1.3.3 Metals: Basic Principles

Metals: Basic Principles

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Introduction to Metals in Medical Devices

The Role of Metals in Modern Medicine

The use of metals in the body has paralleled and enabled the advancement of medicine in the 20th and 21st centuries. A majority of medical devices require a metal alloy to provide the necessary strength and fatigue resistance to perform over the life of the patient.

- Joint replacements
- Spinal devices
- Cardiovascular stents
- Mechanical heart valves
- Fracture fixation devices
- Dental implants

A Historical Perspective

Early Explorations (18th - 19th Century)

The adaptation of metals for skeletal repairs and dentistry has foundations that go back millennia. Early scientific explorations laid the groundwork for modern metallic biomaterials.

1775

Iron wires were explored for use in internal fracture fixation.

1829

Tests in dogs of platinum, gold, silver, and lead showed promise for in-body use.

1908

Research began on the cellular reaction to metal fragments.

Early 20th Century Advances

The Dawn of Modern Alloys

Significant advances in metallurgy up to the 1920s introduced new alloys that became mainstays in medical applications, particularly for internal fracture fixation devices like screws and plates.

Stainless Steels

Versions like AISI-302, AISI-304, AISI-316, and AISI-317 were introduced for medical use.

Stellite

Also known as Vitallium, these cobalt-chromium-molybdenum (CoCrMo) alloys were developed for internal fixation.

Mid-20th Century Innovations

The Titanium Era and Other Key Alloys

The mid-20th century saw the introduction of titanium and its alloys, which exhibited excellent properties for a wide range of medical device applications. Other specialty alloys also found their niche.

- Titanium and its alloys (1950s-1970s): Found to have excellent strength, corrosion resistance, and biocompatibility.
- Platinum-Iridium (Pt-10% Ir): Used for electrodes due to its stability.
- Gold-Copper (Au-Cu) Alloys: Widely used in dentistry.
- Silver-Mercury (Ag-Hg) Amalgams: A common dental filling material for decades.

Why Metals? The Mechanical Demands

The Unparalleled Need for Metallic Strength

Metals are required for many medical devices because they possess requisite mechanical properties that no other class of biomaterials can replicate.
The human body is essentially a fatigue machine, subjecting implants to millions of loading cycles.

Cardiovascular Loading

At 70 beats per minute, the heart contracts about 37 million times per year.

Orthopedic Loading

A person walking 10,000 steps a day loads their leg joints about 1.8 million times per year.

The Hostile Body Environment

Surviving the In Vivo Environment

The internal environment of the body is ***mechanically and chemically hostile***. Implants must withstand significant stresses and degradation-inducing mechanisms.

- *Cyclic Loading*: Leads to fatigue failure modes.
- *Sustained Wear*: Occurs at articulating surfaces like joints.
- *Mechanically Assisted Corrosion*: The interplay of mechanical stress and chemical corrosion.
- *High Stresses*: Can reach hundreds of megapascals in load-bearing applications.

No other biomaterial class can perform at the stress and degradation-inducing levels that metals can, making them an essential part of the biomaterials toolbox for the foreseeable future.

The Major Alloy Systems

Classifying Metallic Biomaterials

The major alloys in use today can be classified into two main categories based on ***their intended lifespan*** within the body.
This classification is partly influenced by regulations like the Medical Device Amendments of 1976, which grandfathered in many existing alloys.

Permanently Implantable

Intended for indefinite use within the body. These are the principal alloys applied to a wide range of medical devices today.

Biodegradable (Biocorrodible-Bioresorbable)

Designed to be temporary, ultimately degrading or biocorroding over time. These are mostly in development or used in a few approved applications.

Permanently Implantable Alloys

The Workhorses of Medical Devices

The three major permanently implantable alloy systems are used across the entire spectrum of medical devices.

Stainless Steels

- Primarily 316L (ASTM F-138)

Cobalt-Chromium-Molybdenum

- CoCrMo (ASTM F-75, F-799, F-1537)

Titanium and its Alloys

- CP Ti (ASTM-F67)
- Ti-6Al-4V (ASTM F-136)

Other permanently implantable alloys include **Platinum** (Pt), **Gold** (Au), and **Silver** (Ag) alloys.

Promising & Degradable Alloys

Metals of the Future

Research continues to explore new metallic elements for both permanent and degradable applications, aiming to improve upon the properties of existing biomaterials.

Promising Permanent Alloys

Zirconium (Zr), Niobium (Nb), Palladium (Pd), Tantalum (Ta), Rhenium (Re), and Molybdenum (Mo) are being investigated for their potential advantages in strength or other properties.

Degradable Alloys

Magnesium (Mg), Tin (Sn), Iron (Fe), and Zinc (Zn) alloys are the primary systems under consideration for temporary implants that corrode away after healing.

Bioresorbable Bone Fixation Devices for Oral and Maxillofacial Surgery

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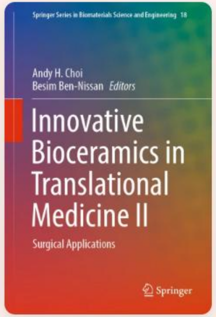

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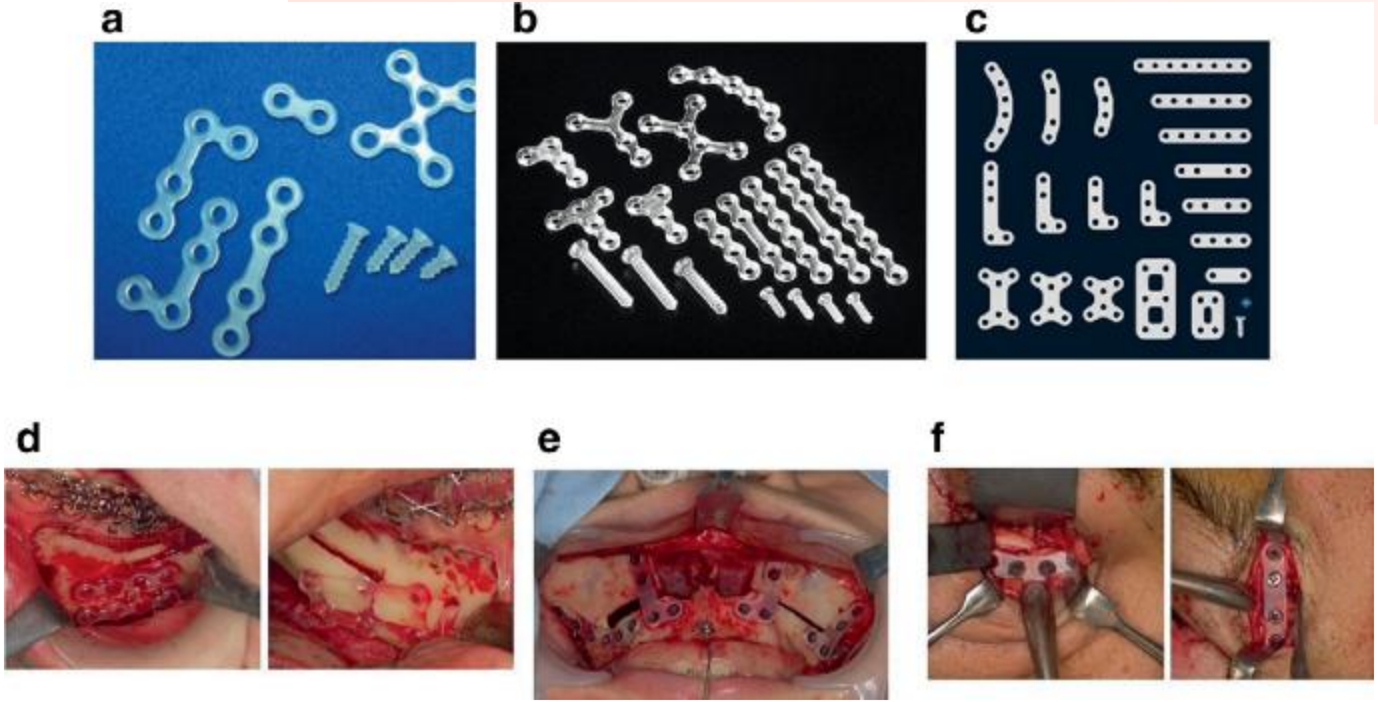

Degradable Alloys in Detail

Designing for Disappearance

The primary goal for degradable alloys is to **provide mechanical support until the body heals, after which they should safely corrode and be resorbed**. Magnesium alloys have been investigated the most for this purpose.

- Known to corrode rapidly in physiological solutions.
- Oxidation products are relatively innocuous: Mg oxide (MgO or Mg(OH)2).
- A potentially problematic byproduct is hydrogen gas, which can form pockets in tissue.
- Other systems like Tin (Sn), Iron (Fe), and Zinc (Zn) are also under consideration.

Noble and Antibacterial Alloys

Specialty Applications

Alloys of **gold, silver, and platinum**—the noble metals—are utilized for their unique electrical and chemical properties in specific medical and dental applications.

- *Electrodes*: The electrical properties of Au and Pt are ideal for stimulation and recording.
- *Corrosion Resistance*: Their noble electrochemical nature makes them highly resistant to degradation.
- Dentistry: Used in various dental applications, including Ag-Hg amalgams.
- Antibacterial Properties: ***Silver is increasingly used for its antibacterial effects***, often as a coating or nanoparticles on other medical devices.

Applications of the "Big Three"

Specific Uses of the Main Alloy Systems

1. Stainless Steel (316LVM)

   Used in surgical instruments and medical devices like **screws, rods, and plates for bone fixation and spinal fusion.**

2. Cobalt-Chromium-Molybdenum (CoCrMo)

   Used where high strength, fatigue resistance, and wear resistance are needed. It is one of the most wear-resistant alloys, used for decades in total joints.

3. Titanium (Ti-6Al-4V)

   Used in dental implants and total joint replacements. Features high strength, low modulus, and excellent biological interfacing, allowing for bone ingrowth (osseo-integration).

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Management of hypertrophic nonunion with failure of internal fixation by distraction osteogenesis

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Metal Processing: From Ore to Alloy

From Raw Material to Usable Metal

The journey of a metal from its natural state to a finished medical device involves several key processing steps.

Step 1: Extraction

Metals are obtained from ore, which consists mostly of metal oxides.

Step 2: Reduction

Metal cations in the ore are reduced to elemental metals, often in high-temperature, low-oxygen furnaces.

Step 3: Alloying

Elemental metals are melted together to form alloys of specific compositions.

Step 4: Casting

The molten mixture is cast into a large block, known as a billet.

Metal Processing: Wrought & Forged Forms

Shaping and Refining the Alloy

Once a metal billet is cast, it undergoes thermomechanical processing to be formed into standard stock shapes like rods, sheets, or plates, and to refine its internal structure.

- Hot Working: Deformation processes like forging, drawing, or extruding are applied at high temperatures.
- Purpose: This allows for large deformations without damaging the alloy.
- Benefit: It refines the grain size of the metal, which improves its mechanical properties.

- Result: The metal is formed into usable stock (rod, bar, sheet, tube) for further manufacturing.

Metal Processing: Thermomechanical Control

Engineering Strength and Ductility

Thermomechanical processing combines heat and deformation to control the final properties of the metal. A key process is cold working.

Cold Working (Work Hardening):

- Definition: Plastic deformation at low temperatures.
- Structural Effect: Generates, moves, and entangles dislocations (crystal defects).
- Property Effect: Increases yield stress (strength) and lowers ductility (flexibility).
- Application: Alloys can be intentionally cold-worked to achieve higher strength for specific device requirements.

Metal Processing: Annealing

Restoring Ductility with Heat

Thermal treatments, known as annealing, are often performed on cold-worked alloys to reverse the effects of deformation.

The Process

The cold-worked alloy is heated, providing thermal energy to the microstructure.

The Result

Dislocations are eliminated (recovery) or new, deformation-free grains form (recrystallization). The resulting annealed alloy has lower strength but higher ductility than its cold-worked counterpart.

Metal Processing: Powder Metallurgy

Building from Powder

Instead of starting with a large billet, some components are made from metal powders, offering unique advantages.

Powder Generation: Molten alloy is sprayed into a fine mist that solidifies into spherical powders.

Hot Isostatic Pressing (HIPing): Powders are placed in a mold and subjected to high temperature and pressure. The particles diffusion bond (sinter) together to form a fully dense part.

- Advantage: The grain size is governed by the small starting particles, resulting in very high-strength alloys.

Metal Processing: 3D Printing

Layer-by-Layer Fabrication

Powder metallurgy is the foundation for modern 3D printing of metals, also known as additive manufacturing. This technology allows for the creation of complex, patient-specific implants.

- Method: A laser or electron beam selectively melts or sinters powdered alloy particles in a pattern, layer by layer, to build the part.
- Techniques: Common methods include Selective Laser Sintering (SLS), Selective Laser Melting (SLM), and Electron Beam Melting (EBM).
- Impact: These methods are gaining significant use and application in the medical device industry for creating custom and complex geometries.

Processing Consideration: Oxygen Contamination

The Challenge of Oxygen

The presence of oxygen during high-temperature fabrication can be detrimental to many alloys, particularly titanium.

Titanium's Affinity for Oxygen:

- A small amount of dissolved oxygen can increase strength (interstitial solid solution strengthening).
- Too much oxygen can make the alloy brittle and prone to fracture.
- Surface diffusion of oxygen can create a brittle 'alpha case' that reduces the alloy's fracture resistance.
- Solution: Processing is often done in inert gas environments to limit oxidation.

Final Manufacturing: Machining

Creating the Final Shape

For many parts, the final step in shaping is machining the metal stock into its precise, final form.

- Techniques: Highly precise milling machines, lathes, and Computer Numerical Control (CNC) machines are used.
- Tools: Very hard and sharp cutting tools are required to make precision cuts.
- Side Effects: The machining process itself induces localized plastic deformation on the surface, which can create residual stresses that may impact the surface strength (hardness) of the alloy.

Surface Treatments Engineering the Implant Surface

The surface of a metallic implant is critical, as it's the interface with the body. Various treatments are used to impart specific, desirable surface properties.

1

Shot Peening

High-velocity particles are blasted at the surface to induce compressive deformation, which can improve fatigue strength.

2

Grinding & Polishing

Mechanical or electrochemical methods to create a smooth, clean surface.

3

Anodizing

Electrochemical process to grow a controlled oxide layer, often used for color-coding or improving corrosion resistance.

4

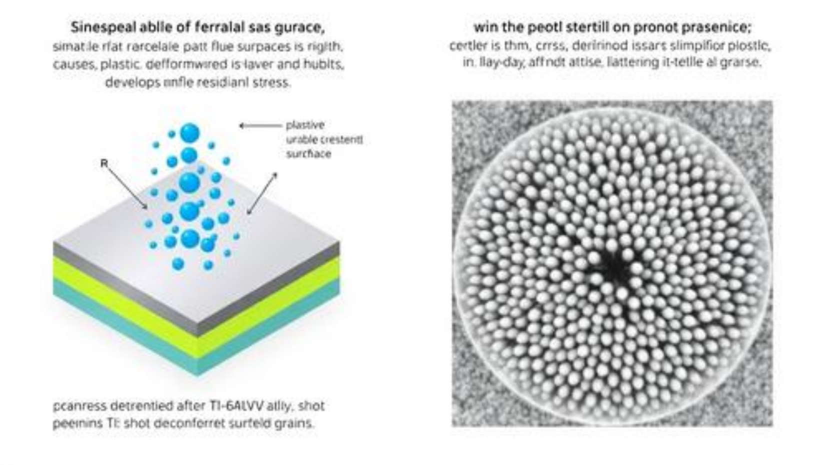
Plasma Coating (PVD/CVD)

Specialized processes to apply thin, hard coatings like nitrides or oxides to the surface.

Surface Treatment: Shot Peening

Improving Fatigue Life

Shot peening is a surface treatment where high-velocity particles (like glass beads) are blasted at a metal surface. This process plastically deforms the outer layer, 'stretching' it against the un-deformed material underneath. This creates large compressive residual stresses on the surface, which are highly beneficial for improving the fatigue strength of the part by making it more difficult for fatigue cracks to initiate.



Surface Treatment: Passivation

Final Cleaning and Protection

A crucial final surface treatment is passivation, which cleans the surface and enhances the protective oxide film.

The Process (ASTM F-86):

- The part is immersed in an acid, typically 30% nitric acid at 130°F for 30 minutes.
- Purpose: To remove unwanted surface contaminants from manufacturing.
- Mechanism: Induces the passive oxide film to become more chemically uniform, increasing corrosion resistance.
- Origin: Initially developed for stainless steel to enrich the surface oxide with chromium (Cr_2O_3). It is now standard practice for CoCr and Ti alloys as well, though its effects may differ.

Final Steps & Surface Dynamics

Preparing for Implantation

At the end of fabrication, sterilization is required. It's also important to remember that the protective surface oxide is not a static layer.

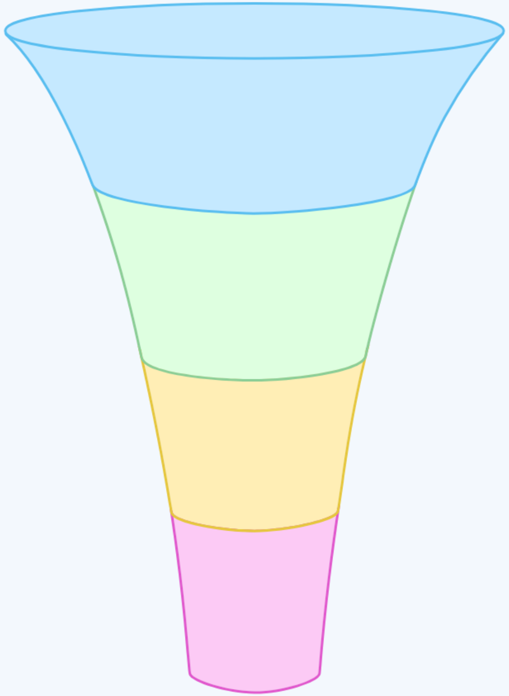
Sterilization

- Gamma Irradiation
- Ethylene Oxide (EtO) Treatment
- Steam Sterilization (Autoclave)

Passive Film Dynamics

Passive oxide films are not static. They are affected by immersion in electrolyte, time, and the electrochemical potential of the environment. They can grow, change chemistry, and incorporate ions from the body like phosphates and calcium.

