Metallic Implant Materials

- 40% of annual 3.6 million orthopaedic operations
- $6 billion market
- 5 out of 100 Americans carry a piece of metal in them!

Metals for Implantation

- Must be corrosion resistant

- Mechanical properties must appropriate for desired application

- Areas subjected to cyclic loading must have good fatigue properties (implant materials cannot heal themselves !!!!)

- Three main categories of metals for orthopedic implants
  - Stainless steels
  - Cobalt-chromium alloys
  - Titanium alloys

- Additional metals used for dental implants
  Amalgam
  Gold

Metal Processing - Heating

- Strengthening by Heat Treatment
  - Possible in alloys to strengthen the material by precipitation- (or age) hardening
  - Material is rapidly cooled from a single phase to a multi-phase structure, with time allowing only small particles of the second phase to form
  - If the particles are uniformly distributed through the first phase, they act to impede dislocation movement and therefore strengthen the material

- Heating can also reduce a metal's strength by allowing grain growth to occur
  - Elevated temperature allows diffusion of atoms, which tend to move from more convex surface of a small grain boundary to a less convex surface of a large grain
  - Grain growth is not reversed by reducing the temperature, but recrystallization can be used to refine the grain size

Metal Processing - Annealing

-Material properties can be altered by processing a material so that it's grain or phase structure changes

- Annealing - heating a material above a material-dependent temperature, allows recrystalization
  - Temperature termed recrystalization temperature
  - Time also plays a role in the amount of recrystalization at any given temperature
  - Materials with more dislocations (higher energies) due to cold-working can be recrystallized at lower temperatures -- WHY?

Answer :Dislocations result in a higher energy at the molecular and grain level.
Recrystalization occurs when enough energy is added to allow the process to occur.
As dislocations already possess a higher energy state,less energy needs
to be added in the result of increasing the material temperature.

  - Reduces strength as dislocations are removed

Metal Processing - Cold Working

Also known as strain hardening

- Mechanical deformation at normal temperatures increases a material's strength (ultimate and yield strengths, plus shear strength) and hardness

WHY?

Answer: Dislocations which occur as a result of mechanical deformation interfere with the progression of other dislocations, resulting in an increase in stiffness, strength, and hardness.

•Amount of cold work (%) is equal to the percent of plastic strain undergone (defined by decrease in cross-sectional area)

•Strain-hardening also reduces ductility

- Part of deformation occurs before gage length is set for material testing

•Cold-working reduces the amount of plastic deformation that a material can undergo in subsequent processing and requires more power for further working

•Cold-working and annealing are often cycled to assist in production

Metal Processing - Hot Working

Mechanical deformation above recrystalization temperature

Metal remains soft and relatively ductile during processing
    - Reduced chance of cracking

Does not introduce permanent dislocations

Metallic Implant Materials

- Reduction of fracture, internal fixation
- Replacement of hip, knee and shoulder
- Oral and maxillofacial surgery

Types of Metallic Implants

- Stainless steel
- Cobalt Based Alloys
- Titanium Alloys

Composition? Properties? Manufacturing?

Stainless Steels

- The most common stainless steel: ***316L (AISI) L=low***
  - Fe 60-65 wt%
  - Cr 17-19 wt %
  - Ni 12-14 wt%

Stainless Steels

- Carbon content reduced to 0.03 wt%:
  - better resistance to *in vivo* corrosion.
- Why reduce carbon?
  - reduce carbide (**$Cr_{23}C_6$**) formation at grain boundary
  - carbide impairs formation of surface oxide

Stainless Steel Processing

- Work harden very quickly, so that cold-working requires intermediate heat treatments to resoften the metal

- Extreme heating can induce chromium carbide ($Cr_{26}C_6$) formation in the grain boundaries which can induce corrosion
    - Heat treatments must be done carefully
    - Welding not recommended
    - Also results in oxide scales on the metal surface, which must be removed by chemical treatment (acid) or sandblasting

- Following cold-working/heat treatment
    - Surface polished and cleaned
    - Metal is passivated with nitric acid
    - Implant is washed, packaged, and sterilized

Type	Condition	Ultimate Tensile Strength [MPa]	Yield Strength [MPa]	Elongation [%]
316	Annealed	515	205	40
	Cold-finished	620	310	35
	Cold-worked	860	690	12
316L	Annealed	505	195	40
	Cold-finished	605	295	34
	Cold-worked	860	690	12

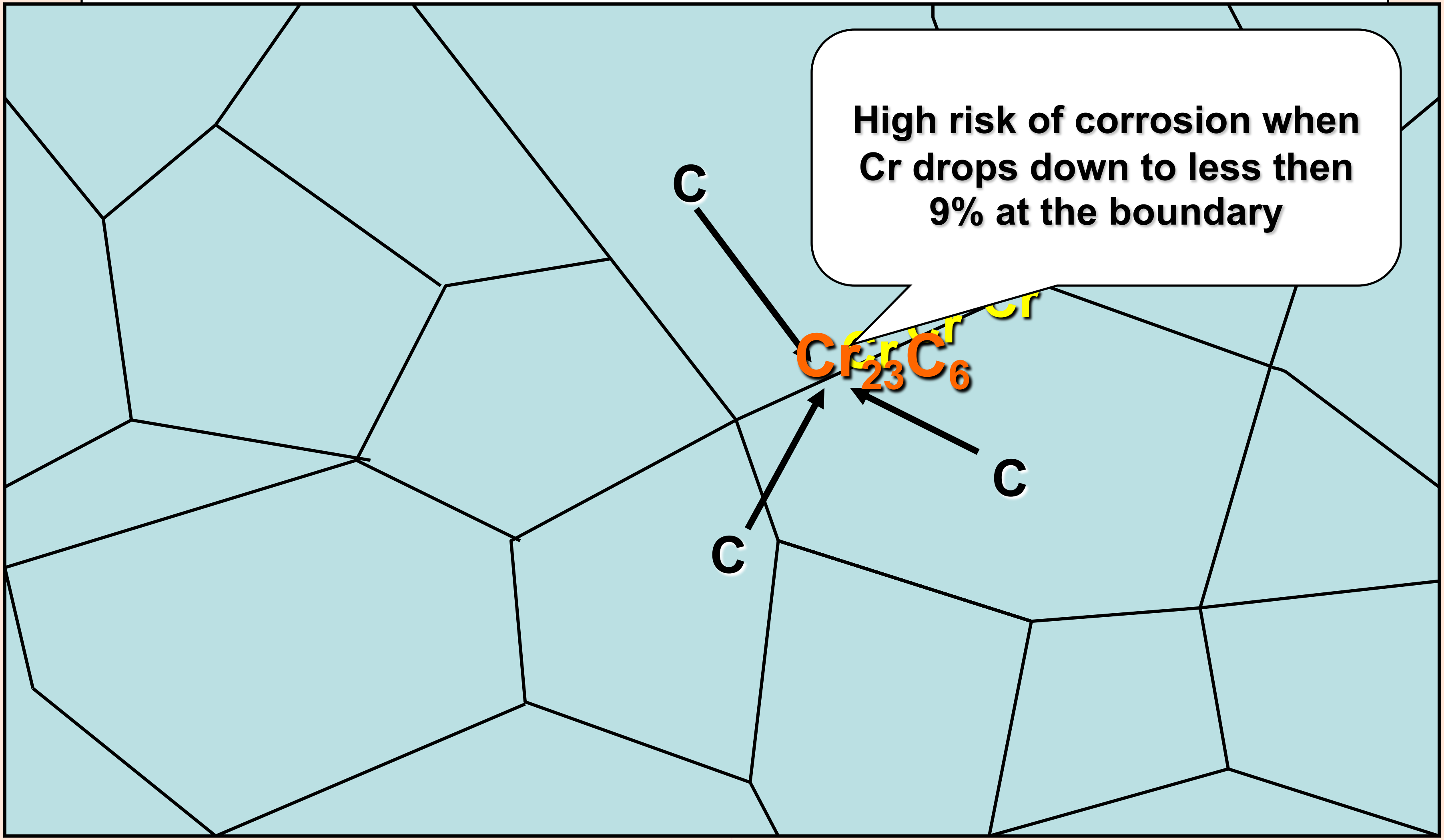
Stainless Steels

- Progression of use
  - Vanadium steel
  - 302 stainless - stronger and more corrosion resistant
  - 316 - addition of molybdenum to improve corrosion resistance in salt water
  - 316L - reduced carbon content from 0.08 wt% to 0.03 wt% to further improve corrosion resistance in chloride solutions

- Chromium is a major component of stainless steels
  - Chromium alloys can be passivated to give excellent corrosion resistance
    - Oxidizes to form transparent film on surface of material, sealing surface and preventing other oxidants from reaching the metal
    - Minimum effective concentration for this effect is 11 wt%

- Today most commonly used stainless steels for implant are 316 and 316L
  - Austentitic category - contain FCC iron
  - Not hardenable by heat treatment, but can be hardened by cold working
  - Non-magnetic
  - Contain Fe, Cr, Ni,Mo, Mn, *Si, C, P, and S*
    - Last four elements are trace elements, with a maximum concentration of 0.75 wt% each

Corrosion at the Grain Boundary



High risk of corrosion when Cr drops down to less then 9% at the boundary

Stainless Steels

- Why add chromium?
  - – corrosion resistance by formation of surface oxide
- Why add nickel?
  - – improve strength by increasing face centered cubic phase (austenite)

Stainless Steels

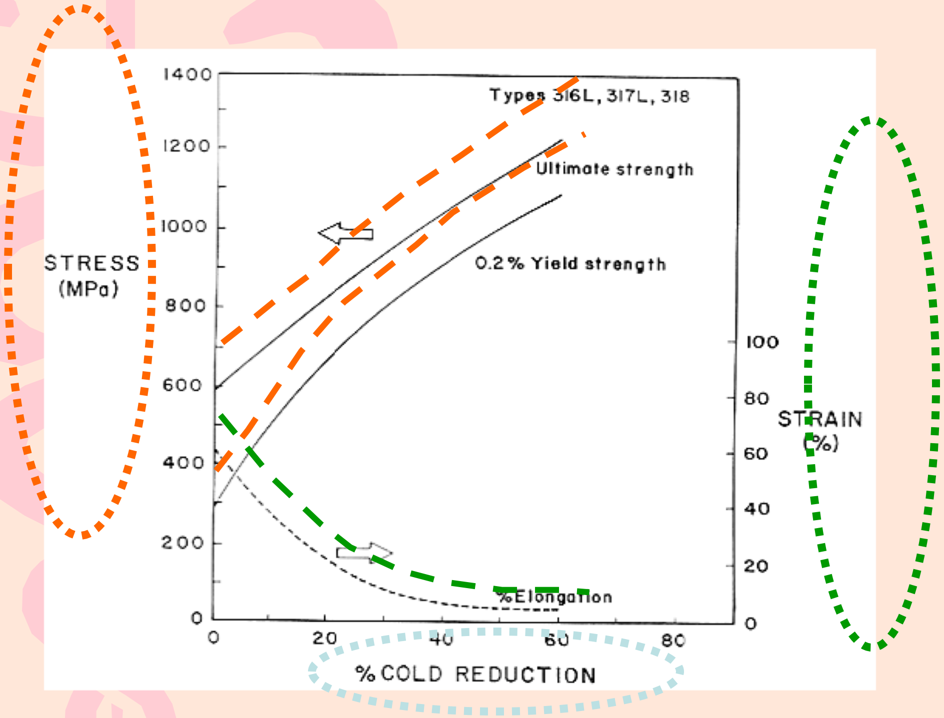
- Good stainless steel:
  - Austenitic (face centered cubic)
  - No ferrite (body centered cubic)
  - No carbide
  - No sulfide inclusions
  - Grain size less then 100 μm
  - Uniform grain size

Stainless Steels

- Improved mechanical properties by *cold working (a.k.a. strain hardening)*
- How? excessive number of dislocations are induced prior to in-vivo use, newer dislocations will be harder to induce

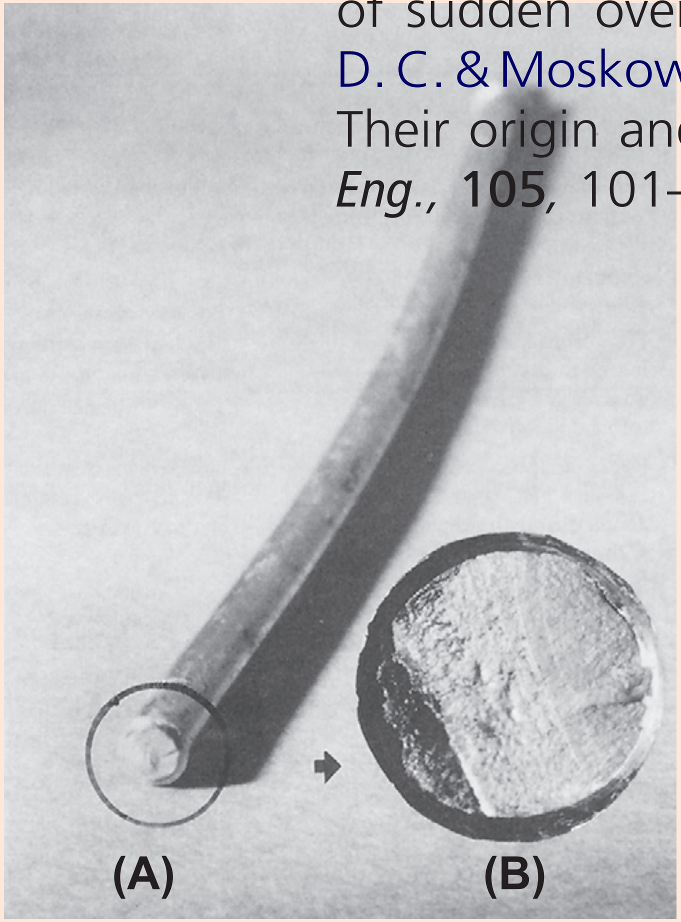
Stainless Steels

- How to cold work: load plastically.
- Pros: increased yield strength, ultimate strength and fatigue strength
- Cons: reduced ductility



Stainless Steels

FIGURE I.2.3.4 The smooth part of a 316L stainless steel Harrington spinal distraction rod that fractured by fatigue *in vivo*. Note the bend in the rod (the rod was originally straight) and (insert) the relationship of the crack initiation zone of the fracture surface to the bend. The inserted photo shows the nature of the fatigue fracture surface, which is characterized by a region of "beach marks" and a region of sudden overload failure. (Photo courtesy of Brunski, J. B., Hill, D. C. & Moskowitz, A. (1983). Stresses in a Harrington distraction rod: Their origin and relationship to fatigue fractures *in vivo*. *J. Biomech. Eng.*, **105**, 101–107.)



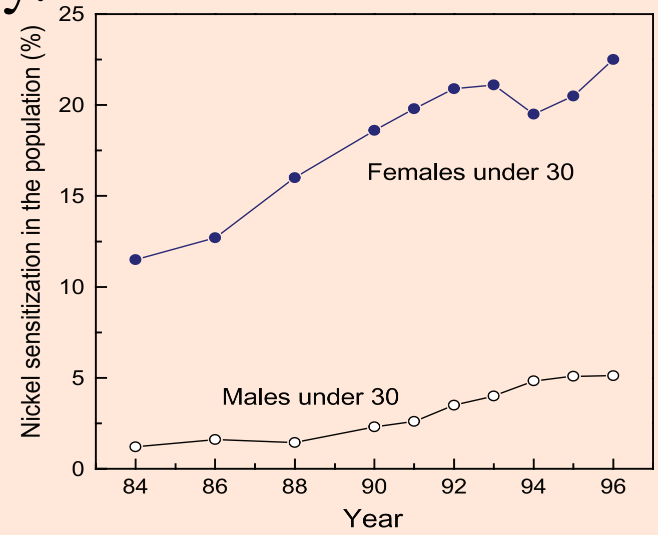
The essential character of Nickel

Although nickel may occur in the valency states -1, 0, +1, +2, +3 and +4, the most common valency of nickel is +2

The main path for divalent nickel (Ni-II) to enter the organism is through the digestive system. Indeed, many kinds of food contain appreciable amounts of nickel. Diets high in chocolate, nuts, dried beans, peas, and grains could supply more than 900 µg/day, while conventional diets usually provide around 150 µg/day. The other routine source of nickel in the diet is found in drinking water. Generally, the levels found in drinking water from sources around the world vary from 5-20 µg/l.

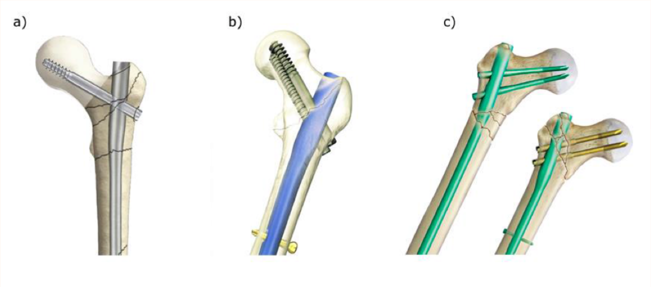
Exposure to Ni can effects human health, among which nickel allergy in form of contact dermatitis is the most common and well-known reaction. Ni ions are the most widespread skin contact allergen in Europe that has become a serious medical problem. The number of women affected by Ni allergy has doubled every year of the last few decades. Dermatologists assumed about 20% of young women and 4% of young men are suffering from the Ni allergy.

The allergic effect of nickel and nickel alloys originates from their easy ionization by **human sweat** upon contact with the skin. The higher prevalence of nickel allergy in women is not genetically determined, but could be related to more frequent daily use of nickel-containing utensils and jewelry. **A higher incidence of lung and nasal cancer among Ni mining, smelting and refinery workers**



In 1994, the European Parliament and Council adopted the Nickel Directive (the European Directive 94/27/EC of 30 June 1994), which entered into full force in 2001. The Nickel Directive limits the nickel content in items used for epithelization after piercing (limit 0.05%), and the nickel release from objects intended for use in direct and prolonged contact with skin ($< 0.5 \mu g\ cm^{-2}\ week^{-1}$)

“NUOVI” ACCIAI PER APPLICAZIONI BIOMEDICALI



It is important to distinguish between stainless steel grades used for implant applications and the commercial grade stainless steels used for other medical devices. In the EU, the Council Directive 93/42/EEC **defines implants as medical devices that are exposed to human tissue for more than 30 days.** Subsequent medical device guidance has, however, provided further clarification by the introduction of following three definitions based on the duration that the medical device is in contact with human tissue.

Transient (normally intended for continuous for less than 60 minutes); **Short term** (normally intended for continuous for not more than 30 days); **Long term** (normally intended for continuous for more than 30 days

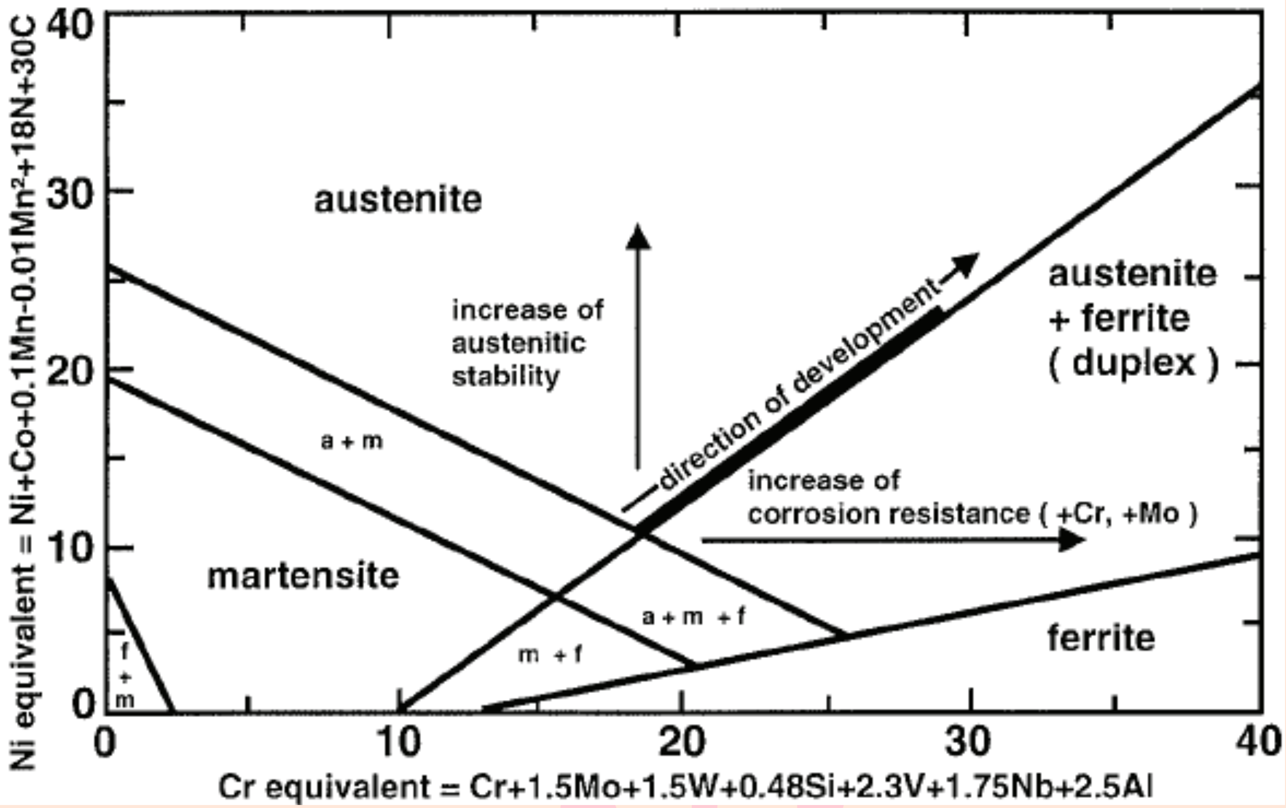


Grafico di Schaeffler

Figure 2. Development of biocompatible nitrogen-containing austenitic stainless steels (reproduced with permission from Iron and Steel Institute of Japan).

Nickel-free austenitic stainless steel is non-ferromagnetic, and the nickel in steels can be replaced by either nitrogen or manganese or both. Both nitrogen and carbon are potent and effective stabilizers of austenite structure; however, small addition of carbon can decrease the corrosion resistance of steel and also enhance its tendency to form precipitates

Nickel-free austenitic stainless steel

Nitrogen (N), which is one of the austenitizing elements, is an important alloying element in austenitic stainless steels in terms of corrosion resistance and strength. Nitrogen dissolved in austenitic stainless steel improves its strength resistance to **pitting corrosion** and **crevice corrosion** in solutions containing **chloride ions**. The related mechanisms are summarized as follows

(1) N in solid solution produces NH^{+4}, hindering oxidation inside a pit;

(2) Concentrated N at the passive film/alloy surface stabilizes the film and prevents the attack by anions (Cl^{-});

(3) Nitrate ions are produced to improve resistance to pitting corrosion;

(4) N addition stabilizes the austenitic phase; and

(5) N blocks kinks and controls the increase of electric current for pit production.

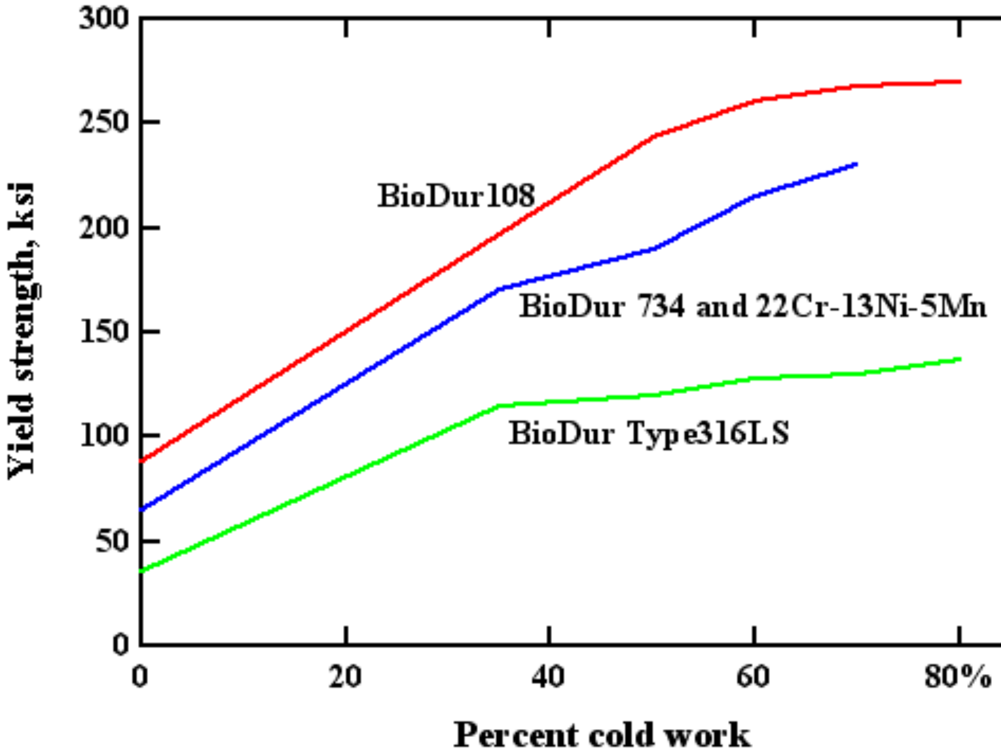
Therefore, austenitic high-nitrogen stainless steels containing over 0.3 wt% N have been developed.

On the other hand, Ni-free austenitic stainless steels have been designed where Ni is replaced by N and Mn; such steels show high strength and corrosion resistance.

23Cr 23Mn 1Mo 0.9N alloy (BioDur 108 - USA)

(Cr18) (Mn18) (Mo2) (N1%) Germany

(Cr15–18) (Mn10-12) (Mo3–6) (0.9 N) Switzerland



A typical yield strength of BioDur 108 alloy is approximately 606MPa in the annealed condition. In comparison, typical yield strength of BioDur 316L is approximately 241MPa. The nitrogen-strengthened BioDur 734 and Fe-22Cr-13Ni-5Mn steels, with more nitrogen than BioDur 316L but less than BioDur 108 alloy, typically exhibit approximately 448 MPa. The high nitrogen content in BioDur 108 alloy enhances the effect of cold working and further increases the strength level

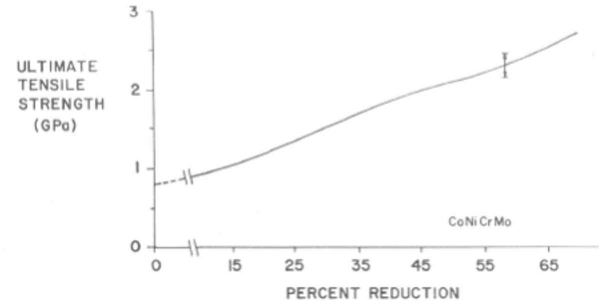
Cobalt Based Alloys

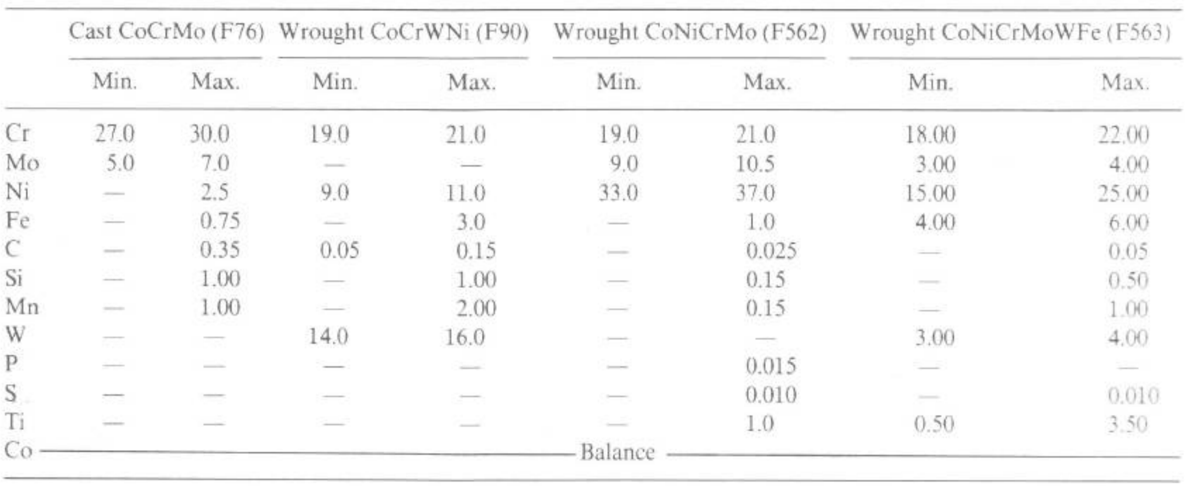
Common types for surgical applications, ASTM designation:

- **Co Cr Mo** (F76) fusione/colata
- Co Cr W Ni (F90) utensili o forgiatura
- **Co Ni Cr Mo** (F562) utensili o forgiatura
- Co Ni Cr Mo W Fe (F563) utensili o forgiatura

I due principali elementi costitutivi Co e Cr formano una soluzione solida solo per percentuali in peso di Cr <35%, Il Mo permette l’ottenimento di una grana fina che a sua volta si traduce in un‘elevata resistenza meccanica delle leghe anche dopo il processo di colata o di forgiatura.

La lega Co Ni Cr Mo presenta un‘elevata resistenza alla corrosione, anche in presenza di cloruri e sotto sforzo. Inoltre, la lavorazione a freddo ed il conseguente incrudimento possono aumentare considerevolmente la resistenza meccanica di tale lega





	Cast CoCrMo (F76)		Wrought CoCrWNi (F90)		Wrought CoNiCrMo (F562)		Wrought 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							

Tab. 6.1.1. Composizione chimica delle leghe di cobalto impiegate per realizzare impianti chirurgici.

