

Corrosion

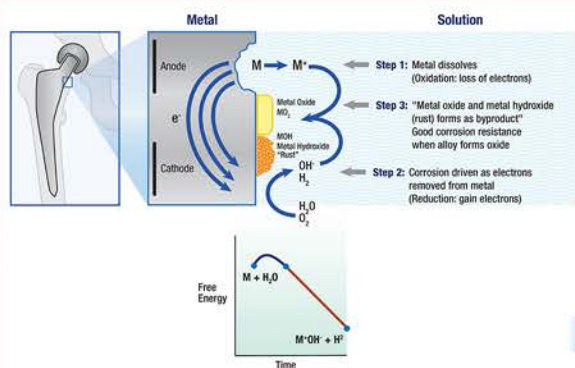


Figure 1: Corrosion on a Surface In theory, maximum corrosion occurs if the complete metal surface was exposed on a surface. Corrosion occurs in three basic steps: 1. Metal dissolves on the surface into the aqueous environment and cations are removed (oxidation). 2. Remaining electrons are attracted to a differential charge at another point on the surface where electrons are removed from the metal driving the reaction (reduction). 3. Metal oxide or metal hydroxide form as byproducts of this reaction. Metal oxides and insoluble metal oxides (rust) form an insulating layer on the metal surface almost instantly that inhibit the kinetics of corrosion and insulate the metal from further corrosion. **Thermodynamics:** Corrosion is a very exothermic process with minimal activation energy. A theoretical bare metal surface where a passive layer is prevented from forming can be explosive. An excellent example of this reaction is the explosive reaction that occurs after placing pure sodium metal in water.

Uniform Corrosion

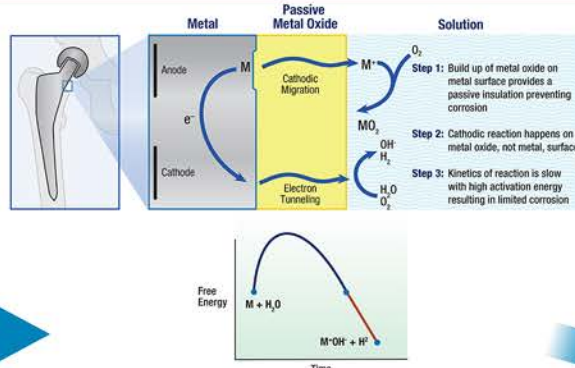


Figure 2: Corrosion on a Surface with a passive film—Uniform Corrosion In reality, a passive film forms almost instantly on the surface of the metal. If the film remains homogenous and undisturbed, corrosion is inhibited as the uniform passive film shields the metal surface from the aqueous reaction. Metal oxide forms a stronger barrier to migration of the positive charged metal and electrons as compared to the insoluble hydroxide (rust). The passive film is in dynamic flux—its thickness is a balance between reactions that erode and build the film. **Thermodynamics:** The free energy released remains identical to maximal corrosion on a surface. The thermodynamics are different because the activation energy is greatly increased with a passive film by inhibiting the reaction kinetics slowing the reaction and the energy released.

