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**PROCEEDINGS OF THE  
ION IMPLANTATION FOR  
ARMY NEEDS WORKSHOP**



June 1984

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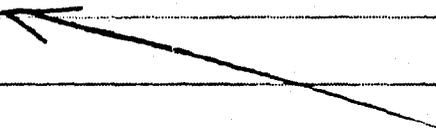
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This paper presents a general overview-  
discussion of materials modification by  
ion beam mixing. This technique consists  
of depositing a thin film on a substrate  
and then using a beam of inert ions to  
mix up this area.



p. 23 (" 410698")

→ This paper concerns the characteristics of ion implanters for fabrication of electronic devices. High voltage implanters have been designed for implanting ions deeper into semiconductor materials. They are now standardized at 400 KEV. ←

p 35

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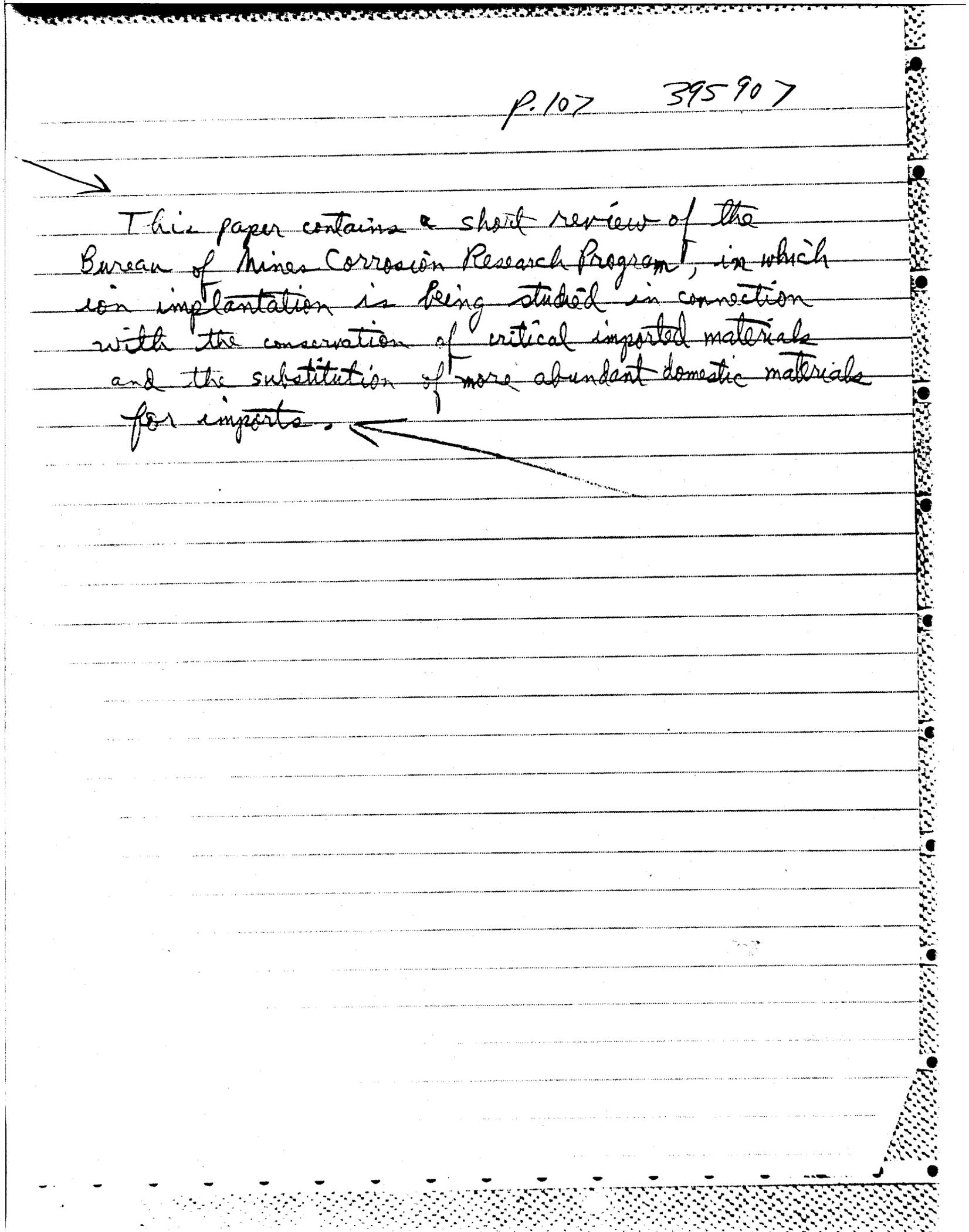
→ This paper presents some highlights of a conference on ion implantation held at the University of Manchester. Some emphasis is put upon the use of ion implantation for materials ~~and~~ other than semiconductors. →

p.53 (10 040900)

