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CORROSION FATIGUE PROPERTIES OF SURGICAL IMPLANT MATERIALS

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SURGICAL IMPLANT MATERIALS

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(M.S. thesis)

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CORROSION FATIGUE PROPERTIES OF SURGICAL IMPLANT MATERIALS

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ABSTRACT

Corrosion resistance studies were done both statically and dynamically on nickel, titanium and stainless steel alloys. The corrosion potentials were recorded as a function of time and interpreted in terms of surface film formation. Titanium alloys proved to be better than either elemental Ti or stainless steel 316.
I. INTRODUCTION

While the use of metals in the human body to correct medical disorders is at least 400 years old, it has only been within the past century that the technique has found widespread use. In the early 1900's, surgeons began experimenting with such materials as annealed iron, copper and magnesium, producing a great number of devices for internal fixation of fractures\(^1\)--screws, rods and metal plates being among the most common. In the 1930's, medicine turned to vanadium steel, and finally stainless steels; the latter produced less trauma in the surrounding tissue. The most common materials in use today are still the stainless steels, 304, 316, and 316L. However, titanium has long been regarded as a very promising candidate--and in fact has found much greater acceptance in Great Britain than in the United States. Vitallium, a Co-Cr-Mo alloy, is also widely used.

Today metals are routinely used in dental fillings, heart valves, knee and hip prosthesis, and even in the rebuilding of jaws! Such widespread use dictates a large number of mechanical and chemical requirements in a material, but it is possible to set down some essential properties.
II. MATERIALS REQUIREMENTS

A. Mechanical Requirements

1. Tensile Strength

In orthopedic applications, the material must maintain a tensile strength at least equal to that of bone (10,000-15,000 psi). Furthermore, it should be noted that bone is a dynamic, living system continually in self-repair. Metals, not having the benefit of an intricate maintenance system, must be sufficiently strong to allow for long term fatigue weakening; Rose suggests an initial tensile strength of 100,000 psi.²

2. Modulus of Elasticity

Implants fixed to bones for the purpose of holding fractures in place are required to bend and flex with the bone. Therefore, we should like a modulus of elasticity comparable to that of the bone itself to avoid creating areas of high stress. This would imply a value of 6500-7800 kg/cm², depending on the loads encountered.³

B. Chemical Requirements

Corrosion Resistance

The implant's resistance to corrosion must be extremely high, as even small amounts of corrosion products are apt to produce painful swelling and inflammation in the surrounding tissue. In surgical applications the damage to implants by corrosion reactions is less important than the toxicity of the products formed by these reactions. Superior corrosion resistance is therefore a primary concern in the implant design.
III. CORROSION PRINCIPLES

A. Thermodynamics

Consider the cell shown in Fig. 1. A typical metal reaction would be:

\[ M_1^{(0)} + \left( \frac{n}{m} \right) M_2^{+n} \rightarrow M_1^{+n} + \left( \frac{n}{m} \right) M_2^{(0)} , \]

where \( M_1 \) and \( M_2 \) are both metals. If the free energy difference for the above reaction is negative it will proceed in the direction written, and the anode, \( M_1 \) will corrode. Corrosion is the movement of ions of \( M \) into solution. Electrons flow to the metal \( M_1 \) and participate in the reduction of \( M_2 \) ions. \( M_2 \) is therefore the cathode. It is the free energy change that drives the electrons from \( M_1 \) to \( M_2 \), i.e., produces the potential difference. The free energy change, \( F \), can be calculated from the potential difference between \( M_1 \) and \( M_2 \), and the number of electrons transferred in the reaction, \( n \), as follows:

\[ F = -nF \]

where \( F \) = the Gibbs free energy, and \( F \) is the Faraday constant.

B. Surface Films and the Oxygen Concentration Cell

Corrosion may be defined as the reaction of a metal or alloy with its environment. Therefore, the corrosion rate is a function of both the specific metal and the surrounding medium. A simple example will serve to illustrate some of the basic phenomena. Consider the reaction of iron with water in an oxygenated medium:

\[ 4Fe + 6H_2O + O_2 \rightarrow 4Fe(OH)_3 \]
Fig. 1. Corrosion cell.

