THE UNIVERSITY OF MANITOBA

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

by

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

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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 1

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 inflamation, 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 wascoperformeded 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, seaswater corrosion, etc.

CHAPTER 21

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] bbased 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]

5.

. continued

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	Со~Сr-Мо 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

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 fatiuge 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 β -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 Foultz [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 corrosionaccelerated 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] whoomonitored, 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 Howemedica, 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, castWiteallium, 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 μ A/cm², but decreasing with time to less than 0.015 μ A/cm² 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 fisotonic saline solutions such as 0.9% NaCl solution, 0.15M NaCl solution or Ringer's physiological solution, abladi which ighoss by 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

11.

TABLE 2

Substance	Interstitial Fluid (m Eq/L)	Intracellular Fluid (m Eq/L)
Na ⁺	141	10
К+	4.1	150
Ca ⁺⁺	4.1	-
Mg ⁺⁺	3	40
C1 ⁻	115	15
HC03	29	10
P0,	2	100
s04	1.1	20
Organic aci d s	3.4	-
Protein	1	60
Plz	Dissolved Gases and pH	20 mm Hg.
P202	35 mm Hg	20 mm Hg
p _{CO2}	46 mm Hg	50 mm Hg.
рH	7.4	7.0

COMPOSITION OF THE BODY FLUIDS [32]

magnesium and the major anions are organic phosphates and sulfates. Table 2 also shows the concentrations of oxygen and carbon-dioxide and the pH of the extra-cellular and intra-cellular fluids. Oxygen and carbon dioxide transport is governed by the respiratory mechanisms. Both oxygen and carbon dioxide diffuse downhill along gradients of decreasing pressure. Hence the pO_2 in the body fluids is less than the partial pressure of ambient oxygen, whereas the reverse is true for carbon dioxide.

The mechanism of buffer action is mainly controlled by the bicarbonate system as outlined in the following equation

$$CO_2 + H_2 0 = H_2 CO_3 = H^+ + HCO_3^-$$
 (1)

If hydrogen ions are added to the system, some will combine with bicarbonate ions and drive the reaction to the left. Thus, not all the hydrogen ions added will stay in solution in the ionic form. Conversely, if a base is added, the reaction will shift to the right causing H_2CO_3 to dissociate into hydrogen and bicarbonate ions. This inverse relationship between the hydrogen and the bicarbonate ion concentration is shown in Figure 1(A) which represents the buffer properties of plasma of which bicarbonate is the principal buffer. The initial point A in the figure represents the normal condition of plasma in the arterial blood, namely a pH of 7.4 and a bicarbonate ion concentration of 24 mM per litre. The effects of adding acid to blood or to plasma are shown by arrows. This however is the picture when CO_2 tension is maintained constant and the acids and bases added are fixed in that they are not removed by respiratory activity.

The effect of CO_2 on the pH and the bicarbonate ion is however very different as shown in Figure 1(B). If CO_2 is added or removed, the



Figure 1 (A) Effect of fixed acid and fixed base on pH and HCO_3 content of separated plasma. (B) Effect of changes in CO_2 on pH and HCO_3 . (C) Combination of the effects shown in (A) and (B) on true plasma [32].

concentration of hydrogen and bicarbonate changes in the same direction, as indicated by equation (1). Figure 1(C) shows the combination of the effects of (A) and (B). The four variations from the normal buffer point as depicted in Figure 1(C) represent the four types of acid-base disturbance observed clinically: respiratory acidosis (CO_2 excess), respiratory alkalosis (CO_2 deficit), metabolic acidosis (fixed acid excess), and metabolic alkalosis (fixed base excess).

To carry the considerations further, it is necessary to analyze the quantitative aspects of various parameters. The relationship between H^+ and the ratio of the constituents of the bicarbonate-carbonic acid buffer system can be expressed from equation (1) as

$$[H^{+}] = KA_{1} \frac{[H_{2}CO_{3}]}{[H CO_{3}]}$$
(2)

where KA₁ is the first dissociation constant of carbonic acid. Rewriting equation (2) in the logarithmic form, the Henderson-Hasselbalch equation is obtained:

$$pH = pK + \log \frac{[H CO_3]}{[H_2CO_3]}$$
 (3)

The pK of the bicarbonate system is known and the pH and the bicarbonate ion concentration can be measured, but the H_2CO_3 concentration, which is extremely low, cannot be directly measured. However, equation (1) reveals that the H_2CO_3 concentration is directly dependent upon the concentration of dissolved CO_2 , which is in turn dependent upon its partial pressure and solubility co-efficient of CO_2 in plasma. Thus equation (3) can be rewritten as follows:

$$pH = pK + \log \frac{[H \ CO_3]}{[a \ pCO_2]}$$
 (4)

where the solubility constant a = 0.0301 and pK = 6.10. Substituting, equation (4) becomes:

$$pH = 6.10 + \log \frac{[H CO_3]}{0.0301 \text{ pCO}_2}$$
(5)

The equation now relates the three measurable quantities; if any two are known, the third may be calculated or obtained from the nomogram of relation between pH, HCO_3^- and pCO_2^- as shown typically for plasma in Figure 2.

The human physiological environment is a complex one. The above discussion shows only the outline of the mechanisms involved in maintaining the acid-base balance of the environment. It is felt that any engineer undertaking an investigation of corrosion or fracture of orthopedic implants should be well conversant with the composition and the chemical kinetics of the intra-cellular and extra-cellular physiological environment.

2.3 Electrochemical Principles of Localized Corrosion

A metal corroding uniformly in an electrolyte usually corrodes at an equilibrium potential called the open circuit potential or corrosion potential, E_{corr}, and at an uniform current density, i_{corr}. However, if an external current is impressed on the material, its potential changes. The applied current density vs. potential curve so generated is called the polarization curve. Electrochemical studies based on anodic polarization (potential increasing in the noble direction) are generally conducted to investigate the susceptibility of an alloy to localized corrosion [34]. These tests are accelerated tests in simulated environments and are designed to predict the corrosion behavior in service. The experimental technique [35] involves a potentiostatic or



Figure 2 Nomogram of relation between pH, $\rm HCO_3^-,$ and $\rm pCO_2$ of human plasma.

potentiodynamic potential scan in the noble direction from the corrosion potential. Figure 3 shows schematically the anodic polarization curve of an active-passive alloy of which stainless steel is an important example. The current density is practically constant and relatively very low over a wide range of potential. This is called the passive current density, $i_{passive}$. The current starts to increase rapidly at a certain potential called the critical pitting potential E_c [34] of the alloy in the environment under investigation. At a potential more noble than E_c pits start to grow and deterioration occurs very rapidly in a localized region. Kolotyrkin [36] has used the breakdown or critical pitting potential to appraise the resistance of several alloys to pit initiation in halide media.

If the potential scan is continued beyond E_c , then on reversing the scan a cyclic hysteresis behavior is observed in some cases [37]. The potential at which the forward and the reversed scans intercept is called the protection potential, E_p Figure 3). Pourbaix and his co-workers [37,38] and later Wilde and Williams [39,40] showed that at a potential more active than E_p , no pit initiation occurs and actively growing pits repassivate. Based on cyclic polarization tests on stainless steel in halide media, Wilde [41] also showed that E_p is not a unique material property but depends on the current density at which the potential scan is reversed, that is, the amount of pit propagation during the forward scan. Wilde concluded that susceptibility of alloys to breakdown of passivity by crevice corrosion may be predicted by the presence or absence of hysteresis during cyclic polarization. It was also observed that the difference between the pitting and protection potential, $(E_c - E_p)$, the difference potential, could be correlated





directly with the extent of crevice corrosion.

Crevice corrosion is generally assumed [42] to be governed by the same kind of mechanism as pitting corrosion, namely the breakdown of passivity. Crevice corrosion however occurs underneath gaskets and shielded areas where the flow of electrolyte and oxygen is limited. Hence, the electrochemical environment within a crevice is more aggressive than the bulk environment, as reflected in a higher chloride ion concentration and lower pH within the crevice [43]. Figure 4 shows schematically the various processes and mechanisms involved in a crevice configuration. The oxidation and reduction reactions are as follows:

Oxidation:	$M \rightarrow M^+ + e$	(6)
Reduction:	$0_{2} + 2H_{2}0 + 4e \rightarrow 40H^{-1}$	(7)

Initially, these processes occur uniformly over the entire metal surface including the crevice interior. After some time, the oxygen within the crevice is depleted because of limited convection but the metal dissolution continues. With the cessation of the cathodic hydroxyle ion-producing re-action, negative chloride ions start moving into the crevice area to maintain a charge balance. The resulting metal chlorides hydrolyze in water to insoluble metal hydroxides and free acid as follows:

 $M^{+} + C1^{-} + H_{2}^{0} = MOH + HC1$ (8)

The acidity lowers the pH within the crevice [44] and a pH as low as 1.0 has been reported [43]. Both the chloride anions and low pH accelerate crevice corrosion in a manner similar to autocatalytic pitting, while the reduction reaction cathodically protects the exterior surface. Also, for active-passive metals that depend on protective oxide films for their



Initial reaction:

Oxidation $M \rightarrow M^+ + e$ (1) Reduction $0_2 + 2H_20 + 4e \rightarrow 40H^-$ (2)

After oxygen is depleted chloride ions migrate into the crevice.

Final reaction:

 $M^{+} + C1^{-} + H_{2}0 = MOH + HC1$ (3)

Figure 4 Schematic diagram showing the mechanism of crevice corrosion [42].

corrosion resistance, the breakdown of passivity and active corrosion in crevices are favoured by the increased concentration of chlorides and hydrogen ions.

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In the laboratory, evaluation of pitting or crevice corrosion resistance is carried out not only by anoddic polarization tests [45] but also by immersing test specimens in aggressive, pit producing environments such as $FeCl_3.6H_20$ or $KMnO_4$ - NaCl solutions [46]. These are highly oxidizing chloride solutions capable of causing pits or crevice corrosion in a short period of time. A somewhat different approach was used by Streicher [47] who applied a potential sufficient to cause pitting initiation on various alloys and counted the number of pits formed under standard conditions. In the general case, interpretation of the results obtained by his technique requires knowing how overall pitting resistance would be expected to correlate with the number of pits found in this type of test.

Pessal and Liu [48] have attempted to determine critical pitting potentials of stainless steels in aqueous chloride environment by another technique. It consists of polarizing the test electrode to the desired potential and then lightly scratching the electrode surface. While the potential is held constant, the current is recorded as a function of time after scratching until the electrode either repassivates or stable pit growth takes place. The potential is gradually raised in the noble direction and the above process is repeated at each potential until the minimum potential is noticed at which the electrode does not repassivate after scratching. This potential is designated as the critical pitting potential. The results obtained by this method are, in general, comparable to those obtained by the scanning technique. Formsome alloys, especially those containing molybdenum, only small differences were observed in the pitting potentials determined by the scratch test and by scanning tests.

Bond [49] has emphasized that pitting potentials of stainless steels are dependent on a variety of factors such as surface preparation, dissolved gases, rate of change of potential, prior history of the electrode, etc. Thus, there is a need for maintaining uniformity in specimen and electrolyte preparations, duration of immersion, and experimental methods.

Suzuki, ett al [50] correlated the critical pitting potential and the critical anodic current density to the chemical and electrochemical characteristics for the anolyte within a pit. Artificial pits were galvanostatically activated in some austenitic stainless steel specimens in 0.5N NaCl solution at 70°C. The acidity and the chloride ion concentration within the pits were measured. Very low pH (0.13 to 0.80) and very high concentration of chloride ions (3.78 to 6.47N) were observed. The concentration of metallic ions in the anolyte within the pit was determined using atomic absorption spectrochemical technique [51]. The distribution of metallic components on weight % agreed well with the respective constituents of the base metal, indicating that no selective dissolution occurred in the process of pitting corrosion.

The electrochemical techniques discussed above help to determine some desirable properties that should be taken into consideration when selecting or developing an alloy for using in a specific environment. However, they do not offer any information regarding the nature and composition of the passive film that imparts corrosion resistance to the alloy. For this reason, spectroscopic studies are necessary to obtain

detailed knowledge of the passive films.