Cobalt Alloys: ASTM F76

- Co-Cr-Mo
- (Co=55-65%, Cr=27-30%, Mo=5-7%)
  (Fe=0.1-0.75%, C=0.1-0.4%, Ni=0.1-2.5%)
- Surface oxide; thus corrosion resistant
- Wax models from molds of implants
- Wax model coated with ceramic and wax melted away
- Alloy melted at 1400 °C and cast into ceramic molds.

Cobalt-Chromium Alloys

Two general compositions

- Co-Cr-Mo - typically cast into desired form
  - Used for many years in dental implants
  - More recently used in artificial joints
  - Good corrosion resistance

- Co-Ni-Cr-Mo - (typically 35% of Co and Ni), normally hot forged
  - Typically used for stems of highly loaded implants, such as hip and knee prostheses
  - High degree of corrosion resistance in salt water when under stress
  - Cold-working can increase strength by more than 100 %, but is impractical for large structures such as femoral stems
  - Poor frictional properties with itself or any other material

    What would this preclude in terms of application?

Answer

Higher fatigue and ultimate tensile strength than Co-Cr-Mo
Good for components with long service life requirements

- Co and Cr are dominant elements, forming a solid solution of up to 65 wt% Co
  - Mo when added, produces finer grains

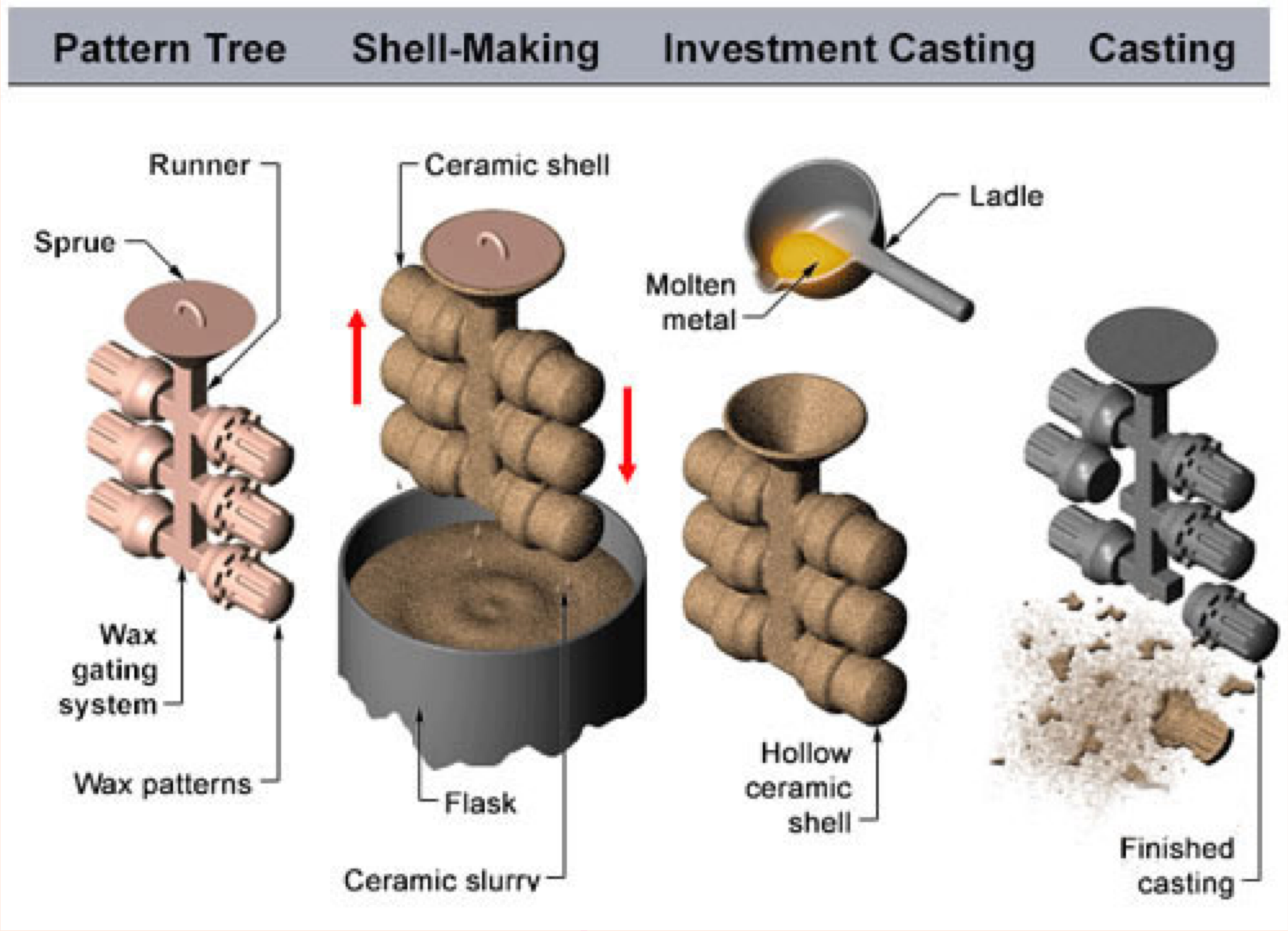
Cobalt-Chromium Processing

- Co-Cr-Mo
  - Cast into molds, originally made from wax patterns
  - The temperature of the mold during casting (800 - 1000° C) determines the grain size
  - Coarse grains at higher temperatures, weaker material but less brittle due to carbide precipitates

- Co-Ni-Cr-Mo
  - Hot forging allows shaping through plastic deformation without inducing crack formation
  - Less energy is required for deformation in heated materials
  - The heated metal is then shaped through compression, often between dies

These dental instruments require alloys that have good corrosion resistance, machinability, and edge retention.

LOST WAX CASTING – INVESTEMENT CASTING



Un metodo per incrementare la resistenza, utilizzato in particolare per la lega Co Cr Mo, è rappresentato dalla pressatura isostatica a caldo (**hot isostatic pressing - HIP**), effettuata una volta che la lega sia stata “atomizzata” sotto forma di piccolissime particelle in un’‘apposita camera. Le particelle, vengono poi setacciate per ottenere una distribuzione granulometrica uniforme ed inserite infine in una camera di pressatura isostatica a caldo. La temperatura della camera è inferiore rispetto alla temperatura di fusione della lega.

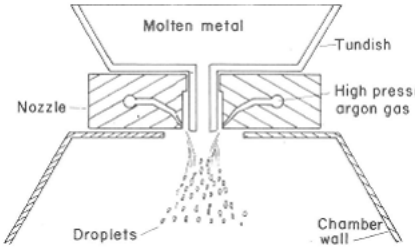


Fig. 6.1.3. Processo di atomizzazione della lega CoCrMo.

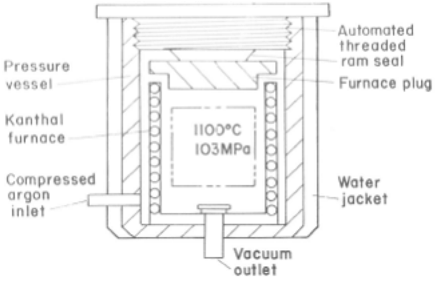


Fig. 6.1.4. Camera di pressatura isostatica a caldo.

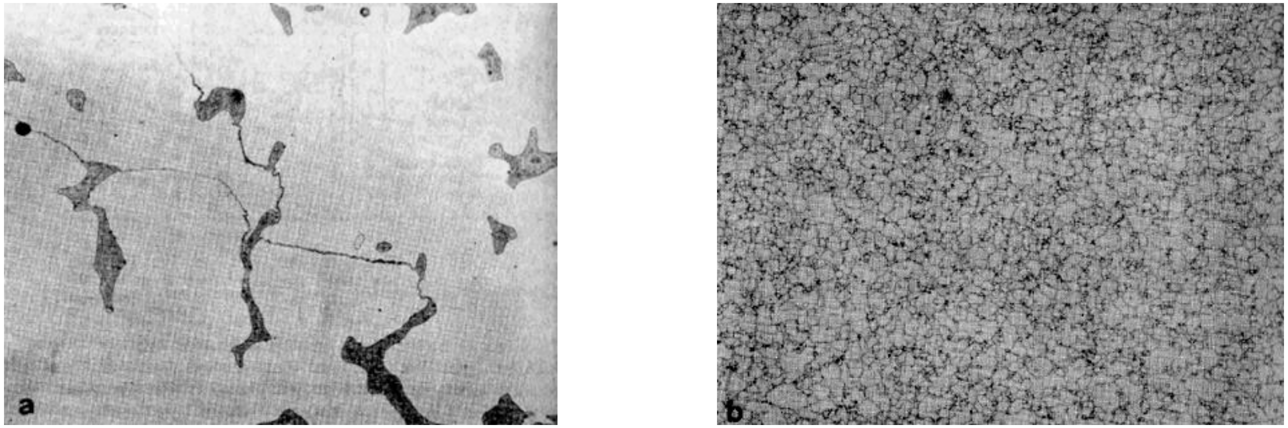


Fig. 6.1.5. Microstruttura della lega CoCrMo ottenuta per: a) colata (500x), b) pressatura isostatica a caldo (500x).

Type	Condition	Tensile Strength [MPa]	Yield Strength [MPa]	Elongation [%]
Cast Co-Cr-Mo (F76)		655	450	8
Wrought Co-Ni-Cr-Mo (F562)	Solution Annealed	795 - 1000	240 - 655	50
Wrought Co-Ni-Cr-Mo (F562)	Cold-worked	1790	1585	8

Produzione delle leghe Co-Cr

Le leghe ottenute per colata contengono una piccola percentuale di C (0,35-0,5% in peso) che ha lo scopo di aumentare la loro “colabilità” abbassando la temperatura di fusione da 1450-1500° C (tipica del sistema binario Co-Cr) a 1350° C.

La microstruttura di colata consiste in una matrice dendritica contenente dei carburi dispersi (M23C6, M7C3, M6C, dove M = Co, Cr, Mo) e altri composti intermetallici. Dopo il semplice trattamento di colata, le leghe presentano una ridotta resistenza e duttilità. Di conseguenza si rende necessaria l’‘esecuzione di un trattamento termico condotto a 1210-1250° C, che permetta la completa dissoluzione dei carburi all’‘interno della matrice. La dissoluzione dei carburi porta alla formazione di elementi che rafforzano per soluzione solida la matrice. Per non ottenere un’‘eccessiva crescita dei grani, si evita di disciogliere completamente i carburi. Queste poche particelle residue si localizzano a bordo grano esercitando un effetto di “pinning” (= ancoraggio) sullo stesso.

Le leghe Co-Cr **lavorate** sono caratterizzate da un minore contenuto di cromo rispetto alle leghe Co-Cr per colata, generalmente compreso tra il 19 e il 21% in peso.

In tali leghe parte del cromo è sostituito dal molibdeno o dal tungsteno. Al fine di stabilizzare la fase fcc è inoltre necessario un certo contenuto di nickel, ferro o manganese.

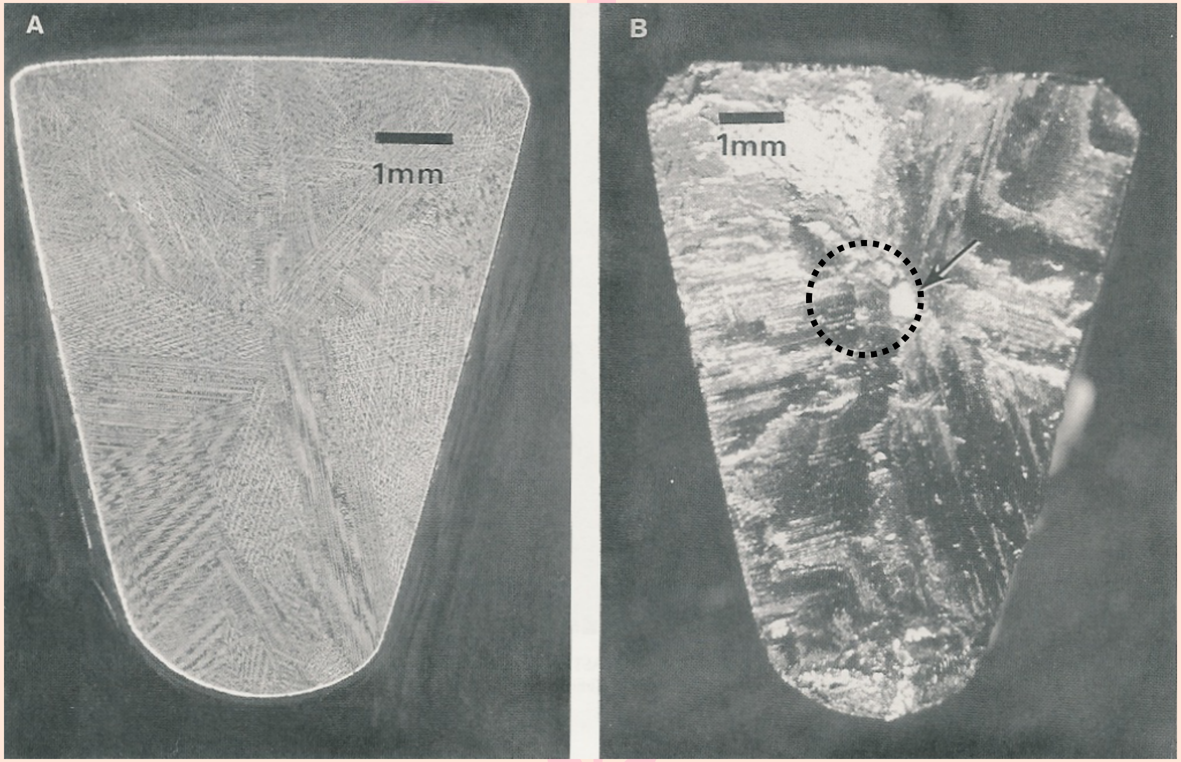
A causa dell'elevata resistenza di queste leghe, è necessario applicare sollecitazioni molto elevate durante il processo di forgiatura. Per ottenere deformazione plastica, le leghe Co-Cr lavorate devono essere sottoposte a ricottura ("annealing") per ottenere una struttura fcc che possa essere mantenuta anche dopo il successivo raffreddamento a temperatura ambiente. La trasformazione hcp, che provoca un incremento delle proprietà meccaniche, può essere indotta mediante la deformazione meccanica impressa. Dopo la lavorazione a caldo (forgiatura), la microstruttura comprende una matrice cubica a facce centrate (fcc) contenente delle piccole piastrine con struttura esagonale compatta (hcp). Un ulteriore incremento delle proprietà meccaniche, in particolare della durezza, può essere ottenuto effettuando una lavorazione a freddo (che produce incrudimento) seguita da un invecchiamento condotto a 500-600° C per 1-4 ore. In tal modo si ottiene la precipitazione di particelle di Co3Mo ed il conseguente aumento della durezza della lega.

Cobalt Alloys: ASTM F 76

- Three caveats:
  - Carbide formation ⌈ corrosion.

  Solution: anneal at 1225 ° C for one hour.
  - Large grain size | reduced mechanical strength
  - Casting defects ⌈ stress concentration, propensity to fatigue failure

The enemy within: Casting defect



Polished-etched view of a cast ASTM F75 femoral hip stem. Note dendrites and large grains

In vivo fracture initiated from a an inclusion formed during the casting process

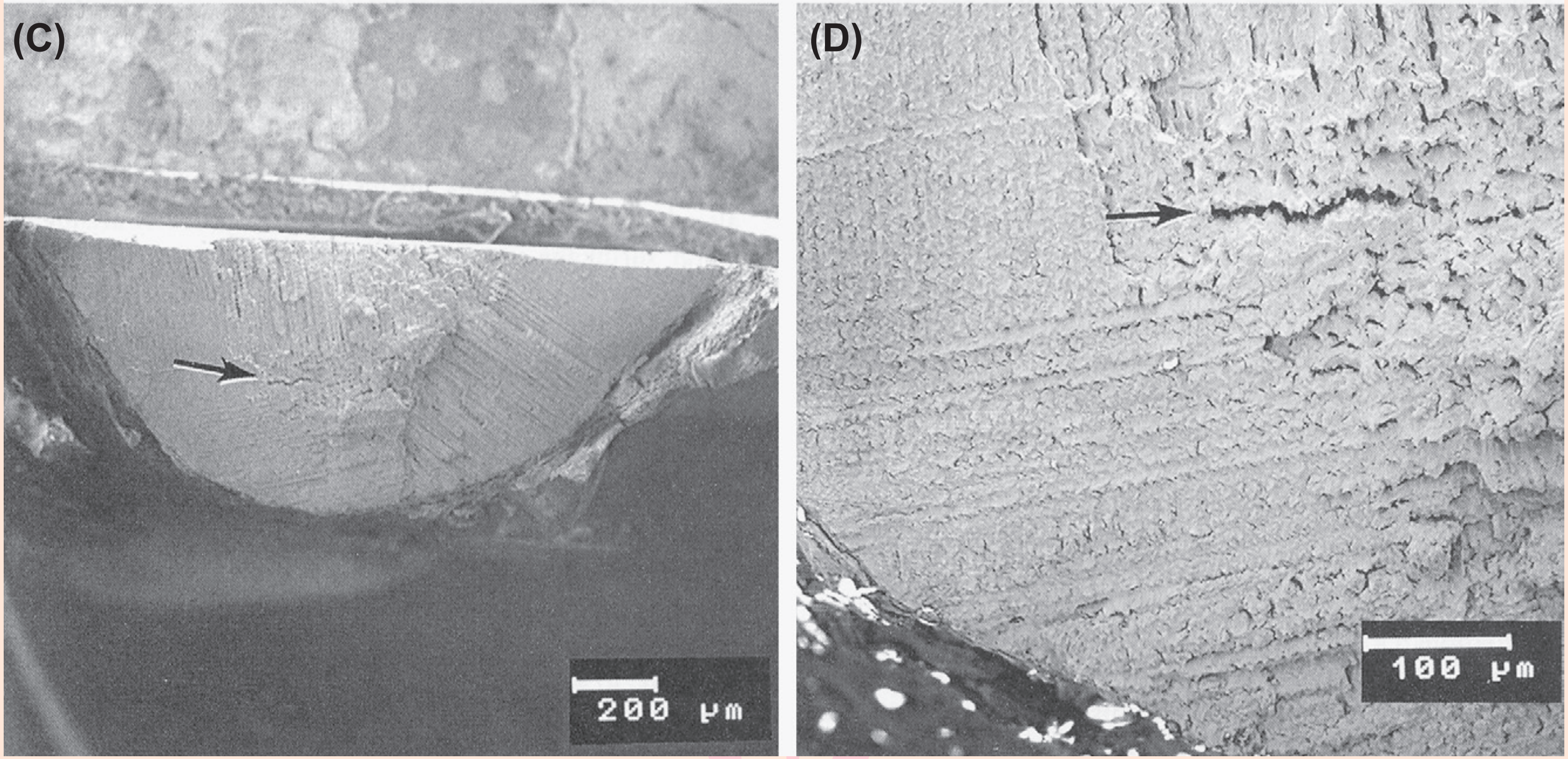


FIGURE I.2.3.2 (A) Macrophoto of a metallographically polished and etched cross-section of a cast Co–Cr–Mo ASTM F75 femoral hip stem, showing dendritic structure and large grain size. (B) Macrophoto of the fracture surface of the same Co–Cr–Mo ASTM F75 hip stem as in (A). Arrow indicates large inclusion within the central region of the cross section. Fracture of this hip stem occurred *in vivo*. (C), (D) Scanning electron micrographs of the fracture surface from a cast F75 subperiosteal dental implant. Note the large grain size, dendritic microstructure, and interdendritic microporosity (arrows).

Cobalt Alloys: ASTM F 799

- Modified form of F75: hot forged after casting
- Mechanical deformation induces a shear induced transformation of FCC structure to HCP.
- Fatigue, yield and ultimate properties are twice of F76.

Cobalt Alloys: ASTM F90

- W and Ni are added to improve machinability and fabrication
- (Co=46-58%, Cr=19-21%, Mo=4-7%)

(W=14-16%, C=0.05-0.15%, Ni=9-11%)

- Mechanical properties similar to F76
- Mechanical properties double F76 if cold worked

Titanium Based Alloys

- Lighter & more elastic
- Good mechanical properties
- Good corrosion resistance due to TiO_2 solid oxide layer

Titanium and Titanium Alloys

High strength to weight ratio

- Density 4.5 g/cm^3 as opposed to 7.9 g/cm^3 for 316 SS and 8.3 g/cm^3 for Co-Cr-Mo or 9.2 g/cm^3 for Co-Ni-Cr-Mo alloys

- Unalloyed titaniums classified based on inclusion of impurities
  - Levels carefully controlled
  - O_2 present has large effect on ductility and strength - more O_2 -> stronger and harder

- Most common alloy is Ti-6A1-4V
  - Al increases transformation temperature between alpha and beta phases
  - V decreases the transformation temperature between the alpha and beta phases
  - Alpha alloys
    - # Good weldability
    - # High strength
    - # Oxidation resistance at high temperatures
    - # Single phased with no two-phase structure at lower temperatures, cannot be heat treated (See Figure 2)
  - Beta alloys - Stronger than alpha phased alloy
    - # Alpha - Beta alloys Alloys formed by heat treating beta solutions are stronger than an annealed alpha-beta alloy

Classification	Tensile Strength [MPa]	Yield Strength [MPa]	Elongation [%]
Titanium - **Class 1 to 4 (CP)**	240 - 550	170 - 485	24 - 15
Ti-6Al-4V Alloy	860	795	10

Titanium Alloy Processing

- Highly reactive with oxygen at high temperatures
  - Will burn easily
  - Will at least absorb oxygen, which has what effect?

Answer

High temperature processing requires an inert atmosphere, often processed in a vacuum

Hot working or forging should be done below 925° C

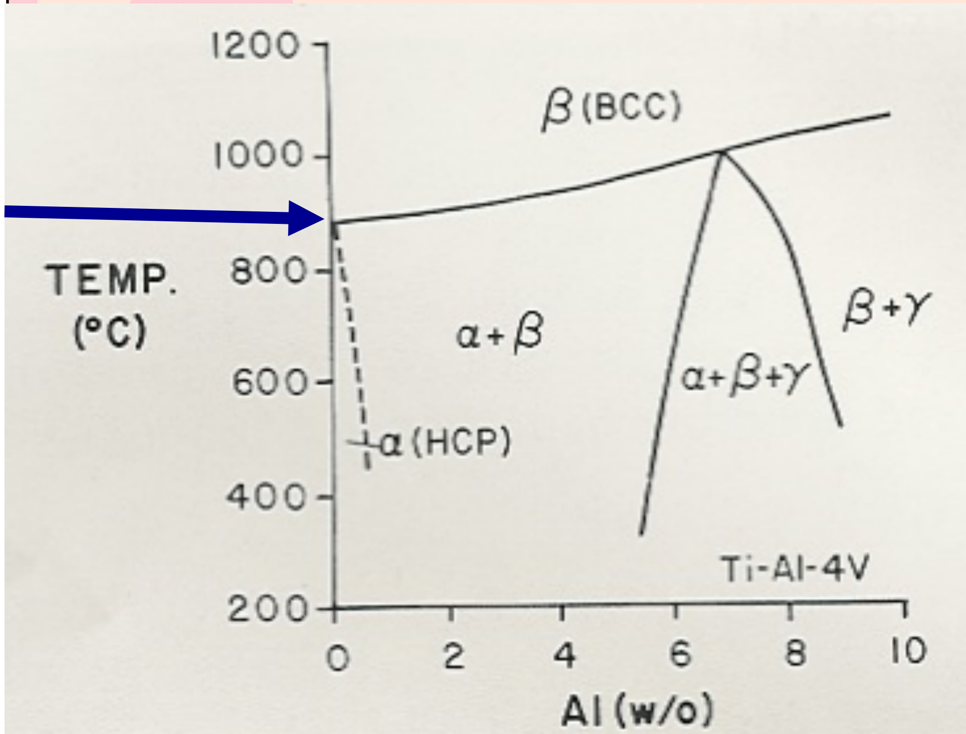
- Machining problems exist due to mechanical reaction with other metals
  - Can be minimized by using very sharp tools at low speeds
  - Electrochemical machining also avoids this problem

Titanium Based Alloys

- Ti-6% wt Al-4% wt V (ASTM F136) is widely used
- Contains impurities such as N, O, Fe, H, C
- Impurities increase strength and reduce ductility

Titanium Alloys: ASTM F136

- HCP structure transforms to BCC for temperatures greater than 882 ° C.
- Addition of Al stabilizes HCP phase by increasing transformation temperature
- V has the inverse effect



The **Ti–6Al–7Nb** alloy has been developed as a replacement for the Ti–6Al–4V alloy. This alloy was developed and is mainly used in Europe because one of its components, **vanadium**, shows strong cytotoxicity, although there has been no report of accidents when using Ti–6Al–4V alloy implants.

Its corrosion resistance and safety are greater than those of Ti–6Al–4V.

Ti–6Al–2.5Fe alloy also developed in Europe, the Ti–13Zr–13Ta alloy (nearly β) developed in the United States, and the Ti–6Al–2Nb–1Ta and Ti–15Zr–4Nb–4Ta alloys developed in Japan have been standardized. These are $\alpha + \beta$ type alloys.

The lower elongation of $\alpha + \beta$ type Ti alloys than that of stainless steel has caused an ‘artificial fracture’ or ‘human error’ in spinal fixators and maxillofacial plates because the elongation to fracture of $\alpha + \beta$ type Ti alloys is only about 10–17%.

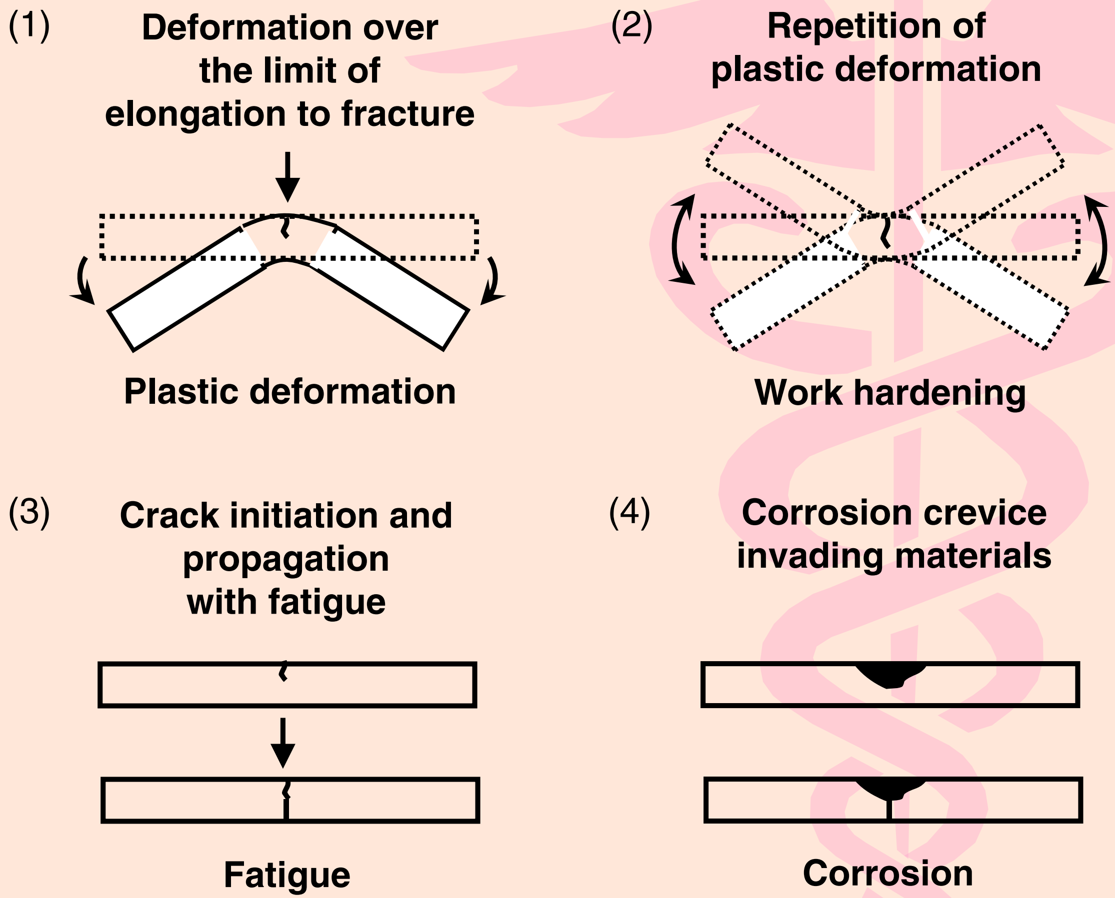
The following four causes of fracture of metals are feasible in medicine:

(i) larger plastic deformation than the elongation to fracture is applied by medical doctor at the operation site,

(ii) multiple plastic deformation is applied if the first bending by the doctor at the operation site is unsuccessful,

(iii) alloy fatigue and

(iv) large crevices as a result of corrosion initiate fracture.



(1) **Deformation over the limit of elongation to fracture**

Plastic deformation

(2) **Repetition of plastic deformation**

Work hardening

(3) **Crack initiation and propagation with fatigue**

Fatigue

(4) **Corrosion crevice invading materials**

Corrosion

Figure 1. Causes of fracture of metals in medicine: (i) larger plastic deformation than the elongation to fracture is applied by medical doctor at the operation site; (ii) multiple plastic deformation is applied if the first bending by the medical doctor at the operation site is unsuccessful; (iii) alloy fatigue; (iv) large crevices as a result of corrosion work initiate fracture.

