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**EFFECTS OF NOBLE-METAL ION IMPLANTATION ON
CORROSION INHIBITION AND CHARGE INJECTION CAPABILITY OF
SURGICAL Ti AND Ti-6Al-4V**

**A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville**

In-Seop Lee

August 1989

Dedicated to

my family

Eun-Ju

Hyun-A

Seung-Joon

my parents

Ki-Taik

Eul-Sook

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ABSTRACT

Studies are described involving effects of noble-metal ion implantation on corrosion inhibition and charge injection capabilities of surgical Ti and Ti-6Al-4V. With surgical alloys, harmful biological responses are principally due to the type and quantity of metal ions released by the corrosion process. One approach to improve long-term biological performance involves surface modifications to significantly reduce degradation rates. With regard to surface-modifications, one of the most effective methods is through ion implantation. Results are presented for ion-implanted Au, Rh, and Ir.

For the static in vitro corrosion properties, the noble-metal ion-implanted Ti-6Al-4V and commercially-pure (CP) Ti were investigated in non-passivating acid and passivating saline solutions. It was postulated that during the early stages of corrosion (or during a corrosion pretreatment) the implanted noble-metal would enrich at the surface and significantly reduce subsequent corrosion rates. The observed behavior for the Ir and Rh implanted materials appeared to follow the postulated mechanism, with both initial and time-dependent improvements in corrosion resistance. However, the Au implanted material yielded early benefits, but the enhanced corrosion resistance deteriorated with time. X-ray photoelectron spectroscopy (XPS) analysis indicated that the implanted Au atoms remained as pure metallic Au, while the Ir and Rh atoms were in some oxide state, which gave the good adhesion of the Ir or Rh enriched surface to the Ti substrate.

For a stimulating neural electrode, the charge density should be

as large as possible to provide adequate stimulation of the nervous system while allowing for miniaturization of the electrode. "Activated" Ir has been known as having the highest charge injection capability of any material known. The increase in charge density of pure Ir on continuous cycling is due to the accumulation of the oxide phase (associated with a large surface area) in which the valence state of iridium changes and the double-layer capacitance increases. The charge densities as measured by cyclic voltammetry (second-cycle values) for the Ir implanted materials increased significantly as a consequence of the H_2SO_4 exposure. Initially, the charge injection capability of 5.0 at.% peak-max Ir implanted Ti-6Al-4V after noble-metal surface enrichment was slightly greater in isotonic saline than that of pure Ir, but remained unchanged on continuous cycling because of the limited number of implanted Ir atoms.

TABLE OF CONTENTS

CHAPTER	PAGE
1. INTRODUCTION.	1
2. LITERATURE REVIEW	4
Thermodynamics and Kinetics of Corrosion.	4
Charge Capacity	12
Ion Implantation.	21
Ion Implantation Equipment.	26
Ion Bombardment Effects on Structure and Composition. .	28
Sputtering.	29
Atomic Mixing	32
Crystallization and Amorphization	33
Effects of Ion Implantation on Aqueous Corrosion. . . .	35
Implantation of Non-Metallic Element.	38
Implantation of Metallic Element.	44
Promoting Passivity	44
Stimulating Cathodic Kinetics	49
3. THEORETICAL TREATMENT	58
4. EXPERIMENTAL PROCEDURES	65
Ion Implantation and RBS Measurements	65
Corrosion Treatment	68
Sample Holder	69
Polarization Cell and Immersion Cell.	71
Polarization Curve Determination.	73
Open-Circuit Corrosion Potential Measurement.	73

CHAPTER	PAGE
Cyclic Voltammetry.	75
X-ray Photoelectron Spectroscopy.	76
Atomic Absorption Spectrophotometer	77
5. RESULTS AND DISCUSSION.	80
Corrosion Behavior of Au, Rh, and Ir Implanted Sample .	80
Au and Rh Implantation.	80
Ir Implantation	91
Charge-Injection Capability of Ir and	
Ir Implanted Ti-6Al-4V.	117
6. CONCLUSIONS	146
LISTS OF REFERENCES	148
VITA.	157

LIST OF TABLES

TABLE	PAGE
1. Advantages and limitations of ion implantation as a surface modification.	24
2. Effect of various implanted ions on the pitting potential of pure Al (unimplanted pitting potential, -0.700 V(SCE)).	48
3. Corrosion current densities and hydrogen evolution currents at $\eta = -100$ mV for implanted iron samples in 1N H_2SO_4	50
4. Furnace conditions for Ti	79
5. Corrosion potential of 2.0 at.% peak-max Au implanted and unimplanted Ti-6Al-4V in isotonic saline after each anodic treatment	82
6. Chemical analyses, before and after corrosion treatments. .	111
7. Charge densities as measured by cyclic voltammetry.	120

LIST OF FIGURES

FIGURE	PAGE
1. Schematic diagram showing the electrode kinetic behavior of metal(M) in deaerated acid solution	6
2. The potentiostat circuit	9
3. Schematic of polarization curves indicating the extrapolations of the anodic and cathodic curves	11
4. Cyclic voltammogram of Pt in aerated isotonic saline	15
5. Cyclic voltammogram (30.8 mV/s at 0.008 Hz) for a smooth rhodium electrode in 1 mol dm ⁻³ NaOH at 25°C. The dashed line represents the behavior of an unactivated electrode whereas the full line illustrates the charge enhancement produced on cycling the potential from 0.01 to 1.55 V for 40 s at 5 Hz.	17
6. Cyclic voltammogram at a sweep rate of 60 mV/s of activated iridium(a) and activated, followed by heat treated iridium for 1 h at 200°C(b), 300°C(c), 400°C(d) in 0.5 mol dm ⁻³ H ₂ SO ₄	19
7. Cyclic voltammogram of an Ir electrode in aqueous 0.5 M H ₂ SO ₄ electrolyte at 25°C. ---, oxide free surface; --- oxide covered electrode after N growth cycle. Potential sweep rate = 150 mV/s.	20
8. Gaussian distribution of implanted atoms	23
9. Schematic of an ion implantation system.	27
10. Backscattering spectra of an 80-KeV Ar ⁺⁺ sputtered(closed circle) and unsputtered PtSi sample(open circle)	31

FIGURE	PAGE
11. Schematic classification of surface alloys produced by ion implantation (T is target temperature)	34
12. Potentiokinetic polarization curves for Ar^+ implanted sample in a borate buffer (pH=8.7) solution: $\cdots$, unimplanted; $---$, 10^{15} Ar^+ ; $- -$, 10^{16} Ar^+ ; $---$, 10^{17} Ar^+ ions/ cm^{-2} implanted iron	39
13. Polarization curves in 0.01 N HCl for Fe-18Cr implanted to various levels of phosphorus.	41
14. Effects of nitrogen ion implantation on the anodic current density at constant potential for Ti-6Al-4V while wearing against UHMWPE in isotonic saline.	43
15. Potentiodynamic polarization curves for pure iron, an Fe-7.3% Cr alloy and Cr^+ implanted iron ($5 \times 10^{16} / \text{cm}^2$) in sodium acetate-acetic acid buffer solution (pH=7.3) after removal of the oxide film.	45
16. Schematic diagram showing how alloying with a noble metal produces a passive mixed potential and a marked reduction in corrosion rate.	52
17. Anodic polarization of Ti and Ti-Pt alloys in boiling 1% H_2SO_4	54
18. Open circuit corrosion potentials as a function of immersion time in boiling 1M H_2SO_4 for pure Ti, Pd, and Pd implanted Ti.	55
19. Driving force for metal corrosion and possibilities for passive film formation in aerated aqueous solutions. . . .	59

FIGURE	PAGE
20. The simplest model showing atomic arrangements of a) as-implanted and b) as-corrosion-treated sample	61
21. Schematic polarization curves to consider the effects of noble-metal implanted Ti in terms of electrochemical kinetics	62
22. Schematic diagram of the sputter source.	66
23. Schematic diagram of the sample holder for corrosion treatments	70
24. Schematic diagram of the polarization cell	72
25. Schematic diagram of the immersion cell.	74
26. Schematic diagram of the cell for AAS measurements	78
27. Rutherford backscattering concentration (2.0 MeV He ions) profile of Au for 2.0 at.% peak-max Au implanted Ti-6Al-4V, as implanted and after corrosion treatments . .	83
28. Anodic polarization behavior of as-implanted and control materials in deaerated 1N H ₂ SO ₄ (1.2 V/h).	85
29. Open-circuit corrosion potential of Au and Rh implanted and control samples in deaerated 1N H ₂ SO ₄	86
30. Open-circuit corrosion potential of 2.5 at.% peak-max Rh implanted Ti, as-polished, and prepassivated Ti-6Al-4V in aerated isotonic saline	89
31. XPS spectra of (a) Rh for 2.5 at.% peak-max Rh implanted Ti, and (b) Au for 2.0 at.% peak-max Au implanted Ti-6Al-4V, after corrosion treatments	90

FIGURE	PAGE
32. Anodic polarization behavior of as-implanted Ti samples and control materials in deaerated 1N H_2SO_4 (1.2 V/h). . .	92
33. Anodic polarization behavior of as-implanted Ti-6Al-4V samples and control materials in deaerated 1N H_2SO_4 (1.2 V/h). . .	94
34. Corrosion potential versus time for 2.5 at.% and 5.0 at.% peak-max Ir implanted Ti-6Al-4V samples along with control samples in deaerated 1N H_2SO_4 . . . :	95
35. Corrosion potential versus time for 2.5 at.% and 5.0 at.% peak-max Ir implanted Ti samples along with control samples in deaerated 1N H_2SO_4	96
36. Corrosion potential versus time for 2.5 at.% and 5.0 at.% peak-max Ir implanted Ti-6Al-4V samples along with control samples in aerated isotonic saline	99
37. Corrosion potential versus time for 2.5 at.% and 5.0 at.% peak-max Ir implanted Ti samples along with control samples in aerated isotonic saline	100
38. Rutherford backscattering yield (2.0 MeV He ions) versus depth of Ir for 2.5 at.% peak-max Ir implanted Ti-6Al-4V, as-implanted and corrosion treatments.	102
39. Rutherford backscattering yield (2.0 MeV He ions) versus depth of Ir for 5.0 at.% peak-max Ir implanted Ti-6Al-4V, as-implanted and corrosion treatments.	103
40. Rutherford backscattering yield (2.0 MeV He ions) versus depth of Ir for 2.5 at.% peak-max Ir implanted Ti, as-implanted and corrosion treatments.	104

FIGURE	PAGE
41. Rutherford backscattering yield (2.0 MeV He ions) versus depth of Ir for 5.0 at.% peak-max Ir implanted Ti, as-implanted and corrosion treatments.	105
42. Simulated profile of Ir with the constituent layer model . .	106
43. Rutherford backscattering yield from Ti versus depth, where the depth calibration assumes stopping-power values for pure Ir	108
44. XPS spectra for 5.0 at.% peak-max Ir implanted Ti-6Al-4V: (a) as-implanted, (b) after corrosion treatments	109
45. Rutherford backscattering yield (2.0 MeV He ions) versus depth of Ir for 5.0 at.% peak-max Ir implanted Ti.	112
46. Current density obtained from AAS analyses and open-circuit corrosion potential for as-polished Ti in deaerated 1N H ₂ SO ₄	114
47. Amounts of Ti dissolved in deaerated 1N H ₂ SO ₄ versus time for 2.5 at.% peak-max Ir implanted Ti and as-polished Ti	116
48. Cyclic voltammograms in aerated isotonic saline.	118
49. Charge density versus atomic concentration of Ir in implanted samples.	121
50. Cyclic voltammogram of as-polished Ir determined with a scan rate of (a) 0.17 mV/s and (b) 100 mV/s in isotonic saline.	123
51. Cyclic voltammograms of a commercial aluminum electrolytic capacitor (1000 μ F-50V).	125

FIGURE	PAGE
52. Equivalent electronic circuit for a simple electrochemical cell	127
53. Bode plots for a commercial aluminum electrolytic capacitor (1000 μ F-50V).	128
54. Bode plots for Ir and Ti-6Al-4V at 0.6 V (SHE) in 0.1M H_2SO_4	130
55. Cyclic voltammograms of an Ir electrode in 0.1M H_2SO_4 (100 mV/s)	132
56. Cyclic voltammograms of the activated Ir between 1.0 V (SHE) and 1.3 V (SHE) in 0.1M H_2SO_4 (100 mV/s)	135
57. Bode plots for Ir activated to 1 cycle and 200 cycles at 1.2 V (SHE) in 0.1M H_2SO_4 (100 mV/s).	137
58. Scanning electron micrographs of anodic Ir oxide films . . .	138
59. Scanning electron micrographs of anodic Ir oxide films grown on Ir by activating 2500 cycles.	142
60. Bode plots for Ir activated to 200 cycles at the applied DC potential of 0.3 V (SHE) and 1.2 V (SHE) in 0.1M H_2SO_4	143
61. Charge density of the activated Ir in isotonic saline. . . .	145

CHAPTER 1

INTRODUCTION

Specific metallic materials have been used in structural load-carrying applications for surgical implants, e.g. orthopedic and dental prostheses, because of their inherent strength, toughness, fabricability, and low corrosion rate. Metals and alloys are also used as neurological sensing and stimulating electrodes because of additional properties including high electrical conductivity and charge-injection capabilities.

By the mid-1960s, nearly every type of surgical implant, previously made with stainless steel or Co-Cr-Mo alloys, had been successfully constructed from titanium (1). More recently, Ti-6Al-4V has found clinical use in the form of articulating orthopedic devices. Titanium and its alloy Ti-6Al-4V are probably the best currently available surgical implant materials, especially for orthopedic devices (2-7). They possess excellent corrosion resistance and biocompatibility, good ductility and low elastic modulus, and low density. Furthermore, the alloy has high tensile and fatigue strengths.

The corrosion rates of titanium and Ti-6Al-4V in the biological environment are sufficiently low that devices will not degrade significantly if they are not subjected to mechanical wear or fretting and if they are not employed for electrostimulation purposes. That is, for mechanically and electrically static conditions, the failure of the material or device due to corrosion is highly unlikely. However, although the corrosion rates are low they are nevertheless finite,

which means that titanium ions, or titanium, aluminum, and vanadium ions are continuously being released to the tissues. Metal ions or metal complexes may then concentrate at the implant site and/or at distant sites in the human body. Although the long-term biological effects of these released elements are not completely understood, reducing the corrosion rates of implants, while maintaining or enhancing their mechanical properties, will lead to better overall long-term biological performance.

The noble metals are the most corrosion resistant metals available in nature; as a family they have the lowest driving forces for corrosion, i.e. the lowest reduction in Gibb's free energy on going from the metallic form to a corrosion product. However, in addition to the problem associated with cost, the mechanical properties of noble metals are generally inadequate for most structural applications. Consequently, in this research, in order to achieve surgical materials having both excellent bulk properties and corrosion resistance, substrates were chosen based on their bulk physical properties, then the surfaces were modified by ion implantation of small amounts of noble metals. The advantages of ion implantation techniques for modification of surface-related properties of materials have been reported (8-10).

Au, Rh, and Ir were chosen for implantation into commercially-pure (CP) Ti and Ti-6Al-4V alloy. The corrosion properties of the implanted materials were evaluated relative to use as static implants. Since "activated" Ir can produce the highest charge density of any known material, the charge injection capabilities of Ir and Ir

implanted Ti and Ti-6Al-4V were also studied relative to use as a possible stimulating neural electrode material. Several investigations have demonstrated the beneficial effects of noble metal (Pd, Pt) ion implantation into Ti when evaluated in strongly acidic nonpassivating solutions (11-15). They have found that the implanted noble metal remains on the surface and accumulates by the preferential dissolution of Ti, which results in substantially improved corrosion resistance. It is an additional objective for biomedical purposes to determine whether the noble-metal surface-enrichment effect can be taken to completion, such that the naturally stable surface of the titanium in passivating saline solution (to simulate tissue fluids) is virtually 100% noble metal. The natural stability of this new surface in a biological environment would be important in view of a desired regeneration mechanism, i.e. if the noble metal surface were locally, mechanically disrupted, it would be desirable to have the enrichment process naturally activate at the local site.

CHAPTER 2

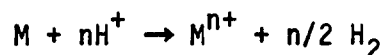
LITERATURE REVIEW

Thermodynamics and Kinetics of Corrosion

Corrosion is defined as the reaction of a material with its environment, with a consequent deterioration in properties. Corrosion of metals in aqueous environment is almost always electrochemical in nature. In essence, the electrochemical reactions are divided into the oxidation and reduction reactions. An oxidation or anodic reaction is indicated by an increase in valence or a production of electrons. A decrease in valence change on the consumption of electrons signifies a reduction or cathodic reaction. Both reactions must occur simultaneously and at the same rate on the metal surface.

The corrosion process must be considered in terms of thermodynamic and kinetic factors. The thermodynamic factors determine what conditions the reactions are at an electrochemical equilibrium and, if there is a departure from equilibrium, in what directions the reactions will proceed and how strong the driving force is. The kinetic factors determine how fast the corrosion reaction occur.

If a metal is placed in a deaerated aqueous acidic solution, it will often corrode as metal ions to the solution. The corrosion reaction can be written in the simplified form:



Hence, the metal reacts with the hydrogen ions of the acid solution to form metal ions of valence 'n' and hydrogen gas. The above reaction can be conveniently divided into two reactions, the oxidation of the metal

and the reduction of hydrogen ions:



Both reactions can be represented as in Figure 1. If a metal electrode is in equilibrium with its ion, the reaction would be represented by the reversible equilibrium potential, E_M , and the corresponding exchange current, $I_{O,M}$. Likewise, when the hydrogen reaction is occurring on the metal surface under equilibrium conditions, it also can be represented by a reversible equilibrium potential, E_H , and the corresponding exchange current, $I_{O,H}$. The reversible equilibrium potential of the hydrogen reaction, E_H^O is defined as having a potential of zero when the concentration of hydrogen ion is maintained at unit activity and the solution is saturated with hydrogen gas at 1 atmosphere pressure at 25°C. The E_M^O value can be calculated from compound free energies of formation when all species are at unit activity at 25°C (standard conditions) by the following relationship.

$$\begin{aligned} |\Delta G^O| &= \text{charge that passed} \times \text{reversible potential} \\ &= nF|E^O| \end{aligned}$$

where 'n' is the number of electrons passed per atom of metal reacted, and F is the charge on a mole of electrons, which is 96,500 C. If the species are not at standard conditions, the half-cell equilibrium potential, E_M , can be calculated through application of the Nernst equation:

$$E_M = E_M^O + (2.303 RT/nF) \log [Ox]/[Red]$$

where R: gas constant

T: absolute temperature

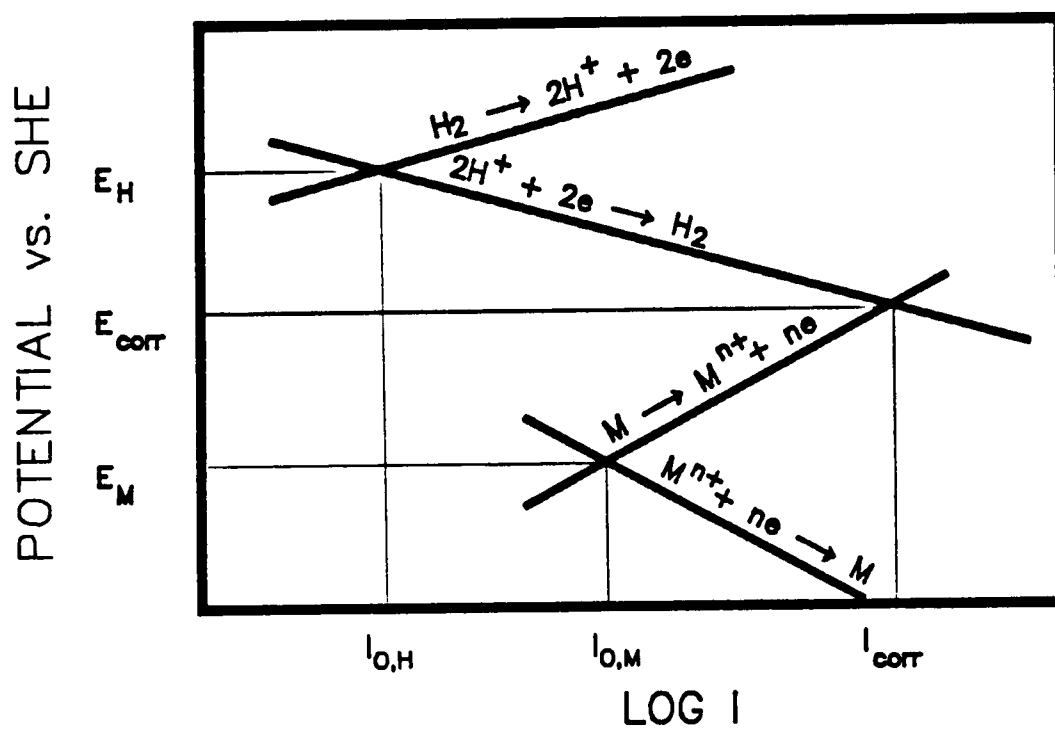


Figure 1. Schematic diagram showing the electrode kinetic behavior of metal(M) in deaerated acid solution.

n : number of moles of electrons transferred

F : Faraday's constant

$[Ox]$: activity product of oxidized species

each raised to its stoichiometric coefficient

$[Red]$: activity product of reduced species,

each raised to its stoichiometric coefficient

The difference in potential between the anodic and cathodic reactions,

$E_H - E_M = E_{cell}$, is the fundamental driving force for the corrosion reaction, $M + nH^+ \rightarrow M^{n+} + n/2H_2$.

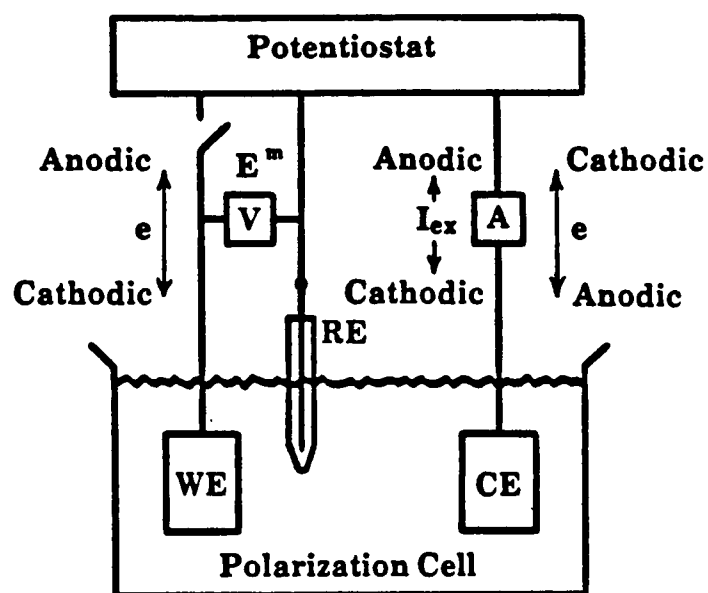
An extremely useful way to study the relation of potential to corrosion is through the use of an equilibrium diagram developed by Pourbaix (16) which plots half-cell potential versus pH, a parameter also of great importance to corrosion processes. A Pourbaix diagram has the advantage of showing at a glance specific conditions of potential and pH under which either a metal surface is in a region of immunity where the tendency for corrosion is nil, in a region where the tendency for corrosion is high, or in a region where the tendency for corrosion may still exist but where there also exists a tendency for a protective or passive film to form. This film does not affect the tendency for corrosion to occur, but it can drastically affect the rate of corrosion, and in some instances, for all practical purposes, stop it.

Since the data are based on thermodynamics, the potential-pH diagrams convey no information on rates of reaction, that is, whether any possible reaction proceeds rapidly or slowly when the energy changes are favorable. Knowing corrosion tendencies from the determination of half-cell potentials is necessary but not sufficient

to ascertain whether a given metal or alloy will suffer corrosion under a given set of environmental conditions. This is so because, while the tendency for corrosion may be strong, the rate of corrosion may be very low, and it may not present any problems. The kinetics of the corrosion reactions are fundamentally related to the activation energies of the electrode processes, mass transport, and basic properties of the metal/environment interface, such as the resistance of the surface film.

The mixed potential theory provides a general method of interpreting or predicting the corrosion potential and reaction rate. As shown in Figure 1, a metal will corrode at E_{corr} after the steady-state conditions are established if it is inserted in a deaerated aqueous acidic solution. At E_{corr} , the open-circuit corrosion potential, the rate of metal dissolution is equal to the rate of hydrogen evolution expressed in terms of current. The current corresponding to this point, I_{corr} , is called the corrosion current since it represents the rate of metal dissolution. It should be noted that I_{corr} also corresponds to the rate at which hydrogen gas is evolved. If the Tafel slope (β) values and exchange currents for this system are known, it is possible to predict the corrosion rate of a metal from the electrochemical data.

To determine the corrosion behavior of a metal experimentally, polarization systems can be used. The system is comprised of a polarization cell (working electrode, reference electrode, counter electrode) and a potentiostat, as schematically shown in Figure 2 (17). The working electrode (WE) is the corrosion sample, i.e. the material



WE = Working Electrode

RE = Reference Electrode

CE = Counter Electrode

V = High Input Impedance Voltmeter

A = Ammeter

Figure 2. The potentiostat circuit.

Source: R. A. Buchanan and E. E. Stansbury, "Aqueous Corrosion", in **Surface Modification Engineering**, ed., R. Kossowsky, CRC Press, (in Press).

under evaluation at which the electrolysis of interest takes place. The counter electrode (CE) is ideally made of a material that will provide the current required to sustain the electrolysis at the working electrode. This arrangement prevents large currents from passing through the reference electrode that could change its potential. The counter electrode should not itself undergo corrosion (and hence should not contaminate the electrolyte) and is often made of platinum. The reference electrode (RE) supplies a constant potential against which the potential of the WE is measured with a high input impedance ($>10^{10}$ ohms) voltmeter or electrometer. Only a negligibly small current is allowed to pass through the RE, so that its reference potential will remain essentially unchanged. The potentiostat is a special direct current (DC) power supply which maintains the potential of the WE relative to the RE at a very constant (preset or set point) value even though the external circuit current, I_{ex} , may change over many orders of magnitude. The potentiostat is employed to control the potential of the WE; while at each set potential, the resultant I_{ex} is measured. When the potential of the metal surface is changed as a result of a flow of current, it is said to be polarized. If it is polarized in a positive direction (potential increase), it is said to be anodically polarized; a negative direction signifies it is cathodically polarized.

Figure 3 (18) shows in a simplified way how the corrosion rate can be determined from anodic and cathodic polarization curves. In this presentation, the currents, I , are divided by specimen area to produce current densities, i . The experimentally measured current densities, i_{ex} , are shown as solid curves. To determine the corrosion current

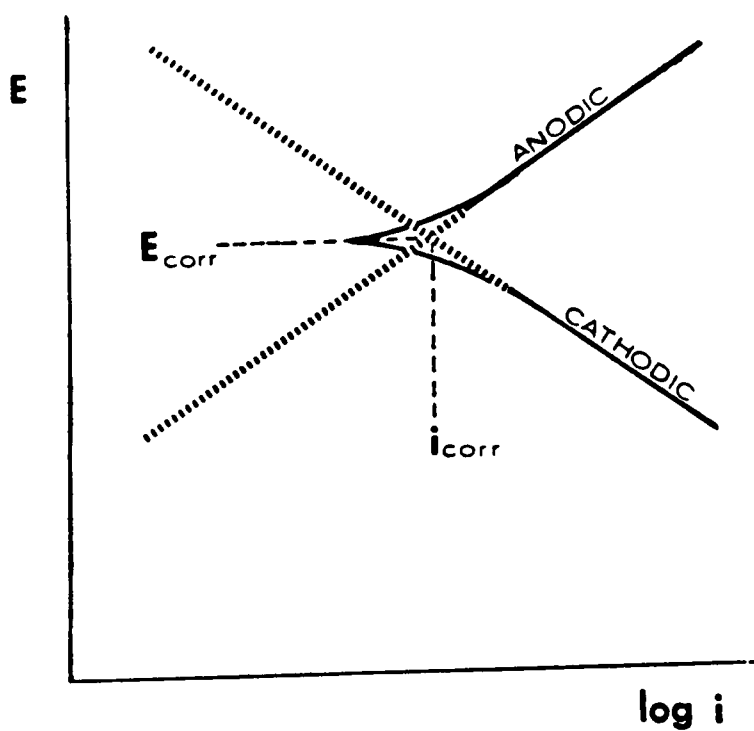


Figure 3. Schematic of polarization curves indicating the extrapolations of the anodic and cathodic curves.

Source: J. Kruger, in **Corrosion and Degradation of Implants Materials**, ASTM STP 684, eds., B. C. Syrett and A. Acharya, ASTM, 107-127, 1979.

density one produces an anodic polarization curve and a cathodic polarization curve. When the logarithm of the current density is plotted as a function of the potential, a portion of the polarization curve will be frequently linear, and it is possible to extrapolate the anodic and cathodic linear portions of the polarization curves to the corrosion potential, where, under ideal conditions, they should intersect. The value of current at their intersection will be the corrosion current density, a measure of the rate of corrosion.

Charge Capacity

When no charge transfer across the metal-solution interface occurs regardless of the potential imposed by an outside source of voltage, the metal electrode is called an ideally polarized electrode. The ideally polarized electrode is characterized by the existence of an electrostatic rather than an electrochemical equilibrium between two phases. While no real electrode can behave as an ideally polarized electrode over the whole potential range available in a solution, some electrode-solution systems can approach ideal polarizability over certain limited potential ranges. A good example is mercury in a deaerated potassium chloride at potentials greater than -1.5 V vs. SHE.

Since charge cannot cross the ideally polarized electrode interface when the potential across it is changed, the behavior of the electrode-solution interface is analogous to that of a capacitor. A capacitor is an electrical circuit element composed of two metal sheets separated by a dielectric material whose behavior is governed by the equation

$$q/E = C$$

where q : charge on the capacitor (C)

E : potential across the capacitor (V)

C : capacitance (F)

When a potential is applied across a capacitor, charge will accumulate on its metal plates until q satisfies the above equation. During this charging process, a current (called the charging current) will flow. The charge on the capacitor consists of an excess of electrons on one plate and a deficiency of electrons on the other.

The electrode-solution interface for an ideal polarized electrode has been shown experimentally to behave like a capacitor. At a given potential the charge on the metal q^M represents an excess or deficiency of electrons and resides in a very thin layer on the metal surface. The charge in solution q^S is made of an excess of either cations or anions in the vicinity of the electrode surface. The whole array of charged species and oriented dipoles existing at the metal-solution interface is called the electrical double layer.

The charge capacity of an electrode-solution interface may be obtained from the determination of a cyclic voltammogram. In cyclic voltammetry, the voltage applied to the stationary working electrode is scanned linearly with a triangular wave form which sweeps the potential of the electrode between two values. The current response is plotted as a function of the applied potential. This technique has been widely used in studying electrochemical reactions and is a convenient tool for obtaining qualitative information about electron transfer processes (19,20).

Figure 4 (21) shows a cyclic voltammogram of Pt in 0.9% NaCl at a sweep rate of 100 mV/s. The area within a given loop is directly proportional to the charge capacity of the platinum electrode under the stimulating action of the applied cyclic potential from -0.4 to 0.8 V vs. SHE. There are three possible processes available for the Pt electrode-saline interface under a selected upper and lower applied potential. The lower potential of -0.4 V (SHE) was selected to preclude water dissociation with H_2 evolution and the upper potential of 0.8 V (SHE) was chosen to prohibit oxygen evolution by water dissociation. The three possible processes (22) are:

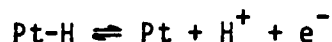
Double layer charging:



Surface oxidation:



H-atom plating:



The double layer charging process involves the attraction and repulsion of ions from the bulk of the solution to the vicinity of the metal. No chemical change takes place, just a redistribution of the ions in the double layer. This process is reversible and acts very much like an electrical capacitor. A second possibility, which does involve chemical change, is the chemically reversible surface oxidation and reduction of the electrode. The H-atom plating process is another possibility. It occurs at low potentials which minimizes possible metal dissolution, and it is kinetically very reversible. Because these three reactions can be reversed, they can act as charge reservoirs for

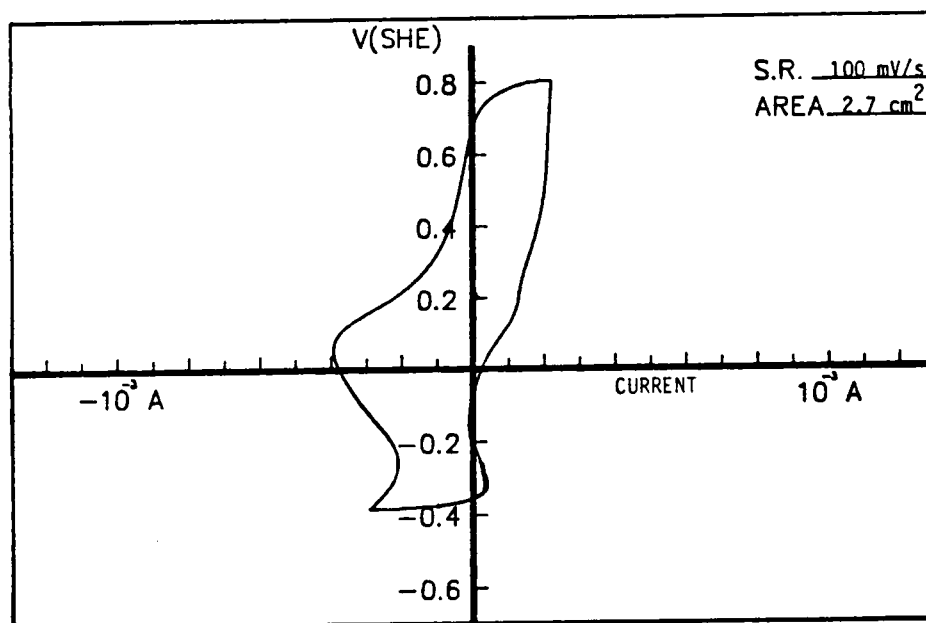


Figure 4. Cyclic voltammogram of Pt in aerated isotonic saline.

biphasic coupling from the electrode to the solution, somewhat like electrical capacitors.

A cyclic voltammogram for deactivated rhodium (immersed in hot aqua regia for 10 minutes in order to remove any thick oxide layers) and a voltammogram recorded after subjecting such an unactivated electrode to a repetitive triangular potential sweep (0.01 to 1.55 V vs. SHE at 5 Hz) for 40 s are shown in Figure 5 (23). This shows that whereas the charge associated with the reversible peaks at about 1.37 V (SHE) increased markedly on cycling, there was little if any corresponding change in the currents recorded at lower potentials. Burke et al. (23) suggest that the films produced by potential cycling are of duplex character, a relatively porous, poorly adherent, outer layer and a film of compact material at the metal-oxide interface. Partial reduction of the latter is assumed to occur below around 0.1 V (SHE) and the consequent weakening of metal-metal and metal-oxygen bonding is likely to leave the surface in a more active state for subsequent reoxidation.

Since iridium exhibits the lowest oxygen overvoltage in acid solutions (24) and activated iridium generates a large charge injection capability, considerable research effort has centered on the behavior of iridium and the iridium oxide-solution interface (25-32). Activated iridium means iridium with a high charge capacity in the potential region where the oxygen-containing species are electroformed and electroreduced. The reverse corresponds to the deactivated electrode. The electrochemical response of the Ir electrode is strongly dependent on the history of the electrode. Vukovic (32) reported that the cyclic

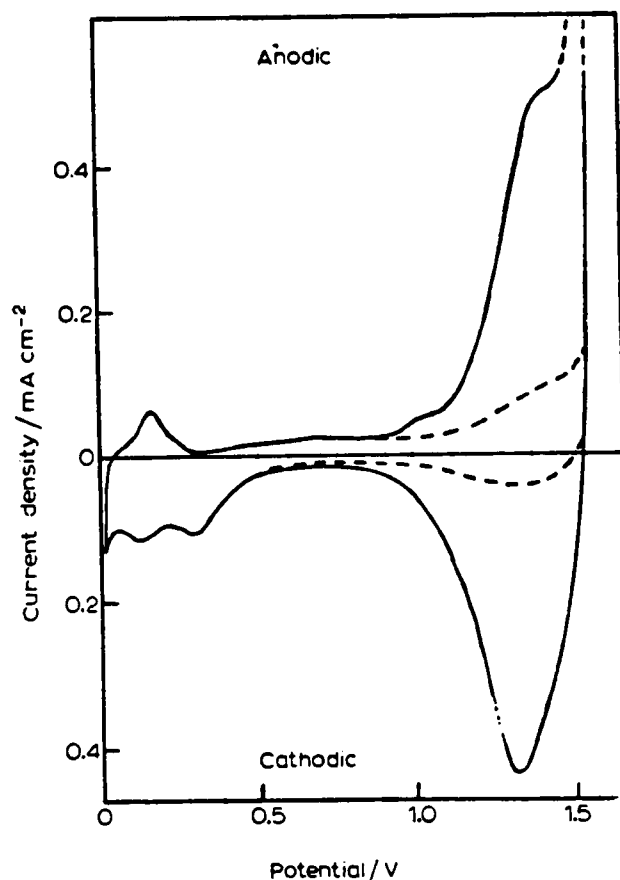


Figure 5. Cyclic voltammogram (30.8 mV/s at 0.008 Hz) for a smooth rhodium electrode in 1 mol dm⁻³ NaOH at 25°C. The dashed line represents the behavior of an unactivated electrode whereas the full line illustrates the charge enhancement produced on cycling the potential from 0.01 to 1.55 V for 40 s at 5 Hz.

Source: L. D. Laurence and E. J. M. O'Sullivan, *J. Electroanal Chem.*, 93, 11-18, 1978.

voltammograms of iridium after thermal treatment at various temperatures are quite different in comparison with that of thermally non-treated electrode. The loss in electrochemical activity of the electrode is evident by thermal treatment as shown in Figure 6. Peaks at 0.75 V (SCE) as well as those at 1.25 V (SCE) decrease with annealing temperature. However, he argued that the heat treated iridium oxide film shows stability during continuous polarization. A thermally non-treated electrode film is a hydrous oxide with its open structure, where water and electrolyte species are trapped. Thermal treatment changes the properties of such a hydrous type of oxide which becomes anhydrous, more compact and with lower surface area.

The activated Ir whose surface is covered with multilayer oxide film formed by repetitive potential cycling shows much larger capacity than the deactivated Ir. Zerbino et al. (26) proposed that the increased capacity of activated Ir is the result of highly reversible H^+ or OH^- transfer reactions and valence transitions within the oxide layer.

