

THE EFFECT OF ION IMPLANTATION  
ON MEDICAL ALLOYS

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THE EFFECT OF ION IMPLANTATION  
ON MEDICAL ALLOYS

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## CHAPTER I

## INTRODUCTION

During the past fifteen years much work has been done in the area of biomedical implants. Often a badly fractured or severed bone must be replaced or strengthened temporarily to allow the bone to heal properly. Artificial structures from plastic materials, but more commonly of several metals, have been used for this purpose: yet no particular metal has been found which is truly compatible in the environment of the body, in vivo, plus exhibiting proper fatigue strength requirements for extended implantation.

The main concern of this thesis is the improvement of fatigue life and corrosion resistance of type 316L stainless steel which is widely used for the fixation of fractured bones. Although it is by no means perfect for implants, it has a reasonable corrosion resistance in body fluids and generally adequate strength. Type 316L stainless steel samples, provided by the Zimmer Mfg. Company, were coated by ion implantation with thin films of molybdenum, platinum, tantalum, and titanium. Tests were made to determine the fatigue life of the samples and any changes in the corrosion characteristics due to the addition of the ion plated surface film.

## CHAPTER II

### BACKGROUND

#### Coating Methods

The coating and plating of metals is a large and varied industry. There are many applications for plating either a thin or thick layer of a suitable coating material on a substrate, some of the most important being for the improvement of lubrication, wear and corrosion resistance, and for decorative purposes.

In order to select a proper coating material and the proper coating technique for a given substrate to provide a specific result, one needs to have a thorough knowledge of the properties of the materials involved and the deposition technique. The deposition method is often the major factor in determining the final properties of a coated surface (1). Coatings of various materials can be deposited on surfaces by many methods such as spraying, impingement, vaporization, electroplating, cladding, and dipping. One of the best methods for plating a thin film on a substrate takes place in a vacuum and is called vacuum deposition. There are three major ways to plate a substrate in a vacuum: a) vapor evaporation, b) sputtering, and c) ion plating.

#### Vapor Evaporation

This method involves the condensation of the substrate of an element or compound from the vapor phase. In vapor deposition techniques, the evaporated atoms have only the thermal energy associated with the

boiling point temperature of the material from which it was evaporated. It has been experimentally shown in a number of cases and agreed in general that during vapor deposition, film formation occurs by nucleation and grain growth (2). The surface has preferred sites where nuclei develop into islands which then grow both laterally and vertically. The islands coalesce and eventually form a continuous film. During this process, the substrate temperature is one of the most important parameters, having an influence on atomic diffusion in the coating material and the width of the interface.

### Sputtering

This may be defined as the ejection of surface atoms from solids or liquids under ion bombardment (3). Sputtering has many applications in industry today and as a result several techniques have been developed. One method, triode sputtering with direct current, will be discussed to provide a general example of the sputtering process.

In sputtering the ion bombardment is done in an inert gas, usually argon, of several microns pressure. A negative potential, usually 2-5 kilovolts, is applied to the material to be coated, with respect to the anode (4). A glow discharge is established in the presence of the sputtering argon gas, and the positive argon ions formed are accelerated toward the specimen, ejecting atoms from the surface thereby etching or cleaning the surface. A shutter is placed between the target, the coating material, and the specimen during d.c. sputter etching to prevent target contamination. After the surface is cleaned, the power source to the target is energized and the positive argon ions then accelerate to the target and thus dislodge atoms from the target surface

by impact. These sputtered atoms are transferred to the specimen surface by a momentum transfer process. When these atoms hit the water-cooled specimen surface, a continuous film forms.

Sputtering is theoretically a line of sight process. A serious disadvantage of sputtering is its low efficiency (3). Less than 5% of the kinetic energy of the bombarding ions goes into the kinetic energy of the sputtered atoms. The other 95% appears mostly as heat in the target. Consequently, if high deposition rates are desired, a means for efficient target cooling must be found.

#### Ion Plating

This method consists of two processes, sputter cleaning and ion implantation, and is basically a diode system consisting of two electrodes in a low pressure inert gas environment. The specimen to be coated is the cathode of a high voltage d.c. circuit, and the boat with the evaporant material is the anode. The specimen or substrate is biased to a high negative potential to start and sustain a glow discharge when gas is fed into the system, especially in the region between the specimen and the evaporating source. The most important region for ion plating is the dark region near the cathode, known as the cathode dark space (5,6). It is in this region where there is the largest potential drop in the plasma. The significance of this dark space is that within this region the ions are accelerated with the highest velocity toward the cathode. The width of this dark space can be expanded or contracted by increasing or decreasing the pressure.

As soon as the discharge is formed, ionized argon ions are accelerated toward the sample and sputtering occurs. While the surface

is being cleaned by sputtering, the discharge current decreases until a constant value is reached which indicates that the surface is cleaned. After the surface has been cleaned, the boat is heated and the plating material evaporated. The evaporated metal atoms are injected into the plasma, ionized, and accelerated toward the cathode along the electric field lines which are produced in the dark space region. These ions reach and deposit on the back side as well as front of the sample, with a kinetic energy proportional to the potential difference between the cathode and anode. While the ion plating process is occurring, sputtering continues. Obviously, the sputtering rate must be less than the deposition rate for a film to be deposited.

Heat Sources and Evaporation. Heat sources and evaporation methods are very important considerations in ion implantation. The uniformity of the plated film, the rate of deposition, the thickness of the film, and the chemical homogeneity of a desired alloy film are all dependent upon the heat source and method of evaporation. Basically there are two types of heat sources used in vacuum evaporation. One is the resistance heated source which is generally used to plate low melting materials at low deposition rates. This source can not operate for long times in a glow discharge environment.

The second type of heat source is the electron beam heat source in which electrons are supplied and emitted by a gun and then accelerated by a potential field to the substrate by a magnetic field. This type of heat source and a method used to evaporate alloys for plating is described further in Appendix I and II.

Process Parameters. The ion deposition process, regardless

of the evaporation method used, requires control of the following process variables to achieve a coating with the desired characteristics (7): 1) glow-discharge pressure, 2) evaporant flux or electron beam power, 3) voltage between the specimen and evaporant, 4) source to substrate distance, 5) substrate temperature, 6) substrate geometry. The glow discharge pressure and the evaporant flux are the most important parameters (8) because the process is very sensitive to their changes and they strongly affect the resulting deposit characteristics.

It has been found that the thickness of a coating on the back as compared with the front of a specimen increases as the discharge pressure increases when the other parameters are held constant, but decreases as the flux of the evaporant material increases to a high level (9). This is due to direct line of sight deposition of un-ionized coating atoms onto the surface facing the evaporating source material. As the evaporant flux is increased, the discharge pressure and/or other process conditions must be changed to maintain uniformity of coating. Another method to obtain optimum coating conditions is to vary the source to substrate distance. It has been found that the ratio between the coating thickness of the front to back surface of a specimen increases as the source to substrate distance increases, an optimum distance being about eight inches.

The deposition rate is an important factor in determining both production capabilities of the process and properties of the deposit. The deposition rate depends on many variables such as the evaporant flux, the source to substrate distance, the system pressure, and the source material and size. When evaporating a material by hot filament

electron beam techniques, the main factor used to control the deposition rate, with other parameters fixed, is the electron beam power, that is, the beam voltage potential and the emission current. The current flowing to the substrate is a measure of the number of ions arriving at the substrate. The current density on the substrate is also a measure of the heat to be dissipated at each voltage level. The temperature of the substrate, particularly of the surface, is directly influenced by the power density of the arriving ions. The substrate temperature is important in controlling the mechanical properties of the deposit, particularly the ductility.

In a diode configuration the voltage is important because it accelerates the vapor ions to the substrate. The potential drop from the ionized plasma to the substrate determines the impact momentum at which the ions arrive at the surface. This affects the number of surface atoms sputtered away and the adhesion of the resultant coating.