To prevent fractures such as those described in (i) and (ii), specific training of medical professionals is required to understand the relationship between the fracture and elongation and work hardening. **In addition, the development of α + β type Ti alloys having large elongation and sufficient strength is required..**

The requirement for a low Young’s modulus to prevent stress shielding in bone fixation is fulfilled by **β-type alloys**, in which the Young’s modulus may decrease to **about 60GPa**. Various β-type alloys,

Ti–12Mo–6Zr–2Fe and

T–15Mo (lega beta)

Ti–15Mo–5Zr–2Al have been developed in the United States.

Ti–29Nb–13Ta–4.6Zr has been developed as a β-type alloy. This alloy has the lowest Young modulus ($\simeq$ 60 GPa)

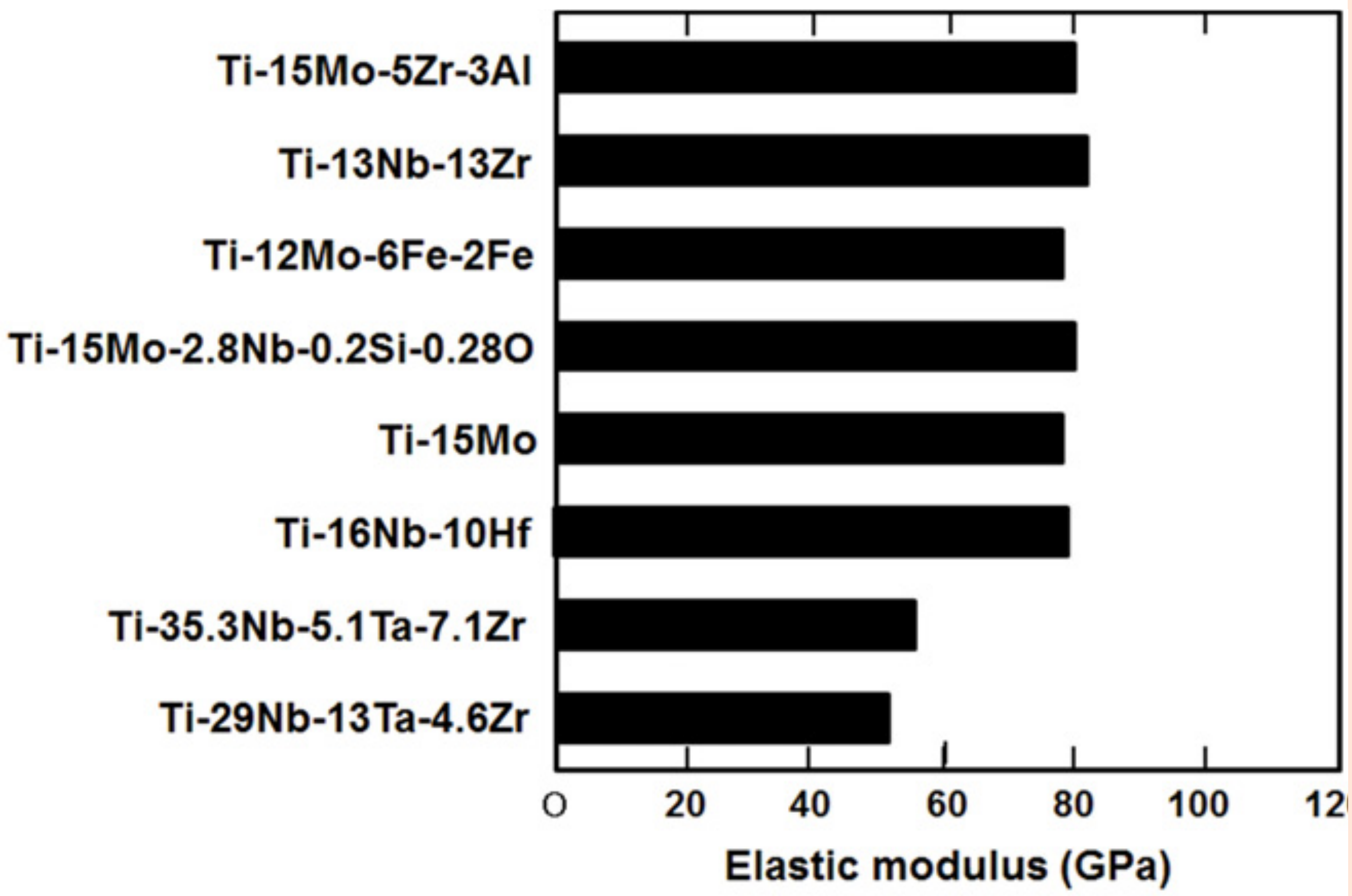
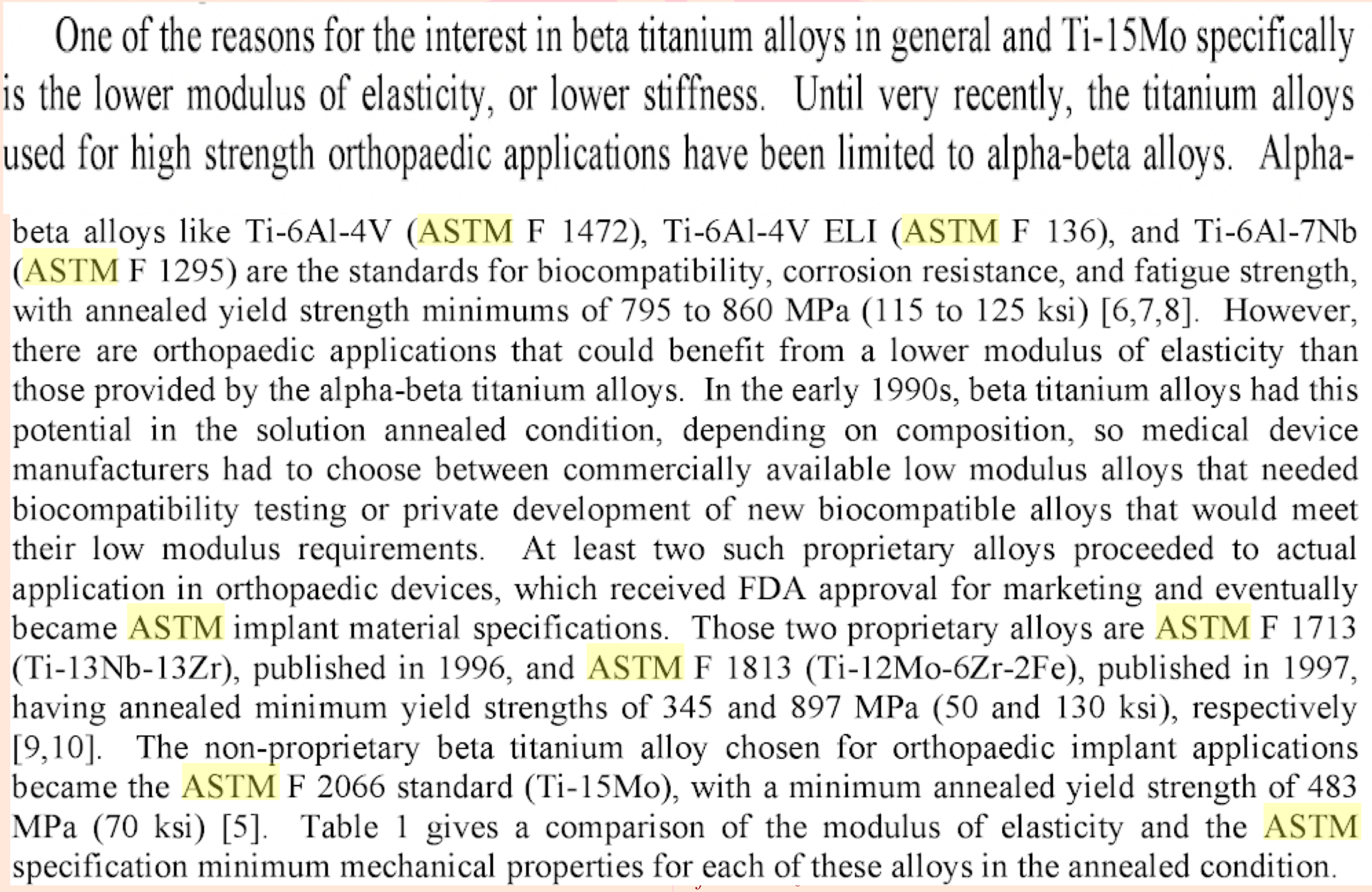


Figure 3. Elastic moduli of β-type alloys [4].

Titanium Alloys



One of the reasons for the interest in beta titanium alloys in general and Ti-15Mo specifically is the lower modulus of elasticity, or lower stiffness. Until very recently, the titanium alloys used for high strength orthopaedic applications have been limited to alpha-beta alloys. Alpha-beta alloys like Ti-6Al-4V (ASTM F 1472), Ti-6Al-4V ELI (ASTM F 136), and Ti-6Al-7Nb (ASTM F 1295) are the standards for biocompatibility, corrosion resistance, and fatigue strength, with annealed yield strength minimums of 795 to 860 MPa (115 to 125 ksi) [6,7,8]. However, there are orthopaedic applications that could benefit from a lower modulus of elasticity than those provided by the alpha-beta titanium alloys. In the early 1990s, beta titanium alloys had this potential in the solution annealed condition, depending on composition, so medical device manufacturers had to choose between commercially available low modulus alloys that needed biocompatibility testing or private development of new biocompatible alloys that would meet their low modulus requirements. At least two such proprietary alloys proceeded to actual application in orthopaedic devices, which received FDA approval for marketing and eventually became ASTM implant material specifications. Those two proprietary alloys are ASTM F 1713 (Ti-13Nb-13Zr), published in 1996, and ASTM F 1813 (Ti-12Mo-6Zr-2Fe), published in 1997, having annealed minimum yield strengths of 345 and 897 MPa (50 and 130 ksi), respectively [9,10]. The non-proprietary beta titanium alloy chosen for orthopaedic implant applications became the ASTM F 2066 standard (Ti-15Mo), with a minimum annealed yield strength of 483 MPa (70 ksi) [5]. Table 1 gives a comparison of the modulus of elasticity and the ASTM specification minimum mechanical properties for each of these alloys in the annealed condition.

Titanium Alloys

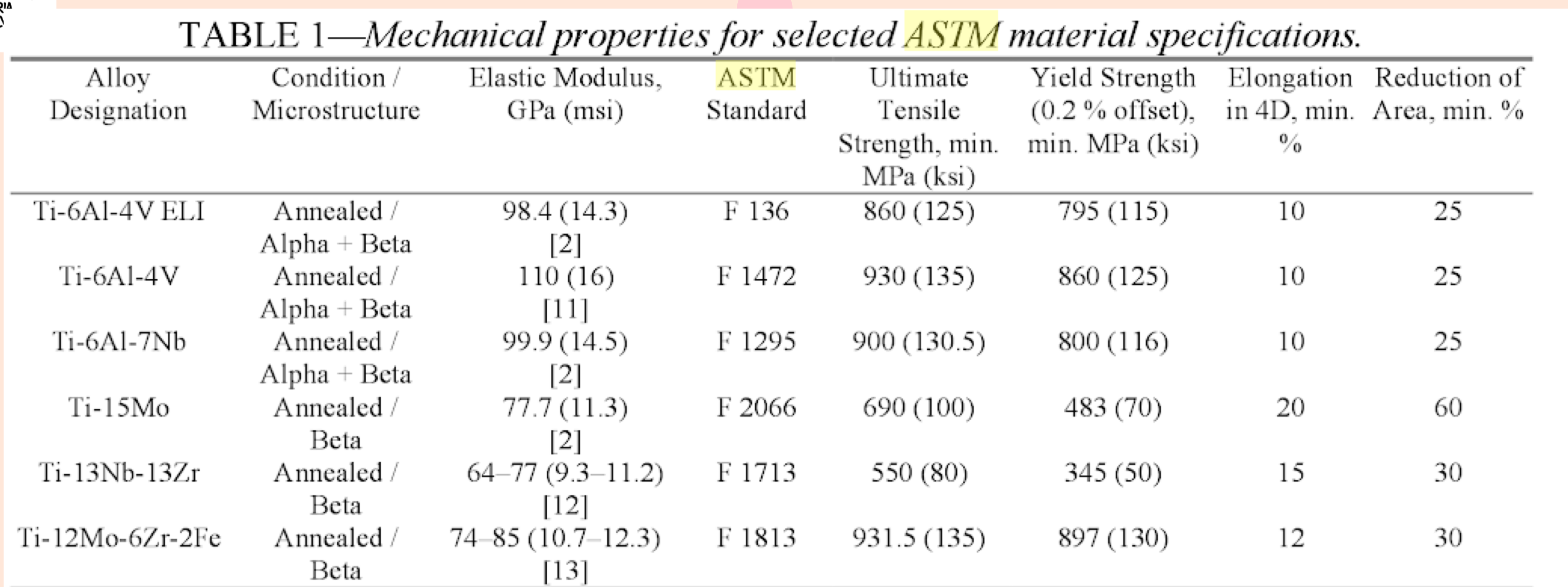


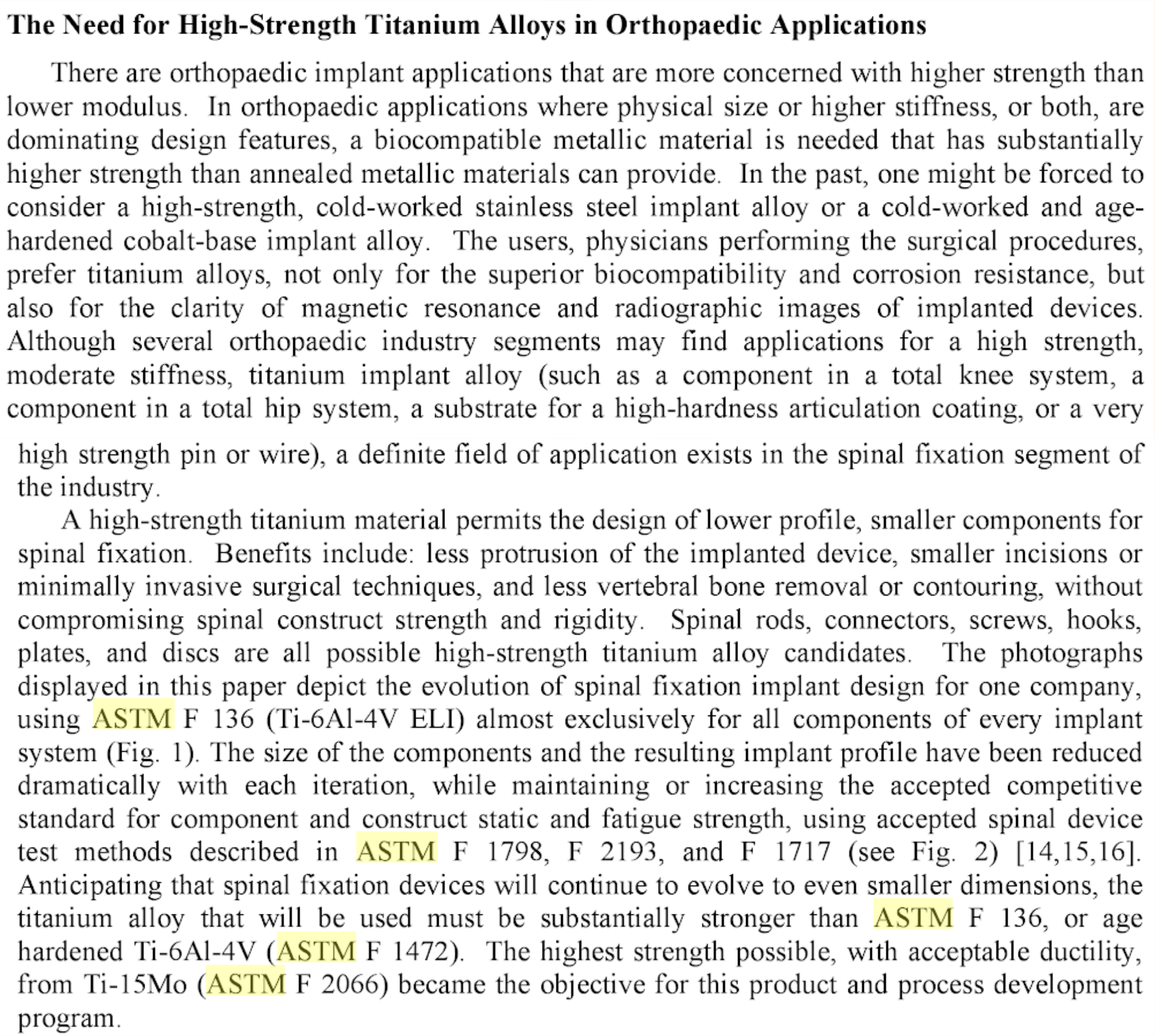
TABLE 1—*Mechanical properties for selected ASTM material specifications.*

Alloy Designation	Condition / Microstructure	Elastic Modulus, GPa (msi)	ASTM Standard	Ultimate Tensile Strength, min. MPa (ksi)	Yield Strength (0.2 % offset), min. MPa (ksi)	Elongation in 4D, min. %	Reduction of Area, min. %
Ti-6Al-4V ELI	Annealed / Alpha + Beta	98.4 (14.3) [2]	F 136	860 (125)	795 (115)	10	25
Ti-6Al-4V	Annealed / Alpha + Beta	110 (16) [11]	F 1472	930 (135)	860 (125)	10	25
Ti-6Al-7Nb	Annealed / Alpha + Beta	99.9 (14.5) [2]	F 1295	900 (130.5)	800 (116)	10	25
Ti-15Mo	Annealed / Beta	77.7 (11.3) [2]	F 2066	690 (100)	483 (70)	20	60
Ti-13Nb-13Zr	Annealed / Beta	64–77 (9.3–11.2) [12]	F 1713	550 (80)	345 (50)	15	30
Ti-12Mo-6Zr-2Fe	Annealed / Beta	74–85 (10.7–12.3) [13]	F 1813	931.5 (135)	897 (130)	12	30

Table 2. Specified titanium alloys.

Composition (mass%)	Type	UNS	ASTM	ISO
Ti–3Al–2.5V	$\alpha + \beta$	R56320	ASTM B 348	–
Ti–5Al–2.5Fe	$\alpha + \beta$	–	–	ISO 5832–10
Ti–6Al–4V	$\alpha + \beta$	R56400	ASTM F 1472	ISO 5832–3
Ti–6Al–4V ELI	$\alpha + \beta$	R56401	ASTM F 136	ISO 5832–3
Ti–6Al–7Nb	$\alpha + \beta$	R56700	ASTM F 1295	ISO 5832–11
Ti–15Mo	β	R58150	ASTM F 2066	–
Ti–13Nb–13Zr	β	R58130	ASTM F 1713	–
Ti–12Mo–6Zr–2Fe	β	R58120	ASTM F 1813	–
Ti–45Nb	β	R58450	AMS 4982	–
Ti–35Nb–7Zr–5Ta	β	R58350	–	–
Ti-55.8Ni	Metallic compound	–	ASTM F 2063	–

Titanium Alloys

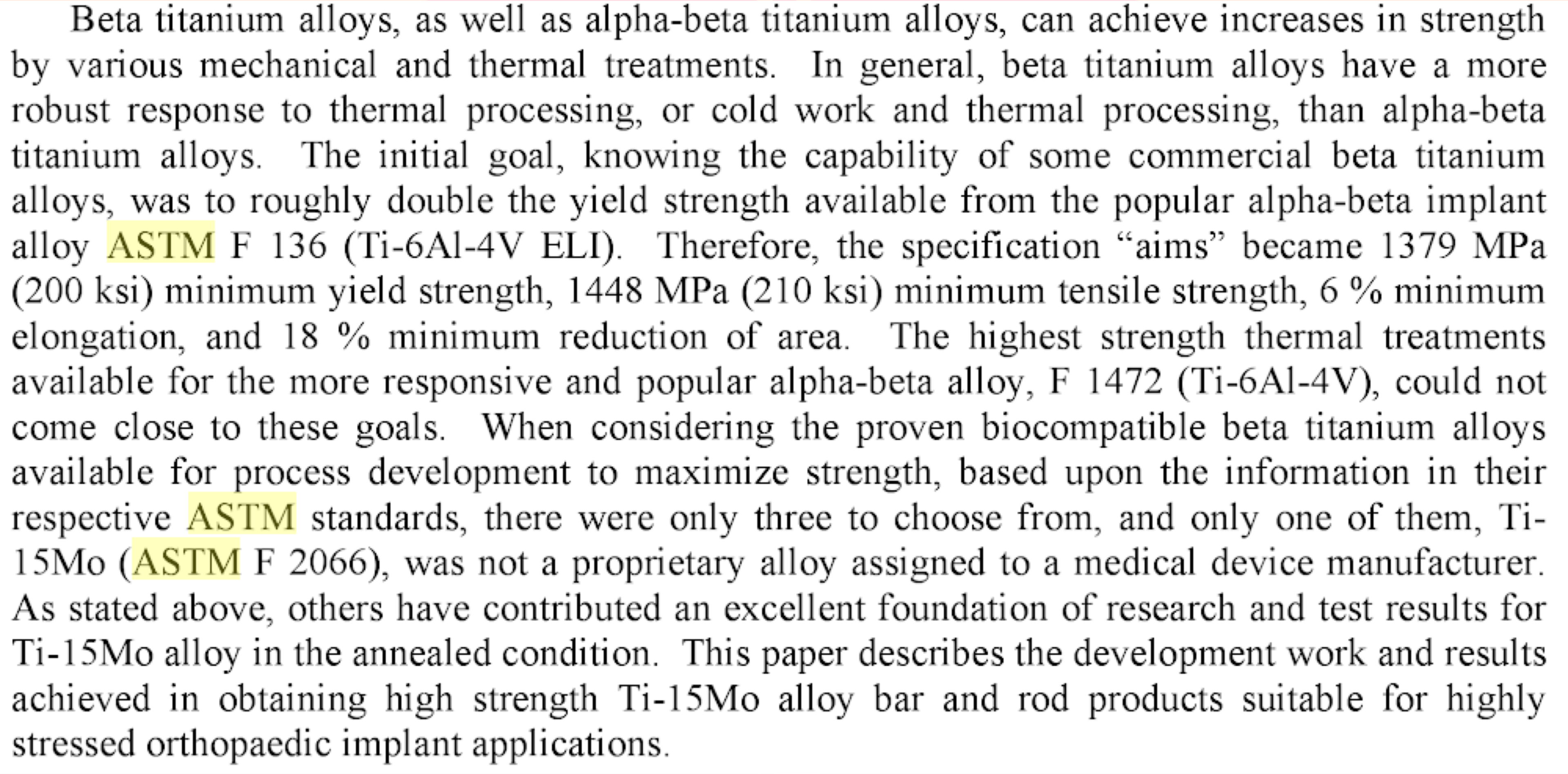


The Need for High-Strength Titanium Alloys in Orthopaedic Applications

There are orthopaedic implant applications that are more concerned with higher strength than lower modulus. In orthopaedic applications where physical size or higher stiffness, or both, are dominating design features, a biocompatible metallic material is needed that has substantially higher strength than annealed metallic materials can provide. In the past, one might be forced to consider a high-strength, cold-worked stainless steel implant alloy or a cold-worked and age-hardened cobalt-base implant alloy. The users, physicians performing the surgical procedures, prefer titanium alloys, not only for the superior biocompatibility and corrosion resistance, but also for the clarity of magnetic resonance and radiographic images of implanted devices. Although several orthopaedic industry segments may find applications for a high strength, moderate stiffness, titanium implant alloy (such as a component in a total knee system, a component in a total hip system, a substrate for a high-hardness articulation coating, or a very high strength pin or wire), a definite field of application exists in the spinal fixation segment of the industry.

A high-strength titanium material permits the design of lower profile, smaller components for spinal fixation. Benefits include: less protrusion of the implanted device, smaller incisions or minimally invasive surgical techniques, and less vertebral bone removal or contouring, without compromising spinal construct strength and rigidity. Spinal rods, connectors, screws, hooks, plates, and discs are all possible high-strength titanium alloy candidates. The photographs displayed in this paper depict the evolution of spinal fixation implant design for one company, using ASTM F 136 (Ti-6Al-4V ELI) almost exclusively for all components of every implant system (Fig. 1). The size of the components and the resulting implant profile have been reduced dramatically with each iteration, while maintaining or increasing the accepted competitive standard for component and construct static and fatigue strength, using accepted spinal device test methods described in ASTM F 1798, F 2193, and F 1717 (see Fig. 2) [14,15,16]. Anticipating that spinal fixation devices will continue to evolve to even smaller dimensions, the titanium alloy that will be used must be substantially stronger than ASTM F 136, or age hardened Ti-6Al-4V (ASTM F 1472). The highest strength possible, with acceptable ductility, from Ti-15Mo (ASTM F 2066) became the objective for this product and process development program.

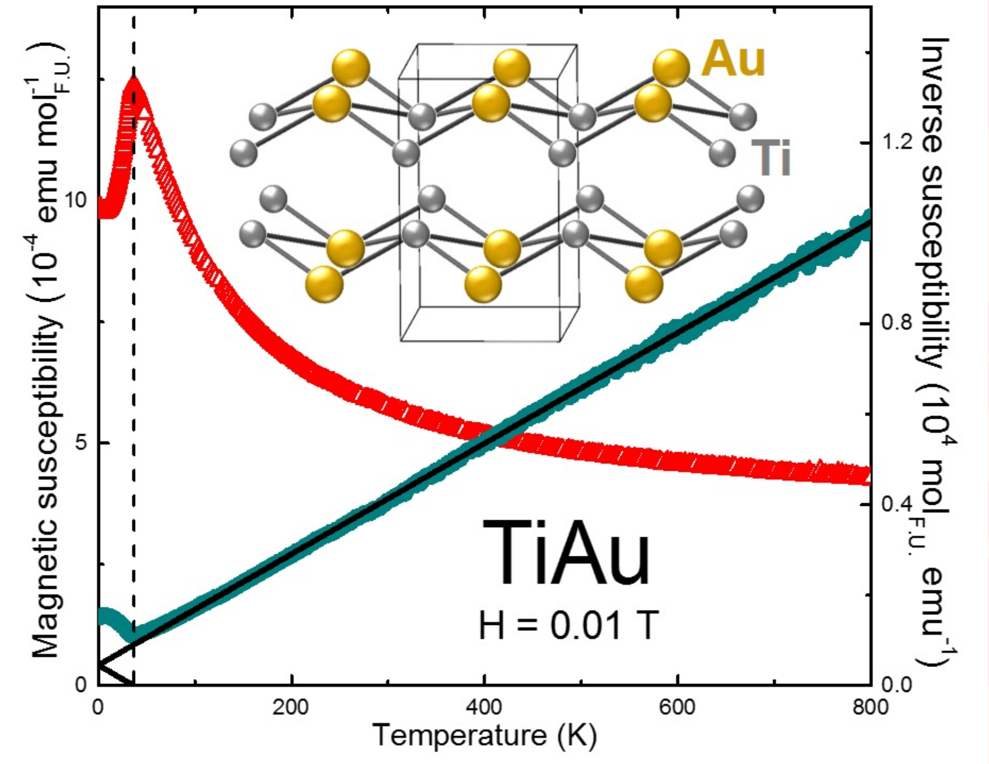
Titanium Alloys



Beta titanium alloys, as well as alpha-beta titanium alloys, can achieve increases in strength by various mechanical and thermal treatments. In general, beta titanium alloys have a more robust response to thermal processing, or cold work and thermal processing, than alpha-beta titanium alloys. The initial goal, knowing the capability of some commercial beta titanium alloys, was to roughly double the yield strength available from the popular alpha-beta implant alloy ASTM F 136 (Ti-6Al-4V ELI). Therefore, the specification "aims" became 1379 MPa (200 ksi) minimum yield strength, 1448 MPa (210 ksi) minimum tensile strength, 6 % minimum elongation, and 18 % minimum reduction of area. The highest strength thermal treatments available for the more responsive and popular alpha-beta alloy, F 1472 (Ti-6Al-4V), could not come close to these goals. When considering the proven biocompatible beta titanium alloys available for process development to maximize strength, based upon the information in their respective ASTM standards, there were only three to choose from, and only one of them, Ti-15Mo (ASTM F 2066), was not a proprietary alloy assigned to a medical device manufacturer. As stated above, others have contributed an excellent foundation of research and test results for Ti-15Mo alloy in the annealed condition. This paper describes the development work and results achieved in obtaining high strength Ti-15Mo alloy bar and rod products suitable for highly stressed orthopaedic implant applications.

Leghe Ti-Au

In the best traditions of great scientific advances, the discovery of the hardness properties of **β-Ti_3Au** was an accident. The team was conducting experiments on making magnetic substances from nonmagnetic materials. Testing various ratios of titanium to gold in these experiments led to beta Ti_3Au being discovered. The alloy has probably been made by accident before (all it requires is a far hotter melting process than normal), but Morosan's team (RICE University – 2016) is the first to obverse its unique properties.



Ti and Au are usually not magnetic and cannot be magnets – unless you combine them.