2.4 Theories of Passivity and Passive Films

Passivity is generally ascribed to a very tenacious passive film on the surface of the material. There are two theories regarding the nature of the passive film [17]. The first suggests that the passive film is always a diffusion-barrier layer of reaction products such as metal oxide or other compound which retards the anodic dissolution. Lead sulfate film on lead immersed in sulfuric acid is a good example. In an alloysprotective oxide films form above the critical alloy composition for passivity, but nonprotective oxide films form below the critical composition. Thus, in Fe-Cr system, it is suggested that a protective Cr_2O_3 type oxide will form only when chromium content is at least 12%.

The second theory regarding the nature of the passive film holds that generally a monolayer or so of a chemisorbed film of oxygen imparts passivity [52] by displacing the normally adsorbed water molecules and thus slowing down the rate of anodic dissolution involving hydration of metal atoms. This theory is based on the fact that most of the metal exhibiting passivity or imparting passivity to an alloy are transition metals having electron vacancies or uncoupled electrons in the d shells of the atom. These uncoupled electrons form strong bonds with oxygen which also contains uncoupled electrons, resulting in electron-pair or covalent bonding supplementary to ionic bonding. The high heats of sublimation of transition metals compared to non-transition metals favor adsorption of the environment because metal atoms tend to remain in their lattice, whereas oxide formation requires metal atoms to leave their lattice. Multilayer chemisorbed passive films, however, react in time

with the underlying metal to form compounds such as oxides.

The chemisorption theory overcomes the difficulty faced by the oxide film theory in explaining the observed Flade potential 0.63 V vs N.H.E. for iron in 1N H_2SO_4 at 25^oC. The reaction that possibly takes place during anodic passivation is [17]:

$$M + H_2 0 \rightarrow 0.M + 2H^+ + 2e^-$$
 (9)

where M represents (a) Fe_2O_3 , (b) Fe_3O_4 , (c) chemisorbed oxygen. Using the data [17]: ΔG^0 of formation for $Fe_2O_3 = -177.1$ Kcal/mole of Fe_2O_3 ; for $Fe_3O_4 = -242.4$ Kcal/mole of Fe_3O_4 ; for H_2O (1) = -56.69 Kcal/mole of H_2O ; for $H^+ = 0$; for chemisorption of oxygen on Fe, $\Delta H^0 = -75$ Kcal/mole O_2 ; $\Delta S^0 = -46.2$ cal/mole $O_2 - {}^{O}C$, (a) and (b) give a Flade potential of -0.051 V vs N.H.E. and -0.086 V vs N.H.E. respectively which are too active compared to the observed value. However, (c) gives a Flade potential of +0.566 V vs N.H.E., in reasonable agreement with the observed value.

The chemisorption theory can also predict quantitantively the critical alloy composition for passivity. Chemisorption on any metal is known to be favored by an unfilled d-band configuration [53]. The following analysis [17] shows how the composition for Ni-Cu system can be predicted. In the gaseous state, nickel has the configuration $3d^84s^2s^2corresponding to two d$ electron vacancies, i.e., two uncoupled d-electrons in the third shell of the atom. In the process of condensing to a solid and forming the metallic bond, uncoupled electrons of neighboring atoms couple with each other, resulting in a vacancy of 0.6 per nickel atom (as measured magnetically). Similarly in the process of alloying, the intercoupling of d-electron increases with the proximity of
nickel atoms in the alloy. Assuming a linear relationship between intercoupling and concentration, the vacancies per nickel atom can be set equal to 2 - (2 - 0.6) at.% Ni/100, corresponding to 2 vacancies for 0% Ni and 0.6 vacancy for 100% Ni. Copper $(3d^{10}4s)$ can donate one electron per copper atom. The alloy loosses its transition metal characteristics and hence passivity when all the d vacancies of nickel atoms are filled up by electrons donated by copper. This is given by:

at.% Ni(2 - 0.014 at.% Ni) = 1 x at.% Cu
$$(10)$$

Using at.% Cu = (100 - at.% Ni) in equation (10) the critical composition is found to be 41% Ni, 59% Cu. This value corresponds closely to the observed value derived from magnetic saturation data. Also electrochemical tests show that nickel imparts passivity to the alloy at around 40 at.% Ni or above [17]. For alloys made up of two or more transition metals, the most passive component of an alloy is assumed to be the acceptor element. The critical compositions for passivity in the Fe-Cr, Ni-Cr and Co-Cr alloys are similarly found to be 12% Cr, 14% Cr, and 8% Cr respectively [54]. In the ternary Cr-Ni-Fe solid solution system electrons are donated to chromium mostly by nickel above 50% Ni but by iron at lower nickel concentrations [55]. Molybdenum similarly exhibits passivity as long as its d bands remain unfilled. In type 316 stainless steel (18% Cr, 10% Ni, 2-3% Mo), for example the optimum weight ratio of Mo/Ni is best maintained at or above 15/85 corresponding to the observed critical ratio for passivity in the binary Mo-Ni system equal to 15 wt.% Mo [56].

A schematic structure of the first-formed chemisorbed film has been proposed by Uhlig [57]. The film consists of a regular array of

oxygen and metal atoms located in the same approximate plane of the surface. This initial layer is found to be more stable thermally than the oxide MO. However with increasing oxygen pressure and passage of time several layers of adsorbed oxygen are formed. Metal ions also migrate into the film which can be considered at this stage to be an amorphous nonstoichiometric oxide. However, eventually it converts into stocchiometric oxides. Thus, both oxide film theory and chemisorption theory predict that the ultimate components of the passive film are stocchiometric oxides.

2.5 Spectroscopic Studies on Oxide Films

Electron diffraction studies have been employed on active, passive, and transpassive oxide films formed on iron by Foley, Kruger, and Bechtold [58] and on oxide films on austenitic stainless steels by Nakayama and Oshida [59]. Soft x-ray spectroscopy has been applied to characterize relatively thick oxide films (> 100 A) on transition metals [60] and thin oxide films (20-40 A) on iron-chromium alloys [61]. Auger electron analysis of the surface reaction film of aluminum has also been carried out [62]. The advantage of the soft x-ray spectroscopy is that it can characterize very thin films. When a metal, alloy, or compound is bombarded with electrons up to 3 KV, soft x-rays originating near the surface are emitted; the depth from which the x-rays come decreases with decreasing electron energy. The wavelength and intensity distribution of the x-ray band spectra are sensitive functions of the electronic structure of the emitter, that is ionization state. Auger electron spectroscopy [63] probes the electronic energy levels of ions undergoing auto ionization and is part of the broader field of secondary electron energy spectroscopy which deals with the analysis of the entire secondary electron energy

spectrum. The secondary electrons, created by bombarding a surface with an electron beam, are energy analyzed to obtain the energy distribution, N(E). Auger spectroscopy is capable of uniquely identifying each element and is essentially a surface probe as the data come from the top five atom layers or so, depending upon the material and the ionizing energy. This method is particularly suitable for surface analysis and characterization of passive films on various alloys.

2.6 Statement of the Problem

Since the present-day orthopedic implant materials such as austenitic stainless steel and Co-Cr-Mo alloys are not totally immune from localized corrosion, further studies were necessary to investigate the mechanisms of the breakdown of passivity and repassivation of these alloys. Most of the previous electrochemical studies [26,29] were limited to determining critical pitting potentials only and surprisingly, no studies on the cyclic polarization behavior have been reported. Critical pitting potential studies give information on breakdown of passivity only. The ability of an alloy to repassivate or interrupt pit propagation can be determined only from the cyclic polarization curve and a knowledge of the protection potential of the alloy. Hence, the susceptibility to corrosion of these alloys was studied, based on cyclic polarization curves. A comparison of the corrosion resistance of the alloys was made on the basis of such electrochemical parameters as the passive current density, the critical pitting potential and the protection potential. A systematic program was undertaken to study the effects of various alloying elements on the corrosion behavior of austenitic stainless steel; the aim was to develop an alloy having a

corrosion resistance superior to that of the present-day austentitic stainless steel. The studies were generally conducted in Ringer's physiological solution which grossly simulates the ionic composition of the extracellular human physiological environment. However, multi-component orthopedic devices are often manufactured with in-built crevices. Due to the restricted flow of oxygen and electrolyte within the crevice, the chemical reactions within a crevice lead to an environment with lower pH and higher chloride ion concentration compared to the bulk electrolyte. Accordingly, tests were conducted in simulated crevice environments prepared by adding to Ringer's solution controlled amounts of hydrochloric acid which increased the chloride ion concentration and decreased the pH at the same time.

Studies were also conducted to analyze the oxide films on various alloys by Auger electron spectroscopic technique. This helped to ascertain the exact nature and composition of the passive films, thus leading to a better understanding of the cause of passivity and its breakdown.

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EXPERIMENTAL PROCEDURES

3.1 Apparatus for Electrochemical Tests

Potentiodynamic anodic polarization tests [64] were conducted employing generally the ASTM recommended practice for polarization measurements regarding equipment, circuitry, and procedures [65]. The apparatus [35] consisted of:

- (i) Polarization cell, salt bridge, and the Luggin probe.
- (ii) Electrode mounting devices.
- (iii) Reference Electrode.
- (iv) Auxiliary electrodes and the working electrode.
- (v) Electrical and electronic equipment, such as
 - (a) Potentiostat
 - (b) Digital voltmeters
 - (c) Motor potentiometer
 - (d) Logarithmic converter
 - (e) X-Y recorder
 - (f) Combined pH meter and $0_2 CO_2$ analyzer
 - (g) Constant temperature bath
- (i) Polarization cell, salt bridge, and the Luggin probe

A multinecked, round bottom, one litre polarization cell [35] was used. This permitted the introduction of electrodes, and gas inlet and outlet tubes. A Luggin probe - salt bridge assembly was used to separate the bulk solution from the reference electrode. The Luggin capillary was filled with an agar gel made by mixing 3-4 gm of agar-agar per 100 ml of 0.2 M potassium chloride solution. The reference electrode was immersed in a thistle tube filled with saturated potassium chloride solution. The thistle tube had a capillary tube end of 1 mm inside diameter with an agar plug to prevent mixing the test solution with the potassium chloride solution. The thistle tube was connected to the Luggin probe by a plastic tube filled with the test solution.

(ii) <u>Electrode mounting</u>

An electrode mounting assembly [66] is shown in Figure 5. Visible is a cylindrical electrode, together with a Teflon compression gasket, electrode mounting rod, and electrode holder. Mounting is accomplished by compressing the electrode against the Teflon gasket by means of the upper nut and washer assembly. Electrical contact is made by the mounting rod. The advantage of this electrode mounting lies in isolating the specimen. It was employed in standardizing our experimental set-up as per ASTM recommendations [65]. However, during subsequent experiments, occasional trouble arose due to crevice corrosion underneath the Teflon gasket. This was avoided by mounting the specimens in acrylic plastic with a single exposed surface of about 1 cm^2 area [45]. Electrical contact was made by drilling a hole into the specimen through the acrylic mount and tapping the specimen. Mounting was done using a Teflonggasket, electrode mounting rod, and glass electrode holder as in Stern-Makrides assembly (Figure 5.). The specimen was mounted eccentrically on the acrylic mount; this allowed the specimen to be completely immersed in the electrolytee, while isolating the rest of the mounting devices, as shown in Figure 6. This holding device proved satisfactory in the present work and was free from any contamination.

Another specimen holder, designed by Pessall and Liu [48], was







tried and found to be very successful. Figure 7 shows this assembly. This holder has the advantage of allowing independent sealing of the specimen and the sample holder, as well as accommodating specimens which are difficult to drill and tap.

(iii) <u>Reference electrode</u>

A Radiometer saturated calomel half cell, model K401, was used as a reference electrode. This electrode is not easily poisoned or contaminated and is insensitive to electrolyte composition; it is almost spill-proof and very rugged, Electrical contact with the electrolyte is maintained by a small crack at the tip of the electrode body. The cell is filled with potassium chloride solution which is always kept saturated by introducing a few crystals of solid potassium chloride.