The Processing-Structure-Properties-Performance Paradigm



Processing

Structure

Properties

Performance

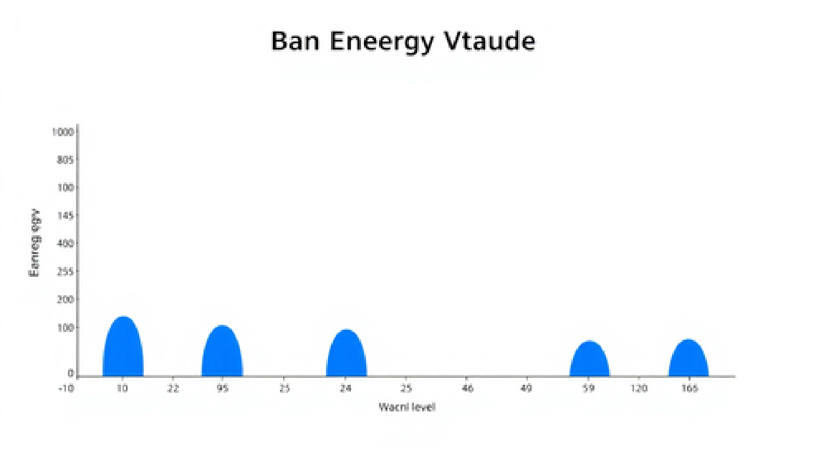
A Foundational Concept in Metallurgy

To understand metallic biomaterials, it is crucial to grasp the relationship between how an alloy is made and how it performs. This is known as the processing-structure-properties-performance paradigm.

Structure of Metals: Electronic Structure

The Basis of Metallic Properties

In a metal, electron energy levels form bands. The outermost valence band is only partially filled with electrons up to the Fermi energy level. The empty levels immediately above the Fermi level allow electrons to easily move and conduct electricity. The energy required to remove an electron from the metal entirely is the 'work function'.



Structure of Metals: Atomic Arrangement

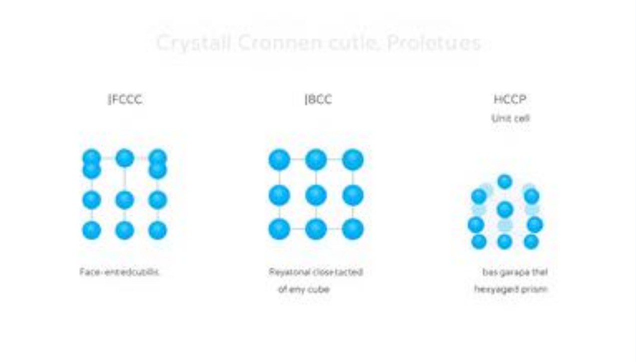
The Crystalline Nature of Metals

Atoms in a metal can be considered as hard spheres. The attractive forces of the metallic bond pull these spheres together into ordered, repeating, three-dimensional patterns called crystalline structures or lattices.

There are 14 possible crystal lattice structures (Bravais lattices). For metallic biomaterials, the most common are:

- Face-Centered Cubic (FCC)
- Body-Centered Cubic (BCC)
- Hexagonal Close-Packed (HCP)

Common Crystal Structures in Biomaterials



Key Crystal Structures

Metallic biomaterials primarily form either cubic or hexagonal structures. For example, austenitic stainless steel is FCC, pure iron at body temperature is BCC, and titanium is HCP.

Temperature Effects & Phase Transitions

The Dance of Energy and Bonds

The stability of a crystal structure is a balance between the electrostatic attractive forces (metallic bonds) and the thermal (kinetic) energy of the atoms.

- Thermal energy (phonons, plasmons) causes atoms to vibrate. Higher temperature means greater vibration.
- At sufficient temperatures, thermal energy can overwhelm bonding forces, causing a phase transition (e.g., solid-to-solid or solid-to-liquid).
- Allotropes: Some metals, like iron, can exist in different solid crystal structures (phases) at different temperatures (e.g., BCC -> FCC -> BCC -> Liquid).

Alloying: Solid Solutions

Creating New Materials

Alloys consist of more than one element combined. The way these elements mix at the atomic level defines the type of solid solution.

Interstitial Solid Solution

Small atoms (like Carbon, Oxygen, Nitrogen) fit into the open spaces (interstices) between the larger metal atoms. Example: Carbon in Iron to make steel.

Substitutional Solid Solution

Atoms of similar size are mixed. The solute atoms (lower concentration) replace the solvent atoms (higher concentration) on the crystal lattice. Example: Nickel in Iron.

Alloying and Microstructure

Controlling Crystal Structure with Alloying

Adding alloying elements can stabilize or destabilize certain crystal structures, leading to complex microstructures.

Example: Ti-6Al-4V

This is a two-phase alloy. Aluminum (an alpha stabilizer) promotes the HCP structure (alpha phase), while Vanadium (a beta stabilizer) promotes the BCC structure (beta phase).

Example: 316L Stainless Steel

Adding ~8% Nickel (an FCC stabilizer) to iron forces the BCC structure to transform into the more stable FCC structure, creating austenitic stainless steel.

Alloying: The Hume-Rothery Rules

Rules of Thumb for Mixing Metals

Not all elements can mix together in any proportion to form a stable substitutional solid solution. The Hume-Rothery rules provide guidelines for when high solubility is likely.

- Atomic Size Factor: The atomic radii of the solute and solvent atoms should be within ~15% of each other.
- Crystal Structure: The solute and solvent should have the same native crystal structure for full solubility.
- Electronegativity: The elements should have similar electronegativity values.
- Valence: The elements should have the same valence.

Introduction to Phase Diagrams

Maps of Material Phases

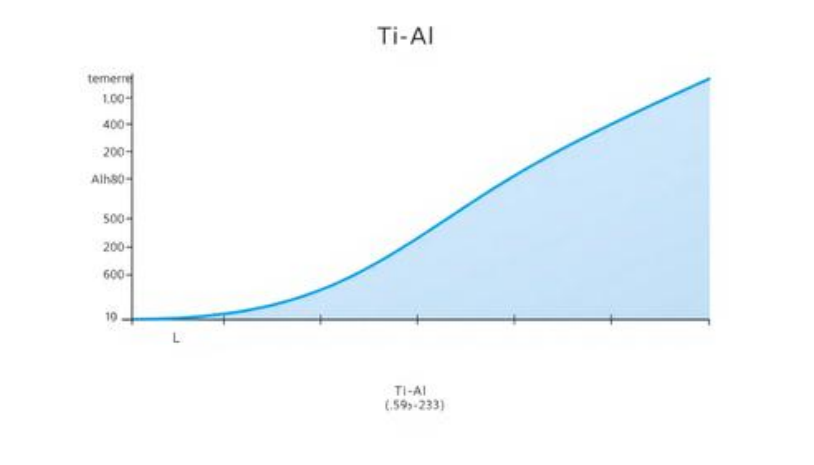
Phase diagrams are a graphical means for showing what phases (crystal structures, liquids, etc.) are present at equilibrium for different temperatures and compositions at a constant pressure. They provide insight into the microstructures that may arise with specific thermal processes.

Important Limitation: Phase diagrams represent equilibrium conditions, which require long times. They do not show metastable or non-equilibrium phases that can arise from rapid processing, like fast cooling (quenching).

Phase Diagrams: Example 1

Ti-Al System

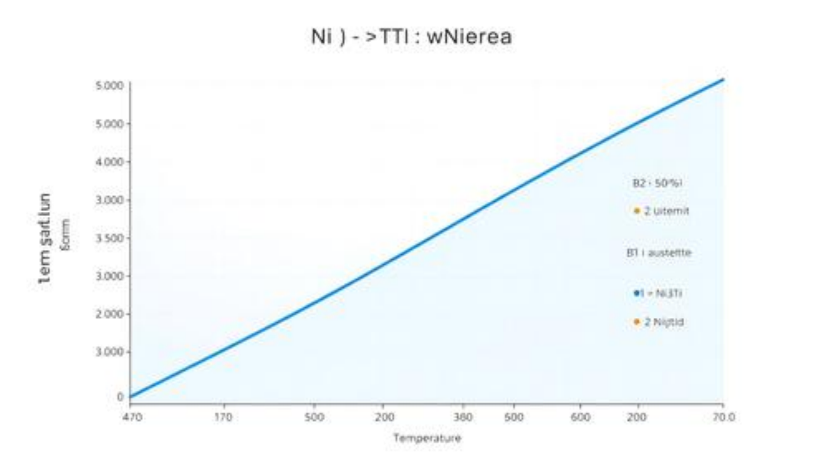
This diagram shows the phases present in Titanium-Aluminum alloys. At low temperatures and up to ~6 wt% Al, the HCP alpha phase is stable. Aluminum acts as an 'alpha stabilizer,' increasing the temperature at which the alpha phase is stable. At higher temperatures (above ~880°C), pure Ti transforms to the BCC beta phase.



Phase Diagrams: Example 2

Ni-Ti System (Nitinol)

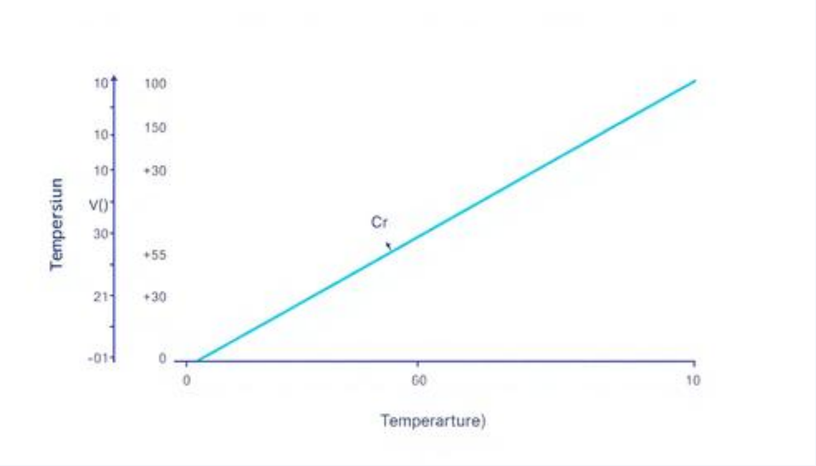
This diagram for Nickel-Titanium shows that near-50% compositions used for biomaterials are a single phase (B2 austenite). However, the famous shape memory and superelastic behavior of Nitinol comes from a non-equilibrium, deformation-induced martensitic phase transformation, which is not shown on this equilibrium diagram.



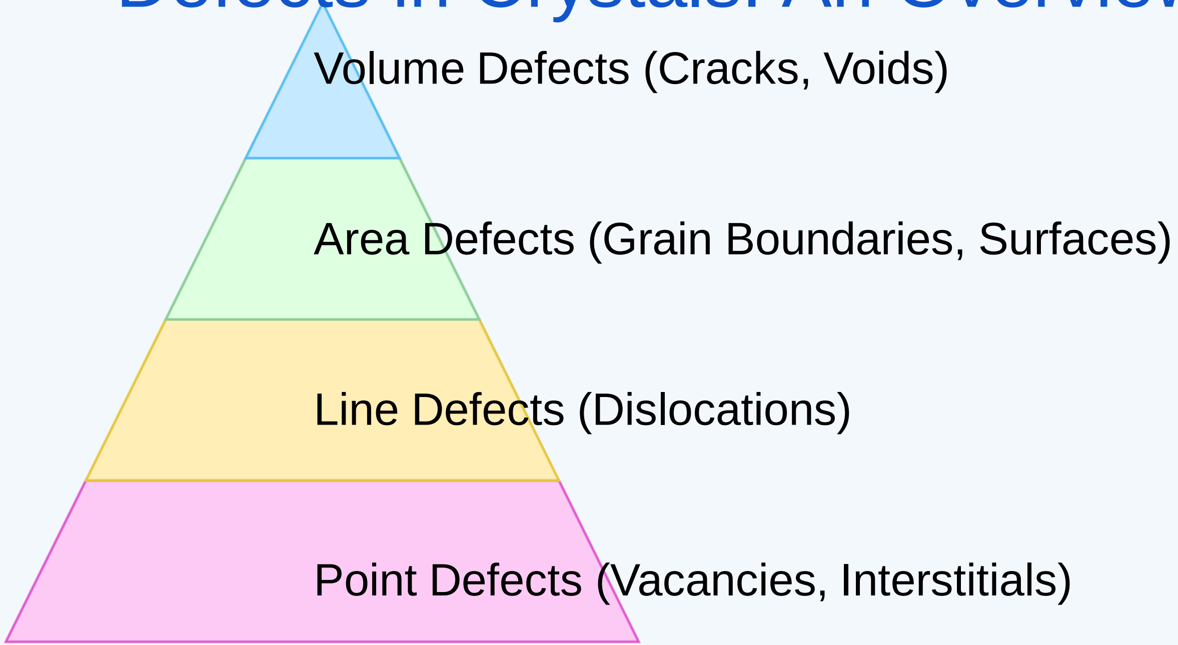
Phase Diagrams: Example 3

Co-Cr System

For Cobalt-Chromium alloys used in biomaterials, the alloy is typically an FCC crystal structure at body temperature. However, it can transform to HCP at higher temperatures. Due to a low stacking fault energy, it's possible for both FCC and HCP structures to be present in the same alloy, especially after heavy deformation.



Defects in Crystals: An Overview



Understanding and controlling these defects is fundamental to controlling the performance of metallic biomaterials.

Real metallic materials are not perfect crystals. They contain various types of defects that arise during processing and have a significant effect on the material's properties.

Point Defects

Atomic-Scale Imperfections

Point defects are defects that occur at or around a single lattice point.

Vacancies

A missing atom at a lattice site. They affect the diffusion of other atoms but have a limited effect on mechanical properties for most biomaterial applications.

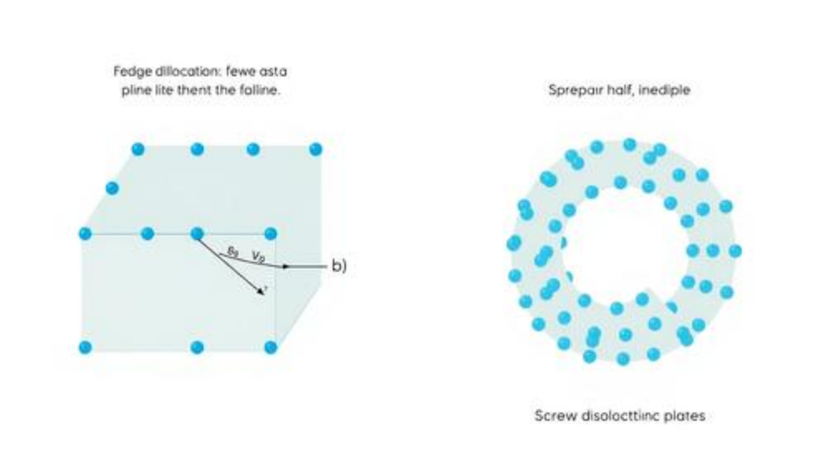
Interstitial Atoms

Small atoms (e.g., Oxygen in Titanium, Carbon in Iron) that occupy spaces between the main lattice atoms. They have a profound effect on strength by pinning dislocations, which makes plastic deformation more difficult.

Line Defects: Dislocations

The Engine of Plastic Deformation

Dislocations are line defects in the crystal structure and are the principal means by which metals deform permanently (plastically). They are essentially a localized elastic distortion associated with the sliding of atomic planes. An edge dislocation can be thought of as the distortion around the end of an extra half-plane of atoms inserted into the crystal lattice.



Dislocation Motion and Slip

How Metals Bend

When a metal is stressed beyond its elastic limit, plastic deformation occurs. This is not caused by entire planes of atoms shearing at once, but rather by the generation and movement of dislocations through the crystal.

- Slip System: Deformation occurs on specific planes (slip planes) and in specific directions (slip directions).
- Critical Stress: Sufficient shear stress must be applied to the slip system to generate and move dislocations.
- Strengthening: Most methods for strengthening metals rely on making it more difficult for dislocations to move (e.g., by creating obstacles).

Area Defects

Two-Dimensional Imperfections

Area defects are boundaries that separate regions of the material with different crystal structures or orientations.

Grain Boundaries

The boundary between adjacent crystals (grains). These disordered regions are effective barriers to dislocation motion. More grain boundaries (i.e., smaller grains) lead to a stronger material.

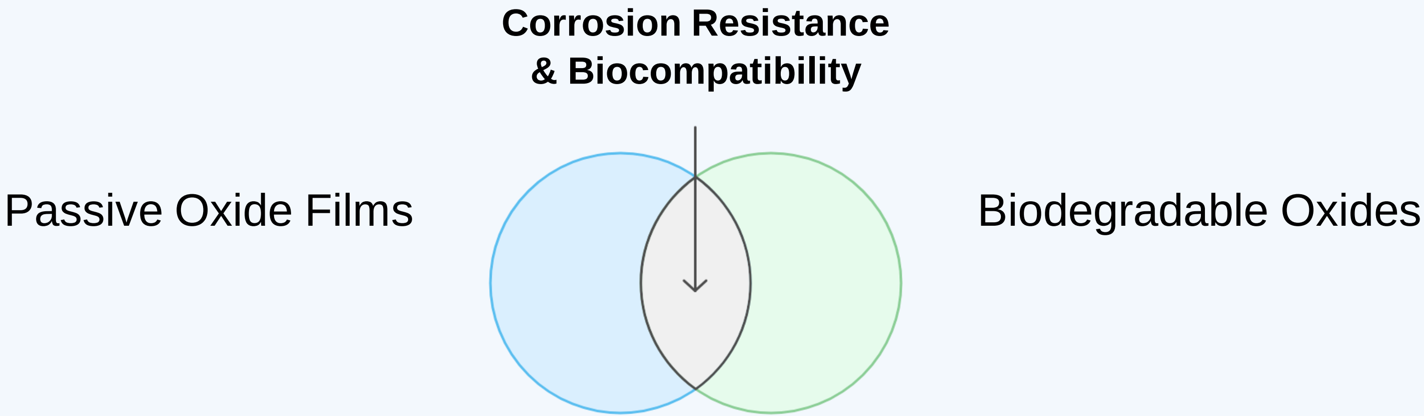
Free Surfaces

The external surface of the material. For biomaterials, this surface is almost always covered with a thin metal oxide layer (passive film) that is critical for corrosion resistance.