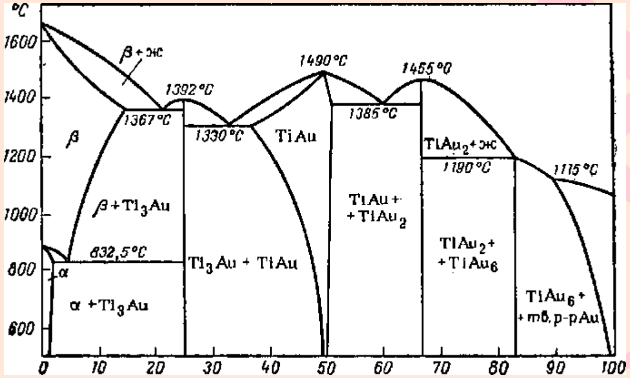
TiAu is not the kind of magnet one would stick to a refrigerator. Magnetic order only appears in TiAu when the metal is cooled to 36 kelvins (-273 C)

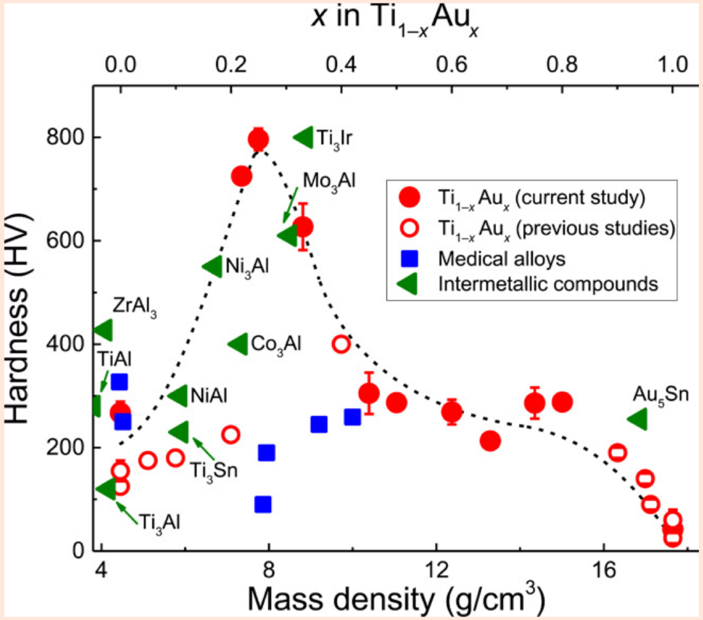
- Titanium coated steel b

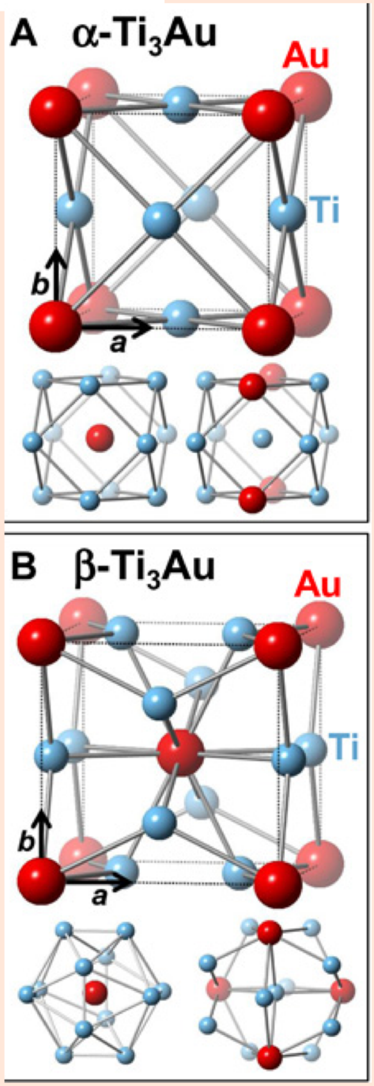
Leghe Ti-Au

Titanium is as strong as steel but 45% lighter, and twice as strong as aluminum but only 60% heavier. ***Unfortunately hardness is not good enough.***

Previously, a twofold increase in hardness has been achieved by alloying Ti with Cu or Ag. This finding suggests that Au is a suitable alloying candidate to increase the hardness in Ti binary alloys, given its nearly twofold density increase over Cu or Ag.







Ti$_3$Au has significantly enhanced hardness while preserving its biocompatibility.

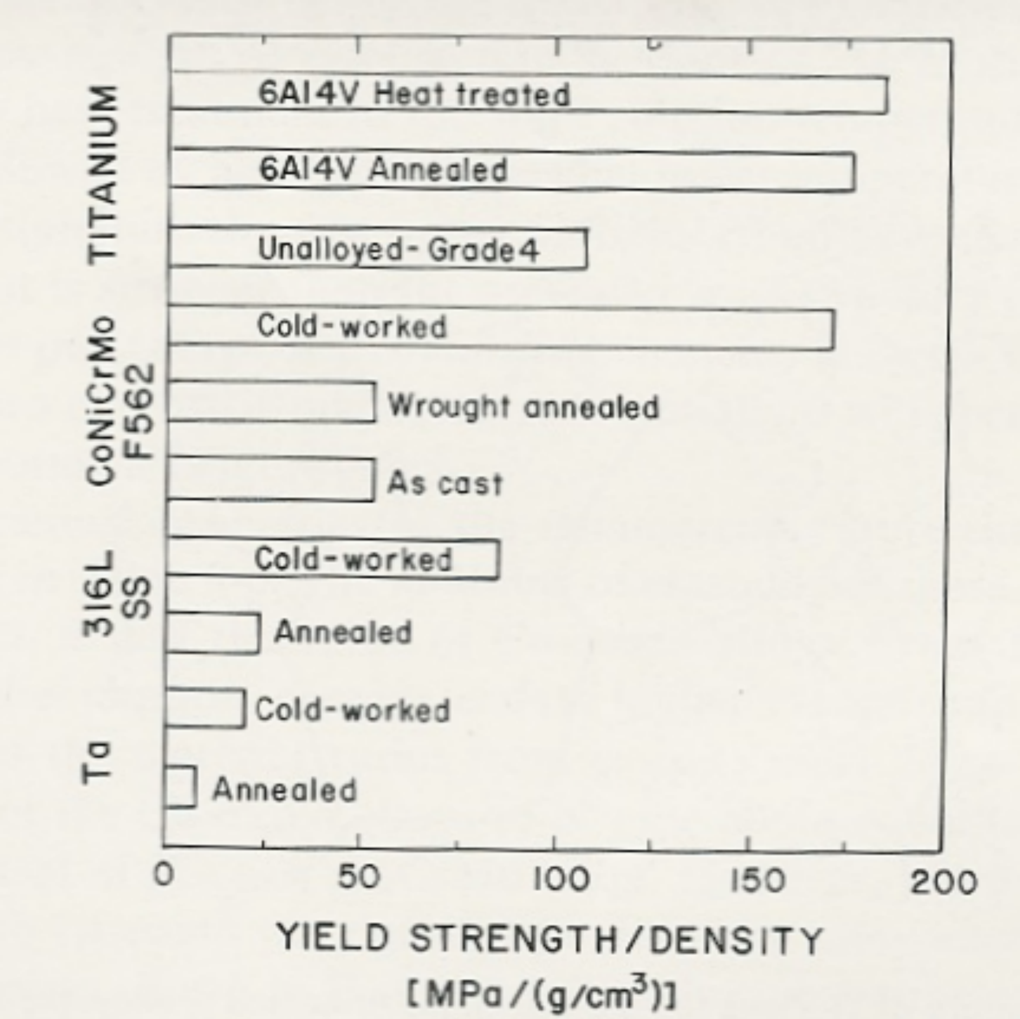
The only other intermetallic compound with a similar hardness value is **Ti$_3$Ir**, the biocompatible properties of which remain unknown

Ti$_3$Au forms in two cubic crystal structures: **α-Ti$_3$Au** and **β-Ti$_3$Au**
β-Ti$_3$Au has higher hardness, considering the Ti coordination and its Ti–Au bond length $d_{\text{Ti–Au}}$ = 2.84 Å being shorter than that of the α-Ti$_3$Au phase [$d_{\text{Ti–Au}}$ = 2.93 Å]

β-Ti$_3$Au has a coefficient of friction that is four times less than titanium.

Hardness is good but toughness is low therefore a 2 phases materials (α-Ti) will be used

Yield Strength of Metals



Dental Metals - Amalgam

- Alloy containing mercury

- Forms a plastic mass at room temp., when mixed with Ag and Sn it hardens with time

- Composition of typical solid alloy (then mixed with liquid mercury)
  - 65% Ag (minimum)
  - 29% Sn, 6% Cu, 2% Zn, 3% Hg (maximum)

- The solid alloy is combined with Hg to give the composition of typical amalgam
  - 45 - 55 % mercury
  - 35 - 45 % silver
  - 15 % tin

- Strength increases with time to an assymptotic level
  - 25 percent of final strength within 1 hour
  - Almost 100 percent of final strength within 1 day

Dental Metals

- Amalgam:
  - Solid alloy
    - silver, tin, copper, zinc and mercury
  - deformable mixture packed in cavity
  - cures over time
    - 25% of total strength in 1 hour
    - full strength in a day
- Gold:
  - Durable, stable, corrosion resistant as fillings

Dental Metals - Gold

- Durable, stable, corrosion resistant

  Why is corrosion resistance especially important in the mouth?

Answer

The mouth is a more acidic and chemically active environment than much of the rest of the body

- Used in fillings via two methods
  - Casting
  - Wax impression taken of cavity and used to construct restoration

- Can also involve use of gold alloys
  - Cu and Pt improve strength
  - Higher Au contents (better corrosion resistance/lower strength) are used in areas not subject to high stresses
  - Lower Au contents are used in crowns and other areas exposed to high stresses

- Malleting
  - Pure Au foil applied in layers and welded together by pressure at room temperature
  - Pure Au soft, limited to areas of low stress

Other Metals - Nickel-Titanium Alloys

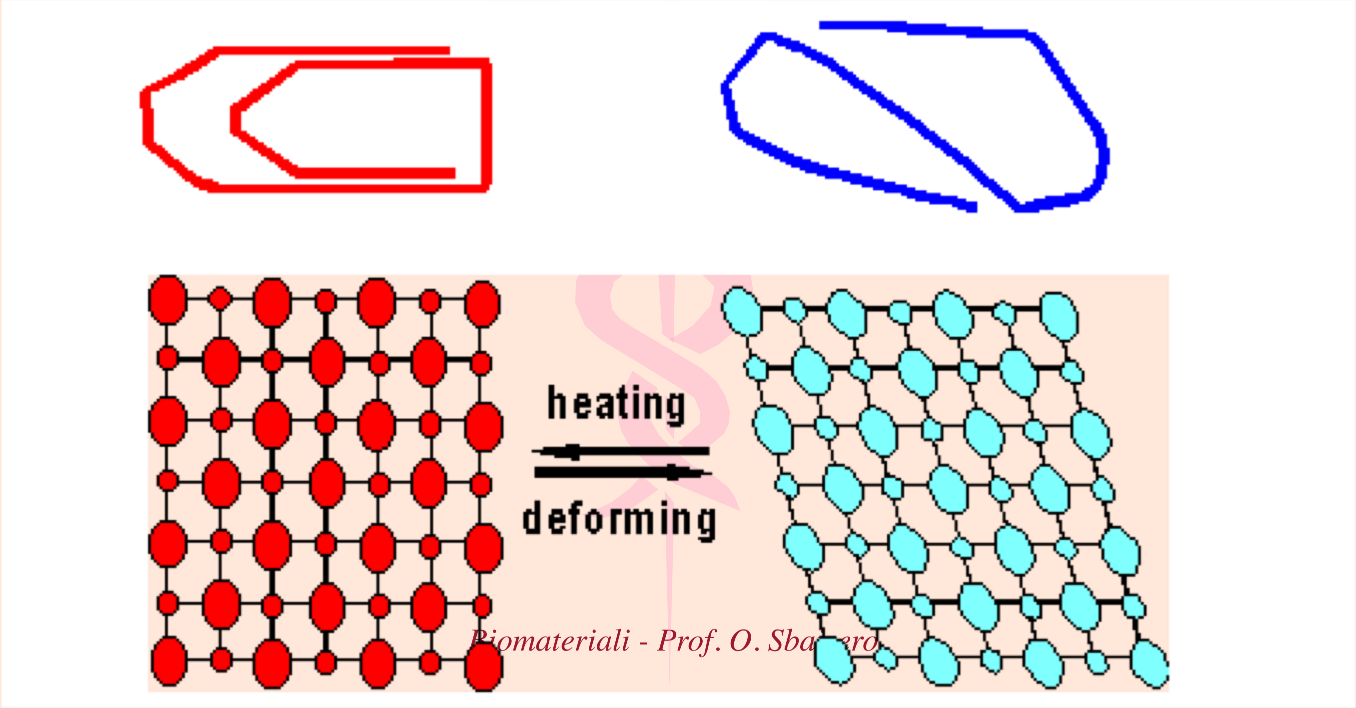
- Possess property known as shape memory effect (SME)
  - After a material is plastically deformed, it will snap back to its previous shape when heated

- **Uses in orthodontic dental archwires, intracranial aneurysm clips, contractile artificial muscles for an artificial heart, orthopaedic implants, stents, heart valves**

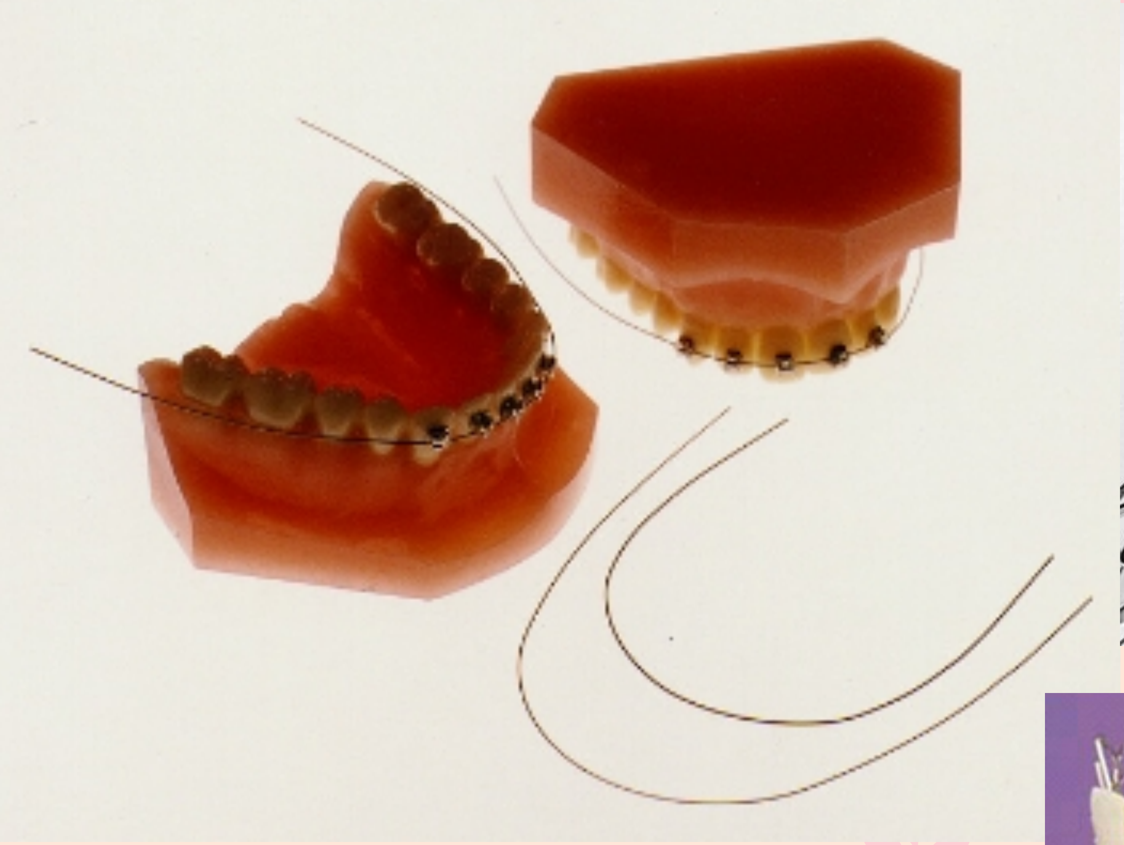
- Generally low modulus of elasticity (about 30 GPa) but high toughness

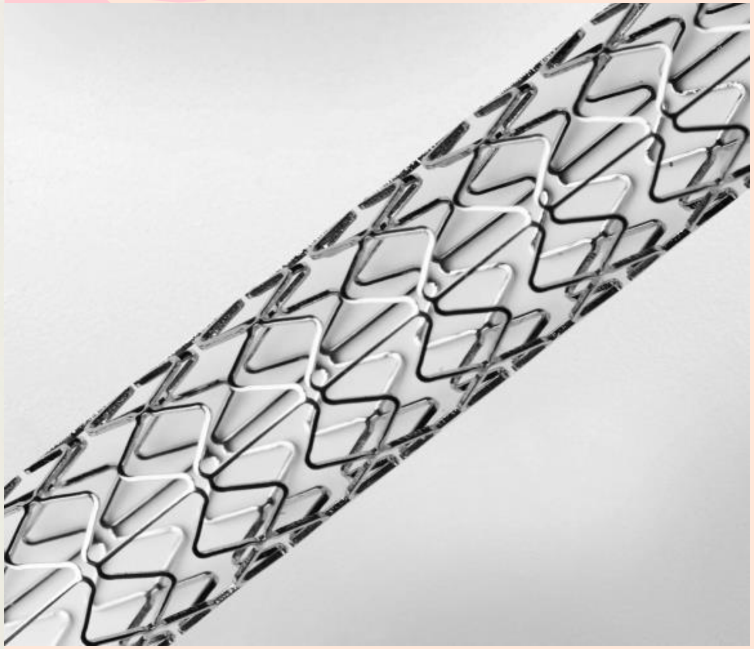
Dental Metals: Nitinol

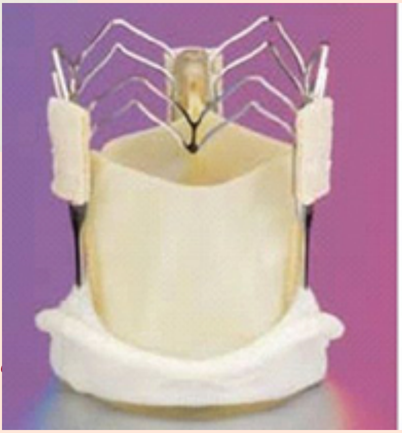
- **NI**ckel-**TI**tanium-**N**aval **O**rdinance **L**ab
- Shape memory alloy (SMA): ability to return to a predetermined shape when heated



Dental Metals: Nitinol







I materiali a memoria di forma (Shape Memory Alloy - SMA) sono materiali funzionali in grado di recuperare elevate deformazioni sfruttando una **trasformazione martensitica** che avviene allo stato solido **senza diffusione**. Essa avviene mediante il passaggio, reversibile, da una struttura ad alta simmetria, detta austenite, ad una a simmetria inferiore, detta martensite. La trasformazione martensitica viene definita mediante quattro temperature caratteristiche, che indicano la temperatura di inizio e fine trasformazione diretta da austenite a martensite (Ms e Mf), e inversa da martensite ad austenite (As e Af). ***Il cambiamento di fase puo' essere provocato da una variazione di temperature del materiale nell'intervallo di trasformazione, o dall'applicazione di un carico al di sopra di un valore critico.*** La fase martensitica e quella austenitica possono coesistere in due intervalli di temperatura: (i) $Mf<T<Ms$ quando il materiale e' sottoposto ad un raffreddamento da una temperatura superiore a Af; oppure (ii) $As<T<Af$ quando il materiale e' sottoposto ad un riscaldamento a partire da una temperatura inferiore a Mf

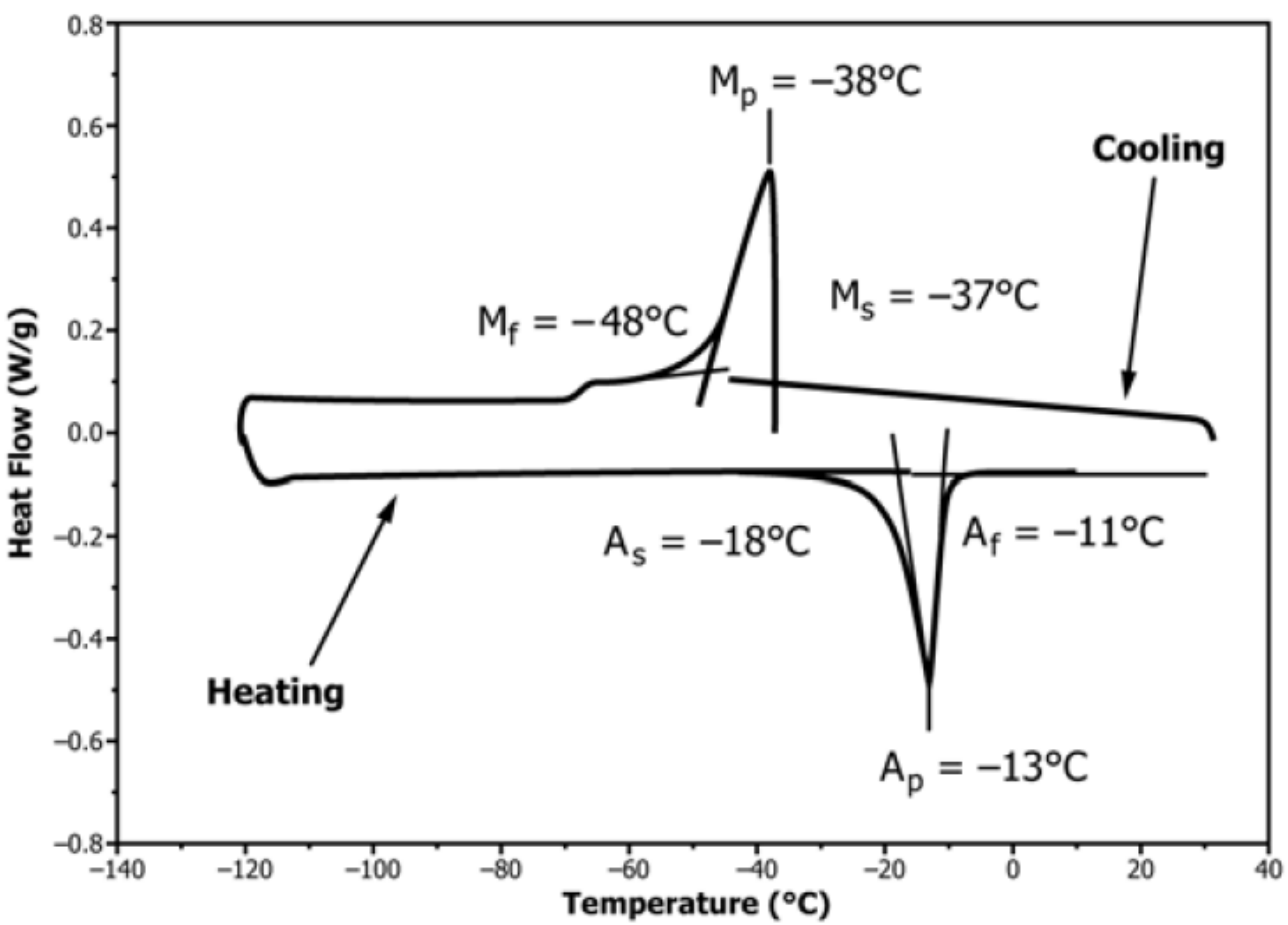
The following technical terms and their definitions are essential for understanding Nitinol and the concepts presented in this document. For an extensive list of standard terminology it is recommended to reference *ASTM F2005 – Standard Terminology for Nickel-Titanium Shape Memory Alloys*.

Austenite – the high temperature parent phase of the Nitinol alloy having a B2 crystal structure.

Austenite finish temperature (Af) – the temperature at which martensite (or R-phase) to austenite transformation is completed on heating of the alloy.

Austenite peak temperature (Ap) – the temperature of the endothermic peak position on the differential scanning calorimetry (DSC) curve upon heating for the martensite (or R-phase) to austenite transformation.

Austenite start temperature (As) – the temperature at which the martensite (or R-phase) to austenite transformation begins on heating of the alloy.



ASTM F2004 – Standard Test Method for Transformation Temperature of Ni-Ti Alloys by Thermal Analysis

Free recovery – unconstrained motion of a shape memory alloy upon heating and transformation to austenite after deformation in a lower temperature phase.

Lower plateau strength/stress (LPS) – the stress measured at 2.5 % strain during tensile unloading of the sample, after loading to 6 % strain per the method described in **ASTM F2516**.

Upper plateau strength/stress (UPS) – the stress measured at 3 % strain during tensile loading of the sample per the method described in **ASTM F2516**.

Martensite – the lowest temperature phase in Nitinol shape memory alloys with a B19’ (B19 prime) monoclinic crystal structure.

Martensite deformation temperature (Md) – the highest temperature at which martensite will form from the austenite phase in response to an applied stress. At temperature above Md the Nitinol shape memory alloy will not exhibit superelasticity it will rather exhibit a typical elastic-plastic behavior when loaded.

Martensite finish temperature (Mf) – the temperature at which the transformation of martensite from austenite (or R-phase) is completed on cooling of the alloy.

Martensite start temperature (Ms) – the temperature at which the transformation from austenite (or R-phase) to martensite begins on cooling of the alloy.

Pseudoelasticity – another name for superelasticity.

Superelasticity – **nonlinear** **recoverable** deformation behavior of Nitinol shape memory alloys that occurs at temperatures above Af but below Md

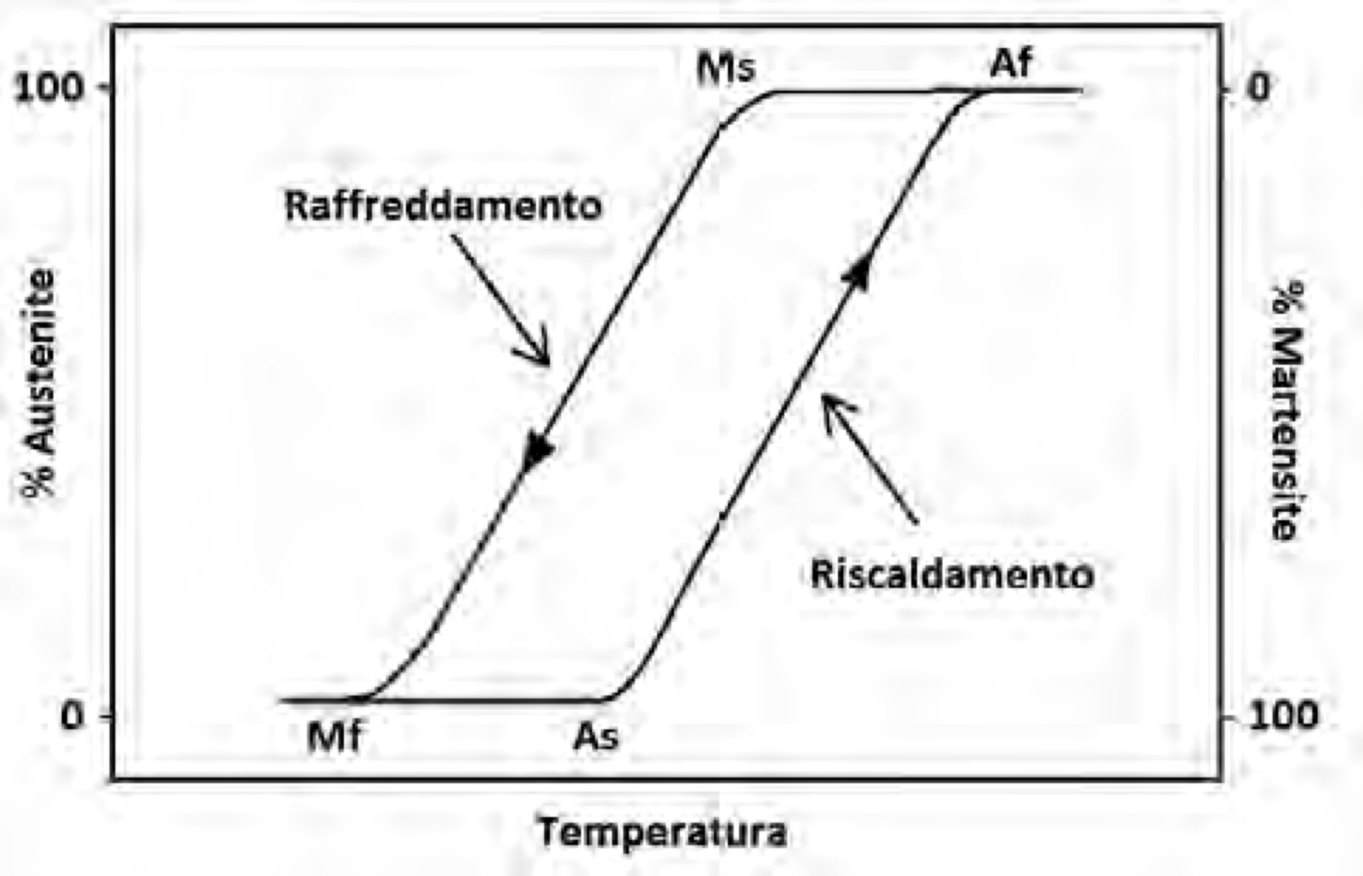
R-phase – the intermediate phase which may form between austenite and martensite. The R-phase occurs in Nitinol alloys under certain conditions. The R-phase has a rhombohedral crystal structure.