(iv) Auxiliary electrodes

Two electrodes of platinum were used as auxiliary electrodes. Platinum was used because of its large exchange current density and its resistance to anodic dissolution. Also, it has the advantage that its polarization is very low in most solutions.

(v) Electrical and electronic equipment

The following equipment waseusedd:

Wenking model 68T53 potentiostat having 11 current ranges, 7 voltage ranges, and a control voltage source of 10 turim, 1000 division precision potentiometer of range ± 2000 mV.

A Kiethley model 160 digital multimeter having 8 current ranges from 100 nA to 1 A, and 7 voltage ranges: 1 mV to 1000 V.

Erwin Halstrup model MP165 motor potentiometer equipped with three sweep ranges, viz. 0 to 1000, 2000 or 5000 mv and with 30 different



Figure 7 Section of a mounting device designed by Pessal and Liu [48].

scan rates ranging from 1 mv/hr to 150 v/hr.

Moseley model 60B logarithmic converter having a dynamic range of 60 db.

Moseley model 6S-A X-Y recorder with two independent servoactuated drives for X and Y axes, isolated and free of ground, each axis having 11 calibrated input voltage ranges: Variable range mode permits arbitrary full scale voltage settings.

Radiometer model PHM71 acid base analyzer having the following ranges:

0₂: 0-30; 0-160; 0-800 mm Hg CO₂: 8-200 mm Hg pH: 0-14; 6.6-8.0

There is independent calibration for 0_2 , $C0_2$ and pH modules and temperature compensation adjustible from 14 to $46^{\circ}C$ calibrated in $2^{\circ}C$ divisions.

Blue M model 1120 A-1 constant temperature heating bath having a temperature range to 100° C calibrated in 1° C divisions starting from 20° C.

3.2 Experimental Methods for Polarization Tests

The experimental methods consisted of the following major steps:

(i) Preparations of specimens and their mountings.

(ii) Preparations of solutions.

(iii) Setting up the apparatus and its calibration.

(iv) Standardizing the experimental set-up.

(v) Conducting the tests and data compilation.

(i) <u>Preparation of specimens</u>

Type 316L stainless steel specimens were prepared from half inch diameter mill annealed rods having a composition of 17.1% Cr, 11.4% Ni,

2.3% Mo, 1.5% Mn, 0.8% Si, and 0.04% C. Cylindrical specimens approximately 2 cm long and 5 cm² surface area were turned from the rod, drilled and tapped for mounting on the Stern-Makrides assembly (Figure 5). They were solution annealed for 1 hour at 1050°C and water guenched. This heat treatment dissolves any chromium carbide along the grain boundary region and thus ensures immunity from sensitization and intergranular attack [67]. The specimens were polished by grinding through a sequence of 220, 320, 400, and 600 emery papers. The dimensions were measured to the nearest 0.001 cm with a micrometer and the surface area was calculated. Similar specimens were mounted on acrylic mounts (Figure 6) and then drilled and tapped. These specimens were mechanically polished to one micron finish. After mounting, specimens were ultrasonically cleaned for two minutes in detergent solution, rinsed in distilled water, cleaned in alcohol, rinsed, dried and immediately immersed in the polarization cell. For tests on the Pessal-Liu type holder [48], about 0.4 inch diameter and 0.1 inch thick disc samples were parted off on a Buehler Model 1010 cut-off machine. The discs were then polished upto 1 micron finish, cleaned as before and mounted on the holder (Figure 7).

For stainless steel alloys cast in the induction furnace in our laboratory, the castings (approximately 5/8 inch diameter and 6 inches long) were homogenized at 1150° C for 24 hours and cold swaged by 20%. Specimens were then prepared as explained above. They were solution annealed at 1050° C for 1 hour and water quenched. Similar mounting and cleaning methods as described above were applied.

Co-Cr-Mo and Co-Cr alloys were also prepared in the induction furance in our laboratory. These alloys were generally tested in the as-cast condition. The Co-Cr-Mo alloy was also tested in the annealed

condition (1200^OC for 24 hours, water quenched). These alloys are hard to drill and tap. Therefore, disc samples were parted off on the cut-off machine and tested on the Pessal-Liu type holder (Figure 7).

(1i) Preparation of solution

The physiological environment of human extracellular fluid has been discussed in chapter II and the principal constituents of extracellular and intracellular fluids are shown in Table 2. The basic physiological solution used in the present-study is shown in Table 3. The composition is so chosen that the ionic concentration of various elements corresponds to that of human extracellular environment where the orthopedic implants are generally placed. The major ionic species are sodium chloride and sodium bicarbonate. Initially 2 mM of CaCl₂ was included in the solution. This was later removed because of CaCO₃ precipitation in the pH range of 7.2 to 7.4.

A two litre stock solution of five times concentration was prepared. During each test, one litre solution of proper strength was prepared by diluting with distilled water. The concentrations of carbon dioxide and oxygen in the solution were regulated by bubbling pure carbon dioxide, oxygen and argon through the solution. The temperature of the solution was generally maintained at 37.1° C, the body temperature, by immersing the polarization cell in a constant temperature water bath.

A Radiometer acid-base analyzer type PHM71 was used to measure pH, dissolved carbon dioxide and oxygen in the test solution. The analyzer operates with a p CO_2 module, type PHA933, and p O_2 module, type PHA930. The corresponding electrodes were individually mounted in thermostatted cells connected to a Haake model TP414constant temperature bath and circulator maintained at 37.1°C. The Radiometer CO_2 electrode,

TABLE 3

COMPOSITION OF PHYSIOLOGICAL SOLUTION

Compound	Amount (g/litre of solution)
NaC1	6.30
NaHCO3	2.44
КС1	0.374
MgC1 ₂ .6H ₂ 0	0.203
MgS0 ₄ .7H ₂ 0	0.123
Na2HP04	0.071
Na ₂ H ₂ PO ₄ .H ₂ O	0.069

type E5036 is a combined glass and silver/silver chloride reference electrode mounted in a jacket and covered by a Teflon membrane which traps a weak electrode solution (0.005 M NaHCO3 per 0.02 M NaCl) in contact with the electrode. The electrode functions like a normal pH electrode and relates the linear change in pH of a bicarbonate solution with its pCO_2 . The pO_2 electrode, type E5046, operates on a Clark type polarographic principle. It consists of a combined platinum and silver/silver chloride electrode mounted in an electrode jacket and covered by a 20 micron thick polypropylene membrane. The electrode traps a phosphate buffer and potassium chloride solution. In operation a constant polarizing voltage of 630 mV vs. S.H.E. is applied to the platinum electrode and current proportional to pO_2 is generated due to the reduction reaction on the cathode. A Radiometer general purpose combination pH electrode, type GK 232C was used to measure hydrogen ion concentration. The electrode was calibrated at 37.1°C.

(iii) Setting up the apparatus and its calibration

The automatic polarization apparatus is shown schematically in Figure 8. The automatic polarization technique was chosen because it improves reproducibility and eliminates timing errors present in manual technique. The set-up shown in Figure 8 is capable of automatically conducting anodic and cathodic polarization measurements under potentiodynamic conditions and automatically recording the results on a semi-logarithmic graph paper. The motor potentiometer is a programmer capable of generating variable voltage which is applied to the input terminals of the potentiostat. This allows the working electrode to be polarized at any predetermined and uniform rate. The potential difference between the working electrode





and the reference electrode is fed into the input terminals of a digital multimeter (set at 1000 mV range and input resistance of 10 meg-ohms). The output of the multimeter is connected to the X axis of the X-Y recorder. The current flowing between the auxiliary electrode and the working electrode is imposed on the input terminal of another multimeter. The resultant potential drop across a precision resistor is impressed via a logarithmic converter on the Y axis of the recorder. A smoothing of current fluctuations was achieved by placing a low-pass R-C filter of time constant (R x C) 1 sec across the input terminals of the logarithmic converter.

The apparatus shown in Figure 8 is capable of measuring polarization curves of normal and active-passive metals over a current range of six decades at potential traverse rates between 1 mV and 150 V/hour. The potential traverse may be automatically arrested at any desired value, and measurements can be conducted through zero volt without the necessity of switching. However, commercially available logarithmic converters are generally limited to an input voltage range where the ratio of maximum to minimum voltage is about 1000:1. As a consequence, for potentiodynamic polarization, calibration of the current axis is necessary. The calibration was done by setting the Y axis of the X-Y recorder in the variable range mode which permitted arbitrary full scale voltage settings. For a particular cell current, the multimeter was set at a fixed voltage and the current range switch of the potentiostat was changed by a decade. The variable control knob of the Y axis of the recorder was then adjusted until one decade change in current corresponded to a shift of the recorder pen by one division on a logarithmic scale. The span between two successive decades on the logarithmic graph paper was so chosen that one turn of the zero control knob the pen moved by one division. Thus ANITOBA

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whenever the current went beyond the scale of the logarithmic converter, the current range setting of the potentiostat was changed by one decade and the recorder pen brought back to the original position by simply giving the zero control knob of the recorder Y axis a one complete turn in the proper direction. The following example will explain this procedure clearly. For the potentiostat, the voltage drop for full scale deflection of the panel instrument is always 200 mV regardless of range. Thus, when the potentiostat is set at 1 mA current range, a 2 mV drop in the multimeter will correspond to 2/200 = 0.01 mA of current. For the same current, the voltage drop in the multimeter will be 20 mV or 0.2 mV respectively for 0.1 mA or 10 mA range setting of the potentiostat. Hence, ffor a properly calibrated recorder, the pen on the current axis will move by one division but in opposite directions if the potentiostat is switched from 1 mA range setting to 0.1 mA and 10 mA settings respectively.

The voltage axis of the recorder was calibrated by setting the X axis of the recorder in the fixed range mode (typically 0.1 V/div) and impressing a 1000 mV voltage from the motor potentiometer. The gain and internal calibration of the recorder were then so adjusted that for 1000 mV of voltage the pen on the recorder moved along the X axis through the corresponding distance (typically 10 divisions). The motor potentiometer was calibrated beforehand as follows. The motor potentiometer was set at 1000 mV and connected to a standard 1000 mV cell to appropriate terminals. The slotted trimmer potentiometer on the motor potentiometer was then adjusted until the needle on the panel indicated "0".

At the beginning of each test the zero adjustment and calibration of the potentiostat were performed. To adjust zero, the range switch

"mA, mV" of the potentiostat was turned all the way clockwise to position 10 mV and the function switch was set at "0" position so that the panel instrument operated as a voltmeter. The zero deviation was corrected by adjusting the trimmer potentiometer (zero control). For calibrating the control potential supply, the vernier of the 10-turn potentiometer was set at position 500 which corresponds to 1000 mV. This was opposed by applying a 1000 mV from the motor potentiometer to the input terminals of the potentiostat whose function switch was now set in " E_c " position so that the panel instrument served as a null detector. If the meter reading was not zero, appropriate correction was made on the calibrating potentiometer located between the control potential terminals.

(iv) Standardizing the experimental set-up

Before conducting any tests, it was felt necessary to check our experimental technique and instrumentation. For this the ASTM recommendations [65] for potentiostatic and potentiodynamic polarization measurements were followed. A corrosion sample (3/8 inch dia x 1/2 inch long) of the standard ferritic Type 430 stainless steel was obtained from the ASTM headquarters. This was drilled, tapped, and mounted on a Stern-Makrides gasket assembly [65]. After proper polishing and cleaning, the specimen was immersed in a hydrogen saturated 1N H_2SO_4 solution maintained at $30^{\circ}C$. The open circuit potential of the specimen was noted 1 hour after immersion. Potential scan was then started beginning at the corrosion potential. Both potentiostatic and potentiodynamic tests were conducted. The experimental set-up including the polarization cell and the specimen is shown in Figure 9. The polarization curves obtained in our laboratory correspond within ±10% to the standard curves shown in the ASTM annual book [65] and were adjudged satisfactory for our purpose.



Figure 9 Photograph showing the experimental set-up for potentiodynamic polarization.