→ This paper, on the research and development requirements for ion implantation, stresses the potential applications for corrosion reduction and conservation of critical materials. ←

p. 63 (31 251950)

✓ The Naval Research Laboratory's involvement in ion implantation is described. Some of the applications emphasized have been linear, bearings and drills. ←



This paper contains a short review of the Bureau of Mines Corrosion Research Program, in which ion implantation is being studied in connection with the conservation of critical imported materials and the substitution of more abundant domestic materials for imports.

→ Studies of ion

1 implantation as a means of modifying the corrosion behavior of alloys should be backed up by fundamental studies which characterize the surface alloys formed. The polarization experiments performed in this work were designed to provide a description of the nature and kinetics of anodic and cathodic reactions which constitute corrosion.

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ABSTRACT

Papers and discussion included in a Workshop on ion implantation held at the Army Materials and Mechanics Research Center, Watertown, MA, are presented. The various sessions contain introductory remarks, fundamentals, current practice, research and development, corrosion studies, and summary review for planning base.

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## INTRODUCTION

This publication contains papers, discussion and associated information from a workshop conducted at the U.S. Army Materials and Mechanics Research Center (AMMRC), Watertown, Massachusetts on 30-31 July 1981. All the papers and attendant discussion were tape recorded. Authors were given the opportunity to revise their presentations for more facile reading in the printed version. The final program of the Workshop is shown on the following page.

The objectives of the Workshop were:

1. To acquaint Army materiel designers and development personnel with potential applications of ion implantation for improvement of surface-related properties;
2. To stimulate interaction and coordination of activities relating to these techniques; and
3. To serve as a mechanism for the generation and cross-fertilization of ideas which might be applied to end items within the various commands and programs.

To a large extent, these objectives have been accomplished. Invitations to attend the Workshop were extended only to Army facilities, except for the speakers. Fourteen Army activities, the U.S. Navy, NASA, and the U.S. Bureau of Mines were represented, as well as the speakers from academia. The discussions were lively and resulted in listing of issues, actions and applications which can be food-for-thought for Army managers considering the need for materials surface modification.

There is an on-going task at AMMRC to investigate surface improvement by ion implantation for Army needs, with objectives similar to those of the Workshop. Consideration is being given to offering another workshop in the future including participation from all the armed services, academia, and industry.





DEPARTMENT OF THE ARMY  
ARMY MATERIALS AND MECHANICS RESEARCH CENTER  
WATERTOWN, MASSACHUSETTS 02172

DRXMR-MDE

FINAL PROGRAM

Chairman - CHARLES LEVY, AMMRC

ION IMPLANTATION FOR ARMY NEEDS WORKSHOP

Thursday, 30 July 1981

- 0800 Registration
- 0830 Introduction - Dr. Robert D. French, Director, Metals and Ceramics Laboratory, AMMRC
- 0835 Welcoming Remarks - Dr. Edward S. Wright, Director, AMMRC
- 0845 "Materials Modification by Ion Beam Mixing," Prof. James Mayer, Cornell University
- 0945 Refreshment Break
- 1015 "Characteristics of Ion Implanters for Fabrication of Electronic Devices," Albert Mark, Electronics Research and Development Command, Ft. Monmouth
- 1100 "Review of the University of Manchester Ion Implantation Conference," Dr. Paul Sagalyn, AMMRC
- 1200 Lunch
- 1330 "Research and Development Requirements for Ion Implantation," Philip Parrish, Army Research Office
- 1415 "Navy Programs on Ion Implantation for Materials Modification," Dr. James Hirvonen, Naval Research Laboratory
- 1500 Refreshment Break
- 1530 Group Discussion

Friday, 31 July 1981

- 0830 Summary Review for Planning Base
- 0900 "Use of Ion Implantation to Modify the Corrosion Behavior of Metals," Bruce Sartwell, Bureau of Mines
- 1000 Refreshment Break
- 1015 "The Modification of Metallic Corrosion by Ion Implantation: Engineering Applications and Fundamental Studies," Prof. Clive Clayton, State University of New York, Stony Brook
- 1100 Concluding Discussion
- 1200 Lunch
- 1315 Tour of AMMRC Facilities
- 1500 Adjournment

All papers and discussions will be unclassified.