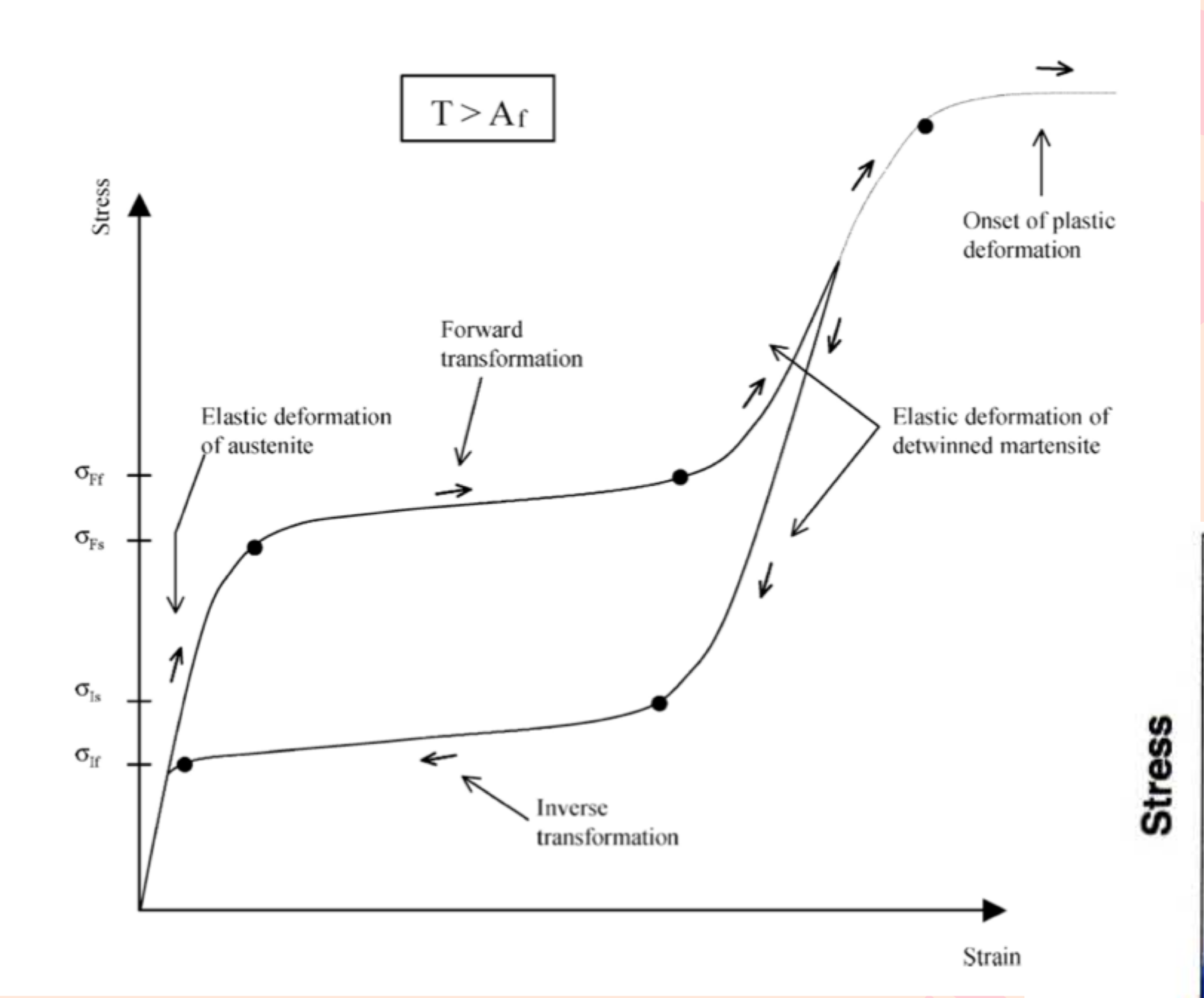
Residual elongation (Elr) – the percent strain measured after tensile loading to 6 % strain and unloading to 7 MPa per **ASTM 2516**.

Uniform elongation (Elu) – the percent elongation (or strain) determined at the maximum force sustained by the test sample prior to necking, or fracture, or both upon tensile loading per **ASTM 2516**.

The R-Phase

Intermediate phases are sometimes present that are stable at temperatures or stresses between the austenite and martensite phases. **A phase known as R-phase, having a rhombohedral crystal structure, is the most common of these phases**; especially when considering traditional binary NiTi Nitinol alloys. The R-phase is an intermediate martensitic phase that competes with the martensite phase transformation that occurs in Nitinol materials that have **high dislocation density** (i.e. cold worked), **Ni-rich precipitates** (i.e. heat treated), or in some **ternary alloys**. Dislocations in the crystal structure as well as Ni-rich precipitates all resist large strains in the crystal lattice. ***Since the R-phase transformation requires much less straining of the lattice it is therefore thermodynamically favorable to occur between the austenite and martensite phases in these cases.***


100
0
% Austenite
Ms
Af
Raffreddamento
Riscaldamento
Mf
As
0
100
% Martensite
Temperatura



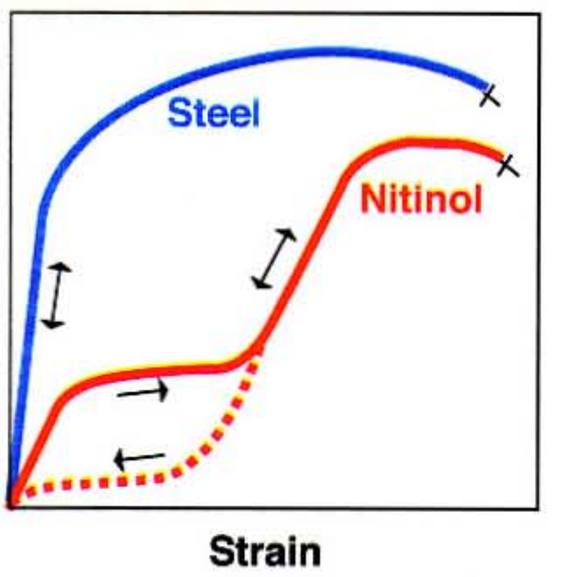


Fig. 3 Schematic stress-strain diagram for Nitinol and stainless steel

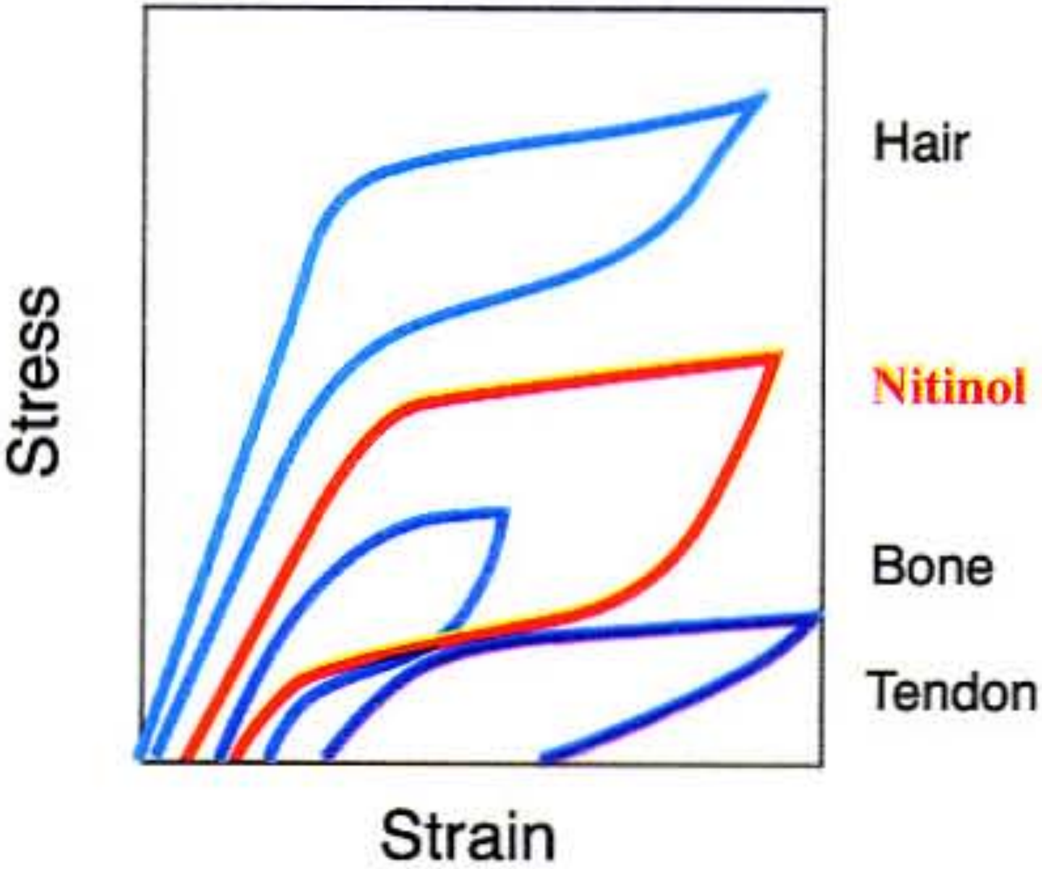
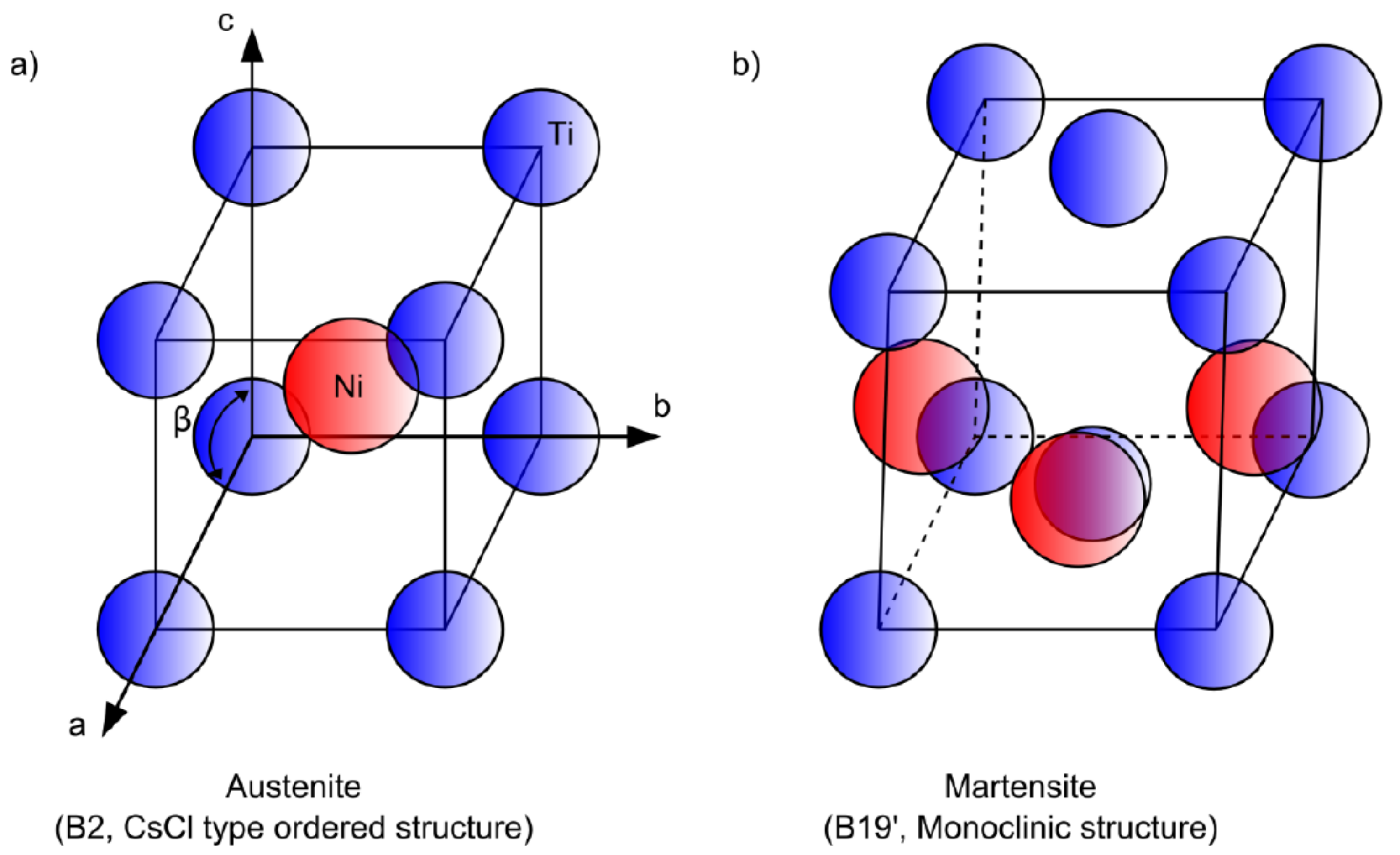


Fig. 2 Biomechanical compatibility of Nitinol: deformation characteristics of Nitinol and living tissues [2]

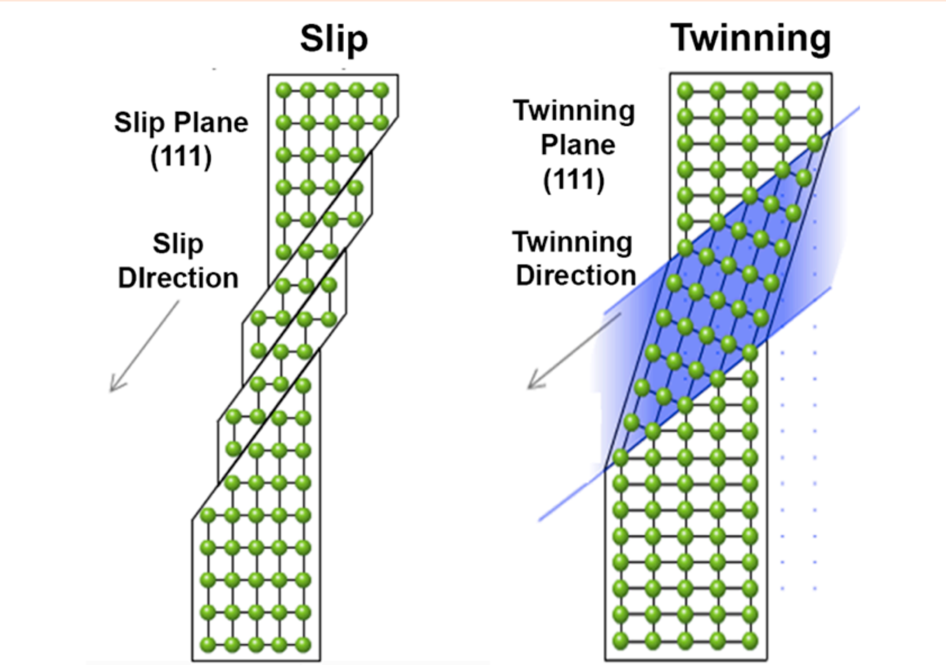


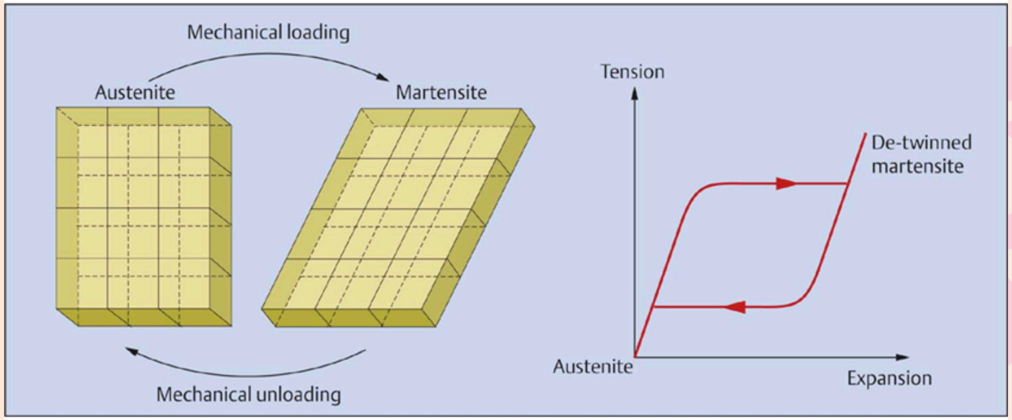
Austenite
(B2, CsCl type ordered structure)

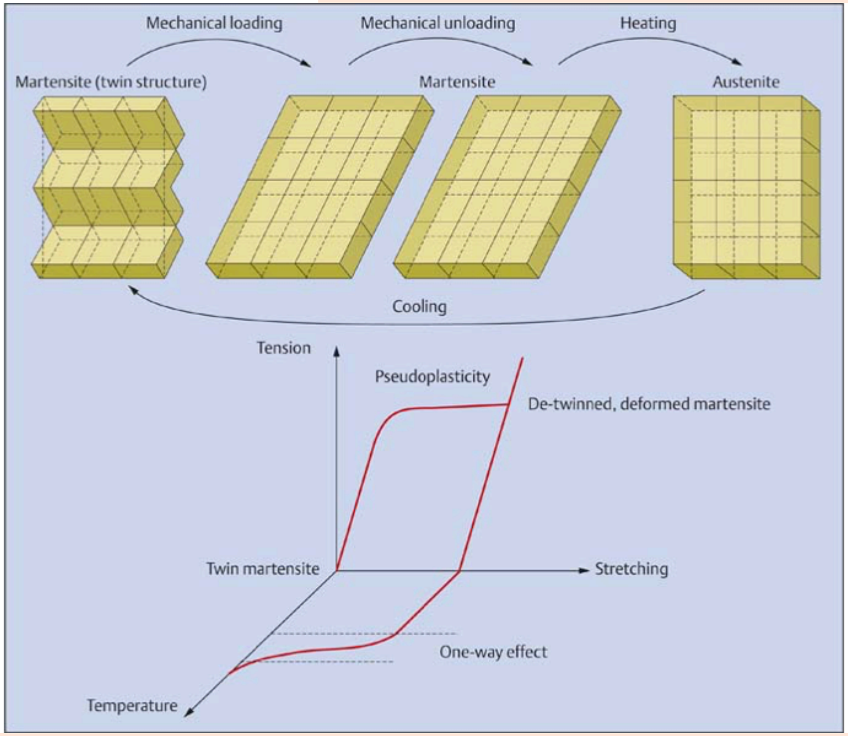
Martensite
(B19', Monoclinic structure)

In Nitinol the diffusionless transformation is an instantaneous distortion in the crystal lattice (B2---B19′) that occurs at the speed of sound; often referred to as a military transformation.

In contrast, diffusion based phase transformations, as common in steel alloys, requires the diffusion of atoms over relatively long distances. Diffusion requires heating the alloy at a high temperature for extended periods of time.


Slip
Slip Plane (111)
Slip DIrection
Twinning
Twinning Plane (111)
Twinning Direction


Mechanical loading
Austenite
Martensite
Mechanical unloading
Tension
De-twinned martensite
Austenite
Expansion


Mechanical loading
Mechanical unloading
Heating
Martensite (twin structure)
Martensite
Austenite
Cooling
Tension
Pseudoplasticity
De-twinned, deformed martensite
Twin martensite
Stretching
One-way effect
Temperature

Functional Properties of Nitinol

The functional properties of Nitinol originate from the thermomechanical response of the material. **The thermomechanical response can be differentiated into two different functional properties depending on whether the austenite--martensite phase transformation is induced thermally or by applied stress. Thermally induced transformation enables the shape memory effect while the stress induced transformation leads to superelasticity.**

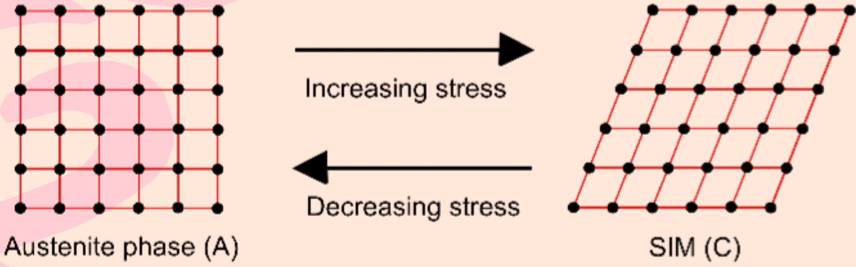
Superelastic and shape memory responses are related. In fact, the response simply depends on the transformation temperature of the Nitinol component coupled with the application temperature. ***Below the Mf temperature the Nitinol alloy will exhibit shape memory while above the Af temperature the Nitinol material will exhibit superelasticity***.

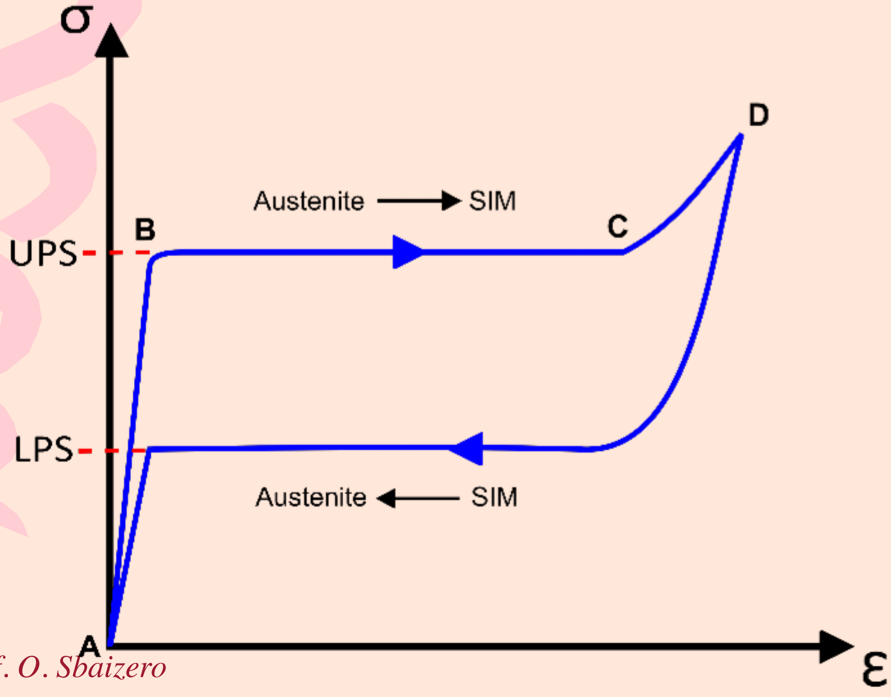
This concept is critical when designing a Nitinol device

Superelasticity

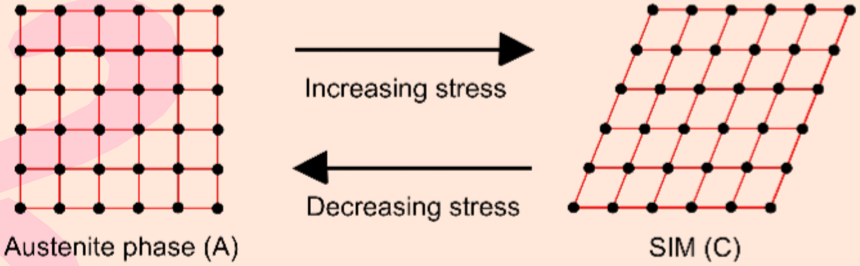
If a stress is applied to a Nitinol component, at a temperature above Af, the austenite phase will be converted to stress induced martensite (SIM-stress induced martensite) resulting in a superelastic response.

A typical cyclic tensile curve for superelastic Nitinol can be broken into several different segments. During initial loading the austenite phase exhibits typical elastic deformation (A → B) up until the UPS is reached. Once the UPS has been reached an isostress condition is observed (B → C) as the cubic austenite structure shears into detwinned SIM, followed by the elastic deformation of the detwinned SIM structure (C → D). Just as for the thermally induced phase transformation, the formation of SIM is reversible.

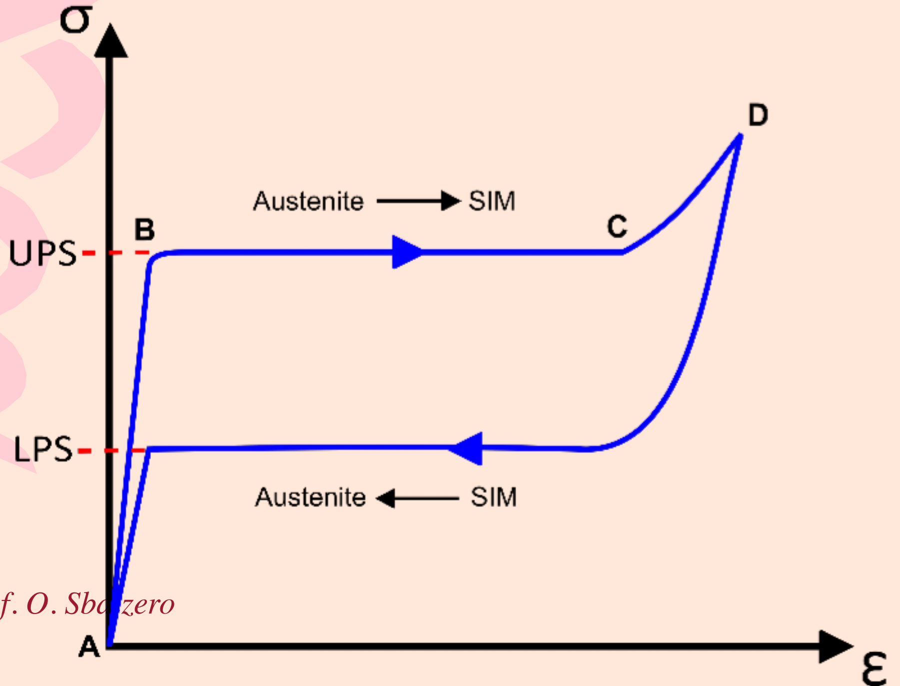




During unloading (D → A) elastic strain is recovered and the SIM transforms back into the parent austenite phase. Note that the recovery stress (or LPS) is lower than UPS. The hysteresis observed arises from internal friction and defects in the crystal structure.



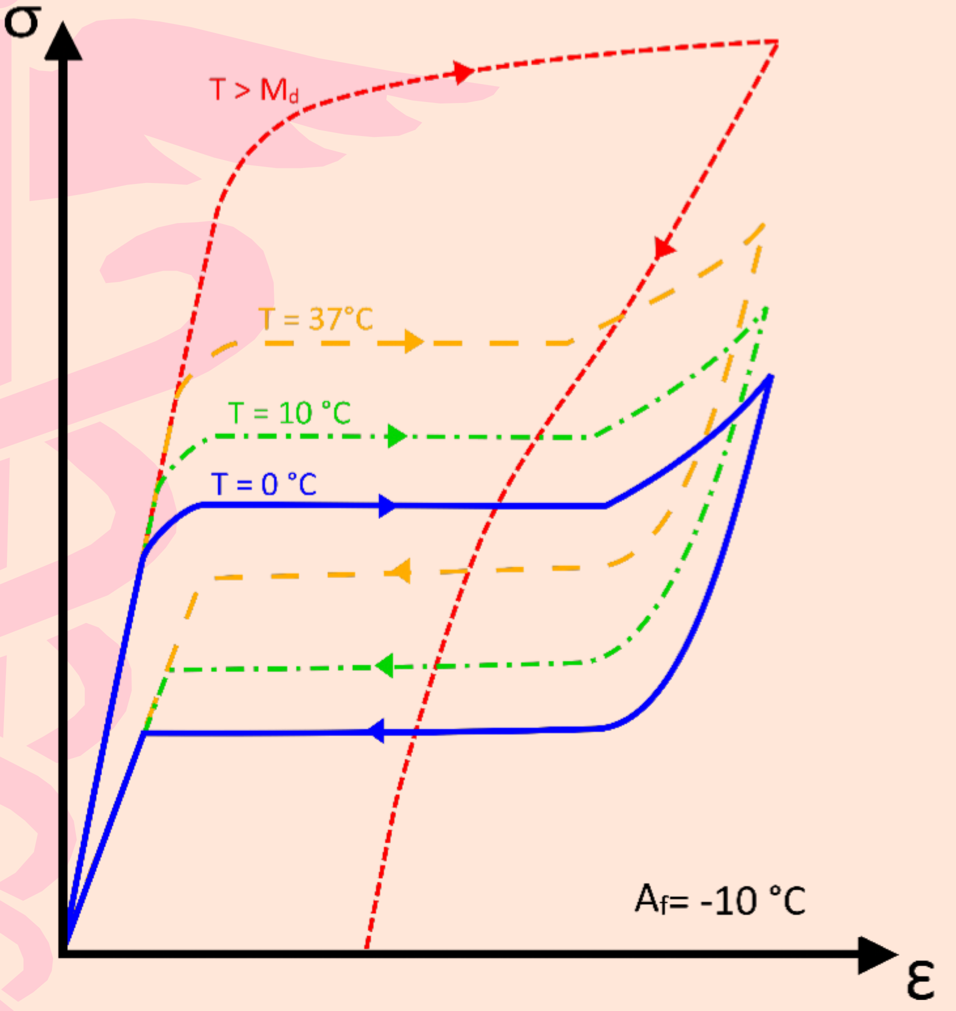
A typical Nitinol alloy will exhibit superelasticity up to **8-10 %** strain before permanent deformation begins. However, there is always some percentage of permanent-set or residual elongation, Elr. The magnitude of Elr depends on the past thermomechanical processing of the material and also the % strain the component was subject to before unloading



The UPS and LPS are not fixed for all temperatures. The superelastic plateaus will increase with application temperature

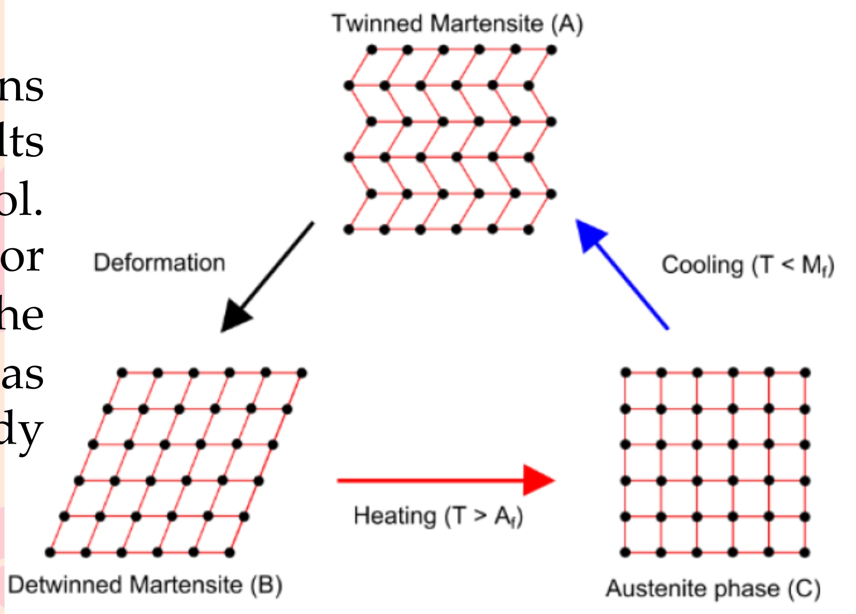
For every C the plateaus can change by 3 – 20 MPa/C; depending on the alloy and processing history. It is therefore important to test the superelastic properties of the final device at the application temperature (ex. 37 ° C for implantable devices).

