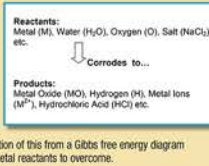


Corrosion is the degradation of a material due to a chemical reaction with its environment, which generally converts a metal to a more stable form, such as its oxide or hydroxide by electrochemical oxidation.

All orthopaedic alloys rely on the formation of passive films to prevent significant oxidation (corrosion) from taking place by providing a barrier to the chemical formation of corrosion product formation. These spontaneously formed films consist of metal oxides (ceramic films) have an atomic structure which limits the migration of ions and electrons across the metal-oxide-solution interface; and are able to remain intact on the surface of these alloys, or reform rapidly during mechanical stressing or abrasion, expected with orthopaedic devices. The depiction of this from a Gibbs free energy diagram perspective is an increased activation energy for the metal reactants to overcome.



Corrosion process with nothing to stop it, i.e. no barrier = metal continually lost from bulk

Thermodynamic Considerations (How corrosion occurs): Metallic corrosion happens through a series of chemical (redox-oxidation) reactions, similar to those of a battery. A "high energy" bulk metal, oxidizes to a lower energy state during corrosion and acts as the anode, i.e. the metal is oxidized, forming metal ions and free electrons. The free electrons "reduce" the oxygen which often times forms hydroxides, phosphates etc, and provides a complementary cathodic reaction. Thus, the dissolution (oxidation) of metal at the anode has basically two possible outcomes: the metal ions can go into solution, becoming hydrated, or the metal ions can form a compound which can form as solids collecting on the surface, e.g. metal-oxide or hydroxides. The basic underlying reaction which occurs during corrosion is the increasing of the valence state (i.e., loss of electrons) of the metal atom to form an ion. Again this metal corrosion (oxidation) event (loss of electrons and increased valence) may result in free ions in solution which can migrate away from the metal surface, or may result in other reactions $M \rightarrow M^+ + e^-$. Such as the formation of metal-oxides, metal chlorides, organo-metallic compounds or other species that typically precipitate out to form solid phases. The solid phases or oxidation products may be subdivided into 1) those which form adherent compact oxide films and 2) those which form non-adherent oxide (or other) particles which can migrate away from the metal surface.

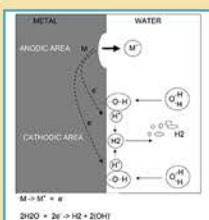


Figure 2: Without any protective layer there is a runaway corrosion reaction of metal in bulk form (high energy) degrading to lower energy and more stable products, e.g. metal oxides and hydroxides.

Corrosion is caused by materials (metals) degrading to a more stable (lower energy) form over time

In all of the possible corrosion reactions there is a thermodynamic driving force for the oxidation of metal atoms to their ionic form. In this case the driving force is given by the free energy of the above reaction.

$$\Delta G_{cell} = nF \ln \frac{[M^{2+}]_{anode} [OH^-]_{cathode}}{[M]_{anode} [H_2O]_{cathode}}$$

The chemical driving force (ΔG) determines whether or not corrosion will take place under the conditions of interest, and for all metals in an aqueous physiologic environment there will always be enough chemical driving force to cause corrosion.

$\Delta G = -nFE$ (1) where n is the valence of the ion, F is the Faraday constant (95,000 coulombs/mole electrons), and E is the voltage across the metal solution interface. This potential, ΔG , is a measure of the reactivity of the metals or the driving force for metal oxidation. It shows that the more negative the potential of a metal in solution, the more reactive it will tend to be (i.e., the greater is ΔG for reduction).

Sadly, the free energy for oxidation (corrosion) is always less than zero under *in vivo* conditions where oxidation is energetically favorable and will take place spontaneously, albeit at very slow rates generally. During corrosion, positive and negative charges (metal ions and electrons respectively) separate to form more chemically stable, lower energy compounds. The metal ions generally leave to form an oxide or another more stable ionic compound (or are released into solution), and the electrons are left behind in the metal and undergo other electrochemical reactions on the surface such as the reduction of oxygen or hydrolysis of water. A charge separation across the metal-solution interface contributes to what is known as the electrical double layer and creates an electrical potential (much like a capacitor). At equilibrium, the chemical energy balances with the electrical energy yielding the Nernst equation which defines the electrical potential across the metal-solution interface when metals are immersed in a solution.

