Metal Corrosion in the Human Body: The Ultimate Bio-Corrosion Scenario

by Douglas C. Hansen

It is not something one usually thinks about until it becomes a personal health issue for most of us. That is, the need for the implantation of a medical device (Fig. 1) to improve our existing medical condition. The majority of these devices are made of a metal alloy (Table I), and for most of us, any concerns about corrosion implications from these implants are secondary to the relief we feel from the anticipated beneficial effect these devices are designed to have. As the global population increases in age, there is a parallel increase in the number of implantation procedures. One study reports that world-wide sales of orthopedic implants alone in 2003 was $8.7 billion and projected to increase at an annual growth rate of 12.5% and reach $17.9 billion by 2009.[1] Clearly, as new devices and technologies are developed, there will be a continuing need for the understanding and characterization of how metal surfaces of implants interact with their surrounding physiological environment.

Implant alloys are typically derived from three materials systems: stainless steels, cobalt-chromium based alloys and titanium alloys.[2] The question "Does corrosion of a metallic implant cause a clinically relevant problem?" is one that probably only an electrochemist or materials engineer will ask when confronted with the prospect of having a metal device implanted into his or her body. While numerous issues may arise with the implant following surgery, one of the most fundamentally important is the interaction between the surrounding physiological environment and the surface of the implant itself. This interaction can lead to either the failure of the implant to function as it was intended, or have an adverse effect on the patient resulting in the rejection of the implant by the surrounding tissue, or both.[3] In either case, explantation of the device is usually required to correct the situation.

Fig. 1. *Knee and hip implant components. (Photo courtesy of Medcast Inc.)*

The human body is not an environment that one would consider hospitable for an implanted metal alloy: a highly oxygenated saline electrolyte at a pH of around 7.4 and a temperature of 98.6°F (37°C). While it is well known that chloride solutions are among the most aggressive and corrosive to metals, the ionic composition and protein concentration in body fluids complicate the nascent understanding of biomedical corrosion even further. Variations in alloy compositions can lead to subtle differences in mechanical, physical, or electrochemical properties. However, these differences are minor compared with the potential variability caused by differences in fabrication methodology, heat treatment, cold working, and surface finishing, where surface treatments are particularly important for corrosion and wear properties. Since metals are inherently susceptible to corrosion, implants are routinely pre-passivated prior to final packaging using an acid bath or some other electrochemical anodizing process (titanium alloys),[4] or an electropolishing method (stainless steel and cobalt alloys).[5] Alloys specific for the intended uses of the implant are determined based upon whether they will be load bearing (wear and fretting resistant) or not. Finally, galvanic couples are routinely encountered in static (*i.e.*, no relative motion) situations where the consideration of the potential difference between the metals involved is secondary to the required yield strength and strength: weight ratio of the implant device, such as stainless steel screws anchoring a titanium alloy bone fracture fixation plate.

The aim of this article, therefore, is to give the reader a broad overview of the different types of metals and alloys used, the corrosion of metals in the human body, the different environments encountered and how well these materials resist degradation in the body.

Table I. Major biomedical metals and alloys and their applications.

Material	Major Application
316L Stainless Steel	cranial plates, orthopedic fracture plates, dental implants, spinal rods, joint replacement prostheses, stents, catheters
Cobalt-Chromium alloys	orbit reconstruction, dental implants, orthopedic fracture plates, heart valves, spinal rods, joint replacement prostheses
Titanium, Nitinol, Titanium alloys (Ti-6Al-4V, Ti-5AL-2.5 Fe, Ti-6Al-7Nb)	cranial plates, orbit reconstruction, maxillofacial reconstruction, dental implants, dental wires, orthopedic fracture plates, joint replacement prostheses, stents, ablation catheters

Implant Materials

The fundamental requirement for choosing a metallic implant material is that it be biocompatible, that is, not exhibiting any toxicity to the surrounding biological system. For more than a hundred years, various metals have been investigated for implantation into

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Table II. Mechanical properties of implant alloys and human bone.