The geometry of the substrate is an important condition because to obtain a desired coating, the process characteristics must be determined for the specific size and shape of the substrate, for each coating application. Each different substrate geometry requires a careful choice of process parameters.

Range and Penetration. One important consideration in determining the effectiveness of ion implantation is the range of the implanted ion. When the energy of an ion falls to about 20eV, it ceases to move through the solid, becoming trapped by the cohesive forces of the material, and the total distance traveled from the surface to this point is called the range (10). Every impinging ion undergoes a slowing down in the

crystal lattice due to energy losses by a series of collisions, and can be backscattered, after one or more collisions, or be trapped in the metal lattice (11). The mean depth at which an ion is trapped is determined by the ion energy and the mass atomic number of the impinging ions and the target atoms. Energy losses are due mainly to elastic Coulomb interactions (electrostatic repulsions) between the nuclear charges of the ions and target atoms, and also the inelastic interactions of the ions with bound or free target electrons. In addition there may be a contribution to the energy loss because of charge exchange between the moving ion and target atom, electrons from one transferring to the other during their close proximity. At low energies, such as in this work, nuclear stopping dominates and is responsible for most of the angular dispersion of the impinging ions. Below the very lowest ion energies, about 10eV, the chemical binding forces can not be neglected and the collisions must be regarded as taking place quantum - mechanically with the lattice as a whole.

When dealing with crystal lattices the phenomenon of channelling and dechannelling play an important role. Ions traveling so that their motion is constrained to the open channels between adjacent close - packed rows of atoms are actually steered by a series of glancing collisions with the atomic rows and therefore their energy loss is reduced. Consequently, if a beam of energetic ions or particles is incident on a crystal lattice, in a low - index direction, increased ion penetration can be expected. Robinson, Oen, and others (12-14) have shown that channelling 5 keV copper atoms along the open channels of a copper lattice can increase the maximum penetration by up to an

order of magnitude. It should be noted that in channelling, the energy loss of a well - channelled ion is dominated by electronic processes rather than nuclear collisions because these ions rarely come close to a nucleus, even for low ion energies. Dechannelling however, which is the ejection of ions from channels, involve relatively close atomic collisions and therefore is mainly an elastic scattering process.

Temperature is also an important variable. Thermal vibration of the lattice plays a major part in determining the range distribution at low ion energies, such as that used in this study. The maximum range will diminish exponentially with increasing temperature at very low ion energies.

A calculation of the range distribution for ions of a given species injected into a given crystal lattice is not yet possible because of uncertainties regarding the energy loss of channelled ions and a lack of full understanding of the dechannelling process. In this study, because of the low energy used in accelerating the ions into the polycrystalline stainless steel, 3 keV, the question arises as to whether these ions were implanted in the surface or just plated on the surface. Although there was a substantial change in the fatigue life of the stainless steel due to the ion plated films, this does not indicate that any penetration occurred. The fatigue data shows no relationship between the relative depths of penetration of the coating materials used and their fatigue life, and no assumption that the ions did penetrate the surface a significant distance can be made.

#### Why Ion Plating?

Ion plating has two unique advantages (5,15,16): 1) Excellent

adherence is usually obtained even between combinations of materials that normally do not form adherent interfaces. The careful cleaning, pretreatment, and handling steps often required for other coating methods are usually not necessary for ion plating. 2) the process results in quite uniform coatings which often can be deposited without rotating the part. Buildup at corners of parts is also not encountered.

### Adhesion

Requirements for Good Adhesion. The adhesion between components of a system depends on three factors: 1) the bonding across the interfacial region, 2) the type of interfacial region, and 3) the fracture mechanism which results in failure. One key to good adhesion is to bring the substrate and coating materials into intimate contact over a large area. In the case of deposited films good adhesion also means that the surface must be free of contaminants which prevent intimate contact or which may have low strengths, and that the nucleation and growth of the films must be such that there is a high interfacial contact area.

Unlike ion plating, most methods require control of both the surface conditions and type of interface formed between the materials for good adhesion. Controlling the surface condition involves: 1) cleaning to remove surface contaminants. This may involve a solvent to remove organics, oxygen firing to oxidize contaminants, hydrogen firing to reduce oxides etc., 2) surface modification to change the physical characteristics of the surface perhaps by etching or abrading, 3) use of adhesion promoters or primers to create a new surface for deposition or to influence the nucleation of the depositing material.

Good bonding does not always mean that there will be good adhesion

in service. The fracture mechanism may be the controlling factor, but this often depends upon the type of interface. For example, the interfacial region may be either continuous or porous. A porous interfacial region generally will be weaker because the pores act as stress concentrators and decrease the effective interfacial area. Nucleation and growth processes of films can give porous interfaces when isolated nuclei must grow to appreciable size before the film becomes continuous and do so without wetting the substrate surfaces.

The most desirable type of interface, from the standpoint of adhesion, is one in which stresses in the interfacial region are distributed over an appreciable volume without the generation of a low strength or brittle region. This can best be done by grading the composition of the interface from that of the bulk material to that of the coating material (4,15).

Adherence. Ion plating has two built-in features which are responsible for the exceptionally strong adherence. The first one is the initial sputter etching. For sputtering, a minimum limit may be set by the requirement that the incoming particle have enough energy to dislodge an atom from its place in the surface crystal lattice, theoretically calculated to be approximately 20-25 e.v. (6,17). Therefore, after sputtering the surface topography changes, bringing out grain boundaries, various surface planes, etch pits and dislocations sputtering thus has a microscopic 'roughening effect' on the surface (4). The surface is cleaned of oxide layers and is free of skin effects of cold working which may be produced by mechanical polishing.

In addition to the cleaning and sputtering effects, the energy of

the sputtered atom is enough to allow the atom to penetrate into the substrate lattice (18-21). Such penetration may create vacancies in the substrate lattice or increase the number of foreign interstitial atoms, and in turn may result in the formation of prismatic dislocation loops.

The end result of these processes is a change in the free energy and structure of the substrate surface. The defect structure in turn affects the number of nucleation sites and the surface free energy which in turn affect the bond strength between the substrate and the film to be plated. These effects change the adhesion properties, sticking coefficient, film stress and structure.

The second feature affecting adherence is the high energy of the impinging coating ions which raise the substrate surface temperature, thus enhancing diffusion without necessitating bulk heating, and alter the surface and interfacial structure by introducing defect concentrations, physically mixing the film and substrate material and producing pseudo-diffusion and chemical reaction at the interface of even normally nonadherent combinations. The interface formed at these high potentials has a graded appearance with a gradual change in composition and lattice parameters. This concentration gradient contributes to the strong adherence of the film (22). The inherent stresses produced during film deposition are due to the differences in lattice parameters and the thermal expansion mismatch between the metal film and the substrate. These stresses are always minimized when a graded interface is formed. Therefore, peeling and blistering effects are not observed on ion plated films.

Throwing Power

Ion plating has good "throwing power" to coat all surfaces of a part and is not a direct line of sight coating process (15). There are two reasons for this. One is that the ionized atoms are accelerated to the substrate along the electric field lines, which are produced in the dark space region, and they reach and deposit on the back side of the substrate as well as the front. Secondly, because the mean free path of the evaporated atom is shorter in the glow discharge environment than the distance between the source and the substrate, atoms of the evaporant on the average make several collisions with gas molecules before they arrive at the substrate surface. Many of these atoms are deflected by the series of collisions to the extent that they can reach all surfaces, including the back side, of the substrate which is not in the line of sight of the evaporating source.

#### Corrosion Aspects

The four coating materials used in this work, Mo, Pt, Ti, and Ta, chosen for their corrosion resistant properties. These properties and how these metals react to different environments are documented in the literature (23-25), and are reviewed in Appendix III.