## CONTENTS

	Page
INTRODUCTION . . . . .	iii
FIRST SESSION: INTRODUCTORY REMARKS	
Dr. Edward S. Wright, Director, AMMRC and Dr. Robert D. French, Director, Metals & Ceramics Laboratory, Army Materials and Mechanics Research Center, Watertown, MA. . . . .	3
SECOND SESSION: FUNDAMENTALS	
Materials Modification by Ion Beam Mixing, Prof. James W. Mayer, Department of Materials Science and Engineering, Cornell University, Ithaca, NY. . . . .	7
THIRD SESSION: CURRENT PRACTICE	
Characteristics of Ion Implanters for Fabrication of Electronic Devices, Albert Mark, U.S. Army Electronics Research and Development Command, Ft. Monmouth, NJ. . . . .	23
Review of the University of Manchester Ion Implantation Conference, Dr. Paul L. Sagalyn, Army Materials and Mechanics Research Center, Watertown, MA . . . . .	35
FOURTH SESSION: RESEARCH AND DEVELOPMENT	
Research and Development Requirements for Ion Implantation, Dr. Phillip A. Parrish, U.S. Army Research Office, Research Triangle Park, NC. . . . .	53
Navy Programs on Ion Implantation for Materials Modification, Dr. James K. Hirvonen, U.S. Naval Research Laboratory, Washington, DC. . . . .	63
FIFTH SESSION: GROUP DISCUSSION . . . . .	95
SIXTH SESSION: CORROSION STUDIES	
Use of Ion Implantation to Modify the Corrosion Behavior of Metals, Bruce D. Sartwell, U.S. Bureau of Mines, Avondale, MD . . . . .	107
The Modification of Metallic Corrosion by Ion Implantation: Engineering Applications and Fundamental Studies, Prof. Clive R. Clayton, State University of New York, Stony Brook, NY . . . . .	127

	Page
SEVENTH SESSION: SUMMARY REVIEW FOR PLANNING BASE . . . . .	155
ACKNOWLEDGMENTS . . . . .	167
RESULTS OF POST-WORKSHOP QUESTIONNAIRE . . . . .	169
RECOMMENDED GENERAL REFERENCES . . . . .	173
RESUMES OF SPEAKER'S BACKGROUNDS . . . . .	175
LIST OF ATTENDEES . . . . .	185

FIRST SESSION:  
INTRODUCTORY REMARKS

## ION IMPLANTATION FOR ARMY NEEDS WORKSHOP

C. Levy: Good morning and welcome to our Ion Implantation Workshop. The proceedings of this workshop are being recorded, so anything you say into the microphone is going on the record, this will facilitate our publishing a printed proceedings. Our first speaker this is Edward S. Wright, AMMRC, Director, who will give us some welcoming remarks.

Dr. Wright: I would like to officially welcome you to AMMRC. Please consider your time here as an investment, that you are one of us, and let us know if there is anything that we can do for you. We will be very glad to help make your visit both enjoyable and productive. As you know from your invitation, this meeting is intended to be a gathering place for professional opinions on the general subject of ion implantation - to find out what we know about ion implantation, what we don't know, and what we should do about it. We are going to use this information in our future planning to decide just exactly what we want to do in this general area. So far, we have been only slightly active in the ion implantation area and mostly in the area of assessment of the mechanisms and other more fundamental aspects of the process. We do not, as yet, have a big program. However, we feel ion implantation is a very important subject and potentially of great value to the Army in the future. As such, we want to develop a feel for where we should be going in this particular area. The idea of using a meeting such as this as a base for planning is appropriate, when you haven't fully developed your train of thought on the subject or the exact direction to pursue. Meetings of this type seem to work out very well. We have used them not only in the R&D side of the house but also to address the manufacturing technology. As for this meeting, it should be used as a time for very serious listening, talking, and thinking and for really objective discussion of where we stand and what we can do in accepting the invitation to come and meet with us and to offer your thoughts on and knowledge of the subject. Hopefully you will take away something in return, in the least a much broader view of the total subject. Thank you again for coming and have a good meeting.