M_1^{+n}, M_2^{+m}
The corrosion product is ferric hydroxide, familiar red-brown rust. As this compound is only slightly soluble in water it forms a precipitate on the surface of the metal. Though the solubility constant is low, some precipitate does go into solution.

The metal is left with an incomplete and bulky layer at the metal/water interface, some surface metal exposed to \( O_2 \), and some in an oxygen deficient environment. Further corrosion will now occur on the metal in the oxygen deficient condition, as can be seen from the following typical reactions:

Cathode Reaction: \[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \]

Anode Reaction: \[ Fe^0 \rightarrow Fe^{+2} + 2e^- \]

As the \( O \) concentration is increased the reaction is driven to the right, producing hydroxyl ions. Therefore the electrode which is exposed to the highest oxygen concentration will become the cathode, and the electrode in the oxygen depleted area the corroding anode. The above example is of course schematic, and as both electrodes were indicated as the same metal we can easily imagine this process occurring on the surface of a piece of iron partially covered by rust. The damage continues most severely under the rust. It should be noted that this concentration cell depends on breaks in the film covering the surface of the metal. A complete film, which is impermeable to oxygen will prevent corrosion.
C. **Effect of Chloride Ions**

If the metal is readily oxidized in air, or if the corrosion products produce an insoluble complete film on the surface of the metal, corrosion will be impeded and the metal is said to be **passivated**. Passivation may be regarded as the abs of any significant corrosion despite favorable free energy changes for the corrosion reactions. Chloride ions and salts present in sea water and physiological solutions accelerate the rate of corrosion reactions and cause intense localized corrosion. This is due to the highly reactive nature of the chloride ion, and its probable reaction with protective films. Such a reaction would leave small areas on the surface exposed to oxygen, with adjacent layers protected. Corrosion would then proceed by action of the differential aeration cell described above. Once a crevice was formed there would be an oxygen deficient area at the base of the crevice or pit, setting up local anodes and cathodes. These pits would then continue to deepen and form mechanical stress raisers as well. Fine cracks are initiated at the sites of these stress raisers, leading to a still further reduction in the oxygen concentration at the bottom of the pit, and further corrosion. This complimentary action of corrosion and mechanical stress is known as **corrosion fatigue**, and can cause rapid deterioration and failure of metals normally showing high tensile strength.
D. Corrosion

The human body is a violently corrosive environment for metals. Body fluids are basically saline (0.1-1M NaCl), with dissolved CO and O and organic acids and compounds. Furthermore, normal activities cause high stress on bones and implants, quickly leading to corrosion fatigue conditions. For satisfactory service under such severe conditions the implant should be highly polished, have smooth and rounded edges, be constructed of only one metal or alloy, and be free of inclusions at the time of implantation. Screws used in fixing plates to bones should be made of the same material as the plate, and secured with screwdrivers of the same material as well. A protective coating over the screw and plate fixture is also recommended as the area directly beneath the screw head will certainly be in an oxygen deficient environment.

The actual failure of an implant due to corrosion is a relatively rare event, though some have been reported. More common is the need to remove the device because of inflammation and infection in the surrounding tissue. This can be caused by a very small amount of corrosion product, as noted previously, and so we are concerned with the development and application of methods of measuring rather low corrosion rates.
IV. MEASUREMENT OF LOW CORROSION RATES

There are several methods available for measuring corrosion. Some are more appropriate than others for low rate measurement. I will first outline some of the more standard methods, and then describe a simple potential vs time method I used in conducting my comparison of metals as candidates for orthopedic implants.

A. Weight Loss

This is the simplest and most direct method of measuring corrosion. It provides an accurate gage of the metal deterioration, but no information as to the type of corrosion, i.e., uniform or pit formation. In addition one must conduct long term experiments before evaluating corrosion by this method.