It should be noted that all the properties listed relate to the metals in bulk form. These properties may differ if the metal is used only as a coating material because, depending on the coating method used, a certain thickness is required of each metal in order to obtain its original bulk properties. Because of the excellent properties of the four metals used in this work, all of them have been extensively used for coating materials, either for electrical, decorative, or protective

purposes (26). Most of these coatings are electroplated, however, and have thicknesses much greater than those obtained with the ion plating process used in this work. Although much work has been done with the ion plating or ion implantation systems, only very little literature regarding the corrosion properties of the thin implanted films studied in this work is available.

Another point well applicable to this work is that for corrosion purposes, each metal must be tested in the environment in which it is to be used. In a general way a metal's corrosion resistance in a projected environment can be forecast, but this supposition can frequently be wrong. A good example is Ti and Ta. Ti has excellent corrosion properties outside the body environment, in vitro, and also in the body environment, or in vivo, as it appears to be very non-reactive in living tissues. Ta is also highly resistant to chemical solutions and has gained a reputation in industry as a highly corrosion resistant metal. In the body however, Ta becomes very reactive and a marked tissue reaction occurs (27).

In relative to this, corrosion testing techniques which will give the most accurate results comparable to, in vivo, testing have been investigated (28,29). The study of implant corrosion requires a sensitive, rapid technique to measure the rate of attack. Electrochemical techniques can be used to accurately determine corrosion rates below .0005 mpy and are ideally suited for implant corrosion studies since they can be performed rapidly and remotely and are adapted easily to, in vivo, corrosion measurements.

#### Biomaterials Background

Man has attempted for hundreds of years to find a material

ideally suitable for medical implant use in the human body, yet none has been found with the properties necessary to replace the remarkable bone material of the body. Not only must a material be compatible to the biological environment of the body, but it must also meet the high strength and fatigue requirements imposed on it by forces encountered in and on the body. Consequently, only a few metals have come close to meeting these requirements: vitallium, titanium and its alloys, and types 316 and 317 stainless steel. These materials all have acceptable strength and corrosion resistance, yet more work must be done to improve the properties. Appendix IV discusses in more detail the problems of compatibility and strength of materials to be used for biomedical implants.

## CHAPTER III

### EXPERIMENTAL PROCEDURE AND RESULTS

#### Ion Plating

##### Materials

An Electron Vapor Deposition Unit (EVD-97) built by the Materials Research Corporation was used for the thin film ion plating process. The Type 316 L stainless steel samples used for this work were kindly supplied and electropolished by the Zimmer Manufacturing Company of Warsaw, Indiana.

Type 316 L stainless steel in the cold worked and annealed condition was used. For tantalum plating, annealed material was used in 1/2" x 3/16" x 4" samples. The Vickers hardness number of this material was 254, or approximately 16 on the Rockwell C scale. Cold worked samples were plated with Mo, Ti, and Pt. Geometrically these samples were 1/2 " x 3/16" x 4 1/2", fully hardened with a Vickers hardness number of 363, Rockwell C 34. Prior to plating, a 1/2" length of each sample was cut off to be used for corrosion experiments.

For the ion plating process, instead of heating the coating material in a boat for evaporation into the ionizing plasma, a 10 mil wire of 99.5% purity was wrapped around a tungsten filament and heated until evaporation occurred. The author feels that this is a poor method to use because of the alloying properties of tungsten with the coating materials, and mainly because during the plating process

sputtering is also occurring and consequently the tungsten filament and the copper rods holding the filament are also being sputtered, creating added impurities in the system and possibly in the coated surface layer.

The choice of Mo, Pt, Ti, and Ta for coating materials was based mainly upon their known corrosion resistance properties, as explained in Section IID.

### Methods

The machine used for the ion plating process uses a diode configuration. The cathode is a round stainless steel plate upon which the steel samples are placed. They are coated by the ionized atoms of the evaporated material which are attracted to the cathode through an applied voltage field. Argon gas was used as the ionizing medium. Each sample was coated separately. In every case, a six inch strip of wire of the desired coating material was wrapped around a tungsten filament attached to a power source. The length of the coating wire was arbitrarily chosen, but was kept constant for reasons of uniformity.

The rate of evaporant flux and consequently deposition rate could not be controlled. This was due mostly to the inaccuracy of the heating power source and the inability to operate the equipment at high temperatures for a long period of time without being able to accurately control the current to the substrate before and during evaporation. Also, the heat required to evaporate the wire was somewhat dependent on how tightly and in what manner the coating wire was wrapped around the tungsten filament. Consequently, it was not possible to control the rate of deposition as accurately as desired.

Previous to every coating run, the vacuum chamber was pumped

down to a pressure of  $1 \times 10^{-6}$  microns or less. The samples were plated at a gas discharge pressure of 20 microns, and at a voltage of 3kV. The current at which plating took place ranged between 50 - 100 milli-amperes. It should be noted that arcing was continuously a problem and often before the required voltage was reached, the current was kept between 200 - 250 ma, for as long as 5 - 10 minutes. Significant heat was generated in the cathode and thus the sample reached several hundred degrees Fahrenheit. This could have an effect in some metals on the diffusion of the surface layer.

In the setup used, the distance between the heat source and the cathode was six inches. The samples to be plated were set flatly on the cathode so that the side opposite the side where the crack initiated was not plated. After the sample was plated, the chamber was pumped down for at least a half hour to a pressure of  $10^{-4}$  microns, after which time the diffusion pump was shut off and the sample was allowed to completely cool down in the bell jar before being removed and prepared for fatigue and corrosion experiments.

#### Evaluation of the Deposits

Hardness. Samples were tested for hardness with the Vickers Hardness Tester and the results are shown in Table 1 below:

Table 1. Hardness Table of 316 L Stainless Steel Samples.  
(All numbers are Vickers Diamond Pyramid Hardness Numbers.)

<u>Fully Work Hardened 316 L Stainless Steel</u>		<u>Annealed 316 L Stainless Steel</u>	
Unspattered Uncoated	363	Unspattered Uncoated	254
Sputtered Uncoated	380	Sputtered Uncoated	270

Table 1. (Continued)

Fully Work Hardened 316 L Stainless Steel		Annealed 316 L Stainless Steel	
Mo Coated	383	Ta Coated	274
Ti Coated	387		
Pt Coated	387		

It is interesting to note that for both types of steel, sputtering and ion plating increase the hardness; however it appears that sputtering alone accounts for most of this hardness increase. This indicates that sputtering in addition to cleaning the surface of oxide and removing stresses due to polishing, creates a surface defect structure which hardens the surface of the substrate.

Thickness. Thickness measurements were made using x-ray fluorescence. First, standards were prepared on 22 square mm thin, glass plates by coating with different thicknesses of each coating material. These were used for standard samples. The glass slides were first cleaned in methanol and acetone and stored in a dessicator at all times except when they were in the evaporation chamber. The thickness of the film on these glass plates was determined by weight measurements using a Mettler electrical balance which had resolution to four decimal places. The films evaporated on the glass slides were very thin, less than 1000 Å, and the weight differences in several cases were very small which led to some inaccuracy in precise thickness calculations. All samples, including steel coated samples were then fluoresced and the numbers of counts were plotted on a graph. The film thicknesses on the coated steel samples were then determined by comparison with the standards. The results are shown in

Table 2. How these thin film thicknesses relate to the fatigue and corrosion characteristics of the samples will be discussed in Section 5.