Figure 7 (27) illustrates the forms of the cyclic voltammograms observed on linearly scanning the potential of an Ir electrode in 0.5M H_2SO_4 between -0.25 and 1.25 V (SCE). The increase of charge capacity with number of potential cycles is evident. The current peaks located in the -0.25~0.15 V (SCE) range mainly pertain to the hydrogen electrode reaction while those found in the 0.15~1.25 V (SCE) range correspond to the electroformation and electrodesorption of oxygen-containing species on Ir. It is evident from Figure 7 that both electrode activation and its deactivation are not sensitive to the

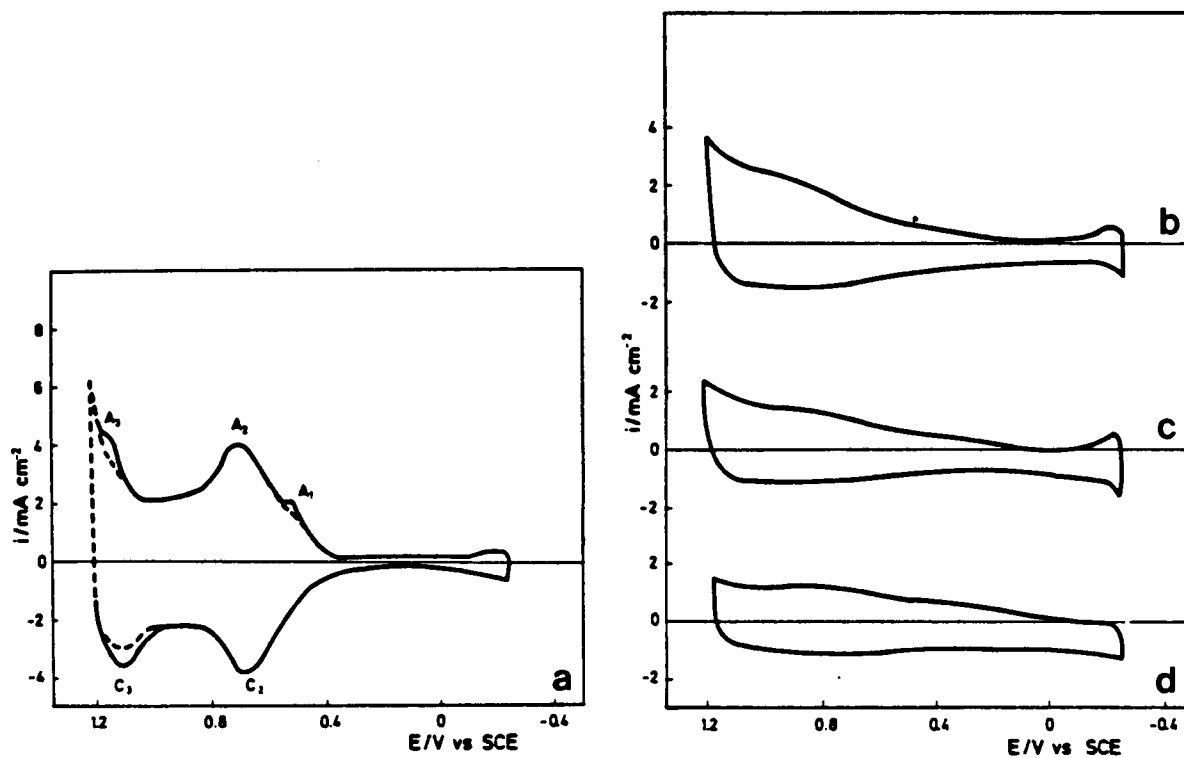


Figure 6. Cyclic voltammogram at a sweep rate of 60 mV/s of activated iridium(a) and activated, followed by heat treated iridium for 1 h at 200°C(b), 300°C(c), 400°C(d) in $0.5\ mol\ dm^{-3}\ H_2SO_4$.

Source: M. Vukovic, J. Appl. Electrochem., 17, 737-745, 1987.

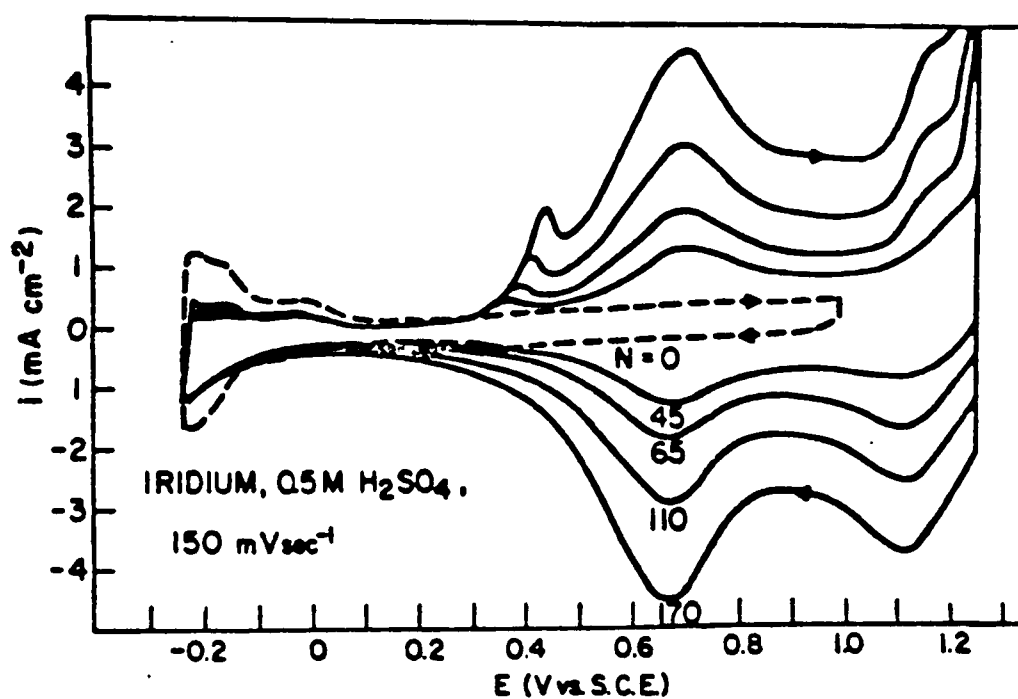


Figure 7. Cyclic voltammogram of an Ir electrode in aqueous 0.5 M H_2SO_4 electrolyte at 25°C. ---, oxide free surface; —, oxide covered electrode after N growth cycle. Potential sweep rate = 150 mV/s.

Source: S. Gottesfeld and J. D. E. McIntyre, *J. Electrochem. Soc.*, 126, 742-750, 1979.

hydrogen gas saturating the electrolytes. The accumulation of charge in the potential range proceeding the oxygen evolution during the repetitive triangular potential sweep is apparently bound to an increase of irreversibility of the various processes either anodic or cathodic, as noticed through the shifts of the corresponding current peak potentials with increasing cycling (26).

Since the phenomena occurring at a metal-solution interface are strongly dependent on the metal surface under the given environments, bulk alloying only for the purpose of providing improved surface properties (e.g., corrosion resistance, charge injection capability, etc.) is potentially wasteful, and surface alloying techniques are in widespread use. Among these, diffusion coating, electrodeposition cladding, hot-dipped coating, metal spraying, vapor deposition, and ion implantation are available. Ion implantation has several unique advantages over the other surface modification processes and was employed in the present study.

Ion Implantation

Ion implantation has been widely and successfully used in the manufacture of semiconductor devices. Recently, this technique, when applied to metals and alloys, has shown unique advantage in the fields of wear and friction, corrosion, oxidation, fatigue, etc.

Ion implantation is a process by which virtually any element can be injected into the near-surface region of any solid by means of a beam of high-velocity ions, usually tens to hundreds of kilo-electron-volts in energy. The ions penetrate the surface producing

both chemical and physical changes in the metal to a depth of several hundred or thousands of angstroms. The resulting depth-concentration profile of implanted dopant atoms can be calculated for most projectile-target combinations from well-established theoretical considerations (33). At low ion fluences (i.e., the number of ions per unit area), the depth concentration profiles are usually well characterized by a Gaussian distribution centered about an average range as shown in Figure 8. The depth of the implanted layer is controlled by the energy or speed of the incident ions. The concentration of ions within the layer is controlled by the length of implantation time. Thus, low implantation energies over short duration would produce shallow ion penetration and minimal ion concentration.

Because ion implantation is a process that modifies surface properties, it is often compared with other conventional techniques, such as vacuum coating, chemical vapor deposition, and ion plating. Some of the advantages and limitations of ion implantation in comparison to other surface treatments (such as coatings) are listed in Table 1 (34).

As for the advantages, first, it is not a coating process and consequently does not have some of the inherent problems associated with surface coating procedures. With a coating (e.g., electroplated coatings, plasm -sprayed coatings, etc.), there is always an interface between the coating and substrate or substrate oxide. The interface represents an abrupt discontinuity between the chemistry and structure of the two materials. It is this interface which is often the source of problems, e.g. lack of strength (poor coating adherence), preferential

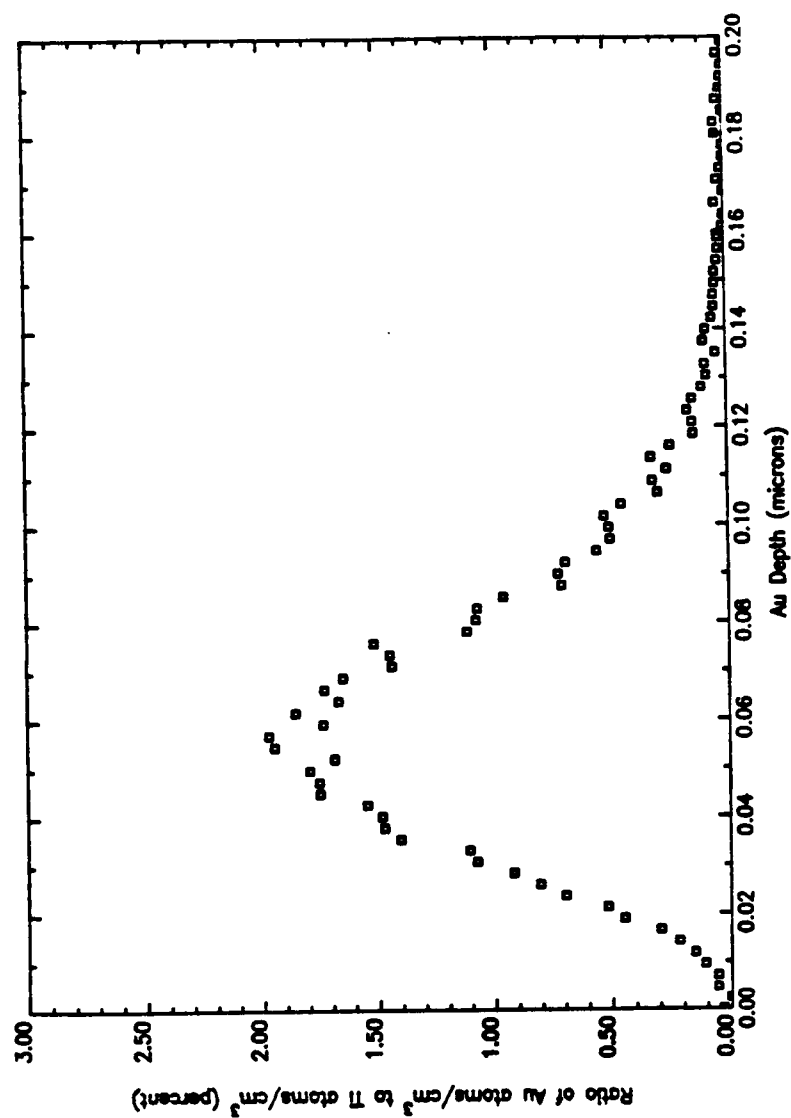


Figure 8. Gaussian distribution of implanted atoms.

Table 1. Advantages and limitations of ion implantation as a surface modification.

Advantages	Limitations
(1) Solid solubility limit can be exceeded	(1) Line-of-sight process
(2) Alloy preparation independent of diffusion constants	(2) Shallow penetration
(3) Allows fast screening of the effects of changes in alloy composition	(3) Relatively expensive equipment and processing costs
(4) No sacrifice of bulk properties	
(5) Low temperature process	
(6) No significant dimensional changes	
(7) No adhesion problems since there is no sharp interface	
(8) Depth concentration distribution controllable	
(9) Clean vacuum process	
(10) Highly controllable and reproducible	

Source: J. K. Hirvonen, in **Treatise on Materials Science and Technology**, Vol. 18, Ion Implantation, eds., J. K. Hirvonen, Academic Press, New York, p. 5, 1980.

corrosion along the interface due to galvanic effects, etc., which can lead to cracking and spalling of the coating. With ion implantation, there is no chemical or structural interface. On the contrary, a continuous transition in chemistry, structure, and properties is produced.

Another important feature of ion implantation is that it is a near-room-temperature processing technique, i.e., the sample temperature, without external cooling, normally does not exceed about 75°C. Consequently, the bulk physical properties of the substrate material remain unaffected. This important feature may be compared with another common surface modification technique for titanium alloys, nitriding, where the required temperature is so high that the excellent fatigue properties of Ti-6Al-4V are significantly reduced. A third unique advantage of the ion implantation process is that it does not alter the surface finish of the substrate. Consequently, it can be employed as a last step in the overall manufacturing process. In other words, the surface-volume properties can be significantly enhanced without altering the geometrical nature of the surface or the device. Ion implantation, therefore, has potential advantages for treating limited-area critical parts. The surface properties (e.g., corrosion resistance, wear performance, etc.) can be enhanced without degrading the bulk properties (e.g., mechanical strength, elastic modulus, etc.)

The following will address the disadvantages of ion implantation. A basic limitation of ion implantation is that it is a line-of-sight process which means the surface to be implanted must be directly in line with the ion source. This necessitates the manipulation of the

object within the vacuum chamber to achieve full coverage of its surface (35). The second relates to the relatively shallow depth of the ion implanted zone, normally about $0.1\text{ }\mu\text{m}$. The other possible disadvantage is cost. It is more expensive than any other surface modification processes.

Ion Implantation Equipment

There exists in the literature detailed articles concerning the various types of implanters, and the production and manipulation of ion beams for implantation (36-38). In this section, a brief description of ion implantation equipment and its operation is given.

Figure 9 (39) shows a schematic of an ion implanter. Ion implantation can be divided into three major stages (39): 1. Production of positive ions 2. Acceleration and mass selection 3. Ion-beam shaping. Although producing an ion beam from a gaseous element is quite straightforward, more sophisticated equipment is required for generating a metal ion beam (40). For a beam from a gaseous elements, the gas is introduced into the ion source in an implanter and, in the presence of electrons accelerated from a hot filament, ionized and a plasma is formed.

Creating a metallic ion beam requires either heating a volatile metal compound in the ion source or using the more common chlorination technique. In this method, chlorine gas is introduced into the ion source, forming metal chloride in situ, which then is volatilized by the heat from the filament. Recently, Moore (41) has developed a sputter source specially for noble metals since the noble metals do not

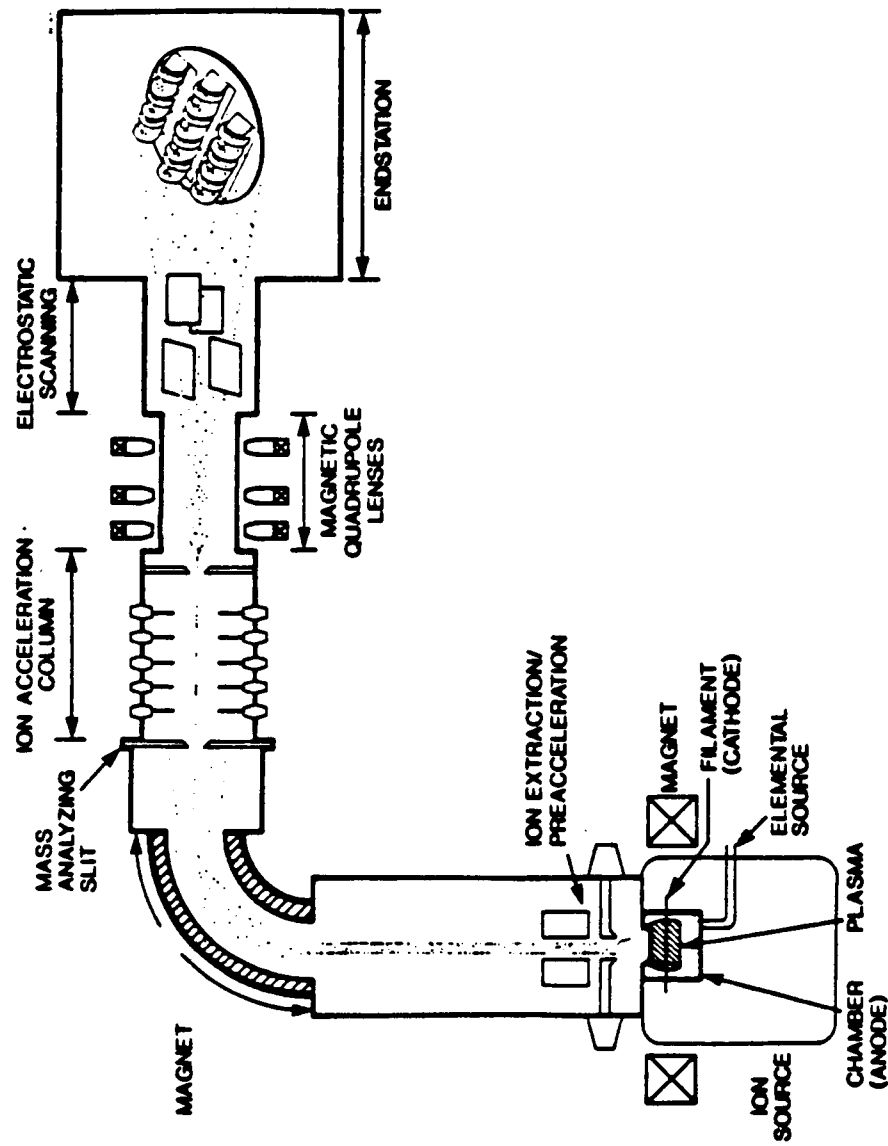


Figure 9. Schematic of an ion implantation system.

Source: P. Sioshansi, *Mat. Eng.*, 1987.

undergo chemical reactions, and very high temperature would be required to achieve a reasonable vapor pressure in the arc discharge chamber of the ion source. The materials are sputtered by argon ions and become ionized in the plasma. Positive ions formed in the ion source are extracted through a slit and, after being accelerated, are directed through a magnetic field that performs the mass analysis. Since ion sources normally produce ions of many species other than those that are desired for implantation, it is ordinarily essential to mass-analyze the beam in order to allow the species of interest to continue toward the target. The magnet pulls out ions of a specific mass and deflects them 90 degree toward the acceleration system. A quality check is performed by mass spectrometry after separation to identify any unknown elements in the beam. Multigap graded tubes accelerate the beam to a high energy level--typically to several kiloelectron volts.

Finally, the ion beam is directed toward the workpiece by a series of specialized eletrostatic and magnetic lensing elements. These lenses ultimately determine the area at the target plane which will be implanted, as well as substrate temperature and important uniformity. The ion beam current passing through the defining aperture is then current integrated to obtain the impurity concentration (in dimensions of atoms per unit area), which in turn can be converted into a volume concentration by knowledge of the range-energy relationships for the particular projectile ion-host combination.

Ion Bombardment Effects on Structure and Composition

Ion implantation is a non-equilibrium solid phase process wherein

an intimate atomic mixture is created within the alloying zone with accompanying high lattice damage. Each bombarding ion creates disorder on a very small scale, and a variety of dynamically created defect structure arises (42). Since ion implantation has the capability of producing materials with compositions and structures unattainable by conventional metallurgical means, there is a growing interest of using ion implantation as a potential method of producing materials with interesting new physical properties. The use of ion implantation for metallurgical purposes calls for implanted concentrations of a few atomic percent or more. This typically requires ion doses approximately 10^{17} ions/cm². At such high doses, sputtering, atomic mixing, and chemical effects will become important in determining the states of the implanted materials.

Sputtering

Sputtering is the removal of material from a target due to bombardment of energetic particles. Since ion implantation is a bombardment of energetic ions, there is always some sputtering. In the case of low-dose ion-implantation, the sputtering effect on the profile can be ignored. However, in the case of high-dose implantation, sputtering effects cause the concentration profile to differ considerably from the profile predicted by range theory due to the sputtering removal effect of implanted ions (43).

The incident ion initiates collisions in a volume surrounding the ion track. The energy of the incident ion is shared among those atoms within that volume and then dissipated. Because energy is shared among

a large number of atoms, only those collisions that take place near the surface of the material are directly effective in knocking atoms out of the material. In other words, the majority of sputtered atoms emerge only from the first few atomic layers. The more collisions taking place in the near-surface region, the higher the sputtering yield will be. Therefore the sputtering yield is proportional to the nuclear stopping power of the incident ion in the near-surface region. Surface binding energies also play a role, and in general, the sputtering yield is inversely proportional to the binding energy (44). In a binary alloy, the two species may not be sputtered at an equal rate because of differences in energy sharing (in the collision cascade), ejection probabilities, or binding energies.

Sputter-induced surface layer composition changes have been observed in many alloys and compounds (45,46). Figure 10 (46) shows a Rutherford backscattering spectrum of a PtSi film sputtered with $1.56 \times 10^{17} \text{ Ar}^{+2}/\text{cm}^2$ at 80 keV and that of an unsputtered sample. The sputtered sample shows an increase of Pt signal height while the corresponding Si signals become lower. This indicates that the sputtered sample is Pt enriched in a layer starting from the surface.

Sputtering makes the sample surface recede; therefore it affects the implantation profile and also removes atoms that have been implanted. This eventually leads to a steady-state condition in which there is no further increase in the amount of implanted species retained in the material. As a rough approximation, the maximum concentration is given by $1/S$ of the total atomic concentration, where S is the sputtering yield. However, this simple rule should be modified

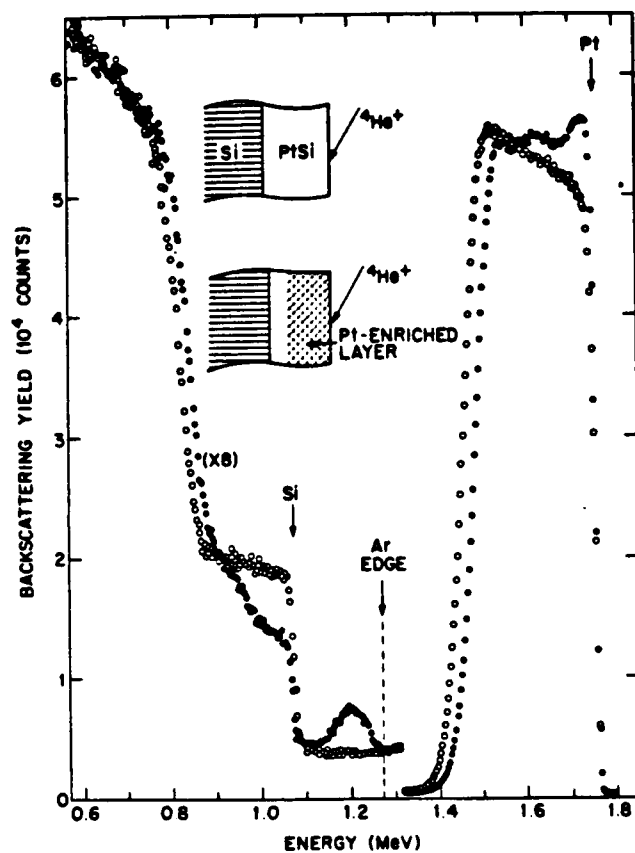


Figure 10. Backscattering spectra of an 80-KeV Ar^{++} sputtered (closed circle) and unsputtered PtSi sample (open circle).

Source: Z. L. Liao, J. W. Mayer, W. L. Brown and J. M. Poate, J. Appl. Phys., 49, 5295-5305, 1978.

if there is preferential sputtering between atoms of the host material and the implanted species.

Atomic Mixing

When an incident ion penetrates through an interface between a thin film (of species A) and a substrate (of species B), ion-induced atomic mixing may result in an intermixed region (which contains both A and B) near the interface as a result of dynamic collision cascades initiated by the passage of the primary ion. This intermixed region may contain definite compound phases. Therefore, it can be called an ion-induced interfacial reaction. For instance, with a thin Pt film on a Si substrate, Poate et al. (47) have observed a mixed layer with relative composition close to PtSi under Ar ion bombardment. Van der Weg et al. (48) found Pd₂Si in the Pd/Si system after the samples had been bombarded by Ar ions of 40-400 KeV energy to doses of about 10^{16} ions/cm² at room temperature. Studies of silicide formation with Pt with low dose (10^{14} /cm²) Xe ion implantation showed that the initial phases formed (Pt₂Si) were the same as those formed with thermal processing (49). However, implantation with high ion dose (10^{16} /cm²) resulted in the formation of a Si-enriched Pt-Si mixed layer. This Si-enriched composition cannot be achieved by normal thermal treatment (50). Subsequent thermal annealing of silicon-enriched Pt-Si mixed layers at 400⁰-500⁰C resulted in the formation of well-defined phases with compositions close to Pt₂Si₃ and Pt₄Si₉. These possess the properties of metastable compounds.

Crystallization and Amorphization

Metastable alloys in crystalline or amorphous phases are readily produced from the melt when the cooling rates are high enough to suppress the normal process of nucleation and growth of equilibrium phases.

Ion implantation, which alters the composition and produces displacement cascades in the host lattice, can also produce metastable surface alloys without heating the host material for introducing alloying species. Although ion implantation is a well-developed technique for modifying surface layers, it is only recently that the concepts of metastable phase formation during the implantation process have been recognized. The phases produced by ion implantation are dictated by the collision cascade process and the many limitations of thermal alloying such as solid solubility (51,52). The metastable phases that are produced may be crystalline with greatly extended solid solubility or may be amorphous (53-55).

Depending on whether or not there is appreciable atomic diffusion within the experimental time used for implantation, Sood (56) divided surface alloys produced by ion implantation in metals into two target temperature regimes as shown in Figure 11. He discussed that in the high temperature regime, the average diffusion length is greater than the lattice constant so that appreciable atomic diffusion occurs and the as-implanted system acquires thermal equilibrium within implantation time. Consequently one or more equilibrium alloy phases are formed, the laws of thermodynamics are applicable, and the equilibrium phase diagram is obeyed. On the other hand, metastable

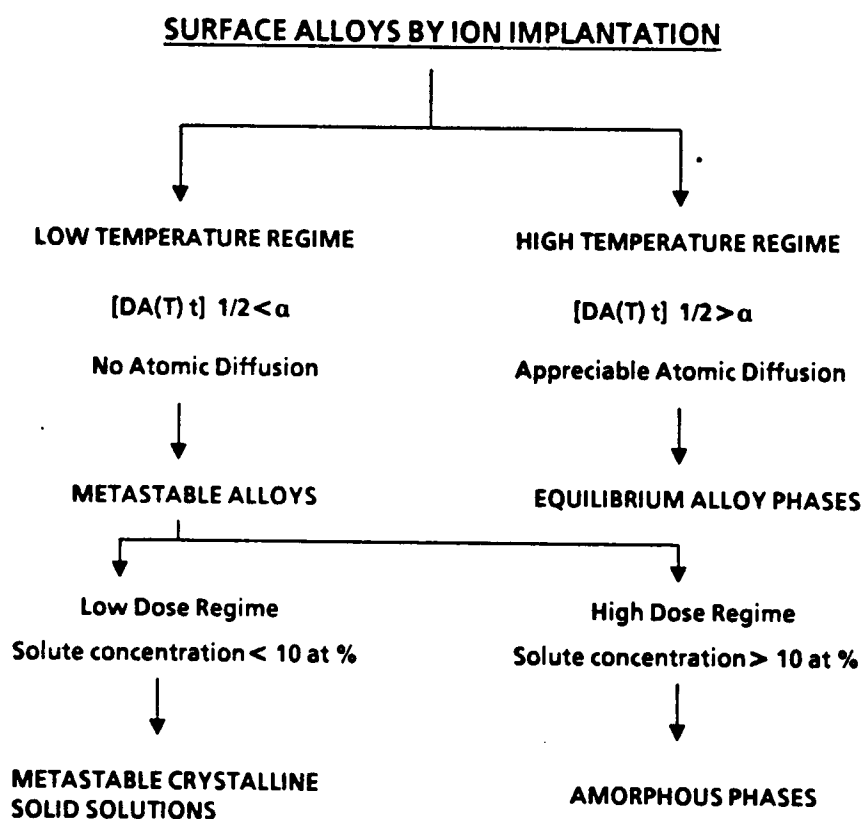


Figure 11. Schematic classification of surface alloys produced by ion implantation (T is target temperature).

Source: S. K. Sood, *Radiation Effects*, 63, 141-167, 1982.

alloys may be formed within the low temperature (room temperature or below) regime where there is no appreciable diffusion.

Two models have been proposed for the mechanism of implantation-induced amorphization: an energy spike model (57), or damage stabilization model (58). However, Limoge and Barbu (59) have argued that the spike model is inadequate and proposed that the lattice becomes unstable above some critical concentration of Frenkel pairs. Above this concentration a transformation from crystalline to amorphous state should occur.

Effects of Ion Implantation on Aqueous Corrosion

Ion implantation, as a surface alloying technique, offers wide scope for alloy design for corrosion resistance since it has been shown that in many cases solid solutions may be made from elements which are normally immiscible under equilibrium conditions. This is an important advantage, since conventional alloys which are not single phase are susceptible to local galvanic attack at phase boundaries.

There are four distinct approaches to using ion implantation in the context of corrosion science and engineering (60):

1. Ion implantation can be used specifically to produce conventional equilibrium surface alloys. In view of the constraints on the technique, however, it is envisaged that this application would, at present, be attractive only when the proposed alloying addition, i.e. the implanted species, is particularly expensive or in extremely short supply, or when surface alloying by some other conventional technique would impair the mechanical (or other) properties of the component.

There does not, currently, appear to be any technical or economic reason for using ion implantation when the alloying addition is relatively cheap and plentiful and when alternative coating techniques are satisfactory.

2. Ion implantation can be used to produce novel, corrosion-resistant surface alloys that are inaccessible by conventional metallurgy techniques. In this application it appears that the optimum approach is to attempt to improve the resistance (possibly with respect to some specific form of localized corrosion, or to general corrosion in a specific environment) of an alloy that already has good corrosion resistance, rather than to attempt use ion implantation to produce a highly resistant surface alloy on a metal that originally exhibits poor corrosion resistance. Again in view of the constraints discussed above, it is envisaged that this approach will, in the first instance, be used to improve the corrosion resistance of small, expensive and/or critical components. When using this approach, the choice of suitable implant species lies among those elements that have very limited solid solubility in the base metal in question and also might be expected to result in improved corrosion resistance. The latter effect may, in principle, be achieved either by inhibiting the anodic or the cathodic kinetics or by inducing or improving spontaneous passivity.

3. Investigations of the corrosion behavior of specific novel alloys produced by ion implantation can result in advances in the understanding of the mechanisms of certain forms of general and localized corrosion.

4. Ion implantation can be used to produce, relatively inexpensively, a

very wide range of conventional alloys of different compositions for corrosion screening tests in conventional corrosion resistant (and other) alloy development programs. This approach could be considerably cheaper than the usual alternative of producing and processing a small melts of each alloy in the range.

Currently, there can be little justification for using ion implantation to introduce alloying additions that can be introduced by more conventional alloying or surface alloying techniques (61). The choice of suitable implant species therefore lies amongst those elements which have very limited solid solubility in the base metal in question, and which might be expected to result in improved corrosion resistance. Identification of the most suitable candidate implant ions can be achieved by a number of approaches. For example, many metals are themselves protected by the spontaneous formation of a protective oxide film, or favour the formation of passive films when present in relatively low concentrations in other metals. An example of this approach would be the implantation of chromium and tantalum into iron (62-64). Some metals can be passivated spontaneously in many environments due to acceleration of the cathodic process. It is possible that the introduction of relatively low concentration of platinum group metals into the surface layers by ion implantation would accelerate the cathodic kinetics sufficiently to facilitate passivation without introducing the danger of localized attack which would inevitably be associated with the two-phase microstructure of conventionally produced alloys (11-15). Alternately, materials of low

corrosion rate might be produced by the implantation of species that poison the cathodic process, e.g., Pb, Hg implantation into Fe (65-68).

Implantation of Non-Metallic Element

Ashworth et al. (69,70) investigated the role of Ar implantation on the corrosion behavior of pure iron in sodium acetate acetic acid buffer solution (pH=7.3) by carrying out a three-sweep polarization experiment. They concluded that Ar^+ implantation into iron resulted in a thickening of the air formed oxide film, which altered the corrosion potential and improved the corrosion resistance of iron. Removal of the oxide layer by cathodic reduction caused the sample to revert back to the original corrosion behavior of pure iron. Bonora et al. (71) have observed the beneficial effect of three nominal doses of argon implantation on the electrochemical behavior of Armco Iron because of the ion-induced radiation damage. Figure 12 (71) shows the polarization curves of implanted (10^{15} , 10^{16} , 10^{17} ions/cm²) and unimplanted samples. Both implanted and unimplanted samples reveal quite similar values for active corrosion and transpassive potential while the samples implanted with 10^{15} and 10^{16} Ar^+ ions/cm² have lower values of I_{crit} and passive current density than the unimplanted sample. Implantation of Ar, which has no appreciable chemical reactivity, can nevertheless produce changes in the electrochemical behavior of metal surface because of the ion-induced radiation damage. The sample implanted with 10^{15} Ar^+ ions/cm², showed the best effects, producing a metal surface with a more uniform initial attack morphology under both chemical etching and pitting attack by chlorides and a more stable

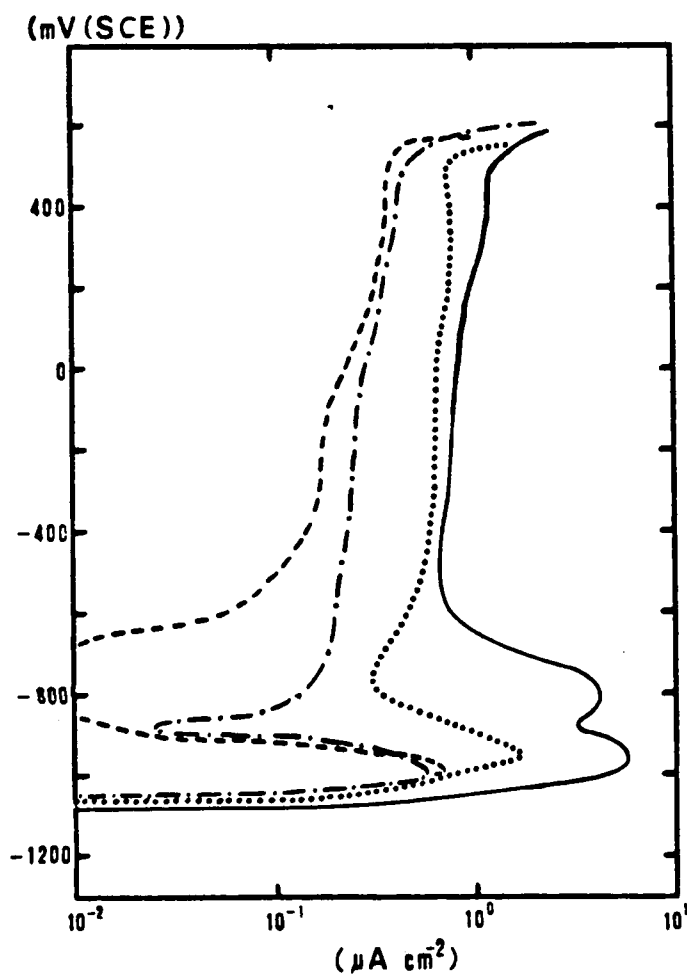


Figure 12. Potentiokinetic polarization curves for Ar⁺ implanted sample in a borate buffer (pH=8.7) solution:
 ···, unimplanted; ---, 10¹⁵ Ar⁺; - · -, 10¹⁶ Ar⁺;
 ---, 10¹⁷ Ar⁺ ions/cm² implanted iron.

Source: P. L. Bonora, G. Cerisola, L. Fedrizzi and C. Tosello,
 Mat. Sci. Eng., 69, 283-287, 1985.

passive film.

Ferber et al. (65) reported that Ne implanted iron samples showed higher corrosion current densities than untreated samples. They also showed that the hydrogen evolution reaction was enhanced by a factor of about 3. The main effect of an inert gas such as Ne during the bombardment is the creation of different defects in the surface layer of the substrate. Therefore, the enhanced corrosion rate can be interpreted as a damage effect due to an intensified surface activity. Moreover, an increase of the surface roughness may result from the irradiation.

Enhanced corrosion resistance due to the formation of amorphous layers by implantation of B, P has been reported (72-77). Polarization curves for several fluences of P-implanted Fe-18Cr in 0.01N HCl are shown in Figure 13 (77). For low (2×10^{16} ions/cm²) and intermediate concentrations (9×10^{16} ions/cm²) P caused an increase in the current density and a decrease in the pitting potential relative to the untreated sample. At high concentrations (2×10^{17} ions/cm²) there was a decrease in the passive current density and a increase in the pitting potential. The structure of the implanted layer, as determined by transmission electron microscopy (TEM), was totally amorphous for Fe-Cr implanted with 2×10^{17} ions/cm². Phosphorous is apparently detrimental in 0.01 N HCl until a critical concentration is exceeded, which causes a change in structure from crystalline to amorphous.

Clayton et al. (73,74) presented similar results for P-implantation into 304 stainless steel. Compositional analysis by auger electron spectroscopy (AES) indicated that the P-implanted

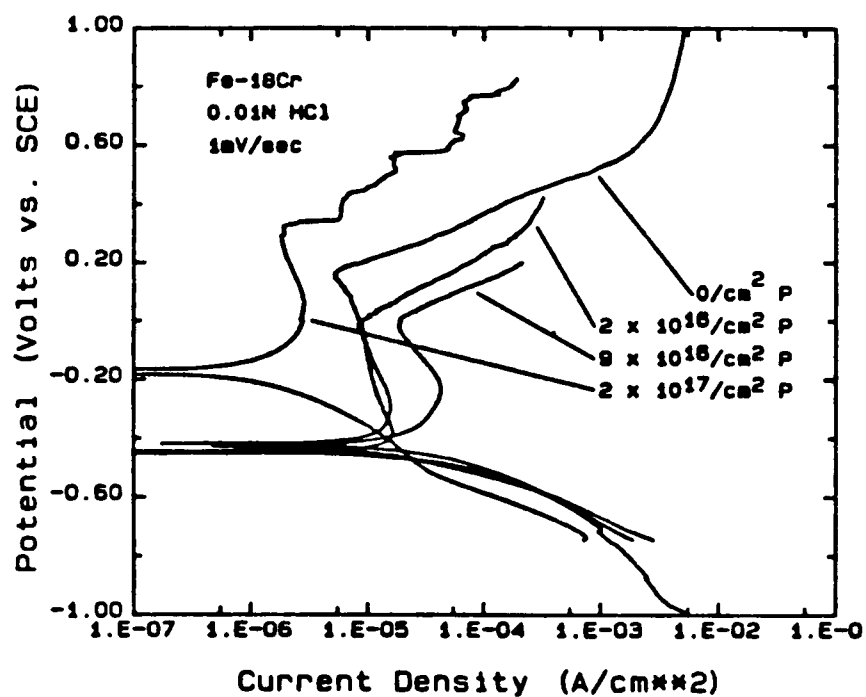


Figure 13. Polarization curves in 0.01 N HCl for Fe-18Cr implanted to various levels of phosphorus.

Source: N. R. Sorensen, R. B. Diegle and S. T. Picraux, *Corrosion*, 43, 2-7, 1987.

amorphous surface alloy formed a much thinner passive film than unimplanted steel. The ability of the amorphous passive film to resist Cl^- ion penetration and structural modification is probably due to the difficulty with which diffusion may take place in the passive film and the inhibitive action of the phosphate anions.

Ashworth et al. (78) found that the corrosion potential of Cl implanted 304L stainless steel was some 80 mV more noble, the breakdown potential was approximately 100 mV less noble, and the current density after breakdown of the passive film was significantly greater; the passive current density, however, was similar to that of the unimplanted sample. They suggested that incorporation of chloride into the passive film did not markedly affect its breakdown and subsequent localized corrosion behavior. Furthermore, these effects must be due to the chemical nature of the implanted Cl, rather than to the implantation process per se.