Surface Films: Passive vs. Biodegradable

The Importance of Passive Films

The surfaces of most metallic biomaterials are covered with a thin, chemically reacted layer of metal oxide. This layer forms when oxygen from air or water reacts with the metal.



For alloys like Ti, CoCr, and SS, these are passive oxide films that are highly protective and slow corrosion. For others, like Mg, the oxide that forms is not passive and does not prevent rapid corrosion, making them biodegradable.

Volume Defects

Three-Dimensional Imperfections

Volume defects are macroscopic imperfections within the bulk of the material.

Voids

Empty spaces left behind during processing, for example, during the solidification of a casting. They act as stress concentrators.

Cracks

Can be introduced during processing or can initiate and grow during service under cyclic loading (fatigue).

Both voids and cracks can significantly reduce the fracture toughness and fatigue resistance of an alloy, potentially leading to catastrophic failure of an implant.

Bulk Mechanical Properties of Metals

Quantifying Material Performance

The mechanical properties of metals, which are highly dependent on their structure and defects, are what make them essential for medical devices. A tensile test is often performed to characterize these properties.

- Modulus: A measure of stiffness (resistance to elastic deformation). Important for stress shielding.
- Strength (Yield & Ultimate): The stress required to cause permanent deformation.
- Fracture Toughness: The ability to resist the propagation of a crack.
- Fatigue Resistance: The ability to withstand cyclic stresses without failing.

Elastic vs. Plastic Deformation

How Metals Respond to Load

When a load is applied to a metal, it first deforms elastically. If the stress is high enough, it will then deform plastically.

Elastic Deformation

Temporary and reversible. Atoms are stretched from their equilibrium positions but remain in the crystal lattice. Think of it like stretching a spring.

Plastic Deformation

Permanent and irreversible. Atoms permanently move within the crystal, primarily through dislocation motion. This changes the shape of the material.

The Yield Stress is the stress required to induce a specific small amount of plastic deformation (typically 0.2%).

Elastic Modulus

Stiffness of Metallic Biomaterials

The elastic modulus (or Young's modulus) is the slope of the elastic portion of the stress-strain curve. It reflects the force required to pull atoms slightly apart from their equilibrium positions.

- Modulus is an intrinsic property dependent on the chemistry (atomic bonding) of the alloy.
  - It is NOT affected by factors like cold work or grain size.
  - Modulus mismatch between an implant and bone can lead to stress shielding.

Alloy	Typical Elastic Modulus (GPa)
316L Stainless Steel	210
CoCrMo Alloy	230
Titanium Alloy (Ti-6Al-4V)	110
Human Cortical Bone	15-20

Strength and Ductility

Measures of Resistance to Deformation

Strength refers to the stress required to induce permanent (plastic) deformation. Ductility measures how much plastic deformation a metal can undergo before it breaks. There is typically a trade-off: increasing strength decreases ductility.

Strength

Includes tensile yield strength, ultimate tensile strength, etc. It measures the stress needed to deform the bulk material.

Hardness

A surface measurement of strength, assessing the stress required to cause a permanent indentation.

Ductility

Measured as percent elongation. High ductility is desirable as it allows for some yielding without fracture, contributing to high fracture toughness.

Strengthening Mechanisms: Alloying

Strengthening through Composition

Adding alloying elements is a primary way to increase the strength of a metal. Pure metals are often very soft.

Interstitial Strengthening

Small interstitial atoms (like Carbon in steel) are highly effective. They accumulate around dislocations, creating 'atmospheres' that pin them in place, requiring much higher stress to initiate movement.

Substitutional Strengthening

Larger substitutional atoms create elastic strain distortions in the crystal lattice, making it more difficult for dislocations to move through.

Strengthening Mechanisms: Cold Working

Strengthening through Deformation

Cold working, or work hardening, is the process of strengthening an alloy by plastically deforming it at low temperatures.

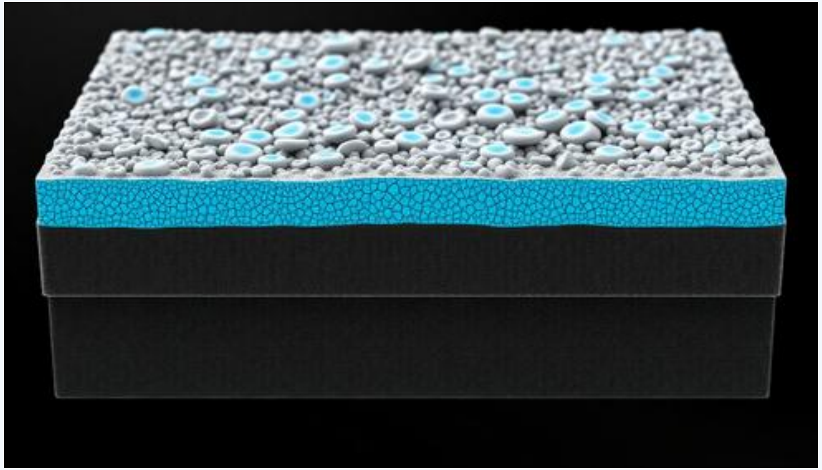
How it works:

- Plastic deformation generates a high density of dislocations.
- These dislocations move and become entangled with each other.
- The entanglement makes it more difficult for further dislocation motion to occur.
- Result: Higher applied stress is needed for more deformation, meaning the yield and ultimate strength increase.
- Trade-off: Ductility decreases, making the alloy more brittle.

Application of Cold Working: Shot Peening

Strengthening the Surface

Shot peening is a surface cold working process. High-velocity particles impact the metal surface, plastically deforming the outer layer. This cold works the surface and imparts beneficial compressive residual stresses, which can significantly increase the fatigue strength of the alloy by resisting the initiation of surface cracks.



Strengthening Mechanisms: Grain Size

Smaller is Stronger

The size of the crystals (grains) in a polycrystalline alloy significantly affects its yield strength. This is described by the Hall-Petch relationship.

Hall-Petch Relationship:

$\sigma = \sigma_0 + k * d^{-1/2}$

Where σ is yield strength, d is grain diameter, and σ_0 and k are material constants.

- Implication: Yield strength increases as grain size decreases.
- Mechanism: Grain boundaries act as barriers to dislocation motion. More boundaries (smaller grains) provide more barriers, thus strengthening the material.
- Application: Titanium and CoCrMo alloys are often fabricated with very fine grains (e.g., 5 μm) to achieve high strength.

Strengthening Mechanisms: Precipitation

Strengthening with a Second Phase

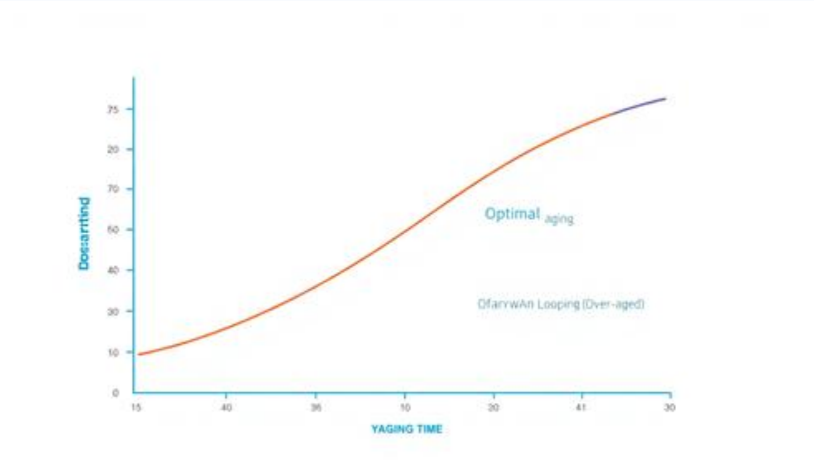
This mechanism involves creating fine particles of a second phase (precipitates) within the primary alloy matrix. These precipitates act as obstacles to dislocation motion, strengthening the alloy.

The precipitates can be intermetallics, carbides, oxides, or other crystal structures. Their effectiveness depends on their size, shape, and distribution within the matrix.

Precipitation Strengthening: Aging

Optimizing Particle Size via Aging

The size of precipitates is controlled by a heat treatment process called aging. As the alloy is aged, the particles grow. There is an optimal particle size that provides the maximum strengthening.



- Particle Shearing: At small particle sizes, dislocations cut through the precipitates.
- Orowan Looping: At larger particle

Fracture of Metals

The Mechanics of Breaking

Fracture is a distinct process from yielding. It requires the initiation of a crack. The tip of this crack then acts as a high-stress concentrator, focusing deformation and eventually leading to crack propagation and failure.

The sharpness of a feature, like a crack or a design notch, can dramatically increase the local stress compared to the overall applied stress. This is called stress concentration.

Stress Concentration

The Danger of Sharp Corners

The stress at the tip of a crack is amplified by its geometry. A sharper, longer crack leads to a higher local stress.

Stress Concentration Formula for an Ellipse:

$\sigma\_local = \sigma\_far * (1 + 2 * \sqrt{(a/\rho)})$

- σ_far is the far-field applied stress.
- a is the crack length (half the major axis).
- ρ is the radius of curvature at the crack tip (a measure of sharpness).

This shows that as a crack gets sharper (ρ decreases), the local stress at the tip increases dramatically, driving propagation.

Fracture Toughness (K_{Ic})

Resistance to Crack Growth

Fracture toughness (K_{Ic}) is a material property that measures its resistance to crack propagation once a crack is already present. It is a critical parameter for predicting the failure of components with existing flaws.

- Testing: Found by loading a pre-cracked sample (e.g., compact tension sample) and measuring the load needed to advance the crack (ASTM E-399).
- Formula: $K_{Ic} = \sigma * \sqrt{a} * Y(a/w)$, where σ is the applied stress, a is crack length, and Y is a geometry factor.
- Significance: A material with high fracture toughness can tolerate larger cracks before failing.

Fatigue of Metals: Introduction

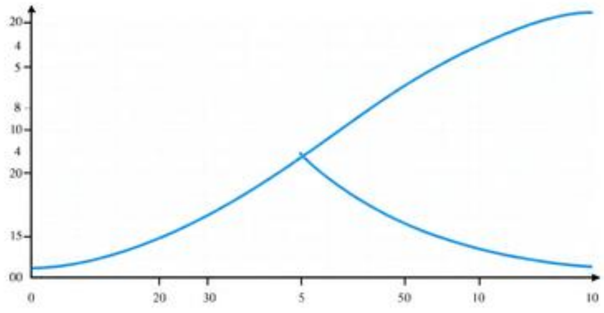
Failure Under Repeated Loading

Fatigue is a process of fracture that results from the initiation and slow propagation of a crack in response to cyclic (repeated) stresses, such as from walking, a beating heart, or chewing.

Key Characteristics:

- Failure can occur at stresses well below the material's ultimate or even yield strength.
- Failure may require millions of loading cycles.
- It is the dominant failure mode for many long-term implants.

Fatigue Life: S-N Curves



Predicting Fatigue Failure

The fatigue strength of a material is assessed using S-N curves (also called Wohler diagrams). Samples are subjected to a cyclic stress (S), and the number of cycles to failure (N) is recorded. Plotting S vs. log(N) shows the relationship.

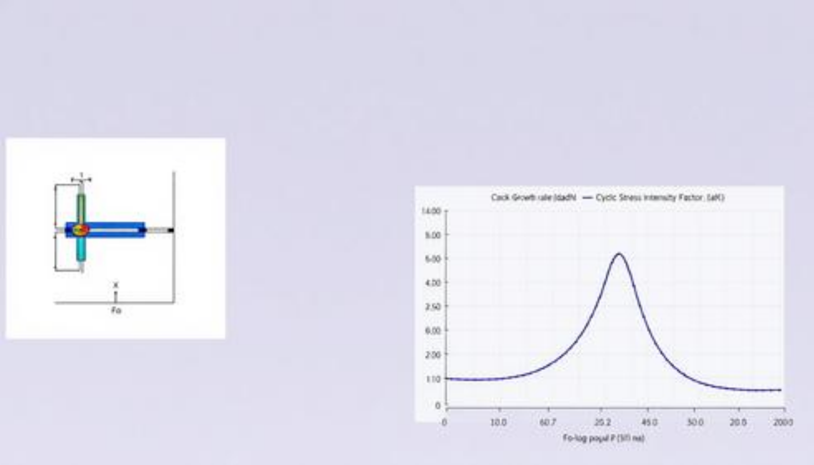
- Fatigue Strength: The stress level below which the material can withstand a very large number of cycles (e.g., 10 million) without failing.
- Fatigue Life: The number of cycles to failure at a specific applied stress level.

Fatigue Crack Propagation

Measuring Crack Growth Rate

An alternative method assesses the rate at which an existing fatigue crack propagates. A pre-cracked sample is cyclically loaded, and the crack growth rate (da/dN) is measured as a function of the applied cyclic stress intensity factor (ΔK). This behavior is often described by the Paris Law:

$$da/dN = C * (\Delta K)^m$$



This law is crucial for predicting the remaining life of a component once a crack has been detected.

High-Cycle vs. Low-Cycle Fatigue

Fatigue in the Context of Biomaterials

For long-term implants, we are primarily concerned with high-cycle fatigue.

Low-Cycle Fatigue

Occurs at high stresses (near the yield stress).

Failure occurs in a low number of cycles (<10,000).

High-Cycle Fatigue

Occurs at lower stresses.

Failure requires a high number of cycles (>100,000).

Dominant concern for medical implants designed to last for years.

In high-cycle fatigue, the vast majority of the lifetime (95-98%) is spent accumulating damage and initiating a crack. Crack propagation is a relatively small portion of the life.

Controlling High-Cycle Fatigue

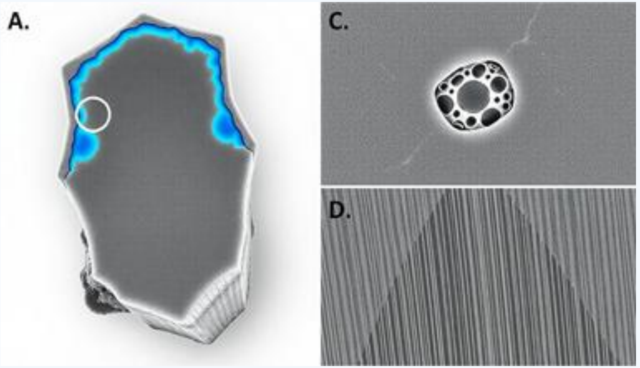
Preventing Fatigue Failure

Since crack initiation dominates high-cycle fatigue life, structural factors that impede nucleation are most important. Almost all fatigue cracks initiate at or near a free surface.

Key Strategies:

- Increase Surface Strength/Hardness: A higher yield stress at the surface makes it harder to initiate a crack.
- Improve Surface Topography: Smooth, polished surfaces have fewer stress concentrators where cracks can start.
- Introduce Surface Compressive Residual Stresses: Processes like shot peening create surface compression that counteracts applied tensile stresses, inhibiting crack initiation.

Fatigue Failure Example: CoCrMo

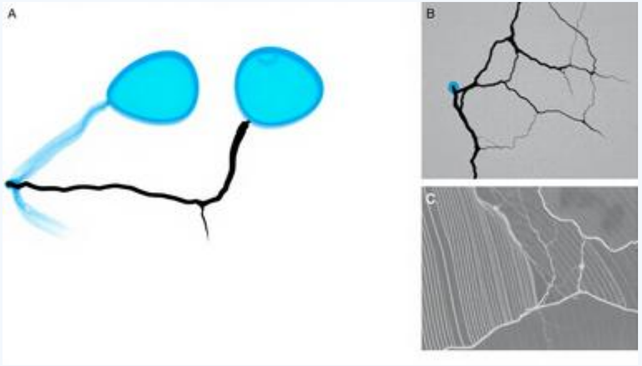


Failure Analysis of a Hip Stem

This scanning electron micrograph shows the fracture surface of a cast CoCrMo alloy femoral component that failed by fatigue in vivo. The failure was initiated at a region of significant casting porosity, which acted as a stress concentrator.

Features include the initiation site, 'clam shell' markings pointing back to the origin, and microscopic fatigue striations.

Fatigue Failure Example: Ti-6Al-4V



Failure Analysis in a Lab Setting

This is the fatigue fracture surface of a Ti-6Al-4V hip stem from a simulated corrosion fatigue test (ASTM F-1612). The distinct regions of failure are clearly visible.

The fracture surface shows a clear fatigue crack initiation site, a region of stable crack propagation, and a final fast fracture region. High magnification reveals characteristic fatigue striations.

Surfaces of Metals: Passive Oxide Films

The Secret to Corrosion Resistance

The three major biomaterial alloys (Ti, CoCr, and stainless steel) owe their excellent corrosion resistance to the spontaneous formation of a very thin (nanometer scale) metal oxide film on their surface.

These passive oxide films are the ultimate smart, self-healing nanobiomaterials:

- Smart: Can be manipulated electrochemically.
- Self-healing: Spontaneously reform if scratched, as long as oxygen is present.
- Nanomaterial: Only a few nanometers thick.

Pilling-Bedworth Ratio

Predicting Film Protectiveness

The Pilling-Bedworth Ratio (PBR) compares the volume of the oxide formed to the volume of the metal consumed. It helps predict whether the oxide film will be protective.

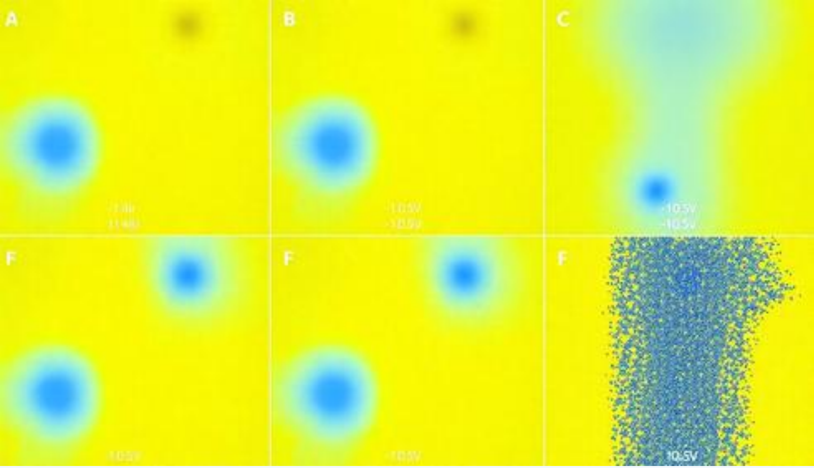
$$PBR = V_{oxide} / V_{metal}$$

- $PBR < 1$: Oxide is porous and non-protective (e.g., Mg, $PBR = 0.8$).
- $PBR > 2$: Oxide is too bulky, flakes off, and is non-protective.
- $1 < PBR < 2$: Oxide is dense, adherent, and creates compressive stress, resulting in a protective passive film (e.g., Ti, $PBR = 1.7$; Cr, $PBR = 2.0$).