C. Levy: Thank you. Dr. Robert D. French, Director of our Metals and Ceramics Laboratory, would like to say a few words of welcome also.

Dr. French: Thank you. I want to join Dr. Wright in welcoming all of you. We are not a large group today, and this was our intent since otherwise discussion can be suppressed. Now it is our Chairman's duty today to try and maintain a schedule, and certainly I don't want to disrupt that. Nor do I want to run over any of the speakers' plans. However, we are very much interested in information today, so I encourage everyone to speak out. I encourage you to greet one another if you do not know each other already. Share your opinions. Your opinions are very important to us. If you do not happen to share the opinion of another speaker, we would like your opinion anyway. We simply do not have the resources within the Army to deal with all the Ion Implantation R&D problems or issues even those we might consider important solely to the Army. Nor should we expect to support everything of potential value to the Army since there are other agencies and other academic institutions supporting work in this area already. So we are going to have to be very selective in planning our R&D Program. We intend, therefore, to accumulate all of the information on past and present activities and interests that we can and it is in that context we are actively seeking your discussion today.

It is not an intention of the workshop to make any funding decisions. This is intended to be a discussion of technical information and interest. We will work out management details later.

I really want to thank the people who helped pull all of this together: our administrative crew that you have already met this morning, certainly the Navy and the Bureau of Mines, very important to us, and our own principle people at AMMRC: notably Charles Levy and Paul Sagalyn.

C. Levy: Thank you - As I mentioned before, we are planning to publish a report of the proceedings from this workshop. Our first technical speaker today is Professor James W. Mayer of Cornell University. Professor Mayer received a Bachelor of Science Degree in Engineering from Purdue University. He has a PhD in Physics from Purdue University in 1960. He has been a visiting scientist in many places and has numerous publications to his credit. Currently he is the Bard Professor of Materials Science at Cornell University in Ithaca, NY.

SECOND SESSION:  
FUNDAMENTALS

## MATERIALS MODIFICATION BY ION BEAM MIXING

Prof. James Mayer  
Cornell University  
Ithaca, NY

It is a pleasure to be here. It has been twenty-eight years since my last visit. Today we're looking at ion implantation. (Figure 1) I would like to discuss two aspects of implantation in a general form. One is highdose implantation and the other is ion mixing. Just to give you a feeling, in one case (highdose implantation) you directly implant species into the material to modify the outer composition. You will hear from researchers like Clayton and Hirvonen on some of their efforts to do this work and their success with corrosion and materials modification. The technique amounts to modifying surface by injecting foreign ions. It takes a large dose, however, because we want to change characteristics by 10% in general. The other aspect of the topic I would like to discuss is ion beam mixing. This consists of depositing a thin metal film on a substrate and then using a beam of inert ions to mix this area up, a two-step process. The advantage of it is that you don't have to have high energy to implant the ions themselves.

In other words, as you will see, you can implant higher concentration of material into the surface and achieve this with lower ion doses. Using both approaches, great successes have been achieved in using implantation to modify the chemical, electrical, and mechanical properties of materials.

I want to give you a feeling, if I may, of some of the crucial ideas lying behind implantation. Regardless of the concentration of ions in a beam impinging on a surface, the simplest view of the impact is that of the single event, one ion coming in creating a collision, cascade and damage. This damage will anneal itself in metals before the next ion comes in so there is generally no overlap of the cascades. Just to remind everyone, one monolayer of coverage is about  $10^{15}$  ions per centimeter square.

In modifying semi-conductors, one is generally dealing with less than a monolayer. The reason for that, of course, is that semi-conductors are very sensitive to small changes in purities. For metals, on the other hand, you have to get one to several atomic percent to be effective. This takes higher beam fluxes. When high beam fluxes are used the resultant distribution of ions from the surface into the bulk metal changes a bit. The normal distribution of ions will follow a rough Gaussian distribution with ions penetrating to depths of 1000 Å with 200 kilovolt potential. This penetration depth is not considered sufficient for many materials applications. Erosion in gun barrels, for example may require near surface modification more than 1000 angstroms in depth; but for many applications, corrosion, fatigue, and the like, as you will hear from later speakers, 1000 Å depths are useful.