B. Linear Polarization

This is an electrochemical method used extensively by N. D. Greene and others. It involves the preparation of a plot of potential vs corrosion current over a small range of potentials about the corrosion potential, that is, the steady state value of the potential for the surface of the corroding metal, measured with respect to some reference electrode. The potential difference between the interior of a metal (assumed approximately equipotential) and its surface will depend on the amount of adsorbed species on that surface. Polarization is the change in the corrosion potential due to adsorption of ions from solution on the surface of the metal. An experiment is run plotting an impressed current value against the measured corrosion potential, the slope of this line allows calculation of the corrosion rate. It should be noted that this method requires rather expensive equipment, namely a potentiostat. Green has recently extended this technique to measurements on implants in vivo.
C. Polarization Diagrams

The preparation of polarization diagrams is also an electrochemical method of evaluating corrosion. It has been used by T. P. Hoar in the evaluation of surgical implants and can be done rather quickly. (Details on the preparation of such diagrams can be found in "Corrosion Engineering" by Fontana and Green, McGraw Hill.) Hoar and Mears have evaluated a series of alloys as candidates for orthopedic implants with this technique and have made some recommendations for alloy choices on the basis of that work. Polarization curves must be determined in solution, and may vary considerably with changes in pH, oxygen concentration, and corrosion product concentration. Once such a diagram has been prepared one compares the steady state or corrosion potential of the metal in that same solution (also determined experimentally) with the diagram, and can then predict future corrosion behavior. A metal in the "active" state will continue to corrode, one in the "passive" area will corrode slowly, if at all, and a specimen in the transpassive state will show pitting. This is a sensitive test, and it can be done rather quickly (a few hours). One must be careful in determining the value of the corrosion potential, however, as this can change dramatically when loads are applied to the specimen.

It was the purpose of this study to develop a simple test for comparing metals as surgical implants under dynamic conditions, and in physiological solutions. We measured the corrosion potential as a function of time, both statically, and when fatigue began (see next section). This curve is valuable in two respects:
1. The steady state value of the corrosion potential after a length of time is needed to determine the state of the metal on the polarization diagram.

2. The shape of the corrosion potential vs the curve can be used to determine the nature of the surface film, as shown below.

D. Potential vs Time Measurements

When a metal is exposed to the atmosphere an oxide layer is formed almost immediately, and this serves to protect the surface. According to Uhlig the steps in the formation of this oxide layer are as follows:

a. physical adsorption of oxygen, followed in most cases by dissociation of \( O_2 \) and chemisorption of \( O \) atoms,

b. nucleation of metal oxide at discrete areas,

c. formation and growth of a continuous oxide layer.

The physical adsorption of oxygen is rapid, but the binding forces are not strong (~6 kcal/mole). Most metals have a high affinity for oxygen, and the \( O_2 \) then reacts further to form a strong chemical bond (~50 kcal/mole), corresponding to chemisorption. A second layer of \( O_2 \) may be chemisorbed to the first, and oxygen adsorbing beyond the second layer is usually physically adsorbed. One may qualitatively follow the formation and breakdown of surface films by measuring the corrosion potential of the sample. The corrosion potential is always that potential at which the total rate of oxidation equals the total rate of reduction for the several reactions occurring on the surface. One can also associate a unique current, the corrosion current with this point. The significance of this parameter may be seen in the
following simple example: 9

Consider a metal immersed in a corrosive medium (such as tin in a salt solution), the potential of this system being measured with respect to a saturated calomel electrode. Since a metal such as tin suffers localized attack, most of the metal remains covered with a protective oxide layer, and the potential difference measured is essentially that across the film. The film is cathodic with respect to the small anodic corroding areas, and our measured potential is higher than that corresponding to the bare metal in solution. Repair of the film decreases the anodic areas and hence the current flowing between the film cathode and anode, lessening the cathodic polarization, and hence raising the measured potential. Inspection of potential time curves can then be used to predict which metals will show film breakdown, and eventual corrosion, in a particular solution. 7

Hoar and Mears have measured the corrosion potentials of various alloys in physiological solutions, and plotted them against time. 7 Their results showed titanium and titanium alloys to be considerably better than vitallium and far superior to stainless steels and nickel alloys. However, these measurements were done under static conditions, and the corrosion potential is seen to change drastically when a stress is applied to the sample. The poor corrosion fatigue resistance of titanium in salt solutions is well known to bridge designers, and suggests further dynamic testing for their use as orthopedic implants.
Fig. 2. Schematic potential-time curves:
(a) general corrosion;
(b) pitting corrosion;
(c) film remains intact.
V. CORROSION FATIGUE TESTING DEVICE