Oxide Film Nanostructure & Evolution

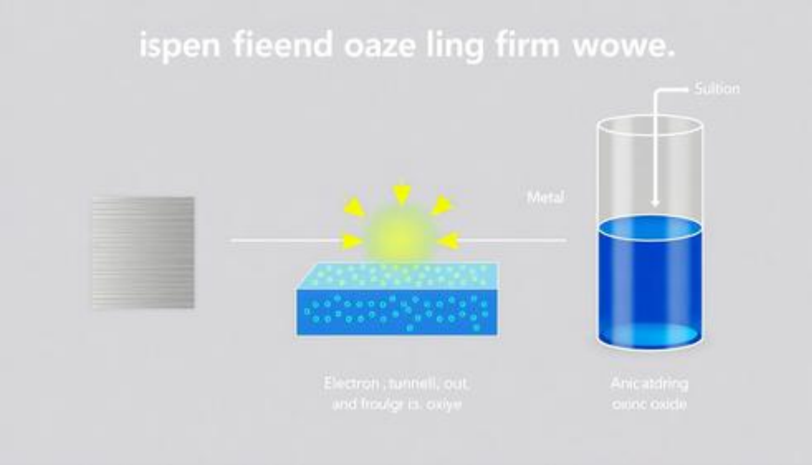
A Dynamic Surface

The nanostructure of a passive oxide film is not static; it evolves based on its environment. These atomic force microscope images show the evolution of the TiO_2 film on Ti-6Al-4V as it is immersed in phosphate-buffered saline and subjected to an increasing electrical potential from -1 V to +1 V. The morphology of the oxide grains clearly changes and grows.



High-Field Oxide Film Growth

How Passive Films Form



The high-field model (Cabrera-Mott theory) explains how passive films grow.

1. Electrons from the metal tunnel to the surface.
2. Oxygen atoms trap these electrons, creating a charge separation.
3. This creates a very high-strength electric field across the thin interface.
4. The field drives positive metal ions outward and negative oxygen ions inward.
5. The ions react to form the metal oxide, thickening the film. As the film thickens, the field strength decreases, and growth eventually stops at a few nanometers.

Film Properties: Point Defects & Anodization

Transport and Modification

Once a passive film is formed, transport of charged species through it is governed by the electric field and the presence of defects.

Point-Defect Model: Describes the atomistic behavior of passive films, where transport occurs via the movement of charged vacancies (missing ions) within the film.

Anodization: An electrochemical process that applies a high positive potential to a metal to intentionally grow a thicker oxide film. On titanium, this process is used to create different colors for medical device identification (e.g., color-coding orthopedic screws). The color is an interference effect dependent on the film thickness.

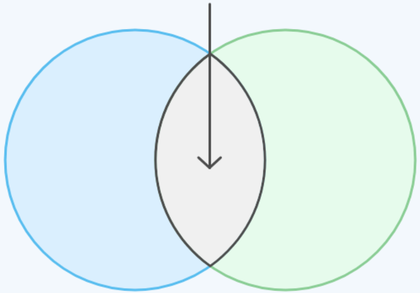
Introduction to Metallic Corrosion

The Electrochemistry of Degradation

Corrosion is an electrochemical process comprised of a coupled set of oxidation and reduction reactions.

Redox Reaction

Oxidation (Anode)



Reduction (Cathode)

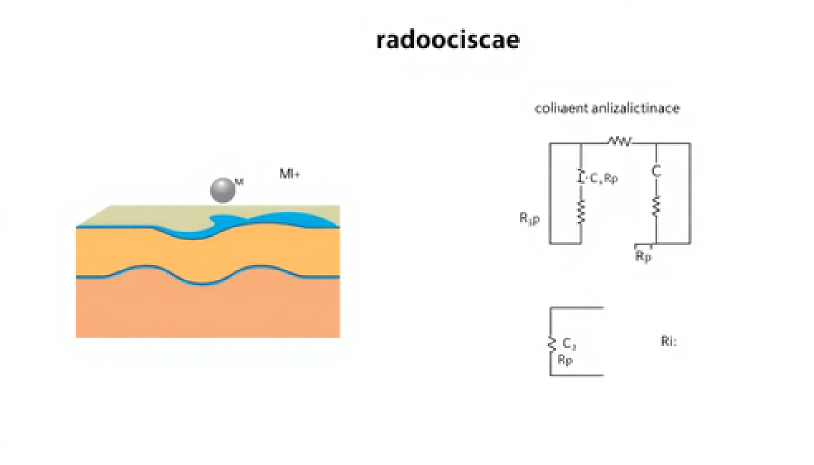
Oxidation: A chemical species loses electrons and its valence state increases (e.g., $Fe \rightarrow Fe^{2+} + 2e^{-}$).

Reduction: A chemical species gains electrons and its valence state decreases (e.g., $O_2 + 4e^{-} \rightarrow 2O^{2-}$).

The Oxidation Half-Cell

The Anodic Reaction

The oxidation half-cell reaction for a metal involves atoms at the surface oxidizing (liberating electrons) and becoming metal cations.



The electrons remain in the metal,
while the cations can be released into the solution.

This separation of charge creates a potential difference at the interface. The electrical circuit shown is a Randles circuit, an analog used to model the resistive (Rp) and capacitive (C) nature of the interface.

The Nernst Equation The Driving Force for Corrosion

At equilibrium, the chemical free energy driving oxidation (ΔG_{ox}) is balanced by the electrical energy that builds up from the charge separation. This relationship is described by the Nernst Equation.

Nernst Equation: $\Delta G_{ox} = n * F * E_{eq}$

- n = charge per cation
- F = Faraday's constant
- E_{eq} = equilibrium electrode potential

This equation measures the driving force for oxidation. A more negative potential means a greater driving force for corrosion. This gives rise to the electromotive or galvanic series, which ranks metals from most active (negative E_{eq}) to most noble (positive E_{eq}).

Nernst Equation: Practical Application

An Important Tool: Reference Electrodes

The Nernst equation shows that electrode potential depends on the concentration of ions in solution. This principle is used to create reference electrodes with stable, known potentials.

Example: Silver/Silver Chloride (Ag/AgCl) Electrode

Reaction: $Ag + Cl^- \rightleftharpoons AgCl + e^-$

- Its potential depends on the chloride ion $[Cl^-]$ concentration.
- When the solution is saturated with chloride, the potential is highly stable and fixed.
- This allows it to be used as a reference point against which other unknown potentials can be measured in corrosion experiments.

The Reduction Half-Cell in the Body

The Cathodic Reaction

For corrosion to proceed, the electrons generated by oxidation must be consumed by a reduction reaction. In most biomaterials applications in the body, the primary reduction half-cell reaction is the reduction of dissolved oxygen.

Oxygen Reduction Reaction:

$$\tfrac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

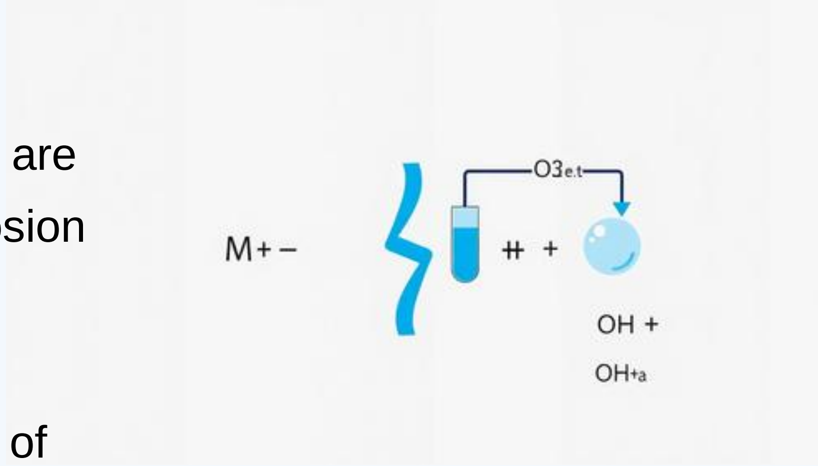
This reaction is simplified and can involve several reactive oxygen intermediates. Other redox-active species in the body can also participate in reduction reactions.

The Full Corrosion Reaction

Putting It All Together

When both oxidation and reduction reactions are present on a metal surface, a complete corrosion circuit is formed.

Electrons generated at the anode (site of oxidation) are consumed at the cathode (site of reduction). This allows current to flow and corrosion to continue. These anodic and cathodic sites can be microscopic and close together, or macroscopic and spatially separated.



Polarizable vs. Nonpolarizable Electrodes

Electrode Behavior Under Current Flow

Electrodes used for stimulation or recording can be classified by how their potential responds to the passage of current.

Nonpolarizable Electrode

Potential remains stable even when current is passed. This is ideal for reference electrodes. Example: Ag/AgCl.

Polarizable Electrode

Potential can be easily shifted by injecting charge. This is useful for stimulation electrodes. Example: Platinum (Pt).

Pourbaix Diagrams (Potential vs. pH)

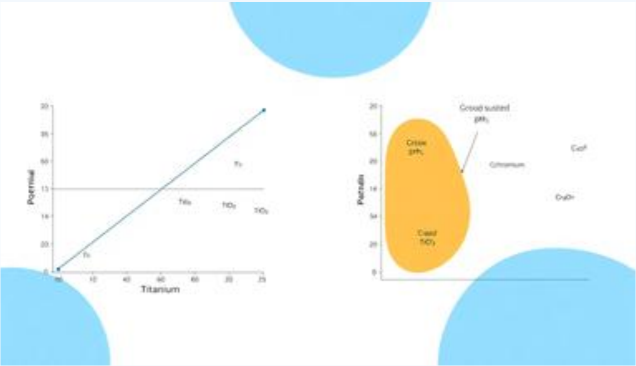
Thermodynamic Stability Maps

Pourbaix diagrams plot electrode potential versus pH. They are powerful tools that depict the combined conditions where specific chemical products of electrode reactions are thermodynamically stable.

They show the regions of potential and pH where a metal is stable (immune), where it corrodes to form ions (corrosion), or where it forms a solid oxide (passivation).

Note: Pourbaix diagrams represent equilibrium and do not provide information about the kinetics (rate) of the reactions.

Pourbaix Diagrams: Examples for Ti & Cr



Visualizing Stability

These Pourbaix diagrams for Titanium and Chromium in chloride-containing solutions show the ranges of potential and pH where the metal, its ions, or its oxides are the most stable species.

Corrosion Kinetics: Evans Diagrams

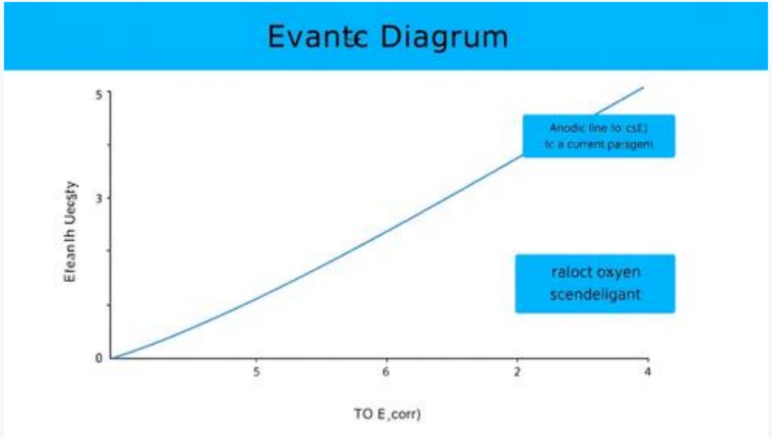
Measuring the Rate of Corrosion

While Pourbaix diagrams show if corrosion is possible, Evans diagrams (or polarization plots) provide information about the kinetics (rate) of corrosion.

Evans diagrams plot electrode potential versus the logarithm of the current density (current per unit area). Current density is a direct measure of the rate of an electrode reaction.

These plots are generated from experiments called potentiodynamic polarization tests.

Evans Diagrams & Mixed Potential Theory



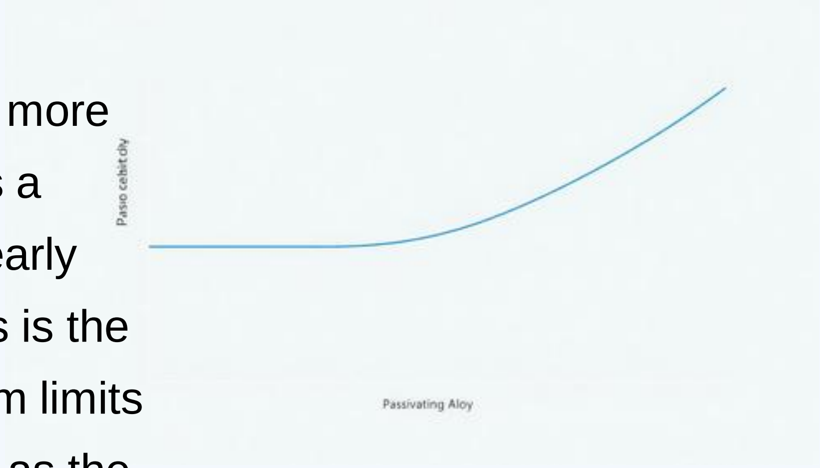
Finding the Corrosion Rate

This Evans diagram shows the behavior of separate oxidation (anodic) and reduction (cathodic) half-cell reactions. According to Mixed Potential Theory, when combined on a single metal surface, the overall potential will settle at the point where the total oxidation current equals the total reduction current. This point defines the corrosion potential (E_corr) and the corrosion current density (i_corr), which is a direct measure of the corrosion rate.

Evans Diagram for a Passivating Alloy

Passivity and Corrosion Rate

For a passivating alloy, the Evans diagram is more complex. The anodic (oxidation) curve shows a region where the current density becomes nearly constant over a wide range of potentials. This is the passive region, where the protective oxide film limits the corrosion rate to a very low value, known as the passive current density. The intersection of the cathodic curve with this passive region determines the corrosion potential and the very low corrosion rate of the alloy.



Introduction to Electrochemical Impedance Spectroscopy (EIS)

A Powerful Technique for Surface Analysis

Electrode interfaces have both resistive character (from charge transfer, or Faradaic processes) and capacitive character (from charge accumulation, or non-Faradaic processes). Electrochemical Impedance Spectroscopy (EIS) is a technique used to measure these properties and characterize the electrode surface.

It provides valuable information about the protective nature of passive films and the corrosion behavior of the material.

EIS: Basic Concepts

How EIS Works

In an EIS experiment, a very small (e.g., 10 mV) alternating current (AC) voltage is applied to the electrode over a wide range of frequencies (e.g., 1 mHz to 100 kHz).

The resulting AC current response is measured. The current will have the same frequency as the applied voltage but will be shifted in phase.

By analyzing the ratio of voltage to current (the impedance) and the phase shift at each frequency, detailed information about the resistive and capacitive properties of the interface can be obtained.

EIS: Equivalent Circuits

Modeling the Interface

To analyze EIS data, the complex behavior of the electrode interface is modeled using simple equivalent electrical circuits composed of resistors (R) and capacitors (C).

The Randles Circuit is the most common and simple analog for an electrode interface. It consists of:

- Solution Resistance (Rs): The resistance of the electrolyte.
- Polarization Resistance (Rp): The resistance to charge transfer (corrosion) at the interface.
- Double-Layer Capacitance (C): The capacitance of the charge accumulation at the interface.

EIS: The Constant Phase Element (CPE)

Modeling Non-Ideal Behavior

Real electrode surfaces, especially those with passive films, often do not behave as ideal capacitors. Their behavior is better modeled by replacing the capacitor in the equivalent circuit with a Constant Phase Element (CPE).

The CPE has an exponent, α, that ranges from 0 to 1:

- If $\alpha = 1$, the CPE behaves like an ideal capacitor.
- If $\alpha = 0$, the CPE behaves like a resistor.
- For passive films, α is typically between 0.7 and 0.95, indicating mostly capacitive but non-ideal behavior, possibly due to surface heterogeneity.

EIS: Mott-Schottky Analysis

Probing the Oxide's Electronic Properties

Mott-Schottky analysis is an impedance-based technique used to investigate the semiconducting properties of passive oxide films.

Method: The capacitance (C) of the surface is measured across a range of DC potentials, and a plot of $1/C^2$ versus potential is constructed.

Analysis: The slope of the resulting line is related to the density of charge carriers (defects) in the oxide film. This provides insight into the quality and electronic nature of the passive layer.

Titanium Alloys,

SERTAN OZAN, KHURRAM MUNIR, ARNE BIESIEKIERSKI, RASIM IPEK,
YUNCANG LI, CUIE WEN

Introduction to Titanium Alloys

The Premier Choice for Orthopedics

Titanium alloys have become indispensable for the biomedical industry, especially for orthopedic implants, due to their excellent combination of mechanical, physical, and biological performance.

The need for these materials is rapidly increasing. Between 2005 and 2030 in the US:

- Total hip replacements are projected to increase by 174% to 572,000.
- Total knee replacements are projected to grow by an enormous 673% to 3.48 million.

Design Criteria for New Ti Alloys

Key Considerations for Implant Design

The primary consideration in designing new biomedical Ti alloys is to select alloying elements with a known, high degree of biocompatibility. After that, mechanical properties must be tailored for the specific application.

Mechanical Criteria

Yield Strength

Elastic Modulus

Fatigue Strength

Wear Resistance

Corrosion Resistance

Biocompatibility: Issues with Traditional Alloys

The Problem of Ion Release

A key aspect of biocompatibility is the potential for metal ions to be released from an implant due to corrosion or wear, and the body's reaction to those ions.