Nitrogen has been shown to be the most effective ion to implant for improving wear properties (79-81). Also, the beneficial effects of nitrogen implantation on corrosion have been reported especially in the corrosive-wear environment (82-89). Figure 14 (87) shows a very significant (up to a factor of 10,000) reduction in corrosion currents of Ti-6Al-4V alloy in wear-corrosion tests as a result of nitrogen implantation (20 at.%). The reduced corrosion may be a result of the reduction in wear due to hardening of the surface which allows the passive film to be retained.

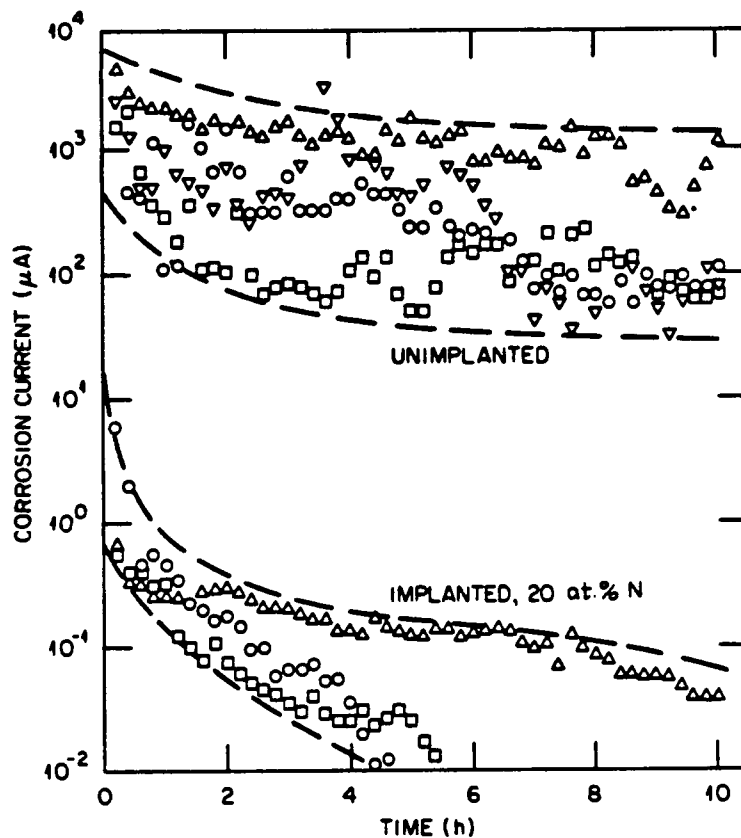


Figure 14. Effects of nitrogen ion implantation on the anodic current density at constant potential for Ti-6Al-4V while wearing against UHMWPE in isotonic saline.

Source: R. A. Buchanan, E. D. Rigney, Jr. and J. M. Williams, *J. Bio. Mat. Res.*, 21, 355-366, 1987.

Implantation of Metallic Element

Promoting Passivity

There may be two approaches to promote the passivity of metals by the implantation process. The first is to introduce elements as in conventional metallurgy and the other approach is to create combinations of elements in the surface layers that can not be produced by conventional metallurgical methods. The prototype of the first approach is Cr implantation into pure iron (90-93). Figure 15 (90) shows the anodic polarization behavior of pure iron, a single conventional alloy (7.3% Cr) and a Cr^+ -implanted material, determined after extensive cathodic treatment which removed any preexisting air-formed oxide film. It is seen that the implantation of Cr^+ produces an order of magnitude reduction in both the critical current density (i_{crit}) and the passive current density (i_{pass}) compared to those of pure iron. There is also a general similarity, but not an identity, between the behavior of the implanted material and the bulk alloy. Covino et al. (91) demonstrated that the effects of chromium implantation on the potentiokinetic polarization behavior of iron were indeed due to the formation of an Fe-Cr surface alloy layer with improved corrosion resistance and that they were not due to some intrinsic effect of the ion implantation process itself on the pre-existing, air-formed oxide films.

Also beneficial effects have been reported for Ni^+ implantation into Fe (91,94). A comparison of the corrosion behavior of pure iron with that of iron implanted with Ni shows three effects due to the

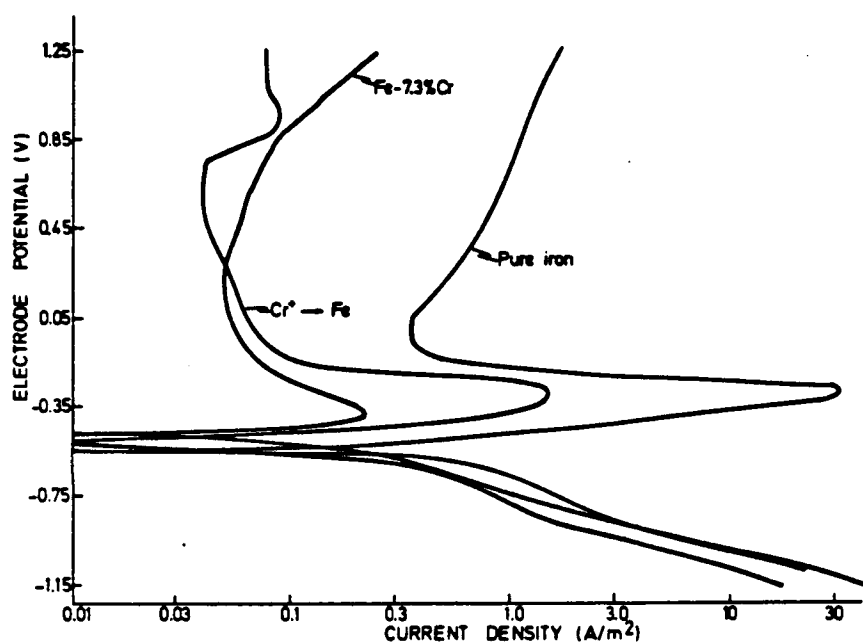


Figure 15. Potentiodynamic polarization curves for pure iron, an Fe-7.3%Cr alloy and Cr^+ implanted iron ($5 \times 10^{16}/\text{cm}^2$) in sodium acetate-acetic acid buffer solution (pH=7.3) after removal of the oxide film.

Source: V. Ashworth, D. Baxter, W. A. Grant and R. P. M. Proctor, *Corrosion Science*, 16, 775-786, 1976.

surface alloying: 1. a substantial reduction in the critical current; 2. a shift of the open circuit corrosion potential toward the noble direction indicating low corrosion rate; and 3. an increase in pitting potential.

Ashworth et al. (63) reported the effect on the corrosion behavior of pure iron of implanting tantalum. Tantalum, known to form a highly protective passive film very readily like chromium, cannot be introduced by conventional alloying techniques because of negligible solid solubility. Ta^+ doses of 5×10^{14} ions/mm² produced a material that compared favorable in corrosion resistance to an acetatic buffer solution (pH 7.2) with an equivalent Cr^+ dosed material. Unlike Cr^+ implantation, however, higher Ta^+ doses did not improve the corrosion resistance further. The reason for the apparent dose independent nature of the corrosion behavior is that the retained tantalum dose and concentration profile were the same in both low and high dose tantalum implanted specimens. The fact that the retained tantalum dose was the same on both low and high dose implanted specimen is indicative of sputtering implantation and of saturation tantalum levels being obtained at doses of $< 5 \times 10^{14}$ ions/mm². Accumulation of implanted Ta at the surface of 304 stainless steel, as a result of the preferential dissolution of the alloy components, has been observed by Ashworth et al. (95). The stable state of retained Ta at all potentials above -0.75 V (SHE) was Ta_2O_5 even at pH=0 (16). The formation of this oxide as an insoluble, coherent, adherent and highly protective corrosion product decreases the critical current density and the passive current density of 304 stainless steel in 0.5M H_2SO_4 .

The beneficial effects of Mo on pitting corrosion has been assessed (96-100). In the presence of Mo, not only does the pitting potential become more positive, but also the critical current densities and primary passivation potentials decrease considerably. Similar results were obtained by surface alloying with implantation of Mo into 304 stainless steel (95,101). The pitting resistance of Mo implanted, dose of 10^{15} ions/mm², 304 stainless steel was superior to that of unimplanted 316 stainless steel, presumably as a result of the higher Mo concentration in the surface layers of implanted specimens.

The pitting resistance of aluminum can be also improved by introducing molybdenum, which is insoluble in aluminum, by implantation techniques. Kim (102) presented the improvement in pitting potential of Al (to as high as 1200 mV) by implantation of Mo. He discussed the enrichment of Mo after corrosion tests based on AES analysis. It appeared that selective dissolution of the aluminum occurred, and that molybdate ions were not dissolving into solution. Thus, protection against pitting corrosion was due to the formation of MoO₂. Extensive studies of pitting behavior of implanted aluminum with several chemical species (Si, Zr, Mo, and Al) at concentrations of 4 or 12 at.% have been performed by McCafferty et al. (103). Table 2 lists pitting potentials in deaerated 0.1M NaCl for aluminum implanted with molybdenum, niobium, zirconium, silicon, and aluminum. The relative beneficial effects of ion implantation with Zr or Si increased with increasing concentration, more so than with Mo or Nb. Implantation of aluminum into aluminum had no effect on the pitting potential as expected. This fact confirmed that the physical effects of implantation

Table 2. Effect of various implanted ions on the pitting potential of pure Al (unimplanted pitting potential, -0.700 V(SCE)).

Implanted ion	Pitting potential (V(SCE)) for the following amounts of implanted ion		pH _{pzc} oxide
	4 at. %	12 at. %	
Mo	-0.560	-0.545	1.95
Si	-0.640	-0.340	2.10
Nb	-0.680	-0.585	2.80
Zr	-0.660	-0.410	6.00
Al		-0.700	9.10

Source: E. McCafferty, G. K. Hubler, P. M. Natishan, P. G. Moore, R. A. Kant and B. D. Sartwell, *Mat. Sci. Eng.*, 86, 1-17, 1987.

are unimportant in this case and that improvements in pitting potential from implantation of various ions can be normally attributed to chemical effects. It should be noted that the pitting potential increased as the pH_{pzc} of the oxide decreased. The pH of zero charge of an oxide (pH_{pzc}) is the pH at which the surface has a net zero charge (104).

Stimulating Cathodic Kinetics

Active corrosion on iron in acids is controlled by the hydrogen evolution reaction. Thus, if the hydrogen evolution reaction were modified by the implantation of an element, the corresponding corrosion behavior would be changed. Ferber et al. (81,82) studied the corrosion behavior of iron implanted with Au^+ , Pt^+ , Pb^+ and Hg^+ . They chose these elements because of their different electrochemical properties. The exchange current density of the hydrogen evolution reaction on Pb and Hg is very low; on the other hand, it is very high on Au and Pt. Table 3 (66) summarizes the data obtained for the active corrosion of unimplanted iron and iron implanted with Hg, Pb, Au, and Pt respectively. The actual corrosion rate of Au and Pt implanted iron electrodes increased by about the same order of magnitude as the hydrogen evolution itself since the main effect of the implantation of Au ions and even more of Pt ions was a strong increase in hydrogen evolution at the implanted surface. The effect of Pb and Hg implantation on the iron corrosion was in the opposite direction: the hydrogen evolution reaction on Pb was in the best case suppressed to nearly one hundredth of the value for unimplanted iron.

Table 3. Corrosion current densities and hydrogen evolution currents at $\eta = -100$ mV for implanted iron samples in 1N H_2SO_4 .

	$i_{\text{H}_2}/\eta = -100$ mV (mA)	$i_{\text{corr.}}$ (mA/cm ²)
Fe_0	3	0.4
Fe/Hg^{2+}	0.03	≈ 0.01
Fe/Pb^{2+}	0.06	0.01 (extrapolated)
Fe/Au^{2+}	80	4
Fe/Pt^{2+}	1000 (extrapolated)	> 10

Source: H. Ferber and G. K. Wolf, in **Ion Implantation into Metals**, eds., V. Ashworth, W. A. Grant and R. P. M. Proctor, Pergamon Press, 1-11, 1982.

The electrochemical behavior of noble-metal ion-implanted Ti has been recently studied (11-15). However, an initial study on the influence of noble-metal bulk-alloy additions on the electrochemical behavior of titanium was done by Stern and Wissenberg in the late 1950's (105). Even before Stern and Wissenberg's study, Tomashov (106) described the influence of Pt and Pd alloying on the corrosion behavior of stainless steel. He reported that alloying of 18% Cr-8% Ni stainless steel or 27% Cr stainless steel with Pt or Pd markedly improved corrosion resistance in room temperature H_2SO_4 by facilitating the cathodic reaction.

Passivation by alternation of the cathodic process kinetics is of special interest when the critical anodic potential of the metal is more active than the reversible hydrogen potential of the solution. Under these circumstances, passivity theoretically can be achieved with the presence of a redox system no more oxidizing than the hydrogen reaction. Under conditions where the metal exhibits a relatively low hydrogen exchange current density (high hydrogen overvoltage), a passive mixed potential may not be obtained directly. However, passivity can be accomplished by alloying such a metal with an element which is essentially insoluble in the environment and which exhibits a high exchange current for the hydrogen ion reduction process (low hydrogen overvoltage). A small amount of corrosion should leave the alloy addition essentially in elemental form on the surface. The surface is now a bi-electrode, or galvanic couple, with one of the constituents presenting a low-hydrogen overvoltage surface. This is shown schematically in Figure 16 (105) which may be considered typical

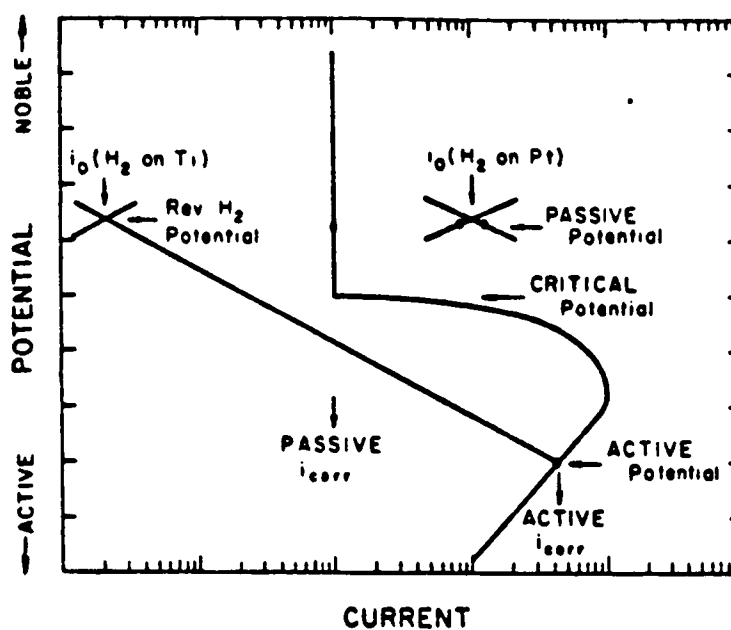


Figure 16. Schematic diagram showing how alloying with a noble metal produces a passive mixed potential and a marked reduction in corrosion rate.

Source: M. Stern and H. Wissenberg, J. Electrochem. Soc., 106, 759-764, 1959.

of the behavior of Ti. The exchange current for the hydrogen reduction reaction of Ti is very small resulting in an active mixed potential. When alloyed with a metal like Pt, regions with very high exchange currents are produced on the surface creating a mixed potential in the passive potential range. This results in a markedly reduced dissolution rate.

Figure 17 (105) shows anodic polarization data for three alloys in boiling 1% H_2SO_4 compared with that of unalloyed Ti. The polarization curve of 0.01% Pt alloy (open squares) is essentially that of a typical active metal because there is not enough time for Pt to accumulate at the surface. However, if this alloy is immersed in solution overnight prior to anodic measurements, the polarization curve parallels the behavior of unalloyed Ti in the passive region. Titanium alloys containing 0.37% or 2% Pt are passive very soon after immersion and show the passive behavior. Similar results were discussed on the surface alloyed Pt-Ti sample by ion implantation (11,12).

Hubler and McCafferty (13,14) demonstrated the enrichment of the noble metal, Pd, at the surface by the preferential dissolution of Ti. They implanted Pd^+ into titanium and exposed the material to boiling 1M H_2SO_4 . Using Rutherford backscattering analysis to obtain Pd profiles after various periods of exposure to acid, they showed a progressive change in the concentration profile. The surface concentration of Pd was initially less than 0.1% in as-implanted samples, rose to 5% after 6 minutes, 10% after 12 minutes and saturated at about 16% after 48 minutes immersion. Figure 18 (14) shows the open circuit corrosion potential for pure titanium, pure palladium, and palladium-implanted

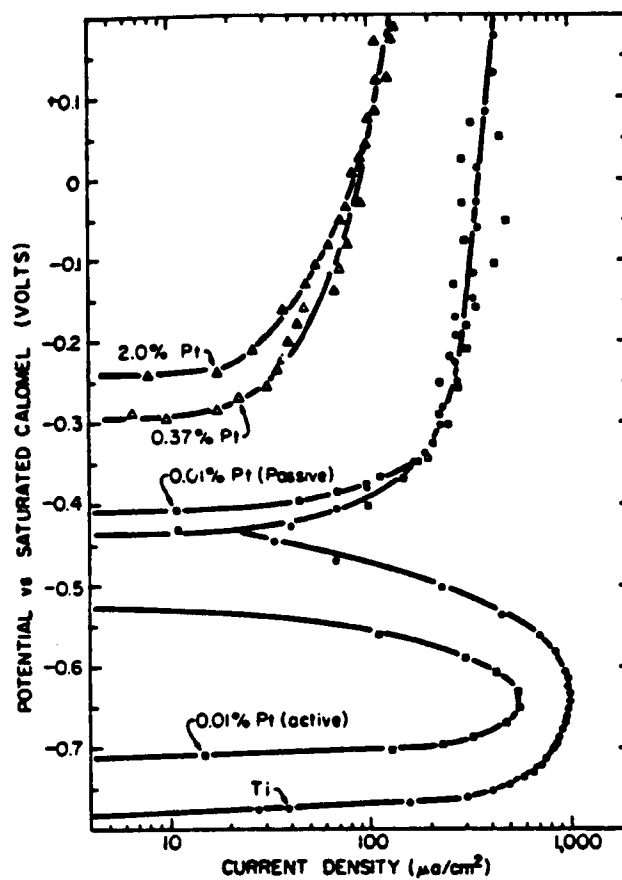


Figure 17. Anodic polarization of Ti and Ti-Pt alloys in boiling 1% H_2SO_4 .

Source: M. Stern and H. Wissenberg, *J. Electrochem. Soc.*, 106, 759-764, 1959.

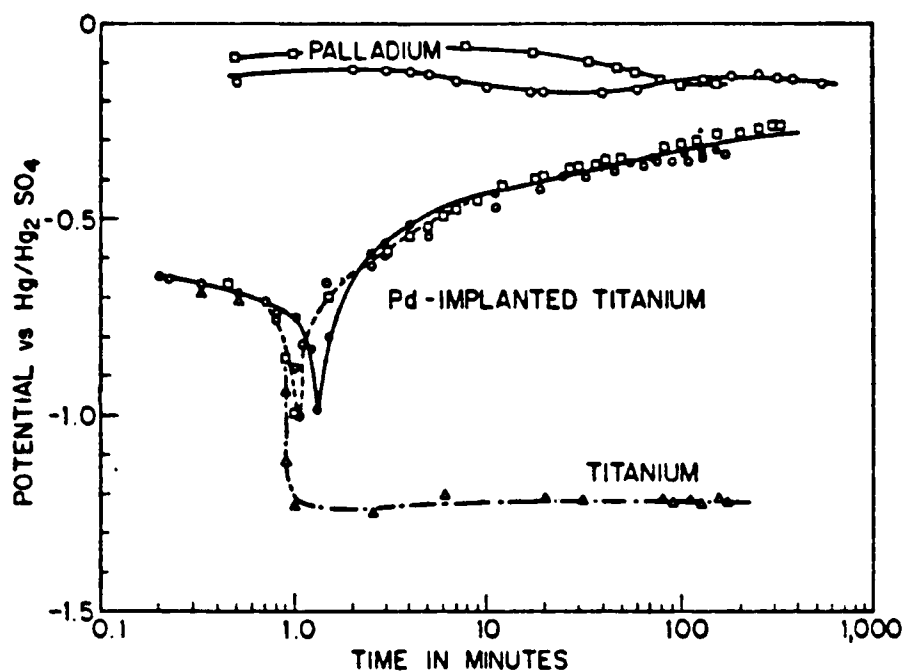


Figure 18. Open circuit corrosion potentials as a function of immersion time in boiling 1M H₂SO₄ for pure Ti, Pd, and Pd implanted Ti.

Source: G. K. Hubler and E. McCafferty, *Corrosion Science*, 20, 103-116, 1980.

titanium as a function of immersion time in boiling (100°C) $1\text{M H}_2\text{SO}_4$. The open-circuit corrosion potential of palladium was approximately 1000 mV more noble than that of pure titanium. The open-circuit corrosion potential of the implanted sample was much closer to that of pure palladium because the Ti-enriched surface dissolved away to expose a new surface region containing an increased concentration of Pd. The role of Pd is to provide cathodic sites for the hydrogen evolution reaction. As the surface concentration of Pd increased, so did the cathodic/anodic area ratio. The electrochemical behavior of this composite electrode is determined by the intersection of the polarization curves for hydrogen evolution on the cathodic Pd sites and dissolution of Ti on the anodic sites. If the mixed potential resides in the passivation region of Ti, Ti will be self-passivated resulting a markedly reduced dissolution rate.

Hubler and McCafferty concluded that immediately after implantation, and on first immersion, the surface concentration of palladium is too low to stimulate the cathodic kinetics sufficiently to permit self-passivation. More prolonged immersion is necessary, to enrich the surface with palladium by selective dissolution of the titanium from the dilute alloy that comprises the immediate parasurface layers before improved corrosion resistance is achieved.

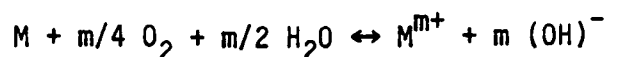
Munn and Wolf (15) have shown that implantation of palladium increases the crevice corrosion resistance of titanium. Test specimens with narrow crevices were immersed in boiling 42% MgCl_2 solution and long-time corrosion tests were carried out. Unimplanted titanium showed crevice attack inside the crevice after 5 days under test. Implanted

samples (10^{16} Pd⁺/cm² at 200 KeV), however, remained passive for 4 weeks under the same conditions. The improved resistance was explained as follows: the palladium on the titanium surface catalyses the hydrogen evolution reaction which is part of the total corrosion process. When this reaction does not take place, the only possible cathodic reaction counterbalancing the anodic dissolution of titanium is oxygen reduction. Since mass transfer inside the narrow crevice is restricted, oxygen is depleted and the pH value inside the crevice falls, rendering the titanium active and thus vulnerable to crevice attack. In the presence of catalytically active palladium on the titanium surface, hydrogen ion reduction takes place, a decrease in the pH value inside the crevice is avoided and the titanium consequently remains passive. As in all cases of cathodic protection, the thickness and uniformity of the palladium-implanted layers are not crucial, as long as enough palladium remains on the surface to stimulate sufficiently the hydrogen evolution reaction. Unimplanted titanium surfaces can also be protected against crevice attack when they are facing palladium-implanted surfaces. This occurs even when the unimplanted and implanted regions are electrically insulated from one another so that directed anodic polarization of the unimplanted titanium cannot occur. It can thus be inferred that the palladium-implanted surface, in catalysing the hydrogen evolution reaction, prevents the electrolyte in the occluded cell from becoming anodic and thus causing breakdown of the passive oxide film on unimplanted titanium.

CHAPTER 3

THEORETICAL TREATMENT

The fundamental driving force for the corrosion reaction involving a metal M in an aqueous, oxygenated solution, with pH as a variable, is the change in Gibbs Free Energy, ΔG , for the reaction:



If ΔG is negative, the free energy of the products will be less than that of the reactants, and the reaction will proceed as written (left to right). Under this condition, the metal will corrode releasing ions of valence m, M^{m+} , to the solution. On the other hand, if ΔG is positive, the reaction will not proceed as written, and corrosion will not occur. The magnitude of ΔG , assuming it to be a negative quantity, may be regarded as the "driving force" for corrosion.

The ΔG values for the above reaction have been calculated for a number of elements as a function of pH, and are presented in Figure 19. The assumptions involved in the calculations included the absence of substances in the aqueous solution with which the metal could form soluble complexes or insoluble salts, initial metal-ion activities of 10^{-6} , and an oxygen partial pressure of 0.2 atmosphere. Figure 19 also indicates whether the initial corrosion will be to increase the metal ion concentration in solution or to form an insoluble corrosion product (oxide or hydroxide) which may behave as a passive film.

Referring to Figure 19, it is thermodynamically impossible for gold to corrode in aqueous solutions under the previous assumptions.

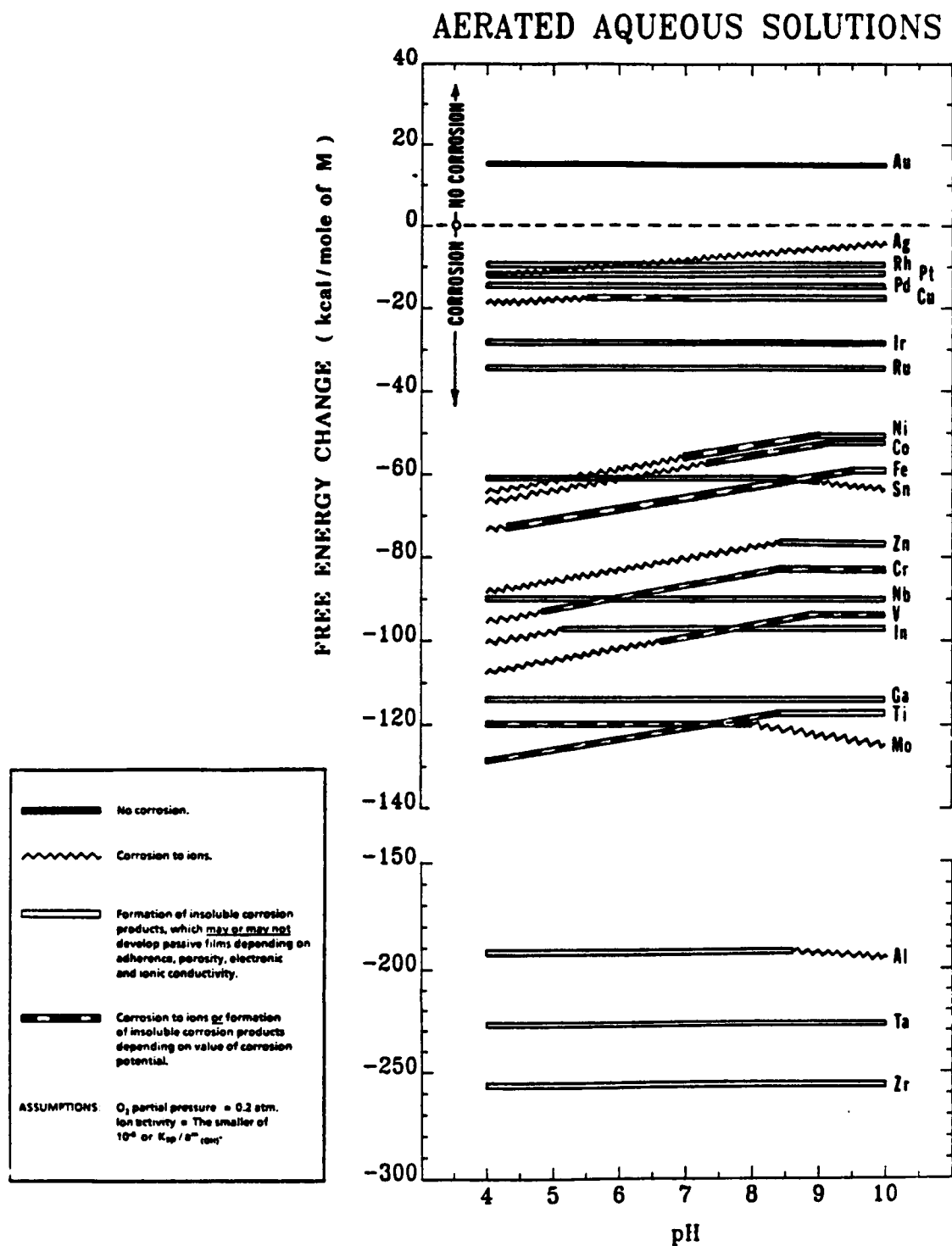


Figure 19. Driving force for metal corrosion and possibilities for passive film formation in aerated aqueous solutions

Consequently, Au was selected for ion implantation. Also Rh and Ir were chosen because they have low driving forces for corrosion and form stable oxides over the pH range of concern, 4 through 10.

The Au-Ti system will be utilized in the following to explain how ion implantation might improve the corrosion resistance. It is evident that ion implantation processing causes atom rearrangements via displacement and replacement sequences, preferential sputtering effects, radiation-enhanced diffusion, and radiation-induced segregation (16). It is, however, assumed for the simplest picture only that Au atoms substitute for Ti atoms during Au implantation into Ti, and a near Gaussian concentration distribution is obtained at a given accelerating potential as shown in Figure 20(a). When the implanted element is more noble than the substrate, the substrate element has a greater tendency to corrode and goes into solution. In the Au/Ti system, the Au will not corrode, as previously shown. Consequently, as Ti goes into solution, the Au should be retained at the surface, continuously increasing in concentration. It might ultimately cover the entire surface as shown in Figure 20(b). As a result of surface enrichment, the Au/Ti system should respond like Au in terms of corrosion behavior and show a zero-metal-ion-release rate.

Figure 21 schematically illustrates electrochemical polarization curves in deaerated acid solution in order to explain how the implanted noble-metal might improve the corrosion resistance of titanium in terms of electrochemical kinetics. Curve A represents the anodic polarization curve of unimplanted titanium showing an active and a passive region. For the noble-metal implanted Ti sample, the surface becomes enriched

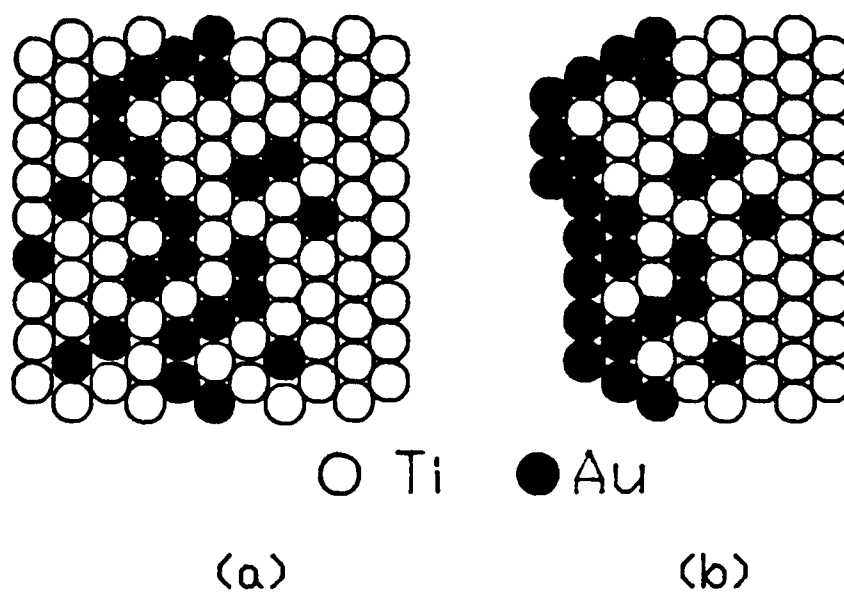


Figure 20. The simplest model showing atomic arrangements of
a) as-implanted and b) as-corrosion-treated sample

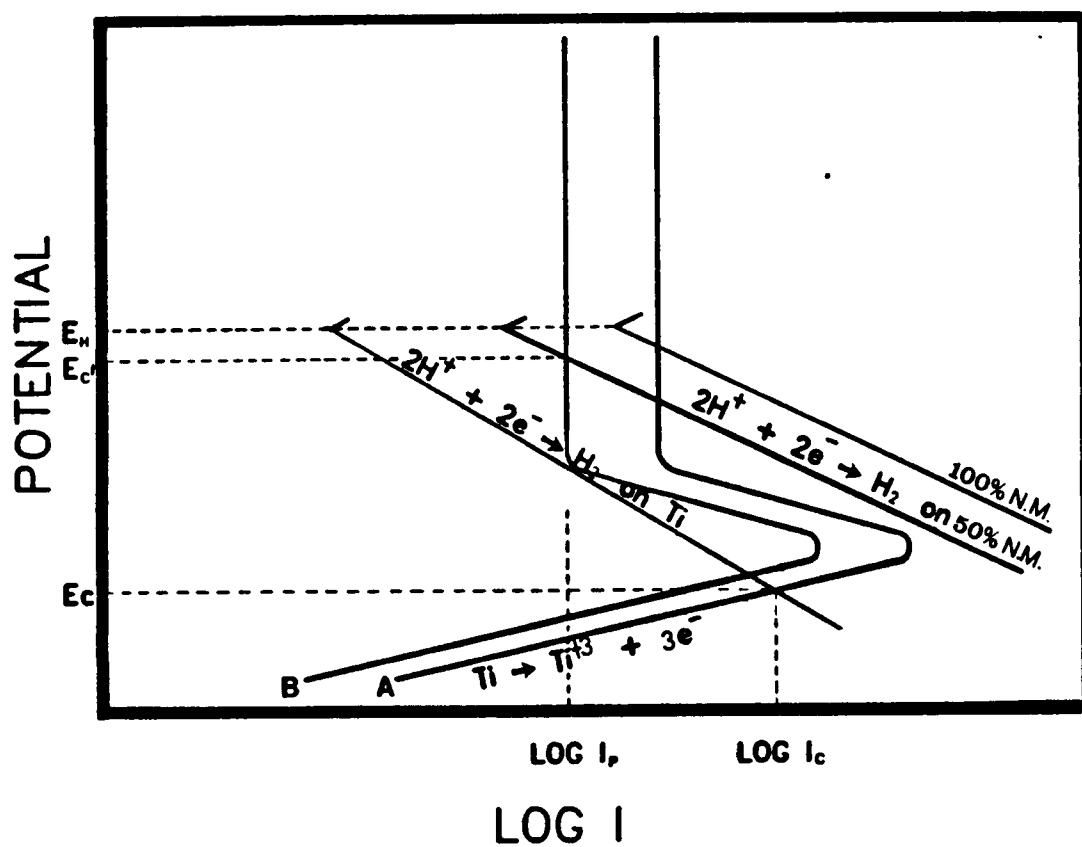


Figure 21. Schematic polarization curves to consider the effects of noble-metal implanted Ti in terms of electrochemical kinetics

with the noble-metal by the preferential dissolution of Ti as pointed out earlier. Curve B denotes the dissolution rates of titanium whose surface is covered to 50% by the noble-metal. The unimplanted titanium is shown to corrode with a corrosion current, I_c , at which the total anodic current is equal to the total cathodic current, and at an open-circuit corrosion potential of E_c . If the surface area of the Ti sample is A_T , the corrosion current is given by the product of the surface area and the corrosion current density, i_c :

$$I_c = i_c \times A_T$$

The open-circuit corrosion potential, for the implanted sample whose surface is covered to 50 % noble-metal, corresponds to the potential at which the cathodic hydrogen current on noble-metal sites (Curve C) is equal to the anodic current for Ti sites (Curve B) (ignoring the anodic and cathodic hydrogen current on Ti sites, and the anodic current on noble-metal sites because of relatively small values). If this mixed potential is in the passive region of Ti, the Ti surface is polarized in the passive region and dissolved at a corrosion current density, i_p . The corrosion current of this composite sample is then:

$$I_p = i_p \times A_T$$

This corrosion current, I_p , is very small compared to the corrosion current of unimplanted titanium sample, I_c , because of the smaller current density(i_p) and the reduced Ti surface area(A_T). Furthermore, in Figure 21, as the noble-metal surface area increases while the Ti surface area decreases, the curve representing cathodic hydrogen

current on the noble-metal shifts to higher currents while the curve representing anodic current for Ti shifts to lower currents. Thus, during noble-metal surface enrichment, the open-circuit corrosion potential, E'_c , represented by the intersection of the prior two curves, continuously increases and reaches the equilibrium potential for hydrogen reaction, E_H , when the surface is covered to 100% noble-metal.

CHAPTER 4

EXPERIMENTAL PROCEDURES

Ion Implantation and RBS Measurements

Samples 2.5 cm in diameter of Ti-6Al-4V (ASTM F136) and commercially pure Ti, with thicknesses of 3.2 mm and 0.5 mm, were cut from annealed rod and plate respectively. The sample surfaces were ground and polished through 1 micron diamond paste. After cleaning with methanol, the polished samples were stored in a desiccator until implantation.

Ion implantation processing and Rutherford backscattering analyses of implanted samples were performed in the Solid State Division, Oak Ridge National Laboratory (ORNL). For implantation, a polished sample was mounted on three of four sides in a square sample holder. The blank side was used for beam calibration. The sample holder was set in the target chamber of a Varian-Extrion 200 KV ion implantation system which extracts noble (Au, Rh, and Ir) ions from a source, accelerates magnetically mass-separated ions, and electrostatically scans the ion beam on the surface of the target metal. During implantation, the substrate was maintained at approximately room temperature.

In order to create the noble ion beam, a special Ar sputter source, developed by J. L. Moore (41) at ORNL, was employed and is shown schematically in Figure 22. When the probe is biased negatively with respect to the arc chamber in the plasma, argon ions are attracted to the probe where they sputter material from the surface. The

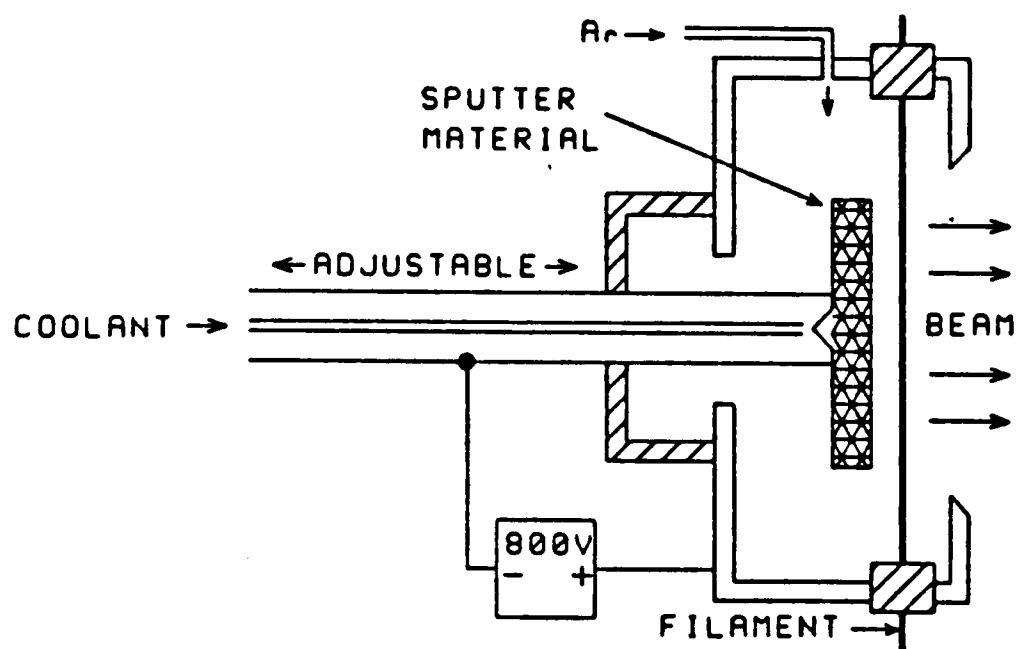


Figure 22. Schematic diagram of the sputter source.

sputtered atoms become ionized in the plasma. The voltage to the probe can be adjusted to control the sputter rate.