Material	Tensile Strength $(MN/m)^2$	Yield Strength $(MN/m)^2$	Vickers Hardness (H_v)	Young's Modulus $(GN/m)^2$	Fatigue Limit $(GN/m)^2$
316L SS	650	280	190	211	0.28
Wrought Co-Cr Alloy	1540	1050	450	541	0.49
Cast Co-Cr Alloy	690	490	300	241	0.30
Ti-6Al-4V	1000	970	---	121	---
Human Bone	137.3	---	26.3	30	---

the human body, such as aluminum, copper, zinc, iron and carbon steels, silver, nickel, and magnesium.[3] All of these were discarded as being too reactive in the body for long term implantation. When stainless steel was introduced into general engineering as a new corrosion-resistant material in the early 1900s, it was soon utilized in surgical applications. However, the 18-8 stainless steel that was initially used was found to exhibit intergranular corrosion due to high (0.08%) carbon content and gross pitting due to low molybdenum content. Of all the stainless steels, only the austenitic molybdenum-bearing 316 was of any use, even though it was described as inherently corrodible.[6] Movement toward 316L alloy, having a much lower carbon content (0.03%), greatly reduced the risk of intergranular attack.

During the same period of time, cobalt-chromium and cobalt-chromium-molybdenum alloys were first introduced and utilized in dental and orthopedic applications due to their corrosion resistance. The most corrosion resistant of the implant materials presently employed is titanium and its alloys. Titanium alloys were first used in the 1960s and their use has been growing steadily since the mid-1970s and continues to increase. Several titanium alloys (α & β phases), such as Ti-6Al-4V, Ti-5Al-2.5Fe, and Ti-6Al-7Nb provide ideal strength and corrosion resistance characteristics. The main advantage of titanium and its alloys is the non-reactivity of the passive film that is formed; the main disadvantages are its susceptibility to fretting as well as oxygen diffusion during fabrication, causing embrittlement.[7] The mechanical properties of the alloys discussed here are presented in Table II.[8]

Biological Environment

When a metal device is implanted into the human body, it is continually exposed to extracellular tissue fluid (Fig. 2, for example). The exposed metal surface of the implant undergoes an electrochemical dissolution of material at a finite rate, due to interactions with the surrounding environment. In the case

Fig. 2. *Dental implants showing anchors and dental prostheses. (Image courtesy of BioHorizons, Inc.)*

of the human body, this environment can contain water, complex organic compounds, dissolved oxygen, sodium, chloride, bicarbonate, potassium, calcium, magnesium, phosphate, amino acids, proteins, plasma, lymph, saliva etc. Upon implantation, the tissue environment is disturbed, disrupting blood supply to the surrounding tissue and the ionic equilibrium. The initiation of corrosion can be the result of various conditions existing along the implant surface, whether it is the formation of localized electrochemical cells resulting in pitting attack, or crevice corrosion at the interface between a plate and a locking screw, or any one of the other forms of corrosion that can occur, which will be discussed later.

Corrosion Testing

Numerous methods have been used to evaluate the corrosion resistance of implant materials in the laboratory, with the majority involving either qualitative measurements of implantation of devices into experimental animals (*in vivo*) or quantitative electrochemical measurements in simulated body fluid (*in vitro*)[9] or a combination of both where qualitative and quantitative corrosion measurements of implants are made *in vivo*. However, to maintain reproducibility and minimize variables, very few *in vitro* studies involve simulated body fluids that contain amino acids, proteins and ions at the proper temperature and pH, simply due to the complexity of the system and the inherent difficulty of reproducing that system in the laboratory. While this approach may appear to be flawed, the overall ranking of biomaterials in terms of corrosion resistance tested *in vitro* does not change when compared to the measurement of the same biomaterials *in vivo* (although in quantitative terms, corrosion rates for each specific alloy may rise or fall).[3]

Implant Corrosion Mechanisms

The types of corrosion that are pertinent to the currently used alloys are: pitting, crevice, galvanic, intergranular, stress-corrosion cracking, corrosion fatigue, and fretting corrosion. These corrosion types will be discussed in relation to the specific alloys and their occurrence.