This increase in plateau stresses is due to increasing thermodynamic stability of the high temperature austenite phase the further the temperature of the Nitinol material is increased above the A_f temperature. In fact, the UPS will continue to increase until the yield stress of the alloy is reached and the material will yield and behave again like an elastic plastic material. Superelasticity therefore cannot occur above this critical temperature termed “martensite deformation temperature” or M_d (~ 80 C > A_f).

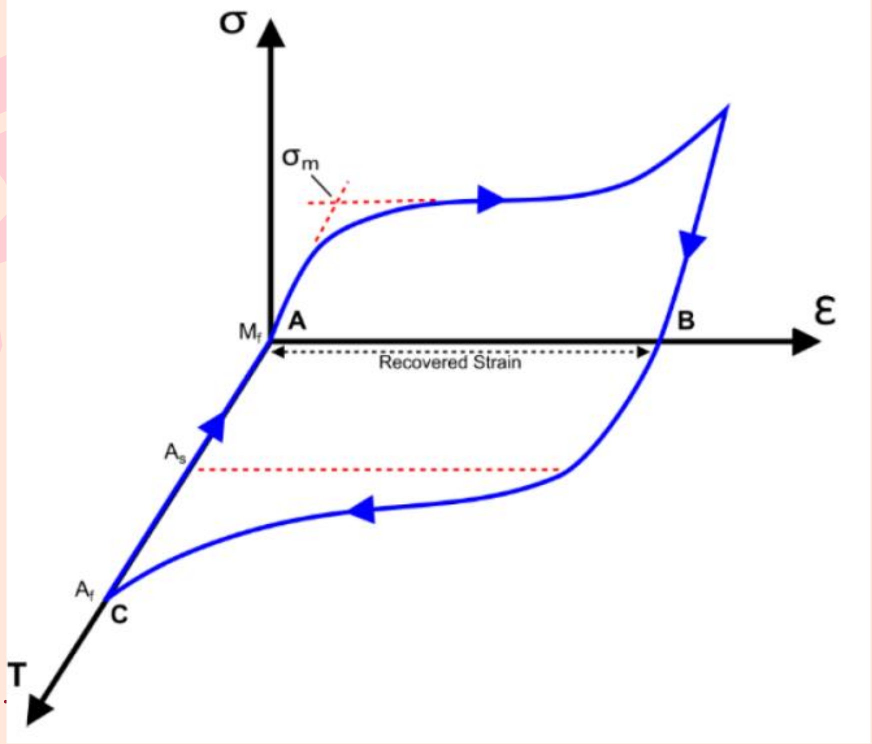


Shape Memory Effect

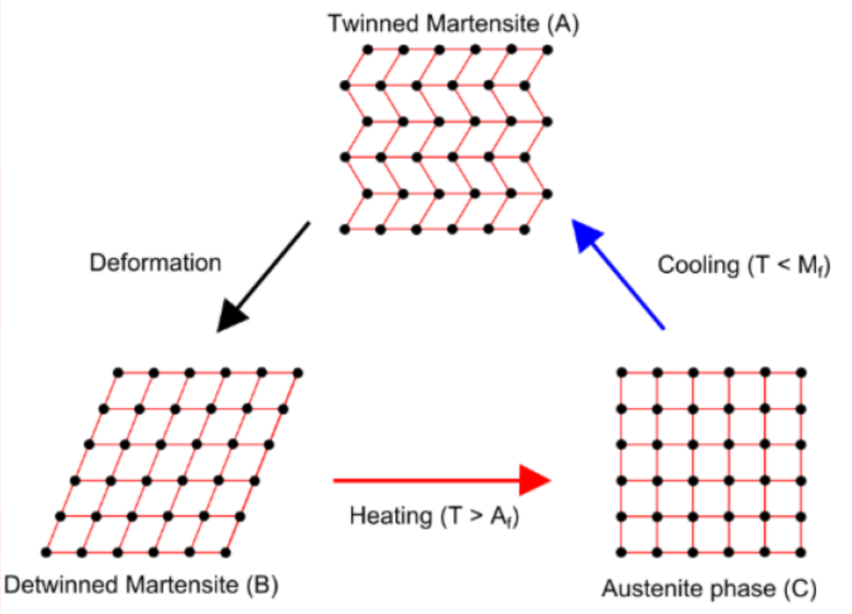
Thermally induced phase transformations between martensite and austenite results in the shape memory response of Nitinol. The shape memory effect is utilized for creating actuators as well as for the deployment of medical devices such as cardiovascular stents as they reach body temperature.

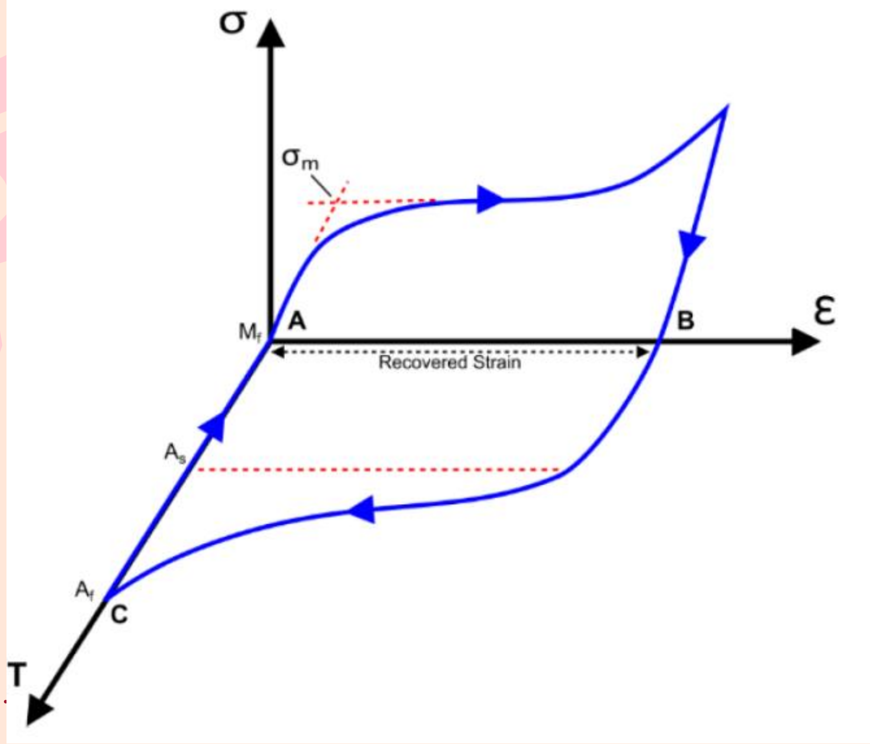


To exhibit shape memory behavior the Nitinol alloy must first be cooled below M_f. Deformation of martensite is visualized moving from point A to point B on the stress-strain-temperature plot. In the early stages of the deformation an elastic region is observed before the martensite detwinning stress (σ_m) is reached where the stress remains almost constant. This constant stress region is followed by the elastic straining of the fully detwinned structure. Once the material is in the deformed state and the stress has been unloaded, heating to a temperature above A_s will cause the detwinned martensite to begin transforming into austenite.



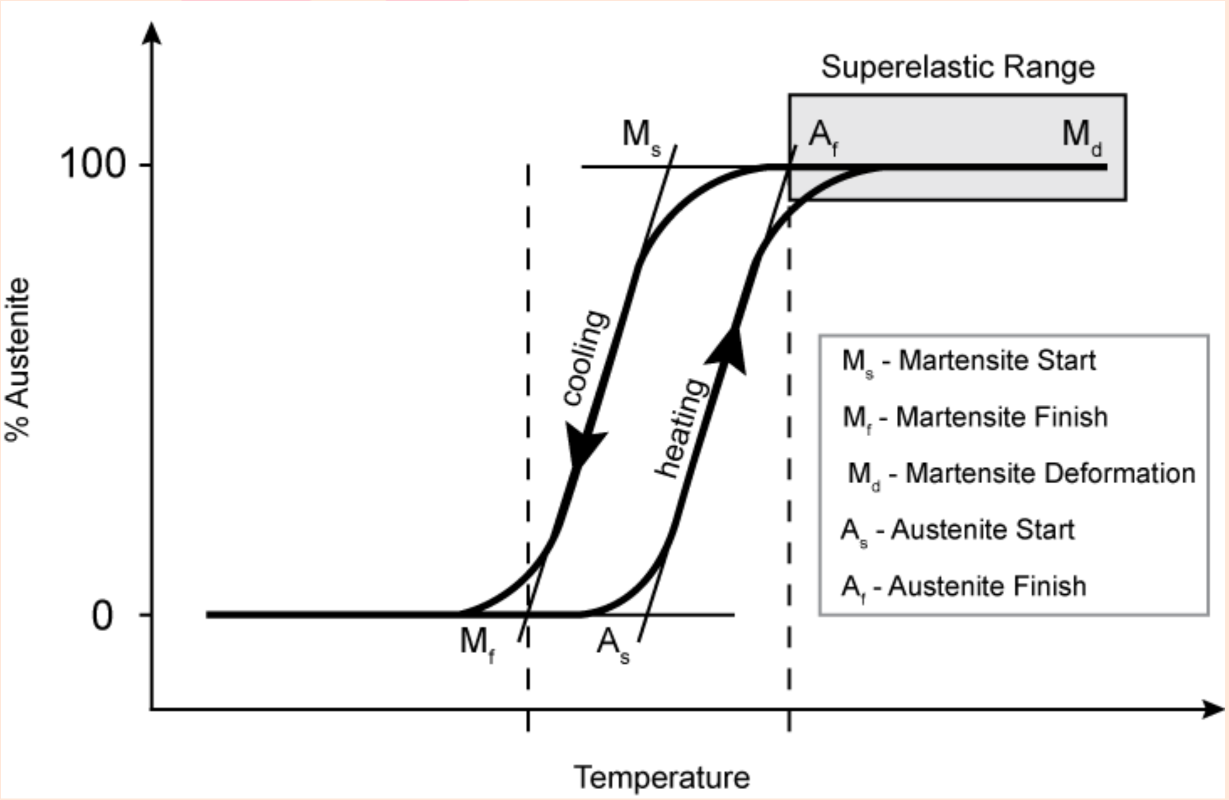
This transformation of the crystal structure translates into the recovery of the original trained shape of the component on the macroscopic scale once the temperature reaches above Af (B → C). The deformed crystal structure remembers its original orientation because of the lattice correspondence. When the temperature is returned to below Mf the austenite structure changes back to martensite (A → B), with no macroscopic shape change, and the cycle can be repeated





Thermal Hysteresis

Thermal hysteresis is the difference in phase transformation temperatures when the alloy is heated versus when it is cooled. This hysteresis is typically around 20 - 30 C for Nitinol superelastic alloys used in medical device applications. The thermal hysteresis is related to mechanical hysteresis of the UPS and LPS during the superelastic response of the alloy at temperatures above Af. A greater thermal hysteresis will yield a greater mechanical hysteresis.



Effect of Cold Work

Also known as work or strain hardening, cold work is the strengthening of a material through plastic deformation.

Cold working is critical in the thermomechanical processing of net-shape raw materials to obtain the desired mechanical and functional properties of the final Nitinol component. The typical final amount of cold work resulting from the final drawing/rolling process step ranges from 30 – 50 %; calculated in terms of reduction of cross sectional area.

In Nitinol, the amount of cold work affects both the mechanical and functional properties of the alloy.

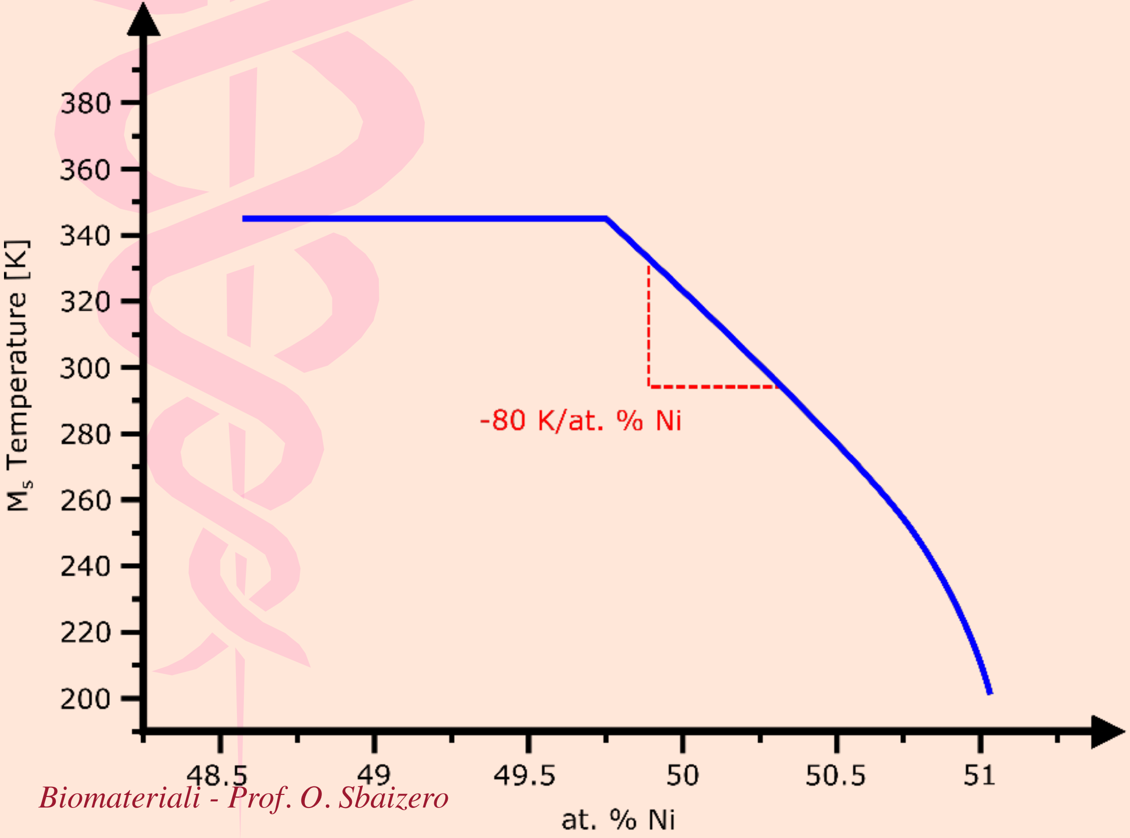
For example, mechanical properties such as the yield stress and ultimate tensile strength (UTS) of the material increase with percentage cold work. This increase in strength however comes at the expense of a reduction in elongation (or ductility).

It is important to note that a final heat treatment is required to allow the Nitinol material to exhibit the shape memory and superelastic properties. **A material with 30 % cold work for example has too high dislocation density within the crystal structure and does not allow the necessary straining to occur for phase transformation.** On the contrary, if the amount of cold work imparted into the material is not high enough the yield stress can be too low where the material plastically deforms below the UPS or martensite detwinning stress, σ_m. The material will therefore not exhibit shape memory or superelasticity in this case.

Alloy Ratio and Ms

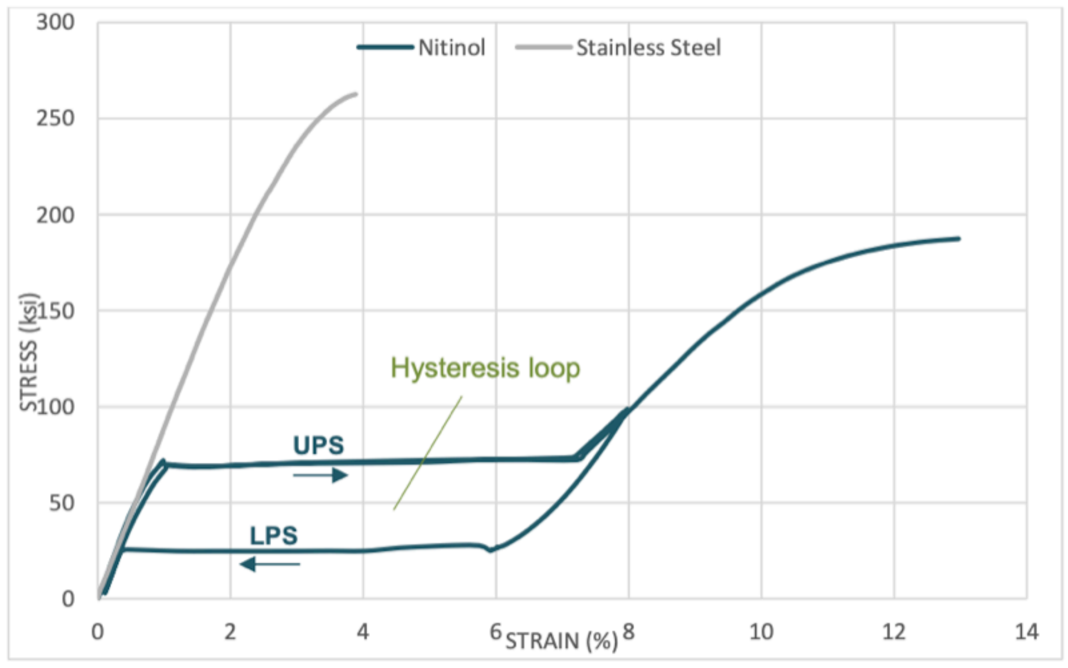
Nitinol is typically composed of approximately 50 to 51 at. % Nickel by atomic percent (i.e. 55 to 56 wt. %). **As can be seen by the following graph, the Ms of the material is highly sensitive to the alloying ratio.** The smallest change in Ni content has a large effect on the transformation temperatures. This is important to understand when considering different wrought Nitinol materials and ageing heat treatments.

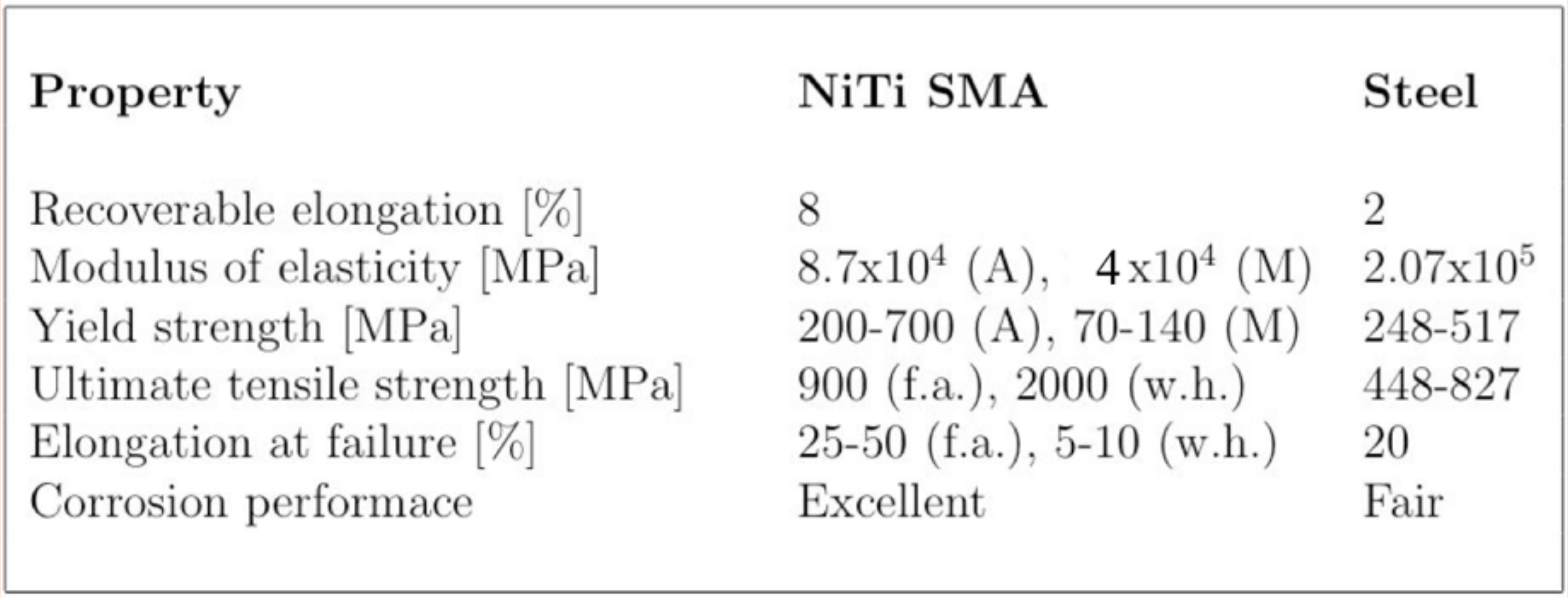
The Ms Temperature changes by approximately 80 degrees Kelvin for every atomic percent change in Ni content. For this reason, great control of the alloy content is required during the casting process



Stress-Strain curves are shown below for a typical **stainless steel alloy and a Nitinol alloy**. A simple comparison of the curves illustrates the difference between elastic-plastic behavior common to engineering metals and the non-linear superelastic behavior of Nitinol. The Nitinol sample shown below was strained to 8%, released back to 0%, and then pulled to failure to illustrate the superelastic loop. The stainless steel sample was pulled straight to failure.

The elastic limit of the stainless steel alloy is around 0.2% before permanent straining occurs **whereas nitinol can be strained up to 8% before permanently straining.**





Property	**NiTi SMA**	**Steel**
Recoverable elongation [%]	8	2
Modulus of elasticity [MPa]	$8.7 \mathrm{x} 10^4$ (A), $4 \mathrm{x} 10^4$ (M)	$2.07 \mathrm{x} 10^5$
Yield strength [MPa]	200-700 (A), 70-140 (M)	248-517
Ultimate tensile strength [MPa]	900 (f.a.), 2000 (w.h.)	448-827
Elongation at failure [%]	25-50 (f.a.), 5-10 (w.h.)	20
Corrosion performace	Excellent	Fair

Corrosion

On the surface of Nitinol, Titanium ions interact with oxygen to form an extremely tenacious and passive Titanium oxide layer (TiO_2). This oxide layer protects the Nitinol material beneath from the external environment which typically gives the Nitinol excellent corrosion resistance and biocompatibility.

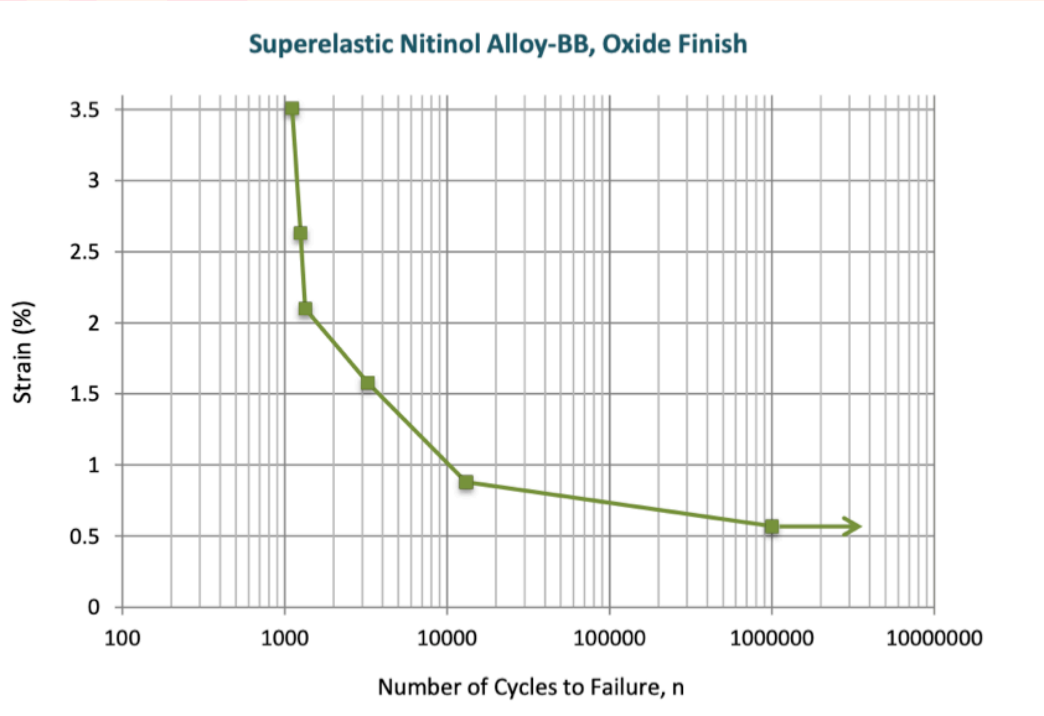
Sterilization of Nitinol

Medical devices made from Nitinol can be sterilized through most typical sterilization methods including **steam** (autoclave), **ethylene oxide** (EtO), or **radiation** (gamma). However, the temperature seen by the device must be considered and maintained below 300 C to ensure no effects on mechanical and functional properties.

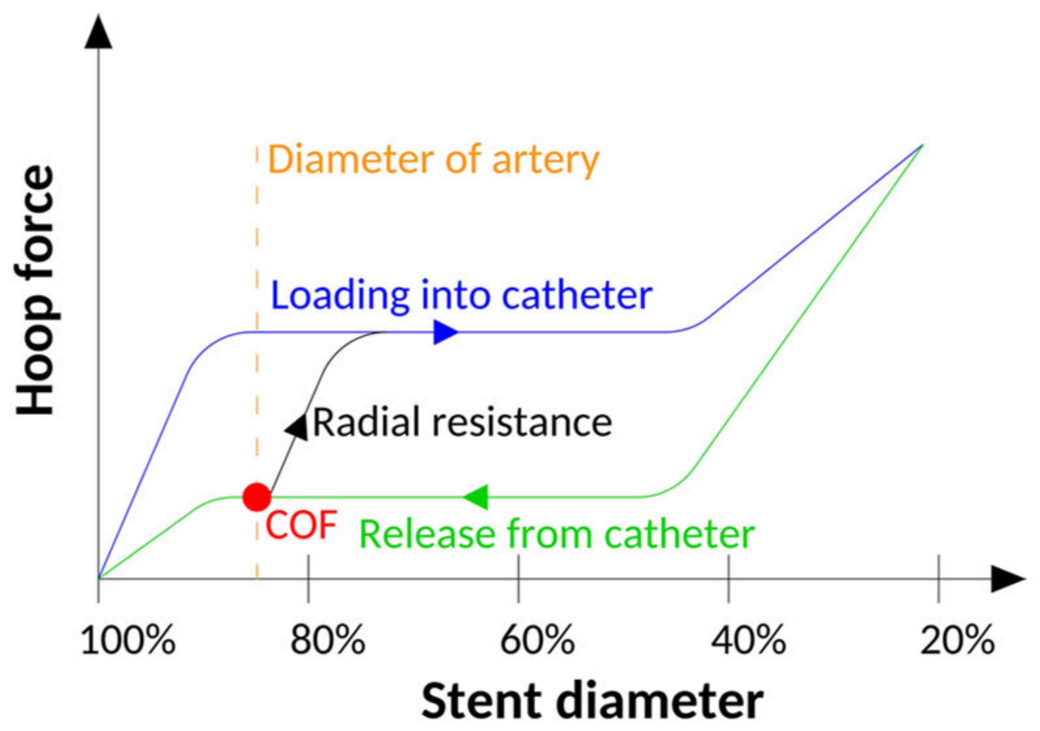
Fatigue

Fatigue needs to be considered for long term, high cycle applications. The chart shown below presents a typical dramatic decrease in fatigue life as the strain level increases. *For example, at 0.57% strain testing was terminated after 1 million cycles and the wire survived. Increasing the strain to just 0.88%, the wire failed at just over 13 thousand cycles.* Fatigue performance is therefore very important to consider when designing a Nitinol component.

If the application uses 0.5% or less strain, such as experience in many cardiovascular stent or heart valve applications, the material will likely survive millions of cycles.



Radial resistive force (RRF) and Chronic outward force (COF) are the two main characteristics that determine the force balance between the vessel wall and the stent. **RRF is a measure of the amount of force required to compress the stent radially, while COF correlates to a measure of the radial force the stent projects outward in its deployed configuration.** Both RRF and COF are determined by the unique force hysteresis of Nitinol. **Hoop strength is another important design parameter that defines the maximum hoop load that can be carried by the stent.**



$$\sigma = p \cdot d / 2\, t$$

Sometimes hoop force, Fd, or hoop force per unit length, fd, is used instead of hoop stress to characterize load acting on the stent

$$F_d = p \cdot d \;\; L / 2$$

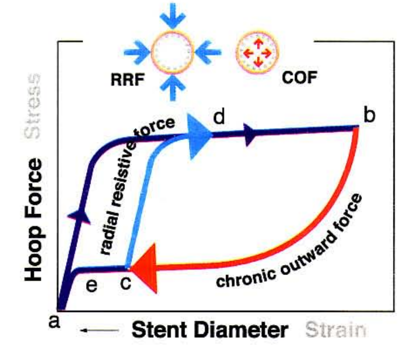


Fig. 7 Schematic stress hysteresis and concept of biased stiffness as demonstrated with the cycle insertion into delivery system/deployment/compression of a stent

Ti–Ni alloys consisting of equal atomic amounts of Ti and Ni (49–51 mol% Ni) show unique mechanical properties, such as **shape memory, superelasticity and efficient damping**. Because of the superelasticity, the Ti–Ni alloy is used for guide wires, stents, orthodontic arch wires, endodontic reamers and files.