The concentration profiles of implanted atoms were determined before (as-implanted) and after corrosion treatments with Rutherford backscattering techniques using He ions accelerated to 2 MeV in a Van de Graff particle accelerator. Backscattering spectrometry is not very sensitive compared to other methods—for example, neutron activation analysis or secondary ion mass spectroscopy. However, backscattering spectrometry furnishes depth profiles without layer removal by ion sputtering or chemical stripping, which is generally required with other profile methods. The concept of a Rutherford backscattering experiment is quite simple and briefly explained in below.

When a beam of monoenergetic and collimated alpha particles (^4He nuclei) impinges perpendicularly on a target, almost all of the incident particles penetrate and finally stop in the target material as a result of losing energy during collision. If the energy of the incident ^4He ion is not too high, nuclear reactions can be ruled out and elastic collisions are assumed during the collision process. However, the few alpha particles that do undergo close encounters with the nucleus of a single target atom are scattered backward and can be detected if the scattering angle is more than 90° from the incident direction. A scattering event at the front surface is detected at an energy $K_M E_0$, where K_M , the kinematic factor, is the ratio of the energy of the projectile after to that before the collision and E_0 is the incident energy of the projectile. The kinematic factor is higher for a heavier element at a given scattering angle.

A scattering event that takes place somewhere inside the target is recorded at a lower energy due to the energy loss of the particle along its inward and outward path. Such energy losses can be calculated from the stopping cross section. Since the energy losses are dependent on the initial energy, two different values of the stopping cross section are used: one along the inward path and one along the backward path which is higher than the former one. Knowing the energy losses allows one to determine where the particles were scattered. Since the beam is unattenuated, the scattering probability at any depth is proportional to the number of atoms of a particular kind present there. Therefore, a concentration profile of a given element is translated into a signal of corresponding height and decreasing energy in the backscattering spectrum.

Corrosion Treatment

The following sequence of corrosion treatments and analyses was employed to characterize the electrochemical behavior of the implanted samples.

1. The anodic polarization curves of the noble metal ion implanted samples in the as-ion-implanted condition were determined in deaerated 1N H_2SO_4 and compared with those of as-polished control samples.
2. The implanted samples, which had previously undergone anodic polarization, along with control samples (pure noble metal, as-polished c.p. Ti and Ti-6Al-4V, and prepassivated Ti and Ti-6Al-4V) were immersed into nitrogen deaerated 1N H_2SO_4

and continuously monitored for changes in open-circuit corrosion potential as an indication of noble metal surface enrichment. To enrich the implanted noble metal at the surface, Ti must be dissolved first. Since Ti shows active corrosion behavior in 1N H_2SO_4 , this solution was selected as a way to accelerate the enrichment process.

3. After H_2SO_4 exposure, the noble metal implanted samples were immersed in O_2 saturated isotonic saline (0.9 wt.% NaCl) to determine whether the noble metal enriched surface is stable or not in this solution as function of time.

Cyclic voltammograms of the implanted samples and control samples were determined after each corrosion treatment in isotonic saline.

Sample Holder

After the corrosion treatments, the samples were subjected to surface analysis by RBS and x-ray photoelectron spectroscopy (XPS). Since both analyses require a bare metal, for the corrosion treatments each sample was mounted in a specially-constructed TeflonTM sample holder (see Figure 23) instead of epoxy. The resulting sample mount allowed the implanted and corrosion treated surface to be preserved without any possible mechanical damage; otherwise, efforts to remove the epoxy would have resulted in mechanical damage to the surface. Special care was given to mount the sample such that the electrolyte was not in contact with the sample except at the exposure area. The sample-holder/sample-contact areas which could provide a crevice geometry were reduced by sharpening the edges as shown in Figure 23.

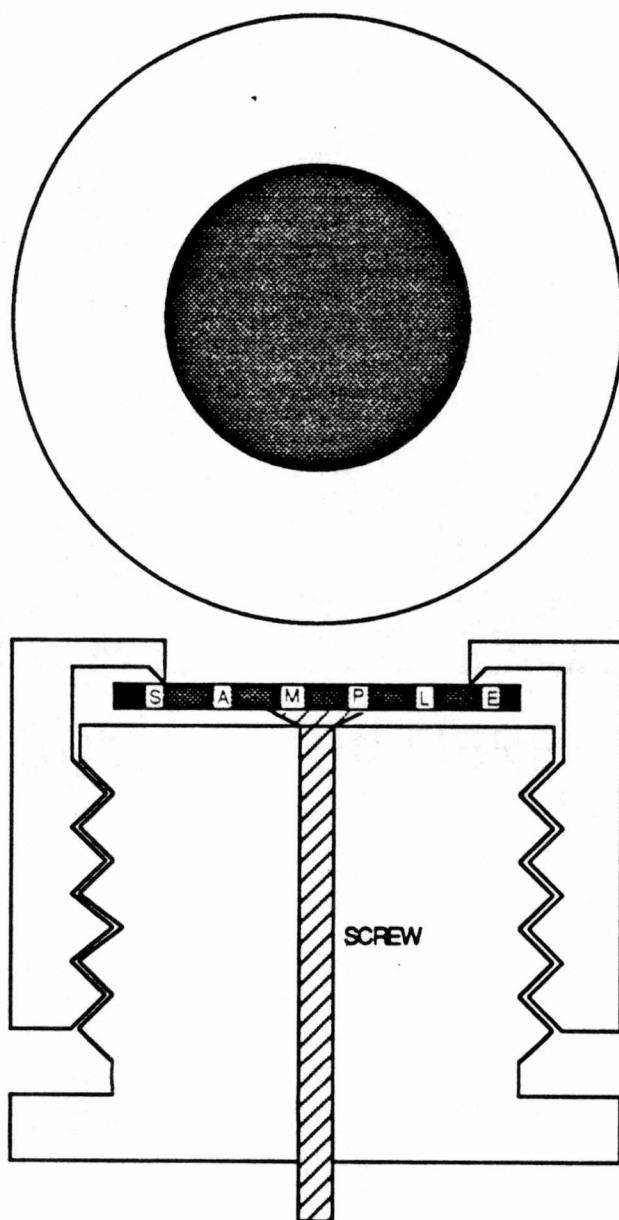


Figure 23. Schematic diagram of the sample holder for corrosion treatments.

TeflonTM tape was wrapped around the male part of sample holder to prevent any electrolyte from penetrating into the sample holder. No electrolyte was found inside the sample holder even after several months exposure.

Polarization Cell and Immersion Cell

The polarization cell used for the anodic polarization determinations and cyclic voltammetry is shown in Figure 24. A 2-liter Pyrex container was closed by a PVC plate containing several drilled and tapped holes for various electrodes (specimen electrode, platinum auxiliary electrode, Ag-AgCl reference electrode) and to allow auxiliary devices such as a thermometer and a sparging tube to be introduced. The fittings were made from a PVC. Brass screws near the edge of the top were used to compress an O-ring between the top and the flange of the 2-liter vessel, thus sealing off the test cell from the atmosphere.

The reference electrode used for all electrochemical measurements was a saturated silver/silver-chloride electrode contained in a capillary tipped glass tube with the tip positioned about 1-2 mm from the surface of the specimen. The silver/silver-chloride reference electrode was checked with respect to a standard saturated calomel electrode before use and the reference electrodes that did not fall within ± 5 mV of the standard value for this electrode were discarded. All potentials, however, were reported relative to the standard hydrogen electrode (SHE) by simply adding 196 mV to the silver/silver-chloride value.

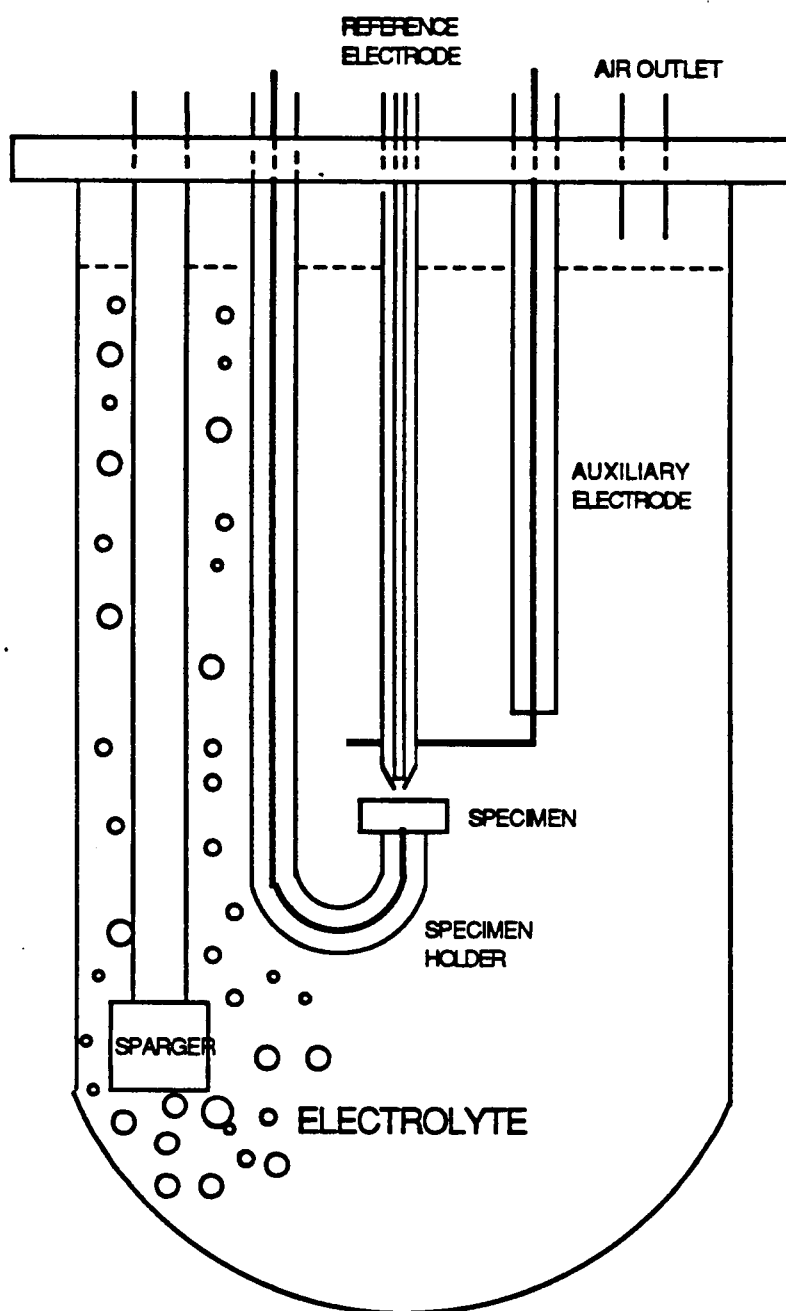


Figure 24. Schematic diagram of the polarization cell.

Seven-liter glass containers were used for the open-circuit corrosion potential measurements. Two or three sample electrodes were immersed simultaneously in each container and the open-circuit corrosion potential of each sample was measured relative to its own silver/silver-chloride reference electrode as indicated in the sketch of Figure 25.

Polarization Curve Determination

All anodic polarization curves were determined with an EG&G Princeton Applied Research Model 273 potentiostat. The test solution, 1N H_2SO_4 , was deoxygenated with nitrogen starting 30 minutes before immersion of the specimen and continuously purged during the test. The potential was changed linearly in the noble direction at a scan rate of 1.2 V/h from the open-circuit corrosion potential after 30 minutes of immersion. For the noble metal implanted samples, the polarization was continued to the potential above which the specific noble metal begins to oxidize. This potential was determined based on the theoretical potential-pH diagram for the corresponding noble metal.

Open-Circuit Corrosion Potential Measurement

The open-circuit corrosion potential is the potential at which the total anodic currents are equal to the total cathodic currents. Since both anodic and cathodic reactions are occurring on the metal surface, the change in open-circuit corrosion potential is a reflection of the change in metal surface reactions. As mentioned in CHAPTER 3 an increase in the open-circuit corrosion potential of the noble metal implanted sample is an indication of noble metal enrichment at the

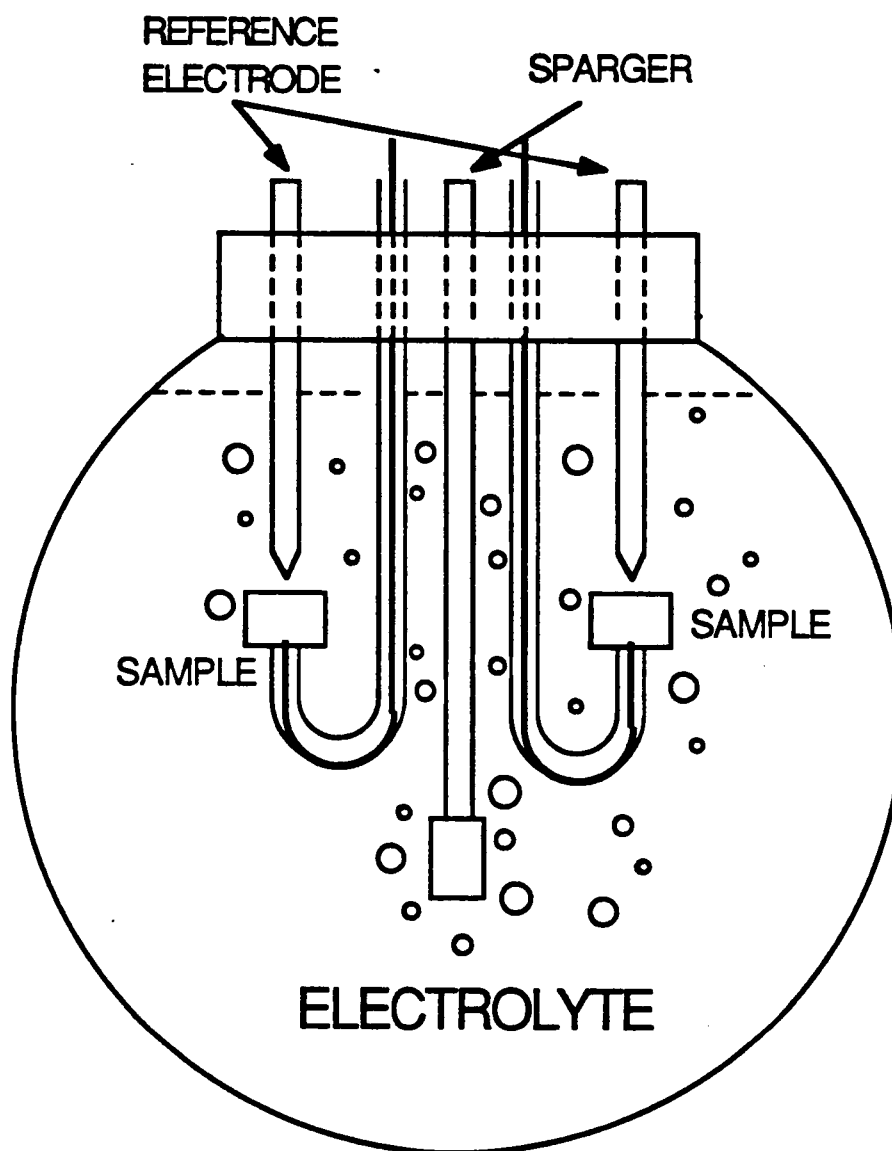


Figure 25. Schematic diagram of the immersion cell.

surface. All open-circuit corrosion potential measurements were made with a programmable 24 channel multiplexer controlled by a personnel computer.

N_2 -deaerated 1N H_2SO_4 and O_2 -saturated saline solutions were used for the noble metal enrichment process and the stability test of the noble metal enriched surface, respectively. Both solutions were made with doubly distilled water. The test solutions were deaerated (aerated) with N_2 (O_2) throughout the test and the silver/silver-chloride reference electrodes were checked periodically against a calomel electrode.

Cyclic Voltammetry

Cyclic voltammetry, which is a common technique for studying electrochemical reactions, was used to compare the relative charge injection capabilities of materials in saline solution. The voltage was scanned linearly with a triangular wave form between two potentials at a rate of 100 mV/s and the resultant current density was plotted on a linear scale. The area inside the loop generated by one cycle was measured with a planimeter, and is directly proportional to the charge density (charge per unit area) of the electrode. After each corrosion treatment, the samples were rinsed thoroughly with distilled water and transferred into saline solution. All cyclic voltammetry was performed with an EG&G Princeton Applied Research Model 273 potentiostat.

X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed for surface characterization of samples before and after corrosion treatments with a Perkin Elmer PHI 5100 ESCA system in the Department of Chemistry at UTK. $MgK\alpha$ x-rays were used to irradiate a sample with an x-ray source power of 250 watts. The specimen was mounted on the end of the sample introduction probe at an angle of 45° with respect to the analyzer.

When the sample is irradiated with monoenergetic soft $MgK\alpha$ x-rays in vacuo ($\sim 10^{-9}$ Pa), the photon is absorbed resulting in the emission of electrons. XPS analysis is accomplished by sorting the emitted electrons by energy. The emitted electrons have kinetic energies given by the Einstein relation:

$$E_k = h\nu - E_{BE}$$

where E_{BE} is the ionization energy or binding energy of the atom for the particular shell involved, $h\nu$ is the energy of the photon, and E_k is the kinetic energy of the ejected electron. The XPS spectra obtained is a plot of the number of emitted electrons per energy interval versus their kinetic energy.

The identification of chemical state is made from the exact positions and separations of the peaks, and the chemical composition of solid surfaces is obtained from the peak heights or areas. Since the mean free path of the electron is very small, the electrons which are detected originate from only about the top 5 atomic layers. As a result, the technique is very useful in investigations of phenomena where surface composition is of great importance.

Atomic Absorption Spectrophotometer

The test solution was analysed with a Perkin-Elmer Zeeman/3030 system utilizing the Zeeman effect for background correction and incorporating an AS-60 autosampler. For this investigation, a small cell which can accommodate as much as 80 ml of electrolyte was constructed (see Figure 26). The 1 cm² of electrode surface was exposed to 70 ml of deaerated 1N H₂SO₄, and approximately 0.5 ml of solution was obtained periodically by opening a valve without disturbing the open-circuit corrosion potential measurements.

The AS-60 autosampler was programmed to deliver 20 microliters of solution from the cup to a pyrolytically coated graphite tube. The Heated Graphite Atomizer (HGA) furnace program that is recommended for Ti is shown in Table 4. For an analysis by furnace atomic absorption spectrometry, the sample must normally be dried, thermally pretreated, and atomized. The drying and thermal pretreatment steps are crucial for an analysis since only when the element under study is largely free from the sample matrix can suitable atomization take place.

The sample is atomized in a pyrolytically coated graphite tube through which monochromatic light of set wavelength (characteristic of the element being analyzed, 276.8 nm for Ti) is being passed. The atomized sample absorbs fractions of the incident light dependent on the amount of the element in question in the atomized sample. In this manner, the concentration of the individual element in the solution is determined.

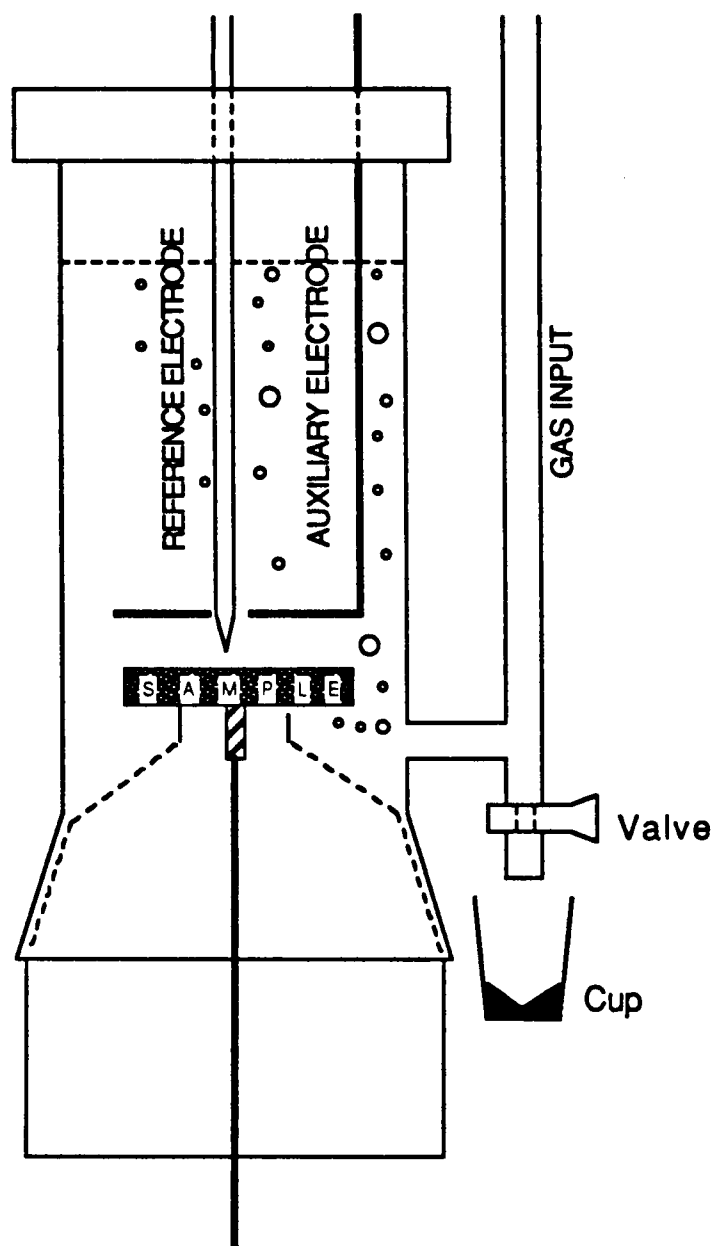


Figure 26. Schematic diagram of the cell for AAS measurements.

Table 4. Furnace conditions for Ti.

STEP	FURNACE TEMPERATURE (°C)	TIME (sec)		INTERNAL GASFLOW (ml/min)
		RAMP	HOLD	
Drying	130	6	60	300
Pretreatment	1400	1	45	300
Atomization	2650	0	5	0
Cleaning	2750	1	5	300
Cooling	20	1	20	300

CHAPTER 5

RESULTS AND DISCUSSION

Corrosion Behavior of Au, Rh, and Ir Implanted Sample

Au and Rh implantation

As mentioned in CHAPTER 3, Au is the only element which will not corrode in pure aqueous solutions, and consequently the initial study was directed toward Au implantation.

Ti-6Al-4V was implanted with Au^{+2} to a fluence of 5.85×10^{15} ions/cm² at an energy of 244 KeV. Sputtering with Ar produced ion beams of 2 to 4 μA and the desired fluences were obtained in less than 40 minutes. The fluence or dose of implanted atoms was calculated from the measured total beam charge. The total beam charge, Q , is given by.

$$Q = F \times V \times e \times A$$

where F : fluence, No. of ions/cm²
 V : valence of each ion
 e : electron charge, $1.602 \times 10^{-13} \mu\text{C}$
 A : area of beam on sample

The area of beam on sample was calibrated to 3.772 cm² for the particular implanter used. By inserting the measured charge of 7067 μC into the above relationship, the fluence of implanted Au atoms, 5.85×10^{15} ions/cm², was calculated. This fluence resulted in a near Gaussian concentration profile with the 2.0 at.% peak-max concentration located at approximately 60 nm from the surface.

To have Au atoms covering the entire surface with at least one

atomic layer, Ti must be dissolved preferentially. Au implanted Ti-6Al-4V was anodized at 0.4 V (SHE) in 0.9% NaCl + 20 Vol.% HCl at 50° C for 113 minutes to accelerate the dissolution of Ti, and the open-circuit corrosion potential of the anodized sample was then measured in aerated saline solution after 2 hrs of immersion. Table 5 shows the open-circuit corrosion potentials of Au implanted and unimplanted Ti-6Al-4V in aerated saline solution after each anodization treatment. The open-circuit corrosion potential of Au implanted Ti-6Al-4V increased after each treatment but the corrosion potential of 215 mV after the third treatment was still lower than that of pure Au, 443 mV.

The concentration profiles of implanted Au atoms before and after corrosion treatments are shown in Figure 27. It is clear from the RBS profiles that Ti was dissolved away and Au was enriched at the surface. The number of Au atoms released by the preferential dissolution of Ti can be calculated through the following equation,

$$\# \text{ of Au atoms released} = \rho_a \text{ of Ti} \times 1 \text{ cm}^2 \times t \times (\text{at. fraction of Au})$$

$$\text{where } \rho_a = \text{atomic density of Ti, } 5.66 \times 10^{22} \text{ atoms/cm}^3$$

$$t = \text{dissolved thickness, cm}$$

By comparing the backshoulder of profiles as shown in Figure 27, it was assumed that the given corrosion treatments corroded 390 Å. Thus, the number of released Au atoms corresponded to the shaded area and was 1.32×10^{15} atoms/cm² from the above equation. The average atomic fraction of Au used was 0.6. If all the released Au atoms were retained and uniformly distributed throughout the surface, they should cover the entire surface and the open-circuit corrosion potential must be that of

Table 5. Corrosion potential of 2.0 at.% peak-max Au implanted and unimplanted Ti-6Al-4V in isotonic saline after each anodic treatment.

	Corrosion Potential (mV vs. SHE)	
	Au implanted Ti-6Al-4V	Unimplanted Ti-6Al-4V
As-received	170	87
After 1st Anodizing	164	97
After 2nd Anodizing	221	125
After 3rd Anodizing	215	137

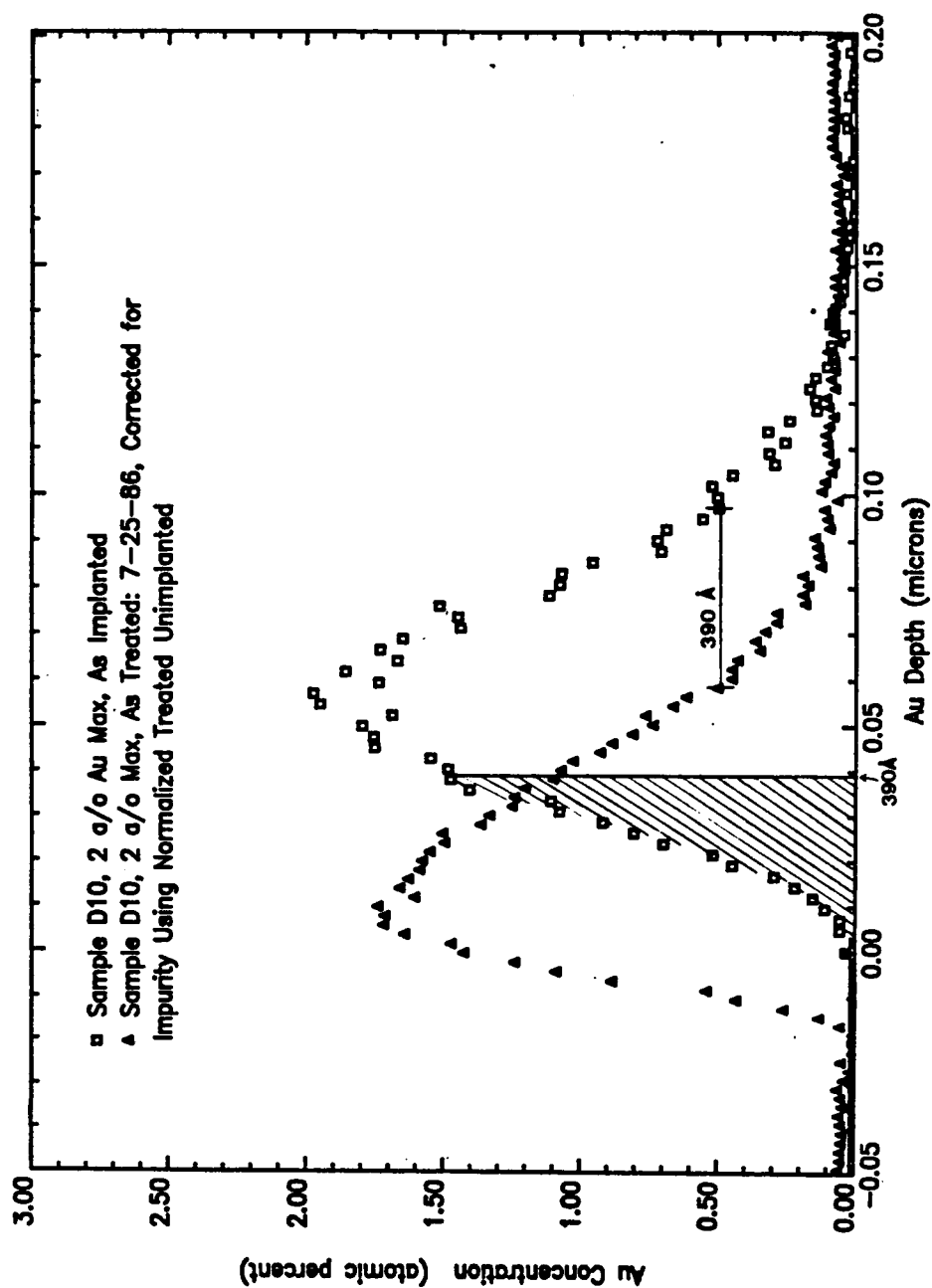


Figure 27. Rutherford backscattering concentration (2.0 MeV He ions) profile of Au for 2.0 at.% peak-max Au implanted Ti-6Al-4V, as implanted and after corrosion treatments.

pure Au. It was not clear at that time why the corrosion treated 2.0 at.% peak-max Au implanted Ti-6Al-4V did not show an open-circuit corrosion potential as high as that of Au, and afterwards more careful corrosion treatments were given to all implanted samples as described in the experimental procedures.

Another Au implanted Ti-6Al-4V was prepared with similar implantation parameters to the earlier sample (5.49×10^{15} ions/cm², 240 KeV), and Ti was also implanted with Rh⁺ to a fluence of 7.38×10^{15} ions/cm² at 122 KeV.

The anodic polarization behavior in deaerated 1N H₂SO₄ of the control material (unimplanted Ti-6Al-4V), and the as-implanted 2.0 at.% peak-max Au implanted Ti-6Al-4V and 2.5 at.% peak-max Rh implanted Ti are shown in Figure 28. The two noble-metal ion-implanted materials responded similarly in the as-implanted condition, with both producing much more noble open-circuit corrosion potentials and much lower anodic current densities than the control material.

The samples were then immersed in the deaerated 1N H₂SO₄ solution for noble-metal surface enrichment. Figure 29 shows the behavior of the open-circuit corrosion potential, E_c , as a function of time over four days. In Figure 29, it is seen that for all three samples the initial open-circuit corrosion potentials were high (noble values) due to the passive film created by the prior anodic polarization curve generation. The noble potentials dropped to more active values over the first 2-7 hours as a result of adjustments in the passive films. The passive film for the control material adjusted to the freely-corroding condition within two hours, with E_c remaining stable and very active thereafter.

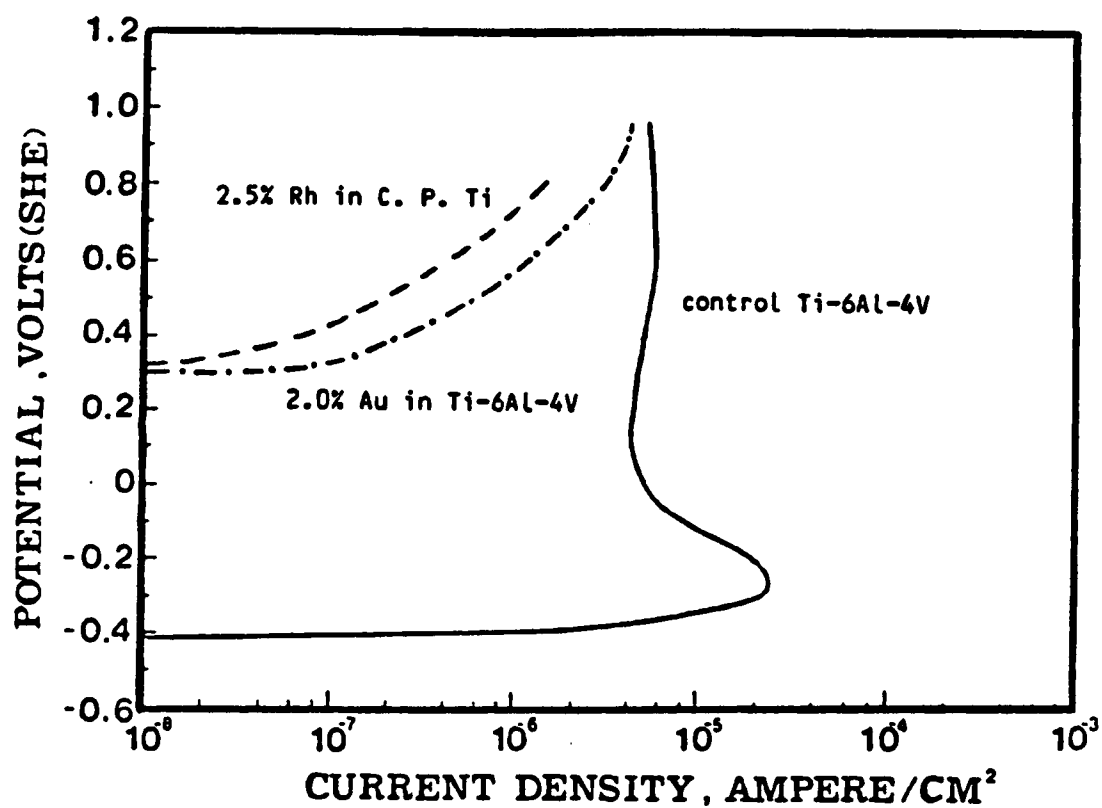


Figure 28. Anodic polarization behavior of as-implanted and control materials in deaerated 1N H₂SO₄ (1.2 V/h).

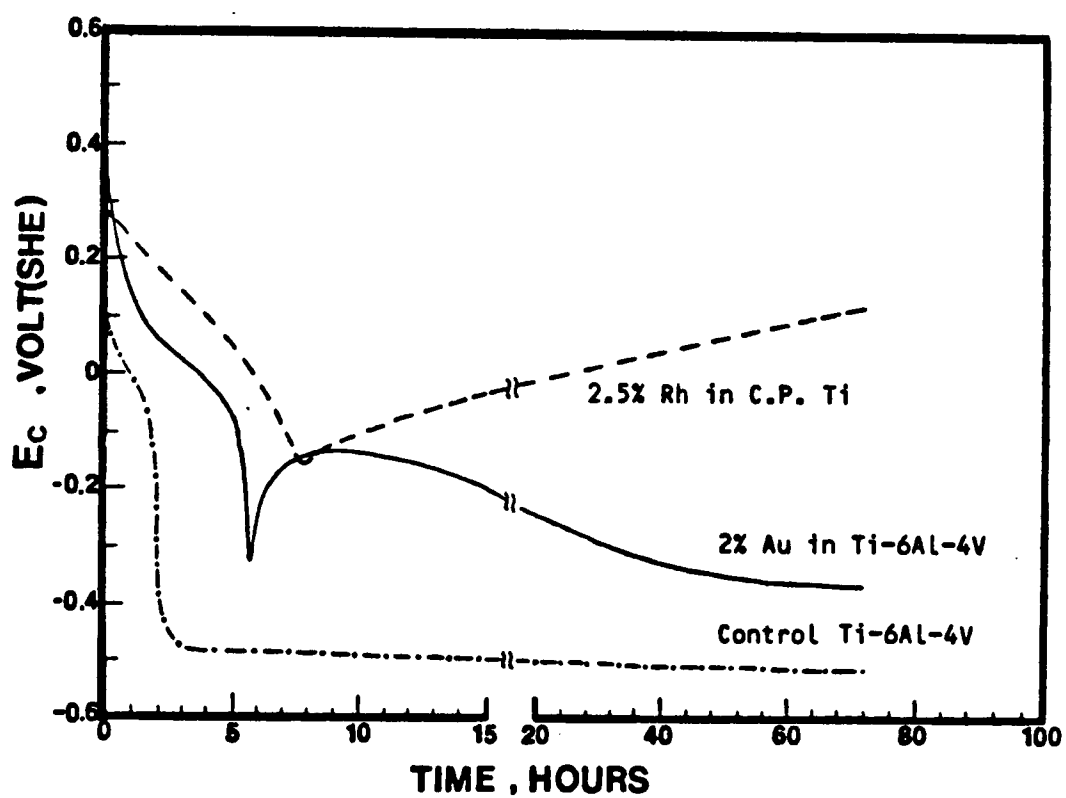


Figure 29. Open-circuit corrosion potential of Au and Rh implanted and control samples in deaerated 1N H_2SO_4 .

The surface characteristics of the 2 at.% peak-max Au implanted Ti-6Al-4V adjusted over a time period of six hours; then the open-circuit corrosion potential, E_c , reversed toward the noble (positive) direction as the Ti dissolved away and Au atoms accumulated on the surface, indicating lower corrosion rates. However, at eight hours, E_c again began to move in the active direction, slowly approaching the value for the control material. Visual examination of the surface indicated that Au enrichment had occurred: the coloration had slowly changed from the bright silver appearance of Ti to the yellowish color of Au. However, it was also noted that the polished Ti-6Al-4V surface under the Au film had undergone etching during the H_2SO_4 pretreatment. Consequently, it was concluded that with this particular pretreatment, the ion implanted Au did indeed enrich at the surface, but it did not adequately adhere to the Ti substrate. Therefore, with reference to Figure 29, it did not produce the desired long-term electrochemical effect. Similar behavior has been reported for Pt implanted Ti sample. Thompson et al. (12) have discussed that the remaining Pt is loosely bound on a dynamically corroding surface and remains in the "inactive" state indefinitely. On the contrary, the 2.5 at.% peak-max Rh implanted Ti, after the initial adjustment period of approximately 7.5 hours, continuously showed an increase in E_c out to the four day duration of the test. This continuous movement of E_c in the noble direction indicated not only that Rh surface enrichment was occurring, but also that the Rh was adhering to the Ti substrate. Also, Rutherford backscattering analysis showed that most of the implanted Rh was retained in the sample after this corrosion treatment.

Finally, the Rh implanted material, the control Ti-6Al-4V material, and prepassivated Ti-6Al-4V were immersed in aerated isotonic saline solution for 37 days. The E_c values were continuously monitored, and are shown in Figure 30. The warm nitric acid prepassivation treatment (60°C, 30 vol.% nitric acid, 30 minutes; ASTM F86) is generally regarded as an optimum means to improve the corrosion resistance of Ti-6Al-4V. However, as seen by the E_c behavior in Figure 30, the passive film developed by the prepassivation treatment was not stable with time in isotonic saline, i.e. the E_c values for the prepassivated and non-prepassivated material approached each other after 37 days. On the other hand, the open-circuit corrosion potential of the 2.5 at.% peak-max Rh implanted Ti increased to more noble values over the entire exposure period, indicating complete stability of the Rh enriched surface in isotonic saline.