- Stainless Steels and Co-Cr alloys can release Nickel (Ni), Cobalt (Co), and Chromium (Cr) ions.
- There are serious concerns regarding the carcinogenic effects of Ni and Co.
- Metal allergies, particularly to Nickel, are a significant and growing issue.

Metal Allergies in Orthopedics

When the Body Rejects an Implant

Metal allergies can cause significant problems for patients, sometimes requiring revision surgery to remove the offending implant and replace it with one made from a more biocompatible material like a titanium alloy.

Biocompatibility Issues with Ti-6Al-4V

Even Titanium is Not Perfect

Even some titanium alloys are now considered less suitable because they contain potentially non-biocompatible alloying elements.

The most common Ti alloy, Ti-6Al-4V, contains:

- Vanadium (V): Noted to be carcinogenic.
- Aluminum (Al): Has displayed neurological side effects and potential genotoxicity.

This has driven research into developing new, 'biocompatible' Ti alloys using only elements with no known biological concerns.

Biocompatible Alloying Elements for Titanium

A Palette of Safe Elements

Based on comprehensive reviews of carcinogenic, mutagenic, allergenic, and other effects, a set of transition elements has been identified as highly biocompatible for use in new titanium alloys.

Highly Biocompatible Alloying Elements:

- Titanium (Ti)
- Gold (Au)
- Tin (Sn)*
- Tantalum (Ta)
- Niobium (Nb)
- Ruthenium (Ru)

Biocompatible Titanium Alloys: Classification

Alpha, Alpha-Beta, and Beta Alloys

Titanium alloys are classified based on their room temperature microstructure, which dictates their properties.

α and α-β Alloys

Alpha alloys cannot be strengthened by heat treatment. Alpha-beta alloys, like Ti-6Al-4V, have a mix of phases and offer a good balance of properties.

β-Type Alloys

These alloys have attracted significant attention for orthopedics. They have much better cold-formability (reducing production costs) and a lower elastic modulus, which is closer to that of bone.

Mechanical Properties of Biocompatible Ti Alloys

Comparing Mechanical Properties

This table compares the mechanical properties of common and developmental titanium alloys.

Note the lower Young's Modulus of the β-type alloys compared to the α+β alloy Ti-6Al-4V.

Ti Alloy (wt%)	Microstructure	Young's Modulus (GPa)	Yield Strength (MPa)
Ti-6Al-4V ELI	α+β	110	875
Ti-6Al-7Nb	α+β	105	800
Ti-15Mo	β	78	544
Ti-35.3Nb-5.1Ta-7.1Zr	β	55	547
Ti-13Nb-13Zr	α+β	79-84	836-908

Fabrication: Powder Metallurgy (PM)

Near-Net-Shape Manufacturing

Titanium alloys are expensive to manufacture due to their high reactivity (requiring special environments) and poor machinability. This has led to an increasing preference for Powder Metallurgy (PM) methods.

- Advantage: PM enables the production of net shape or near-net shape parts, minimizing costly machining.
- Benefit: Avoids melting the alloy, reducing reactivity issues.
- Methods: Include die pressing, cold/hot isostatic pressing (HIP), etc.
- Goal: Produce compacts with high density and excellent mechanical performance.

Fabrication: Porous Structures

Mimicking Nature's Design

Nature often uses porous structures (like bone, wood, coral) to optimize mechanical properties. Biomedical engineers are adopting this approach to create porous metal implants.

Advantages of Porous Structures:

- Reduced Elastic Modulus: Increasing porosity decreases the implant's stiffness, reducing stress shielding.
- Bone Ingrowth: Pores allow bone to grow into the implant, providing strong biological fixation.
- Challenges: Porosity compromises the bulk mechanical strength and can reduce fatigue life.

Fabrication: Space-Holder Sintering

Creating Pores with a Placeholder

One effective method for creating high-porosity metals is space-holder sintering. This method provides some control over the final pore morphology.

Process:

- 1. Mix metal powder with particles of a 'space-holder' material.
- 2. Compact the mixture into the desired shape.
- 3. Heat the compact to burn out or dissolve the space-holder material, leaving behind pores.
- 4. Heat further to sinter the remaining metal powder together.

Common Space-Holders:Carbamide,Magnesium,Ammonium Bicarbonate,Sodium Chloride.

Fabrication: Additive Manufacturing (AM)

Printing Metal Implants

Porous materials with desired porosity and complex pore structures can be produced directly, without space-holders, using additive manufacturing (AM) or 3D printing methods. These techniques build parts layer-by-layer from a digital model.

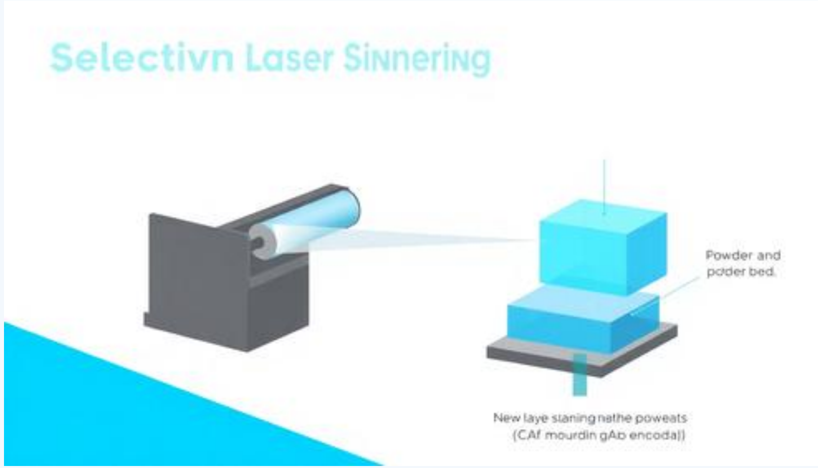
Common Methods:

- Selective Laser Sintering (SLS)
- Selective Laser Melting (SLM)
- Electron Beam Melting (EBM)

AM Processes: SLS & SLM

Laser-Based 3D Printing

In Selective Laser Sintering (SLS), a thin layer of metal powder is spread out. A computer-controlled laser then sinters the powder in a specific pattern to form one layer of the part. The platform is lowered, a new layer of powder is added, and the process repeats until the part is complete. Selective Laser Melting (SLM) is similar, but fully melts the powder for a denser part.



AM Processes: EBM & LENS

Other Additive Manufacturing Processes

Electron Beam Melting (EBM)

Similar to SLM, but uses an electron beam instead of a laser. Must be performed under high vacuum.

Laser-Engineered Net Shaping (LENS)

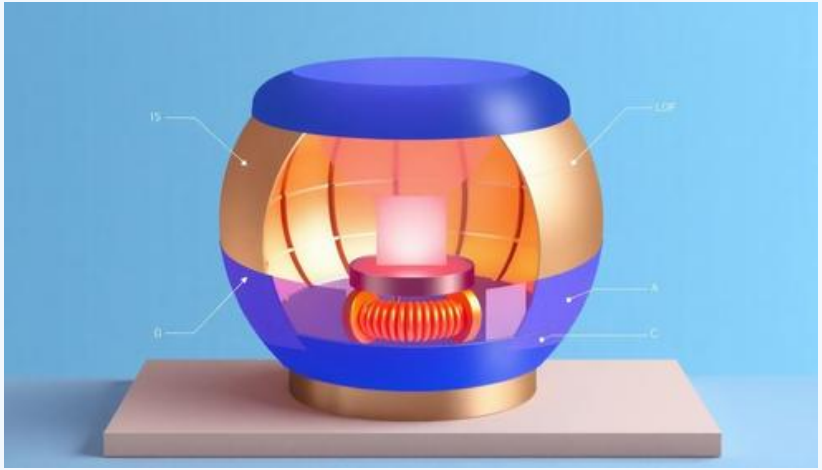
Powder is fed through a nozzle directly into the focal point of a high-power laser, where it melts and deposits onto the part. This method doesn't require a powder bed.

All of these methods require atmospheric control (typically Argon) due to the high reactivity of titanium powder.

Fabrication: Cold Crucible Levitation Melting

Advanced Casting

Casting reactive, high-melting-point metals like Ti, Nb, and Ta is difficult with traditional methods. Cold Crucible Levitation Melting (CCLM) is a solution. In CCLM, electromagnetic forces both heat and levitate the molten metal, mixing it effectively and preventing contamination from contact with a crucible. This yields a very clean and uniform alloy.



Mechanical Properties: Stress Shielding

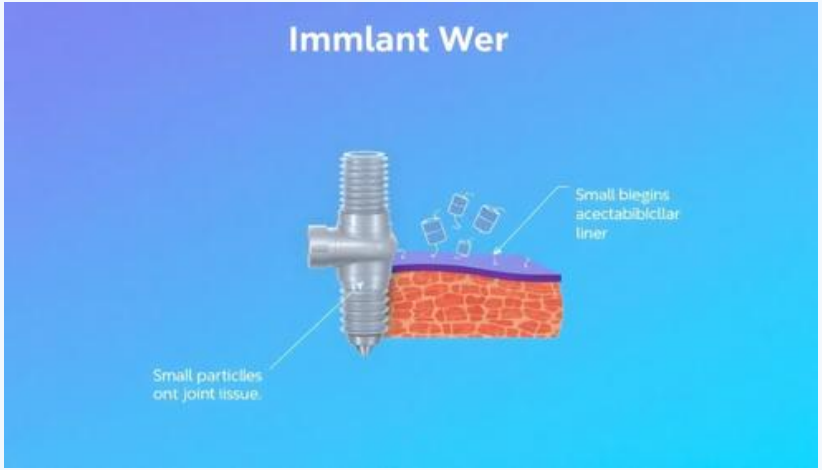
The Problem of Mismatched Stiffness

When an implant material is much stiffer (has a higher elastic modulus) than the surrounding bone, it carries a disproportionate share of the load. This 'shields' the bone from the mechanical stress it needs to stay healthy. The lack of stress can lead to bone resorption and atrophy, potentially causing implant loosening. This phenomenon is called stress shielding.

Mechanical Properties: Wear Resistance

The Downside of Wear

Titanium alloys are known for their poor tribological (wear) properties. When used in articulating joints, they can generate wear debris.



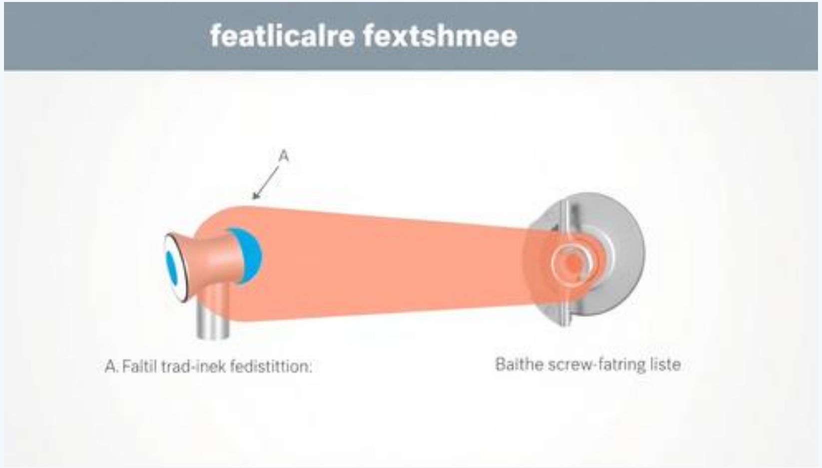
Consequences of Wear Debris:

- Inflammation
- Osteolysis (bone resorption)
- Metallosis (tissue staining)
- Implant loosening

Mechanical Properties: Fatigue Behavior

Endurance Under Cyclic Loading

High fatigue strength is crucial for the long-term success of load-bearing implants. Failures often occur at stress concentration points like screw holes or on the joints of hip prostheses.



Strengthening Ti Alloys without Increasing Modulus

A Balancing Act

Improving the strength of β-type Ti alloys is often done by aging treatments, which precipitate harder secondary phases (α or ω). However, this significantly increases the elastic modulus, which is undesirable.

An alternative is interstitial strengthening by adding controlled amounts of oxygen:

- Oxygen atoms dissolve into the β-phase, strengthening it via solid-solution strengthening.
- This can improve tensile and fatigue properties.
- Crucially, if oxygen content is kept low (< 0.33 wt%), this strengthening can be achieved with little to no increase in the elastic modulus.

Surface Modification for Bone Bonding

Enhancing the Implant-Bone Bond

While Ti alloys are biocompatible, they are bioinert, meaning they don't actively bond with bone. This can lead to the formation of a fibrous tissue layer at the interface, which can cause loosening.

The Goal: Osseointegration & Bioactivity

- Osseointegration: A direct structural and functional connection between living bone and the surface of a load-bearing implant.
- Bioactivity (or Osteoconductivity): The ability of a material to promote the formation of a bone-like apatite layer on its surface, creating a chemical bond with the host bone.

Surface Modification Methods

Creating a Bioactive Surface

Various surface modification methods are used to make the surface of titanium alloys bioactive and improve their bond to bone.

1. **Alkali-Heat Treatment**

   Treating the surface with a strong base (like NaOH) and heat to form a sodium titanate hydrogel layer.

2. **Anodic Oxidation (Anodization)**

   Electrochemical process to grow a nanoporous or nanotubular oxide layer.

3. **Plasma Spray**

   Applying a coating of a bioactive ceramic like hydroxyapatite (HA).

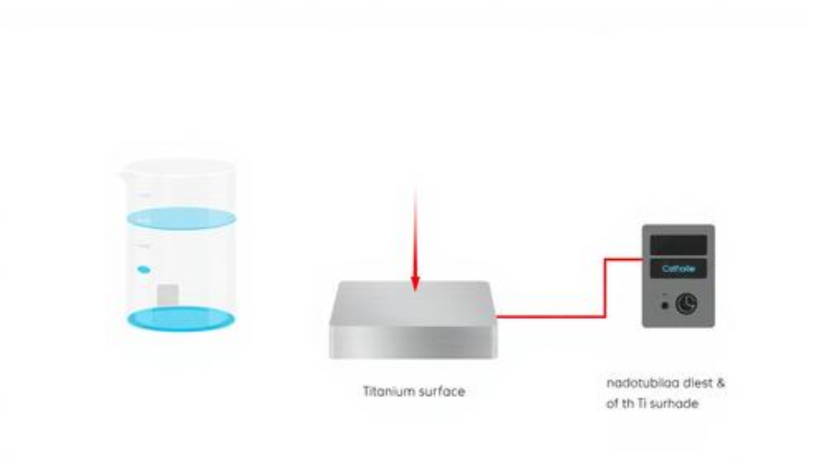
4. **Sol-Gel Coating**

   Using a liquid precursor (sol) to deposit a thin ceramic film.

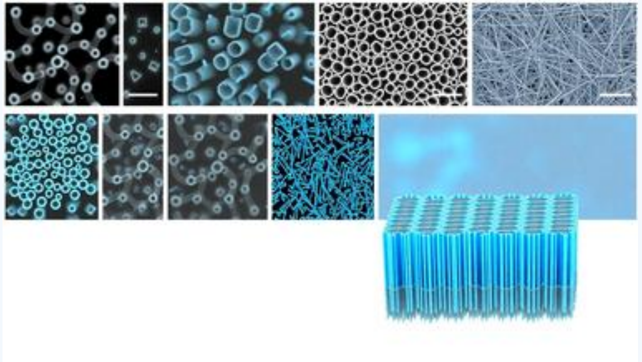
Anodization for Bioactivity

A Promising Surface Treatment

Anodization is an electrochemical technique that tailors the self-protective oxide layer on titanium. In fluoride-containing electrolytes, it can be used to grow highly organized, patterned, nanoporous, or nanotubular structures on the surface. These nanostructures have been shown to significantly enhance osseointegration and cell response.



Anodized Nanostructures



Controlling the Nanotopography

The characteristic dimensions of the TiO_2 nanotubes—such as diameter, length, and wall thickness—can be precisely controlled by adjusting the anodization parameters (potential, time, electrolyte type). These dimensions, in turn, can affect cell adhesion, proliferation, and differentiation.

Stainless Steels for Biomedical Applications

1.3.3B Stainless Steels

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Overview of Stainless Steel

What is Stainless Steel?

Stainless steel refers to a family of iron-based alloys that contain significant amounts of chromium and nickel. The name 'stainless' comes from its excellent corrosion resistance, which is due to a protective surface oxide layer formed by these alloying elements.

Why is it used in Biomedicine?

Specific types of stainless steel are ideal for biomedical devices because of their desirable properties:

- Excellent shaping and joining capabilities.
- Good mechanical properties and durability.
- Acceptable corrosion resistance in the body.

History: The Strengths and Weaknesses of Iron

The Age of Iron

Iron-based tools and weapons have been in use since the Bronze Age. Iron's key advantage is that its hardness and tensile strength can be easily controlled through heating and quenching processes.

The Major Drawback

The primary disadvantage of iron is its tendency to rust (corrode) when reacting with oxygen, causing it to lose its mechanical properties. This propensity limited its use for many applications for over two millennia and made it unsuitable for biomedical implants.

The Dawn of Stainless Steel

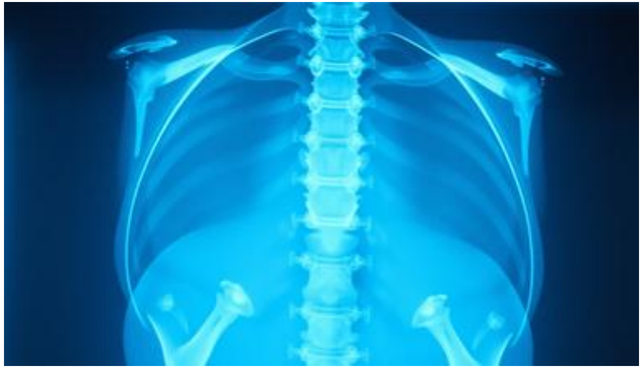
A Revolutionary Discovery

A major technological breakthrough occurred within the last century. It was discovered that adding significant amounts of chromium and nickel to iron created a new alloy with remarkable corrosion resistance, now known as stainless steel.

Impact on Technology

This development was an extraordinary technological advancement that opened up new possibilities for iron-based alloys in nearly every field, including, most notably, biomedical applications.