Titanium alloys.—The shape memory alloy, Nitinol, is composed of near equi-atomic amounts of Nickel and Titanium. Since the early 1970s it has found widespread clinical use as

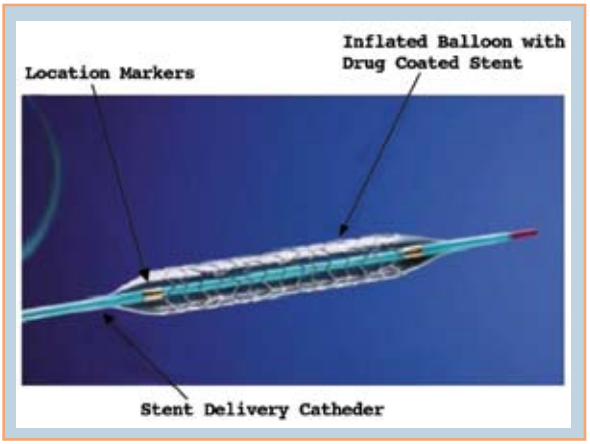

Fig. 3. *Fully expanded endovascular Nitinol stent. (Image courtesy of FDA)*

an orthodontic material[10] and more recently as vascular stents due to its exceptional mechanical characteristics and its high biocompatibility[11] (Fig. 3). Several studies have highlighted the variation in the corrosion performance of Nitinol depending upon the surface condition of the test specimens used and the surface condition given.[12,13] Since heat treatment is involved during the manufacturing process, the passivating oxide present on Nitinol is polycrystalline in nature, and has been found to exhibit severe pitting and crevice corrosion, whereas surface treatment to form amorphous oxide results in excellent corrosion resistance.[14] Other surface treatments, such as electrochemical polishing, has also been found to be a good surface treatment prior to implantation, resulting in significantly increased corrosion resistance and extremely low levels of Ni dissolution, well below the estimated average dietary intake levels of 200–300 µg per day.[11,15]

Titanium-aluminum-vanadium alloys have exhibited very good corrosion resistance, but are subject to fretting and wear, with particles of the alloy found in surrounding tissue, rather than precipitated corrosion products due to uniform or localized corrosion.[16,17] A current problem related to orthopedic alloys is corrosion at the taper connections of modular joint replacement components. With the large and increasing number of total joint designs that include metal-on-metal conical taper connections, the effect of crevices, stress and motion take on increasing importance. Retrieval studies have shown severe corrosion attack can occur in the crevices formed by these tapers *in vivo*.[18,19] Gilbert, *et al.* reported that approximately 16–35% of 148 retrieved total hip implants showed signs of moderate to severe corrosive attack in the head-neck taper connection.[18] Dental implants and root pins made of this alloy are used by dental surgeons due to its low corrosion rate, however particular care must be taken to avoid galvanic couples, particularly between pure titanium and the Ti-6Al-4V alloy.[20]

Cobalt-chromium-colybdenum alloys.—These alloys are being used in orthopedic implants due to their hardness, strength and resistance to corrosion and wear (Fig. 4). There are three different types of Co-Cr-Mo material currently in use: cast (low carbon), wrought, and wrought (high carbon) alloys. Each variety has a different microstructure and different properties optimized for a specific design or function. The cast alloy is used for complicated shapes that cannot be machined (such as the stem of a total hip replacement) whereas the femoral head can be machined from the harder wrought (high carbon) alloy. High and low carbon Co-Cr-Mo alloys have been studied to determine

Fig. 4. *Orthopedic hip replacement implant showing femoral stem and head. (Image courtesy of Wines Medical)*

the effect that carbide inclusions have on the corrosion behavior of the alloy. Results indicate that while the inclusions were significant features on the alloy surface, they did not affect the corrosion or dissolution mechanisms, rather the presence of proteins caused ligand-induced dissolution thereby increasing the Cr concentration in the surrounding extracellular tissue fluid.[21] Laboratory studies where Co-Cr-Mo alloy has been immersed in a simulated body fluid (Hank's salt solution) showed that cobalt dissolved from the surface and the remaining surface oxide consisted of chromium oxide (Cr^{+3}) containing molybdenum oxide (Mo^{+4}, Mo^{+5}, and Mo^{+6}).[22] XPS analysis of the samples in that study revealed that chromium and molybdenum were more widely distributed in the inner layer than in the outer layer of the oxide film. In body fluids, cobalt is completely dissolved, and the surface oxide changes into chromium oxide containing a small amount of molybdenum oxide.