From this equation, a scale of metal reactivity can be established by just measuring the voltage difference in known solutions and thus a ranking, known as the electrochemical series, has been established of those metals with the least to greatest voltage differences from most positive or least reactive or most noble to most negative most reactive, most base. But this is an idealized ranking, based only on thermodynamic equilibrium. That is, if we assume that there are no barriers (surface oxides) to the oxidation (loss of electrons) of the metal, these potentials would be the ones that would exist across the metal-solution.

Corrosion process is impeded with protective oxide layer barrier that forms over all orthopaedic metals

Kinetic Barriers to Corrosion
There are two central controlling (and opposing) forces that control metal implant corrosion are: 1) the driving forces (chemical, electrical, i.e. thermodynamic), which cause corrosion (oxidation/reduction) reactions, and 2) the physical barriers which limit the rate of these reactions. The thermodynamic driving forces correspond to the energy required or released during a reaction. Barriers to corrosion impede or prevent the kinetics of corrosion reactions from taking place. Thus, to understand corrosion processes it is necessary to understand both the driving forces and the kinetic barriers.

The second factor that governs the real world corrosion of metallic biomaterials is the formation of stable surface barriers or kinetic limitations to corrosion. This barrier to corrosion is more important by the corrosion of orthopaedic metals. These physical kinetic barriers prevent corrosion by limiting the rate at which oxidation or reduction processes can take place. Metal-oxide passive films on metal surfaces are the typical example of a kinetic limitation to corrosion. In general, kinetic barriers to corrosion prevent either the migration of metallic ions from the metal to the solution, the migration of anions from solution to metal, or the migration of electrons across the metal-solution interface. Passive oxide films are the most common form of kinetic barrier in orthopaedic implant corrosion, but other kinetic barriers exist including polymeric coatings.

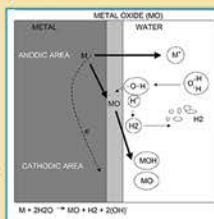
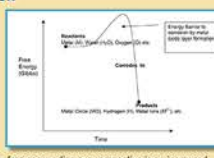


Figure 4: The formation of a protective layer of "corrosion products" such as metal oxides, quickly limits the chemical reaction and release of metal ions.

Corrosion is limited by the formation of chemically stable (lower energy) corrosion product layer (e.g. metal oxide) on the surface forming a barrier.

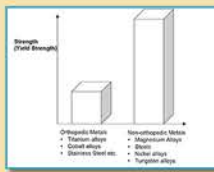
All orthopaedic alloys rely on the formation of passive films to prevent significant oxidation (corrosion) from taking place by providing a barrier to the chemical formation of corrosion product formation. These spontaneously formed films consist of metal oxides (ceramic films) have an atomic structure which limits the migration of ions and/or electrons across the metal-oxide-solution interface; and are able to remain intact on the surface of these alloys, or reform rapidly during mechanical stressing or abrasion, expected with orthopaedic devices. The depiction of this from a Gibbs free energy diagram perspective is an increased activation energy for the metal reactants to overcome.



Orthopaedic alloys have NOT been selected over the past century because they have the best mechanical properties (e.g. not the strongest)

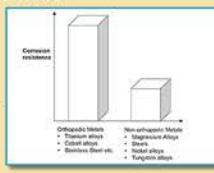
Implant alloys were originally developed for maritime and aviation uses where mechanical properties such as high strength and corrosion resistance are paramount. There are 3 principal metal alloys used in orthopaedics and particularly in total joint replacement: 1) titanium based alloys, 2) cobalt based alloys and 3) stainless steel alloys. Alloy specific differences in strength, ductility, and hardness generally determine which of these three alloys is used for a particular application or implant component.

Although, high strength, high wear resistance, high toughness, and high ductility are all desirable mechanical properties of orthopaedic implants, orthopaedic alloys do not come close to the metals with the highest values of these (e.g. that have the highest strength etc).



Orthopaedic alloys have been selected over the past century for their superior Corrosion Resistance

However it is the high corrosion resistance of all three alloys, more than anything, which has led to their widespread use as load bearing implant materials. Both stainless steel, such as 316L, and Co-Cr alloys were the early materials of choice, because of their availability, relatively good corrosion resistance and reasonable fatigue life. However, in certain applications, owing to size restrictions and design limitations fatigue failures did and do still occur.



