

THE UNIVERSITY OF MANITOBA
EFFECT OF COMPOSITION ON THE ELECTROCHEMICAL
POLARIZATION BEHAVIORS AND ON THE OXIDE FILMS
OF ORTHOPEDIC IMPLANT ALLOYS

by
Rabin Bandy

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A dissertation submitted to the Faculty of Graduate Studies of
the University of Manitoba in partial fulfillment of the requirements
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ABSTRACT

Localized corrosion, namely pitting and crevice corrosion, is the major cause of failure of metallic orthopedic implants. Crevice corrosion occurs in shielded areas and is very common in multi-component implants, e.g., corrosion between screws and plates in stainless steel fixation devices. Pitting corrosion generally occurs in active-passive metals in chloride environment due to the breakdown of passivity. Pits initiate when the potential of the metal is more noble than the critical pitting potential, E_c , of the metal in the environment under investigation. Actively growing pits repassivate at a potential called the protection potential, E_p . Both pitting and crevice corrosion are generally governed by a similar mechanism except that due to restricted flow of electrolyte and oxygen the crevice environment has a lower pH and higher chloride ion concentration.

Electrochemical tests in Ringer's physiological solution on Type 316L stainless steel and 65% Co, 30% Cr, 5% Mo alloy show that the cobalt based alloy has nobler values of E_c and E_p . Addition of more chromium, nickel and molybdenum shifts the E_c values of stainless steel in the noble direction. However, lower pH and higher chloride ion concentration drive both E_c and E_p in the active direction. The E_c and E_p values of the cobalt based alloy are rather insensitive to changes in pH and chloride ion concentration. Therefore, the cobalt based alloy appears to be more desirable in multi-component orthopedic devices where the chances of crevice corrosion are high.

Atomic absorption analyses of Ringer's solution containing corrosion products of Type 316L stainless steel and 65% Co, 30% Cr, 5% Mo

alloy show that no selective dissolution occurs during the localized corrosion of these alloys.

Results of Auger electron spectroscopic analyses show that the oxide film of Type 316L stainless steel contain metals in higher valence states compared to those of more corrosion resistant stainless steel and the cobalt based alloys. This possibly accounts for the more active critical pitting potential of Type 316L stainless steel. It is also observed that for two stainless steel alloys containing the same amount of chromium in the bulk, the oxide film of the higher molybdenum bearing alloy has more chromium than that of the less molybdenum bearing alloy. This implies that molybdenum improves the passivity of stainless steel alloys by stabilizing more chromium on the oxide film.

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CHAPTER I

INTRODUCTION

Orthopedic devices have been reported to have failed due to corrosion [1,2], low cycle fatigue [3,4], poor design, and manufacturing defects [5]. While general corrosion inevitably occurs even when the metal is in the passive state and may not cause any serious problem, localized corrosion such as pitting and especially crevice attack is the predominant cause for failure in service [6-8]. Crevice corrosion occurs in shielded areas and is very common in multi-component implants, e.g., corrosion between screws and plates in stainless steel fixation devices [9]. Pitting corrosion occurs in active-passive alloys such as austenitic stainless steels in chloride environments. These types of corrosion cause severe contamination of the tissues around an implant, leading to inflammation, pain and related complications [10]. Pits may also act as stress raisers which could initiate fracture [11]. Recent studies [12] have shown that an immune reaction may develop in the tissues adjacent to buried metallic implants. This may lead to vascular changes, local bone necrosis and even loosening of the prosthesis. The reason may be the high level of metallic ions generally found within and around crevices. Recently, carcinogenic properties of corrosion products from prosthetic devices have also been reported [13].

Though Type 316L stainless steel seems to be significantly prone to pitting and crevice corrosion [12,14], there are a number of recorded cases in which Co-Cr-Mo devices [7,15] and Co-Cr-W-Ni devices [16] had to be removed for reasons which were subsequently ascribed to corrosion. Both Type 316L stainless steel and cast Co-Cr-Mo alloys are extensively used

as metallic implant materials.* While both have adequate mechanical properties and excellent general corrosion resistance, none are immune from localized corrosion. Stainless steel however is considerably more prone to localized attack than cast Co-Cr-Mo alloys.