Biomedical Applications Emerge



Early Medical Use

The use of stainless steel for medical implants began in the 1920s and 1930s. As new medical procedures were developed and the material itself was refined, the applications for stainless steels in medicine expanded significantly.

Selective Suitability

While there are many different types of stainless steels available commercially, only a select few possess the specific combination of properties that make them suitable for use as biomaterials in implantable devices.

Composition and Types

Alloy Composition

Stainless steel is fundamentally an iron-based alloy containing an appreciable percentage of chromium and nickel.

Three Main Classes

Stainless steels are categorized into three main classes based on their microstructure, which is the arrangement of their internal crystalline structure:

- Austenitic
- Ferritic
- Martensitic

Austenitic Stainless Steels

The Primary Choice for Implants

Austenitic stainless steels have austenite (gamma-phase iron) as their primary phase. They are alloyed with chromium and nickel, and sometimes manganese and nitrogen.

The 300-Series

The 300-series of stainless steels (e.g., Types 301, 304, 316, 347) are the most commonly used for biomedical purposes. This is due to their excellent combination of toughness, durability, weldability, corrosion resistance, and favorable manufacturing economics.

Material Properties: Hardening and MRI Safety

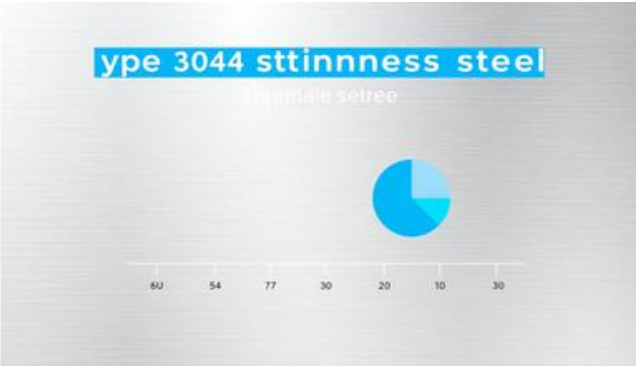
Hardening Methods

Austenitic steels are amenable to work hardening (strengthening through mechanical deformation) but cannot be hardened by heat treatment.

MRI Compatibility

A key advantage of austenitic stainless steel for implanted devices is that it is nonmagnetic. This means it has minimal or no interactions with the intense magnetic fields used in Magnetic Resonance Imaging (MRI), ensuring patient safety during scans.

Focus on Type 304 Stainless Steel



The Workhorse of Surgical Implants

Type 304 is the most familiar austenitic stainless steel used for surgical implants. Its composition is a key factor in its performance.

Composition

- Chromium: 18% - 20%
- Nickel: 8% - 10%
- Iron: Remainder

An example of a basic austenitic steel is Type 302, which is composed of iron with 18% chromium and 8% nickel.

Limitations of Other Stainless Steels

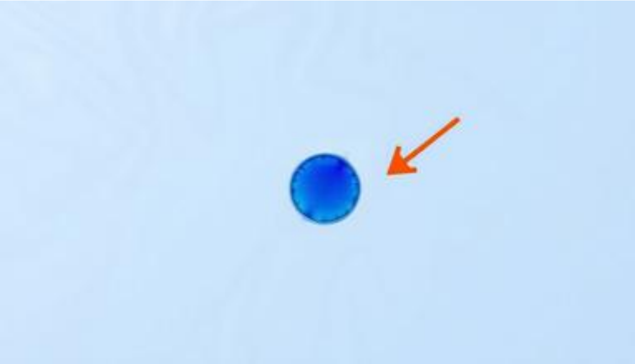
Why Not Other Types?

Ferritic and martensitic stainless steels are not commonly used for biomedical applications. This also applies to precipitation-hardened and cast stainless steels.

Key Deficiencies

These other classes of stainless steel lack the desirable combination of corrosion resistance and mechanical properties that are essential for long-term, safe performance inside the human body, which austenitic steels provide.

he Importance of Composition Control



The Risk of Phase Changes

The composition of stainless steels for biomedical use must be closely controlled. Under certain processing conditions, it's possible for undesirable phases to form within the austenitic alloy.

Delta Ferrite: A Magnetic Problem

One such phase is delta ferrite, which is magnetic. If an implant containing delta ferrite is exposed to the strong magnetic fields of an MRI, it can lead to localized heating or material motion. This is deleterious to the patient, highlighting the critical need for precise compositional control in alloys used for implants.

Crystalline Structure of Stainless Steel

The Crystalline Nature of Metals

Metals, including stainless steel alloys, are characterized by a high degree of crystallinity. The atoms are arranged in a regular, repeating pattern called a crystal lattice.

Unit Cell Structures

There are three basic types of unit cells, the smallest repeating unit of a crystal lattice:

- Face-Centered Cubic (FCC)
- Body-Centered Cubic (BCC)
- Hexagonal Close Packed (HCP)

Stainless steels used for implants have a Face-Centered Cubic (FCC) structure.

The Role of Key Alloying Elements

A Balancing Act

Chromium (Cr)

Its primary purpose is to form a protective Cr_2O_3 surface layer (passive film) that provides corrosion resistance. However, chromium is a ferrite stabilizer, which promotes the less-desirable body-centered cubic phase.

Nickel (Ni), Manganese (Mn), and Nitrogen (N)

These elements are added to counteract chromium's effect and stabilize the desired austenite (face-centered cubic) phase.

The Role of Key Alloying Elements

A Balancing Act

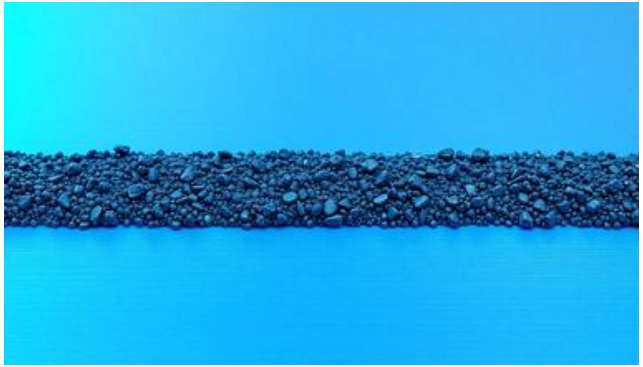
Nitrogen (N)

In addition to stabilizing austenite, nitrogen also increases the mechanical strength and corrosion resistance of the alloy.

Molybdenum (Mo)

Molybdenum additions have a beneficial impact on the resistance of stainless steels to a specific type of corrosion known as pitting.

The Problem with Carbon: Sensitization



Limiting Carbon Content

The carbon content in stainless-steel alloys for implants must be limited to very small percentages. The 'L' in grades like 316L stands for 'Low Carbon' (<0.030%).

The Phenomenon of Sensitization

If too much carbon is present, chromium carbides can form when the steel is held at temperatures between 450-815°C (e.g., during slow cooling after welding). These carbides preferentially form along grain boundaries, depleting the adjacent areas of chromium. These chromium-depleted zones become highly prone to corrosion, which can lead to implant failure.

The Evolution of Implant Alloys

Beyond 316L

While 316 and 316L stainless steels have been used successfully for decades, stronger and more corrosion-resistant alloys have since been developed.

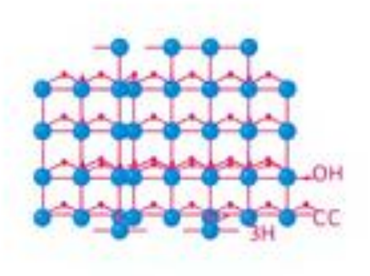
Higher Performance Alloys

Alloys like Rex 734 (Ortron 90) and 22-13-5, developed in the 1980s, contain higher levels of chromium, manganese, and nitrogen compared to 316L. This results in improved mechanical properties and enhanced corrosion resistance.

Nickel-Free Alternatives

Concerns about adverse patient allergic responses to nickel have driven the development of essentially nickel-free stainless steels. An example is BioDur 108, which uses high levels of manganese and nitrogen instead of nickel to stabilize the austenite phase.

Mechanical Properties: The Role of Deformation



Influencing Factors

The mechanical properties of metals and alloys depend on a trio of factors: structure, chemical composition, and processing history.

Plastic Deformation and Dislocations

Permanent (plastic) deformation occurs when mechanical stress causes atoms to move within the crystal structure. This movement creates defects or disturbed regions in the crystal lattice known as 'dislocations.' Subsequent movement of atoms becomes more difficult in the presence of these dislocations, which in turn changes the material's mechanical properties, typically increasing yield strength and decreasing ductility.

Strengthening Mechanisms: Composition Effects

Solid Solution Strengthening

Alloying elements like chromium and nickel replace iron atoms in the crystal structure. Since these replacement atoms have different sizes, they distort the crystal lattice. This distortion makes it more difficult for dislocations to move, thus increasing the material's yield strength.

Interstitial Strengthening

Smaller atoms, like nitrogen, don't replace iron atoms but instead fit into the gaps (interstices) between them. These 'interstitials' cause significant lattice strain, leading to substantial increases in strength by impeding dislocation movement.

Strengthening Mechanisms: Processing Effects

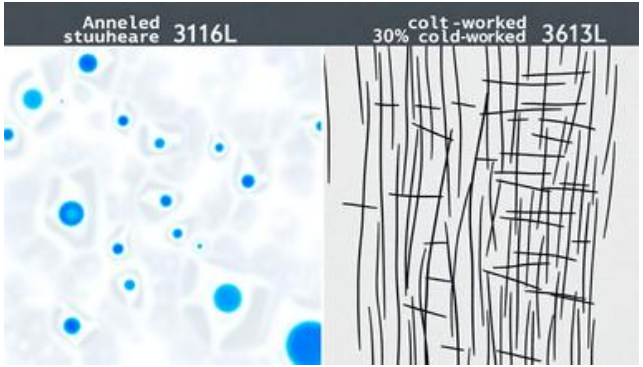
Cold Working

Austenitic stainless steels cannot be hardened by heat treatment. Instead, they are strengthened by a process called work hardening, or 'cold working.' This involves applying repeated mechanical stresses to the material while it is unheated.

Mechanism

Cold working introduces a high density of dislocations into the material. As the dislocation density increases, the dislocations begin to interact and tangle, making it progressively more difficult for them to move. This leads to an increase in the material's strength and a decrease in its ductility.

Microstructure: Annealed vs. Cold-Worked 316L



A Tale of Two Structures

This figure compares the microstructure of 316L stainless steel in two different states. The amount of cold work is specified by the percentage reduction in the material's cross-sectional area.

The image on the right shows a sample that has been cold-worked by about 30%. The deformation within many of the grains of the cold-worked material is clearly evident as slip bands or deformation twins.

Limitations of Cold Working

Non-Uniformity

For large components, cold working may not be uniform. The exterior regions can become more heavily worked than the interior, creating a gradient of properties.

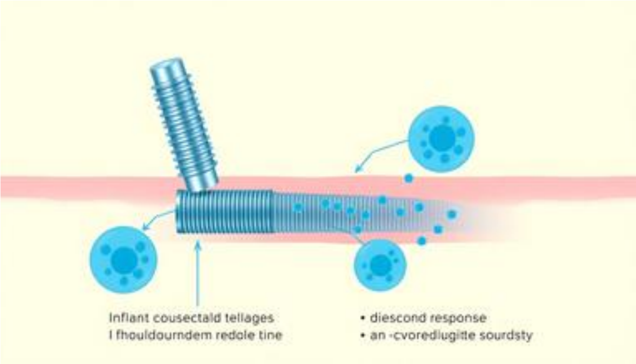
Stress-Induced Transformation

Heavily cold-worked stainless steels (like Type 304) can undergo a crystal structure transformation from nonmagnetic austenite to magnetic martensite. This is a major concern for devices like guide wires, as fragments can become magnetic and cause issues if they break off during a procedure.

Effect of Welding

High-temperature processes like welding will locally heat the material, causing it to recrystallize. This softens the cold-worked material and reduces its mechanical properties back to annealed levels in the heat-affected zone.

Corrosion: The Basics



A Persistent Challenge

Corrosion, or oxidation, is a universal process that causes materials to lose their desirable properties. It's an especially critical consideration for biomedical applications.

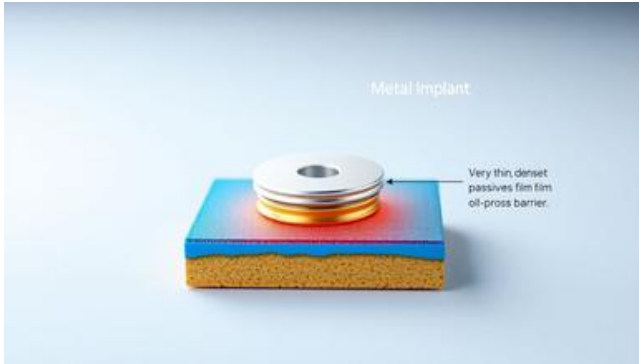
Why It Matters for Implants

- Loss of Material Properties: Corrosion can weaken the implant, leading to mechanical failure.
- Adverse Biological Response: Metal ions released during corrosion can interact with biological tissues, causing inflammation, allergic reactions, or other adverse cellular responses.
- Implant Failure: Either of the above can ultimately lead to the failure of the implant.

The Role of Passive Films

The Protective Shield

Most implantable metals (except noble metals like gold) rely on a protective oxide film, known as a passive film, to limit corrosion to acceptable levels.

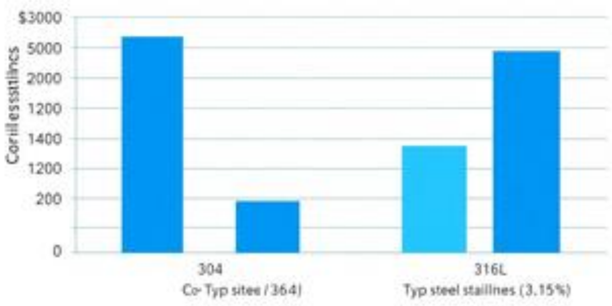


Properties of Passive Films

- Thin (typically < 100 microns)
- Dense
- Strongly adhered to the metal substrate
- Limit the transport of metal ions into the body

Different alloys form different passive films. Austenitic stainless steels and cobalt-base alloys form a chromium oxide (Cr_2O_3) film, while titanium alloys form a titanium dioxide (TiO_2) film.

Corrosion in the Body and Type 316L



A Hostile Environment

The internal environment of the human body, with its chloride-rich fluids, is highly corrosive. For many applications, the corrosion resistance of Type 304 stainless steel is insufficient.

The Superiority of Type 316/316L

Type 316 or 316L stainless steel is used for more demanding applications. The higher nickel and molybdenum content in Type 316 provides superior overall corrosion resistance compared to Type 304, especially against pitting and crevice corrosion in chloride environments. It also offers excellent formability and weldability.

Newer Alloys and Pitting Potential

Comparative Corrosion Resistance

In general, even 316L stainless steel is not as corrosion resistant as cobalt-chromium or titanium alloys. However, newer stainless-steel alloys like 22-13-5, Rex 734, and BioDur 108 show improved corrosion resistance due to their higher concentrations of Chromium (Cr) and Nitrogen (N).

Measuring Resistance: Pitting Potential

A metric for relative corrosion resistance is the pitting potential, measured by an anodic polarization test. Higher values indicate better resistance. One study observed the following pitting potentials:

- 316L: 346 mV
- 22-13-5: 1030 mV
- BioDur 108: 1120 mV

The Impact of Inclusions

What are Inclusions?

Inclusions are foreign particles, typically oxides like alumina or silicates, that form during the initial melting of the alloy and become trapped within the material during processing.

Role in Corrosion

These inclusions have different corrosion behavior compared to the host alloy. If they occur on the implant surface, they can act as initiation sites for corrosion, compromising the integrity of the passive film.

Minimizing Inclusions

To minimize the presence of inclusions, careful control of the alloy melting and subsequent processing steps is required. Standardized specifications, such as those from ASTM, provide guidelines for these processes.

Forms of Corrosion

Mechanisms of Corrosion

- Uniform Corrosion: A relatively even layer of corrosion, like rust on an iron bar.
- Pitting Corrosion: Localized failure of the passive film, leading to small holes (pits).
- Crevice Corrosion: Occurs in tight spaces with stagnant fluid.
- Intergranular Corrosion: Corrosion along grain boundaries (related to sensitization).
- Stress Corrosion Cracking: Cracking caused by the combined effect of tensile stress and a corrosive environment.
- Galvanic Corrosion: Occurs when two dissimilar metals are in electrical contact.

Pitting Resistance Equivalent (PRE)

What is PRE?

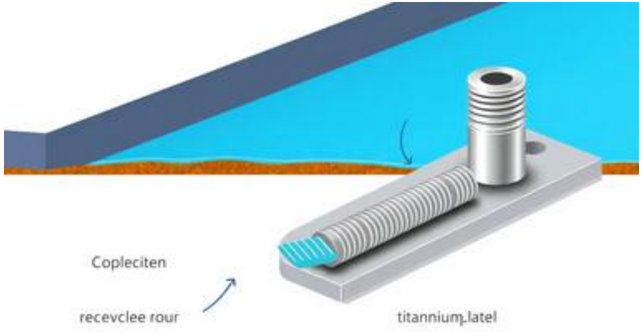
The Pitting Resistance Equivalent (PRE) number is an empirical relationship used to estimate the contribution of key alloying elements to the pitting corrosion resistance of austenitic stainless steels. A higher PRE number indicates better resistance.

The PRE Formula

The formula varies slightly based on nitrogen content, but a common approximation is:

$$PRE = \% Cr + 3.3 \times \% Mo + 16 \times \% N$$

Crevice and Galvanic Corrosion



Crevice Corrosion

This is another localized form of corrosion that occurs due to a stagnant microenvironment (e.g., under a screw head or in a modular joint). Corrosive agents can enter the crevice, but oxygen is prevented from entering, which stops the protective passive layer from reforming (repassivation). It can be minimized by careful implant design.

Galvanic Corrosion

This occurs when two dissimilar metals are in electrical contact in a conducting fluid (like body fluids). The potential difference between the metals drives corrosion of the less noble metal. It can even occur between two 'similar' alloys if they have different compositions or processing histories. This is avoided by careful material selection and management.

Summary: Stainless Steels

Revolution in Biomaterials: The introduction of chromium and nickel created corrosion-inhibiting stainless steel, making iron-based alloys suitable for implants.