Table 2. Results of Thickness Measurements

Coated Steel Samples	Thickness (Angstroms)
Ti 1	740 ± 25
Ti 2	705 ± 50
Pt 1	540 ± 50
Pt 2	545 ± 50
Ta 1	340 ± 50
Ta 2	400 ± 50
Ta 3	800 ± 100
Mo 1	200 ± 100
Mo 2	70 ± 70

### Fatigue

One of the main purposes of this work was to find the effect of the various ion plated films on the fatigue life of Type 316 L stainless steel. As noted earlier, strength and fatigue life are very important considerations for medical implants. All the fatigue experiments conducted in this work were high-cycle fatigue studies using a Sonntag Universal Fatigue Testing Machine which vibrates at a frequency of 1800 cpm. A special attachment to the machine was made for three point bending of the steel sample. The static and dynamic loads were applied through a 3/16" diameter roll pin at the top center of the sample. The samples were supported by two roll pins, 3/16" diameter, one quarter inch from each end, on the coated side of the sample. Also on this plated side of

the sample, directly beneath the center load pin, is where the fatigue cracks initiated for all the samples. See the schematic diagram in Figure 1.

The results of the fatigue tests are shown in Table 3. The samples were tested in the order of the groups observed in Table 3. After a group of coated samples were fatigued, uncoated samples were also fatigued to check sample and machine consistency. It can be noted that the fatigue values for the uncoated samples in the Mo, Pt, and Ti groups are erratic. As the machine conditions were checked for uniformity before every fatigue test, some of the scattered values obtained for these uncoated samples can not be explained.

It should be noted that because no extra samples were available, the effect of sputtering on fatigue life was not included in this work, therefore no sputtered but uncoated samples were fatigued. It has already been mentioned that sputtering has a microscopic roughening effect on the surface of the substrate and that sputtering may harden the substrate surface to a small degree. Each coated sample in this work was cleaned by sputtering before the actual plating process occurred. Samples were sputtered for various periods of time varying from 5-20 minutes, depending usually on the sporadic arcing which occurred. The effect of sputtering could partly account for the difference in fatigue values observed in the plated specimens.

Cold worked stainless steel plated with Mo, Pt, and Ti was studied first. In the Mo group, three uncoated samples were first tested. Then three Mo coated samples were tested followed by two uncoated samples to establish sample and machine consistency. All Mo coated samples

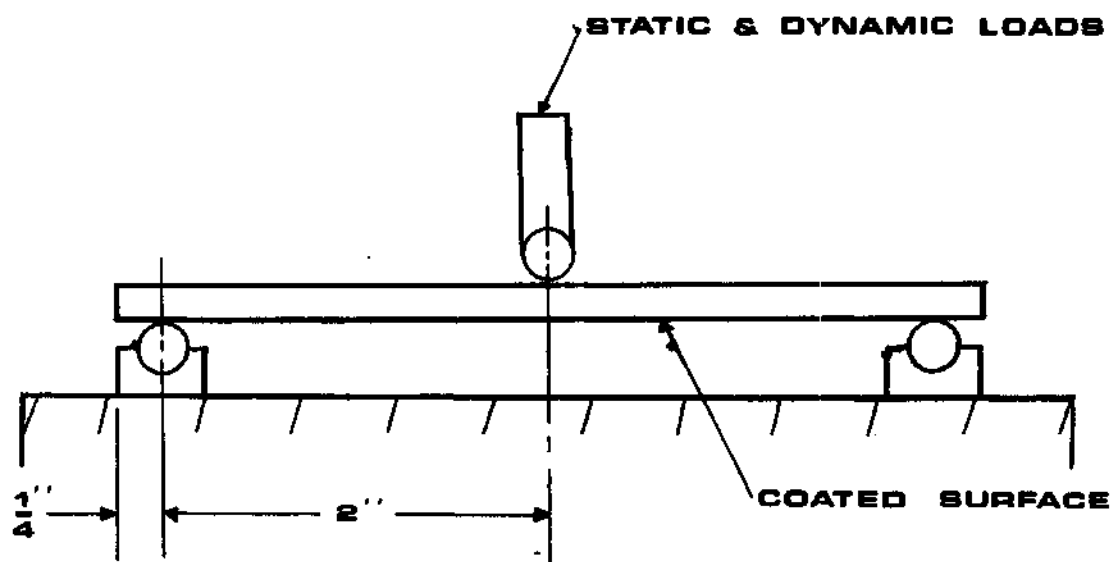


Figure 1. Schematic Diagram of the Fatigue Apparatus Used in the Fatigue Tests

Table 3. Fatigue Life in Cycles of the Uncoated and Pt, Ta, Mo, and Ti Plated Samples

<u>Cold Worked</u> <u>316 L Stainless Steel</u>						
	<u>Mo Coated</u>		<u>Pt Coated</u>		<u>Ti Coated</u>	
	<u>Uncoated</u>	<u>Uncoated</u>	<u>Uncoated</u>	<u>Uncoated</u>	<u>Uncoated</u>	<u>Uncoated</u>
Load: 160 lbs. Static, 140 lbs. Dynamic						
1.	10,363,000*	383,000	806,000	1,516,500	14,693,000*	6,914,000*
2.	10,016,000*	320,000	669,000	563,000	710,000	865,000
3.	10,211,000*	353,000	1,125,000		13,741,000*	394,000
4.		488,000			3,145,000	5,557,000
5.		393,000				
Avg.		<u>395,400</u>	<u>866,666</u>	<u>1,039,750</u>		
<u>Annealed</u> <u>316 L Stainless Steel</u>						
	<u>Ta Coated</u>		<u>Mo Coated</u>		<u>Uncoated</u>	
	<u>Uncoated</u>	<u>Uncoated</u>	<u>Uncoated</u>	<u>Uncoated</u>	<u>Uncoated</u>	<u>Uncoated</u>
Load: 118 lbs. Static, 100 lbs. Dynamic						
1.	1,520,000	392,000	10,146,000*	955,000		
2.	549,000	329,000	10,473,000*	1,078,000		
3.	861,000	361,000	10,083,000*	957,000		
4.	484,000	391,000				
5.		334,000				
6.		277,000				
7.		352,000				
Avg.	<u>853,000</u>	<u>348,000</u>				<u>996,666</u>

\*These samples were removed from the tester before fracture.

achieved more than 10,000,000 cycles without failure, an order of magnitude difference in life over the uncoated samples.

Next a set of Mo coated and uncoated samples were vacuum annealed at 800 C for 8 hours and air cooled. There appeared to be some oxidation of these samples. The purpose of these tests was two-fold: 1) to allow diffusion and equilibrium to occur in the surface film, and 2) to note the effect of an annealing on fatigue life. Again the three Mo samples showed an order of magnitude improvement in life over the uncoated samples.

Next three Pt coated samples were tested, followed by the two uncoated samples. It can be seen that the results here were inconclusive due to scatter of the data. In view of the scatter in corrosion data reported in the next section and to the limited samples available, it was decided to preclude any further tests with Pt coated samples.

The Ti samples were tested next but in a different manner. First one uncoated sample was tested followed by a Ti coated sample, etc. The results are not consistent, but it can be noted that the best Ti coated samples show an order of magnitude improvement in fatigue life over the uncoated samples. Therefore it appears that a Ti coating may increase the fatigue life, but no additional samples were available to confirm this trend. It should also be noted here that an oxide film was observed on Ti samples 1 and 2, while the oxide film was not observable on samples 3 and 4. Also it is known that oxygen is soluble in Ti and can form a solid solution at fairly high temperatures. If oxygen combined with the Ti to a small degree during plating, this could have a significant affect on fatigue life and possibly account for the inconsistent fatigue values

measured for the Ti specimens.

Several annealed, uncoated samples were tested next, followed by Ta coated samples tested in the same manner as the Ti samples. The results here are fairly consistent and the fatigue life approximately doubles as a result of the Ta film.

In summary, it can be seen from the fatigue results that the Mo coated samples show a large increase in fatigue life. Ta also improves fatigue life but to a smaller degree. The data for Ti are inconsistent but it appears that a Ti film may increase the fatigue life. No trend can be determined for the Pt coated samples because of the scattered results.