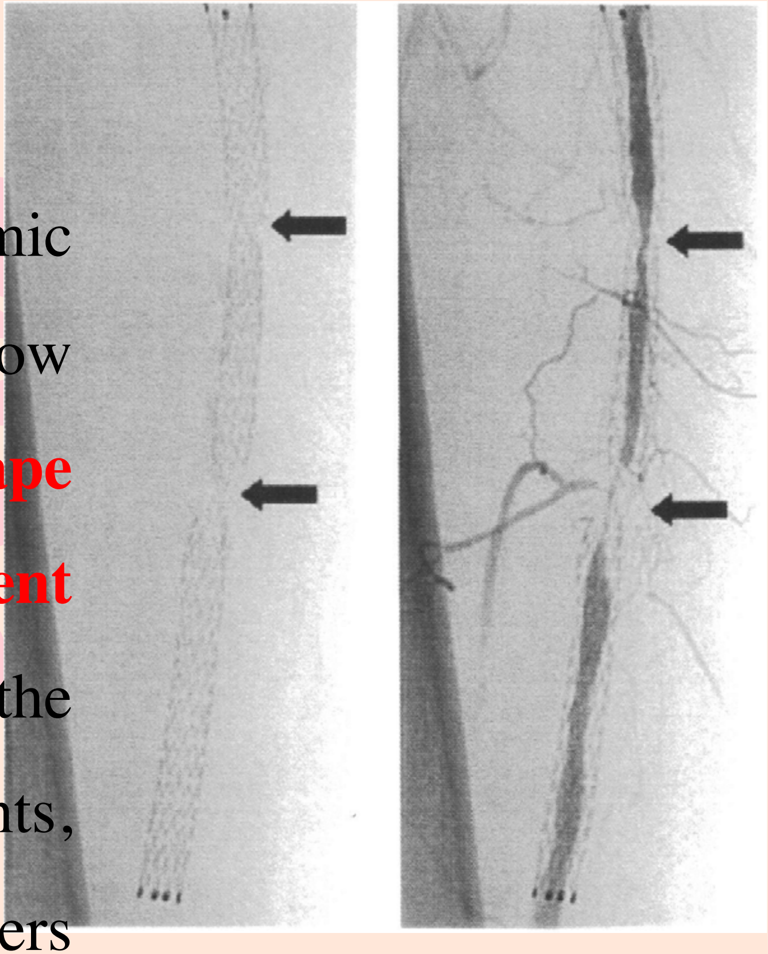


Figure 6. Early-stage fractures of self-expanding Ti–Ni femoral stents in service observed by x-ray examination [10].

Early-stage fractures of stents in service have been reported. Among self-expanding Ti–Ni femoral stents, 37.2% fractured within 10.7 months of implantation, The use of Ti–Ni alloy with about 50 mol% Ni in medicine is limited by safety. Therefore, there is a great demand for Ni-free shape-memory and superelastic alloys to solve such problems.

Ti–Sn–Nb

Ti–Nb–Al

Ti–Mo–Ga

Ti–Mo–Sn

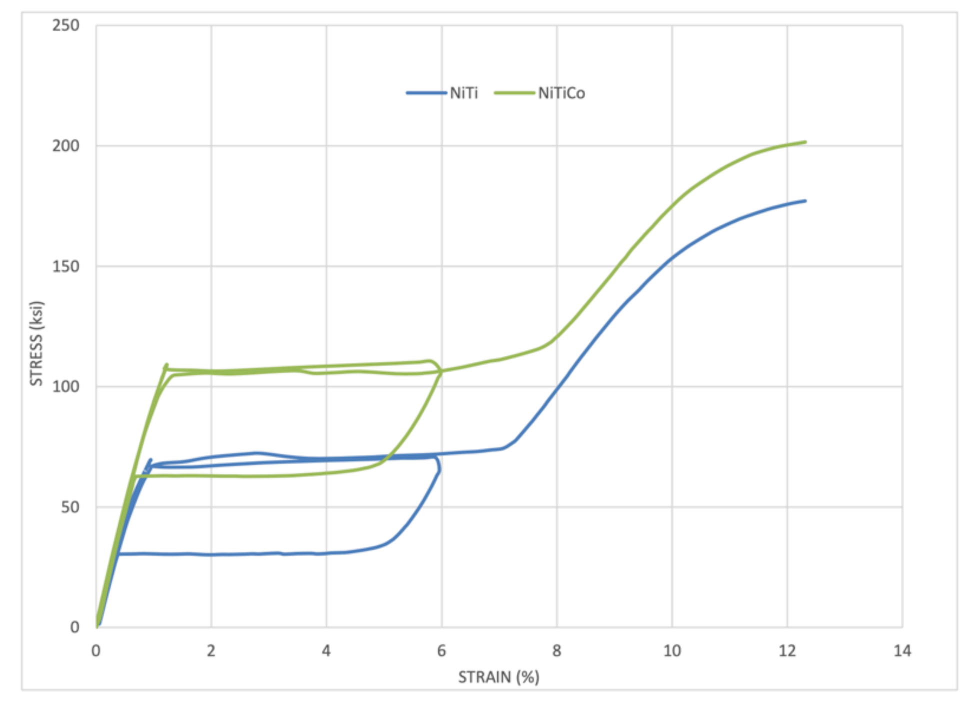
Ti–Nb–O

Ti–Nb–Zr exhibit shape-memory effect and superelasticity, while the recovery strain and superelastic deformation stress of these alloys are still lower than those of the Ti–Ni alloy.

The Nickel Titanium Cobalt (NiTiCo) Alloy

NiTiCo is a relatively new shape memory alloy with “stiffness” properties that exceed that of standard Nitinol. From an application perspective, there are significant advantages for certain medical devices in utilizing an alloy that exhibits the superelasticity of standard Nitinol in combination with an increase in modulus of elasticity and UPS/LPS. **For example, the higher elastic modulus, UPS and LPS will allow for smaller device profiles, thus enabling new opportunities for device development**.

NiTiCo alloys contains 1.2-1.5 wt. % Cobalt.



Other Metals

- Tantalum
  - High biocompatibility in animal studies
  - Low strength to density ratio restricts applications to those such as wire sutures and radioisotopes

- Platinum and other noble metals
  - Corrosion resistant but poor mechanical properties
  - Used mostly as alloys for electrodes such as pacemaker tips

Low magnetic susceptibility alloys for MRI

Magnetic resonance imaging (MRI) is widely used as an important diagnostic tool, especially for orthopedic and brain surgery. This method has remarkable advantages for obtaining various cross-sectional views and for diagnosis of the human body with no invasion and no exposure of the human body to x-ray radiation**. However, MRI diagnosis is inhibited when metals are implanted in the body, since metallic implants, such as stainless steels, Co–Cr alloys and Ti alloys become magnetized in the intense magnetic field of the MRI instrument, and artifacts occur in the image.** Such artifacts can disturb the images of organs and tissues around the implant, preventing exact diagnosing. **The area affected by the artifacts is related to the magnetic susceptibility of the implants and decreases with decreasing magnetic susceptibility.** Therefore, metals with low magnetic susceptibility should be developed as MRI continues to increase in popularity.

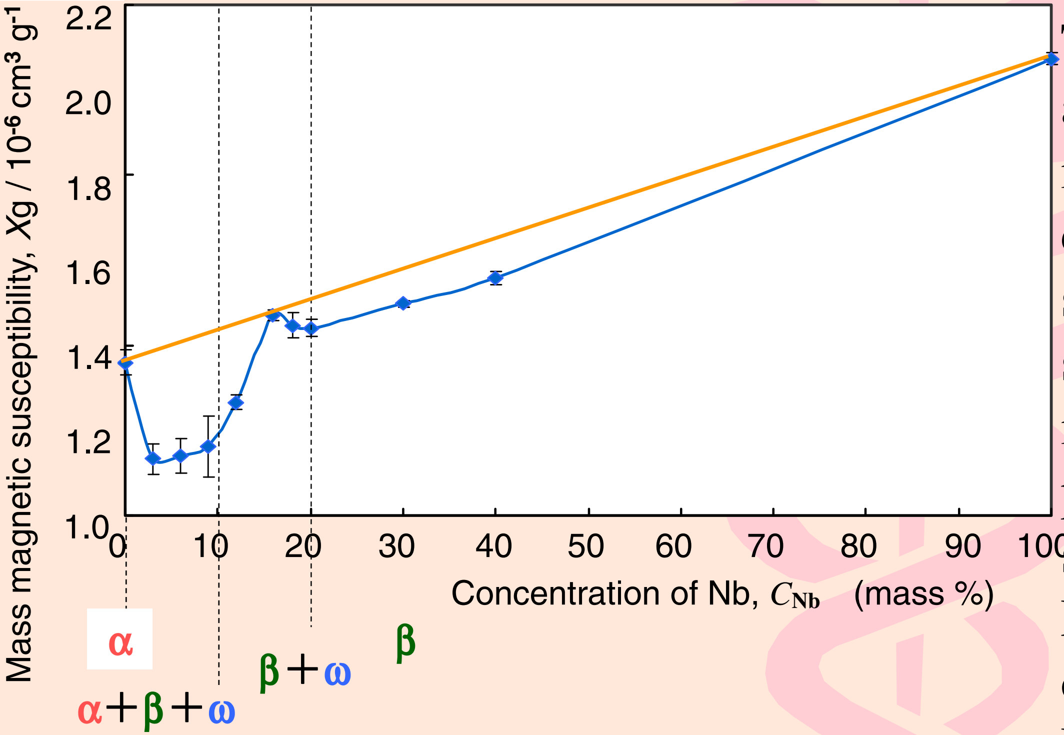


Figure 9. Effects of Nb content and constituent phases on the magnetic susceptibility of Zr–Nb alloy.

The magnetic susceptibility of a Au–Pt–Nb alloy is similar to that of water.

To reduce artifacts Ti–Zr, Zr–Nb, and Zr–Mo alloys with low magnetic susceptibility have been developed. The magnetic susceptibility of the Zr–Nb alloy is shown in figure; it exhibits minimum values where the ω phase is formed. The magnetic susceptibility was reduced in Zr–Nb and Zr–Mo alloys up to about one-seventh of that of the Co–Cr–Mo alloy and one-third of that of Ti and Ti alloys.

Among Zr-based alloys, Zr–9Nb and Zr–3Mo possess low magnetic susceptibility Although Zr–3Mo and Zr–9Nb alloys have low magnetic susceptibilities, it is difficult to apply plastic deformation to these alloys during processing for medical devices because their tensile strength and elongation are limited by the ω phase.

Surface modification of metallic biomaterials

To add biofunction to metals, surface modification is necessary because a biofunction cannot be added during manufacturing processes such as melting, casting, forging and heat treatment. **Surface modification is a process that changes a material's surface composition, structure and morphology, leaving the bulk mechanical properties intact**. With surface modification, the tissue compatibility of the surface layer can be improved.

Usually two methods might be used:

(I) **a calcium phosphate layer with the thickness in the micrometer.** Plasma spraying of apatite on metallic materials is widely used to form the apatite layer. In this case, however, the apatite –Ti interface or the apatite itself may fracture under relatively low stress because of low interface bonding strength and low toughness of the sprayed layer.

(II) surface-modified layer with the thickness in the nanometer scale

hard-tissue compatibility can be improved by modifying the Ti surface instead of the apatite coating.

-Mechanical anchoring

In the stems of artificial hip joints and dental implants, the chemical bonding of metal surfaces with bone is not expected. In other words, it is impossible for metals as typical artificial materials to chemically and naturally bond with bone as living tissue, especially in the human body with body fluid. Therefore, the surface morphology is sometimes controlled, and rough and porous surface is formed in biomaterials. Living tissue, such as bone, is expected to grow into the rough porous surface, and the materials and bone are strongly connected as a result of the so-called anchoring effect.

First generation: grind machining of the surface.

Second generation: blast, acid etching, anodic oxidation and laser abrasion.

Nanostructured titanium oxide and titanium oxide nanotube

Third generation: chemical treatment and hydroxyapatite coating.

Fourth generation: Immobilization of biofunctional molecules (collagen, bone morphogenetic protein and peptide).

When Ti alloys are used for bone fixators, such as bone screws and bone nails implanted in bone marrow, Ti alloys form callus on their surfaces and sometimes assimilate with bone. Therefore, bone may be refractured when the fixators are retrieved after bone healing because Ti easily forms calcium phosphate on itself. **Stainless steel is used for complete retrieval after healing**. Therefore, surface treatments that do not cause callus formation are necessary for the safe utilization of Ti alloy devices. It has been reported that Zr forms zirconium phosphate but not calcium phosphate.

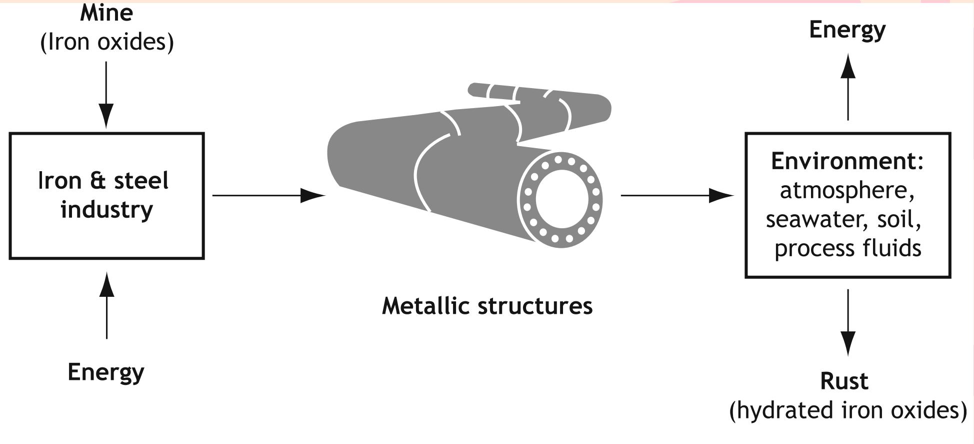
(Degrado)
Corrosione

Materials exposed to aggressive environments may undergo chemical and physical degradation.

This degradation is called "**corrosion**" when the material concerned is a **metal**. The term corrosion derives from Medieval Latin [corrosionis, from the verb corrodere].

Corrosion is often defined as "destruction or degradation of a material caused by a reaction to its environment" and also "***the spontaneous tendency of a metallic component to return to its original state as found in nature***".

For this reason, corrosion is also called ***metallurgy in reverse***, because the corrosion process returns metals to their more thermodynamically stable natural state as oxides or sulphides or other compounds, from which metallurgy transforms to metal by supplying energy.



While You Are Reading This Message, 10 Tons of Iron Is Corroding Around the World

Cost of corrosion accounts for around 3–4% of the GNP of industrialized countries. A recent study by NACE (IMPACT 2016) estimates the global cost of corrosion to be US$ 2.5 trillion.

Corrosion cannot be halted but only reduced. The costs of corrosion could be reduced by 15–35% simply by applying basic knowledge of corrosion principles, adopting the most familiar techniques such as cathodic protection, corrosion inhibitor injection or selecting a resistant material and improving design.

Corrosion Forms

Corrosion damage presents two main morphologies with regard to the environmentally exposed surface: on the whole surface, so-called **generalized corrosion**, only on a small portion of it, so-called **localized corrosion**. Moreover, in specific conditions and in the presence of a tensile load, attacks can cause cracks perpendicular to the tensile stress to form, so-called **stress corrosion cracking**. In general, corrosion processes bring all the constituents of the material into solution even if in some cases only one constituent is dissolved (selective corrosion) or only the grain border is attacked producing **intergranular corrosion**.

Uniform or Generalized Corrosion

This is a form of corrosion which affects the whole surface. Material thinning, called also thickness loss, is generated at a typically predictable rate provided that the environmental conditions are known. For example, the corrosion of carbon steel exposed to the atmosphere takes place at a rate varying from a few tens to a few hundred μm/year depending on humidity, temperature, the **presence of chlorides** and other pollutants. When zinc coatings are used in the same environment, the corrosion rate drops to a value about 10–30 times lower.

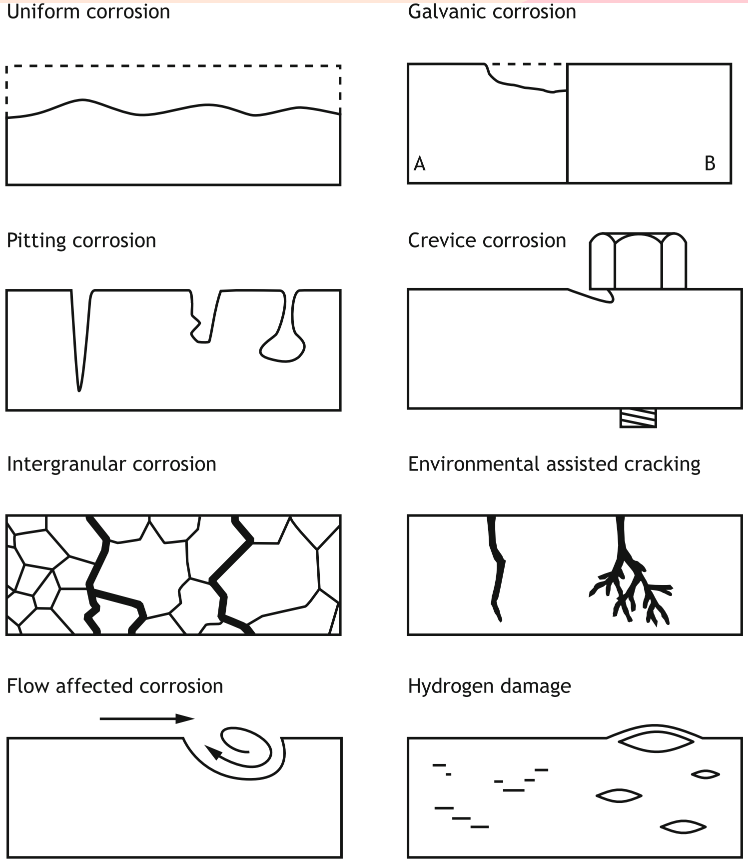


Fig. 1.3 Figure showing typical corrosion forms occurring on metals

Corrosion

- Corrosion is the degradation of metals to oxide, hydroxide or other compounds through chemical reactions.
- Human body is an aggressive environment:
  - Water H_2O
  - dissolved oxygen (O_2)
  - proteins
  - chloride
  - hydroxide
  - pH (after surgery pH around 5.3-5.6)
  - flow rate

Corrosion: Basic Reactions

La condizione indispensabile affinché si manifesti la corrosione su di un manufatto ferroso è quindi la presenza di umidità e di ossigeno. In presenza di umidità, infatti, si hanno fenomeni di corrosione in quanto l'acqua, anche se poco, si dissocia:

H_2O ---> $H^+ + OH^-$

mentre il metallo, in presenza di acqua, tende a ossidarsi:

Fe ---> $Fe^{++} + 2e^-$

ne consegue che può avvenire la seguente reazione:

$2Fe^{++} + 4OH^-$ ---> $2Fe(OH)_2$

A sua volta $Fe(OH)_2$ può ulteriormente reagire con l'ossigeno per formare la ruggine: **$4Fe(OH)_2 + O_2$ ---> $2Fe_2O_3 \cdot nH_2O + 3H_2O$**

Ma questa non è l'unica reazione possibile:

$4Fe + 3O_2 + 2H_2O$ ---> $2Fe_2O_3 \cdot H_2O$

$2Fe + O_2 + 2H_2O$ ---> $2Fe(OH)_2$ $4Fe + 3O_2 + 6H_2O$ ---> $4Fe(OH)_3$

$6Fe + 4O_2$ ---> $2Fe_3O_4$

Corrosion: Basic Reactions

Il tutto è aggravato dal fatto che gli elettroni formatisi nella seconda reazione, circolando nel metallo, reagiscono con gli ioni H^+ presenti per formare Idrogeno:

$2H^+ + 2e^- \dashrightarrow H_2$

Il quale Idrogeno, allontanandosi dall'ambiente di reazione, fa aumentare il pH, che, a sua volta, favorisce la terza reazione.

In un **ambiente salmastro** il fenomeno di corrosione è aggravato dalla presenza di NaCl e altri sali che si dissociano in acqua:

$NaCl$ ---> $Na^+ + Cl^-$ **e lo ione Cloro che si forma può reagire con il Ferro:**

$Fe^{++} + 2Cl^-$ ---> $2FeCl_2$ mentre al catodo si forma l'idrossido di sodio:

$Na^+ + OH^-$ ---> $NaOH$ il quale reagisce con il cloruro ferroso per dare nuovamente l'ossido ferrico:

$4FeCl_2 + 8NaOH + O_2$ ---> $2Fe_2O_3 + 8NaCl + 4H_2O$ come aggravante si riforma il cloruro di sodio che ritorna quindi in reazione.

Corrosion: Basic Reactions

1) **processo anodico (ossidazione)**. Trasferimento del metallo in ioni idratati, con un numero equivalente di elettroni "lasciati" sulla superficie del metallo.

$Me \rightarrow Me^{++}(nH_2O) + 2e^-$

2) **processo catodico (riduzione)**. Assimilazione dell'eccesso di elettroni da parte di depolarizzatori (atomi, molecole o ioni capaci di essere ridotti al catodo), in questo esempio ossigeno, tramite la semireazione

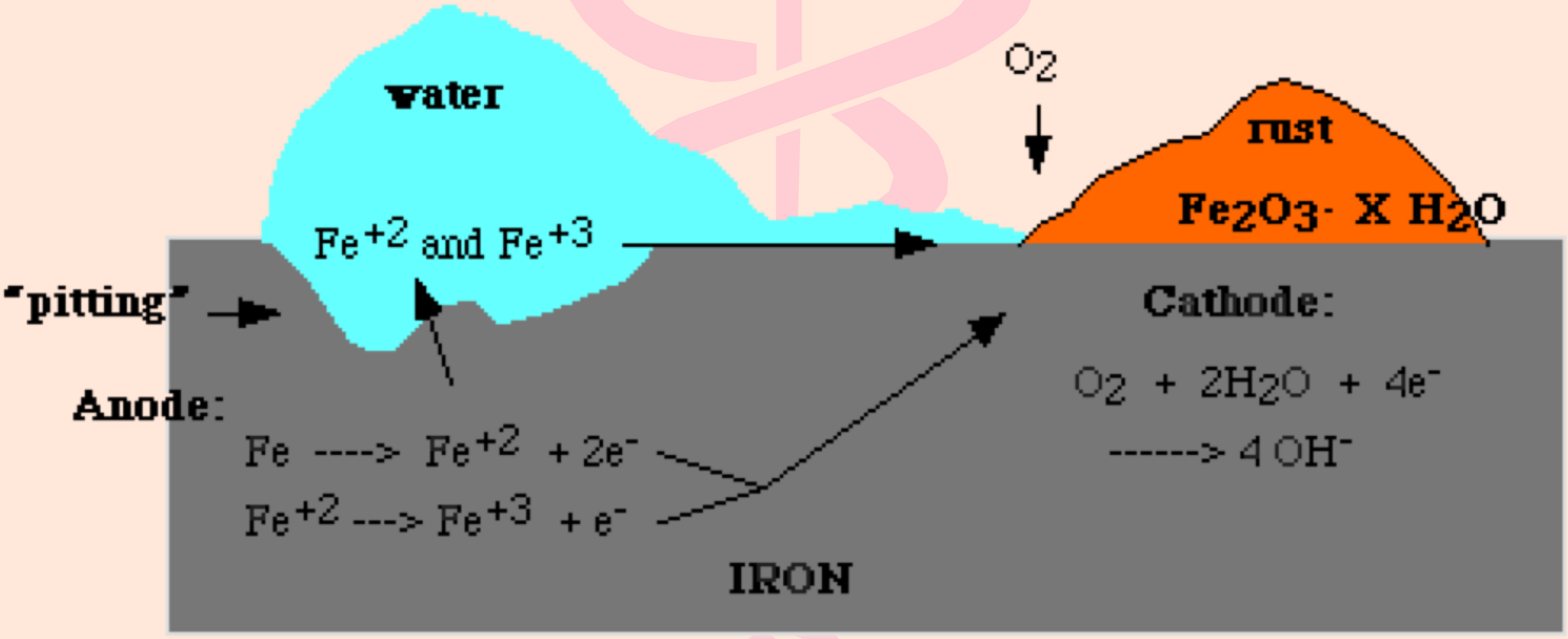
$O_2 + 2e^- + H_2O \rightarrow 2OH^-$

Questi due processi sono indipendenti ma complementari, nel senso che il numero di elettroni nell'unità di tempo lasciati sulla superficie metallica dalla reazione anodica deve essere uguale al numero di elettroni nell'unità di tempo consumati dal depolarizzatore nella semireazione catodica [$v_{ox} = v_{red}$]. Infatti, se così non fosse, si avrebbe un accumulo di carica elettrica nel metallo.

Queste relazioni avvengono entrambe all'interfaccia metallo-soluzione acquosa, zona nella quale esse possono comportare modificazioni sensibili dell'ambiente acquoso (ad esempio un sensibile aumento di pH).

Corrosion: Terminology

How it happens on the surface?



La corrosione localizzata per aerazione differenziale si instaura quando sulla superficie del materiale metallico sono presenti zone che presentano una differente permeabilità nei confronti dell'ossigeno.

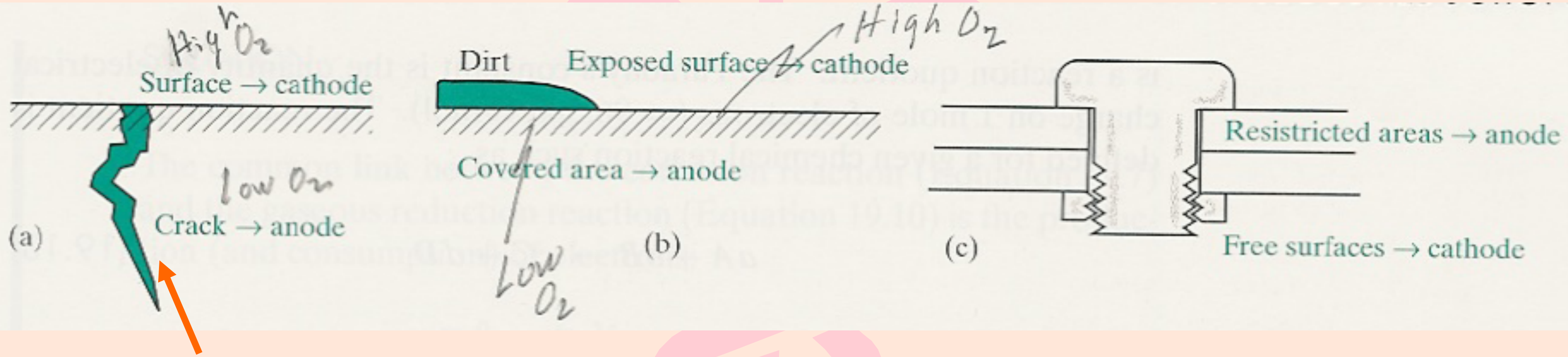
La parte della superficie metallica meno permeabile all'ossigeno si comporta da regione anodica, quindi è sede del processo di dissoluzione del metallo; ad esempio nel caso dell'acciaio si ha il seguente processo di ossidazione:

$Fe \rightarrow Fe^{++} + 2e^-$

mentre la parte della superficie metallica più permeabile all'ossigeno si comporta da regione catodica, quindi è sede del processo di riduzione dell'ossigeno:

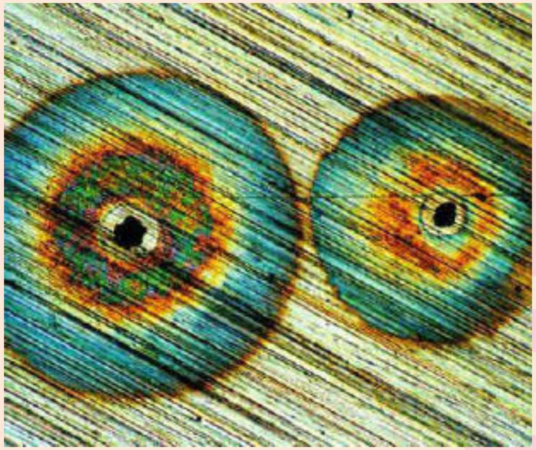
$1/2\ O_2 + H_2O + 2e^- \rightarrow 2\ OH^-$

Corrosion: Closer look at the "gaseous reduction":



Crevice Corrosion

- Pitting Corrosion: special case of crevice corrosion where corrosion is induced by handling damage such as scratches. Surgeons should be careful about this type of corrosion.



Corrosion in the crevice between the tube and tube sheet (both made of type-316 stainless steel) of a heat exchanger in a seawater desalination plant

An example of corrosion damages with shared responsibilities was the sewer explosion that killed 215 people in Guadalajara, Mexico, in April 1992. Besides the fatalities, the series of blasts damaged 1,600 buildings and injured 1,500 people.

Galvanic Corrosion

Il meccanismo della **corrosione galvanica** si produce secondo un processo ad umido e si innesca quando due materiali avente un diverso valore di nobiltà (oppure due parti dello stesso materiale esposte a condizioni differenti), vengono posti a diretto contatto (formando un *accoppiamento galvanico*), in presenza di un terzo elemento (detto "elettrolita").