In order to most nearly duplicate physiological conditions a device was constructed to produce a stress normal to the surface of the sample, at low frequency (1 hertz), and in physiological saline solution. This essentially provided a 3 point bending test, as diagrammed in Fig. 3. Sample size was controlled to produce a stress of 160 psi, and slight flexure (0.010 in.) of the specimen. The testing machine consisted of lucite basins to hold six such specimens simultaneously. Each basin holds one sample, and the corrosive solution can be identical to or different than the other basins. In addition, the stress applied to each of the specimens can be independently controlled through adjustments on the "driver" length as shown in the photo. The force is applied to each of the specimens through the depression of a strap spring, as seen in Fig. 4. Nylon wheels were fitted to the ends of the driver to reduce the rolling friction on the strap spring. The lucite basins were held parallel by metal guides on the aluminum base, and fixed down by a wing nut bar assembly resting on a carefully fitted lid. Holes were drilled in the lid for the plexiglass push rods and salt bridge tubing. The corrosion potentials of the six samples were scanned at intervals ranging from 3 to 20 minutes, and recorded with the Vidar Data Acquisition System. This system provided both a paper readout for computer work, and a printout for visual inspection. Numerous problems were encountered with the paper tape, and it is strongly suggested that future users of this system have the Tallye Punch checked before running an experiment.
Fig. 3. Point bending fatigue.
Fig. 4. Schematic diagram of spring assembly.
Fig. 4 (continued) Front view of fatigue machine.
Fig. 4 (continued) Top view of fatigue machine.
VI. SAMPLE PREPARATION

The first set of samples was cut and milled to size (4 in. x 1/2 in. x 1/8 in.) and then etched at 50% HCl-50% HF solution. This "pre-corrosion" of the specimen was later considered unwise, and samples in the second run were polished to #600 paper and not etched. Both sets of samples were washed and then dried with 200 proof ethanol before being placed in the basins.
VII. EXPERIMENTAL PROCEDURE

After the samples were prepared each was calibrated on the testing machine to a stress of 160 psi. This was necessary to insure a uniformity of stresses on all samples, and seemed roughly to correspond to typical loads placed on an implant in a 150-200 lb patient. Calibration was difficult as we were interested in the force applied to the sample, and not merely the force necessary to deflect the strap spring a fixed distance. This point seems to have been overlooked in previous work of a similar nature by J. Cohen while working on a weight loss experiment to measure corrosion fatigue in implants. As the samples all varied in their modulus of elasticity it was necessary to apply a 10 lb force to each sample in the basin with a standard weight, and then measure that sample's deflection. The deflection, about 0.005 to 0.010 in. was measured with a Starret Dial Indicator, and the driver was then set to produce this same deflection. As expected, the nickel alloys and the steels showed different deflections (by almost 0.005 in. in a measurement 0.010 to 0.015 in.) when the standard load was applied to each.

The six basins were then filled with Ringer's Solution (Cutter Labs, Berkeley, CA), and the lids and push rods put in place. Ringer's Solution is commonly used for in vitro work to simulate body fluids, and its composition is as follows:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.86 g/100 ml</td>
</tr>
<tr>
<td>KCl</td>
<td>0.03 g/100 ml</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>0.08 g/100 ml</td>
</tr>
</tbody>
</table>
Salt bridges were fitted between each of the basins and a saturated calomel electrode, also immersed in Ringer's Solution. Corrosion potentials were then measured, first statically and then with the corrosion testing machine running. Static readings were generally taken for two days before beginning the fatigue experiment, which was run for at least one million cycles. The apparatus was checked periodically, and the basins refilled to prevent any composition change due to evaporation. Little evaporation was actually noticed.

A "scratch test" was performed following the fatigue test in Run #2. This is simply the physical scratching of the metal surface with a sharp object (a nail was used), breaking the protective layer. The potential is measured following the scratch, and quick repair of the injury is indicated by a rapid rise in potential following its initial decrease. This simple test gives one an idea how metals will behave under dynamic "in service" conditions, those that do not show a quick rise in the potential will corrode locally and soon fail.