The superior corrosion resistance of the above mentioned alloys is ascribed to the passive films that form on the surface of these alloys and impart passivity to them [17]. Localized corrosion presumably occurs due to the breakdown of the passive film. In the laboratory, electrochemical tests are performed to investigate the susceptibility of different materials to localized corrosion. These tests are accelerated tests in simulated environments and are designed to predict the corrosion behavior in service. The present study sought to determine the electrochemical parameters involved in the passivity and the breakdown of passivity of commonly used metallic implant materials such as Type 316L austenitic stainless steel and Co-Cr-Mo alloys. The effect of individual alloying elements on the electrochemical behavior was also studied. The purpose was to compare the existing alloys on the basis of their corrosion resistance and to develop and recommend better alloys relatively or totally immune from localized corrosion in the environment under consideration, namely human interstitial fluid. It is however felt that to obtain an insight into the complex nature of the passivity of an alloy, investigation of the electrochemical parameters alone is not sufficient. Therefore, an attempt was made to characterize the passive film itself by the Auger electron spectroscopic technique. This might lead to a better understanding of the nature of passivity and the cause of its breakdown.

*A list of metallic implant materials and their chemical composition is shown in Appendix I.

Though the study was performed on orthopedic implant materials, it has a much broader implication in that stainless steel and many active passive alloys are highly susceptible to localized corrosion in halide environments of which human extra-cellular fluid is a typical example. In this respect, this study will encompass many industrial problem areas such as corrosion in chemical plants, refineries, nuclear plants, seawater corrosion, etc.

CHAPTER 2

LITERATURE SURVEY

2.1 Metallurgical and Corrosion Studies on Metallic Implants and Implant Materials

The compatibility of metallic implants in the human physiological environment has been studied from different aspects such as investigations on failed orthopedic devices and various in-vivo and in-vitro tests. Table 1 shows the results of a detailed study conducted by Scales [7] on implants removed from 667 patients treated in England. The implants were inserted during 1962-65 and a follow-up was made in 1969. Stainless steel, Co-Cr-Mo, and titanium implants conforming to B.S. 3531 were used. Bacteriological and metallurgical examination revealed that a high percentage of all the alloys had to be removed due to corrosion. Colangelo and Greene [2] also noticed corrosion damage in 91% of all multi-component devices that they studied.

Cahoon and Paxton [1] based their investigations on metallographic and electron microprobe analyses of failed implants. In multi-component devices corrosion was generally observed within the crevices such as screw hole areas. It was revealed that the inclusion content of some of the failed stainless steel implants was prohibitively high, thus impairing the fatigue strength of the material. In some cast implants, failure was ascribed to porosity. In some of the stainless steel implants the molybdenum content was found to be below the minimum A.S.T.M. specification of 2.0%, thus lowering the pitting corrosion resistance.

X-ray studies to analyze the corrosion products obtained from a high carbon steel implant were conducted by Cahoon [18]. The corrosion

TABLE 1 [7]
STUDIES ON RETRIEVED METALLIC IMPLANTS

TABLE 1(a)
PERCENTAGE OF CORRODED IMPLANTS AMONG 667 REMOVED

	S.S.	Co-Cr-Mo	Titanium
Number and percentage of total number of implants	478 (71.6%)	83 (12.4%)	106 (15.8%)
Percentage corrosion or fretting	62.6	21.7	22.6

Table 1(b) shows the incidence of contact/crevice corrosion and fretting and mechanical failure of components of implants used in weight-bearing bones.

TABLE 1(b)
313 MULTIPIECE IMPLANTS = 1,759 COMPONENTS USED
IN WEIGHT-BEARING BONES ONLY

	S.S. 1,410	Co-Cr-Mo 184	Titanium 165
Percentage with contact/crevice corrosion and/or fretting	87	59.3	65.4
Percentage with fatigue or torsion failure	0.5	6.5	4.8

. . . continued

Table 1(c) shows the percentage of contact/crevice corrosion and/or fretting and mechanical failure of screws used with intertrochanteric devices and bone-plates in weight-bearing bones.

TABLE 1(c)

1,232 SCREWS USED WITH INTERTROCHANTERIC AND BONE PLATES
IN WEIGHT-BEARING BONE

	S.S. 1,002	Co-Cr-Mo 112	Titanium 118
Percentage with contact/crevice corrosion and/or fretting	55	41.9	43.2
Percentage with fatigue or torsion failure	0.2	8.03	4.2

From Table 1(d) it could be seen that there is no correlation between corrosion or fretting and the incidence of sepsis.