Austenitic Steels Dominate: This class of stainless steel is especially suitable due to its favorable corrosion resistance, MRI compatibility, and desirable mechanical properties.

Engineered Properties: The performance of stainless steel is determined not just by alloy composition, but also by processing (e.g., cold working), allowing properties to be tailored for specific applications.

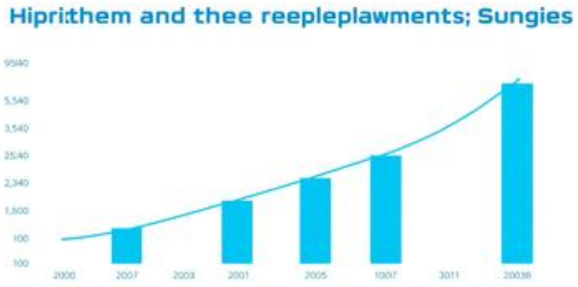
Continuous Improvement: While 316L is a common standard, newer alloys offer improved strength and corrosion resistance. Development is ongoing.

Importance of Standards: ASTM and ISO standards, along with data from retrieval studies, are crucial for advancing the design and application of stainless-steel implants.

CoCr Alloys in Biomedical Applications

AMIT BANDYOPADHYAY, KELLEN D. TRAXEL, JOSE D. AVILA, INDRANATH MITRA, SUSMITA BOSE

Introduction to CoCr Alloys



Primary Applications

Cobalt-chromium (CoCr) implants are most commonly used to treat clinical conditions like degenerative joint disease and rheumatoid arthritis.

Growing Demand

Arthroplasty (joint replacement surgery) has seen a significant increase in recent years. Projections show a massive growth in demand for total hip arthroplasty (THA) and total knee arthroplasty (TKA), driving the need for more and better implants.

Clinical Issues and Testing

The Challenge of Wear

A major issue with implants, particularly in articulating joints, is the release of metal ions due to wear-induced damage. This process is known as ionic leaching.

Focus on Testing and Understanding

Significant regulatory development has led to extensive studies to understand the cellular response to the release of Cobalt (Co^{2+}) and Chromium (Cr^{3+}) ions. This has spurred the development of new testing methods to evaluate:

- Bio-tribological performance (friction, wear, and lubrication)
- Mechanical properties
- Electrochemical behavior (corrosion)

Common CoCr Alloy Types

Key Alloy Systems

The most common CoCr-based alloys are of the cobalt-chromium-tungsten (Co-Cr-W) and cobalt-chromium-molybdenum (Co-Cr-Mo) types.

Role of Alloying Elements

1. Cobalt (Co): The base metal.
2. Chromium (Cr): Provides a passive Cr_2O_3 surface oxide film for corrosion resistance (same as in stainless steel).
3. Tungsten (W) and/or Molybdenum (Mo): Act as strengthening elements within the alloy.

The best-known system is the Co-27Cr-6.1Mo alloy, designated ASTM F75, due to its excellent combination of properties.

Common Biomedical CoCr Alloy Grades and Compositions (wt%)

ASTM Designation	Co	Cr	Mo	W	Si	Mn	C	Ni
F75 (CoCrMo)	Bal.	27.0-30.0	5.0-7.0	-	0.0-1.0	0.0-1.0	0.0-0.35	1.0
F799 (CoCrMo)	Bal.	26.0-30.0	5.0-7.0	-	0.0-1.0	0.0-1.0	0.0-0.35	0.0-1.0
F90 (CoCrW)	Bal.	19.0-21.0	-	14.0-16.0	0.4	1.0-2.0	0.05-0.15	9.0-11.0
F562 (CoNiCrMo)	Bal.	19.0-21.0	9.0-10.5	-	0.0-0.15	0.0-0.15	0.0-0.025	33.0-37.0
F90 (CoCrWNi)	Bal.	19.0-21.0	-	14.0-16.0	-	-	-	9.0-11.0

Studying Corrosion: Electroanalytical Methods

Quantifying Performance

Electroanalytical Methods (EMs) are used to analyze and quantify the electrochemical performance (i.e., corrosion behavior) of biocompatible materials.

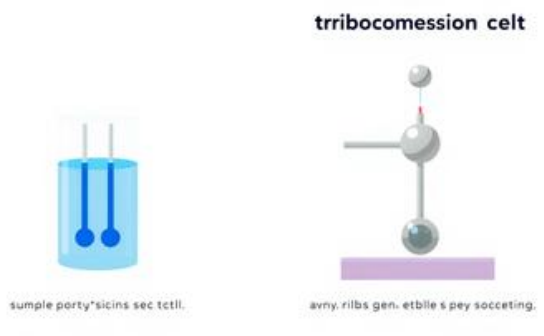
The Three-Electrode Setup

Testing is typically done in a 'corrosion cell' with a three-electrode convention:

- Working Electrode (WE): The material sample being tested (the analyte).
- Reference Electrode (RE): Provides a stable potential to measure against.
- Counter Electrode (CE): Completes the electrical circuit, often made of platinum.

A potentiostat instrument controls the potential and measures the resulting current.

Corrosion and Tribocorrosion Test Setups

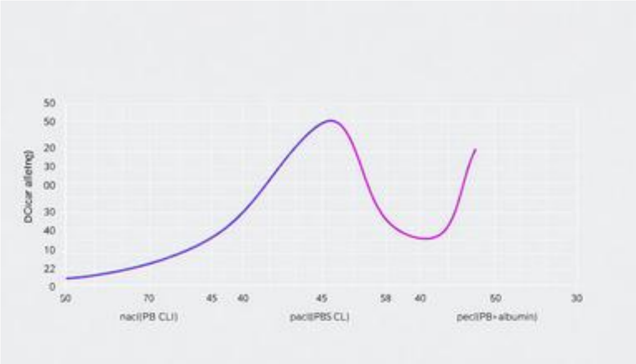


Simulating the Body

A corrosion cell can be configured to work in biologically relevant media (e.g., simulated body fluid). It can be combined with wear testing to study 'tribocorrosion' - the interaction of wear and corrosion.

(A) A standard corrosion cell setup. (B) A tribocorrosion setup incorporates a counter wear material and applied load to simulate joint movement.

Potentiodynamic Polarization Curves



Understanding Corrosion Behavior

Potentiodynamic Polarization (PDP) curves are generated by sweeping the potential applied to the sample and measuring the resulting current. These curves reveal key corrosion parameters.

This example shows that in more physiologically relevant media (like PBS + albumin), the corrosion potential (Ecorr) shifts, indicating the material has a lower resistance to corrosion compared to a simple salt solution. This highlights the importance of testing in relevant environments.

Microstructure and Role of Alloying Elements

Contribution of Each Element

Cobalt (Co)

Serves as the base FCC (α-Co) crystal structure. It provides high strength, good work-hardening, and can undergo a stress-induced phase transformation to HCP (ε-Co), which contributes to its excellent wear and corrosion resistance.

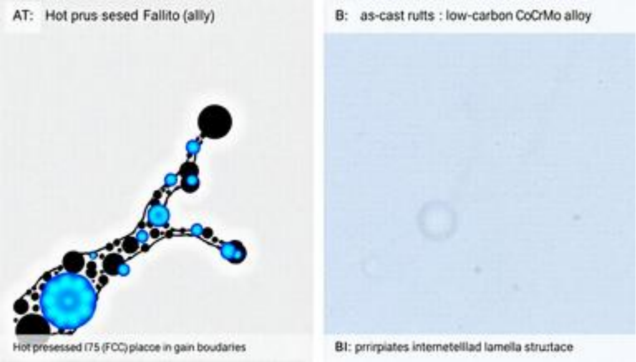
Chromium (Cr)

Provides oxidation resistance via the Cr_2O_3 passive film. It also strengthens the alloy and is a major source for forming metal carbides (e.g., Cr_7C_3, $Cr_{23}C_6$).

Tungsten (W) & Molybdenum (Mo)

These large atoms provide significant solid-solution strengthening by impeding dislocation motion. They also contribute to the formation of metal carbides along grain boundaries.

Microstructural Features of F75 Alloy

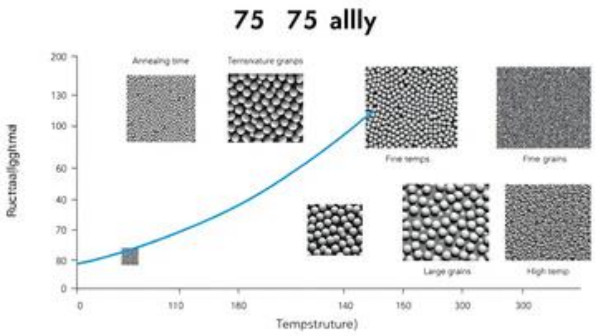


A Closer Look at the Microstructure

High-magnification images reveal the different phases that form within CoCr alloys, which dictate their properties.

(A) A hot-pressed F75 microstructure with a carbide network. (B) An as-cast microstructure showing various precipitates, including the undesirable σ phase, which can be removed with heat treatment.

The Effect of Heat Treatment

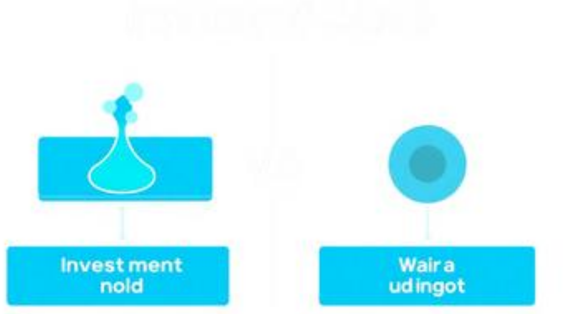


Tailoring Properties with Heat

The microstructure of CoCr alloys can be precisely controlled through heat treatment (annealing). This allows for a trade-off between strength and ductility.

- High-temperature annealing results in large, equiaxed grains, leading to high ductility.
- Lower-temperature annealing results in highly refined (small) grains, leading to higher hardness and tensile strength.

Traditional Manufacturing Methods



Investment Casting

A traditional method where liquid metal is cast into a ceramic mold created from a wax pattern. It's ideal for high-volume production but can result in variations in microstructure and mechanical properties.

Wrought Processing

Materials are formed from solid ingots and shaped through various techniques (e.g., forging, rolling). This generally produces a more uniform microstructure and more consistent properties compared to casting.

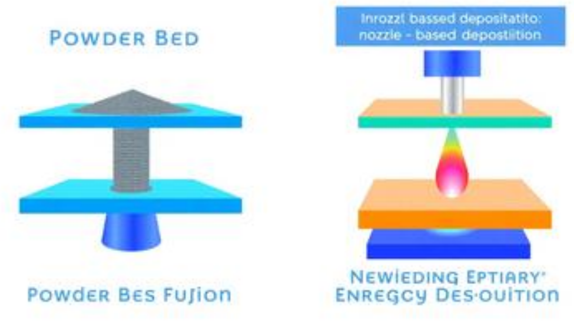
Additive Manufacturing (3D Printing) of CoCr

A New Paradigm in Manufacturing

Additive manufacturing (AM), or 3D printing, is a layer-by-layer process that offers new possibilities for biomedical implants, including:

- Patient-specific designs tailored to individual anatomy.
- Complex geometries and surface modifications (e.g., porous structures for bone ingrowth) that are impossible with traditional methods.

AM Techniques: DED vs. Powder-Bed



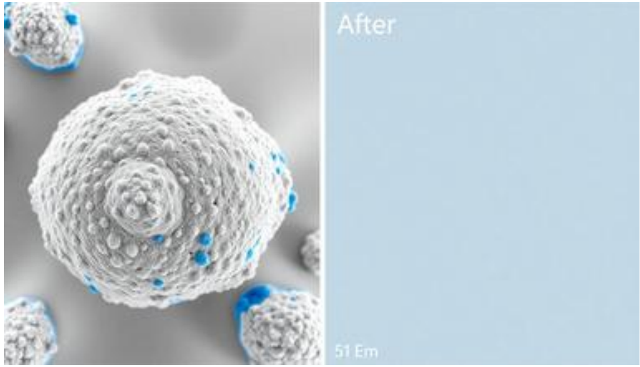
Powder-Bed Fusion (PBF)

A laser or electron beam melts powder in a thin layer. The build platform drops, a new layer of powder is spread, and the process repeats. This method is great for creating fine, detailed features and internal porosity.

Directed Energy Deposition (DED)

A deposition head melts powder or wire as it is fed into a melt pool on the part's surface. This process is well-suited for creating large parts, repairing components, or developing new materials by changing the feedstock material on the fly.

Challenges in AM of CoCr Alloys

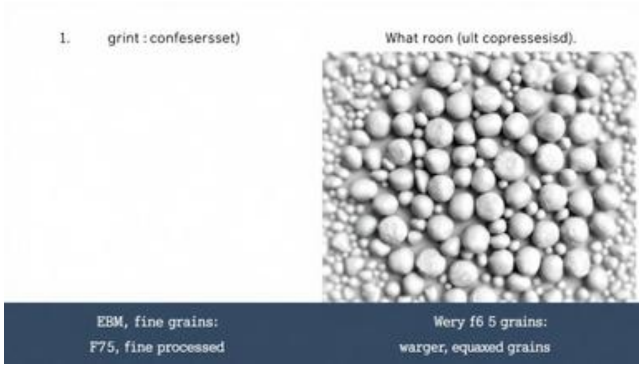


Surface Finish and Powder Removal

A key challenge in AM is surface roughness and the presence of partially melted or loose powder particles, which must be removed to ensure patient safety. Chemical etching is one method used to smooth surfaces and remove sintered particles.

Comparison of a 3D-printed F75 scaffold surface before (left) and after (right) chemical etching to improve surface finish.

AM Microstructure and Machinability



Fine Grains and Tough Machining

The very high cooling rates inherent in laser-based AM create a very fine-grained microstructure. This is different from the larger grains of traditionally processed alloys.

This fine-grained structure can make the as-processed AM parts much more difficult to machine compared to their wrought counterparts, leading to issues like extensive tool wear and cracking of the part.

Materials Innovation with AM

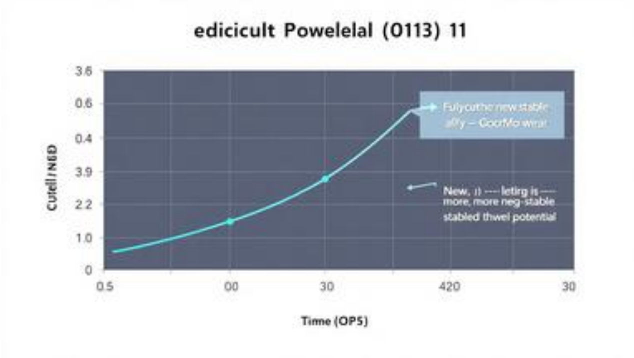
Functionally Graded Materials

DED systems allow for the composition to be changed dynamically during printing. This can create functionally graded materials, for example, transitioning from a titanium alloy base (for bone integration) to a CoCr alloy surface (for wear resistance) in a single component.

In Situ Composites

It's also possible to pre-mix powders to create novel composites. One study showed that adding calcium phosphate powder to CoCrMo alloy during laser AM resulted in an in-situ tribofilm forming during wear testing. This film lowered friction and wear, demonstrating the potential to design materials with enhanced biomedical performance.

Bio-Tribocorrosion: Open-Circuit Potential



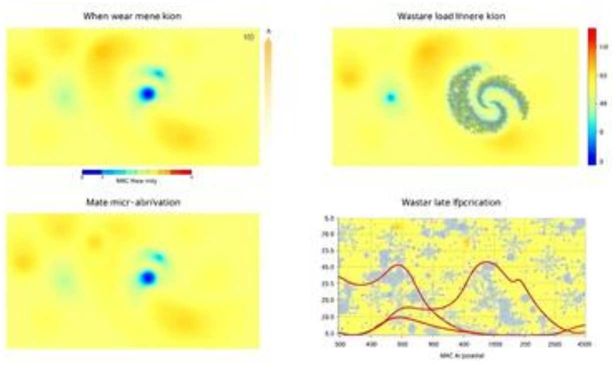
Equilibrium Potential

Open-Circuit Potential (OCP) measures the natural potential difference that exists between the material and the testing solution when no external current is applied. It represents an equilibrium state.

The Effect of Mechanical Wear

When mechanical wear begins, the protective passive layer on the material is destroyed. This exposes the fresh, more reactive metal underneath to the solution. This activation causes a sudden drop in the OCP to a more negative potential, indicating an increased tendency to corrode.

Wear Regimes and Wastage Maps



Depassivation/Repassivation Cycle

Under constant mechanical wear, the passive film is continuously removed (depassivation) and then attempts to reform (repassivation). This cycle of 'wear-accelerated corrosion' leads to synergistic material loss.

Micro-Abrasion Corrosion (MAC) and Wastage Maps

These maps are created by testing under various loads and potentials. They define different wear regimes and quantify the severity of material loss, providing a powerful tool for predicting implant performance under different conditions.

Key Advantages of CoCr Alloys in Tribocorrosion

Lower Wear Rates

Across comparable tests, CoCr alloys consistently show lower wear rates than other common implant alloys like Ti6Al4V. For example, when tested against UHMWPE (the plastic cup in a hip replacement), the wear rate for CoCr is approximately six times lower than for Ti64. This translates to a longer implant life and less wear debris.

Higher Corrosion Resistance

CoCr alloys typically exhibit a more positive Open-Circuit Potential (OCP) than Ti64. A more positive (or less negative) potential indicates a higher resistance to corrosion. This reduces the driving force for the corrosion process to occur.

Applications of CoCr Alloys

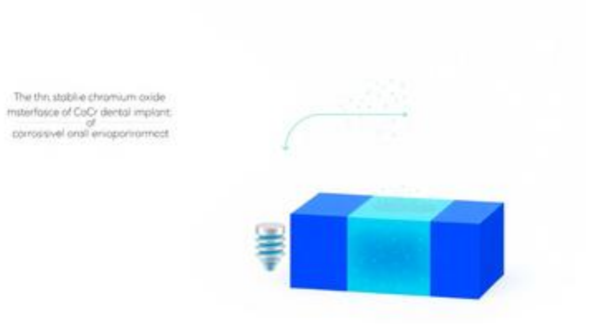
Historical Context

CoCr alloys were first introduced in the 1930s for dental applications under the brand name Vitallium. Their excellent corrosion resistance and biocompatibility soon led to their adoption by the orthopedic industry.