Two complete runs were made on the following materials:

<table>
<thead>
<tr>
<th>Run #1</th>
<th>Run #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>Cu</td>
</tr>
<tr>
<td>Ti-8Al-1Mo-1V</td>
<td>Ti</td>
</tr>
<tr>
<td>Inconel 825</td>
<td>Ti-8Al-1Mo-1V</td>
</tr>
<tr>
<td>Inconel 600</td>
<td>S.S. 316</td>
</tr>
<tr>
<td>Inconel 400</td>
<td>S.S. 304</td>
</tr>
<tr>
<td>Ti-2.5Sn-5Al</td>
<td>Inconel 825</td>
</tr>
</tbody>
</table>

The titanium, obtained from Reactive Metals Corp., L. A. was commercially pure; no chemical analysis was available. Ti-8Al-1Mo-1V and Ti-2.5Sn-5Al were obtained from the machine shop, again with no
chemical analysis available. The stainless steel alloys were a courtesy of the Eisco Corp., S. F., California, and the Inconel alloys were courtesy of the International Nickel Co., N. Y., again of commercial grade.
VIII. RESULTS

The potential vs time plots for the two runs are shown as Figs. 3-21. Run #1 consisted of a 48 hour static test (fatigue machine not running), followed by 336 hours (about 1,400,000 cycles) of dynamic testing. Run #2 also began with 48 hours of static corrosion, followed by 260 hours of corrosion fatigue, and ended with 40 hours of a "scratch" test, again under static conditions. Some of the very sharp peaks in the plots were caused by stray data points; many of these were caused by incorrect transcription of readings from the paper tape to computer cards. They are therefore of no significance and should be ignored.

Some characteristics are common to most all plots, and are clearly correlated with surface phenomenon on the metals. During the static portion of the test, the potential is seen to rise, and this is indicative of the formation of protective layers. At the onset of fatigue the potential drops sharply, presumably due to the rupture of these protective films. During fatigue the potential is seen to have two characteristic features: a slow oscillation and a rapid oscillation in time. One may postulate that the small oscillations are caused by the rapid formation and repair of micro-fissures in the metal, these fissures being caused by the fatiguing process. We would expect these small cracks to be formed at approximately the cycling frequency (1 hertz) and repaired rather quickly. The larger oscillations, which form the envelope of the graph, might well be related to the formation and subsequent repair of larger cracks, or the creation of many small fissures and their subsequent repair.
Titanium (see Figs. 5 and 6) was tested in both runs, and seemed to fare rather differently in each. In the first run we observed severe oscillations, both rapid and slow. However, the potential always rose to about its initial (pre-static test) value, leading one to hope for good long-term performance. Response to the scratch injury was good, repair occurring in a few hours. The oscillations were much quieter in the second run, with only four peaks being clearly prominent. These were probably caused by rather small cracks, which were all repaired in 2-3 hours.

Inconel 825 (see Figs. 7 and 8) gave similar results for both runs, with the second run again showing smaller oscillations than the first. The sharp peaks during the static portion of Run #2 should be ignored. Repair of the scratch damage was somewhat slower than in titanium. The steady state corrosion potential in Run #2 is about 250 millivolts higher than the pre-test value, but only about 50 mV higher in Run #1. One can see rather easily that the effect of fatigue in Run #2 was to set the steady state potential below the value reached during the static test, encouraging corrosion. Inconel 825 and titanium behaved rather similarly, with titanium doing somewhat more poorly under fatigue conditions.

Ti-8Al-1Mo-1V (see Figs. 9 and 10) was also run twice, and exhibited protective film formation during the static runs. Many more peaks were present in the plots, indicating extensive crack formation and repair. However, the steady state corrosion potentials were at least 100 mV higher than the static value, and were still rising at
the end of the test. Fatigue therefore seemed to produce many small fissures, but not an increase in the overall corrosion resistance. One might expect pitting from such considerations, making this alloy unsuitable for surgical implants.