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(v) Conducting polarization tests and data compilation

Having standardized the technique and instrumentation, systematic polarization tests were performed as follows:

(a) Cyclic potentiodynamic behavior of Type 316L Stainless Steel in Ringer's solution

The initial program was to conduct potentiodynamic tests in normal physiological environment. The aim was to establish various electrochemical parameters such as the open circuit potential E corr, passive current density $i_{passive}$, critical pitting potential E_c , and protection potential ${\rm E}_{\rm p}.$ The specimen was immersed in the solution whose composition is shown in Table 3. Sufficient time (20 hours) was allowed for the system to stabilize. From time to time the open circuit potential of the specimen was noted. When its fluctuation became less than ± 5 mV in half an hour it was adjudged to be steady. The open circuit potential Ecorr was obtained at this point. Anodic polarization was started in each case from ${\rm E}_{\rm corr}.$ A scan rate of 600 mV/hour was used. This corresponds to 50 mV shift of potential in 5 minutes, which is often followed in potentiostatic tests [59]. The polarization curve was automatically recorded on the X-Y recorder. In the passive region, the current density ipassive was very low and uniform. At the onset of the breakdown of passivity current fluctuations were noticed and at the critical pitting potential E_c , current started increasing very rapidly. In order to investigate the cyclic polarization behavior, the potential scan was reversed at some desired potential beyond E_c . The potential where the reverse scan curve intercepted the forward scan curve, namely the protection potential E_n, was obtained. The reverse scan was continued until the current became low and comparable to i passive. The polarization

process was stopped at this point and the open circuit potential of the specimen was noted after 10 minutes. This completed one set of observations. For each polarization run, the specimen was repolished after necessary light machining, mounted, cleaned, and immersed in a freshly prepared solution. A number of runs was obtained but each time the potential scan was reversed at different current densities. The purpose was to ascertain whether the cyclic polarization behavior was dependent on the extent of the forward scan.

> (b) Effect of composition on the polarization behavior of austenitic stainless steel

Starting from Type 316L stainless steel as the base material several stainless steel alloys were cast in our laboratory. The amount of any one of the three alloying elements, namely chromium, nickel and molybdenum was systematically increased keeping the percentage composition by weight of the rest of the alloying elements at the base level. Thus, three different sets of alloys - high chromium, high nickel and high molybdenum type stainless steels were prepared. A few samples with some copper were also prepared. The compositions of the various alloys are shown in Table 4. Specimens were prepared from these alloys and cyclic polarization tests were conducted as described in the preceding section.

(c) Effect of low pH and high chloride ion concentration on the electrochemical behavior of stainless steel

It has been discussed in Chapter II that in a crevice configuration low pH and high chloride ion concentration are generally observed due to hydrolysis of metal ions. Accordingly, specimens were immersed as before in the Ringer's solution and after a period of stabilization, controlled amounts of hydrochloric acid of 0.2 N strength were added to the solution. Hydrochloric acid was chosen because it lowers the pH and increases the

TABLE 4

COMPOSITBON OF ALLOYS FOR CYCLIC POLARIZATION CURVES, COCOMBOSITEON (WEX)

	Cr	I.	Mo	U	Si	Mn	Сu	Remainder
1.(316L)	17.1	11.4	2.3	0.04	0.8	1.5	L i N	Fe
*2.	21	11.4	2.3	0.04	0.8	1.5	ΝiΊ	Fe
*3.	24	11.4	2.3	0.04	0.8	1.5	NiT	Ч Ч
4.	17.1	20	2.3	0.04	0.8	1.5	N i J	ъ С
5.	17.1	11.4	3.5	0.04	0.8	1.5	Nil	е
6.	17.1	11.4	വ	0.04	0.8	1.5	Nil	Fe
*7.	17.1	11.4	ω	0.04	0.8	1.5	Ni 1	Ч
	17.1	11.4	2.3	0.04	0.8	1.5	1.5	Ч
9.	17.1	11.4	2.3	0.04	0.8	1.5	က	E E
10.	20	25	4.5	0.04	0.8	1.5	1.5	F F

*Two-phase alloys containing & ferrite.

48.

chloride ion concentration at the same time. Each time the open circuit potential of the specimen shifted immediately after the addition of HCl; and its variation with time was recorded. The open circuit potential became steady again in 2-3 hours and approached the potential registered before HCl had been added. Potentiodynamic cyclic polarization tests were conducted each time after the potential became steady.

(d) Potentiodynamic tests on 25% Ni, 20% Cr, 4.5% Mo, 1.5% Cu alloy

This alloy, generally similar to Type 904L stainless steel manufactured by Uddeholm steel Co. of Sweden, was prepared in our laboratory. This austenitic stainless steel is widely used in structural applications in chemical and other process industries. It has mechanical properties comparable to those of Type 316L stainless steel. But in view of its superior corrosion resistance, it was investigated as a possible orthopedic implant material. Cyclic polarization tests, similar to those on other specimens explained before were conducted on samples of this alloy.

> (e) Effect of higher chloride ion concentration and temperature on the corrosion resistance of 25% Ni, 20% Cr, 4.5% Mo, 1.5% Cu alloy

The above alloy did not exhibit any breakdown of passivity either in Ringer's solution with or without hydrochloric acid. Hence, it was felt necessary to test it in a more aggressive chloride environment where the passivity of the alloy might break down. Previous studies have shown that higher chloride ion concentration and higher temperature impair the corrosion resistance of stainless steel. Leckie and Uhlig [68] observed that higher chloride ion concentration and temperature shifted the critical pitting potential of Type 18-8 stainless steel in the more active direction. Uhlig and Morril [69] noticed an increase in the

corrosion rate of Type 18-8 stainless steel with increase of chloride ion concentration and temperature. Their results indicated maximum pits occurring at 4% sodium chloride solution at 90° C. Trabanelli and Zucchi [70] and Szklarska-Smialowska [71] also reported that with increase in temperature the critical pitting potential of Type 316L stainless steel shifted towards more active direction in 3% sodium chloride solution. In view of the above findings, the 20% Cr, 25% Ni, 4.5% Mo, 1.5% Cu alloy was potentiodynamically tested in 4% sodium chloride solution at 37.1°C and also at 60° C.

(f) Cyclic polarization behavior of 65% Co, -30% Cr, -5% Mo alloy

Co-Cr-Mo alloys under various trade names such as Vitallium and H.S. 21 are widely used in orthopedic implants. These alloys are generally used in the as-cast condition though sometimes annealing and thermomechanical treatments are also performed [9,16]. Disc samples of the as-cast and annealed (24 hours at 1200° C) alloy were mounted on the holder shown in Figure 7 and potentiodynamically tested in Ringer's solution. A number of tests was also performed in Ringer's solution containing various amounts of hydrochloric acid. A few samples were also tested in 4% sodium chloride solution at 37.1° C and 60° C. Hot working was performed on some specimens. A portion of the 65% Co=30% Cr-5% Mo casting was cut off, hot swaged at 1150° C by 20% on diameter, annealed at 1050° C for 2 hours and quenched in water. A disc sample was obtained and cyclic polarization tests were conducted in the usual way.

(g) Polarization tests on 70% Co-30% Cr alloy

To investigate the effect of molybdenum, or the absence of it, on the corrosion resistance of Co-Cr-Mo alloys, the above molybdenum free Co-Cr alloy was prepared. Polarization tests were conducted on an as-cast specimen.

(h) Polarization tests on individual alloying elements

Iron, chromium, nickel, and molybdenum are the principal constinuents of austenitic stainless steel and cast cobalt based implant materials are generally composed of cobalt, chromium, and molybdenum. Though the corrosion characteristics of an alloy are determined by its overall composition, the behavior of each constituent element might also be significant. So cyclic polarization tests were conducted on pure Fe, Cr, Ni, Mo, and Co. The purpose of these tests was to correlate the electrochemical parameters of an alloy to those of each element and to determine whether any specific element has a predominance over the rest of the constituents in governing the corrosion resistance of the alloy.

3.3 Atomic Absorption Analysis of Corrosion Products

To study further the role of each of the alloying elements in the corrosion process, atomic absorption analysis of the corrosion products was carried out. The tests were conducted in two stages. The first stage consisted of analyzing the Ringer's solution itself for various trace elements. The Ringer's solution, although prepared from reagent grade chemicals of highest purity available, contains trace elements. Accordingly, a freshly prepared one litre Ringer's solution was first analyzed on a Perkin-Elmer Model 306 atomic absorption spectrometer in the department of chemistry to determine the concentrations of various trace elements.

In the second stage of the tests, the Ringer's solution was analyzed for corrosion products formed during anodic polarization processes. Specimens of Type 316L stainless steel and as-cast 65% Co, 30% Cr, 5% Mo alloy were separately polarized anodically. In each case, the potential scan was reversed at a current density 2 decades higher than the passive

current density. During reversal, the potential was held steady for 2 hours at 200 mV more active to the critical pitting potential. This allowed sufficient amount of ions to flow into the solution. After 2 hours, the reversal scan was continued until the current became very small and comparable to the passive current. In the case of Type 316L stainless steel, some precipitates were observed in the corrosion cell. These corrosion products were filtered handidissored and concentrated hydrochloric acid and the solution was mixed with the filtrate so that both the dissolved and the undissolved portions of the corrosion products were available for analysis. The electrolyte in which Co-Cr-Mo alloys were tested was clear and no filtering was necessary. The electrolytes were analyzed for each element on the atomic absorption spectrometer.

3.4 Auger Electron Spectroscopic Analysis of the Oxide Films on Stainless Steels and Co-Cr-Mo Alloys

Three different stainless steel alloys and one Co-Cr-Mo alloy were analyzed to characterize the oxide films. The stainless steel alloys are Type 316L stainless steel, the alloy with 17.1% Cr, 11.4% Ni and 5% Mo, and the 20% Cr, 25% Ni, 4.5% Mo, 1.5% Cu alloy. 1 cm x $\frac{1}{2}$ cm x 1 mm specimens were obtained by stages of cold rolling and annealing. They were finally annealed at 1050°C for 1 hour and water quenched. A specimen of similar dimension was also obtained from a 65% Co-30% Cr-5% Mo casting. The sample was annealed for 24 hours at 1200°C. The specimens were mechanically polished upto 0.05 micron finish, cleaned ultrasonically in a detergent solution, rinsed in distilled water, cleaned in alcohol, rinsed, dried and immersed immediately in separate cells containing Ringer's solution at 37.1°C. These were kept in the solution for 4 days for sufficient growth of the passive films on the surface. After withdrawal,

the specimens were rinsed in distilled water and dried. These were then sent to the Educational and Research Services of Carnegie-Mellon University for Auger electron analysis of oxide films. Typicalaresultssares are shown in the Appendix II.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Electrochemical Polarization Tests:

Cyclic Polarization Behavior of Type 316L Stainless Steel in Ringer's Solution

Potentiodynamic cyclic polarization curves for Type 316L stainless steel are shown in Figure 10. Three seaprate runs, each under identical conditions of pO_2 , pCO_2 and pH are shown. The potential scan was reversed at a different current density in each run. Table 5 shows the open circuit potentials at the beginning and 10 minutes after the potential scan, the current densities at which the potential sweeps were reversed, and the difference potentials, $(E_c - E_p)$ [41] for these runs. It is observed that the hysteresis behavior varies with the range of the potential scan, i.e., the amount of pit propagation. Thus, no hysteresis was observed when the scan was reversed at approximately 5 μ A/cm² but a large hysteresis loop was noticed for a high reversal current ($\simeq 200 \ \mu A/cm^2$), and an intermediate behavior was observed for an intermediate value of current reversal. As the forward scan beyond the critical pitting potential, E_{c} , increases, the amount of localized attack within minute pits increases due to more time available for the reaction involving hydrolysis of corrosion products and chloride ion build-up within pit cavities [43]. Thus, the protection potential, E_p , is not a unique material property but varies with the amount of localized attack induced by polarization, as was also observed by Wilde [41] for stainless steel in halide media.