TABLE 1(d)

THE INCIDENCE OF SEPSIS RELATED TO CORROSION OR FRETTING
IN 667 IMPLANTS REMOVED FROM PATIENTS

	S.S.	Co-Cr-Mo	Titanium
Percentage of sepsis with corrosion or fretting	8.3	11.1	4.2
Percentage of sepsis with no corrosion or fretting	6.7	10.9	3.6

products were determined to comprise FeCO_3 and $\beta\text{-FeOOH}$ which appear to have formed due to the carbon dioxide content of the interstitial fluid and potassium ions of the intra-cellular fluid respectively.

Williams [19] conducted combined metallurgical and histological studies on tissue-prosthesis interactions in orthopedic patients. He has emphasized the skill and competent workmanship needed in conducting orthopedic surgery. The conventional countersunk profile of a screw-plate interface can only result in good mating if the screw is inserted perpendicularly through the plate. If inserted obliquely, a crevice results leading to localized corrosion. This was clearly demonstrated by laboratory experiments conducted with the conventional arrangements; but when hemispherical countersunks were used, thereby producing even mating, the corrosion was eliminated. He also noticed that the stress-induced martensitic transformation which occurs during the production of bone screws is responsible for severe corrosion. The magnetic moment of the various components of implants were compared with the occurrence of corrosion and it was noticed that the interfaces associated with the most martensitic of the screws, as measured by the degree of magnetism, were most susceptible to corrosion. Correlating the amount of martensitic transformation with the nickel content, he concluded that a minimum 11% nickel would be desirable for austenitic stability. Cohen and Hammond [20] also noticed a higher incidence of pitting corrosion in samples having non-austenitic compositions, as determined by magnetic permeability.

In the above studies [20], galvanic and stress corrosion were not evident. Cohen and Foulz [21] studied the failure of an AISI type 420 Steinman pin which was used as an intramedullary rod for fixation of a fracture of the fibula. The screw used was made of AISI type 316 steel.

Upon examination, a series of pits was observed on the shaft of the pin whereas the screw revealed no corrosion. However, the pits on the pin were localized at a distance from the screw and not on the surface closest to the screw which in this case is the cathodic metal. The authors concluded that galvanic corrosion, namely corrosion due to the dissimilarity of the metals played very little, if any, part in the corrosion in this case. They also chemically analyzed the corrosion products within the pits of the pin and characterized them as principally iron salts.

Rostoker et al [22] studied the galvanic compatibility of present-day orthopedic implant materials. Using a metallographic technique to identify and count corrosion pits, the tendency for passive film breakdown was studied under conditions that simulated a crevice and a combination of two different materials. Galvanic corrosion due to contact between any two dissimilar materials did not arise.

Corrosion in orthopedic implants is often designated as "face" corrosion. This however has been properly identified as a form of fretting corrosion or crevice corrosion or a combination [2].

Failures due to corrosion fatigue have been reported by several authors. Metallographic and fractographic examinations using electron microscopy revealed distinct evidence of fatigue failure in 316 SMO implants removed from human subjects [2,4]. On metallographic examinations of bone nails made of austenitic stainless steel, Fabler noticed distinct evidence of fatigue failure initiation [3]. On adding 0.18% nitrogen to austenitic stainless steel, superior fatigue corrosion resistance was obtained [3]. Metallographic studies on retrieved intramedullary bone pins made of Type 316 stainless steel also showed

evidence of corrosion fatigue failure [23]. Corrosion pits may act as stress raisers leading to fatigue crack nucleation and corrosion-accelerated mechanical failure. Rose et al [11] investigated the failure of a Vitallium* nail-plate device which had been used to fix an intertrochanteric fracture of the hip. The nail was composed of cast Vitallium and the plate of wrought Vitallium. Scanning electron microscope studies revealed the presence of microscopic cracks nucleated by corrosion pits in the nail-plate contact area. The authors suggested that the possibility of galvanic corrosion due to the contact of dissimilar metals could not be ruled out; however, it appears that crevice corrosion was responsible for pit initiation.

Greene and Jones [24] discussed the applicability of the linear polarization technique of measuring corrosion rate to in-vivo corrosion of surgical implants and concluded that this technique might be useful in detecting the onset of localized corrosion in buried implants. Thus, an implant can be removed before extensive tissue damage occurs. In-vivo studies were performed by Colangelo and Greene [25] who monitored, by the linear polarization method, the corrosion rate of a SAE type 1018 steel specimen surgically implanted in the thigh muscle of a mongrel dog. They observed that the corrosion rate was highest during the first few days after implantation and it gradually fell off with time. The decrease in the corrosion rate is believed due to either surface precipitation of proteins and other organics or formation of protective oxide films on the steel surface.