After corrosion treatments, the surfaces were characterized with x-ray photoelectron spectroscopy (XPS). Figure 31 shows (a) $3d_{5/2}$ line of Rh and (b) $4f_{7/2}$ line of Au. An important advantage of XPS is the ability to obtain information on chemical states from the variations in binding energies, or chemical shifts, of the photoelectron lines by comparing binding energies with the experimental data on standard materials.

The $3d_{5/2}$ line of Rh was not positively identifiable in terms of chemical state because of lack of experimental data, but it was definitely not related to metallic Rh. It was presumed that the Rh is in some oxide state which gives the good adhesion of the Rh enriched surface to the substrate. On the other hand, the Au peak on the

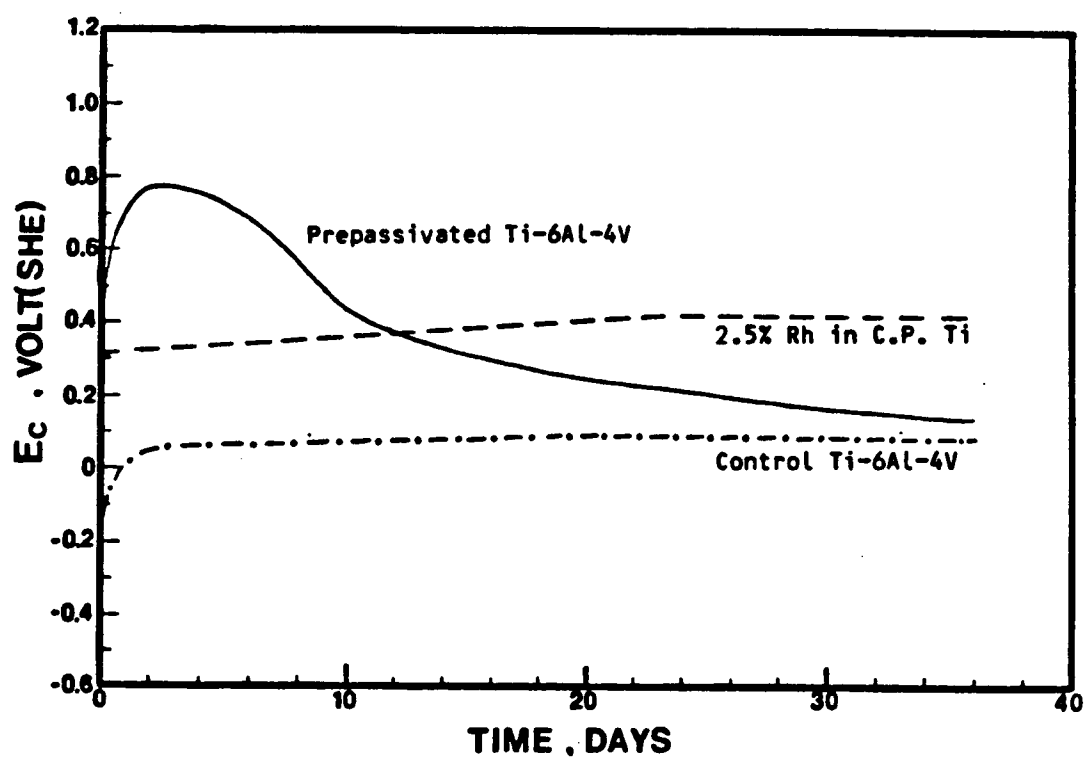
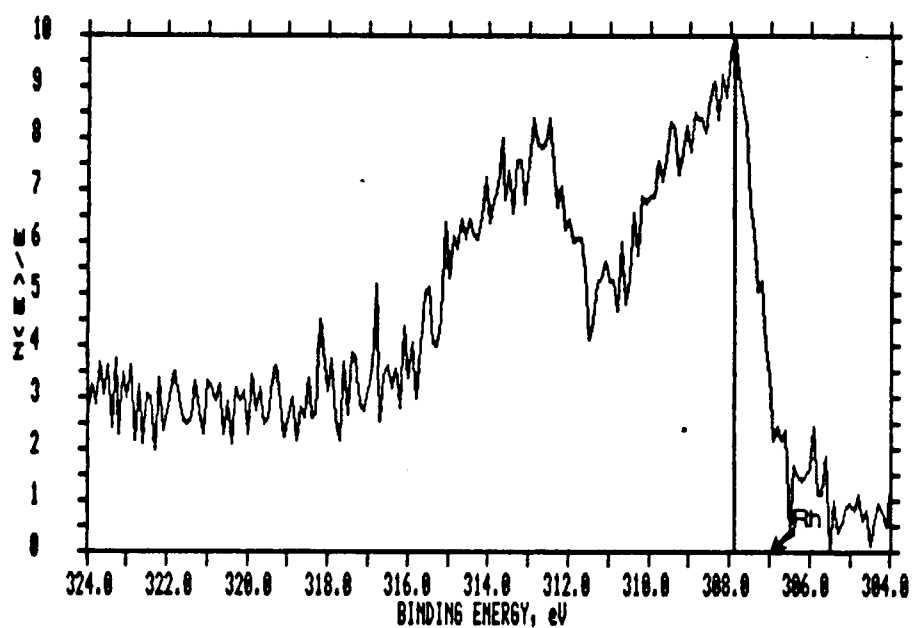
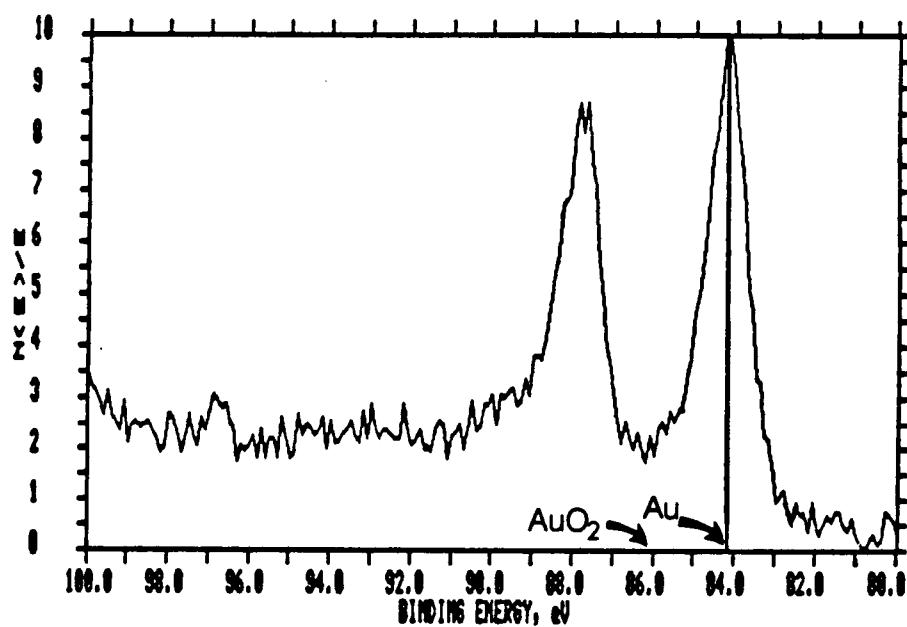


Figure 30. Open-circuit corrosion potential of 2.5 at.% peak-max Rh implanted Ti, as-polished, and prepassivated Ti-6Al-4V in aerated isotonic saline.



(a)



(b)

Figure 31. XPS spectra of (a) Rh for 2.5 at.% peak-max Rh implanted Ti, and (b) Au for 2.0 at.% peak-max Au implanted Ti-6Al-4V, after corrosion treatments.

corrosion treated implanted sample remained at the same binding energy value as pure metallic Au, which explains why the enriched Au layers did not properly adhere to the Ti substrates and did not show the long-term improvements in corrosion resistance.

Ir implantation

Iridium, as a specific noble metal, offers certain potential advantages. It has been characterized as the most corrosion resistant metal known (107) and as having good biocompatibility, i.e. good biological performance (108). With regard to the possible use of pure iridium, there are number of disadvantages. Not only is iridium expensive, but also it is very brittle, and therefore difficult to mechanically fabricate. Furthermore, because of its extreme resistance to corrosion, chemical processing is very difficult, e.g. etching and lithography of miniature devices. This section describes the studies involving effects of Ir implantation.

Beam currents of 20-30 μA were achieved from a Ar sputter source. Implantation of Ir^{+2} was accomplished at an energy of 244 KeV and at fluences of 0.74×10^{16} and 1.48×10^{16} ions/cm². With 2.0 MeV He^{+} Rutherford backscattering (RBS) analysis, the peak Ir concentrations at the two fluences were determined to be 2.5 and 5.0 at.% peak-max, respectively. The peaks in the Ir concentration profiles occurred at a depth of approximately 30 nm.

The first characterization involved analysis of anodic polarization behavior of as-implanted samples in N_2 -deaerated 1N H_2SO_4 at room temperature. Results are shown in Figure 32 for 2.5% and 5.0%

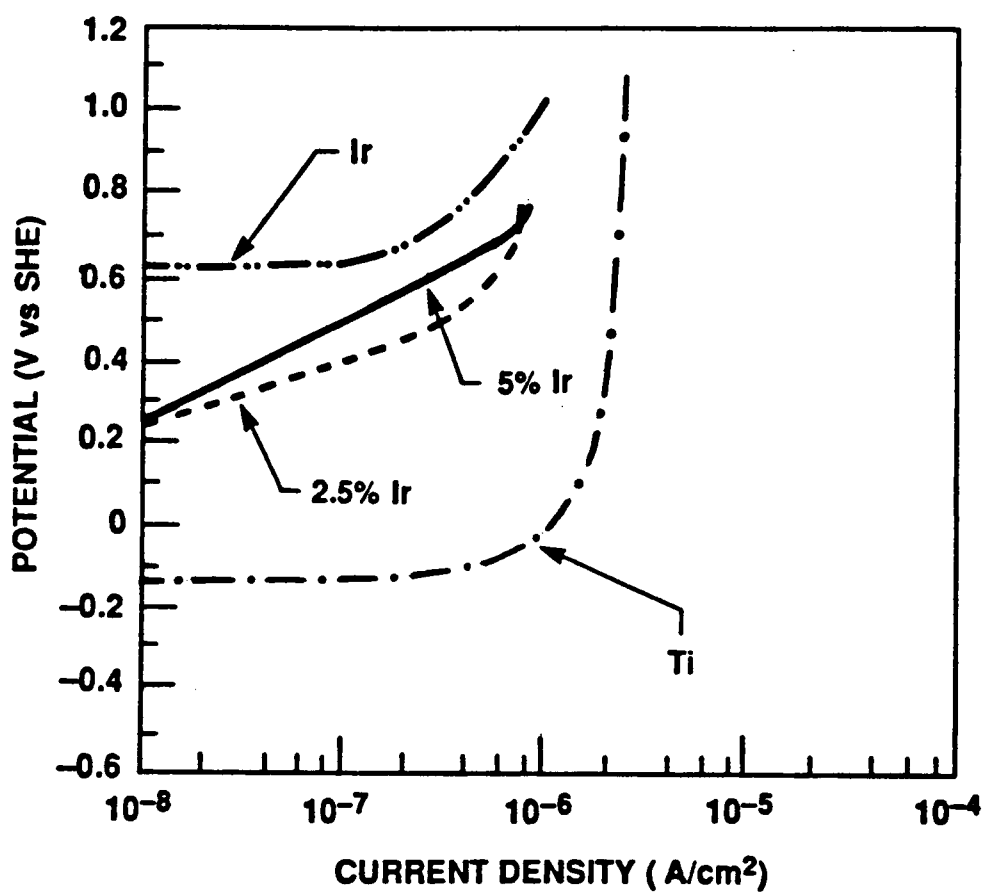


Figure 32. Anodic polarization behavior of as-implanted Ti samples and control materials in deaerated 1N H₂SO₄ (1.2 V/h)

peak-max Ir implanted Ti, and in Figure 33 for 2.5% and 5.0% peak-max Ir implanted Ti-6Al-4V along with references (unimplanted Ti and Ti-6Al-4V, pure Ir). Each anodic polarization curve was determined by increasing the potential from the open-circuit corrosion-potential measured after 30 minutes of immersion. The implanted samples were polarized to 0.8 V (SHE) just above which Ir oxidizes to IrO_2 at $\text{pH}=1$. The Ir implanted materials produced more noble open-circuit corrosion potentials and lower anodic current densities relative to unimplanted Ti and Ti-6Al-4V. These initial beneficial effects were probably due to the air formed oxide film produced during the implantation process rather than the chemical effects of implanted Ir atoms since the concentration of Ir at the surface in the as-implanted condition is much less than the peak-max values and actually near the zero value. The enhanced corrosion resistance of implanted materials due to the formation of thick air oxide films has been observed by Ashworth et al. (69,70). They reported that the removal of the oxide layer by cathodic reduction caused the sample to revert back to the original corrosion behavior.

The next step was to immerse the implanted samples, which had previously undergone anodic polarization, into N_2 -deaerated 1N H_2SO_4 and to continuously monitor the open-circuit corrosion potential as an indicator of Ir surface enrichment. Use of the H_2SO_4 solution was viewed as a way to accelerate the enrichment process. Results are shown in Figures 34 and Figure 35. Fresh control samples, i.e. samples that had not undergone anodic polarization, were also included: pure Ir, as-polished Ti and Ti-6Al-4V, and prepassivated Ti and Ti-6Al-4V. The

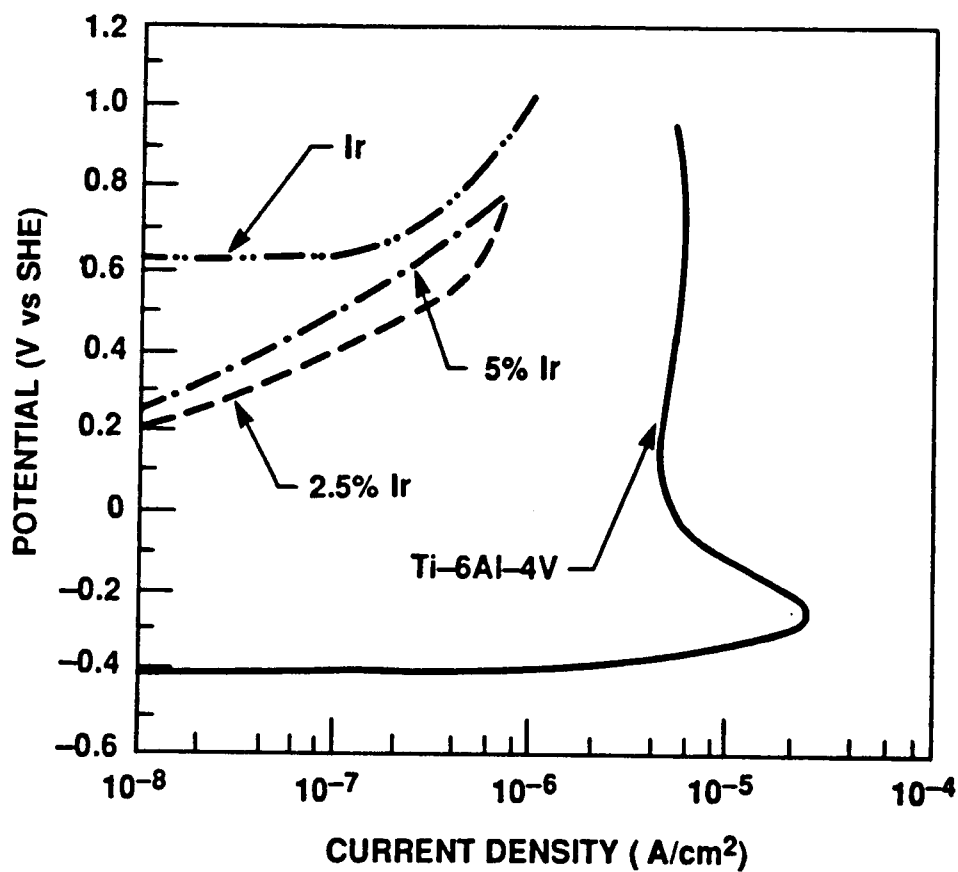


Figure 33. Anodic polarization behavior of as-implanted Ti-6Al-4V samples and control materials in deaerated 1N H₂SO₄ (1.2 V/h).

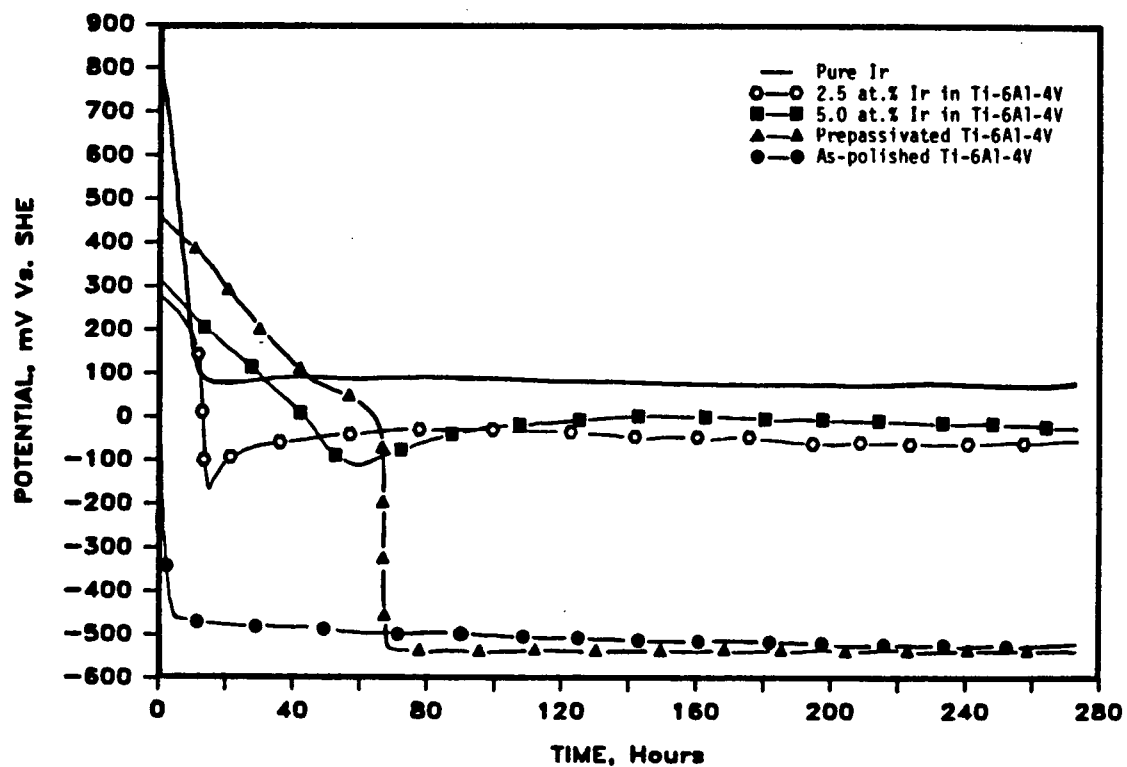


Figure 34. Corrosion potential versus time for 2.5 at.% and 5.0 at.% peak-max Ir implanted Ti-6Al-4V samples along with control samples in deaerated 1N H₂SO₄.

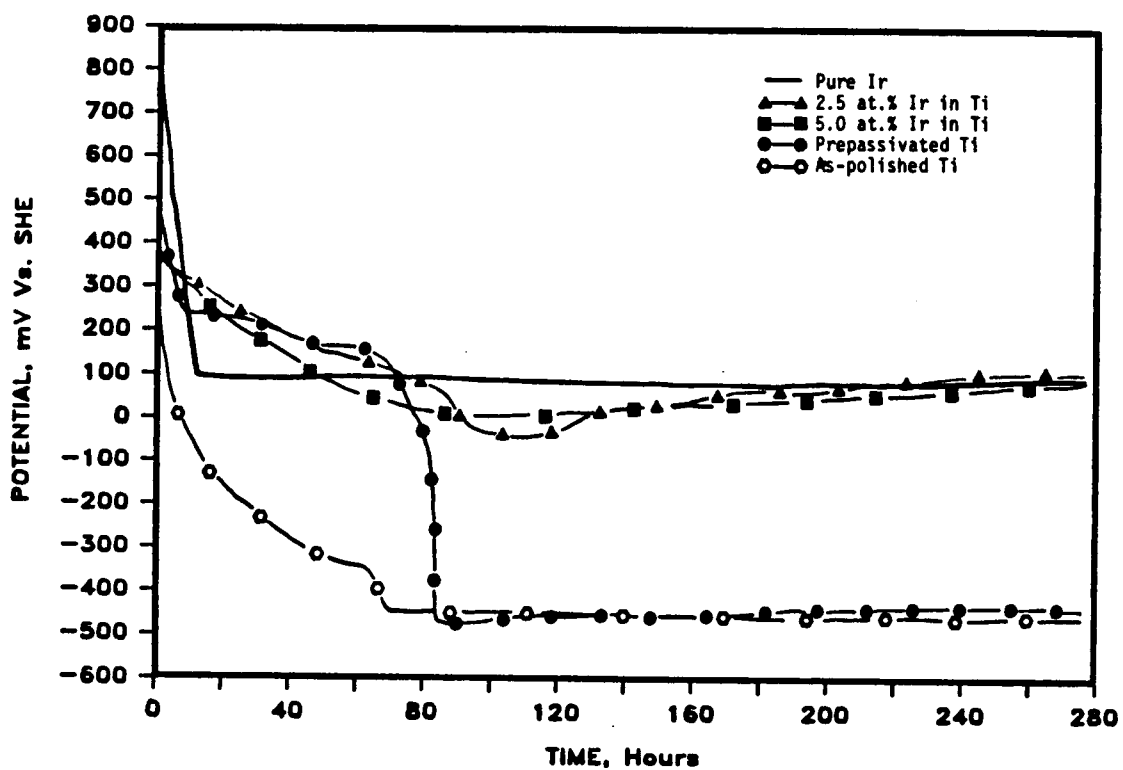


Figure 35. Corrosion potential versus time for 2.5 at.% and 5.0 at.% peak-max Ir implanted Ti samples along with control samples in deaerated 1N H_2SO_4 .

prepassivated materials had been immersed in warm nitric acid for 30 minutes-- the primary step in a treatment often given to surgical devices to improve corrosion resistance (ASTM F86). As shown in Figure 34, the corrosion potentials of the as-polished and prepassivated Ti-6Al-4V were essentially the same at about -520 mv (SHE) after approximately 70 hours. Both samples underwent corrosion in the active state at a very low potential indicating the instability of pre-formed passive films in 1N H_2SO_4 . However, the Ir implanted materials produced continuous increases in open-circuit corrosion-potential toward that of pure Ir after initial adjustments in the anodically-formed and air-formed oxide to the freely corroding conditions in H_2SO_4 . The initial adjustment periods for 2.5 at.% and 5.0 at.% peak-max Ir implanted Ti-6Al-4V was 16 hours and 58 hours, respectively.

Even in the initial adjustments, the implanted Ir atoms were accumulating at the surface by the preferential dissolution of Ti, Al, and V, which would continuously change the open circuit corrosion potential to noble direction. However, the increments in open-circuit corrosion potential due to the Ir surface enrichments were smaller compared to the drops due to the adjustments in preformed oxide films. Therefore, the overall open-circuit corrosion potential decreased in the adjustment period. Since the 5 at.% peak-max Ir implanted Ti-6Al-4V was exposed to the ion beam longer than the 2.5 at.% peak-max Ir implanted Ti-6Al-4V, in order to obtain higher fluences, the air formed oxide on the 5 at.% peak-max Ir implanted Ti-6Al-4V was probably thicker, which required a longer adjustment period. If the samples were implanted with an inert gas, they would corrode in the active state at

around -520 mV (SHE) after the initial adjustments because the implanted inert atoms would not give any chemical effects but would result in a thickened air formed oxide. The lowest open circuit corrosion potential of the 5 at.% peak-max Ir implanted Ti-6Al-4V, -98 mV (SHE), is higher than that of the 2.5 at.% peak-max Ir implanted Ti-6Al-4V, -171 mV (SHE), because of the higher concentration of implanted Ir at a given depth.

Similar results are shown for 2.5 at.% and 5.0 at.% peak-max Ir implanted Ti in Figure 35. After approximately 84 hours, the corrosion potentials of the as-polished and prepassivated Ti were essentially the same around, -450 mV (SHE), while the Ir implanted samples produced continuous increases in the open-circuit corrosion potential toward that of pure Ir indicating continuous Ir surface enrichment.

Following the H_2SO_4 exposure, the Ir implanted samples were placed in the aerated isotonic saline (0.9 wt% NaCl). In addition, fresh control samples (prepassivated Ti and Ti-6Al-4V, as-polished Ti, Ti-6Al-4V, and pure Ir) were prepared and evaluated. The open circuit corrosion potentials were continuously monitored for 45 days. The results are shown in Figures 36 and 37 for Ir implanted Ti-6Al-4V and Ti, respectively. The open-circuit corrosion potentials of the as-polished and prepassivated samples approached each other indicating instability with time for the prepassivated surface. This effect has also been reported by Fraker et al. (7). However, the corrosion potentials of the Ir implanted materials were stable in the saline solution, with small increases in the noble direction after initial adjustments, approaching the value for pure Ir.

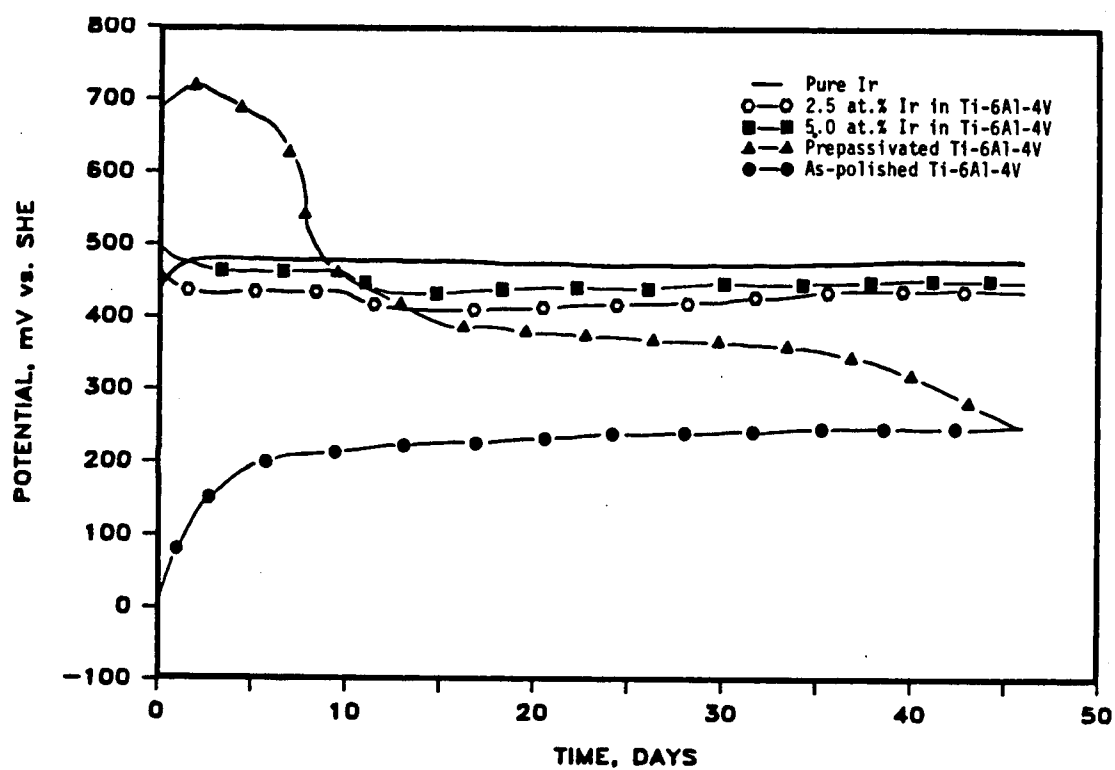


Figure 36. Corrosion potential versus time for 2.5 at.% and 5.0 at.% peak-max Ir implanted Ti-6Al-4V samples along with control samples in aerated isotonic saline.

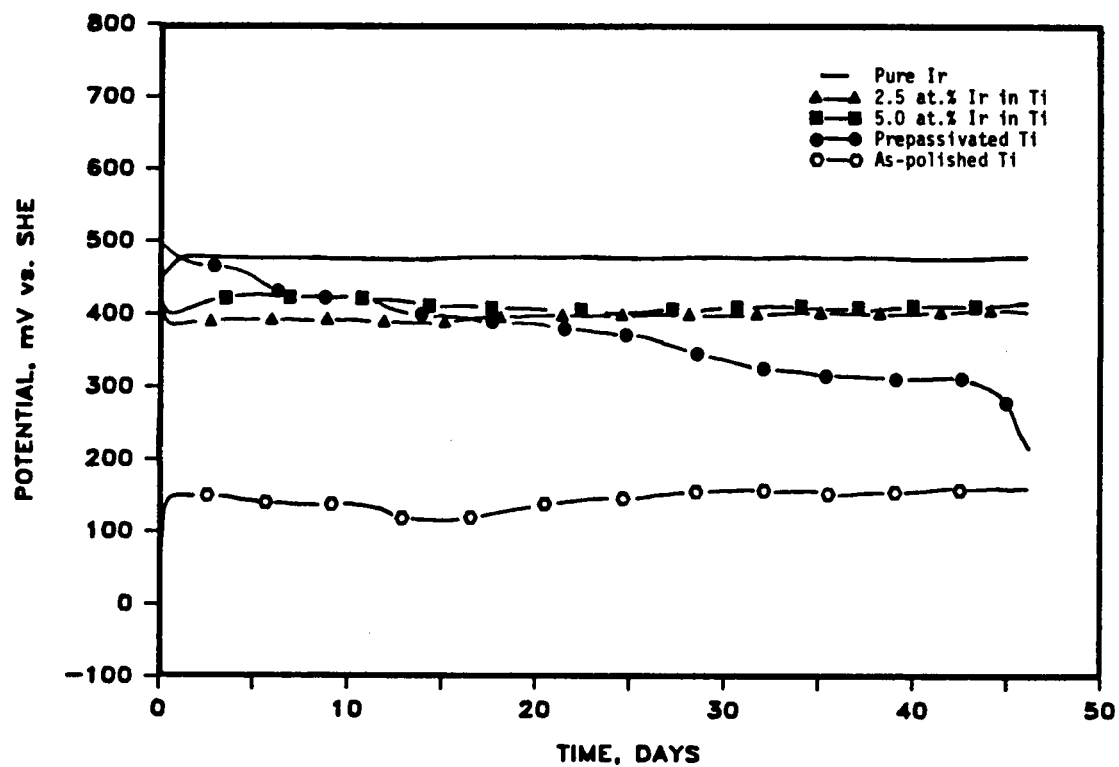


Figure 37. Corrosion potential versus time for 2.5 at.% and 5.0 at.% peak-max Ir implanted Ti samples along with control samples in aerated isotonic saline.

The electrochemical results indicated substantial enrichment of Ir at the surface of the Ir implanted Ti and Ti-6Al-4V samples. Surface analyses by XPS and RBS supported the evidence of the electrochemical results.

Figures 38-41 show RBS concentration profiles for Ir in the 2.5 at.% and 5.0 at.% peak-max Ir implanted Ti-6Al-4V and in the 2.5 at.% and 5.0 at.% peak-max Ir implanted Ti for the as-implanted condition and then after the corrosion treatments described above. RBS profiles do not show clearly the degree of Ir enrichment at the surface by the corrosion treatments. However, the total area beneath the Ir profile for the as-implanted condition and after the corrosion treated condition is constant to within the $\pm 5\%$ error in the measurement indicating that the most of the implanted Ir atoms were retained in the material. Also, the shift of peak to the surface after corrosion treatments indicates that the surface was indeed enriched with Ir atoms, especially for the 2.5 at.% and 5.0 at.% peak-max Ir implanted Ti-6Al-4V (see Figures 38 and 39).

The RBS profile of Ir for the corrosion treated sample in Figure 39 can be simulated with constituent layer models. The simulation shown in Figure 42 was obtained with the model in which the first two layers are 100% Ir, and layers of increasing depth have progressively less percentages of Ir. Naturally such a calculation of expected RBS response from a model of constituent layers, in comparison with the actual response, does not provide a unique determination of the constitution. However, it does show that the ion-implanted Ir, after the corrosion treatments, is a major element in the near surface.

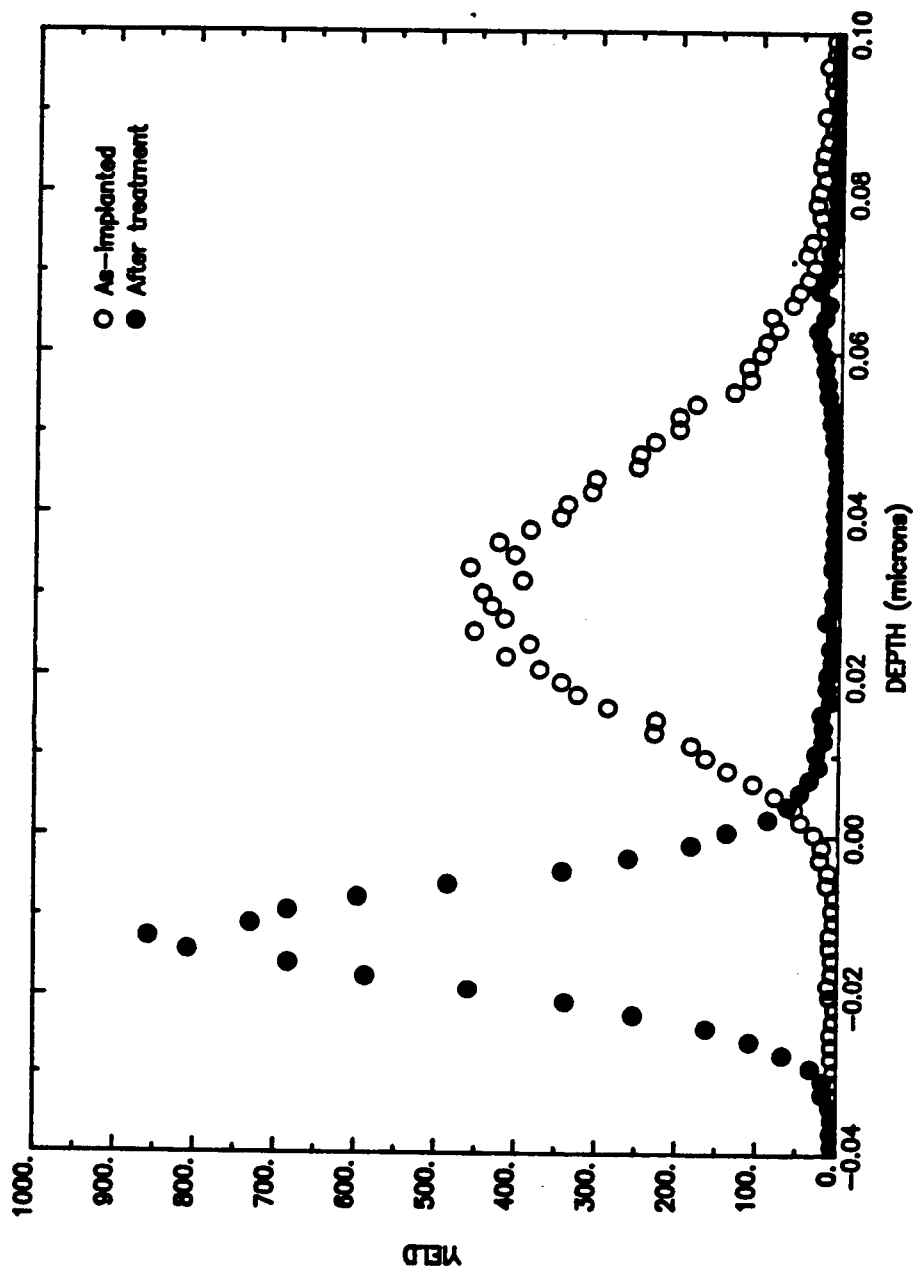


Figure 38. Rutherford backscattering yield (2.0 MeV He ions) versus depth of Ir for 2.5 at.% peak-max Ir implanted Ti-6Al-4V, as-implanted and corrosion treatments.

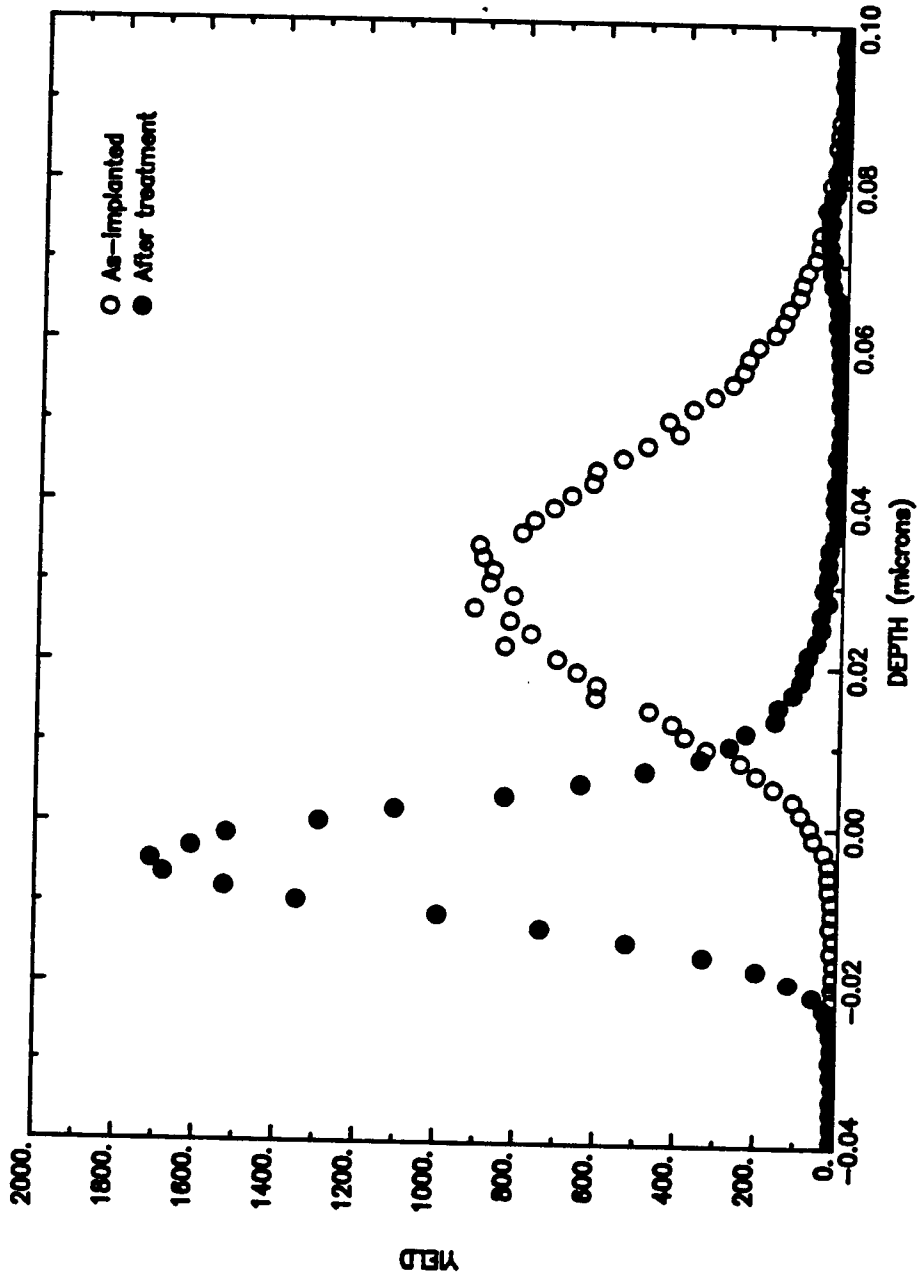


Figure 39. Rutherford backscattering yield (2.0 MeV He ions) versus depth of Ir for 5.0 at.% peak-max Ir implanted Ti-6Al-4V, as-implanted and corrosion treatments.