Examination of Table 5 and Figure 10 reveals that in spite of some hysteresis in the intermediate case, the open circuit potential at



TABLE 5

RESULTS ON THE POTENTIODYNAMIC CYCLIC BOLARIZATION OF TYPE 316L STAINLESS STEEL IN RINGER'S SOLUTION

Difference Potential (E_c ^{-E} p) (mV)	0	200	420	
Open Circuit Potential 10 Minutes After the Scan (mV vs SCE)	09+	+47	-62	
Current Density at Scan Reversal (µA/cm ²)	4	60	120	
Open Circuit Potential at the Beginning of Experiment (mV vs SCE)	+65	+57	09+	

56.

the end of the scan quickly comes back to the value at the beginning of the experiment; whereas for the more severe case, the open circuit potential remains at about 120 mV more active than the original rest potential. In this case visible pits on the surface of the specimen were observed at the end of the experiment. This is in agreement with Jones and Greene [72] who also observed a drift of potential in the active direction for localized corrosion of stainless steel in chloride media.

The absence of hysteresis for up to a certain range of forward scan (Fig. 10) indicates that for each sweep rate there may be a unique current density below which a reversal of current gives $E_p = E_c$. Thus, this current density is an index of resistance of the alloy to localized corrosion in that hysteresis starts only after this current density is exceeded. For the Type 316L stainless steel in Ringer's solution this index appears to be somewhere between 5 and 10 μ A/cm². Beyond this current density, the difference potential (E_c-E_p) indicates the resistance of the area in the hysteresis loop increases, the magnitude of (E_c-E_p) increases, and eventually E_p becomes more active than the rest potential (Fig. 10).

From the point of view of corrosion resistance, a desirable alloy should have not only a very noble value of E_c but also a very noble value of E_p . A noble value of E_p ensures that even if the passivity of the material is somehow destroyed, the material has an excellent chance of repassivation and restricting pit propagation. The low passive current density of Type 316L stainless steel ($\simeq 0.2 \ \mu A/cm^2$) as observed in this study (Fig. 10) and by others [26,29] only indicates that the alloy has an excellent general corrosion resistance, attributed to a very tenacious

passive film on its surface. This however does not furnish any information regarding the resistance of the alloy to localized corrosion which occurs due to the breakdown of passivity. A very active protection potential exhibited in the case where the potential scan is reversed at about 200 μ A/cm² (Fig. 10) indicates that if passivity is destroyed and pits start to grow, they will continue growing instead of being repassivated. In orthopedic devices where the so-called "face" corrosion or fretting corrosion [2] is very common due to mechanical rubbing, it is likely that the passive film will be destroyed causing some pit propagation. Therefore, in determining the resistance of an alloy to crevice corrosion using the cyclic polarization technique it would appear that the alloy must exhibit a very noble protection potential even when the potential scan is reversed at current densities exceeding about 2 decades that of the passive current density. The active protection potential exhibited by Type 316L stainless steel at a scan reversal of about 200 μ A/cm² implies that chances of repassivation of growing pits in implants made of this alloy are limited.

In order to determine whether the large current density observed during hysteresis (Fig. 10) is due to increased surface area of the specimen caused by pitting, the following experiment was performed. A cyclic polarization test, as shown in Figure 10, was first carried out. The rest potential of the specimen was then allowed to stabilize for 2 hours. A second polarization run was then obtained in the same solution. Two such successive runs are shown in Figure 10(a). It is observed that the two consecutive runs yield almost identical results; particularly, the $i_{passive}$ of the two curves are identical. Had there been a large increase in the surface area caused by pitting during the first polarization run,



the i_{passive} in the second run would have been larger than that in the first run. The absence of any difference of i_{passive} between the two runs however rules out the possibility that the high current density during hysteresis is due to the increase in the overall surface area of the specimen.

Effect of Composition on the Polarization Behavior of Stainless Steel

Figure 11 shows typically how various alloying elements influence the polarization behavior of stainless steel. Each polarization curve in the figure represents that of an alloy developed from Type 316L stainless steel as the base material. Copper content between 0 to 3% had no influence on the polarization behavior and all curves were similar to that for the 3% Cu alloy shown in Figure 11. Cr, Ni, and Mo, all improve the corrosion resistance by raising E_c towards the noble direction, while Cu does not cause any significant change. While large hystereses are observed in high Cr and high Ni alloys, hysteresis cannot be observed in the 5% Mo alloy (alloy No. 6 in Table 4) since the breakdown potential for this alloy is above that for the decomposition of water (the increase in current occurring at about 1000 mV vs. SCE for the 5% Mo alloy is due to the breakdown of water).

However, as will be described later, a noble value for the breakdown potential regardless of the value for the protection potential is a desirable feature in limiting crevice corrosion and therefore larger amounts of Cr, Ni and particularly Mo would seem desirable. Unfortunately, high Cr and Mo contents give rise to the formation of δ ferrite and the resultant undesirable two phase microstructures as shown typically in


Figures 12 and 13. However, higher Ni contents prevent the formation of δ ferrite and therefore a single phase austenitic alloy (microstructure shown in Figure 14)with 20% Cr, 25% Ni, 4.5% Mo, and 1.5% Cu was prepared and tested. This alloy is also passive throughout the potential range studied (Figure 11). All the alloys shown in Figure 11 and Type 316L stainless steel in Figure 10 have almost the same value of passive current, indicating that their general corrosion resistances are similar.

Effect of Low pH and High Cl⁻ on the Polarization Behavior of <u>Stainless Steel</u>

Controlled amounts of HCl were added to 1 litre of Ringer's solution containing the specimen and the variation of the open circuit potential was recorded as shown in Figure 15. Addition of 200 ml of 0.2N HCl decreased the pH to 1.5 and added 40 milli equivalents of chloride ion in a solution already containing about 115 meq of Cl $^-$ [33]. The pH of 1.5 and the new Cl⁻ concentration are consistent with those generally observed in crevices [42,43]. All the three alloys in Figure 15 exhibited similar potential fluctuations upon adding HCl. The potential quickly rose in the noble direction, fell off to a very active value and then gradually increased towards the original rest potential. For Type 316L, the potential went as high as +302 mV vs. SCE. The significance of this will be clear on examination of Figure 16 which shows the polarization curves for the three alloys in the above-mentioned acidic medium. The 20% Cr, 25% Ni, 4.5% Mo, 1.5% Cu alloy remained passive while both 17.1% Cr, 11.4% Ni, 5% Mo alloy and Type 316L steel showed hysteresis with a very active value of $E_{\rm p}$. Comparison of Figures 15 and 16 reveals that for Type 316L stainless steel the peak open circuit potential in the noble







Figure 13 Microstructure of 17.1% Cr, 11.4% Ni, 8% Mo alloy (X100).



Figure 14 Microstructure of 20% Cr, 25% Ni, 4.5% Mo. 1.5% Cu alloy (X100).







direction (+302 mV vs. SCE in Fig. 15) exceeds the critical pitting potential (\approx 260-280 mV vs. SCE, Fig. 16) in the same medium. This implies that if sufficient free HCl is generated within a crevice, the potential of Type 316L stainless steel may be temporarily more noble than the critical pitting potential, causing a spontaneous breakdown of passivity. This makes Type 316L stainless steel a less-than-ideal material for use in multi-component orthopedic devices where the chances of crevice corrosion are very high [1].

Effect of Higher Chloride Ion Concentration and Temperature on the Corrosion Resistance of 25% Ni, 20% Cr, 4.5% Mo, 1.5% Cu Alloy

The above alloy remains passive and does not exhibit any hysteresis in Ringer's solution with or without hydrochloric acid (Fig. 11, 16). Therefore, it was felt necessary to study its behavior in a more aggressive chloride medium. Figure 17 shows the results of a polarization test in 4% NaCl solution at 60° C. This solution was chosen because higher chloride ion concentration and higher temperature impair the corrosion resistance of stainless steel [68,69]. The 4% NaCl solution is about 4 times stronger in chloride ion concentration than Ringer's solution. But even this high chloride ion concentration may sometimes be expected within crevices [42,43]. Figure 17 shows that the above alloy indeed breaks down in an aggressive chloride environment, and pronouced hysteresis with a very active value of E_n is observed. The tests in Ringer's solution containing HCl and in 4% NaCl at 60° C were designed to study the polarization behavior of the specimens in simulated crevice environments, rather than the bulk environment. Multi-component orthopedic devices are generally manufactured with in-built crevices. Thus, tests in the crevice environments are likely to give more



realistic information regarding the actual service performance of the alloys under consideration. The results of these studies imply that hysteresis phenomenon is a common feature of austenitic stainless steels in chloride media, and the resulting active protection potentials render them highly susceptible to localized corrosion.

Polarization Tests on Individual Alloying Elements of Austenitic Stainless Steel

Fiugre 18 shows the cyclic polarization curves for iron and molybdenum and Figure 19 shows the curves for nickel and chromium, in Ringer's physiological solution. The purity of all the elements was more than 99.9%. The purpose of these tests was to correlate the polarization characteristics of the individual elements with those of the alloy itself. It is observed that all the four elements exhibit varying degrees of passity and all have different critical pitting potentials. The open circuit potentials and the passive current densities also differ widely. The passivity of chromium is most pronounced; its passive region most extended and the $i_{passive}$ the least of all the elements. All the four elements show varying degrees of hysteresis. The difference potential, (E_c-E_p) , for Cr and Mo is rather small compared to Ni and Fe both of which have E_p values more active than the respective open circuit potentials.

It seems difficult to predict the cyclic polarization behavior of an alloy from that of the constituent elements. Thus, Type 316L stainless steel having a composition of 17.1% Cr, 11.4% Ni, and 2.3% Mo shows considerable hysteresis in Ringer's solution while another austenitic stainless steel having 20% Cr, 25% Ni, 4.5% Mo does not show any hysteresis





in the same solution (Fig. 11).

The above experiments reveal that the polarization behaviors of the individual alloying elements of stainless steel alloy differ. It is also noticed that the bulk composition of the alloy influences its polarization behavior. However, these tests do not explain how the change of composition is correlated to the polarization behavior. The need to investigate the role of the passive film on the surface of the alloy was felt at this point. It is reasonable to believe that depending on the bulk composition of the alloy the composition of the passive film varies; and ultimately the composition of the passive film, rather than the bulk composition, determines the corrosion behavior of the alloy. Subsequent studies to analyze the passive films of various alloys by Auger electron sepectroscopic technique were prompted by this need to ascertain the composition of the passive films.

Cyclic Polarization Behavior of 65% Co - 30% Cr - 5% Mo Alloy

Figure 20 shows the polarization curve for the as-cast alloy which is widely used in orthopedic implants. The $i_{passive}$ of this alloy is similar to that of Type 316L stainless steel (Fig. 10), as was also observed by Mueller and Greener [29] and Cahoon et al [9]. This signifies that the general corrosion resistance of these two alloys is probably the same. However, the cast Co-Cr-Ho alloy has a nobler critical pitting potential (\approx 500 mV in Fig. 20) compared to Type 316L stainless steel (320 \approx 340 mV in Fig. 10). This implies that the cast Co-Cr-Mo alloy has greater resistance to pitting corrosion than Type 316L stainless steel. A nobler critical pitting potential for the Co-Cr-Ho alloy was also reported by other authors [9,73,74]. An examination of the transpassive region in



Figure 20 shows that after about 10 μ A/cm², the transpassive current increases less rapidly, giving rise to a secondary passivity. The secondary passivity however can be predicted from the two phase microstructure of the as-cast alloy as shown in Figure 21.

The cyclic polarization curve in Figure 20 gives very significant information. It is noticed that the cast Co-Cr-Mo alloy has a relatively noble protection potential and also the E_p for this alloy is very insensitive to the amount of pit propagation during the forward scan. For the two different values of scan reversal, E_p varies from about 420 mV to 400 mV vs. SCE and the difference potential $(E_c - E_p)$ varies from 80 to 100 mV. A noble value of ${\rm E}_{\rm p}$ implies that the chances of repassivation of growing pits are higher. And the fact that ${\tt E}_{\tt p}$ is not sensitive to the amount of forward scan ensures that irrespective of the amount and duration of pit propagation the potential range where the material can be repassivated remains relatively constant. Compared to Type 316L stainless steel, the Co-Cr-Mo alloy is thus more desirable. For Type 316L stainless steel (Fig. 10) E_p is not only more active but also very much dependent on the amount of pit propagation during the forward scan. When the scan was reversed at about 200 μ A/cm², E_p for Co-Cr-Mo alloy was about 400 mV and that for Type 316L about -50 mV vs. SCE giving a difference of 450 mV.