Only half of the fatigued samples could be measured for the ion plated film thicknesses. Except for tantalum there was no apparent correlation between the fatigue life of the samples and the thicknesses of the films. The Ta data are shown in Table 4.

Table 4. The Fatigue Life and Thickness for Ta Coated Samples

Fatigue Life (Cycles)	Thickness (Angstroms)
1,520,000	340
861,000	400
484,000	800

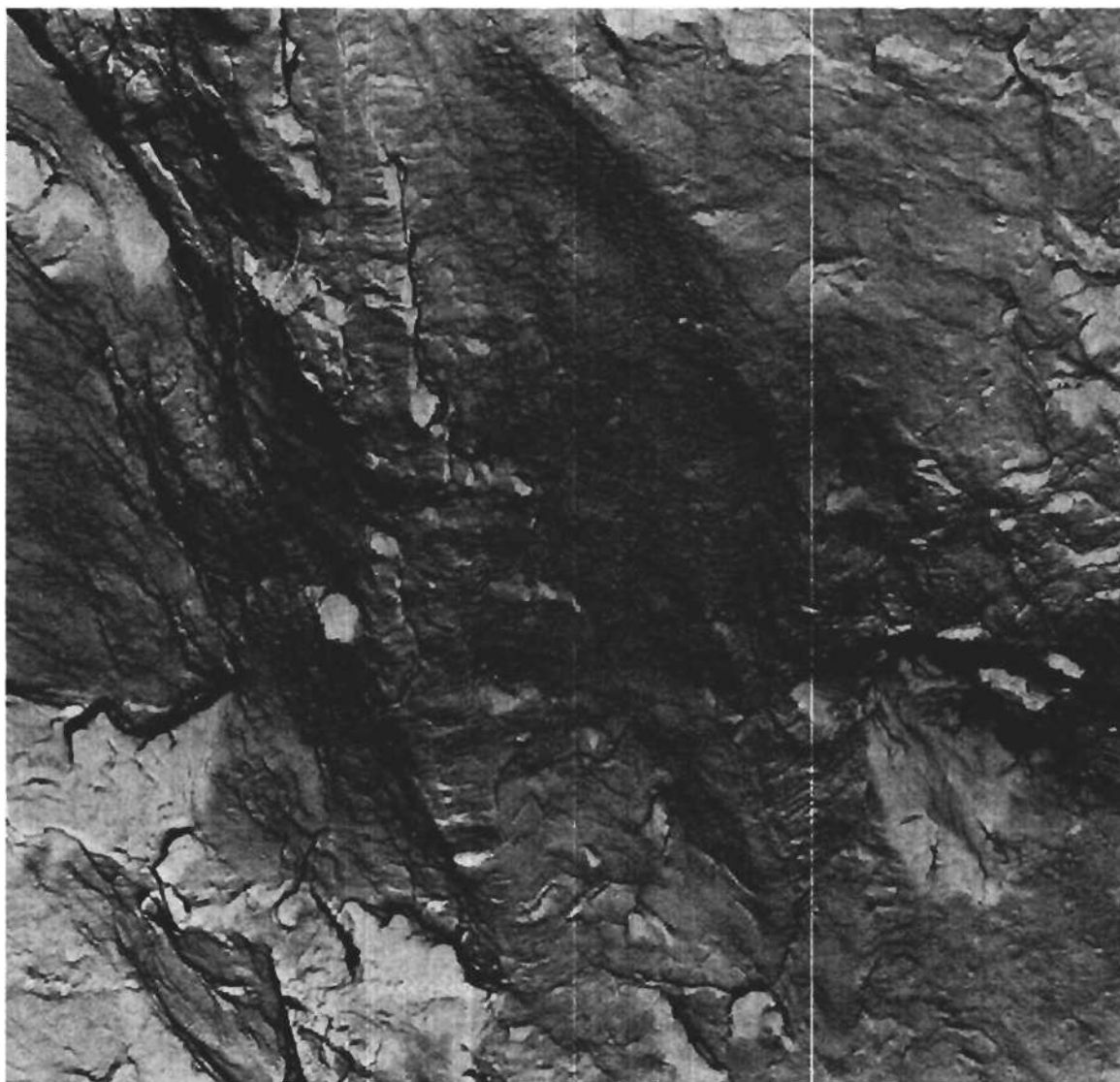
It can be seen that the fatigue life decreased as the Ta film thickness increased, however this increase is not linear. The Mo films, which were most effective, were extremely thin: 200 and 70 angstroms.

To examine the fatigue phenomena, pictures of the crack surface

and adjacent external surfaces were taken in the scanning electron microscope (SEM). The pictures showed slip lines on the external surfaces but lack of resolution and contrast did not allow crack surface pictures to be interpreted for observations related to the fatigue effects. Therefore replicas for the transmission electron microscope were prepared from plated and unplated samples. Figure 2 shows typical broad band fatigue striations characteristic of a ductile material on the fracture surface of a Ti plated sample which fractured at 3,145,000 cycles. Striations were first observable at a distance of about 1 micron from the crack initiation site. This picture was taken at a distance of 1.2 microns from the crack initiation site. Other pictures taken of fracture surfaces, including those of the unplated samples, were not significantly different from Figure 2 and allowed no conclusions to be made for the differences in fatigue life due to the addition of the thin plated films.

#### Corrosion

In this work, anodic polarization curves were determined using a Beckman Electroscan 30 Potentiostat. The test cell contained a platinum auxillary electrode and a saturated calomel electrode used as the reference electrode. A neutral Ringer's solution consisting of .9 grams of NaCl, .4225 gm KCl, .239 gm CaCl<sub>2</sub>, .20 gm NaHCO<sub>3</sub>, and 1000 ml H<sub>2</sub>O, was used as the electrolyte to simulate the extracellular fluids of the body. The tests were taken at room temperature and N<sub>2</sub> was bubbled through the solution for forty minutes before testing to produce deaeration; it was bubbled at a slower constant rate for stirring



See - G - 1.2 from edge  
20,500X

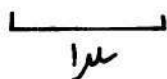


Figure 2. Micrograph of The Fracture Surface Ti Plated Stainless Steel Sample. (Taken at a depth of 1.2 microns from the crack initiation site.) Magnification - 20,500X.