Corrosion process is impeded with protective oxide layer barrier that forms on orthopaedic metals

Orthopaedic Alloys
Orthopaedic alloys rely on the protective barrier of the passive films to reduce oxidation (corrosion) from taking place. Since the electrical potential across the body-fluid-metal solution interface for these reactive metals can be 1-2 volts and the distances are so small, the results electric field gradient across the oxide is very high, on the order of 10⁶ to 10⁷ V/cm. Different metal oxides are more stable than others. Titanium oxide is particularly chemically stable and is the reason why titanium and titanium alloy process such superior corrosion resistance. This is also related to the electric field differences across the metal oxide (also known as charge difference, also known as chemically available electrons in the bulk metal). This means that measurable voltage differences and electric currents can be used to predict and measure chemical stability and corrosion rates.

The oxide film growth depends on the electric field across the oxide(1). If the voltage potential across a metal-oxide-solution interface is decreased then the oxide film thickness decreases by a reductive dissolution processes resulting from electrochemical interaction that act to compensate and keep the electric field strength constant. Increasing the voltage across an interface will correspondingly increase the thickness of the film.

In fact, oxide thickness is often determined by the "anodization rate" which is defined as the oxide thickness per volt(2). If the interfacial potential of an implant interface is made sufficiently negative (or similarly if the pH of the solution is made low enough), then metal oxide films will no longer be thermodynamically stable and will undergo reductive dissolution, resulting in no barrier to active corrosion. These barrier oxide films are not flat smooth continuous sheets of adherent oxide covering the metal; they are consist of dense (3) or dome (4) shapes.

Several treatments are used to increase the barrier effect of protective oxide films, which include hot, concentrated nitric acid baths, boiling in distilled water(5), and anodization. However, detailed investigators into how to optimize oxide film structure to maintain and protect the surface of orthopaedic alloys in vivo remains incomplete and is an area of active research/technological development.

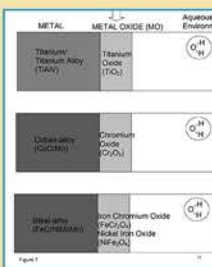
Corrosion resistant orthopaedic alloys

There are 3 principal metal alloys used in orthopaedic implant alloys were originally developed for maritime and aviation uses where mechanical properties such as corrosion resistance and high strength are paramount.

Stainless Steel Alloys
The form of stainless steel most commonly used in orthopaedic practice is designated 316L (American Society for Testing and Materials F138, ASTM F138). Molybdenum is added to enhance the corrosion resistance of the grain boundaries, while chromium dispersed evenly within the microstructure allows the formation of chromium oxide (Cr₂O₃) on the surface of the metal. Stainless steels are surface treated (e.g. in nitric acid) to promote the growth and thickening of this passive oxide layer (6-9)

Cobalt-Chromium Alloys
Of the many Co-Cr alloys available, there are two most commonly used as implant alloys (Table 2): 1) cobalt-chromium-molybdenum (CoCrMo), which is designated ASTM F-75 and F-76; and 2) cobalt-nickel-chromium-molybdenum (CoNiCrMo) designated as ASTM F-562.

Titanium Alloys
The stability of the oxide layer formed on CP-Ti (and consequently its high corrosion resistance)



disolution, resulting in no barrier to active corrosion. These barrier oxide films are not flat smooth continuous sheets of adherent oxide covering the metal; they are consist of dense (3) or dome (4) shapes.

Several treatments are used to increase the barrier effect of protective oxide films, which include hot, concentrated nitric acid baths, boiling in distilled water(5), and anodization. However, detailed investigators into how to optimize oxide film structure to maintain and protect the surface of orthopaedic alloys in vivo remains incomplete and is an area of active research/technological development.

Comparison of common Orthopaedic Alloy Corrosion resistance and wear resistance

Why Co-alloy is used for articulating surfaces and not Ti-alloy (protective surface oxide layer gets the credit)

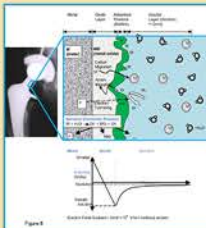
There are 3 principal metal alloys used in orthopaedics and particularly in total joint replacement: 1) titanium based alloys, 2) cobalt based alloys and 3) stainless steel alloys. Differences in strength, ductility, and hardness generally determine which of these three alloys is used for a particular application or implant component. Stainless Steel Alloys: The most common orthopaedic stainless steel, 316L (American Society for Testing and Materials F138, ASTM F138) includes molybdenum to enhance the corrosion resistance of the grain boundaries, while chromium dispersed evenly within the microstructure allows the formation of chromium oxide (Cr₂O₃) on the surface of the metal. Stainless steels are surface treated (e.g. in nitric acid) to promote the growth and thickening of this passive oxide layer (6-9)