Fiugre 22 shows the cyclic polarization curve of a hot worked and annealed specimen of 65% Co - 30% Cr - 5% Mo alloy. The ingot was hot swaged at 1150° C by 20% on diameter, annealed for 2 hours at 1050° C and water quenched. Similar treatments [16] improve the corrosion resistance because of improvement in microstructure as shown in Figure 23. A more homogeneous finer grained matrix structure and more uniform distribution



Figure 21 Microstructure of as-cast 65% Co, 30% Cr, 5% Mo alloy (X100).

1 : 1





Figure 23 Microstructure of hot worked and annealed 65% Co, 30% Cr, 5% Mo alloy (X100).

of carbides are obtained. The polarization curve of the hot-worked alloy is however very similar to the as-cast alloy except for a marginal improvement of E_c , about 540 mV for the hot-worked alloy compared to about 500 mV for the as-cast one. There is also a slight improvement of E_p by about 30 mV in the case of the hot worked alloy. Furthermore, the hot-worked sample does not exhibit any secondary passivity. This appears to be due to its uniform microstructure.

Effect of Low pH and High Cl^- on the Polarization Behavior of 65% Co - 30% Cr - 5% Mo Alloy

Figure 24 shows the effect of HCl addition on the as-cast 65% Co -30% Cr - 5% alloy, as was also done for stainless steels (Figure 15). The variation of the open circuit potential, shown in Figure 24 is caused by the addition of 200 ml of 0.2 N HCl to one litre of Ringer's solution containing the specimen. It is observed that compared to the stainless steels (Fig. 15) the fluctuation of potential for the Co-Cr-Mo alloy is considerably less severe, implying that the cobalt based alloy may be less sensitive to hydrochloric acid.

Figure 25 shows the polarization curve for the cast Co-Cr-Mo alloy in Ringer's solution with hydrochloric acid added. It is observed that the critical pitting potential E_c in this solution is about 800 mV vs. SCE and the protection potential E_p is approximately 750 mV vs. SCE. Thus both E_c and E_p are nobler than in the case where no hydrochloric acid is added (Fig. 20). On the other hand, in Type 316L stainless steel both E_c and E_p move in the active direction when HCl is added to Ringer's solution (Fig. 16). The difference of behavior between Type 316L stainless steel and the Co-Cr-Mo alloy in the above acidic medium is thus very significant. While the stainless steel becomes more susceptible to localized corrosion,







the Co-Cr-Mo alloy exhibits an opposite tendency. Also, one observes that the peak potential of about 150 mV in Figure 24 is considerably less than 800 mV, the critical pitting potential in the same medium (Fig. 25). Thus, in the Co-Cr-Mo alloy, unlike the stainless steel, there is no danger of a spontaneous breakdown of passivity due to the accumulation of hydrochloric acid in a crevice configuration.

The cyclic polarization curve for the as-cast Co-Cr-Mo alloy in 4% NaCl solution at 60° C is shown in Figure 26. The values of E_{c} and E_{p} are slightly active to those in Ringer's solution (Fig. 20). This implies that the E_{c} and E_{p} values of the cobalt based alloy are rather insensitive to higher chloride ion concentrations and temperature.

In comparison to Type 316L, or even more corrosion resistant stainless steels, the 65% Co - 30% Cr - 5% Mo alloy has a number of distinct advantages. It has nobler values of E_c and E_p . Also its difference potential, E_c-E_p , is very small, about 80 mV compared to about 400 mV for Type 316L stainless steel. Its E_p is insensitive to the amount of pit propagation. Also its E_c and E_p are not much sensitive to higher chloride ion concentrations and higher temperature. Thus, the Co-Cr-Mo alloy appears to be more immune to localized corrosion than any of the stainless steel alloys investigated in the present study.

In order to determine the influence of molybdenum on the polarization behavior of the cobalt based alloy, tests were conducted on a molybdenum free 70% Co - 30% Cr alloy. Figure 27 shows the cyclic polarization curve of the as-cast alloy. It is readily observed that the polarization curve of this molybdenum-free alloy is similar to that for the alloy containing 5% Mo. The values of E_c (\simeq 420 mV vs. SCE) and







 E_p (~ 360 mV vs. SCE) of the 70% Co - 30% Cr alloy are however somewhat more active than the 65% Co - 30% Cr - 5% Mo alloy (Fig. 20). Also the rest potential in the Co-Cr alloy is +40 mV vs. SCE compared to about -100 mV vs. SCE for the Co-Cr-Mo alloy (Fig. 20). But the influence of molybdenum in the cobalt based alloy is not as significant as in the case of stainless steel (Fig. 11).

The cyclic polarization curve in Ringer's solution of pure cobalt, the major constituent of the Co-Cr-Mo alloy, is shown in Figure 28. It is observed that cobalt has a very active rest potential (\simeq -600 mV vs. SCE), has a passive region with an i passive in the range of 30 to 60 $\mu\text{A/cm}^2$ and an E $_{\text{C}}$ of about -180 mV vs. SCE. The hysteresis in the polarization curve is not pronounced and the resulting E_p is about -240 mV vs. SCE. The difference potential, $(E_c - E_p)$ is thus only 60 mV which is comparable to the magnitude of that of the 65% Co - 30% Cr - 5% Mo alloy (Fig. 20). The polarization curves for Mo and Cr are shown in Figures 18 and 19 respectively. It appears that as in the case of Type 316L stainless steel the Co-Cr-Mo alloy also exhibits a polarization curve which cannot be correlated explicitly to that of any one of the constituent elements. However, it can be qualitatively predicted that the major constituents namely, Fe in Type 316L stainless steel and Co in 65% Co - 30% Cr - 5% Ho have a major influence in governing the shape of the polarization curves of the respective alloys.

4.2 Atomic Absorption Analysis of Corrosion Products of Type 316L Stainless <u>Steel and 65% Co - 30% Cr - 5% Mo Alloys</u>

The purpose of the atomic absorption tests was to determine the amount of each elements of an alloy going into the electrolyte during a



dissolution process. Contrary to polarization curves which give only the overall dissolution characteristics of the alloy, the atomic absorption tests show how much of each of the constituent elements is involved in the process of dissolution. Table 6 shows the results of analyses of solutions after polarization tests were conducted - one for a Type 316L stainless steel and the other for an as-cast Co-Cr-Mo alloy. During cyclic polarization tests, the potential was held constant for 2 hours at 200 mV more active to the critical pitting potential, as already explained in section 3.3 of chapter III. The solution was analyzed for individual elements after the end of the polarization tests. The Ringer's solution, although made of reagent grade chemicals of highest purity available, contains trace elements. Accordingly the solution itself was analysed for various elements on the atomic absorption spectrometer. Table 7 shows the concentrations of various elements in Ringer's solution before polarization tests. The concentrations shown in Table 6 are the values after necessary corrections for the trace elements are already done.

It is readily seen that the percentage composition of each of the elements in the solution after completion of the polarization test corresponds approximately to that in the bulk composition of the alloy, especially in the Type 316L stainless steel. In the case of the Co-Cr-Mo alloy the % of Mo in the solution (13%) seems to be rather high compared to the Mo content of the alloy (5%). The above results of atomic absorption analysis generally confirm the observations of Suzuki et al [50] who also analyzed by atomic absorption technique the distribution of metallic ions within the anolytes of various artificially induced stainless steel pits. They observed that the distribution of various elements in

TABLE 6

RESULTS OF ATOMIC ABSORPTION ANALYSIS OF RINGER'S SOLUTION AFTER ANODIC POLARIZATION OF TYPE 316L STAINLESS STEEL AND 65% Co - 30% Cr - 5% Mo ALLOY

Type of Alloy	Elements	Amount (ppm)	Арр %
316L Steel 17.1% Cr, 11.4% Ni, 2.3% Mo)	Fe	1.31 ± 0.04	65
	Cr	0.41 ± 0.02	20
	Ni	0.25 ± 0.01	12
	Мо	0.06 ± 0.03	3
65% Co - 30% Cr - 5% Mo	Со	0.47 ± 0.02	53
	Cr	0.30 ± 0.01	34
	Мо	0.12 ± 0.03	13

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TABLE 7

ATOMIC ABSORPTION ANALYSIS OF TRACE ELEMENTS IN RINGER'S SOLUTION

Elements	Amount (ppm)
Ni	0.13 ± 0.01
Cr	0.005 ± 0.001
Со	0.33 ± 0.02
Fe	0.09 ± 0.01
Мо	too low for analysis

the anolyte was in the same proportion to that in the bulk metal. These results imply that no selective dissolution occurs in localized corrosion of stainless steels.

4.3 Auger Electron Spectroscopic Tests on the Oxide Films of Stainless Steel and Co-Cr-Mo Alloys

Figure 29 shows the profile curves obtained by Auger electron spectroscopic analysis on oxide films of a Type 316L stainless steel sample which was kept, prior to Auger analysis, in the Ringer's solution for about 4 days. Si, Mo, O, Cr, Ni and C profiles are shown on the diagram where the height of each mark above the 0-0 zero line is approximately proportional to the concentration. The X axis (0-0 line) represents the time which can be correlated to the penetration of the electron beam into the oxide layer and beyond. The distance - milliamp current relationship is linear when the accelerating voltage is held constant. Thus, if a 2 KV 1 MA beam penetrates about 3 Å/minute in the oxide layer, a 2 KV 5 MA beam will penetrate 15 Ă/minute. Oxide films on samples of 17.1% Cr, 11.4% Ni, 5% Mo alloy (no. 6 in Table 4) and 20% Cr, 25% Ni, 4.5% Mo, 1.5% Cu alloy (no. 10 in Table 4) and a 65% Co, 30% Cr, 5% Mo alloy were also analyzed. Typical spectra and profile curves, including the one shown in Figure 29 are shown in the Appendix II.

It is readily seen from Figure 29 that the oxygen concentration is very high on the surface, signifying the presence of the oxide layer. The oxygen concentration however soon falls off very rapidly to a steady level. The entire oxygen profile thus gives a picture of oxygen diffusion from the surface to the bulk material. An interval of 5 minutes is shown between two arrows in the diagram. If it is assumed that the 1 mA beam

90.



penetrates roughly 3 \AA /minute [75], the thickness of the oxide layer is approximately 30-50 \AA . It is also observed that the diffusion affected zone is large compared to the oxide layer thickness.

Examination of the profiles of the major alloying elements reveals that the nickel concentration reaches a maximum value somewhere between the surface and the bulk material, probably between 50 and 150 $\stackrel{0}{\text{A}}$ below the surface. The molybdenum concentration is very low on the surface and increases steadily from the surface to the bulk material, save for minor fluctuations. The chromium concentration reaches a maximum in the vicinity where the oxygen concentration is decreasing and the nickel concentration is increasing. The peak occurs at roughly 30-40 $\stackrel{0}{\text{A}}$ from the surface.

Since the height of the profile curve above the zero line in Figure 29 is approximately proportional to the concentration, a plot of composition along the profile relative to the bulk composition can be obtained. Figure 30 shows such a plot for chromium for two runs each of the three stainless steel alloys. The curve corresponding to 316L, Run 1 is obtained from Figure 29 where the bulk chromium composition corresponding to the point at the end of the spectrum is assumed to be 17.11%, the chromium content of the alloy. The rest of the curves in Figure 30 has been obtained from profile curves shown in the Appendix II. The distance along the X axis is obtained on the basis of penetration of a 1 mA beam by roughly 3 Å/minute. Though the composition vs. distance correlation in Figure 30 is not exact, it appears to be quite suitable for comparison purposes. Figure 31 shows the chromium composition vs. distance on a linear scale to permit a closer examination of the first 50 Å, i.e., essentially





the oxide layer. The similarity between the chromium profiles of all the three alloys is very striking. It is noticed that within first 10 Å, the amount of chromium is relatively constant and is generally lower than that in the bulk. Between 10 and 50 Å, the amount of chromium increases very sharply to a peak value of 20-25% except in 316L Run 1 where the peak is about 35%. In 316L, Run 1 and Run 2 correspond to the first run on two different samples. For the other two alloys, Run 1 and Run 2 correspond to two separate runs on two different spots of the same sample. It appears that for these two alloys, the profile for Run 2 is different from that of Run 1. This is possibly due to some cleaning of the entire sample during the first run. The profiles for Run 2 of these two alloys however follow a similar pattern. It is interesting to note that the chromium peaks in these cases are not so pronounced. This may be due to the depletion of chromium on the oxide layer caused by the cleaning action.