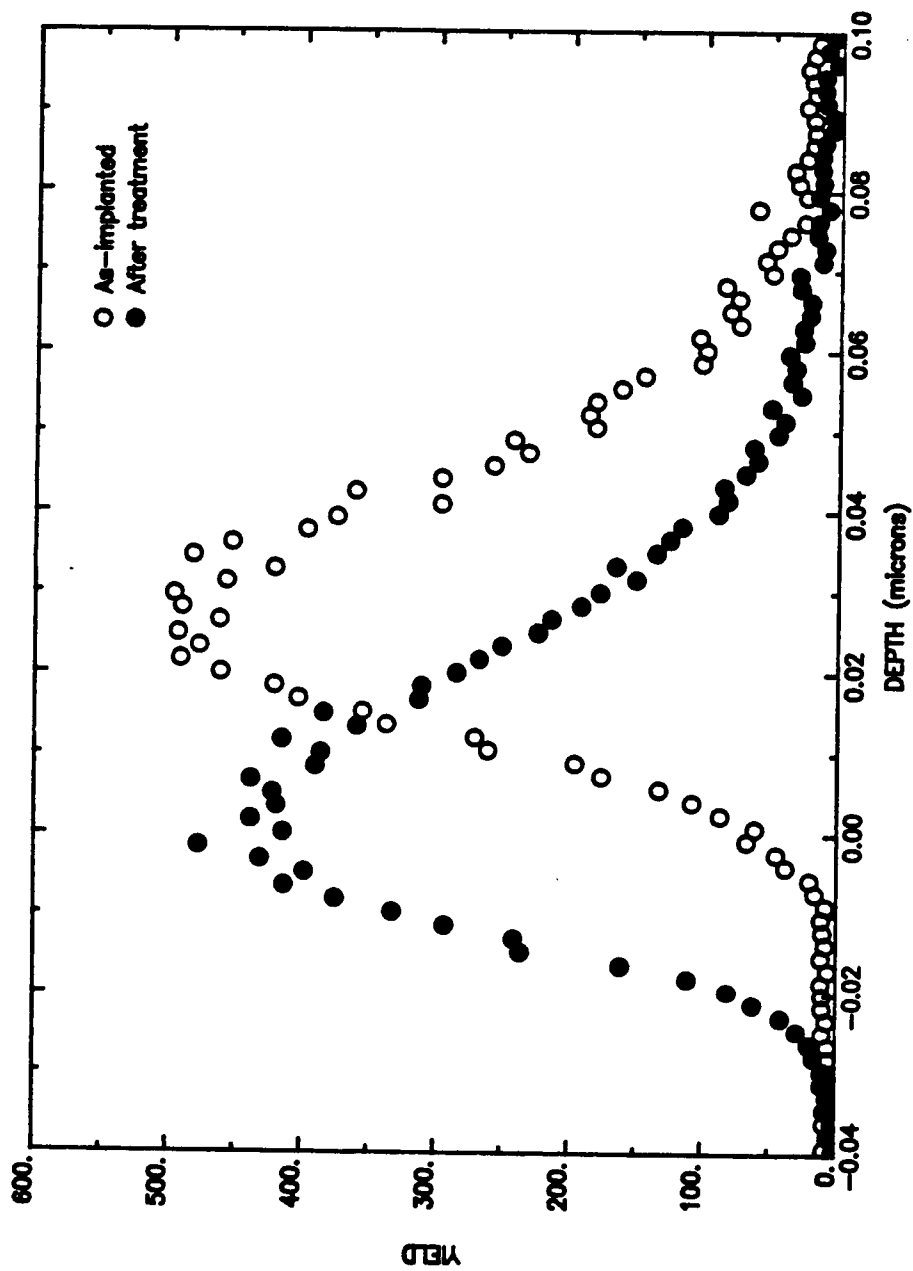


Figure 40. Rutherford backscattering yield (2.0 MeV He ions) versus depth of Ir for 2.5 at.% peak-max Ir implanted Ti, as-implanted and corrosion treatments.

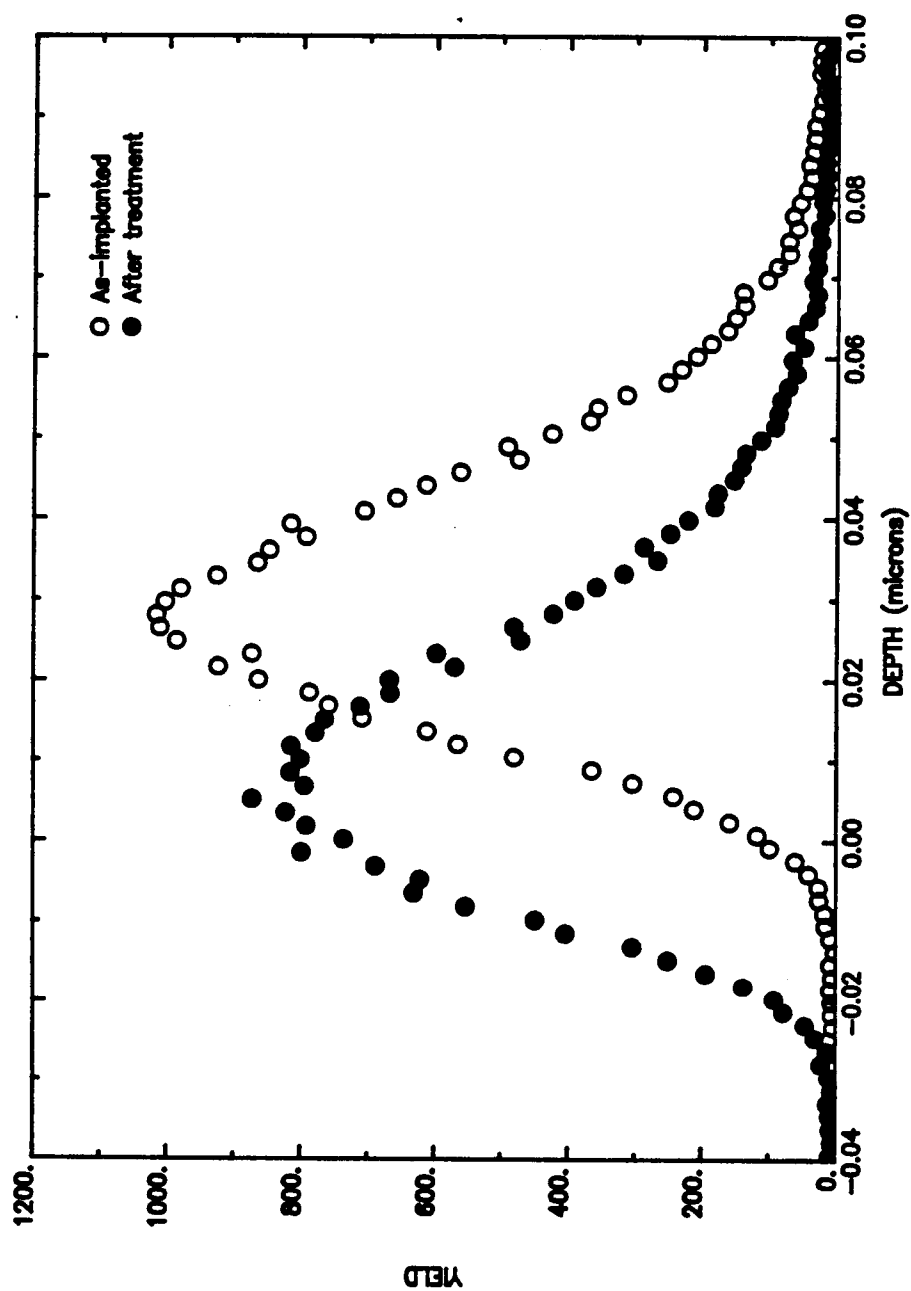


Figure 41. Rutherford backscattering yield (2.0 MeV He ions) versus depth of Ir for 5.0 at.% peak-max Ir implanted Ti, as-implanted and corrosion treatments.

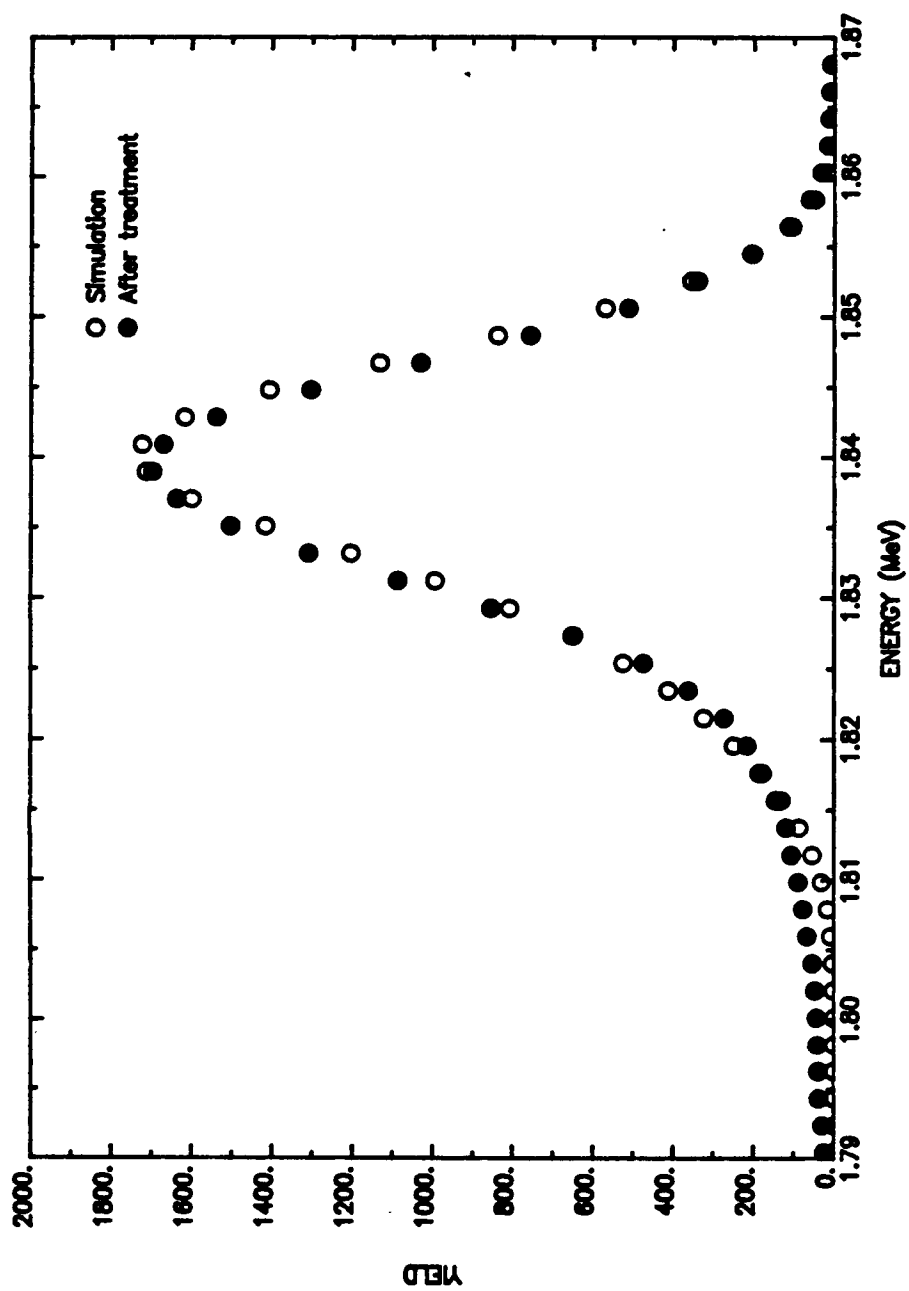


Figure 42. Simulated profile of Ir with the constituent layer model.

Figure 43 shows the Ti edge in the RBS profile of the 5 at.% peak-max Ir implanted Ti-6Al-4V before and after corrosion treatments. The Ti edge in the RBS histogram of the corrosion treated sample was offset in energy (depth) indicating that it was below the surface due to Ir coverage. This effect, represented by only two channels of spectrometer resolution, was nevertheless unmistakable. It is consistent with a depth of 2 or 3 nm of Ir, or perhaps nearly all of the implanted Ir in oxidized form. No such offset was found for the implanted Ti samples, in which case the Ir was distributed as indicated in Figures 40 and 41.

Following RBS analyses, the surfaces of the implanted samples were analyzed by x-ray photoelectron spectroscopy (XPS), which provides both the chemical composition and the chemical state of elements at/near the solid surface over a very shallow depth, approximately 2 nm. Surfaces were not sputtered prior to XPS analysis. Figure 44 compares the XPS survey spectra for the 5 at.% peak-max Ir implanted Ti-6Al-4V in the as-implanted condition (a), and after the series of electrochemical treatments (b). The $2P_{3/2}$ line for Ti on the corrosion treated sample was almost completely suppressed, while the $4f_{7/2}$ line for Ir was very prominent. The XPS results were also consistent with the RBS results, indicating that the surface of the 5 at.% peak-max Ir implanted Ti-6Al-4V had practically solid coverage with Ir after the corrosion treatments. The $4f_{7/2}$ line for Ir occurred at a higher energy than either that of metallic Ir or IrO_2 . It was not identified but was assumed to reflect some oxide state involving mostly IrO_2 with some TiO_2 , which was responsible for the good adhesion of the Ir enriched

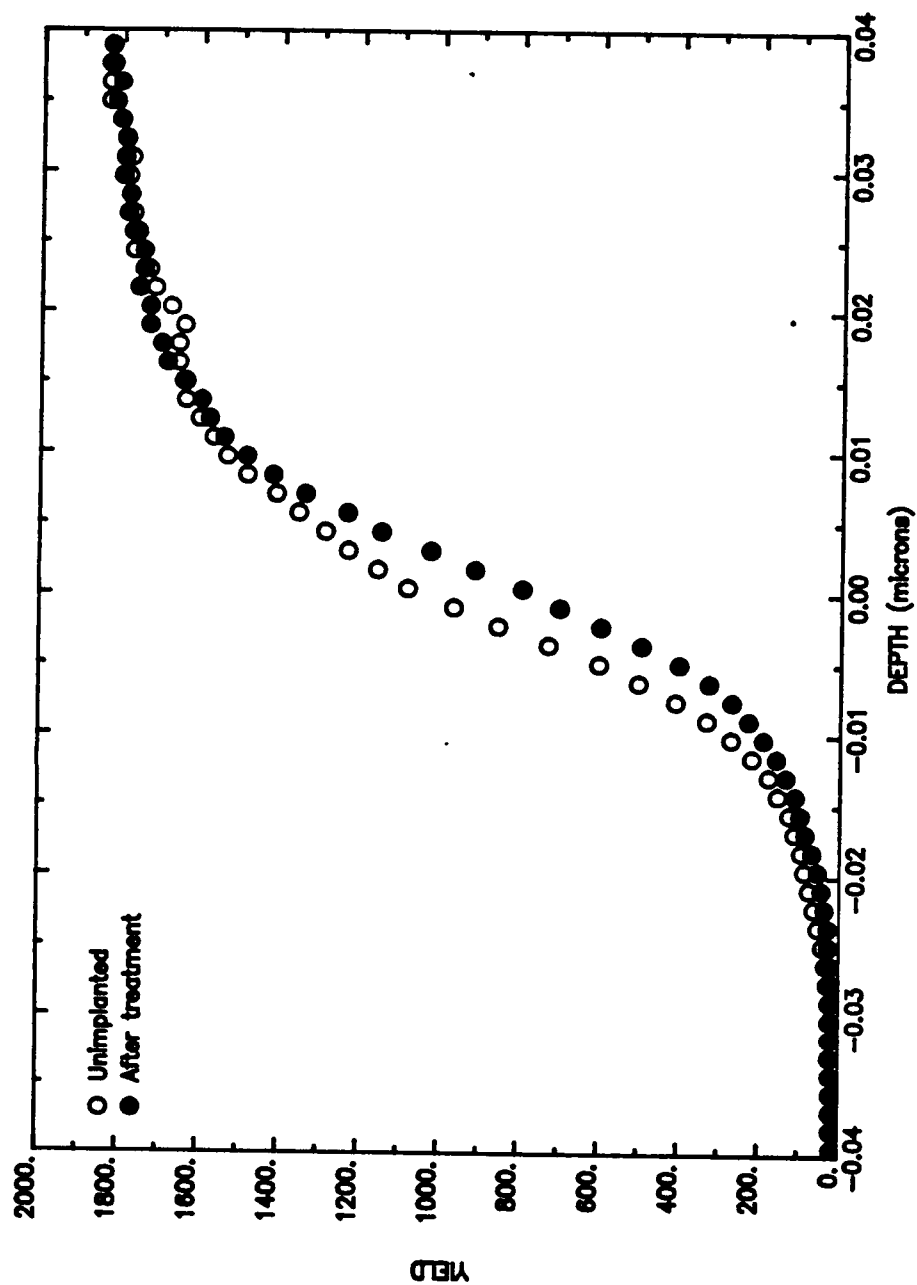
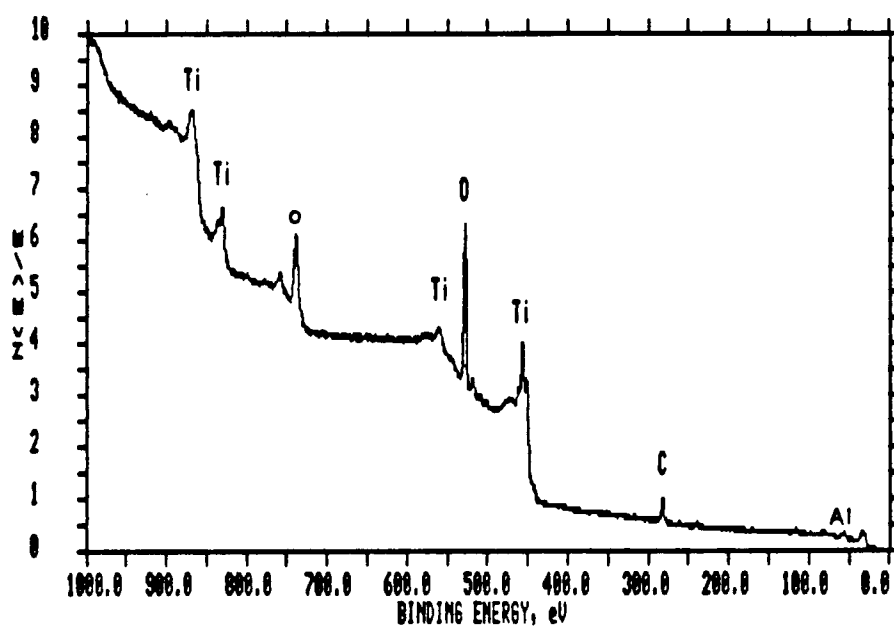
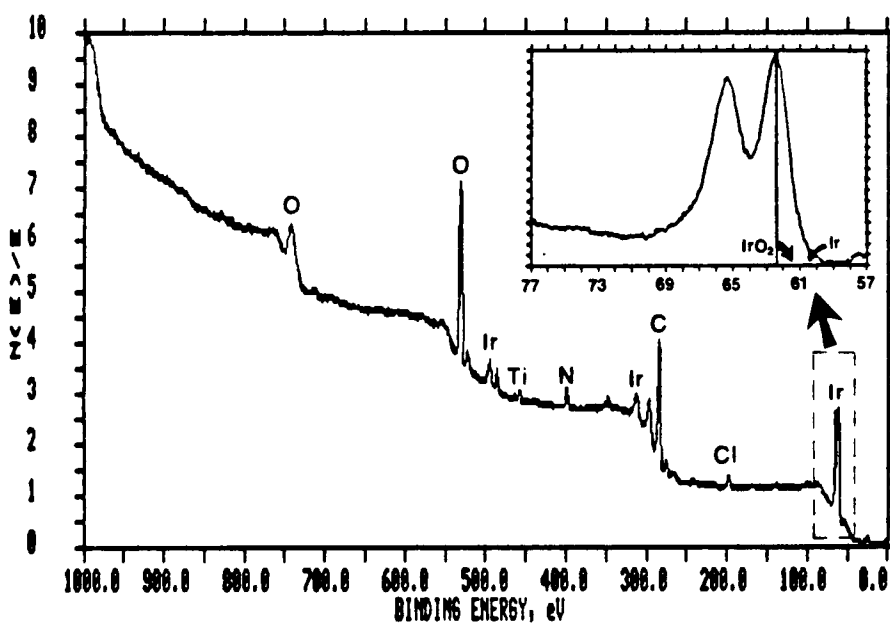


Figure 43. Rutherford backscattering yield from Ti versus depth, where the depth calibration assumes stopping-power values for pure Ir.



(a)



(b)

Figure 44. XPS spectra for 5.0 at.% peak-max Ir implanted Ti-6Al-4V: (a) as-implanted, (b) after corrosion treatments.

surface to the Ti substrate.

Averaged Ir concentrations over a depth of approximately 2 nm were obtained from XPS analysis and are shown in Table 6, expressed in terms of Ir/Ti atom ratios and atomic % Ir (determined as $(\text{Ir}/(\text{Ti}+\text{Ir})) \times 100$ to indicate the degree of Ir surface enrichment at the expense of Ti). It is seen that as a consequence of the corrosion treatments and tests, Ir had concentrated at and near the surface to average values of 33% and 87% for the 5.0 at.% peak-max Ir implanted Ti and Ti-6Al-4V, respectively. Since the XPS analysis averaged concentration over about 5 atomic layers, the actual surface concentrations of Ir were likely higher than the values of 33% and 87%.

Even though all the Ir implanted Ti and Ti-6Al-4V samples were corrosion treated in same way, Ir was more enriched at the surfaces of the implanted Ti-6Al-4V samples than the implanted Ti samples. Since CP Ti has better corrosion resistance than Ti-6Al-4V, the dissolution of Ti is lower for a given immersion time, and consequently the enrichment process is slower for implanted Ti samples. Following this rationale, the 5 at.% peak-max Ir implanted Ti was double exposed to the deaerated 1N H_2SO_4 , and the average Ir concentration was bound to increase from 33% to 56%. Also, the RBS concentration profile of the Ir, shown in Figure 45, clearly shows the continued shift of the peak to the surface indicating more Ir surface enrichment by the double corrosion treatment.

It was discussed in CHAPTER 3 that the increase in open-circuit corrosion potential of the implanted sample indicates noble metal enrichment at surface, and consequently reflects improvements in

Table 6. Chemical analyses, before and after corrosion treatments.

Material	BEFORE TREATMENTS Peak-Max Values at 30nm Depth Ir/Ti (Atomic % Ir)	AFTER TREATMENTS XPS Results ~2nm Depth Average Ir/Ti (Atomic % Ir)
2.5% Ir Peak-Max In Ti-6Al-4V	0.026 (2.5%)	1.53 (60%)
5.0% Ir Peak-Max In Ti-6Al-4V	0.053 (5.0%)	6.45 (87%)
2.5% Ir Peak-Max In Ti	0.026 (2.5%)	0.383 (28%)
5.0% Ir Peak-Max In Ti	0.053 (5.0%)	0.498 (33%)

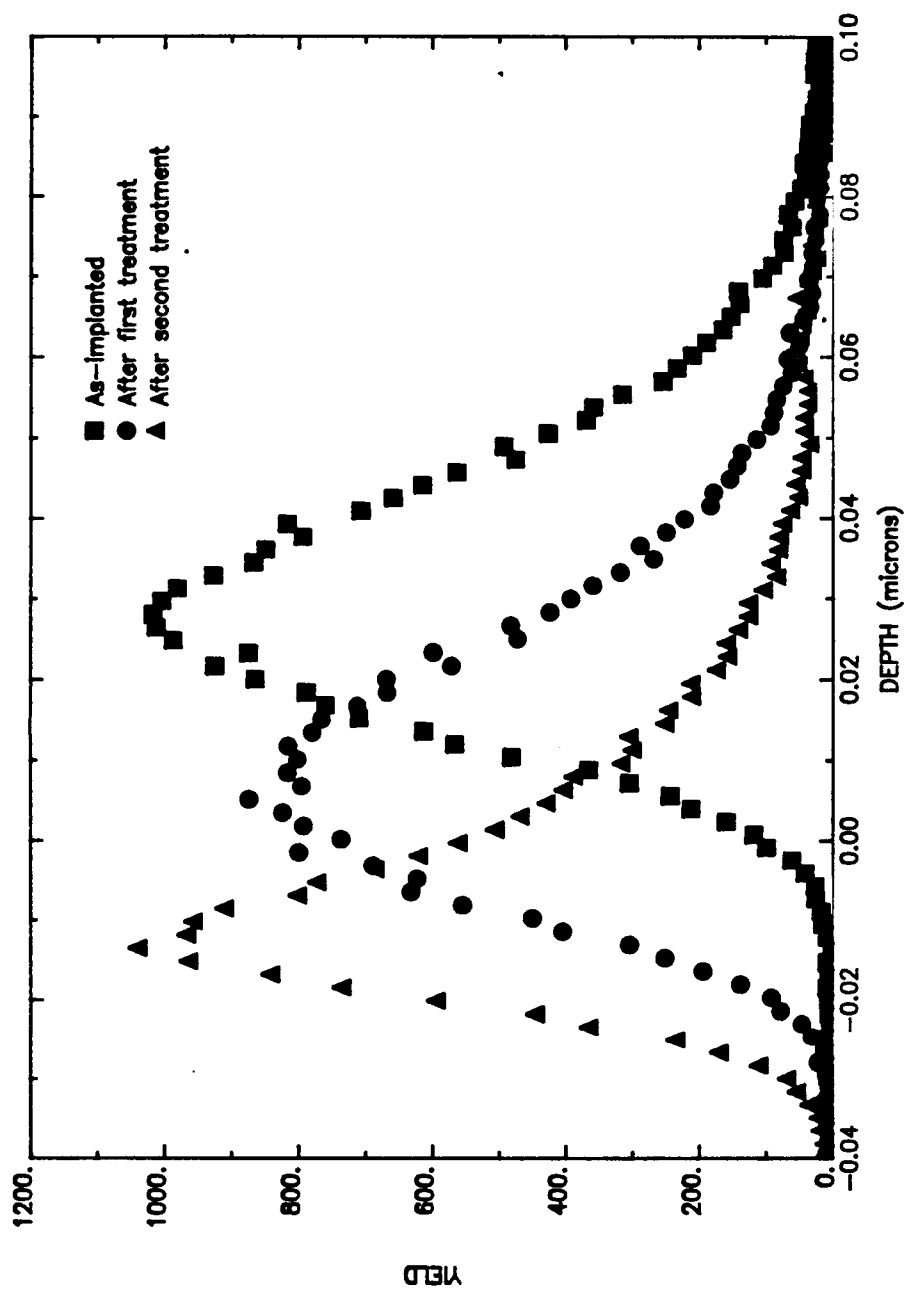


Figure 45. Rutherford backscattering yield (2.0 MeV He ions) versus depth of Ir for 5.0 at.% peak-max Ir implanted Ti.

corrosion resistance. Since current measurements could not be made while monitoring the open-circuit corrosion potential of samples, chemical analysis of the test solution was performed with atomic absorption spectrophotometer (AAS). In this technique, the dissolved amounts of individual elements in the solution are determined, which can be converted to the corresponding corrosion current density from the Faraday's law shown below.

$$I = [(W_i \times m_i \times F)/(M_i \times t)]$$

where I : current density, $\mu\text{A}/\text{cm}^2$

W_i : dissolved amounts of i element, $\mu\text{g}/\text{cm}^2$

m_i : valence of i element

M_i : atomic weight of i element

t : time, s

This technique is very useful for considering the contribution of each element to the current density that is determined at any potential from the polarization curve, since the current represents the net current density for all elements at the sample surface. The determination of the contribution of each alloy element to the dissolution current density also indirectly yields information about the surface composition of the alloy. For example, if the ratio of A element to B element is high relative to the bulk ratio in a test solution, the surface is enriched in the B element.

The as-polished Ti sample was immersed in deaerated 1N H_2SO_4 and the test solution was analyzed for the dissolved amount of Ti at each given time while monitoring the open-circuit corrosion potential.

Figure 46 shows the open-circuit corrosion potential and the current

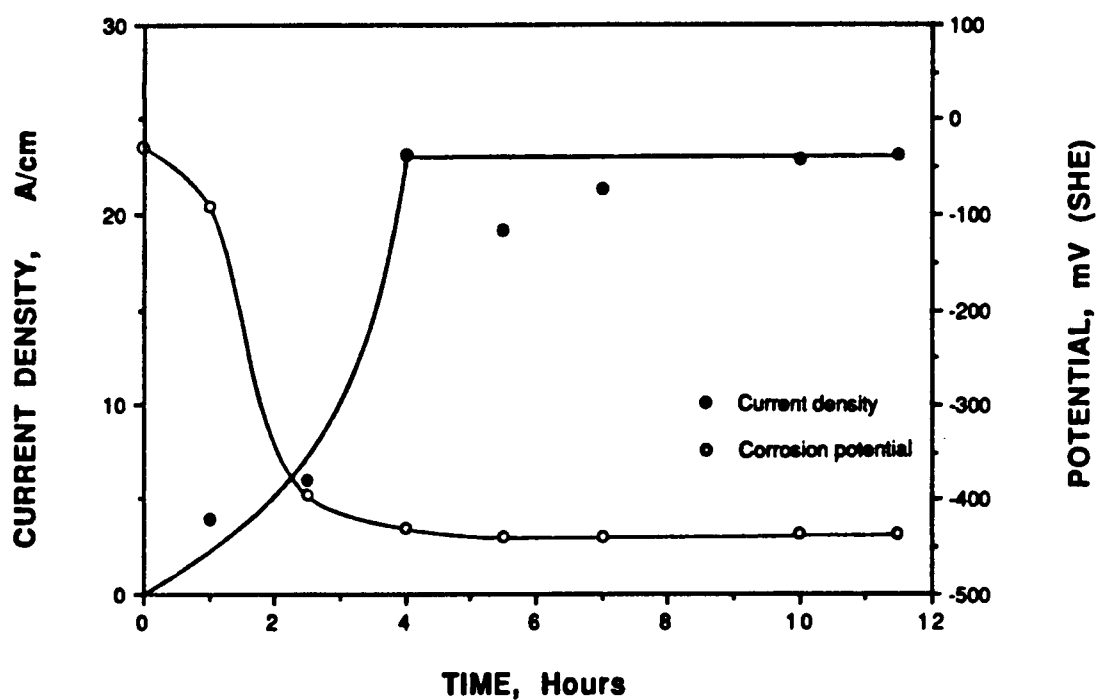


Figure 46. Current density obtained from AAS analyses and open-circuit corrosion potential for as-polished Ti in deaerated 1N H_2SO_4 .

density calculated using the Faraday's law at each given time. The valence used was +4 for the passive and +3 for the active state of Ti (109). In transient periods, the open-circuit corrosion potential decreased due to dissolution of the air-formed oxide film, while the current density increased. After approximately 4 hours of immersion, both the current density and the open-circuit corrosion potential reached stable values of around $23 \mu\text{A}/\text{cm}^2$ and -440 mV (SHE) , respectively. The current density obtained from AAS measurements is very close to the value of $21.3 \mu\text{A}/\text{cm}^2$ reported by Kelly (109).

The AAS measurements were also performed with the 2.5 at.% peak-max Ir implanted Ti, in the as-ion-implanted condition, in deaerated $1\text{N H}_2\text{SO}_4$ at the open-circuit corrosion potential. Figure 47 shows the amount of Ti dissolved as a function of time along with a reference sample (as-polished Ti). The dissolution rate of Ti was tremendously decreased by the small amounts of Ir implantation. Two major factors are responsible for such low dissolution rates of the implanted Ti sample. One factor is the stimulation of the hydrogen evolution rate on Ir, which brings the mixed corrosion potential of the implanted sample to the passive region of Ti so that Ti does not dissolve actively. The other factor is the continuous decrease in Ti surface area due to Ir surface enrichment, even in the passive region. If the surface of the implanted Ti sample is covered to 100% with Ir, the Ti dissolution rate will be zero.

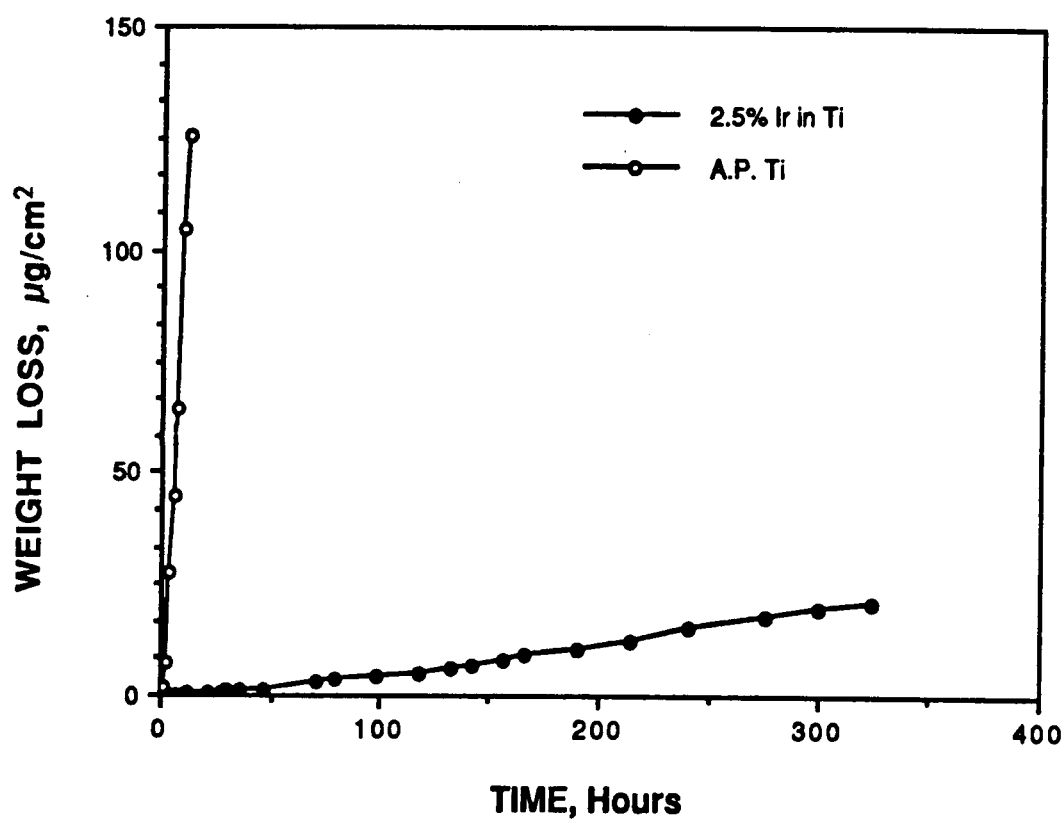


Figure 47. Amounts of Ti dissolved in deaerated 1N H_2SO_4 versus time for 2.5 at.% peak-max Ir implanted Ti and as-polished Ti.

Charge-injection Capability of Ir and Ir Implanted Sample

Considerable research has been performed on the electrochemistry of Ir because of its two distinct properties. The first property is associated with its high affinity for hydroxide ions which gives superior catalytic activity for oxygen evolution (110,111). The second property is related to its electrochromic behavior, where a change of color takes place between oxidative and reductive states of the metal, which makes it of interest for use in electro-optic display devices (26-28, 112-119).

Recently, there is also great interest in Ir for prosthetic applications, especially as an electrical neural stimulation electrode (30,120,121). Neural prostheses are devices which use electrodes to interface directly with the nervous system for supplementing or replacing function in the neurologically handicapped (108). The electrical neural stimulation electrode requires a reversible charge injection without causing any neural damage by the formation of toxic faradaic reaction products. It has been found that Ir subjected to repetitive potential sweeps in acid over a certain potential range results in the formation of a thick oxide film and produces as much as a 100-fold increase in the charge injection than a bare Ir electrode (26).

In this section, the charge injection capability of Ir implanted samples will be presented and the increase in charge injection of activated Ir (thick oxide film formed on Ir) will be discussed in terms of the capacitance via the faradaic reactions.

Figure 48 shows the cyclic voltammograms of unimplanted

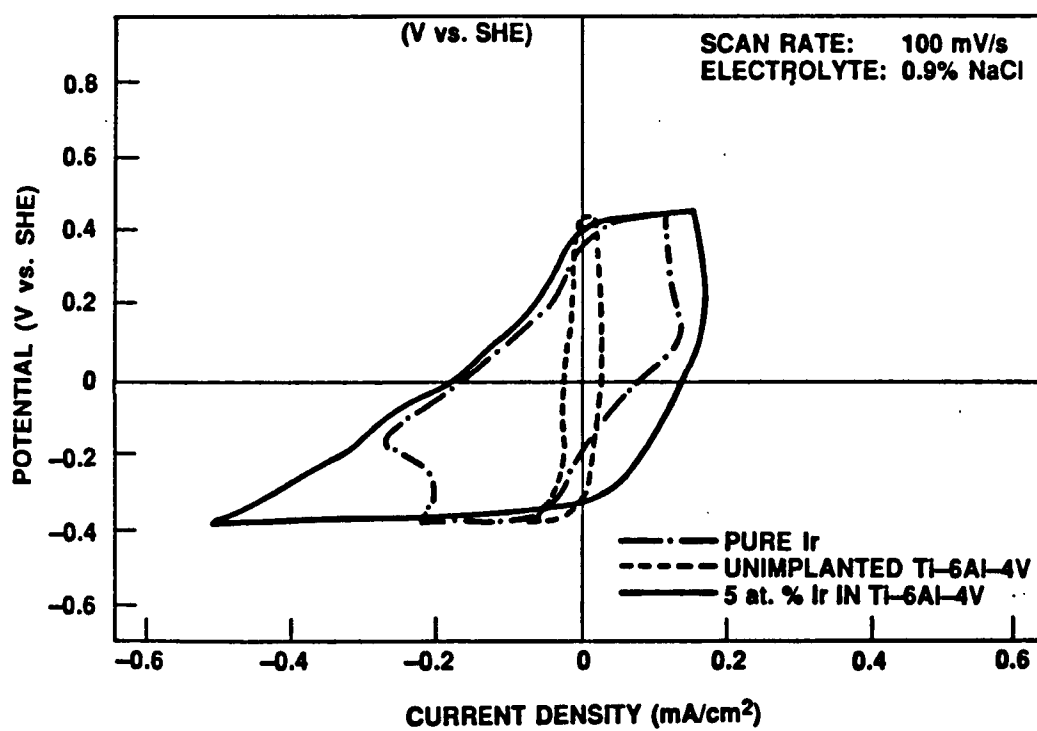


Figure 48. Cyclic voltammograms in aerated isotonic saline.