The point to this is the following: useful surface modification technique today requires a rather high concentration of high energy impinging ions. I have a feeling that full surface processing will involve more than implantation, and might be followed with some rapid deep quench technique using a pulsed ion beam or a laser as has been done with semi-conductors. This means implanting a species and then driving it further.

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A key aspect of ion implantation in semi-conductors is the level of control. I think the same will ultimately be true in metallurgical applications: control over the ion species put in, and control on driving ions in further to get deep below the surface. This may mean higher energy machines and each of these new high-energy, high-current implant machines typically costs about \$700,000.

Having discussed ion beam direct action on a surface, it is easier to see that when you put an ion beam through a metal/semi-conductor then film, as long as it penetrates the interface, intermixing will take place (Figure 2). At high enough temperatures, thermodynamic driving forces take over and new phases form between the two. This is a most efficient process since for every ion put in below the original surface are displaced.

Ion mixing, therefore, is a way of increasing the concentrations of added materials for the same beam energy. With ions penetrating deeply, an intermixing of the top metal layer and the substrate takes place (Figure 3). As beam energy and ion flux go up and as mixing of the surface atom layers with the near surface bulk takes place, effectively diluting the metal. Eventually, at high enough beam energy the process becomes sputter limited. That is, material is driven off the surface as fast as it arrives. The remainder of my talk will focus on mixing where, depending on the dose, one can get various concentrations of added materials in roughly the 20 to 40 percent region.

When using direct ion implanting for materials surface modifications, it is rather straightforward to raise the added material concentration to 10-20 atomic percent. So one approach is to make base alloys that are almost the right composition and then improve the surface with implantation. Direct ion beam implantation can be used for very fine control of material composition and microphase formation since the collision and atomic structure re-stabilization is rather like a very fast quench (Figure 4). So what you can do with lasers, you can do with an ion beam.

Whether hitting the surface with ion beams or lasers, considerable energy is being added to the system in a short time. With the beam off, the affected material can relax to either an amorphous or metastable state. This means that new, non-equilibrium phases can be made and I will show you a few examples. There are many such examples around as you will see from the other speakers. I will talk about a sort of micro-alloying by ion beam mixing (Figure 5). In this case we consider the collision cascade volume around the ion track in which we have ion induced mixing and enhanced diffusion along with a fast quench.

Development work in ion beam mixing is being carried on in two regimes. First is collision cascade mixing which is essentially a high energy process (Figure 6). The incident ion collides with many atoms. The number of atoms struck depends on input energy per unit path. So a heavy ion like xenon has a greater effect than a light ion like argon. The second regime would be recognized by those familiar with radiation damage. It is analogous to radiation enhanced diffusion. An incoming ion creates both vacancies and interstitials driven from their original crystal structure sites. Diffusion of these defects helps the added species spread. This regime requires a lower ion dose for a given amount of reaction.

Here is an example of chrome on silicon by B. Y. Tsaur, at Lincoln Laboratory, showing the amount of mixing as the reciprocal of temperature (Figure 7). Low temperature collision cascade mixing is more or less independent of temperature.

We can measure the extent of mixing by looking at the dilution of a surface film with atoms from the base metal. Figure 8 shows the results of bombarding a surface film of platinum on a substrate of silicon then measuring surface dilution. You can see how the extent of mixing increases with higher dosages of the  $Xe^+$  ion beam.

I must state that our ability to predict exactly how much mixing there is still primitive. This field is just about two years old and still in an exploratory stage. There is a lot of work yet to be done in mixing. Figure 9 shows that the crystal structure lattice parameters of mixtures of elements with similar structural symmetry vary in a nicely linear fashion. This finding will most certainly help our ability to predict the product of mixing. Again, this shows you can get mixing from a metastable solution. We have measured resistivity of these metal films to pick up the transformation (Figure 10). Implanting layers of two metals, forms a single phase solid solution. Heating the mixture drives it back to equilibrium. This is a good example of control over both composition and structure.

