

Manufacturing Methods

Post-Processing

- Hot Isostatic Pressing (H.I.P.); a pressurised heat treatment process, can be used to enhance the mechanical properties of metallic implants.



U

Summary

B

Summary

- The biological performance of metallic medical implants depends on the alloy/material type, chemistry, and processing.
- The biocompatibility of the various metallic systems can be expressed in a number of factors:
 - Mechanical biocompatibility
 - Bio-inertness or Bio-tolerance
 - Mechanical performance (e.g. fatigue, wear, strength, etc...)
- Conventional processing techniques (e.g. investment casting, forging, and machining) have achieved consistent performance for the majority of implant classes.
- Novel processing techniques (e.g. metal 3D printing) offers the advantage of customisation.

Thank You. Questions?



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