Ti-6Al-4V, 5 at.% peak-max Ir implanted Ti-6Al-4V, and pure Ir in saline solution after H_2SO_4 exposure. The electrochemical potential of the electrodes was cycled with a scan rate of 100 mV/s between upper and lower values of 0.45 V (SHE) and -0.4 V (SHE), respectively. This procedure is useful in characterizing and comparing materials for possible use as neural stimulating electrodes. The lower potential was selected to preclude water dissociation with H_2 evolution, which begins at approximately -0.41 V (SHE) at pH=7. The upper potential was chosen to restrict the electrochemical oxidation of Ir, which should theoretically begin at 0.5 V (SHE). Results shown in Figure 48 were measured during the second cycle in each case. The area within a given loop is directly proportional to the charge density of the material under the stimulating action of the applied cyclic potential. For a stimulating neural electrode, the loop and therefore the charge density should be as large as possible to provide adequate stimulation of the nervous system while allowing for miniaturization of the electrode. It is seen from Figure 48 that the charge density of pure Ir was considerably higher than that of unimplanted Ti-6Al-4V and that the charge density for the 5% peak-max Ir implanted Ti-6Al-4V was even greater than that of pure Ir.

The charge densities as measured by cyclic voltammetry (second-cycle values) after each treatment in the course of this study are presented in Table 7. It is seen that the charge densities for the Ir implanted materials increased significantly as a consequence of the H_2SO_4 exposure and they increased slightly even after saline exposure.

Figure 49 shows the charge densities versus the atomic

Table 7. Charge densities as measured by cyclic voltammetry.

	A. P. Ti	P. P. Ti	A. P. Ti-6-4	P. P. Ti-6-4	E3	E6	D23	D26	Ir
After anodic polarization	0.10	0.19	0.1	0.14	0.04	0.04	0.06	0.07	1.2
After H ₂ SO ₄ exposure	0.18	0.19	0.28	0.24	0.15	0.17	0.88	2.5	1.6
After saline exposure	0.13	0.08	0.08	0.09	0.15	0.19	1.24	3.72	1.6

Unit; mC/cm²

E3; 2.5 at.% peak Ir in Ti

E6; 5.0 at.% peak Ir in Ti

D23; 2.5 at.% peak Ir in Ti-6Al-4V

D26; 5.0 at.% peak Ir in Ti-6Al-4V

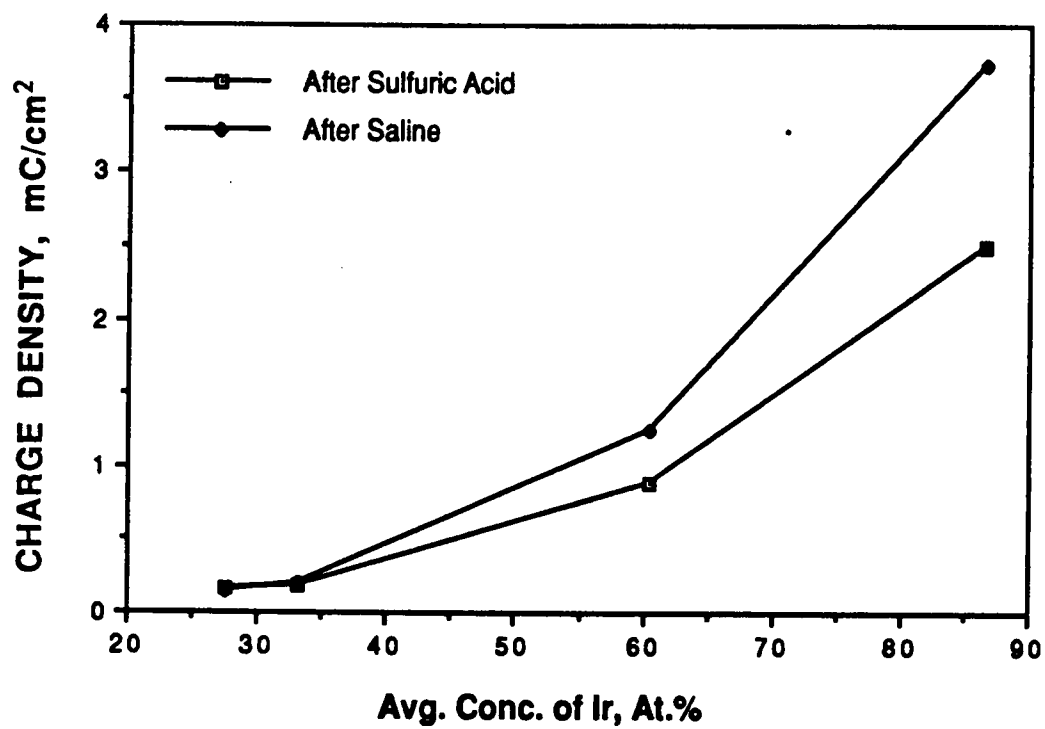
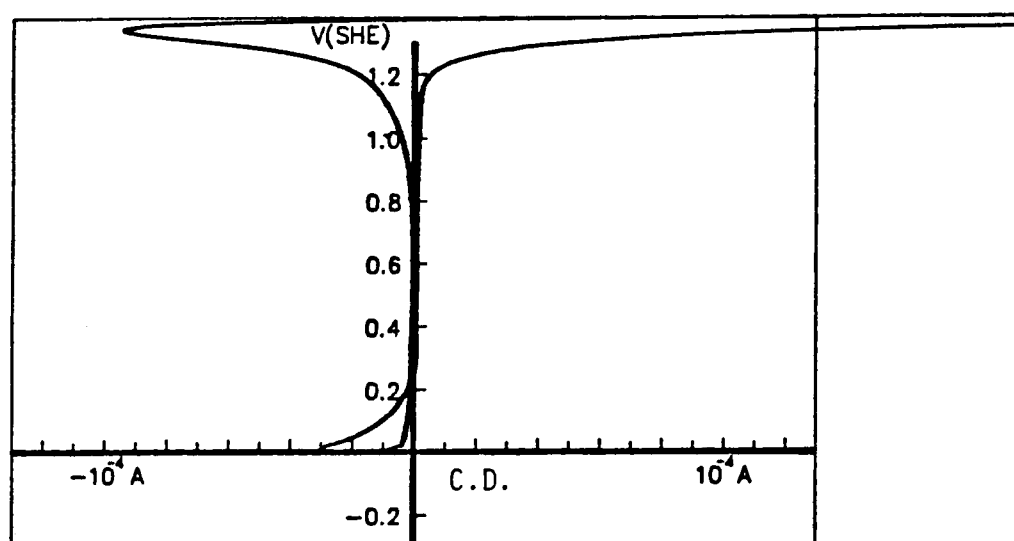


Figure 49. Charge density versus atomic concentration of Ir in implanted samples.

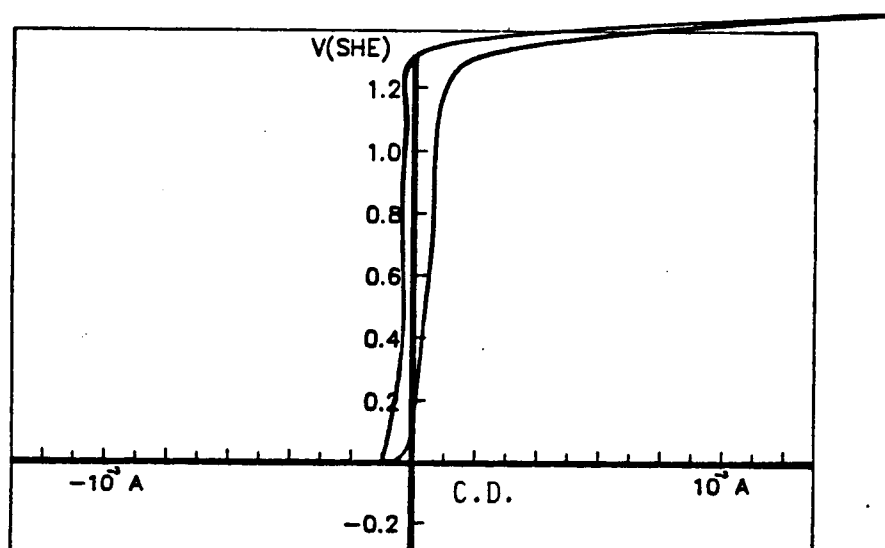
concentrations of Ir determined with x-ray photoelectron spectroscopy on implanted samples. The same concentration was used for the sulfuric acid and saline exposure since XPS analyses were done only after saline exposure and Ir was enriched mostly after the sulfuric exposure. The 5 at.% peak-max Ir implanted Ti-6Al-4V which had the highest average atomic concentration of 87% produced the largest charge densities after both sulfuric acid and saline exposures indicating that the enriched Ir at the surface was responsible for the high charge densities.

Robblee et al.(30) discussed that the large charge density on Ir is the result of faradaic reactions due to the highly reversible H^+ or OH^- transfer reactions and valence transitions within the oxide layer. However, the effects of the nonfaradaic processes must be taken into account in using electrochemical data to obtain information, especially in the experiments used a high scan rate.

Figure 50 shows cyclic voltammograms for Ir cycled between 0.0 V (SHE) and 1.45 V (SHE) in saline solution with a scan rate of (a) 0.17 mV/s and (b) 100 mV/s. The scan rate, 0.17 mV/s, is recommended in ASTM G5 to determine polarization curves since it is slow enough to give near-equilibrium conditions at each applied potential. Thus, the linear polarization curve determined with 0.17 mV/s can be assumed to be the equilibrium polarization curve and truly represents the charge transfer processes at the Ir electrode/solution interface. On the other hand, the scan rate of 100 mV/s is so fast that it does not allow oxidation or reduction reactions to occur under equilibrium conditions at a given potential. The linear polarization curves generated with the two different scan rates are quite different, and consequently the



(a)



(b)

Figure 50. Cyclic voltammogram of as-polished Ir determined with a scan rate of (a) 0.17 mV/s and (b) 100 mV/s in isotonic saline.

charge densities produced by Ir with the two different scan rates are not the same.

Under some conditions a given electrode-solution interface will show a range of potential where charge transfer reactions (faradaic processes) do not occur, although the nature of the electrode-solution interface can change with potential or solution composition. Although charge does not cross the interface under these conditions, external currents can flow when the potential changes. This behavior is related to the double layer capacitance. The double layer capacitance of most smooth metal surfaces has a value ranging from about 10 to 40 $\mu\text{F}/\text{cm}^2$ (122). Therefore, if the anodic polarization curve was determined with a high scan rate over the range of potential in which the faradaic current is very small, the capacitance current is much larger and is the current primarily measured. Then, one must be careful in interpreting the experimental results.

A certain type of capacitor, known as an electrolytic capacitor, utilizes a metal oxide film as a dielectric. The electrolytic capacitor was developed to have the advantage of small physical size for a relatively large capacitance. It owes its high capacitance per unit area to the thinness of the oxide film and to its high dielectric constant. The most common metal oxide used is either Al_2O_3 or Ta_2O_5 since they are stable over a wide range of potential. The dielectric constants of Al_2O_3 and Ta_2O_5 are about 10 and 15 respectively (123).

Figure 51 shows cyclic voltammograms of a commercial aluminum electrolytic capacitor (1000 μF -50V) determined with different scan rates. The currents during an upscan (downscan) are called charging

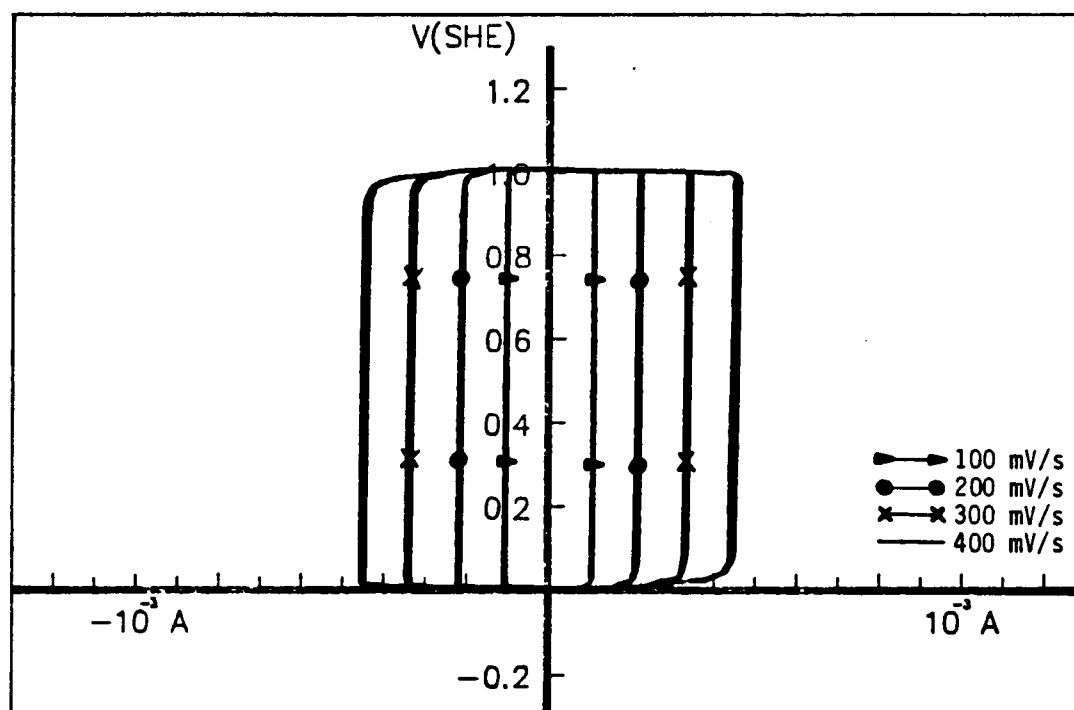


Figure 51. Cyclic voltammograms of a commercial aluminum electrolytic capacitor ($1000 \mu\text{F}$ -50V).

currents (discharging currents) and can be determined from the following relationship,

$$i = C \times dV/dt$$

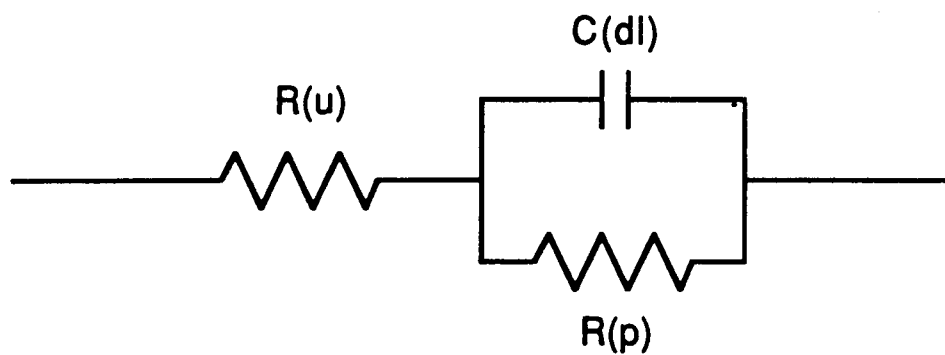
where C : capacity, F

dV/dt : scan rate, volts/s

The external current is a direct function of scan rate, but the charge of the capacitor during a given cycle is 2 mC regardless of scan rate.

Figure 52 is a simplified equivalent circuit of an electrolytic capacitor which is identical to the electrical circuit of a simple electrochemical system. In the electrochemical system, $R(u)$ is the uncompensated resistance between the working electrode and the reference electrode. $R(p)$ is the polarization resistance at the electrode/solution interface. $C(dl)$ represents the double layer capacitance at this interface. These three parameters can be obtained from electrochemical impedance spectroscopy (EIS) measurements which are able to provide data on both electrode capacitance and charge kinetics.

Figure 53 is an EIS Bode plot for the commercial aluminum electrolytic capacitor (1000 μ F-50V). Impedance data were obtained over the range of 5 to 20,000 Hz with an AC voltage amplitude of 5 mV. Impedance measurements at much lower frequencies are required for the polarization resistance, $R(p)$, which permits the calculation of electrochemical reaction rates. Generally, the capacitance is determined by extrapolating the high frequency data from a Bode plot to 0.16 Hz where $C = Z^{-1}$ as shown in Figure 53.



$R(u)$: Uncompensated resistance
 $R(p)$: Polarization resistance
 $C(dl)$: Double-layer capacitance

Figure 52. Equivalent electronic circuit for a simple electrochemical cell.

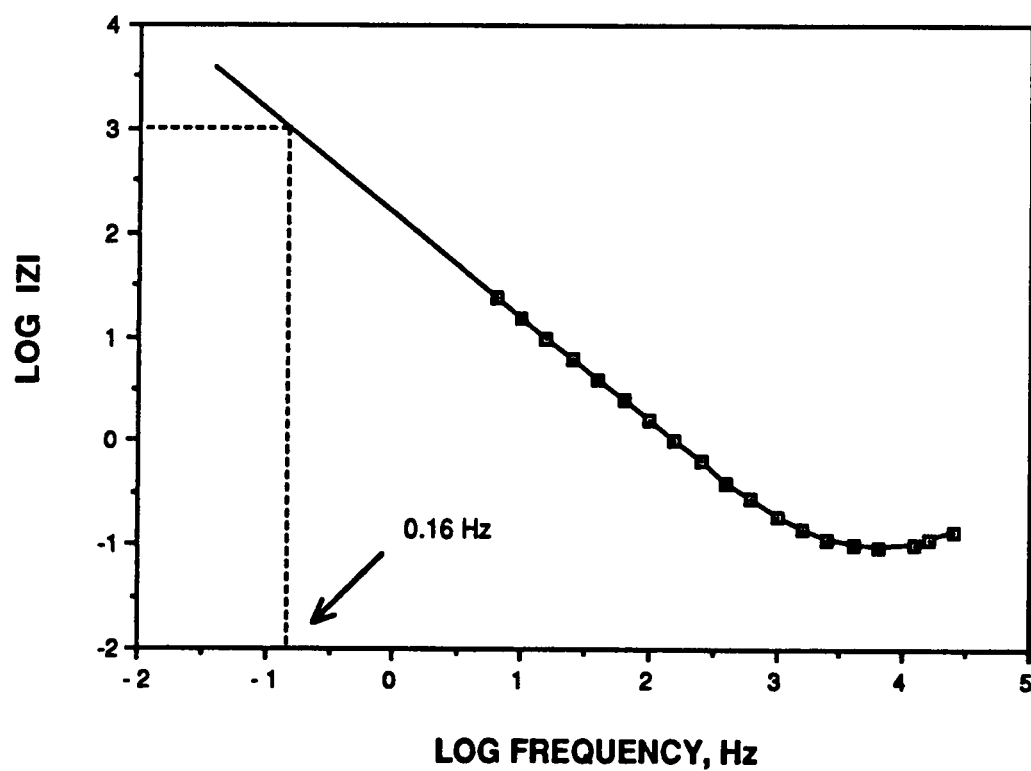


Figure 53. Bode plots for a commercial aluminum electrolytic capacitor (1000 μF -50V).

$$C = 1/1000 = 1000 \mu F$$

The capacitance can be obtained very precisely from electrochemical impedance spectroscopy measurements.

Figure 54 shows Bode plots for the Ti-6Al-4V and pure Ir at the applied DC potential of 0.6 V (SHE) in 0.1 M H_2SO_4 . Both Ti-6Al-4V and Ir, polished to 1 μm with a diamond paste, were anodized in order to form oxide films in deaerated 0.1M H_2SO_4 at 1.1 V (SHE) for 1 hr. Extrapolating the straight portions to the LOG |Z| axes at $f = 0.16$ Hz as shown in Figure 54 yielded the capacitances of Ti-6Al-4V and Ir as 18 μF and 100 μF , respectively. Since the capacitance of Ir is higher than that of Ti-6Al-4V, it can produce higher charge densities. The higher capacitance of Ir could be related to either a higher dielectric constant for the oxide or a thinner oxide film, as shown by the relationship below for a parallel-plate capacitor.

$$C = Q/V_c = \epsilon_r \epsilon_0 A/d \text{ farads}$$

where A : the area of the dielectric, m^2

d : the thickness of the dielectric, m

ϵ_r : the relative permittivity of the dielectric

ϵ_0 : constant, $1/(36\pi \times 10^9)$ farads/m

It is well known that an iridium electrode subjected to potential cycling between two selected values forms a thick oxide film, which is significantly different from that of other noble metals such as platinum and gold. The oxide formed on platinum, palladium and gold during a upscan can be readily reduced back to the metal at cathodic potentials. However, iridium oxide formation is irreversible since it

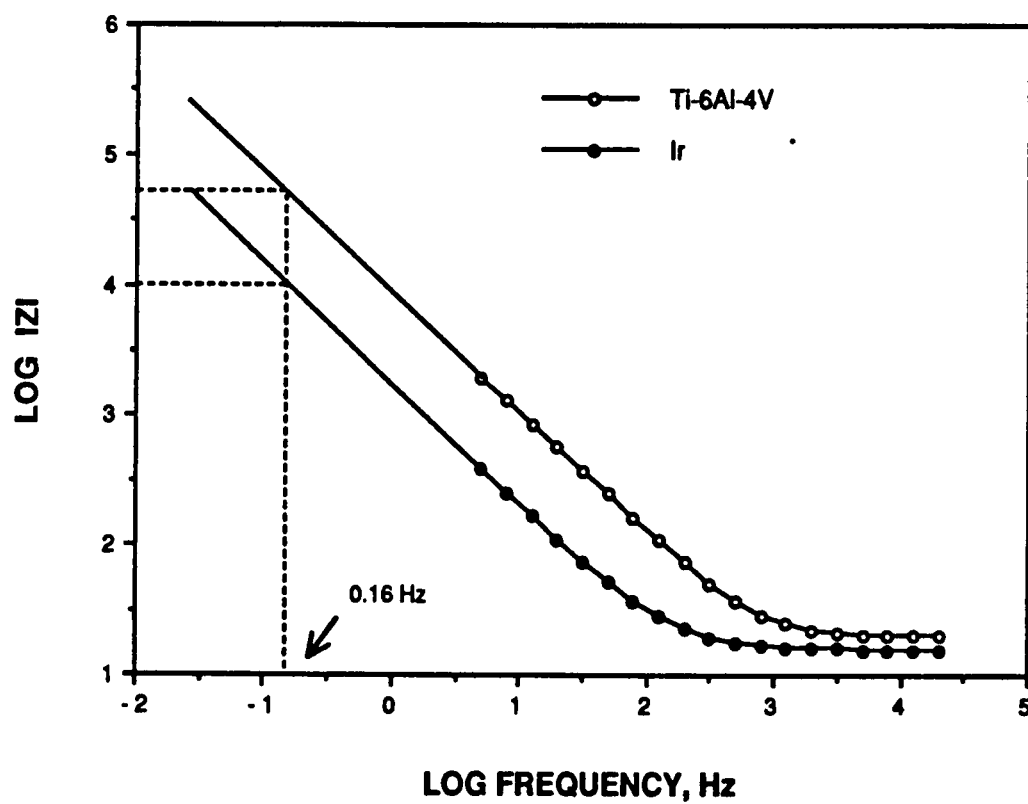


Figure 54. Bode plots for Ir and Ti-6Al-4V at 0.6 V (SHE) in 0.1M H_2SO_4 .

is not reduced back to the metal at cathodic potentials during the sweep. This effect allows the production of a progressively thicker oxide (124). The growth of a hydrous oxide film in aqueous solution requires either diffusion of metal cations to the oxide/solution interface or diffusion of hydroxide ions to the metal/oxide interface. Since Ir ions do not diffuse easily through the oxide (117) hydroxide ions must diffuse through the oxide during its growth.

The efficiency of oxide growth has been found to be very dependent on the upper and lower limits of the activating potential sweep (27,110). Gottesfeld and McIntyre (27) showed that the oxide film does not grow for anodic limits less than 0.9 V (SCE) with a fixed cathodic limit of -0.25 V (SCE) in 0.5 M H_2SO_4 . Also, they observed no film growth for cathodic limits greater than 0.0 V (SCE) with a fixed anodic limit of 1.25 V (SCE) and concluded that the optimum anodic and cathodic potential limits for film growth in 0.5M H_2SO_4 are 1.25 V and -0.25 V (SCE), respectively.

Figure 55 shows cyclic voltammograms of Ir in 0.1M H_2SO_4 . The 1 μm surface finished Ir electrode was potentiodynamically cycled between 0.0 V (SHE) and 1.45 V (SHE) with a linear potential sweep rate of 100 mV/s. A very considerable enhancement of the charge densities produced by Ir with increasing number of cycles is shown, and the voltammogram became almost symmetrical with regard to charge density (i.e. area) about the potential axis. It has been stated that the increase in charge density on continuous potential cycling is due to the accumulation of the oxide phase in which the valence state of iridium atoms changes (28,32,125).

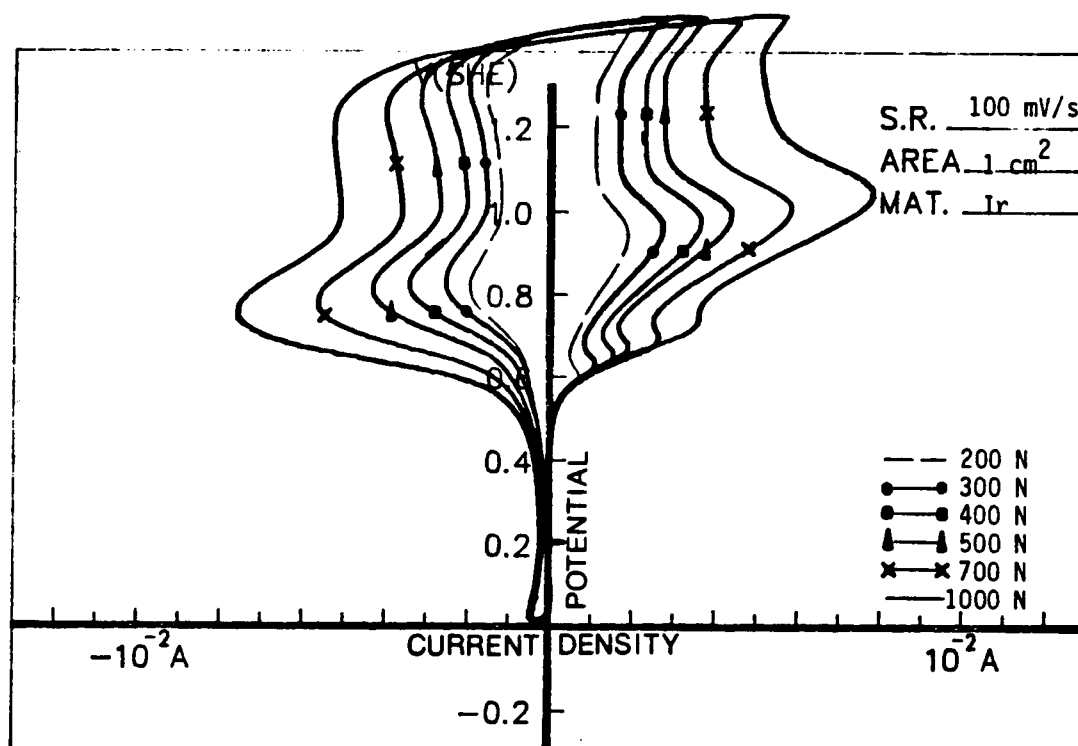
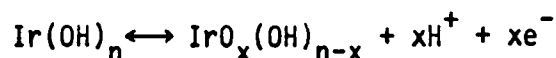


Figure 55. Cyclic voltammograms of an Ir electrode in 0.1M H₂SO₄ (100 mV/s).

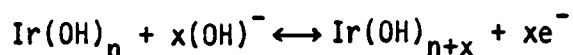
During the anodic sweep, the color of the oxide started changing from metallic to blue around 0.4 V (SHE), became darker and remained dark blue above near 0.9 V (SHE). The bleaching process occurred during the cathodic sweep. The dark blue became lightened around 1.0 V (SHE) and no blue color could be observed below 0.4 V (SHE). The electrochromism of the anodic iridium oxide film is similar to the electrochromism in WO_3 , albeit with opposite polarity (27,114). The anodic iridium oxide film is a more promising material for passive display devices than WO_3 because of its stability in contact with water and its fast coloring-bleaching times (20-40 ms) (114).

Two different mechanisms have been proposed to explain the electrochromism of the anodic iridium oxide film: the double proton-electron injection mechanism by Gottesfeld et al. (27), and the anion mechanism by Beni et al. (28). Gottesfeld et al. (27) postulated the following reaction to describe the film conversion processes:



In this mechanism, during the coloration process, electrons are removed from the oxide across the metal-oxide interface by application of a suitable anodic potential to the metal substrate. Charge repulsion causes an equivalent amount of mobile positive charge carriers (protons) to be ejected across the oxide-electrolyte interface, thus preserving electroneutrality inside the oxide. Similarly, during bleaching, electrons are injected into the oxide film from the metal while the compensating positive charge is injected at the oxide-electrolyte interface. On the other hand, Beni et al. (28) have observed that the speed of coloration and bleaching in anodic iridium

oxide films is independent of pH and the coloration-bleaching process occurs in water-free solutions containing F^- or CN^- . Thus, they have proposed the hydroxide mechanism for anodic iridium oxide film electrochromism, represented by a half reaction of the form:



However, both mechanisms agreed that the coloration is associated with a change in valence of iridium from 3 to 4, and that the reduction of iridium from 4 to 3 relates to the bleaching process.

Since "activated" Ir is able to produce high charge densities while preventing undesirable reactions due to charge storage, it has become a promising material for neural prostheses. Robblee et al. (121) studied the charge injection capabilities of thermally-prepared multilayer oxide films on Ti and stated that the valence transition of iridium within the oxide layer resulted in the high charge density. Also, Foods et al. (126) catalogued IrO_2 as a faradaic stimulation electrode referring to its fast reversible redox reaction. However, it was found in this study that the double layer capacitance is equally or even more responsible for the high charge density of anodically formed Ir oxide.

After Ir was activated to a selected number of cycles between 0.0 V (SHE) and 1.45 V (SHE) with a scan rate of 100 mV/s in 0.1 M H_2SO_4 , cyclic voltammograms of the activated Ir were determined in the same solution at the same scan rate but between 1.0 V (SHE) and 1.3 V (SHE), over which the change in valence state of Ir does not occur. As shown in Figure 56, the activated Ir behaved like a capacitor in the region of 1.0 V (SHE) and 1.3 V (SHE), and the charge density increased with

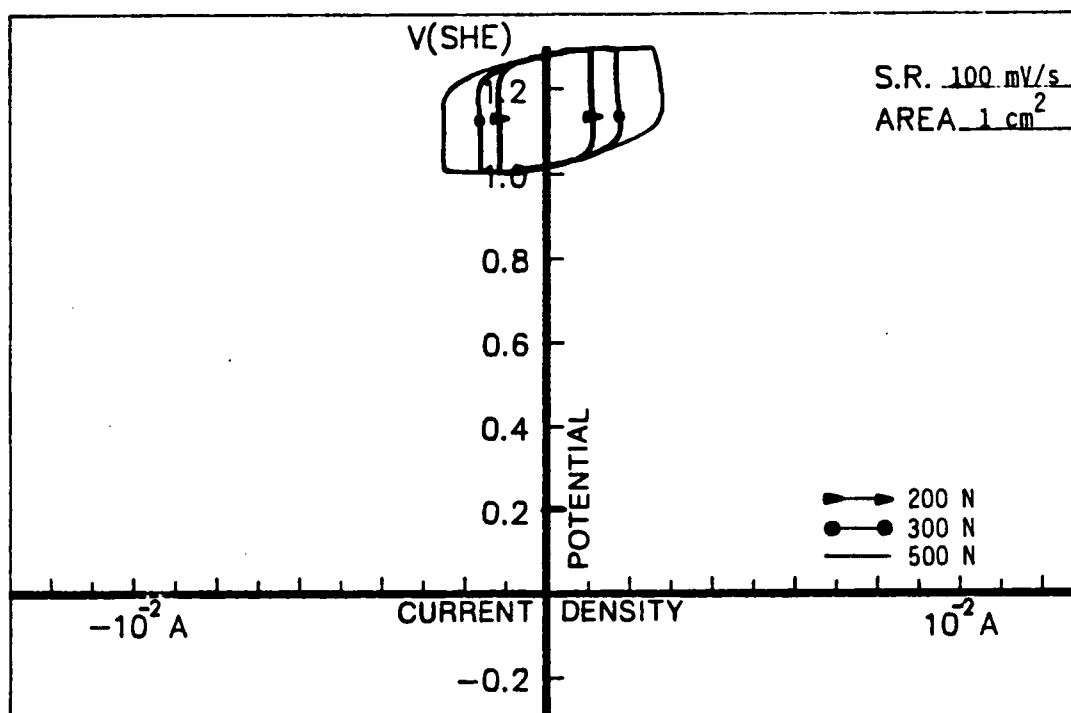


Figure 56. Cyclic voltammograms of the activated Ir between 1.0 V (SHE) and 1.3 V (SHE) in 0.1M H_2SO_4 (100 mV/s).

increasing number of cycles. Since there is no valence transition of Ir in this region of potentials, the charge density produced by the activated Ir must be related to the double layer capacitance.

EIS measurements were performed on Ir electrodes, which had been activated to 1 cycle and 200 cycles, at an applied DC potential of 1.2 V (SHE) in 0.1 M H_2SO_4 . The Bode plots are shown in Figure 57. The double layer capacitance was increased from 280 μF to 25 mF for the Ir electrode on going from 1 to 200 cycles. From the relationship shown on page 129 for a capacitor, the area of the dielectric, i.e. the surface area of the anodic oxide film must be increased to account for the higher double layer capacitance assuming a constant thickness of oxide (although the average oxide thickness probably increases, this effect alone would produce lower capacitance values).

Scanning electron micrographs of Ir activated to the different numbers of cycles in 0.1 M H_2SO_4 are shown in Figure 58 (a)-(f). It is clearly seen that the oxides were more accumulated on the Ir electrode activated to higher numbers of cycles. The surface topography of the oxide on Ir cycled to 100 N began to show some dissimilarities from the as-polished Ir electrode. With the increase in activating cycles, the surface became more uneven and oxide films of very high real surface area were developed. This roughening was probably due to either the reduction of some oxides to bare metal on each cathodic scan or the strain introduced in the surface layer by virtue of the greater volume occupied by the oxide layer relative to the metal it replaced. Continuous potential cycling for a long period of time may result to the flaking of the oxide. As a matter of fact, the anodic dissolution

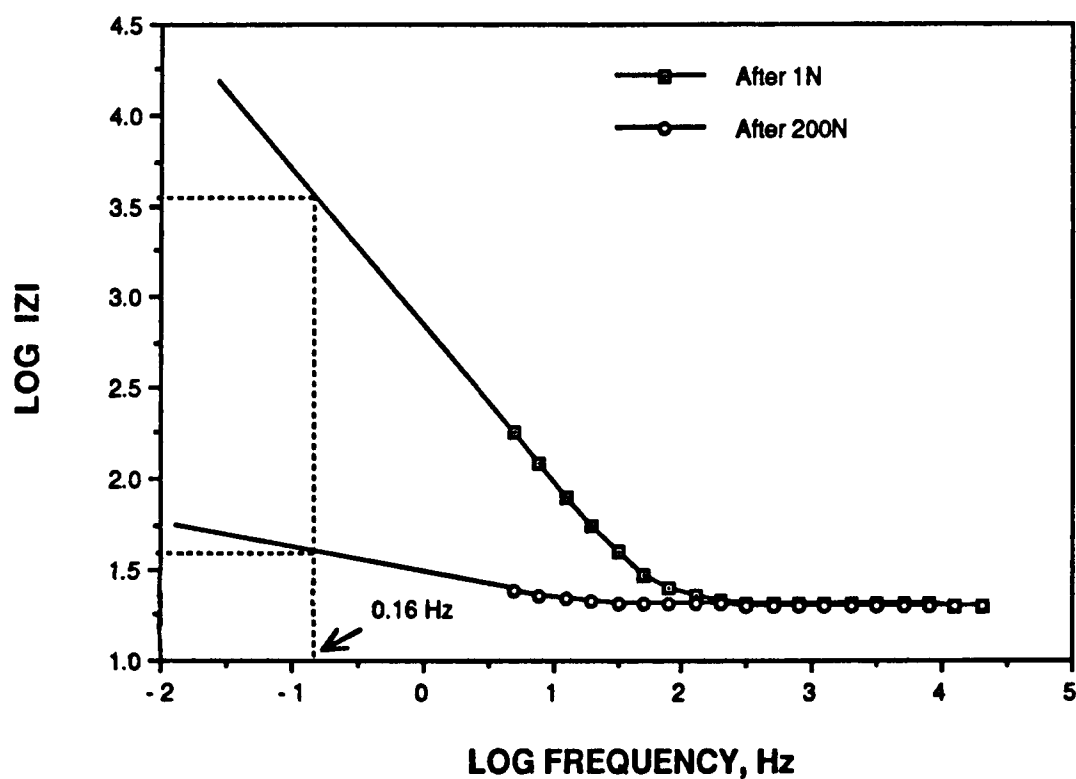
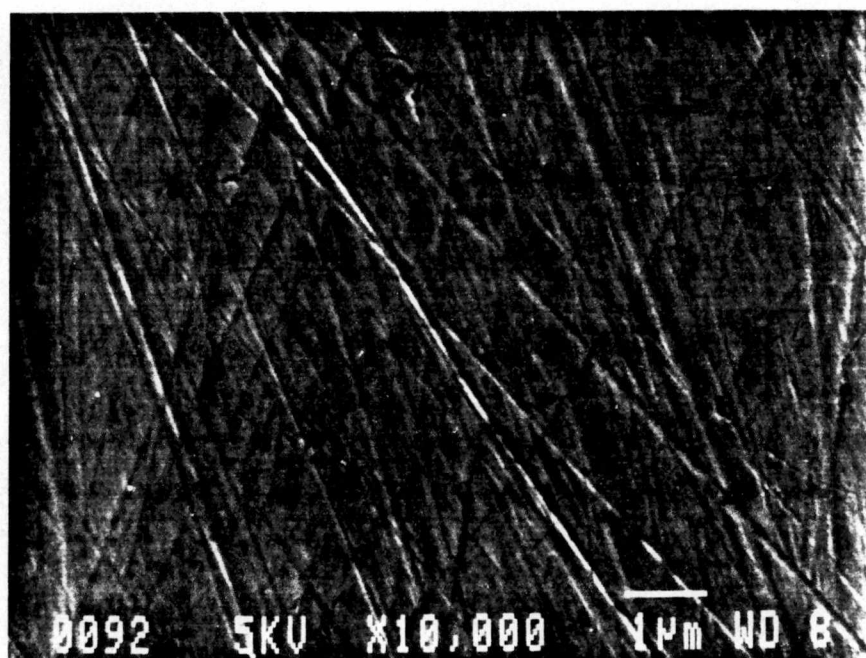
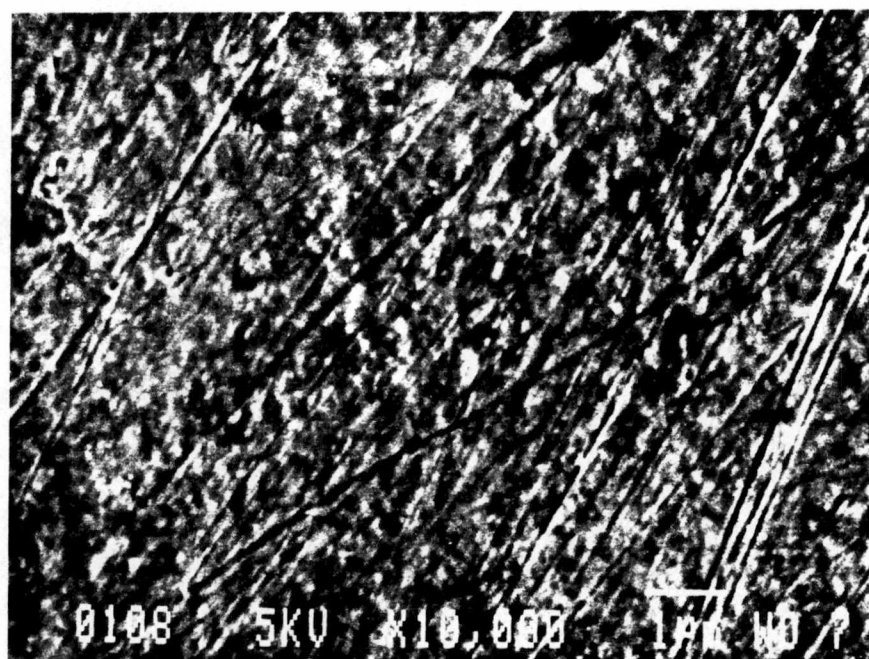


Figure 57. Bode plots for Ir activated to 1 cycle and 200 cycles at 1.2 V (SHE) in 0.1M H_2SO_4 (100 mV/s).