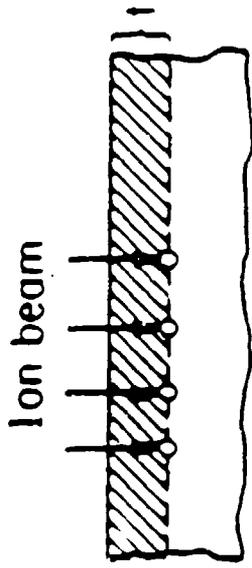
Our laboratory has carried out other studies with gold-cobalt, looking at the transformation from the face-centered cubic (FCC) to hexagonal. When mixed at liquid nitrogen temperatures, an amorphous layer forms. Heating this up produces first a single phase solution. Heating further, creates two phases. From resistivity measurements (Figure 11) one first sees an amorphous-FCC transformation around  $200^\circ C$ . At higher temperatures one finds a single phase which has been confirmed by microscopy. At higher temperatures a two-phase structure appears. Here in one system we have shown layers, metastable mixed phases, a super-saturated solid solution, and an amorphous structure (Figure 12). One can also form super lattices.

Gold-vanadium is a system we are still studying at Cornell. This is an interesting system because it puts together a FCC material like gold and a body-centered cubic (BCC) material like vanadium (Figure 13). When rich in gold atoms, the result is a FCC solid solution. When vanadium rich, the result is a body centered cubic solid solution. In between, we get an amorphous layer. This was not predictable from our present knowledge base. In some cases we form, instead of a solid solution, a well defined phase.

There is obviously a lot to be done and, naturally, there is a role for the Army and the other services to play. I have discussed the subject in general ways and covered our laboratory developments right up to the present. There is, of course, much other development work going on, some of which will be covered here today. This is a most promising technology and I am looking forward to its expanding developments and use. Thank you.

# Ion beam modification of materials

## A.) High dose implantation

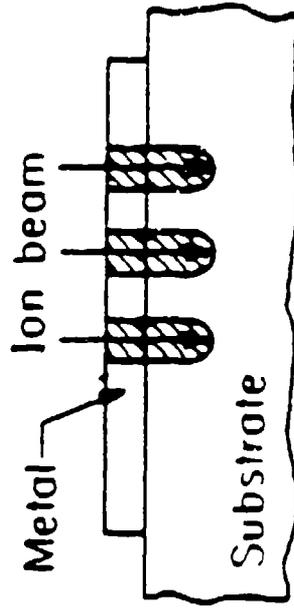


$$I = 5 \times 10^{-5} \text{ cm} \rightarrow 3 \times 10^{18} \text{ host at./cm}^2$$

- To introduce 10% change in composition  $\rightarrow 3 \times 10^{17}$  ions/cm<sup>2</sup> (equivalent to 300 monolayers of ions)

High current implantation systems required.  
(0.1 amp at 400 kV to implant  $10 \times 10$  cm in 1 min)