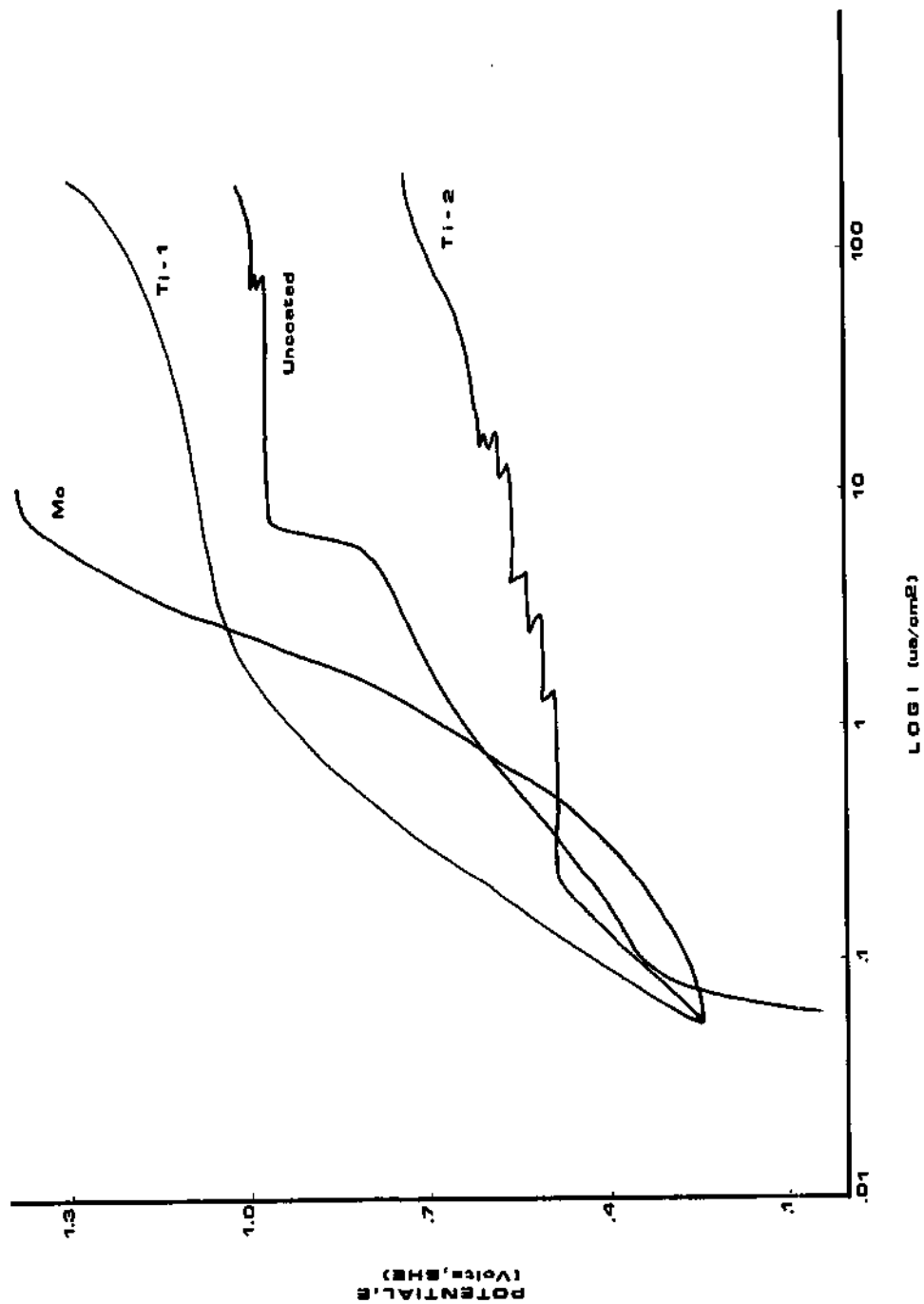


Figure 3. Polarization Curves of Uncoated and Mo and Ti Coated Stainless Steel Samples Measured In Ringer's Solution. (Curve Ti-1 represents a 740 angstrom Ti film with a visible oxide layer. Curve Ti-2 represents a 705 angstrom Ti film with no apparent oxide film.)

purposes during testing.

The test samples were set in quickmount molds and were outlined with epoxy so that the surface area of all the samples was equal. After being set in the solution the samples were prepolarized at a potential of  $+0.1V$  for two minutes and then the polarization curves were measured at a speed of  $.06$  volts per minute. Mo and Ti coated 316 L samples and uncoated 316 L stainless steel samples were tested. Several tests were performed with different test samples of each type, and Figure 3 on page 28 represents composite curves of the data obtained.

## CHAPTER IV

## DISCUSSION

Fatigue

Several observations can be made based on the results of the fatigue experiments. The data show that an ion plated film can have a large effect on the fatigue life of a metal. Although the mechanism of the effect was not a topic of investigation in this study, a few observations can be made. Refer to Table 5 below.

Table 5. Properties of Metals Which Could Affect the Fatigue Life (30-32).

	316 S.S.	Mo	Ti	Ta	Pt
Stacking Fault Energy (ergs/cm <sup>2</sup> )	13	--	--	--	95
Crystal Structure	FCC	BCC	HCP	BCC	FCC
Modulus of Elasticity (psi x 10 <sup>6</sup> )	28	47	15	27	21.3
Atomic Radius (Angstroms)	1.26	1.39	1.47	1.46	1.38
Hardness Annealed (Vickers)	254	180	180	100*	40*
Cold Worked	363				

\*These values were converted from other scales.

The first observation concerns the influence of the crystal structure. The two coating materials which produced the greatest and most consistent fatigue life increases, Mo and Ta, are both BCC. Pt, which did not seem to affect the fatigue life, is FCC. Ti is HCP and the data indicate

that perhaps a Ti coating may improve the fatigue, but no definite conclusions could be made.

Second, the relationship to the stacking fault energy can be considered. It is known that cross slip occurs more easily in materials with a high stacking fault energy than in materials with a low stacking fault energy. It has been postulated (33,34) that fatigue crack initiation and growth is dependent upon cross slip and therefore upon stacking fault energy. Stainless steel has an extremely low stacking fault energy,  $13 \text{ ergs/cm}^2$ , and although no comparative values could be found for Mo, Ti and Ta in the literature, it can be noted that Pt, which has a high stacking fault energy, had apparently little effect on the fatigue life of the 316 L stainless steel.

The third point to be observed is the hardness. It can be noted that the hardness of cold worked stainless steel is greater than that of Mo and Ti, yet large increases in fatigue life resulted. Pt has a much lower hardness and its effect on fatigue was minimal. Ta also has a lower hardness than the annealed steel it was plated on, yet Ta did have a significant effect on the fatigue life. Thus, there is no trend observable which would indicate that hardness is the major factor in increasing the fatigue life.

The fourth observation concerns the atomic radii, modulus of elasticity, and the importance of the surface layer stresses in the fatigue resistance of metals, which could possibly account for the observed fatigue increases in this work. This topic has been studied by Kramer (35,36) who claims that the surface layer stress increases during cycling and therefore the dislocation density is greatest in the

surface region. When the surface stress reaches, locally, a value equal to the fracture strength, a crack is initiated. Because there is a gradient of stress in the surface layer, the crack extends until the stress in front of the crack tip is less than the fracture strength. Therefore, reducing the surface stress or prohibiting the egress of dislocations from the surface will delay crack initiation and therefore increase the fatigue life. It has also been shown that when an alloy on the surface is formed on a specimen and properly heat treated, the dislocations become pinned and dislocation motion is impeded, thereby increasing the fatigue life.

Referring to Table 5 and considering atomic radii differences, it is observed that all the metals possess a radius larger than stainless steel, Ti and Ta being the largest. When these atoms are driven into the metal surface as an ion implant, a small stress field could be created at the surface or act as pinning points for dislocations. Although one of the advantages of ion implantation is the formation of a psuedo-diffused layer between the substrate and coating material regardless of the compatibility or size of the combining atoms, this does not mean that the bombarding ions will not create stresses and strains in that layer due to atom size differences.

In the case of Mo and Pt, the atomic size may make no difference; however the large difference in modulus of Mo would enable the film to inhibit the egress of dislocations from the surface and thereby increase the fatigue life. Pt has a lower modulus and no increase in fatigue is shown. Ta has a modulus comparable to that of the steel, however the Ta atoms may have created a large enough surface stress or acted as pinning

dislocation points and therefore a small increase in fatigue can be seen. Ti, unlike Ta, has a much smaller modulus than steel. Although fatigue results on Ti coated specimens do show a trend toward increasing fatigue life, their inconsistency does not allow any definite conclusions.

### Corrosion

In view of the increase in fatigue life of the Mo and Ti plated samples, polarization curves were obtained to study the probable corrosion behavior of these ion plated steels in the human body. The steel coated with the thin Mo film, although exhibiting no definite passive region, shows an improvement in the corrosion behavior above .6 volts SHE, with respect to the uncoated sample. It is interesting to note that the thickness of the Mo film on these samples was determined to be only 70 angstroms. Polarization tests taken by Ashworth et al. (37) indicate that ion implantation results in a film that is more resistant to breakdown than thin films coated by other methods.