There is little information in the literature about cobalt levels and metal-on-metal bearing for total hip replacements. Coleman, *et al.* reported an increase in the level of cobalt in the blood in the first year after implantation of an all metal cast Co-Cr-Mo hip prostheses.[23] Wear at the bearing surfaces seems to be responsible for generating release of the cobalt, but corrosion of the implant materials or of the wear particles may also contribute to the release of cobalt into the surrounding tissue fluid. However, there has been a correlation between elevated cobalt levels in the blood due to corrosion in patients having mixed-alloy modular metal-on-polyethylene hip implants.[16]

316L stainless steel.—Surgical grade 316L implants (Fig. 5) corrode in the human body environment and release Fe, Cr and Ni ions and these ions are found to be powerful allergens and carcinogens.[24] Studies on retrieved implants show that more than 90% of the failure of implants of 316L stainless steel are due to pitting and crevice corrosion attack.[25] This fact alone deems that a better material be used for even temporary implant devices.

The corrosion of 316L in the human body can take many forms and the following are the more important corrosion mechanisms that have been identified.[3]

Intergranular corrosion.—More than 30 years ago, heterogeneous intergranular distribution of carbon was observed in surgical grade 316, resulting in intergranular corrosion due to the formation of chromium carbides. Since then, surgical specifications have demanded lower and lower carbon content. It is only when the carbon content of austentitic stainless steel is below 0.03% are the carbides reproducibly absent, thus greatly reducing the risk of corrosion.[26]

Pitting.—Pitting is the most common form of corrosion arising from the breakdown of the passivating oxide film, which can be enhanced by the presence of proteins in the tissue fluid and serum.[27,28]

Fretting.—Corrosion products due to fretting on 316L immersed in extracellular tissue fluid are oxides containing chromic chloride and

Fig. 5. *316L Stainless steel bone fracture fixation plate and screw. (Image courtesy of Synthes, Inc.)*

potassium dichromate[29] as well as variable amounts of calcium, chloride, and phosphorous, with nickel and manganese being absent, indicating preferential release of these metal ions into the surrounding solution.[30] These results indicate that for 316L implant surfaces, nickel and manganese are depleted in the oxide film and that the surface oxide composition changes to mostly chromium and iron oxide with a small percentage of molybdenum oxide in the human body.

Crevice corrosion.—316L is highly susceptible to crevice corrosion attack as compared to the other implant alloys.[31] The occurrence of corrosion on the bone plate and screws made of 316L at the interface between the screw heads and the countersink holes is a common feature.[7,16]

Galvanic corrosion.—While reports in the literature concerning galvanic couples and their effect on the corrosion behavior of the metal components involved are mixed,[32-35] one has to consider whether the implant systems involved are exposed to static or cyclical load conditions (*i.e.*, relative motion). In cases where there are galvanic couples arising from the combination of dissimilar metals, such as 316L stainless steel and the Co-Cr-M alloy or Ti-6Al-4V alloy, the stainless steel will be attacked and these combinations should be avoided. Galvanic effects can also occur by using metal alloys that have undergone slightly different metal processing (cast vs. wrought Co-Cr-Mo). The placement of polymeric inserts between metal-metal interfaces will eliminate galvanic corrosion and would considerably reduce fretting corrosion, however alloy selection is critical since a crevice situation would certainly be the result and a more aggressive corrosion issue could develop.

Stress corrosion cracking.—There continues to be a debate as to whether stress corrosion cracking takes place in 316L in the body. While fractures of this alloy have been found to exhibit the classical stress corrosion cracking appearance,[36] in other cases it has been determined that intergranular corrosion had weakened the device, thus facilitating the fracture.[37]

Conclusions

Corrosion is one of the major issues resulting in the failure of biomedical implant devices. The nature of the passive oxide films formed, and the mechanical properties of the materials form some of the essential criteria for selection of alternative or development of new materials. In clinical terms, the biggest improvements could be made by better material selection, design, and quality control to reduce, or possibly eliminate corrosion in implant devices. Surface modification of 316L stainless steel is one alternative that is already in practice. That is, the coating of the alloy with hydroxyapatite plays a dual role: minimizing the release of metal ions by making it more corrosion resistant, as well as making the surface more bioactive and stimulating bone growth. Other surface modification techniques, such as hard coatings, laser nitriding, bioceramics, ion-implantation, and biomimetic coatings and materials all have great potential to improve the performance characteristics of biomedical implants and improving the lives of their recipients. It is becoming clear that there are real risks associated with the use of metals as long term chronic implant devices, and with the continuing research and development of new biomaterials, these risks can be managed, and one day eliminated.

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