The Inconel alloys, #400 and #600 (see Figs. 11 and 12) behaved very similarly to each other in the first run. The strap spring broke at about 150 hours on #600, leading to the potential rise seen from 150 to 200 hours. Here the spring was replaced, and the potential quickly fell to its previous fatigue value. The final portion of the graph seems to indicate that from about 270 hours to the termination of the run, there was no stress on the sample. Inconel 400 behaved quite similarly, although the strap spring did not break during the run. The very sharp peak at about 115 hours is a stray data point. Both Inconels maintained steady potentials during fatigue, with the expected oscillations due to fissure creation and repair. The corrosion behavior is estimated as poor, with pitting expected, and similar to that of Inconel 825.

Ti-2.5Sn-5Al (Fig. 13) was the final alloy tested in Run 1, and showed somewhat better electrochemical behavior. Once more the very sharp peaks are bad data points, and the gradual rise beginning at 150 hours was due to a failure in the strap spring. However, it is clear that the potentials during fatigue were higher than during the static run, and at no time did they drop too sharply. Ti-2.5Sn-5Al, therefore, seems a good choice for an implant alloy, and its light weight tends to recommend it over the inconels. It should be noted that the strong potential shown here during fatigue is actually better than that exhibited by pure titanium. This is interesting as most testing, (e.g., Hore and
Mears tends to recommend elemental Ti as superior to alloyed Ti. This fatigue test is, therefore, most significant, but must be interpreted cautiously. The sharp peaks between 140 hours and 200 hours are difficult to explain, as the machine was not fatiguing at this point. The data from about 260 hours on is adjusted so as to remain on the graph's scale. It is actually much more peaked—this is also difficult to explain without further experiments. The important point to note, though, is that the potential did rise throughout the run, recommending titanium alloys for further consideration.

Copper (Fig. 14) was run as a control in Run #2, and showed some interesting features. Immediately noticeable is the absence of both large and small oscillations in the potential. In addition, no sharp drop in the potential was observed following the scratch test. In short, copper did not seem to form any protective layer at all, and hence never passivated. The potential remained almost constant and negative with respect to the calomel electrode. Corrosion proceeded uninhibited, and was easily visible on the surface. This is a most satisfying result, and gives confidence in the gross interpretation of these curves.

The last two alloys tested in Run #2 were the stainless steels, #304 and #316 (Figs. 15 and 16). Their results were similar to each other, but of the two, #316 appeared somewhat superior. The 316 steel developed a protective coating more rapidly, and suffered a less severe drop in the corrosion potential at the onset of fatigue. The oscillations in the 316 seemed to be damping out more quickly than in 304 as well. It was also noted that #316 repaired its surface film much more quickly after the scratch injury, the calmness of the oscillations
being especially pronounced here. In short, the 304 would be expected to develop pitting before the 316.
IX. SUMMARY AND CONCLUSIONS

One of the initial purposes of this study was to compare titanium and stainless steel for use as orthopedic implants. Reviewing the results of Run #2 it seems that titanium is a superior metal in terms of corrosion resistance. The corrosion potential during this run remained steady, and did not drop severely during fatigue. The lack of small peaks in the graph indicates much better pitting resistance from the stainless steels. Titanium did not do as well during the first run, however, and this is attributed to "slapping" of the strap spring on the push rod. (Adjustments made after the first run provided a more uniform distribution of the force on all the samples.)

It is significant that the Ti alloy, Ti-2.5Sn-5Al, seemed better than elemental titanium. This would contradict data taken on static testing of titanium, but not be surprising as Ti is known to be subject to corrosion fatigue in salt solutions. With the reservations previously mentioned, one may speculate that titanium alloys hold promise as candidates for surgical implants, and proceed with further testing and alloy design in that direction. This would be opposed to the current trend in the United States to use stainless steel exclusively.

Electrochemical methods of evaluating corrosion are effective in measuring corrosion rates too low to be detected optically in a short experiment. Photographs were taken of the samples both before and after the second run with the metallurgical microscope. No evidence of corrosion was visible under a magnification of 40x. The value of this simple electrochemical measurement is therefore particularly well demonstrated in this experiment.
Fig. 14
ACKNOWLEDGMENTS

I am very happy to acknowledge the friendly and professional help of my advisor, Professor J. W. Morris, Jr. on this project. A special thanks also goes to Julien Patenaude, without whom the apparatus would never have been constructed, and Stanley Kohn, who helped with the computer program.

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REFERENCES


4. R. M. Rose and J. Wulff, Structure and Properties of Materials


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