A comparison of the chromium content in the vicinity of the oxide layer for the three alloys in Figures 30 and 31 reveals some interesting results. It is observed that between 0 to 10 Å, type 316L stainless steel has the minimum chromium content, varying between 5 to 7%. The other two alloys namely 20% Cr, 25% Ni, 4.5% Mo, 1.5% Cu and 17.1% Cr, 11.4% Ni, 5% Mo have considerably higher chromium in the 0 to 10 Å region. The higher chromium content in the oxide layer of the 20% Cr, 25% Ni, 4.5% Mo, 1.5% Cu alloy is expected because of its higher bulk chromium content. However, the 17.1% Cr, 11.4% Ni, 5% Mo alloy has the same amount of chromium in the bulk as in Type 316L stainless steel. But it has almost 2 to 3 times more chromium in the oxide layer than that of Type 316L steel. The passivity of an alloy is generally governed by the surface passive

film. The higher chromium content in the outer oxide layer of the 17.1% Cr, 11.4% Ni, 5% Mo steel thus accounts for its greater passivity over Type 316L stainless steel in Ringer's solution (Fig. 11). The major difference between these two alloys is that while 316L has 2.3% Mo in the bulk, the 17.1% Cr, 11.4% Ni, 5% Mo alloy has 5% Mo. This suggests that a higher amount of molybdenum improves the composition of the oxide layer by astabilizingg a higher amount of chromium in the oxide layer. This appears to be one of the possible explanations of the beneficial effect of molybdenum in combating localized corrosion of stainless steel.

Figures 32 and 33 show the nickel profiles obtained by the same procedures as for chromium profiles of Figures 30 and 31. All the three alloys exhibit a similar course for nickel, namely a relatively low and steady value between 0 to 20 \mathring{A} , a peak at roughly 50 to 70 \mathring{A} which levels off to a lower value around 100 $\mathring{\text{A}}$. The 20% Cr, 25% Ni, 4.5% Mo, 1.5% Cu alloy has a considerably higher amount of nickel throughout its course. This is expected because of the higher amount of nickel in the bulk of this alloy. It is interesting to note that maximum concentration of chromium and nickel occurs at different distances from the surface. Nickel reaches a peak value at a distance where the chromium begins to level off from the peak value and chromium concentration reaches a peak value in the vicinity where nickel concentration begins to increase towards a peak value. This indicates an overall balance of nickel plus chromium in the oxide and diffusion layer.

Figures 34 and 35 show the molybdenum concentration profiles for the three alloys. It is observed that the molybdenum concentration is very low and has practically the same value between 0 to 10 $\stackrel{\circ}{A}$ for all the three












alloys. Roughly beyond 10 Å, the concentration of molybdenum increases gradually accompanied by very minor fluctuations. The molybdenum concentration for the 17.1% Cr, 11.4% Ni, 5% Mo alloy is generally higher throughout because of its higher bulk molybdenum.

Figures 36 and 37 show the profiles for iron concentration for the three alloys. The amount of iron in the bulk was obtained by subtracting the sum of the amount of various alloying elements from 100%. The rest of the iron profile was then obtained by comparison with the bulk iron concentration. The iron signal was monitored only in Run 2 for each of the three alloys. It is observed that iron concentration is low and relatively constant within 0 to 10 \mathring{A} beyond which the concentration rises very quickly to a maximum value at about 50 \mathring{A} and remains practically steady throughout.

Figures 38 and 39 show the oxygen profiles in arbitrary units for the three alloys. The oxygen concentration is relatively steady at a high value within the initial 10-20 Å. The concentration then falls off sharply and becomes very low at about 50 Å. Thus, the oxide film may be assumed to extend up to anywhere between 10 to 50 Å. The depth of the oxide layer is more or less the same for all the three alloys, though for 316L it appears to be slightly more extended than the other two alloys.

Figures 40 and 41 show the carbon profiles for the three alloys. The concentration is high at the outer 5 $\stackrel{\circ}{A}$ of the oxide layer. The concentration then falls off but rises again and fluctuates. Part of the higher carbon concentration at the outer oxide layer is due to contamination from handling and cleaning. On examination of the various spectra corresponding to Run 2 on Type 316L stainless steel (details in Appendix II)





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it is observed that the carbon peaks for spectra 1 and 2 are different from those for the remaining four spectra. The carbon peaks in spectra 1 and 2 have a sharp positive maximum before the large negative minimum. The ratio of these are about 4/23 for spectrum 1. Spectra 4-6 all show two small negative peaks before the large negative peak. This is related to carbon in a "bound" state, as opposeddto being an "adsorbed" molecule. Thus, the carbon observed is not simply contamination from handling and or cleaning, but a good part of it is integral with the oxide layer.

The silicon profiles are shown in Figures 42 and 43. The silicon signal was monitored in Run 1 only of all the three alloys. Silicon was present at detectable levels up to approximately 40 Å from the surface.

Sulphur, phosphorus, calcium and occasionally copper were detected in the outermost layer of the oxide film. All of these elements disappeared in the bulk region.

In the profile curves discussed so far, it is assumed that the height of each mark above the 0-0 line (X-axis) is proportional to the concentration. However, interpretation in terms of composition depends on the gain set for each channel and relative spectral line strength. For the lines used for the analyses of the three alloys discussed so far the channel gain settings and the relative spectral line strength are shown in Appendix II (Table II, Appendix II). Also, one should remember that the sensitivity of a signal may not be linear. However, for a comparative study of various alloys the approximation in the present study is acceptable.

Since the composition of the major constituents in the oxide layer has been approximately determined, an attempt can be made to formulate the





overall composition of the oxide film. The percentage composition by weight of each of the constituents has been converted to the atomic composition and the following results have been obtained:

Type 316L	stainless	steel:	10% M,	90% 0	
		· · ·	· ·		
17.1% Cr,	11.4% Ni,	5% Mo alloy:	29% M,	71% 0	

20% Cr, 25% Ni, 4.5% Mo, 1.5% Cu alloy: 36% M, 64% O where M and O stand for the combined metallic elements and oxygen respectively. Detailed calculations are shown in Appendix III. It is interesting to note that in Type 316L stainless steel the amount of oxygen is highest, about 9 times that of the combined metallic elements; whereas in the 20% Cr, 25% Ni, 4.5% Mo, 1.5% Cu alloy the amount of oxygen is the lowest among the three alloys, roughly twice that of the metallic elements. This suggests that in the oxides of Type 316L steel the metals are in higher valence statesr than in the other two alloys. In view of the discussions in section 2.4 of Chapter II regarding the nature of the passive film, it is felt justified not to assign a definite formula because not only amerthere complex_oxides; but there have beyomesoxygenyignthe adeoubed state tate.

It seems likely that the oxides with metals in higher valence states in the passive film of Type 316L stainless steel render this alloy less stable compared to the other two alloys. The higher oxides can be readily reduced to the lower ones and in the process can provide an electron sink for the anodic dissolution reaction of the exposed regions of the basis metal. Thus the following reactions can easily take place [76]:

$$Fe_20_3 + 6H^+ + 2e = 2Fe^{++} + 3H_20(E_1^0 = +0.723)V)$$
 (1)

Fe = Fe⁺⁺ + $@e(E_2^0 = -0.44V)$ (2)

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The large ddrivingg e.m.f. $E = E_1^0 - E_2^0 = 1.17V$ gives rise to a large negative net chemical free energy change for this reaction. This implies that the overall reaction can take place spontaneously. The net result is that Fe^{+++} ions in the lattice are either removed directly into solution as Fe_{aq}^{++} or reduced to the ferrous state while still in the lattice. Either process promotes the formation of vacancies, where the lattice energy is abnormally large, in the surface, e.g. [76]:

$$2Fe_{lattice}^{+++} = 2Fe_{lattice}^{++} + \Box_{oxygen}$$
$$+ Fe_{aq}^{++} + H_2^0 \qquad (3)$$

and so facilitates dissolution.

Similarly CrO₄ ions, where chromium is at a higher valence state, can provide an electron sink to facilitate the reaction:

 $2Cr0_4^{-} + 2Fe + 4H^+ = Fe_20_3 + Cr_20_3 + 2H_20$ (4)

This causes Fe_20_3 to precipitate alongsidele Cr_20_3 .

It appears that the difference of composition of the passive film may well explain the difference of electrochemical polarization behavior of the bulk specimens of the three alloys, namely 17.1% Cr, 11.4% Ni, 2.3% Mo (Type 316L); 17.1% Cr, 11.4% Ni, 5% Mo; 20% Cr, 25% Ni, 4.5% Mo, 1.5% Cu, as observed earlier (Fig. 11). Type 316L has a film composition where the metals are in their higher valence states to form the oxides. As explained in equation (3), these oxides will promote formation of vacancies on the surface. Since conductivity is directly related to vacancy concentration, the film in this case is initially more conducting. With the application of an external potential in the noble direction, the conductivity progressively increases. Polarizable aggressive anions

such as Cl⁻ introduce an additional electrical field. When the electric field in the passivating film is sufficiently great, which will occur at a lower applied potential in Type 316L stainless steel than in the other two alloys, metal cations are pulled outwards or Cl⁻ pulled inwards [77] through the film. Thus, there exists a critical pitting potential, E_c , above which appreciable corrosion occurs at the "contaminated" points and pitting initiates locally. The strength of the induced field is greater at higher concentration of the aggressive chloride anion. Therefore, a lower applied potential is necessary to break down the film. The results of the electrochemical polarization tests supports this theory. The 20% Cr, 25% Ni, 4.5% Mo, 1.5% Cu alloy does not exhibit a breakdown of passivity in Ringer's solution (Fig. 11), whereas in 4% NaCl solution at 60° C, it readily breaks down (Fig. 17).

Figure 44 shows the profiles of various elements monitored in a 65% Co, 30% Cr, 5% Mo specimen. As in the case of stainless steel, here also the oxygen concentration is very high on the surface and falls off rapidly. For the chromium signal, a chrome depletion behind the chrome oxide band is noticed. Cobalt content is low on the surface, but soon rises to a high steady value. Also, cobalt makes up the difference in the chromium depletion zone. Initially Cl and Mo signals interfere. It was assumed that the Cl was a surface contaminant and the Cl signal was monitored. It fell and rose again. The increase was interpreted as the Mo signal. Typical spectra and sprofiles nare shown in the Appendix II.

Profiles of individual elements were obtained applying procedures similar to those of the stainless steel alloys. The cobalt profile is



shown in Figures 45 and 46. The amount of cobalt is low up to about 10 Å, then it increases rapidly and reaches a maximum at about 60-70 Å. The chromium composition as shown in Figures 47 and 48 is steady between 0 to 10 Å; it reaches a maximum at around 30-40 Å but then falls off to a smaller value and fluctuates along the diffusion layers. The chromium composition on the surface in the second run is found to be higher than in the first run. This may be due to the cleaning of the entire sample during the first run. It is interesting to note that similar effect for chromium also occurred in the stainless steel alloys (Figs. 30, 31). Molybdenum (Figs. 49, 50) on the contrary exhibits an opposite behavior from chromium. Here the Run 2 shows a lower composition compared to Run 1. In both cases there is a Mo depletion zone around 20-25 Å beyond which the composition increases steadily all along the diffusion zone. The oxygen profile is shown in Figures 51, 52 and Figures 53,54 show the carbon profile.