Versatile Applications

CoCr alloys are used in a wide range of biomedical devices due to their high wear resistance, strength, and long-term stability.

Biocompatibility: Corrosion Resistance



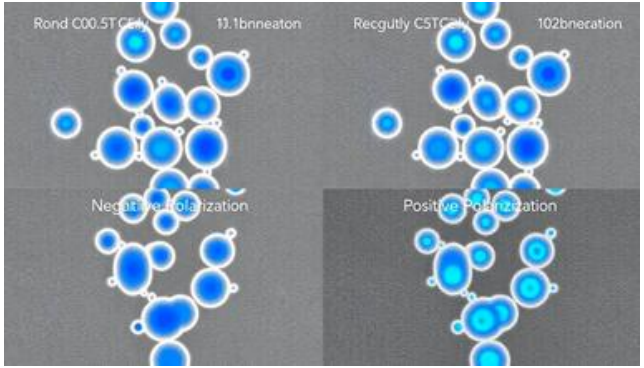
Self-Passivation

The presence of chromium allows the alloy surface to self-passivate, forming a protective, corrosion-resistant oxide layer. This is crucial in environments like the mouth, where devices are exposed to chemical reactions from food and enzymes.

Importance in Medical Implants

This corrosion resistance is also critical for medical implants, as it reduces the release of metal ions that can cause irritation, inflammation, and immune responses in the surrounding tissue, thereby increasing the service life of the implant.

Biocompatibility: Cellular Interactions



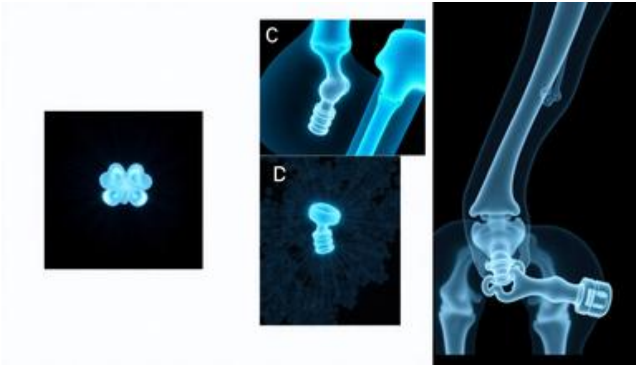
Enhanced Cell Proliferation

Electroactive Effects

Electroactive metals like CoCr alloys can influence cellular processes such as adhesion, proliferation, and membrane transport. Voltage changes on the material surface, which occur during corrosion, can have a direct effect on nearby cells.

Studies have shown that applying a positive potential to CoCr alloys can enhance the attachment and proliferation of preosteoblast cells (cells that form bone).

In Vivo Biocompatibility



Tissue Engineering Approaches

Promoting Bone Growth

In in-vivo conditions, CoCr alloys show good biocompatibility, characterized by new bone formation around the implant as early as 3 weeks post-implantation. They promote lamellar contact and the formation of bony bridges, leading to good fixation.

The surface of CoCr implants can be seeded with stem cells or osteoblasts prior to implantation. This has been shown to improve bone interlocking and accelerate the healing process.

Clinical Concerns: Metal Ion Release

Reasons for Revision Surgery

Although popular, CoCr implants can require revision surgery due to issues like wear-induced osteolysis (bone loss), aseptic loosening, and metal ion release.

Toxicity Concerns

Wear and corrosion can release Co^{2+} and Cr^{3+} ions from articulating joints, which can potentially cause local tissue reactions (metallosis) and have been linked to an increased risk of some cancers. High levels of Co^{2+} have also been associated with neurological, endocrine, and cardiac damage. Due to these concerns, the use of metal-on-metal CoCr bearings has significantly declined.

Conclusion on CoCr Alloys

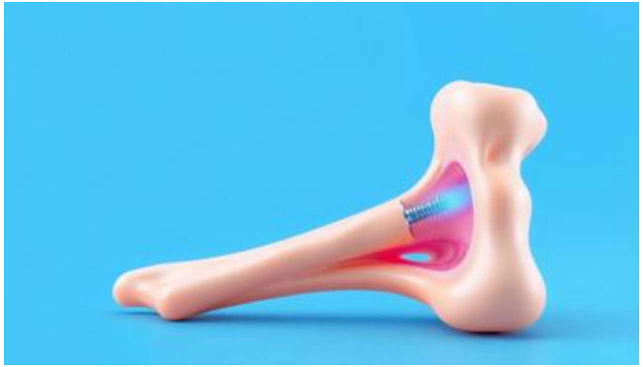
A Unique Combination of Properties

CoCr-base alloys are widely used in various arthroplasty applications due to their excellent combination of strength, wear resistance, corrosion resistance, and fatigue properties.

The Path Forward

While CoCr alloys are well-established, recent advances in manufacturing (like 3D printing) and testing methods provide new insights. Understanding the fundamental relationships between alloying, microstructure, mechanical/electrochemical properties, and the biological response is crucial for developing the next generation of improved, safer implants.

Biodegradable Metals



FRANK WITTE, Professor for Bioactive Implants,
Berlin, Germany

Definition and Rationale

What are Biodegradable Metals?

Biodegradable metals are metals designed to corrode gradually in the body and dissolve completely once they have fulfilled their function, such as supporting tissue during healing. The corrosion products should be safely metabolized or assimilated by the body with an appropriate host response.

The Rationale

Many implants are only needed temporarily to support healing (e.g., fracture fixation plates). Permanent implants may require a second surgery for removal, or they can cause long-term complications. Biodegradable implants eliminate the need for removal surgery and leave no permanent foreign body behind.

Advantages and Material Selection

Key Advantages

Biodegradable metals have a high specific strength (strength-to-density ratio). This allows for the design of thin, low-volume implants that are still stronger than biodegradable polymer alternatives. This is attractive for devices like cardiovascular stents or small bone screws.

Selecting the Base Metal

From a toxicological standpoint, the base metal should be chosen from elements that are naturally present and essential in the body. The main candidates are:

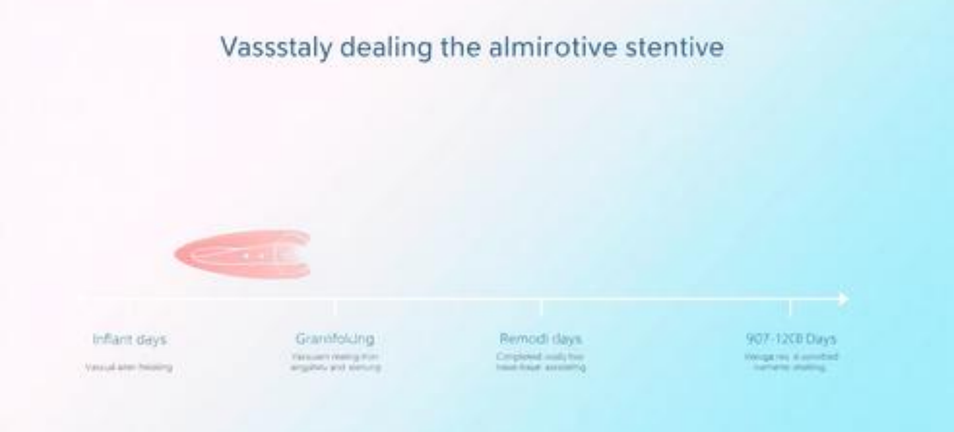
- Magnesium (Mg)
- Iron (Fe)
- Zinc (Zn)

Design Consideration: Service Lifetime

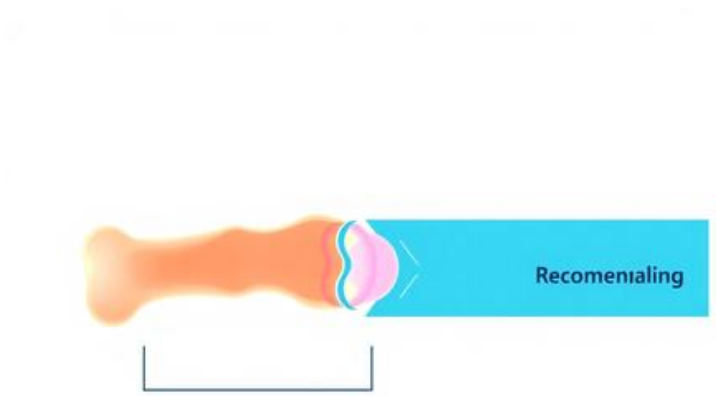
Matching Degradation to Healing

The primary goal is for the implant to provide sufficient mechanical support until the tissue has healed. Understanding the healing timeline is crucial for designing the implant's degradation rate.

Vascular Healing



Bone Healing



Corrosion Design

Controlling the Corrosion Rate

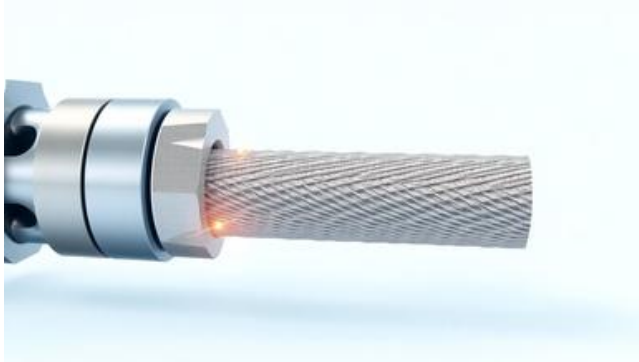
The tendency of a metal to corrode is given by its standard electrode potential, but the actual rate (kinetics) depends on factors like the surface film and the local environment (pH, fluid flow).

Key Challenges

Local Tissue Perfusion: Blood flow around the implant can be dramatically reduced after surgery, affecting the transport of ions and oxygen.

Cyclic Fatigue: Predicting the fatigue life of a degrading implant under changing loads in vivo remains a 'holy grail' of the field.

Improving Material Properties



Alloying and Microstructure

The mechanical properties and corrosion behavior are strongly influenced by alloying elements and the resulting microstructure.

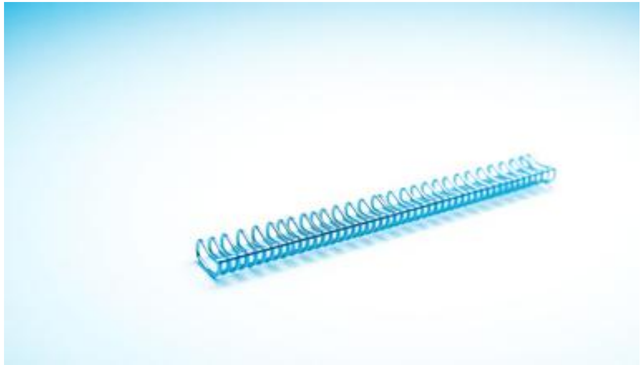
Mechanical Deformation

Techniques like extrusion, rolling, and drawing are used to refine the microstructure and improve the mechanical and corrosion properties of Mg and Zn-based metals.

Advanced Structures

Materials with amorphous (metallic glass), nano-, or quasicrystalline structures can exhibit very high strength and corrosion resistance compared to their conventional crystalline counterparts due to their unique atomic arrangements.

Iron-Based Biodegradable Metals



Properties and Applications

Iron-based biodegradable metals can provide high strength and ductility, making them favored candidates for high-strength applications like cardiovascular stents.

The Corrosion Challenge

The main drawback is that pure iron corrodes very slowly in the body. Incomplete corrosion can lead to residual implant material, defeating the purpose of a biodegradable device.

Modifying Iron's Corrosion Rate

Alloying Strategies

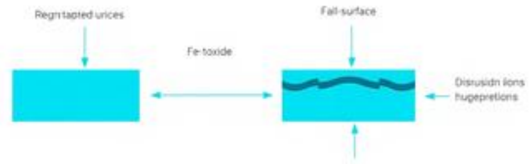
Alloying is the primary method to accelerate the corrosion of iron while maintaining mechanical strength. Alloying with manganese (Mn) has been successful, as it increases the corrosion rate and also makes the iron nonmagnetic, which is beneficial for MRI compatibility.

Other Approaches

Other techniques to increase the corrosion rate include:

- Ion implantation with elements like silver.
- Creating composites with bioceramics.
- Creating porous structures or nano-porous surfaces to increase the surface area available for corrosion.

Iron Degradation Process



The Electrochemical Process

Iron corrodes via an anodic reaction ($Fe \rightarrow Fe^{2+} + 2e^{-}$) and a cathodic reaction that consumes oxygen. The rate is limited by the local availability of oxygen.

Formation of Degradation Products

The process involves the formation of iron hydroxides, which are then oxidized to form various iron oxides. A complex layer of oxides, phosphates, and carbonates forms on the surface.

Zinc-Based Biodegradable Metals

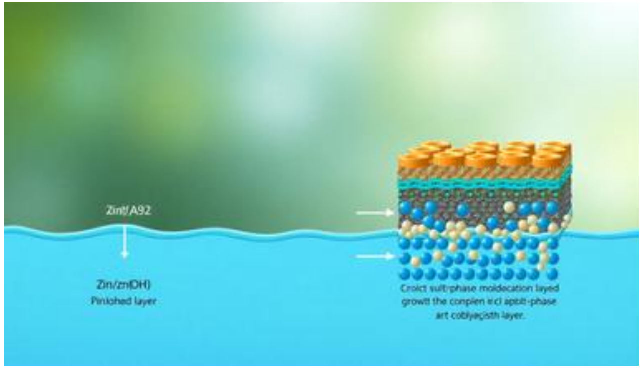
Properties and Applications

Zinc's corrosion rate is intermediate, falling between the fast rate of Magnesium and the slow rate of Iron. This makes it a promising candidate for applications like stents.

The Mechanical Challenge

The main limitation of pure zinc is its low mechanical strength and plasticity, making it unsuitable for most load-bearing devices without modification.

Zinc Degradation Process



The Electrochemical Process

Similar to iron, zinc degradation occurs via anodic dissolution of the metal and cathodic reduction of oxygen.

Formation of Degradation Products

This process produces a surface layer of zinc hydroxide ($Zn(OH)_2$) and zinc oxide (ZnO). In the body, chloride ions can convert this layer into soluble salts, promoting further corrosion. Over time, a complex layer containing zinc oxide, zinc carbonate, and calcium phosphate can form.

Magnesium-Based Biodegradable Metals

From Research to Clinic

Magnesium-based biodegradable metals are the most advanced and have successfully reached the clinic. They are used in regulatory agency-approved devices for both cardiovascular and orthopedic applications.

The two leading commercial implants, the Magmaris stent and the Magnezix screw, are both made from Mg-Y-RE (Magnesium-Yttrium-Rare Earth) alloys, demonstrating the success of this alloy family.

Magnesium Alloying and Processing

Controlling Properties

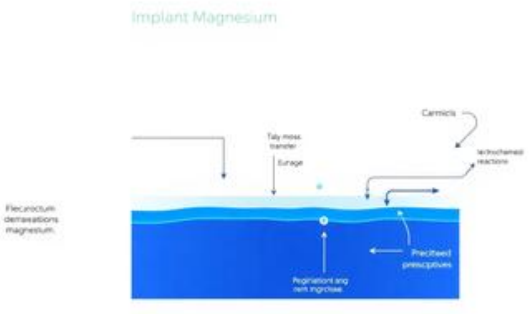
The corrosive and mechanical properties of magnesium are controlled by the choice of alloying elements and the processing route. Only a few elements are considered biocompatible for alloying.

Key Alloying Strategies

- Rare Earth Elements (REEs): Elements like Y, Gd, and Nd are used to refine grains, improve strength, and enhance corrosion resistance. They are used in the clinically successful WE-series alloys.

Magnesium Corrosion Process

The Basic Reaction



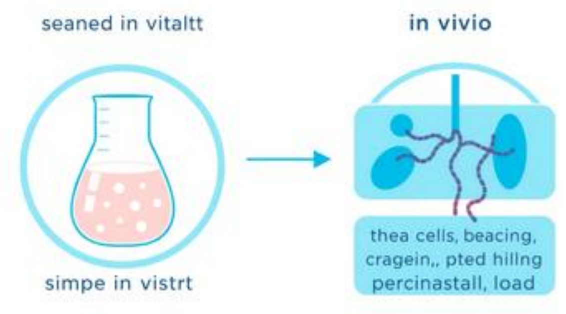
When magnesium is immersed in an aqueous medium, it corrodes rapidly, producing magnesium hydroxide ($Mg(OH)_2$) and hydrogen gas (H_2). This also causes the local environment to become more alkaline (higher pH).

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2\uparrow$$

A Complex Process

The overall degradation process is complex, involving electrochemical reactions, mass transfer of ions and products, precipitation of various compounds (like magnesium carbonate), and acid-base reactions, all influenced by the local fluid dynamics.

In Vivo vs. In Vitro Corrosion of Magnesium



The In Vitro vs. In Vivo Gap

Magnesium corrosion rates measured in simple lab tests (in vitro) are often 1-5 times higher than what is observed in the body (in vivo).

Why the Difference?

The in vivo environment is far more complex. The formation of a stable corrosion layer containing phosphates and carbonates, the adhesion of proteins and cells, and changes in local tissue perfusion all act to slow down the corrosion process compared to simple in vitro setups.

Clinical Observations of Mg Implants

Bone Promoting Effects

A key finding is that degrading magnesium actively promotes bone growth. Mg^{2+} ions stimulate sensory nerves to release CGRP, which promotes osteogenic differentiation. They also activate the Wnt signaling pathway in bone marrow stem cells, pushing them to become bone-forming cells.

Hypomineralized Zones

A common clinical observation is the appearance of temporary, hypomineralized (less dense) zones around Mg implants in bone 6-12 weeks after surgery. These zones disappear as bone healing completes, but their exact cause and effect are still under investigation.

Summary and Regulatory Outlook

A New Class of Biomaterials

Biodegradable metals are now established as a new class of biomaterials, with magnesium-based devices already in clinical use. Iron and zinc-based devices remain promising but are at an earlier stage of development.

The Future is 'Absorbable'

To harmonize with the language used for polymers, the regulatory term 'absorbable metals' is now being used.

New ISO and ASTM standards are under development to provide a framework for testing and comparing these materials, which will promote faster clinical translation.