## B.) Ion beam mixing



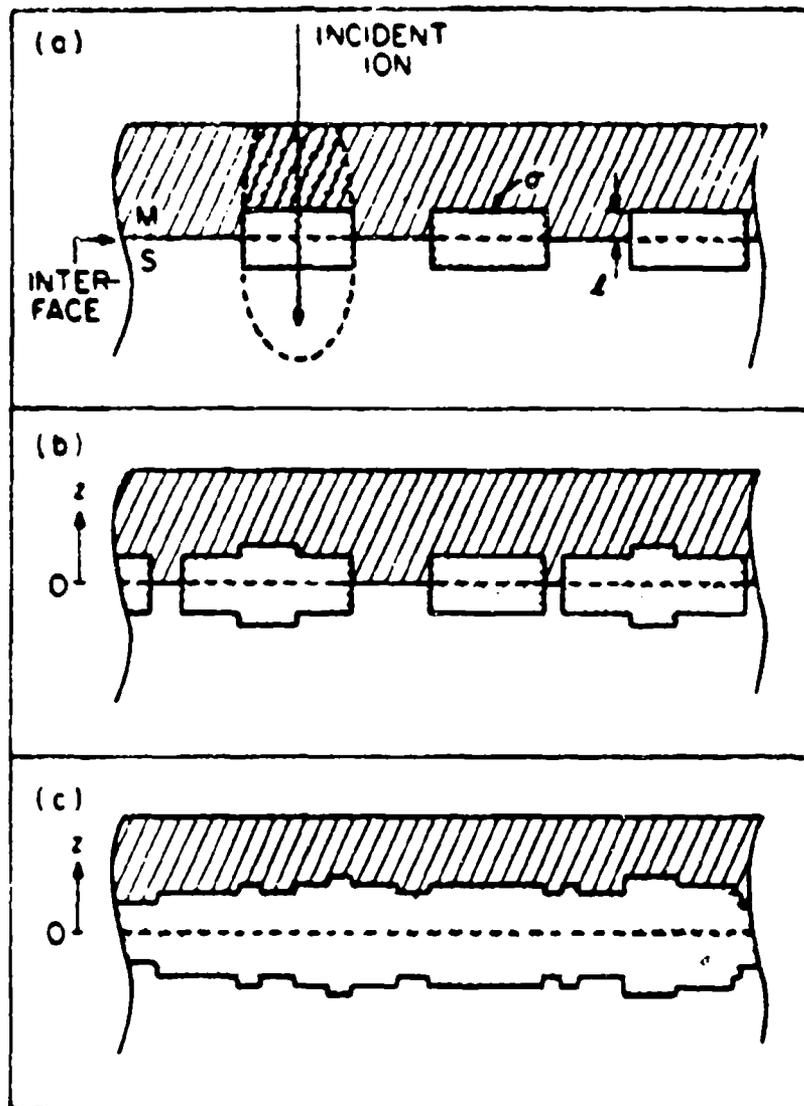
- Deposit metal film
- Implant "inert ions"
- Enhanced diffusion around ion track

Figure 1

## Ion-Induced Interfacial Reactions

If the ion range ( $W$ ) penetrates through an interface, atomic mixing can result in an interfacial reaction.

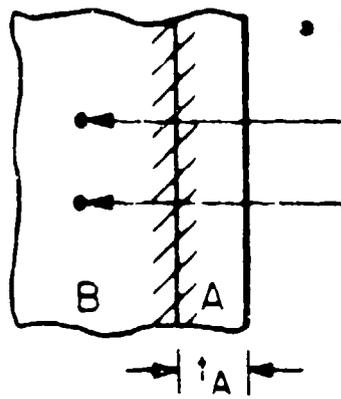
We consider such reaction as being composed of many localized elemental processes, each generated by one ion :



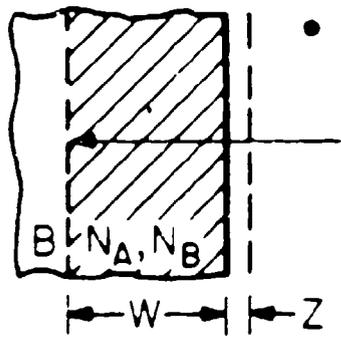
Then, kinetics of the reaction can be exactly predicted by Poisson statistics.

Figure 2

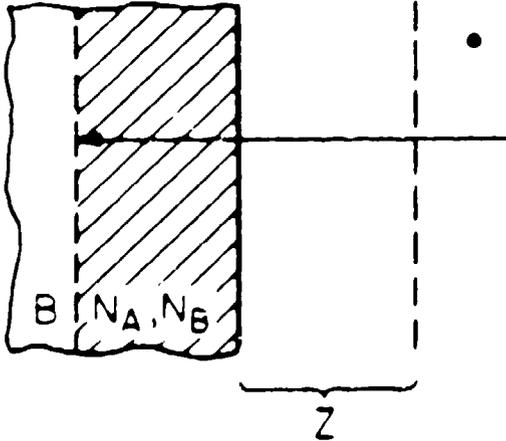
# Ion Beam Mixing



- Low Dose ( $\Phi \lesssim 10^{15} \text{ Xe/cm}^2$ )
  - Interfacial Reaction
    - inter diffusion, phase formation
  - Collision Cascade
    - ion species, energy
    - radiation-enhanced diffusion



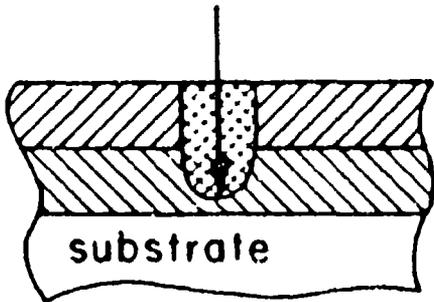
- Intermediate Dose ( $\Phi \approx 10^{16} \text{ Xe/cm}^2$ )
  - Uniformly Mixed Layer
  - $\frac{N_A}{N_B} \approx \frac{(t_A - Z)}{W - t_A} = N_s$
  - $W \approx R_p + 2\Delta R_p$
  - $Z \approx \frac{1}{N} S \cdot \Phi$