Pitting Corrosion

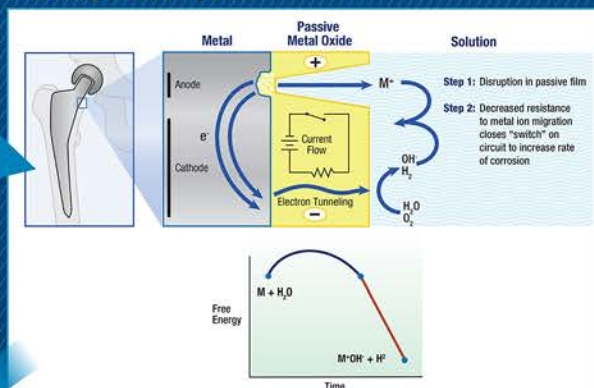


Figure 3: Pitting Corrosion Slight inconsistencies that develop in the passive film lead to breakdown in small areas, development of a focused anode, and localized galvanic corrosion. For example, if one area of the passive film has a small amount of more permeable hydroxide (rust) than impermeable oxide, then a defect can develop over this area of the passive surface (pitting) creating a more permeable and less protective film. A larger flow of metal ions can escape in this small area creating a focused anode. A differential cathode will develop over a large surface at a distant point in response to the point anode that develops. This creates a large difference in potential charge at distant points on the metal surface. The current flow between these two charges is similar to the voltage difference across a battery or galvanic corrosion. **Thermodynamics:** Compared to uniform corrosion, thermodynamics are identical except the small disruption on the passive film decreases the activation energy making the more favorable environment for corrosion reaction more favorable speeding the kinetics.

MACC Corrosion

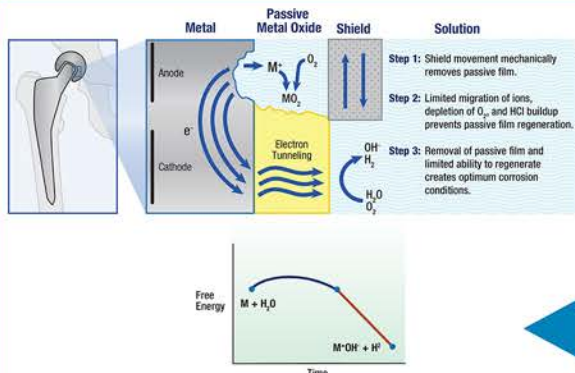


Figure 5: Fretting Corrosion or Mechanically Assisted Crevice Corrosion (MACC) Physical shearing forces removes the protective passive film that serves as a barrier for the metal surface from corrosion. The optimal environment in crevice corrosion can be further optimized by removing even more biofilm creating a larger surface for crevice corrosion to occur. For example, at the trunnion interface, possible shear movement between the taper surfaces can remove additional passive film. Increased head sizes and femoral stem offset increase the force across the trunnion and the potential for shear movement between the surfaces. A lack of passive film to protect the metal surface and the optimal environment for corrosion from the limited diffusion of crevice corrosion setup optimal conditions for aggressive corrosion. Fretting corrosion or MACC are essentially identical terms. **Thermodynamics:** Except for the theoretical conditions when there is no passive film, fretting (MACC) has the lowest activation energy and increased kinetics from a larger surface area of metal. Again, the energy released (overall free energy) remains the same.

Crevice Corrosion

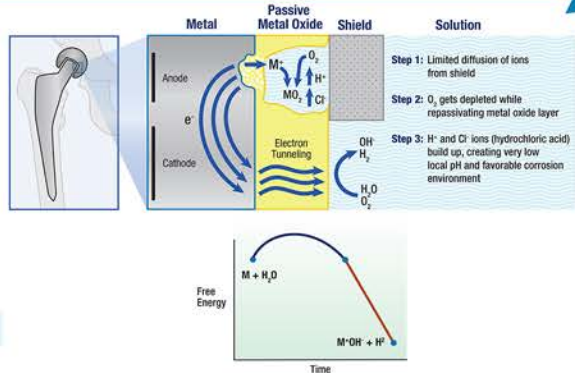


Figure 4: Crevice Corrosion Pitting corrosion that occurs with limited diffusion of ions creates optimal conditions for corrosion. The total hip arthroplasty trunnion is a closed environment that prevents ion diffusion. A water-tight seal is established at a finite point on the neck-head taper connection, not across the entire taper surface. This water-tight seal prevents the diffusion of ions. Oxygen becomes depleted, limiting the ability of a passive layer to regenerate itself (repassivation). Hydrogen and chloride ions (hydrochloric acid) concentration increases. This creates a low pH environment that accelerates corrosion by preventing repassivation from the increased rate of corrosion and the low concentration of oxygen to create metal oxide. The metal surface has a small inconsistent passive film that is not insulated from an aqueous solution ideal for corrosion. Essentially, crevice corrosion is pitting corrosion under an ideal corrosion environment. **Thermodynamics:** Compared to pitting corrosion, the activation energy is lower given the more favorable conditions for corrosion increasing the reaction kinetics, however the energy released (overall free energy) remains the same.