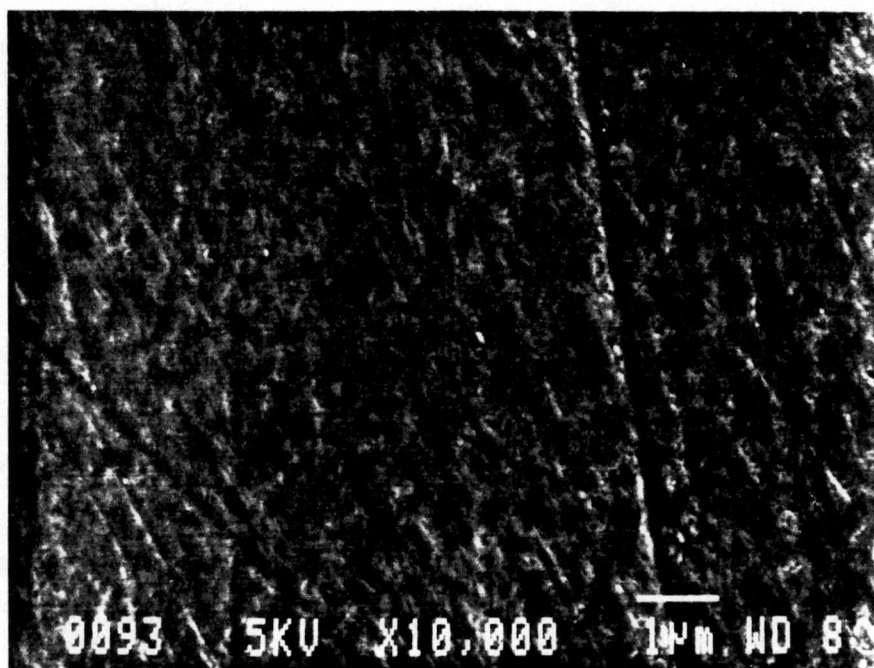


(a) As-polished

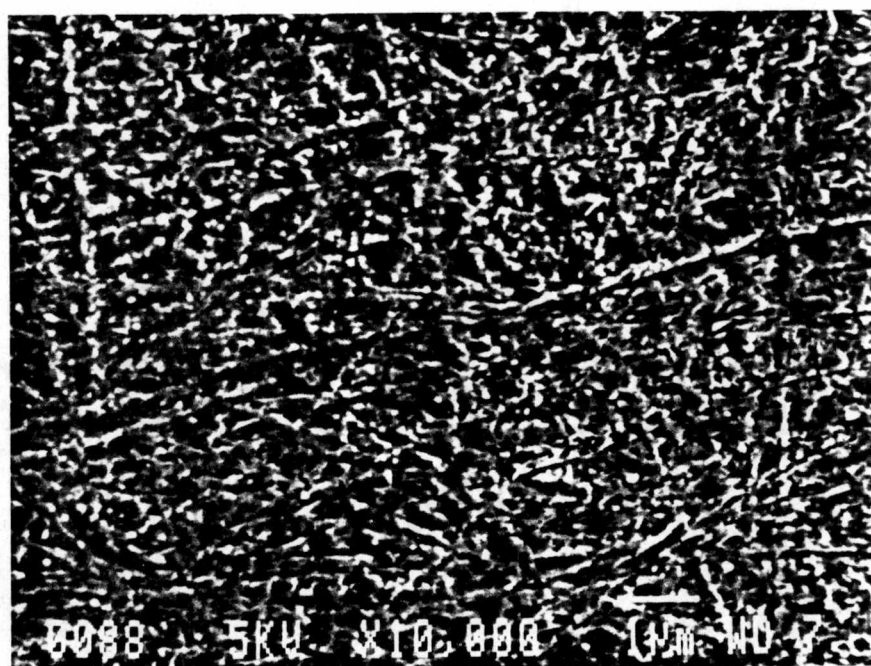


(b) 100 cycles

Figure 58. Scanning electron micrographs of anodic Ir oxide films.

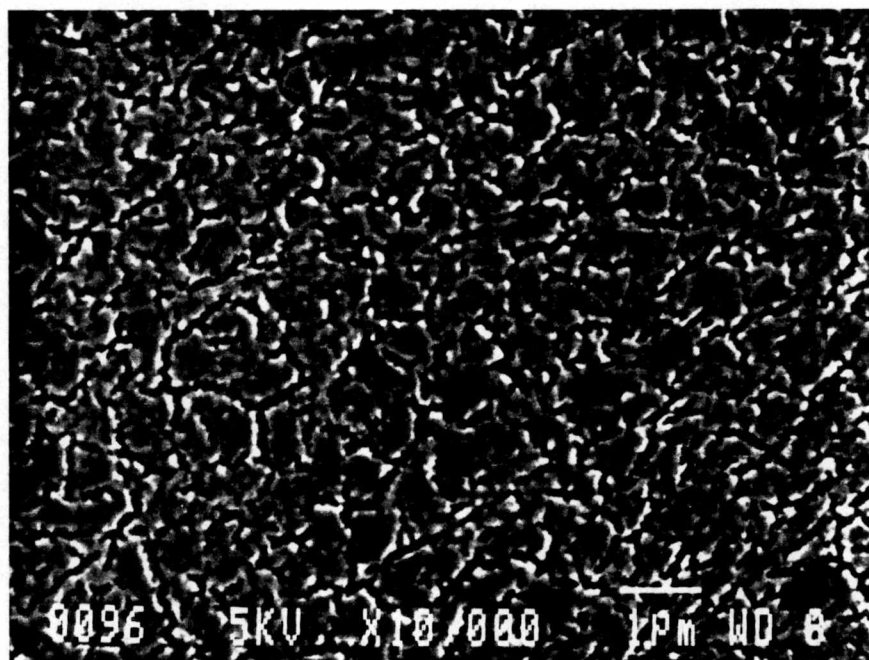


(c) 200 cycles

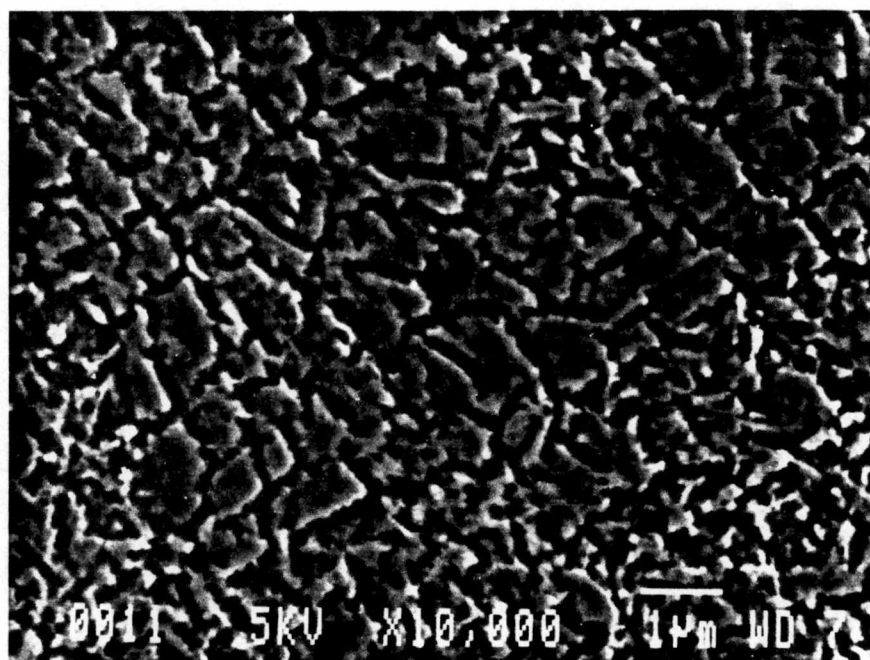


(d) 300 cycles

Figure 58 (Continued)



(e) 500 cycles



(f) 1000 cycles

rate of Ir on potential cycling in 1M H_2SO_4 was claimed to be 8-9 times that found for Pt under comparable experimental conditions (125).

The porous-natured oxide is shown in Figure 59. The oxide morphology possibly allowed the bare Ir to contact with the electrolyte and the oxide to grow continuously with increasing cycles. This oxide was grown on Ir by activating the Ir electrode to 2500 cycles. Whether the underlying regions (marked A in Figure 59) correspond to bare Ir or an oxide layer is not known. However, Rand et al. (125) suggested that a large portion of bare Ir must be exposed since the quantity of charge passed in adsorbing hydrogen, which is a measure of the area of the bare metal surface exposed to the solution (127), decreased by only 25 % after Ir was activated to 2500 cycles between 0.06 V (SHE) and 1.5 V (SHE) with sweep rates of 40 mV/s in 1 M H_2SO_4 .

As shown in Figure 55, page 132, the charge density of the activated Ir was mostly produced in the upper portion of each potential cycle even though the morphology of the oxide (high surface area) was not significantly changed with the applied potential at each cycle. EIS measurements were made on Ir activated to 200 cycles, at the applied DC potentials of 0.3 V (SHE) and 1.2 V (SHE). Figure 60 shows the much lower double layer capacitance of Ir at the lower potential. The only possible explanation is the different dielectric properties of the oxides. The higher valence Ir oxide must be characterized by a much higher dielectric constant.

For charge injection into the nervous system from an iridium electrode, several types of potentially harmful reactions must be avoided. Among these are electrolysis of water, oxidation of saline,

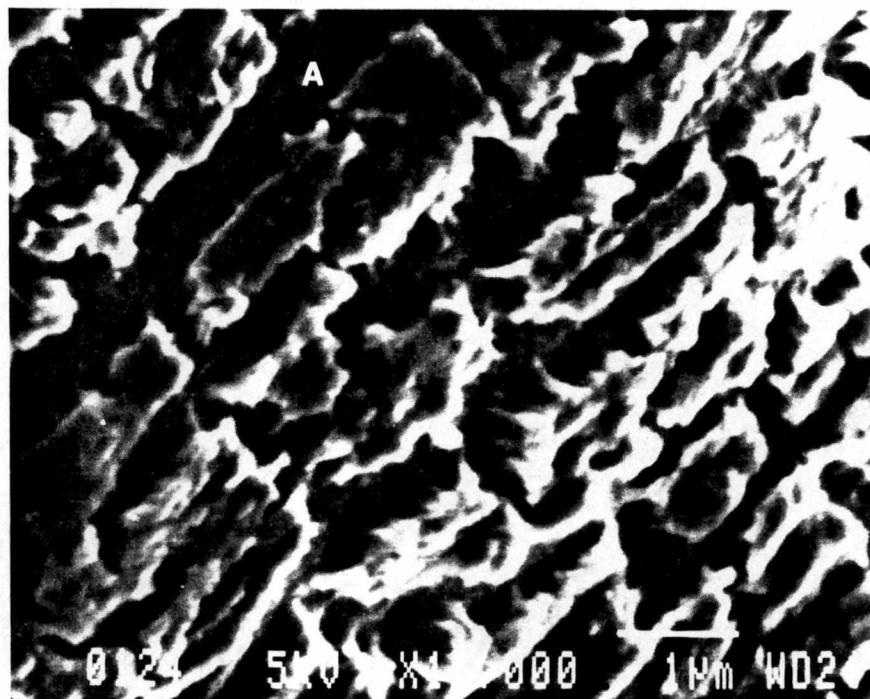


Figure 59. Scanning electron micrographs of anodic Ir oxide films grown on Ir by activating 2500 cycles.

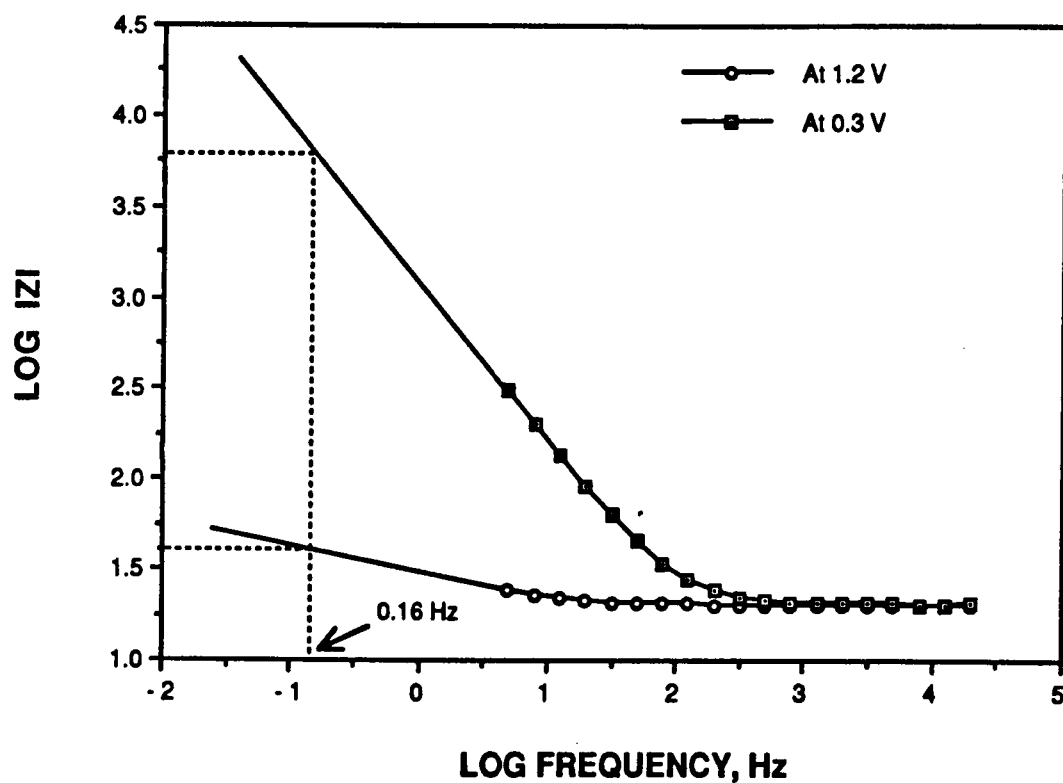


Figure 60. Bode plots for Ir activated to 200 cycles at the applied DC potential of 0.3 V (SHE) and 1.2 V (SHE) in 0.1M H_2SO_4 .

oxidation of metal to form complex ions, and oxidation of organics. When the applied potential to Ir is too high (low), oxygen (hydrogen) evolution occurs. These reactions should be excluded because of possible physical damage from the gas produced and from the local pH change near the electrode. Consequently, the upper and lower limits of the potential for charge injection of Ir in saline solution are 0.8 V (SHE) and -0.4 V (SHE), respectively. The upper (lower) potential was selected to preclude water dissociation with O_2 (H_2), which begins at approximately 0.815 V (-0.41 V) (SHE) at pH=7. By choosing these limits of potential, the first two of the above listed four harmful reactions can be avoided. The latter two require additional study.

With regard to performance in saline, Ir electrodes, polished to $1\ \mu\text{m}$ with diamond paste, were first activated to a selected number of cycles between 0 V (SHE) and 1.45 V (SHE) in 0.1 M H_2SO_4 . Then, each electrode was carefully rinsed with distilled water and transferred into saline solution. The charge densities of the activated Ir in saline solution at the second cycle between applied potentials of -0.4 V (SHE) and 0.8 V (SHE) with a scan rate of 100 mV/s are shown in Figure 61 as a function of the number of activation cycles in 0.1M H_2SO_4 . The efficiency of activation per cycle decreased with increasing number of activating cycles. The charge density of $10\ \text{mC}/\text{cm}^2$, as is required by future prostheses (128), can be obtained by activating Ir in 0.1M H_2SO_4 to 300 cycles.

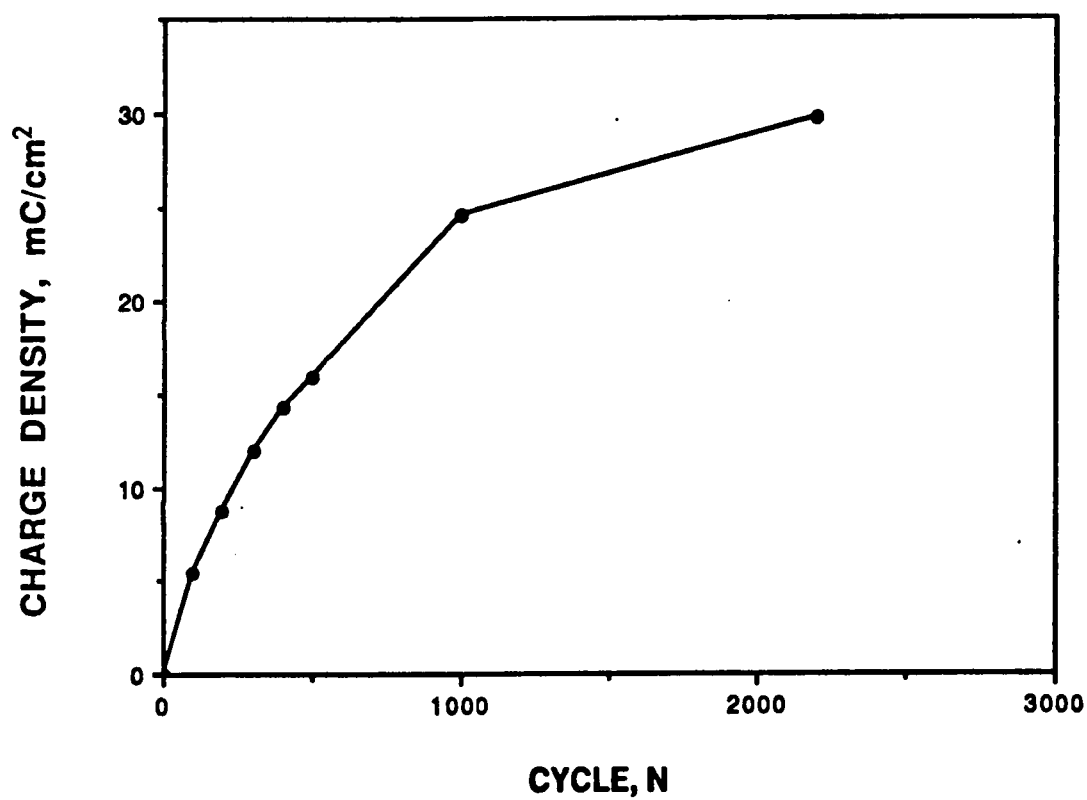


Figure 61. Charge density of the activated Ir in isotonic saline.

CHAPTER 6

CONCLUSIONS

The electrochemical characteristics of Au, Rh, and Ir implanted CP Ti and Ti-6Al-4V alloy were evaluated. The following conclusions can be made by considering the results presented in this study.

1. All noble-metal implanted samples showed improved corrosion properties even in the as-implanted condition. With regard to anodic polarization behavior in deaerated 1N H_2SO_4 , they produced more noble open-circuit corrosion potentials and lower anodic current densities relative to unimplanted samples.
2. The 2.5 at.% peak-max Rh implanted Ti, and the 2.5 at.% and 5.0 at.% peak-max Ir implanted Ti and Ti-6Al-4V showed improvement in corrosion resistance throughout immersion in deaerated 1N sulfuric acid solution resulting from the preferential dissolution of Ti with a subsequent build-up and retention of the implanted noble atoms at the surface. Also, the Rh or Ir enriched surface demonstrated stability and continuous improvement in corrosion resistance in isotonic saline solution, in contrast to a surface prepared by warm nitric acid prepassivation.

Both Rutherford backscattering and x-ray photoelectron analysis provided additional evidence for the accumulation of Rh or Ir on the surface after the corrosion treatments. For example, the average surface concentrations of Ir as measured

over a depth of approximately 2 nm by x-ray photoelectron spectroscopy was 87% for the 5.0 at.% peak-max Ir implanted Ti-6Al-4V sample after exposure in H_2SO_4 and saline solutions. The actual surface concentration could easily have approached 100% Ir.

3. The 2.0 at.% peak-max Au implanted Ti-6Al-4V produced short-term, but not long-term improvements in corrosion resistance. During H_2SO_4 exposure, the ion implanted Au did indeed enrich at the surface, but it did not adhere to the Ti substrate.
4. The charge densities of Ir were enhanced by cycling between 0.0 V (SHE) and 1.45 V (SHE) in 0.1M H_2SO_4 with a scan rate of 100 mV/s. The increase in charge density on continuous potential cycling is due to the accumulation of the oxide phase (associated with a large surface area) in which the valence state of iridium atoms changes and the double-layer capacitance increases.
5. Initially, the charge injection capability of 5.0 at.% peak-max Ir implanted Ti-6Al-4V after noble-metal surface enrichment by acid pretreatment was slightly greater in isotonic saline than that of pure Ir. However, the charge density of pure Ir increased with the number of cycles due to the formation of a thick oxide, but the oxide of the implanted Ti-6Al-4V could not grow because of the limited number of implanted Ir atoms. Consequently, the charge injection capabilities of the implanted material remained unchanged.

LIST OF REFERENCES

LIST OF REFERENCES

1. G. H. Hille, **J. Mat.**, 1, 373 (1966).
2. F. W. Rhineland, M. Rouweyha, and J. C. Milner, **J. Bio. Mat. Res.**, 5, 81 (1971).
3. P. J. Aragon and S. F. Hulbert, **J. Bio. Mat. Res.**, 6, 155 (1972).
4. F. Escales, J. Galante, W. Rostoker, and P. Coogan, **J. Bio. Mat. Res.**, 10, 175 (1976).
5. E. J. Kaminski, M. W. Shenk, and R. J. Oglesby, **J. Bio. Mat. Res.**, 11, 871 (1977).
6. M. A. Imam, A. C. Fraker, and C. M. Gilmore, **Corrosion and Degradation of Implant Materials**, ASTM STP 684, 128 (1979).
7. A. C. Fraker, A. W. Ruff, A. C. Van Orden, and K. M. Speak, **Titanium Alloys in Surgical Implants**, ASTM STP 796, 206 (1983).
8. N. E. W. Hartley, **Radiation Effects**, 44, 19 (1979).
9. C. R. Clayton, **Nuclear Instruments and Methods**, 182/183, 865 (1981).
10. C. J. Mchargue, **International Metals Reviews**, 31, 49 (1986).
11. B. R. Appleton, E. J. Kelly, and C. W. White, **International Metals Reviews**, 26, 991 (1981).
12. N. G. Thompson, B. D. Lichter, B. R. Appleton, E. J. Kelly, and C. W. White, in **Ion Implantation Metallurgy**, C. W. Preece, and J. K. Hirronen eds, New York, AIME, 181 (1980).
13. E. McCafferty and G. K. Hubler, **J. Electrochem. Soc.**, 125, 1892 (1978).
14. G. K. Hubler and E. McCafferty, **Corrosion Science**, 20, 103 (1980).
15. P. Munn and G. K. Wolf, **Materials Science and Engineering**, 69, 303 (1985).
16. M. Pourbaix, **Atlas of Electrochemical Equilibria in Aqueous Solutions**, Houston, NACE (1966).
17. R. A. Buchanan and E. E. Stansbury, in **Surface Modification Engineering**, R. Kossowsky ed., CRC press (in press).
18. J. Kruger, **Corrosion and Degradation of Implants Materials**, ASTM STP 684, 107 (1979).

19. G. A. Mabbott, **J. Chem. Ed.**, 60, 697 (1983).
20. P. T. Kissinger and W. R. Heineman, **J. Chem. Ed.**, 60, 702 (1983).
21. I-S. Lee and R. A. Buchanan, Unpublished research at University of Tennessee (1987).
22. S. B. Brummer and M. J. Turner, **IEEE Trans. Biomed. Eng.**, BME-24, 59, (1977).
23. L. D. Burke and E. J. M. O'Sullivan, **J. Electroanal. Chem.**, 93, 11 (1978).
24. S. Trasatti and G. Lodi, in **Electrodes of Conductive Metallic Oxides**, Part B, S. Trasatti ed., Elsevier, Amsterdam, 521, (1981).
25. D. N. Buckley and L. D. Burke, **J. Chem. Soc. Faraday 1**, 71, 1447 (1975).
26. J. O. Zerbino, N. R. de Tacconic, and A. J. Arvia, **J. Electrochem. Soc.**, 125, 1266 (1978).
27. S. Gottesfeld and J. D. E. McIntyre, **J. Electrochem. Soc.**, 126, 742 (1979).
28. G. Beni, C. E. Rice, and J. L. Shay, **J. Electrochem. Soc.**, 127, 1342 (1980).
29. S. Ardizzone, A. Carugati, and S. Trasatti, **J. Electroanal. Chem.**, 126, 287 (1981).
30. L. S. Robblee, J. L. Lefko, and S. B. Brummer, **J. Electrochem. Soc.**, 130, 731 (1983).
31. L. D. Burke and D. P. Whelan, **J. Electroanal. Chem.**, 162, 121 (1984).
32. M. Vukovic, **J. Appl. Electrochem.**, 17, 737 (1987).
33. D. K. Brice, **Ion Implantation Range and Energy Deposition Distributions**, Vol. 1 High Incident Ion Energies, IPE/PLENUM, New York (1975).
34. J. K. Hirvonen, in **Treatise on Materials Science and Technology**, Vol. 18 Ion Implantation, J. K. Hirvonen eds., Academic Press, New York, 5 (1980).
35. J. C. Bittence, **Materials Engineering**, April, 57 (1982).

36. H. Ryssel and H. Glawishing eds., **Ion Implantation Techniques**, Springer-Verlag, Berlin (1982).
37. L. Wegmann, **Ion Implantation**, Academic Press, 3 (1984).
38. G. Dearnaley, J. H. Freeman, R. S. Nelson, and J. Stephen, **Ion Implantation**, North-Holland Pub., Amsterdam (1973).
39. P. Sioshansi, **Mat. Eng.**, 104, 19 (1987).
40. P. Sioshansi, **Machine Design**, 58 (1986)
41. J. L. Moore, ORNL-6453, ORNL, Oak Ridge, TN, 167 (1987).
42. L. E. Rehn, R. S. Averback, and P. R. Okamoto, **Materials Science and Engineering**, 69, 1 (1985).
43. Y. Okabe, M. Iwaki, S. Namba, and K. Yoshida, **Nuclear Instruments and Methods**, 182/183, 231 (1981).
44. N. Anderson and H. L. Bay, **Radiation Effects**, 19, 139 (1973).
45. M. L. Tarng and G. K. Wehner, **J. Appl. Phys.**, 42, 2449 (1971).
46. Z. L. Liao, J. W. Mayer, W. L. Brown, and J. M. Poate, **J. Appl. Phys.**, 49, 5295 (1978).
47. J. M. Poate and T. C. Tisone, **Appl. Phys. Lett.**, 24, 391 (1974).
48. W. F. van der Weg, D. Sigurd, and J. W. Mayer, in **Applications of Ion Beams to Metals**, S. T. Picraux, E. P. Eernisse, and F. L. Vook, eds., Plenum Press, New York, 209 (1974).
49. B. Y. Tsaur, Z. L. Liao, and J. W. Mayer, **Appl. Phys. Lett.**, 34, 168 (1979).
50. B. Y. Tsaur, Z. L. Liao, and J. W. Mayer, **Phys. Lett.**, 71A, 270 (1979).
51. J. A. Borders and J. M. Poate, **Phys. Rev.**, B13, 969 (1976).
52. D. K. Sood and G. Dearnaley, **Radiation Effects**, 39, 157 (1978).
53. C. W. White, S. R. Wilson, and B. R. Appleton, **J. Appl. Phys.**, 51, 738 (1980).
54. W. G. Johnson, A. Mogro-Campero, J. L. Walter, and H. Bakhr, **Mater. Sci. Eng.**, 55, 121 (1982).
55. P. Moine, J. P. Eymery, R. J. Gaborlaud, and J. Delafond, **Proc. Conf., Ion Beam Modification of Materials: Nucl. Instrum. Meth.**, 209-210, 267 (1983).

56. D. K. Sood, **Radiation Effects**, 63, 141 (1982).
57. G. Carter, D. G. Armour, S. E. Donnelly, and R. Webb, **Radiation Effects**, 36, 1 (1978).
58. W. A. Grant, **J. Vac. Sci. Technol.**, 15, 1644 (1978).
59. Y. Limoge and A. Barbu, **Physical Review B**, 30, 2212 (1984)
60. V. Ashworth and R. P. M. Proctor, in **Treatise on Materials Science and Technology**, J. K. Hirvonen ed., 18, 195 (1980).
61. V. Ashworth, D. Baxter, W. A. Grant, and R. P. M. Proctor, **Corrosion Science**, 16, 661 (1976).
62. V. Ashworth, D. Baxter, W. A. Grant, and R. P. M. Proctor, **Corrosion Science**, 16, 775 (1976).
63. V. Ashworth, D. Baxter, W. A. Grant, and R. P. M. Proctor, **Corrosion Science**, 17, 947 (1977).
64. Y. Okabe, **Nuclear Instruments and Method**, 182/183, 231 (1981).
65. H. Ferber, H. Kasten, G. K. Wolf, W. J. Lorenz, and H. Folger, **Corrosion Science**, 20, 117 (1980).
66. G. K. Wolf and H. Ferber, **Nuclear Instruments and Methods**, 209/210, 197 (1983).
67. H. Ferber and G. K. Wolf, in **Ion Implantation into Metals**, V. Ashworth, W. A. Grant, and R. P. M. Proctor eds., Pergamon Press, 1 (1982).
68. G. K. Wolf, **Radiation Effects**, 48, 237 (1980).
69. V. Ashworth, G. Garter, W. A. Grant, P. D. Jones, R. P. M. Proctor, N. N. Sayegh, and A. D. Street, in **Ion Implantation in Semiconductors and Other Materials**, F. Chernow, J. A. Borders, and D. K. Brice eds., Plenum, New York, 443 (1977).
70. V. Ashworth, W. A. Grant, R. P. M. Proctor, and T. C. Wellington, **Corr. Sci.**, 16, 393 (1976).
71. P. L. Bonora, G. Cerisola, L. Fedrizzi, and C. Tosello, **Materials Science and Engineering**, 69, 283 (1985).
72. Q. M. Chen, H. M. Chen, X. O. Bai, J. Z. Zhang, and H. H. Wang, **Nucl. Instrum. Methods**, 209-210, 867 (1983).

73. C. R. Clayton, K. G. K. Doss, Y-F. Wang, J. B. Warren, and G. K. Hubler, in **Ion Implantation into Metals**, V. Ashworth, W. A. Grant, and R. P. M. Proctor eds., Pergamon Press, 67 (1982).
74. C. R. Clayton, K. G. K. Doss, H. Herman, S. Prasad, and Y-F Wang, in **Ion Implantation Metallurgy**, C. M. Preece and J. K. Hirvonen eds., AIME, 65 (1980).
75. Y. F. Wang, C. R. Clayton, G. K. Hubler, W. H. Lucke and J. K. Hirvonen, **Thin Solid Films**, 63, 11 (1979).
76. H. J. Kim, W. B. Carter, R. F. Hochman, and E. I. Meletis, in **Proc. Int. Conf. on Surface Modification of Metals By Ion Beams**, G. K. Wolf, W. A. Grant, and R. P. M. Proctor eds., Heidelberg, September 17-21, 1984, in **Mater. Sci. Eng.**, 69, 297 (1985).
77. N. R. Sorensen, R. B. Diegle, and S. T. Picraux, **Corrosion**, 43, 2 (1987).
78. V. Ashworth, E. Baron, W. A. Grant, P. Munn, and R. P. M. Proctor, in **Ion Implantation into Metals**, V. Ashworth, W. A. Grant, and R. P. M. Proctor eds., Pergamon Press, New York, 77 (1982).
79. W. C. Oliver, R. Hutchings, J. B. Pethica, E. L. Paradis, and A. J. Shuskus, **Mat. Res. Soc. Sym. Process**, 27, 705 (1984).
80. R. Hutchings and W. C. Oliver, **Wear**, 92, 143 (1983).
81. F-Z. Cui, H-D. Li, and X-Z. Zhang, **Nuclear Instrument and Methods**, 209/210, 881 (1983).
82. P. L. Bonora, **Nuclear Instrument and Methods**, 182/183, 1001 (1981).
83. P. L. Bonora, G. Cerisola, C. Tosello, and S. Tosto, in **Ion Implantation into Metals**, V. Ashworth, W. A. Grant, and R. P. M. Proctor eds., Pergamon Press, 35 (1982).
84. J. M. Williams, R. A. Buchanan, G. M. Beandsley, and R. K. Bacon, in **Ion Beam Processing of Materials**, G. K. Hubler, O. W. Holland, C. R. Clayton, and C. W. White eds., Elsevier, New York, 735 (1984).
85. J. M. Williams and R. A. Buchanan, **Mat. Sci. & Eng.**, 69, 237 (1985).
86. J. M. Williams, R. A. Buchanan, and E. D. Rigney, Jr., **Proceedings, ASM Conference on Applications of Ion Plating and Implantation to Materials**, Atlanta, Georgia, June 3-5 (1985).

87. R. A. Buchanan, E. D. Rigney, Jr., and J. M. Williams, **J. Bio. Mat. Res.**, 21, 355 (1987).
88. R. A. Buchanan, E. D. Rigney, Jr., and J. M. Williams, **J. Bio. Mat. Res.**, 21, 367 (1987).
89. J. Zhang, X. Zhang, G. Zintang, and L. Hengde, in **Biomedical Materials**, J. M. Williams, M. F. Nichols, and W. Zingg eds., MRS 55, 229 (1986).
90. V. Ashworth, D. Baxter, W. A. Grant, and R. P. M. Proctor, **Corr. Sci.**, 16, 775 (1976).
91. B. S. Covino, B. D. Sartwell, and P. B. Needham, **J. Electrochem. Soc.**, 125, 366 (1978).
92. K. Takallashi, Y. Okabe, and M. Iwaki, **Nuclear Instruments and Methods**, 182/183, 1009 (1981).
93. Y. Okabe, M. Iwaki, and K. Yakahashi, **Materials Science and Engineering**, 90, 223 (1987).
94. B. S. Covino, P. B. Needham, and G. R. Conner, **J. Electrochem. Soc.**, 125, 370 (1978).
95. V. Ashworth, W. A. Grant, A. R. Mohammed, and R. P. M. Proctor, in **Ion Implantation Metallurgy**, C. M. Preece and J. K. Hirvonen eds., AIME, 47 (1980).
96. P. E. Morris, in **Galanic and Pitting Corrosion-Field and Laboratory Studies**, ASTM STP 576, 261 (1976).
97. N. D. Greene and G. Judo, **Corrosion**, 21, 15 (1965).
98. M. Pourbaix, L. Klimzack-Mathieu, C. Martens, J. Meunier, C. Vanleughenaghe, L. de Munck, J. Laureys, L. Nellmans, and M. Warzu, **Corr. Sci.**, 3, 239 (1963).
99. H. C. Man and D. R. Gabe, **Corr. Sci.**, 21, 713 (1981).
100. J. B. Lumsden and R. W. Staehle, in **Passivity and Its Breakdown on Iron and Iron Base Alloys**, NACE, 75 (1976).
101. E. McCafferty and P. G. Moore, **J. Electrochem. Soc.**, 133, 1090 (1986).
102. S. Kim, PhD Dissertation, North Carolina State University (1986).
103. E. McCafferty, G. K. Hubler, P. M. Natishan, P. G. Moore, R. A. Kant, and B. D. Sartwell, **Materials Science and Engineering**, 86, 1 (1987).

104. T. P. Hoar, **J. Electrochem. Soc.**, 117, 17c (1970).
105. M. Stern and H. Wissenberg, **J. Electrochem. Soc.**, 106, 759 (1959).
106. N. D. Tomashov, **Corrosion**, 14, 229t (1958).
107. R. C. Weast, M. J. Astle, and W. H. Beyer eds., **CRC Handbook of Chemistry and Physics**, 67th, CRC Press, B-21 (1986).
108. F. T. Hambrecht, in **Biomedical Materials**, J. M. Williams, M. F. Nichols, and W. Zingg eds., MRS 55, 265 (1986).
109. E. J. Kelly, **J. Electrochem. Soc.**, 123, 162 (1976).
110. D. N. Buckley and L. D. Burke, **J. Chem. Soc. Faraday Trans. 1**, 72 2431 (1976).
111. G. Beni, L. M. Schiavone, J. L. Shay, W. C. Dautremont-Smith, and B. S. Schneider, **Nature**, 282, 281 (1979).
112. D. Michell, D. A. J. Rand, and R. Woods, **J. Electroanal. Chem.**, 84, 117 (1977).
113. S. Gottesfeld and S. Srinivasan, **J. Electroanal. Chem.**, 86, 89 (1978).
114. S. Gottesfeld, J. D. E. McIntyre, G. Beni, and J. L. Shay, **Appl. Phys. Lett.**, 33, 208 (1978).
115. L. M. Schiavone, W. C. Dautremont-Smith, G. Beni, and J. L. Shay, **Appl. Phys. Lett.**, 35, 823 (1979).
116. G. Beni and J. L. Shay, **Physical Review B**, 21, 364 (1980).
117. J. L. Shay, G. Beni, and L. M. Schiavone, **Appl. Phys. Lett.**, 33, 942 (1978).
118. G. Beni and J. L. Shay, **Appl. Phys. Lett.**, 33, 567 (1978).
119. W. C. Dautremont-Smith, G. Beni, L. M. Schiavone, and J. L. Shay, **Appl. Phys. Lett.**, 35, 565 (1979).
120. L. S. Robblee, J. Marston, J. McHardy, and S. B. Brummer, **Biomaterials**, 1, 135 (1980).
121. L. S. Robblee, M. J. Mangaudis, E. D. Lasinsky, A. G. Kimball, and S. B. Brummer, in **Biomedical Materials**, J. M. Williams, M. F. Nichols, and W. Zingg eds., MRS 55, 303 (1986).
122. K. J. Vetter, **Electrochemical Kinetics**, Academic Press, New York, 79 (1967).

123. G. V. Samsonov ed., **The Oxide Handbook**, 2nd, IFI/PLENUM, New York, 212 (1982).
124. D. A. J. Rand and R. Woods, **J. Electroanal. Chem.**, 31, 29 (1971).
125. D. A. J. Rand and R. Woods, **J. Electroanal. Chem.**, 55, 375 (1974).
126. J. S. Foods and S. M. Erker, in **Biomedical Materials**, J. M. Williams, M. F. Nichols, and W. Zingg eds., MRS 55, 281 (1986).
127. R. Woods, **J. Electroanal. Chem.**, 49, 217 (1974).
128. S. B. Brummer, L. S. Robblee, and F. T. Hambrecht, **Annals of the New York Academy of Sciences**, 405, New York Academy of Science, New York, 159 (1983).

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