Two distinct polarization curves were obtained for the Ti coated samples. Curve 1 shows a definite improvement in the corrosion behavior, while curve 2 exhibits early breakdown of the film and pitting. Measurements showed that the thickness of the films on the samples for which composite curve 1 was obtained was 740 angstroms while composite curve 2 was measured on samples with a 705 angstrom thick film. It seems unlikely that a small difference in coating would cause such large difference in corrosion behavior. Upon closer examination of the samples a light golden hue was observed on the former samples (curve 1) which is indicative of a relatively thick Ti oxide film. This would

provide better protection and could account for the difference between curve 1 and 2. The other sample though, shows no improvement over the unplated one. Instead, early breakdown of the passive layer and pitting are exhibited. This may have been caused by a very nonuniform or porous Ti film, although the exact nature of the breakdown could not be verified.

## CHAPTER V

## CONCLUSIONS

1. A thin film of Mo ion plated on 316 L stainless steel increased the fatigue life by an order of magnitude even in the annealed condition. Corrosion studies show improved corrosion resistance compared to the unplated steel.

2. The results with Ti plated samples show that the Ti film can have a large effect on fatigue life, but since the results were erratic and the number of samples tested limited, no definite conclusion can be drawn. Two distinct polarization curves were obtained for the two different film thicknesses. Samples with the thicker Ti film, also covered by a thick oxide layer, exhibited improved corrosion resistance over the 316 L unplated samples. Samples with the thinner Ti film, on which no oxide layer was visible, exhibited decreased corrosion resistance with early breakdown of the passive layer and pitting.

3. Ta plating approximately doubled the fatigue life of the 316 L samples.

4. Samples plated with Pt showed little or no increase in fatigue life. This is possibly due to the low modulus of elasticity of Pt and/or its high stacking fault energy which promotes cross slip.

## CHAPTER VI

## RECOMMENDATIONS

1. Unfortunately in this work, no uncoated but sputtered samples were fatigued, but this should be studied to determine what effects sputtering may have on fatigue life.

2. The effect of the film thickness of each material should be studied closely and the author believes that measurements determining the stress on the surface of the samples plus measurements determining the penetration depth of the film would be helpful in understanding the mechanism of the plating effect on fatigue life.

3. SEM and TEM fractographs should also be taken to study at what depth from the crack initiation site fatigue striations occur so that the effect of the film on Stage 1 fatigue may be determined.

4. More precise data should be obtained if linear polarization methods were used to determine the effect of the coated samples in the solution as a function of time.

## APPENDIX I

## HEAT SOURCES

Resistance Heated Sources

There are two principal types of heat sources used in vacuum evaporation (10,8). One is the resistance heated source which is generally limited to the deposition of low melting materials and low deposition rates. This is because the resistance heated source is not powerful enough to operate for long times in the glow discharge environment. To overcome this limitation a second type of heat source was developed utilizing an electron beam heat source.

Electron Beam Heat Sources

Several E.B. heating techniques have been investigated for melting and vaporizing materials within a glow discharge atmosphere. The two pertinent common techniques will be described here. The first one is the conventional hot filament E.B. heat source in which the hot filament supplies electrons by the mechanism of thermionic emission. The electrons emitted are accelerated through a potential of a few kilovolts and focused onto the source material by a magnetic field. In this type of gun the electron emitter requires a good vacuum because at higher pressures the emitter is subject to extensive sputtering, and arc discharge tends to occur between the high voltage leads and ground surfaces.

The second E.B. heating technique is the hollow-cathode E.B. technique. In this technique the gun is a hollow cylinder which is

placed in an argon atmosphere and biased to a negative potential to initiate a glow discharge. As soon as a gaseous discharge is initiated, an electron beam is emitted from the aperture. The electrons are not supplied by a hot filament in this type of gun. Instead they are generated by 1) the electric field and thermionic emissions from the inner surface of the cathode which is heated to a very high temperature by ion bombardment, 2) the ionization of the argon gas inside the hollow region of the gun, and 3) the emission of secondary electrons from the inner surface of the cathode wall due to ion bombardment. In the case in which electrons are generated by the combination of the field emission thermionic emission and secondary electron emission due to ion bombardment, the discharge is characterized by a high current and low voltage. It is referred to as the hollow discharge mode (HDC) and the gun is commonly called a hog hollow-cathode gun. The electron density inside the hollow region is several orders of magnitude higher than that near a plane cathode in a normal glow discharge for the same discharge current density.

In the case in which electrons are generated by the ionization of the argon gas inside the hollow region of the gun and the emission of secondary electrons is due to ion bombardment, the discharge is characterized by low current and high voltage. It is known as the electron-beam mode discharge (EBMD), and operating in this mode, the gun emits a well collimated electron beam from the aperture. The steady HDC can be easily obtained when the gas pressure is above 20 millitorr. As pressure is reduced, the discharge voltage will remain constant until a critical pressure is reached at which the discharge switches over

to EBMD, which is also steady but is operative over a much narrower pressure range.

## APPENDIX II

## FLASH EVAPORATION

When alloys or compounds have to be deposited, the deposited film must retain its stoichiometry to the evaporant material. In this situation resistance heating cannot be used because of thermal decomposition and dissociation. Alloys and compounds consist of components which have different vapor pressures. Because of these differences in vapor pressure, the components of the vapor vary continuously during the evaporation time, and the resultant film formed is chemically inhomogeneous. To retain the stoichiometry of the film during the evaporation of alloys and compounds, a method called ion plating with flash evaporation (38) can be used for low melting alloys and compounds. To evaporate high temperature materials i.e. stainless steels, ceramics and glass, electron beam sources can be used.

In flash evaporation, the material to be coated is in powder form, and is continuously fed into a preheated boat. The temperature of the boat is set as high as necessary to evaporate the least volatile component of the material. The constituents of the powder when coming in contact with the boat have to be vaporized instantly. This instantaneous evaporation prevents fractional decomposition of the material. The feed of the powder into the boat should be continuous during the evaporation process. No material should accumulate in the boat and the vapor which is produced from the uniform powder feed into the boat forms a film

with the same composition as the original one.

The parameters to control here are the particle size of the powder, rate of powder delivery to the preheated boat, and the temperature of the boat.

## APPENDIX III

## PERTINENT PROPERTIES OF Ti, Mo, Pt, AND Ta

Titanium

Titanium is intrinsically reactive and immediately acquires a thin coating of oxide,  $TiO_2$ , as soon as it is exposed to the atmosphere, titanium has excellent corrosion resistance because of its ability to repair this protective oxide film. Provided oxygen is present, the film is self-healing and reforms as soon as it is damaged mechanically. Titanium is particularly resistant to chemical that have normally strong oxidizing actions, and is virtually immune to sea-water. Titanium can be used with all concentrations of nitric acid, provided the temperature of the acid remains below about  $120^{\circ}C$ . Titanium corrodes in liquified fluorine but withstands gaseous fluorine up to about  $100^{\circ}C$ . It has better resistance to chlorine compounds than virtually any other construction material. Chlorides have no effect on titanium at temperature below about  $100^{\circ}C$ . The resistance of Ti to non-oxidizing acids is not very good and its resistance to sulphuric acid and hydrochloric acid is poor, and it corrodes very rapidly in contact with even the most dilute hydrofluoric acid solutions. Its resistance to organic acids is excellent and it is totally inert in nearly all basic solutions at almost any temperature and any concentration. Ti is virtually unattacked by salts and is inert against almost all organic materials at all temperatures.

### Molybdenum

Mo has good resistance to hot and cold concentrated HCL, HF, and  $H_2SO_4$  acids and nitric acid below  $100^\circ C$ . Mo has good resistance to cold and hot aqueous alkalis, and chlorine, bromine and iodine have no effect at all at normal temperatures. Fluorine though, tends to attack Mo even at room temperature. Mo is quite stable in oxygen or air at low temperatures. Water, salt solutions and organic materials have no effect on Mo whatever, nor is Mo attacked by such gases as sulfur dioxide, hydrogen sulphide, CO,  $CO_2$ , or ammonia gas, below  $1000^\circ C$ . Ammonium hydroxide, though, attacks Mo slowly.