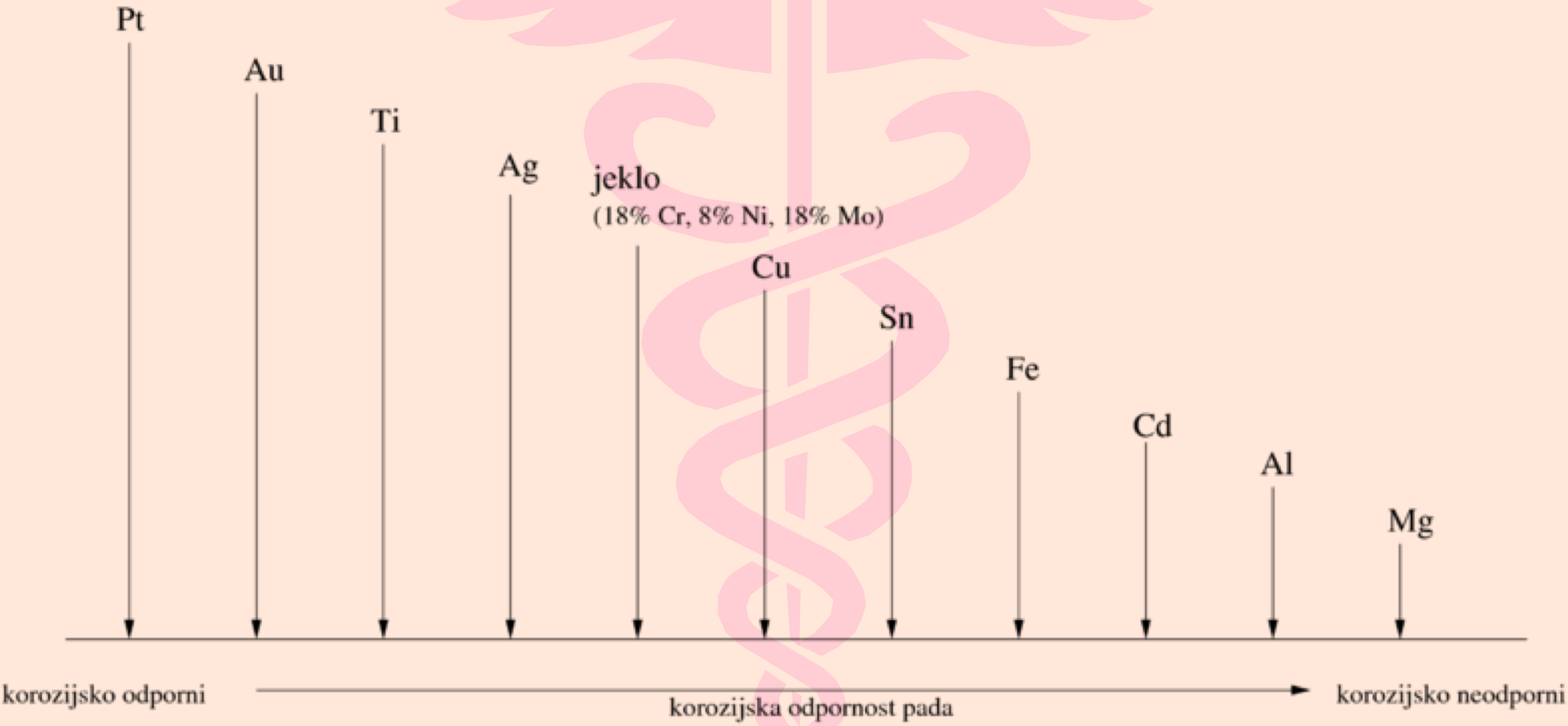
Si viene a formare una cella galvanica in cortocircuito (detta **macrocoppia**) nella quale gli elettrodi sono costituiti dai due materiali accoppiati. Si genera un flusso di elettroni dal materiale meno nobile (avente potenziale minore), denominato anodo (o polo negativo) che si ossida, verso quello più nobile avente potenziale maggiore, denominato catodo (o polo positivo), dove avviene la riduzione dei cationi, che può rivestirsi di strati metallici.

Le reazioni che avvengono durante il processo di corrosione sono tutte redox (dall'inglese ***reduction*** e***ox****idation*).

Galvanic Corrosion

- Occurs when there are two dissimilar metals
- Much more rapid than corrosion by gaseous reduction
- **Avoid implantation of dissimilar metals**

Galvanic Corrosion



Pt

Au

Ti

Ag

jeklo
(18% Cr, 8% Ni, 18% Mo)

Cu

Sn

Fe

Cd

Al

Mg

korozijsko odporni

korozijska odpornost pada

korozijsko neodporni

mechanism:

$Fe \rightarrow Fe^{++} + 2e^-$

$2H^+ + 2e^- \rightarrow H_2$ acid medium

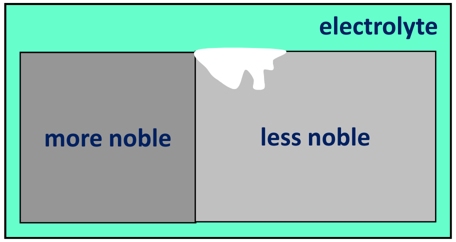
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ alcaline medium

preconditions:

- conductive surrounding (even a very thin water film is enough)
- homogeneity of surrounding & material

! anodic and cathodic reactions are parallel !

→ dissimilar conducting materials are connected electrically and exposed to an electrolyte



electrolyte

more noble

less noble

preconditions:
- **electrochemically dissimilar metals**
- **metals are in electrical contact**
- **metals are exposed to an electrolyte**

metals in electrolyte → different corrosion potentials of different metals
→ potential difference = driving force for galvanic current flow

less noble material	**= anode**	**→ acceleration of corrosion**
more noble material	**= cathode**	**→ reduction of corrosion**

→ Kathodic reaction at the periphery of the drop

→ Passivation of border area by increasing pH

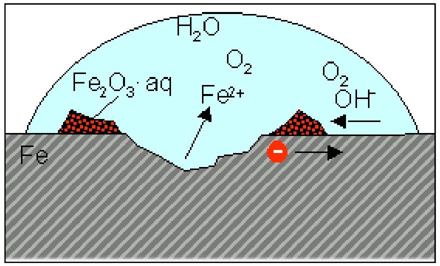
→ Low pH & low O_2-concentration in the middle → dissolving of ion

→ around anodic area: formation of rust

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

$Fe^{++} + 2OH^- \rightarrow Fe(OH)_2$

$4Fe(OH)_2 + O_2 \rightarrow 4FeO(OH) + 2H_2O$



↑Corrosion with **↓O_2 concentration**

Un processo corrosivo ha luogo quando sono verificati determinati presupposti termodinamici e cinetici. Come prima detto, la reazione tra un metallo M e l'ambiente:

$$M + 1/2\ O_2 + H_2O \ = \ M(OH)_2$$

è termodinamicamente possibile solo se accompagnata da una diminuzione dell'energia libera ΔG del sistema, variazione che esprime inoltre il lavoro motore disponibile per il processo stesso.

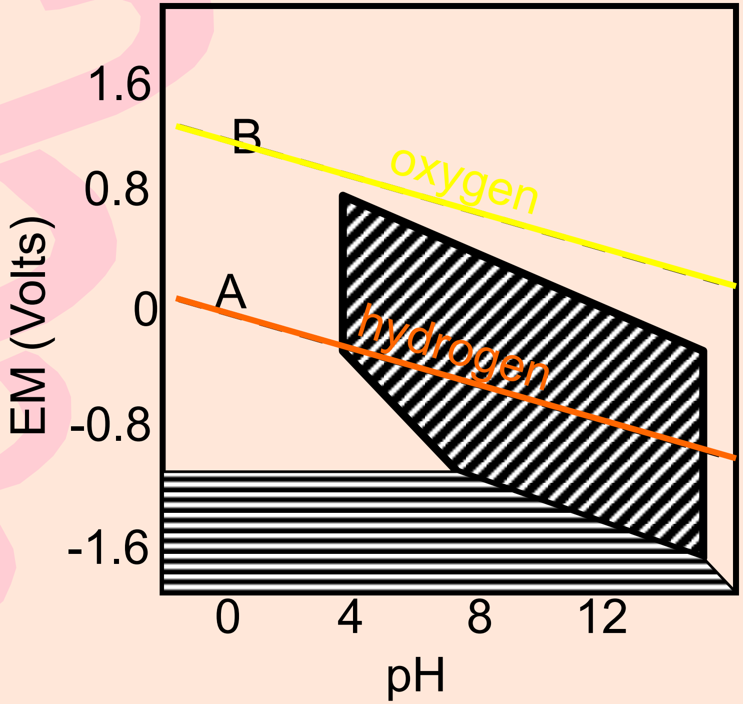
Questa condizione è verificata nel caso del ferro puro nell'atmosfera: in questo caso si parla di stato di **ATTIVITA**'.

Quando la reazione **non è termodinamicamente possibile** ($\Delta G > 0$), il materiale si dice in stato di **IMMUNITA'** (ad es. oro in atmosfera).

Vi sono però casi in cui la reazione è T.D. possibile, ma estremamente lenta dal punto di vista cinetico e si parla allora di stato di **PASSIVITA'** (è il caso del Cr e degli acciai INOX che si ricoprono di un film protettivo di ossido di cromo).

Pourbaix Diagram

- classification of all possible reactions between a metallic element and water for combinations of pH and electrical potential difference
- above B oxygen is released
- below A hydrogen is released
- between A and B water is stable

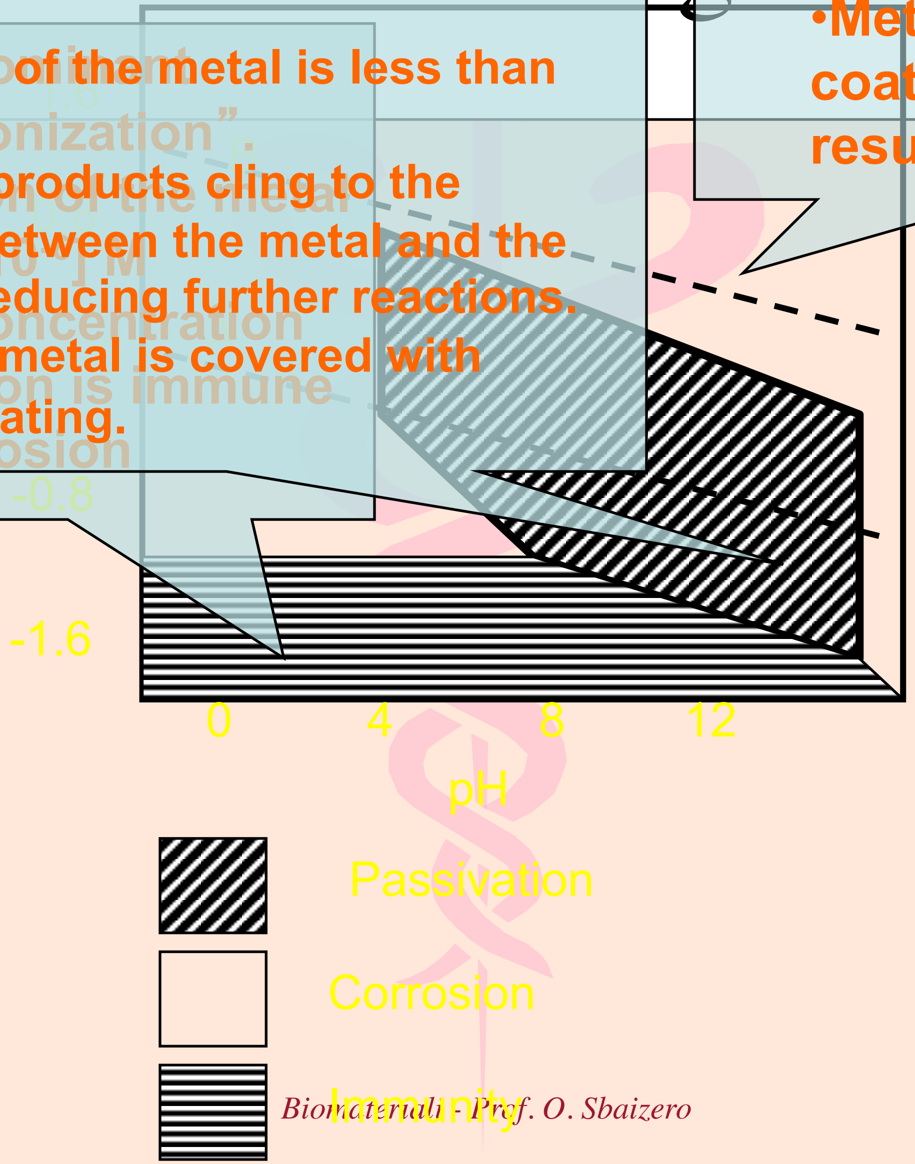


Pourbaix Diagram

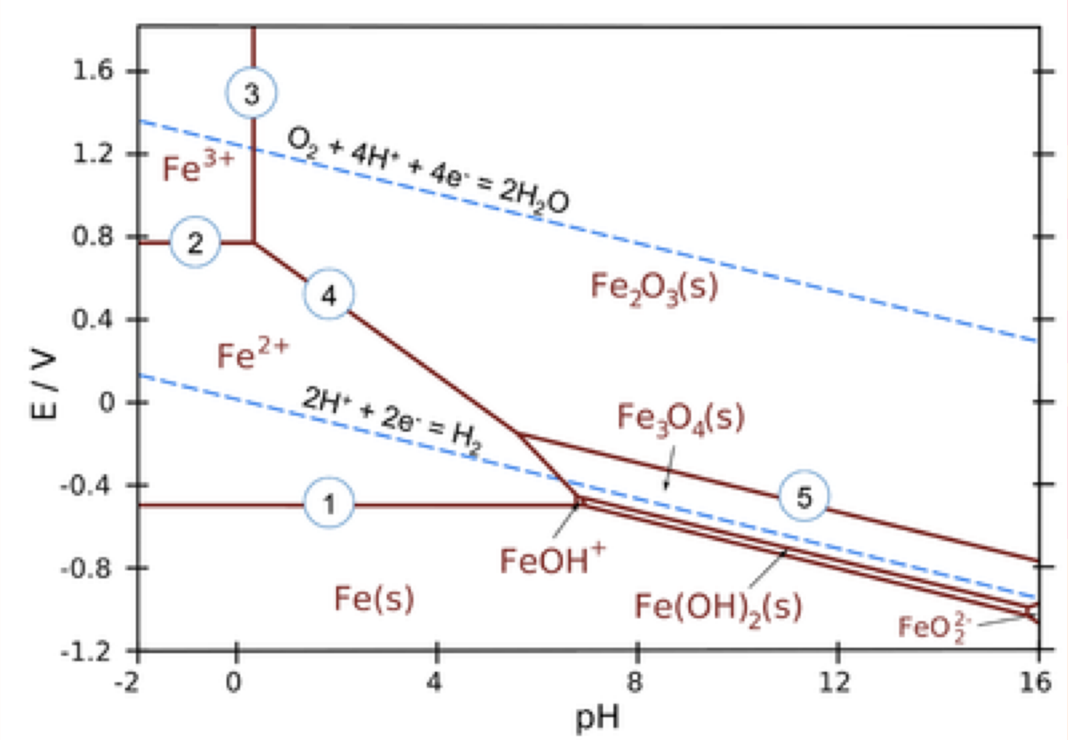
- Passivation: formation of "oxides and hydroxides"
- Concentration of the metal is less than $[10^{-6}]$ M
  - Reaction products cling to the interface between the metal and the solution, reducing further reactions.
  - Thus, the metal is covered with passive coating.

- Immunity Dominant reaction is "ionization".
- Concentration of the metal is less than $[10^{-6}]$ M
  - At this concentration the reaction is immune from corrosion

- Corrosion: concentration of the metal is greater than 10^{-6} [M]
  - Metal and the passive coating is attacked resulting in corrosion.



Pourbaix Diagram



in the Pourbaix diagram for Fe, the horizontal line between the Fe^{3+} and Fe^{2+} regions represents the reaction

$$Fe^{3+}{}_{(aq)} + e- \rightleftharpoons Fe^{2+}{}_{(aq)}$$

which has a standard potential of +0.77 V.

- **Areas** in the Pourbaix diagram mark regions where a single species ($Fe^{2+}{}_{(aq)}$, $Fe_3O_{4(s)}$, etc.) is stable. More stable species tend to occupy larger areas.
- **Lines** mark places where two species exist in equilibrium.
  - **Pure redox** reactions are **horizontal** lines - these reactions are not pH-dependent
  - **Pure acid-base** reactions are **vertical** lines - these do not depend on potential
  - Reactions that are **both** acid-base and redox have a slope

Pourbaix Diagram

The water redox lines have special significance on a Pourbaix diagram for an element such as iron.

Recall that liquid water is stable *only* in the region between the dotted lines.

Below the H_2 line, water is unstable relative to hydrogen gas, and above the O_2 line, water is unstable with respect to oxygen.

For active metals such as Fe, the region where the pure element is stable is typically below the H_2 line. This means that iron metal is unstable in contact with water, undergoing reactions:

$Fe(s)+2H+\rightarrow Fe_2+(aq)+H_2$ (*in acid*)

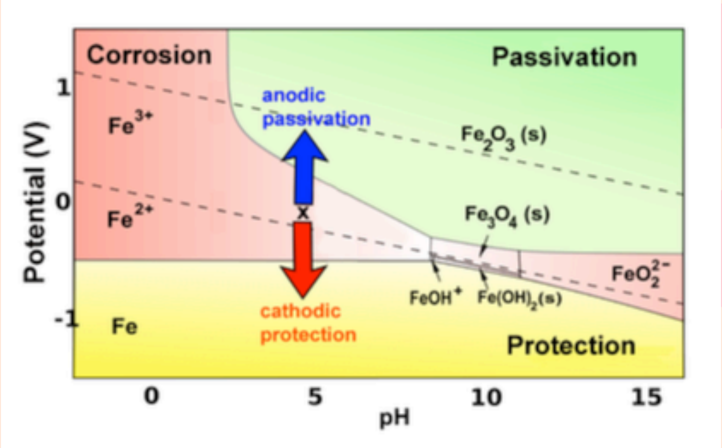
$Fe(s)+2H_2O\rightarrow Fe(OH)_2(s)+H_2$ (*in base*)

Iron (and most other metals) are also thermodynamically unstable in air-saturated water, where the potential of the solution is close to the O_2 line in the Pourbaix diagram. Here the spontaneous reactions are:

$4Fe(s)+3O_2+12H^+\rightarrow 4Fe^{3+} + 6H_2O$ (*in acid*)

$4Fe(s)+3O_2\rightarrow 2Fe_2O_3(s)$ (*in base)*

Pourbaix Diagram



Draw a vertical line through the iron Pourbaix diagram at the pH of tap water (about 6) and you will discover something interesting:
at slightly acidic pH, iron is quite unstable with respect to corrosion by the reaction:

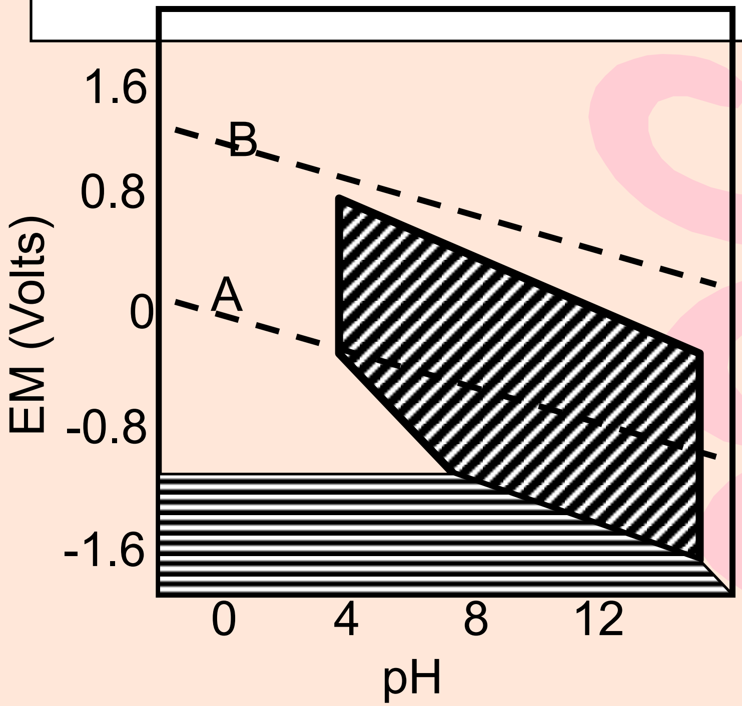
$$Fe(s) + 2H+ \rightarrow Fe^{2+}_{(aq)} + H_2$$

but *only in water that contains relatively little oxygen,* i.e., in solutions where the potential is near the H_2 line. Saturating the water with air or oxygen moves the system closer to the O_2 line, where the most stable species is Fe_2O_3 and the corrosion reaction is:

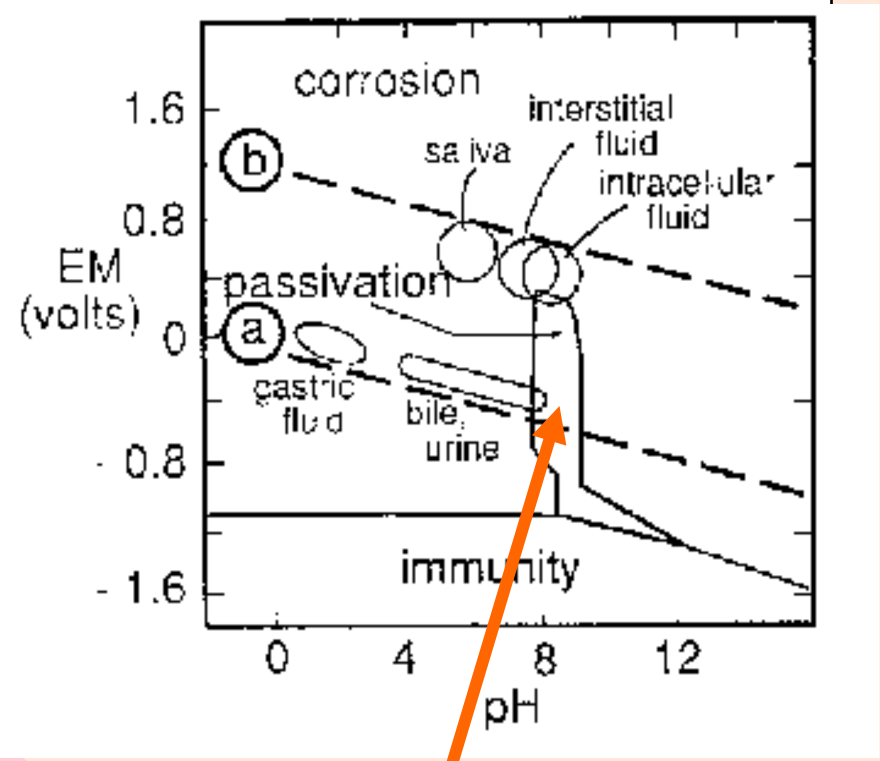
$$4Fe(s) + 3O_2 \rightarrow 2Fe_2O_3(s)$$

This oxidation reaction is orders of magnitude slower because the oxide that is formed *passivates* the surface. **Therefore iron corrodes much more slowly in oxygenated solutions**. More generally, iron (and other active metals) are passivated whenever they oxidize to produce a solid product, and corrode whenever the product is ionic and soluble. This behavior can be summed up on the color-coded Pourbaix diagram below:

Pourbaix Diagram



Chromium in water



Chromium in water + chloride

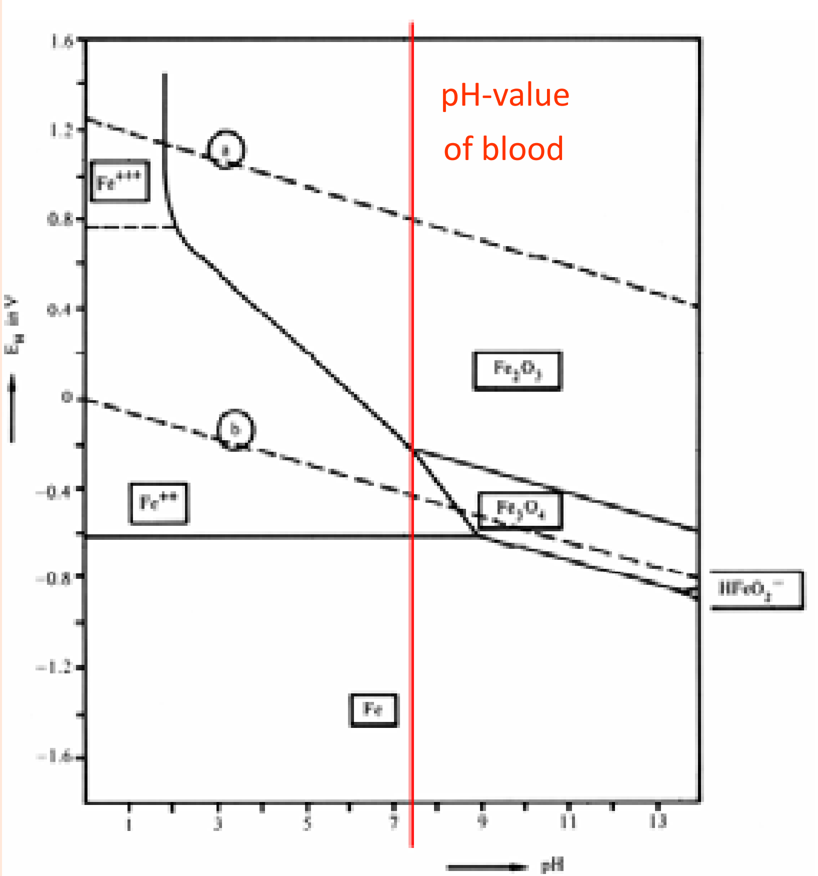
- Note smaller passivation region. Greater chance of corrosion.
- Most physiological solutions in the corrosion region

Corrosion of implants in human body:

→ **Blood = complex electrolyte**
* pH = 7,4 (±0,05)→ generated with a buffer-system
* blood consists of cells and plasma (proteins and electrolytes like Cl^- *or* PO_4^{3-} *dissolved in water*)
→ **more aggressive than seawater**!

→Corrosion increased at areas with **mechanical stress**

→ Can provoke an **inflammation**



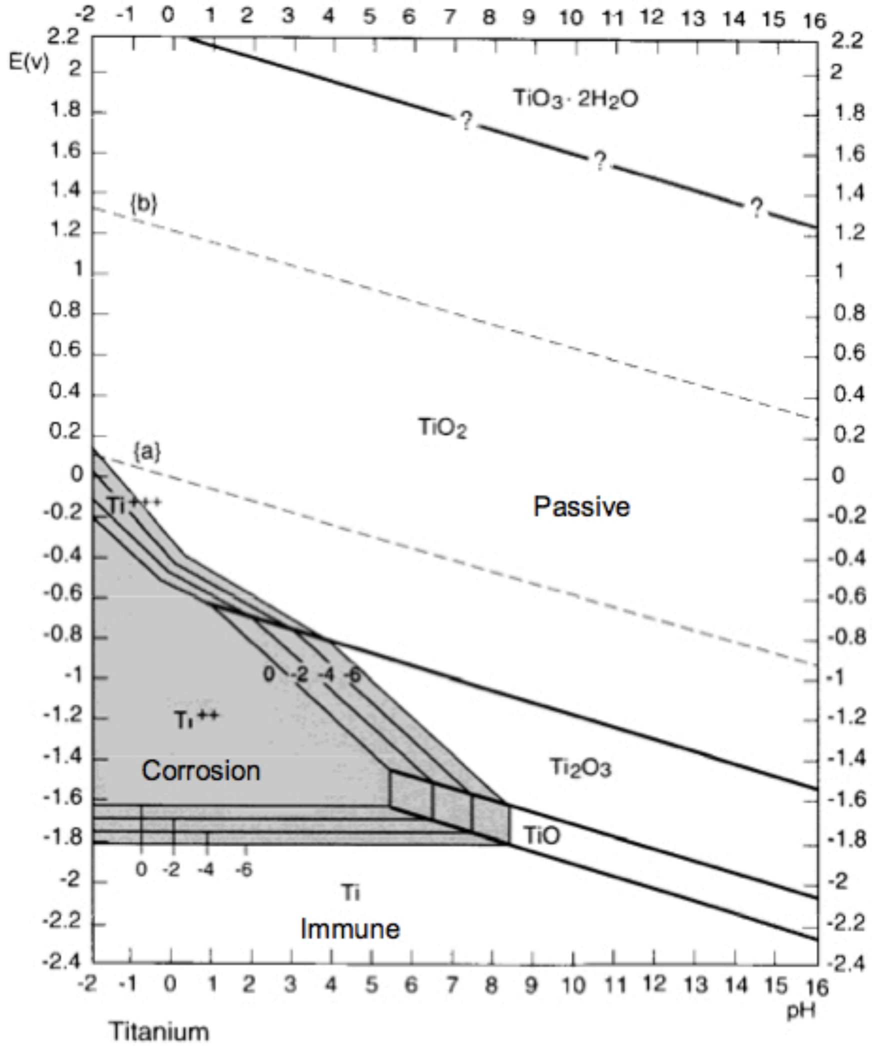


Fig. 2.1. The Pourbaix diagram for the titanium-water system [1] .

Against Corrosion

- Use appropriate metals
- Avoid implantation of dissimilar metals
- Minimize pits and crevices
- Avoid transfer of metal from tools to the implant during surgery
- A metal that does not corrode in one part of the body may corrode somewhere else