Cobalt-Chromium Alloys: Cobalt-chromium implant alloys fall into one of two categories, those with nickel and other alloying elements, and those without: 1) cobalt-chromium-molybdenum (CoCrMo), which is designated ASTM F-75 and F-76; and 2) cobalt-nickel-chromium-molybdenum (CoNiCrMo) designated as ASTM F-562. Titanium Alloys: While pure titanium is generally the most corrosion resistant metal, titanium alloy Ti-6Al-4V (ASTM F-136) is used for part replacement components because of its superior mechanical properties in comparison to pure titanium cpTi. The Ti-6Al-4V alloy microstructure is generally composed of a fine-grained CP phase with a sparse distribution of the BCC phase to maintain strength and corrosion resistance.



In vivo Corrosion is impeded with protective oxide layer AND a protein biofilm barrier that forms on orthopaedic metals, but oxidation still occurs

The complex interface between a metal and the proteaceous fluid in vivo environment can be summed up with the following description (see Fig. 9). The metal surface spontaneously reacts with its surroundings to form a passive metal-oxide film which may be nonuniform in cross section (dome or needle shaped) and, at least initially, amorphous. The oxide film is nucleated and grown on the metal surface and contains within it defects which allow for electronic and ionic transport of charged species across the film. There also exists a large electric field which is the driving force for the movement of these ions across the film. If the electric field strength is changed (by changing the applied potential for instance) then the oxide film will grow or shrink to attempt to maintain a constant field strength (at least at low temperatures). Also, depending on conditions, the oxide film will change crystal structure, size and thickness.



In the solution, in the immediate vicinity of the interface, there exists what is known as the electrical double layer. This layer contains an excess of charged species to balance the net charge present on the surface of the oxide. This double layer also contains water molecules which have their dipole moments oriented to minimize the electric field. These effects reduce the influence of the electric field from the metal so that only the first 10 nm or so of solution will be affected by the electric field.

Oxide films have the characteristics of semiconductors with an atomic defect structure which determines the ability for ionic and electronic transport across films (14). Metal cations (M+) and oxygen anions (O-) require the presence of cationic or anionic vacancies (respectively) in the oxide for transport of these species across the film. If there is a deficit of metal ions in the oxide film (i.e. there are cationic vacancies), for example, then metal ion transport is possible and these oxides are known as p-type semiconductors. Chromium oxide (Cr₂O₃) is such a metal-deficit oxide. On the other hand, if there is an excess of metal ions in the oxide (or a deficit of oxygen) then cation transport is limited but anion transport can occur. These oxides will also have excess electrons and are known as n-type semiconductors. TiO₂ is one such n-type semiconductor(14). The greater the number of defects (vacancies or other valence species) the less the oxide film can prevent migration of ionic species and thus the lower is the kinetic barrier to corrosion. TiO₂ is very close to being balanced stoichiometrically and thus does not have many ionic defects and is a very effective barrier to why Ti alloys are so corrosion resistant. Other defects (e.g. other metal ions) may be present in these passive oxide films which may alter their ability to kinetically limit corrosion. These additions may enhance or degrade the ability of the oxide to prevent corrosion.

Fairly self evidently, the ratio of the oxide specific volume to metal alloy specific volume (Pilling Bedworth ratio) will determine if the oxide will adhere to the metal or not. If there is a large mismatch between the metal and oxide lattice parameters then significant stresses will be generated. The magnitude of the internal stress will vary with the thickness of the oxide. There can be too much of a good thing where too great an oxide thickness can result in spontaneous fracture or spalling of the oxide and decrease the kinetic barrier effect of the oxide to corrosion.

When an oxide film is ruptured from the metal substrate fresh, unoxidized metal is exposed to solution. In orthopaedic alloys these films will reform or reprecipitate and the magnitude of the reprecipitation currents may momentarily be large. This is due to the fact that large driving forces are present for the oxidation process and when the kinetic barrier is removed these large driving forces can operate to cause oxidation. Thus, the mechanical/physical stability of the oxide films as well as the nature of their reprecipitation process are central to the performance of oxide films in orthopaedic applications.