### Platinum

Pt is one of the most corrosion resistant metals known, because it is cathodic to virtually every other metal except gold. Pt has complete resistance to alkaline, neutral, or acid aqueous solutions at virtually all concentrations and temperatures. The only conditions under which Pt can be attacked are very acidic conditions with a combination of extremely strong oxidizing action. Cyanides tend to form complex salts with Pt and for this reason Pt is dissolved by very hot alkali cyanides. The metal is also attacked slightly by chlorine gas and somewhat more vigorously by bromine. Pt resists  $H_2SO_4$ , HCL, and nitric acids at all concentrations and temperatures.

### Tantalum

Ta in general has excellent corrosion resistance. It is however attacked badly by HF and fluorosilicic acid and care must be taken when Ta is kept in long term contact with non-oxidizing acids to prevent

hydrogen embrittlement. It is attacked badly by 40% NaOH as well as by fused alkalis. Ta though shows excellent corrosion resistance to phosphoric acid at all strengths, and to all inorganic salts. Chlorine and bromine have little effect except at high temperatures, but the resistance to fluorine gas, even at fairly low temperatures, is not too good. Tantalum has excellent corrosion resistance to hydrochloric, hydrobromic and hydroiodic acids at all concentrations and temperatures and has excellent resistance to dilute and concentrated  $H_2SO_4$  even at very high temperatures.

## APPENDIX IV

## BIOMATERIALS BACKGROUND

Fatigue

The application of metals and alloys for use as implantable bioassists, such as pacemakers and heart valves, and orthopedic devices (fixtures and prostheses) has a long history, dating back even to the time of the Egyptians (39). Since that time many different metals have been used for implants but no material yet has been able to duplicate the properties of bone. One remarkable property of bone is its ability to repair itself by simultaneous resorption and replacement. Even though bone undergoes repeated bending due to the multiple forces to which it is constantly subjected, the process of continuous self-repair prevents an eventual fatigue of the bone. It is this quality of resistance to fatigue which has not been possible to reproduce in metal implants (40).

When considering a metal for use as an implant, its compatibility in the body environment is of prime importance. Many metals react with the surrounding body tissue, or corrode due to the influence of the body fluids. In time the mechanical properties of the material will change due to the environment. The stringent combination of requirements of proper mechanical properties and compatibility to the biological environment, have narrowed the choice of clinically usable metals and alloys to a small number: vitallium, titanium and its alloys, and types 316 and 317 stainless steel (41). Although the materials have

shown acceptable strength and corrosion resistance, there is still much to be learned about these and other materials for biomedical use.

The shape of a prosthetic device must conform closely to the body structure with which it interfaces. The resulting complicated geometry and size limitations can create large net section stresses. Fracture failures of orthopedic implants occur mainly in those fixation devices used as aids in healing bone fractures. This can be directly correlated with the implant's size, shape, and stress concentration which is a result of the limited area where it is applied. An order of magnitude difference in elastic module between bone and most metals also transfers the bulk of the bone structural load to the metal appliance causing bending stresses. For this reason most implant devices must be constructed of high-strength materials. Also, most weight bearing prostheses are subject to severe, long-term cyclic stresses from normal body movements and muscle pull.

Cyclic stressing is particularly important when the metallic devices are immersed in corrosive body fluid which can cause crevice or pitting type corrosion. Fatigue cracks generally initiate at points of geometrical stress concentrations. In all prosthetic devices and particularly in those having multicomponents, these regions of stress concentration often coincide with crevice areas where localized corrosive attack is quite likely. Such conditions tend to promote initiation and propagation of corrosion-accelerated fatigue cracking.

Fractography has verified that fatigue is the major cause of most implant failures (42,43). It usually occurs in devices of small cross section, in the areas of concentrated stress. Although the corrosive

influence of body fluids does have an effect on fatigue life, fatigue itself is the major problem. Fatigue loading is a result of known and unknown stress factors which exist in the body during dynamic weight transfer. These may load a device to several times the body weight during only small changes in the position of the body. An implant, therefore, is subjected to a wide range and frequency of stress cycles, and due to its limitation in size and because of the confines in which it must be implanted, fatigue failure may result.

Forces on artificial joints were measured on two patients carrying hip prostheses by Paul (44). The greatest force measured was 4.33 times the body weight when the subject was running. In level walking, the greatest force was 3.3 times the body weight. Bechtol (45) has estimated that a person puts his full weight on each leg about 1000 times while walking one mile. These loads are repeated between 5000 and 10,000 times daily or 1-3 million cyclic loads per year. Thus the forces and cyclic loading experienced typically by the hip joint and femur are large. Despite these loads, fatigue failures in medical implants are rare. In one study researched by Colangelo and Greene (46), it was observed that out of over 50 Type 316 stainless steel multi-component devices used as implants, only five fractured, and only three of these fractures were fatigue failures. Although fatigue failures of orthopedic implants are few on a percentage basis, there are still numerous cases, and all are important. Implants are used for humans, and ideally no failures should occur.

### Corrosion

The corrosion resistance of metals used for biomedical implants is a subject of much study. Corrosion problems in the human body are usually due to the various elements or chemicals in the body to which different metals may not be compatible. It has been generally accepted that corrosion of implants is mainly due to the NaCl content of the body fluids. However, an investigation by Cahoon (47) showed that the corrosion of stainless steel implants is affected not only by NaCl but also by both carbon dioxide and potassium. The corrosion problem therefore can be very complex and more research needs to be done.

A metal implant is subjected to very different environments in the human body than outside the body. Lang (48), in his publication "Bone Grafting and Surgical Implants", explains that after a metal implant is inserted, it is bathed with an extracellular fluid of the body, and is in intimate contact with living cells, and in many cases with dead cells and stagnant pools of blood. This bathing fluid is a solution of many salts including chlorides and has been called more corrosive than sea water as far as metal implants are concerned.

After operation or fracture the acid-base balance of the body is disturbed locally and a so-called acid tide occurs. The normal tissue pH of 7.38 to 7.42 is overbalanced to the acid side, even as low as pH 6 or 5.5. If dead tissue lies in contact with the implant, such acidity may persist for many days or weeks. Gradually, however, balance is restored and living cells come into contact with the whole surface of the implant and the environment returns to balance. The acid tide

could be an important factor in the behavior of metal implants as it may be accompanied by removal of the surface oxygen layer which protects the metal and allows corrosion to start.

The extracellular fluid has an oxygen tension which is a little lower than that of arterial blood. Dead soft tissue or bone, however, soon loses its oxygen as no blood reaches it, and poisons such as carbon dioxide, lactic acid and other organic acids accumulate which are ordinarily removed by the blood stream. Little oxygen can penetrate where two metal surfaces lie in contact and therefore very different oxygen tensions may exist over different areas of the surface of an implant.

A study by Scales et al. (49), showed that 30% of the implants they examined had been corroded to some degree. Colangelo and Greene (29) observed that 37% of 53 component devices had corroded, and a major percentage (91%) of the multicomponent devices showed corrosion of varying degrees in one or more locations. They noted that the predominant form of corrosion was crevice attack, which occurred in 42% of all possible sites. They also noted that pitting was not generally observed with surgical implants and was not considered a major problem area. This is a controversial point though. Mueller and Greener (50) noted that the form of corrosion often observed on surgical implants, especially stainless steels, is a pitting form of attack.

The general mechanism of crevice corrosion is thought to be understood, but the corrosion agent or agents in body fluids responsible for crevice corrosion have not been fully investigated. The phenomena of crevice corrosion has been responsible for the failure of many implants and the occurrence of crevice corrosion is the major disadvantage

of the type 316 stainless steel used for implants.

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