Anodic polarization studies on implant materials have been

*Vitallium is a registered trademark of Howmedica, Inc.

conducted by Hoar and Mears [26], Aragon and Hulbert [27], Cahoon et al [9], Revie and Greene [28], Mueller and Greener [29], etc. On the basis of tests over a period of 100 hours Aragon and Hulbert [27] observed that the Ti-6Al-4V alloy corrodes 176 times slower than Type 316L stainless steel. Cahoon et al [9] observed that the cast Co-Cr-Mo alloy has a nobler critical pitting potential than Type 316L stainless steel. In-vitro corrosion rates of Type 316L stainless steel, cast Vitallium, and titanium, all under passive condition in Ringer's solution, were measured by Mueller and Greener [29]. They appeared to be the same for all three materials placed at $0.5 \mu\text{A}/\text{cm}^2$, but decreasing with time to less than $0.015 \mu\text{A}/\text{cm}^2$ as also indicated by Revie and Greene [28]. Furthermore, in-vivo corrosion rates have been placed at only about one-tenth of the in-vitro corrosion rates.

Cohen and Wulff [16] investigated the clinical failure of a surgical implant (a Thornton plate and Smith-Peterson nail) caused by crevice corrosion of the plate. In this implant which was composed of wrought and cast Vitallium, it was the wrought Vitallium that showed the most significant deterioration. It was shown that superior resistance to crevice corrosion could be imparted to the currently used cast Co-Cr-Mo alloy such as H.S. 21, Vitallium etc, by alteration of fabrication methods, thereby giving it over-all superiority as a surgical implant material. The authors subjected the cast alloy H.S. 21 to various types of hot working such as press forging, extrusion, hot rolling, etc. followed by annealing in each case. They observed that alloys with mechanical properties similar to those of wrought H.S. 25 but with resistance to crevice corrosion equivalent to or better than that of the cast type H.S. 21 or cast Vitallium might be produced by the above process.

The superior properties were attributed to the more homogeneous, finer grained matrix structure and more uniform distribution of carbides achieved by hot working and heat-treatment.

Cameron et al [30] tested the reactivity of porous Vitallium in-vivo and in-vitro. No harmful tissue reaction or evidence of crevice corrosion was noticed.

Researches aimed at developing superior quality of metallic implant materials are in progress throughout the world. It appears that present-day orthopedic implant materials, if manufactured conforming to prescribed recommendations [31], have adequate strength and general corrosion resistance. However, they are still not totally immune from pitting and crevice corrosion.

2.2 Physiological Environment of Human Extra-Cellular Fluid [32-33]

In-vitro corrosion studies [26-29] are generally conducted in isotonic saline solutions such as 0.9% NaCl solution, 0.15M NaCl solution or Ringer's physiological solution, all of which grossly simulate the extra-cellular environment. Therefore, it is felt necessary to discuss the ionic components and various dissolved gases in the extracellular fluid, e.g., blood plasma, interstitial fluid, etc. The principal constituents of extra-cellular and intra-cellular fluids are shown in Table 2. Ionic concentrations in blood chemistry are generally expressed in equivalents; and as the concentrations encountered are very small it is convenient to use the unit milli equivalents per litre (m Eq/l). Among the ionic species found in the extra-cellular fluid, the major cation is sodium, and the major anions are chloride and carbonate. The predominant cations of the intra-cellular fluid are potassium and

TABLE 2
COMPOSITION OF THE BODY FLUIDS [32]

Substance	Interstitial Fluid (m Eq/L)	Intracellular Fluid (m Eq/L)
Na ⁺	141	10
K ⁺	4.1	150
Ca ⁺⁺	4.1	-
Mg ⁺⁺	3	40
Cl ⁻	115	15
HCO ₃ ⁻	29	10
PO ₄ ⁻⁻⁻	2	100
SO ₄ ⁻⁻	1.1	20
Organic acids	3.4	-
Protein	1	60
	Dissolved Gases and pH	20 mm Hg.
P _{O₂}	35 mm Hg	20 mm Hg
P _{CO₂}	46 mm Hg	50 mm Hg.
pH	7.4	7.0