As in the case of stainless steel, the composition of the surface film has been calculated. Calculations for Run 2 is shown in Appendix III. The composition is found to be 17% M; 83% 0. Thus, the film in this alloy has oxides with metals in their high valency states. The critical pitting potential of this alloy in Ringer's solution is roughly 500 mV vs. SCE (Fig. 20), a value in between the critical pitting potentials of Type 316L and 20% Cr, 25% Ni, 4.5% Mo, 1.5% Cu alloy (Fig. 11). This is expected because of the oxide composition of the cobalt based alloy also lies in between that of the above two stainless steel alloys. However, in 4% NaCl solution at 60° C (Fig. 17), the 20% Cr, 25% Ni, 4.5% Mo, 1.5% Cu alloy starts to break down at about 4506mV vs. SCE, whereas the cobalt





















based alloy is relatively immune in higher chloride concentration (Fig. 26). The possible reason for this may be the high concentration of chromium (30%) in the Co-Cr-Mo alloy. It was discussed in section 2.4 in Chapter II that the critical chromium content for the Co-Cr system is only 8%. Thus with 30% Cr, this alloy has considerable amount of d electron band unfilled which favours chemisorption of oxygen. The Cl⁻ ion competes with oxygen ion for preferential adsorption on the metal surface. As long as the affinity for oxygen remains greater than that for Cl⁻, passivity is maintained. This probably accounts for the immunity of the 65% Co, 30% Cr, 5% Mo alloy to higher chloride ion concentration.

After the reversal of the potential scan in a pobarization process, the current density becomes very low and comparable to the $i_{passive}$ at a potential called protection potential, E_p . It is likely that at E_p the film completely regains its original passive structure. If the passive film is completely destroyed during the pitting process, repassivation necessitates the formation of the film again. Thus the repassivation process may be similar to that of the formation of the passive film in the initial stages of immersion of the specimen.

Accordingly, the open circuit potential vs. time curves of a Type 316L stainless steel and a 65% Co, 30% Cr, 5% Mo sample were obtained as shown in Figure 55 in log scale and Figure 56 in linear scale. It appears that in the initial period the potential changed very differently for the above two alloys. In the Type 316L sample, the potential fell off by about 100 mV in the active direction in about 40 seconds after immersion of the specimen. The potential remained steady at about -200 mV vs. SCE for about 300 seconds and then rose gradually in the noble direction. The





potential of the Co-Cr-Mo alloy changed by a very small amount from -368 mV to -382 mV in the first 10 seconds. It remained steady at -382 mV for only 30 seconds and then rose gradually in the noble direction.

It is reasonable to believe that the passive film in the electrolyte forms soon after its immersion. Therefore, the potential-time curve in the initial period reflects a mechanism of formation of the passive film. It is clearly seen that the films on the stainless steel and on the Co-Cr-Mo alloys form by different mechanisms. The large drift of potential towards the active direction for the stainless steel probably implies a large activation energy barrier for the formation of the film, whereas the energy barrier for the Co-Cr-Mo alloy is much smaller.

A comparison of the protection potentials of the above two alloys (Figs. 10 and 20) shows that the protection potential, E_p , for Type 316L stainless steel is about -60 mV vs. SCE, that is roughly 120 mV active to its rest potential. On the other hand the E_p of the Co-Cr-Mo alloy is about +400 mV vs. SCE, that is roughly 80 mV active to its pitting potential. The rapid increase in current at the critical pitting potential, E_c , for the 316L stainless steel (Fig. 10) suggests that the pitting attack is quite severe and the passive film is probably completely destroyed. The reverse process of the film formation may not be thermodynamically possible in this case until the applied potential reaches a sufficiently active value so that the large energy barrier against the film formation is overcome. For the Co-Cr-Mo alloy, the passive film appears not to be completely destroyed even beyond the critical pitting potential. This is evident from the relatively gradual rise of current beyond E_c (Fig. 20). Hence, a change of applied potential in the active

direction by about 80 mV reduces the electrostatic field across the film sufficiently to enable a complete reconstruction of the passive film.

One final point regarding the Auger analysis is in order. All the spectroscopic analyses were performed on passive films formed during a period of 3-4 days' immersion of the specimens. More information can be obtained if the specimens are progressively anodically polarized to various ranges of potential up to and beyond the critical pitting potential and back to the protection potential, and the films on the surface are Auger analyzed at each stage. This may give a detailed picture of the dynamic processes involved in passivity, its breakdown and the repassivation process. Further studies in this direction are highly recommended.

CHAPTER 5

CONCLUSIONS

The following conclusions can be drawn from the various investigations and results of this study.

- It is confirmed that the protection potential is not a unique material property but varies with the amount of localized attack induced by polarization.
- 2. If sufficient free HCl is generated within a crevice, the potential of Type 316L stainless steel may exceed in the noble direction the critical pitting potential, causing spontaneous breakdown of passivity. Thus, Type 316L stainless steel does not appear to be ideal for use in orthopedic implants.
- 3. All the three alloying elements, namely Cr, Ni, and Mo improve the corrosion resistance of stainless steel by shifting the critical pitting potential, E_c , in the noble direction. However, molybdenum appears to be the most effective in imparting resistance to localized corrosion.
- 4. Hysteresis and a very active protection potential are common features of all the stainless steel alloys considered. Thus, if passivity is somehow destroyed in these alloys, pits would propagate without interruption. Therefore, austenitic stainless steels should not generally be recommended in multi-component orthopedic devices where the risk of crevice corrosion is very high.
- 5. It is confirmed that in Ringer's solution 65% Co, 30% Cr, 5% Mo alloy has a critical pitting potential about 150 mV nobler than Type 316L

stainless steel. This implies that the above cobalt based alloy has greater resistance to pitting corrosion in human physiological environment than Type 316L stainless steel.

- 6. For the same value of current reversal ($\simeq 100 \ \mu A/cm^2$), the Co-Cr-Mo alloy exhibits about 450 mV nobler protection potential than Type 316L stainless steel. This indicates that chances of repassivation of growing pits in the cobalt based alloy are considerably higher.
- 7. The protection potential of the Co-Cr-Mo alloy is relatively insensitive to the amount of impressed current during the forward scan, and the chloride ion concentration and acidity of the electrolyte. The protection potential of the stainless steel alloys varjesoconsiderably with the babove aparameters. The hus, here Co-Cr-Mo alloy is more desirable as an orthopedic implant material.
- 8. The atomic absorption analysis shows that the distribution of various elements in Ringer's solution after the anodic polarization test is generally in the same proportion to that in the bulk 316L and Co-Cr-Mo alloys. This implies that no selective dissolution occurs duing anodic polarization of these alloys.
- 9. The composition of the protective film on the surface of three stainless steel alloys and one Co-Cr-Mo alloy has been investigated by Auger spectroscopic analysis. It appears that the composition of the film varies with the bulk composition. For Type 316L stainless steel, the film appears to have oxides with metals in higher valence states compared to the oxides of the other two stainless steel alloys. This possibly accounts for the more active

critical pitting potential of Type 316L stainless steel.

10. Comparison of the chromium profile of Type 316L stainless steel having 17.1% Cr, 11.4% Ni, 2.3% Mo and the alloy having 17.1% Cr, 11.4% Ni, 5% Mo shows that the latter alloy has roughly 2 to 3 times more chromium on the outer first 10 Å of the film. This accounts for the greater stability of the passive film, leading to a nobler critical pitting potential of the latter alloy. Both the alloys have the same amount of chromium in the bulk; but the latter has 5% Mo compared to 2.3% Mo in the former. Therefore, it appears that molybdenum imparts passivity to stainless steel by stabilizing mome chromium on the outer surface of the protective film.
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APPENDIX I

METALLIC IMPLANT MATERIALS AND COMPOSITIONS 31

1. Stainless Steel Bars and Wire

Element	Percent		
	Туре А	Туре В	
Carbon	0.08 max	0.03 max	
Manganese	2,00 max	2.00 max	
Phosphorus	0.03 max	0.03 max	
Sulfur	0.03 max	0.03 max	
Silicon	0.75 max	0.75 max	
Chromium	17.00 - 20.00	17.00 - 20.00	
Nickel	10.00 - 14.00	10.00 - 14.00	
Molybdenum	2.00 - 4.00	2.00 - 4.00	
Iron	Balance	Balance	
Element	Min. %	Max. %	
Chromium	27.0	30.0	
Molybdenum	5.0	7.0	
Nickel	-	2.5	
Iron	-	0.75	
Carbon	-	0.35	
Silicon	-	1.00	
Manganese	-	1.00	
Cobalt	Balance	Balance	

2. Cast Co-Cr-Mo alloys.

Element	Min. %	Max. %
Chromium	19.0	21.00
Tungsten	14.0	16.0
Nickel	9.0	11.0
Iron		3.0
Carbon	0.05	0.15
Silicon		1.00
Manganese		2.00
Cobalt	Balance	Balance

4. Ti 6 Al-4 V alloys.

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Element	Composition %
Nitrogen, max.	0.05
Carbon, max.	0.08
Hydrogen, max.	0.0125
Iron, max.	0.25
Oxygen, max.	0.13
Aluminum	5.5 - 6.5
Vanadium	3.5 - 4.5
Other elements	0.1 each max. or 0.40 total
Titanium	Remainder

5. Titanium

Element	Composition %	Tolerance
Nitrogen	0.07	+0.02
Carbon	0.15	+0.02
Hydrogen	0.02	+0.002
Iron	0.50	+0.15
0xygen	0.31 to 0.40	+0.04

APPENDIX II

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Table II

Element	F 5	Relative Signa Strength, Pure	al e Std.	Chemical Setting	Gàin	- - -
С		1/2		5		
0		4		1		
Si		2		10		
Cr		1/4		10		
Ni		1		10		
Fe		1		2		
Мо				5		
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APPENDIX III

CALCULATIONS FOR APPROXIMATE COMPOSITION OF OXIDE FILMS

1. Type 316L staindess steel

The weight percentage of the major elements are (from Run 2) as follows.

Hence, $0 = 100 - 27.9 \approx 72\%$. Let M stand for all the metals

combined.

Hence, At% M =
$$\frac{\frac{17}{56} + \frac{7}{52} + \frac{3.5}{59} + \frac{0.4}{906}}{\frac{17}{56} + \frac{7}{52} + \frac{3.5}{59} + \frac{0.4}{96} + \frac{72}{16}} \simeq 0.10 = 10\%$$

Hence, the composition is

2. 17.1% Cr, 11.4% Ni, 5% Mo alloys

The weight percentage of the major elements are as follows (Run 2).

Fe - 25%
Cr - 25%
Ni - 7%
Mo -
$$0.6\%$$

57 6

Hence, $0 = 100 - 57.6 \simeq 42\%$.

Therefore, At% M =
$$\frac{\frac{25}{56} + \frac{25}{52} + \frac{7}{59} + \frac{0.6}{96}}{\frac{25}{56} + \frac{25}{52} + \frac{7}{59} + \frac{0.6}{96} + \frac{42}{16}} \simeq 0.29 = 29\%$$

Hence, the composition is:

29% M, 71% O.

3. 20% Cr, 25% Ni, 4.5% Mo, 1.5% Cu alloy

The weight percentage of the major elements are as follows (Run 2).

Hence, $0 = 100 - 65.6 \approx 34\%$.

~ /

Therefore: A Million

At% M =
$$\frac{\frac{24}{56} + \frac{20}{52} + \frac{21}{59} + \frac{0.6}{96}}{\frac{24}{56} + \frac{20}{52} + \frac{21}{59} + \frac{0.6}{96} + \frac{34}{16}} \simeq 0.36 = 36\%$$

Hence, the composition is:

36% M, 64% O.

4. 65% Co, 30% Cr, 5% Mo alloy

The percentage by weight of the major elements are obtained from Run 2.

Co - 17%Cr - 23%Mo - <u>1%</u> 41%

Hence 0 = 100 - 41 = 59%.

Therefore At% of the combined metals.

At% =
$$\frac{\frac{17}{59} + \frac{23}{52} + \frac{1}{96}}{\frac{17}{59} + \frac{23}{52} + \frac{1}{96} + \frac{59}{16}} \simeq 0.17 = 17\%$$

Hence, the oxide film consists of;

17% M, 83% O.