- High Dose ( $\Phi \approx 10^{17} \text{ Xe/cm}^2$ )
  - Sputter Erosion
  - $\frac{N_A}{N_B} = N_s \cdot \exp\left(\frac{-Z}{W}\right)$
  - (no preferential sputtering)

Figure 3

# MICRO-ALLOYING BY ION BEAM MIXING



- collision cascade volume around ion track
- ion induced mixing & enhanced diffusion
- fast quench rate

Formation of: 1) single phase (silicides)  
 metastable 2) amorphous (metal/Si)  
 3) solid solution (metal/metal)

Figure 4

## Metastable phase formation

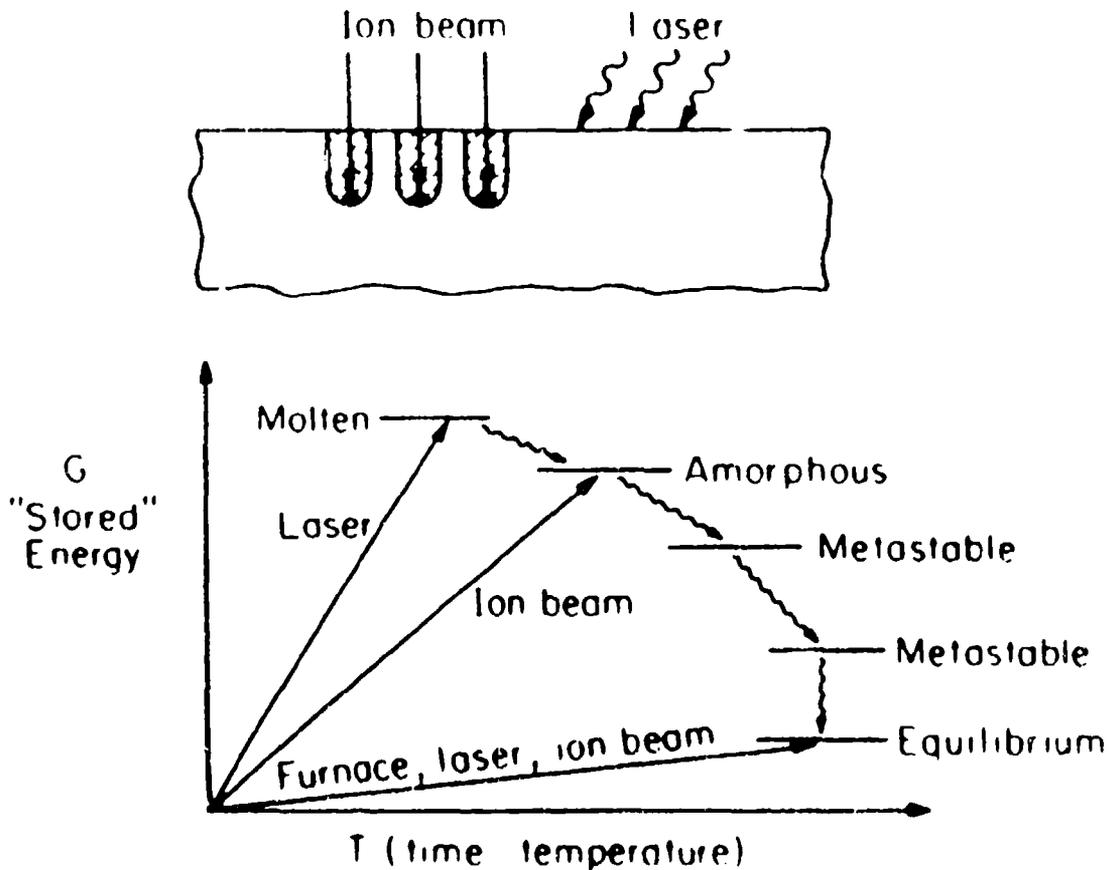


Figure 5

### Ion Beam Mixing

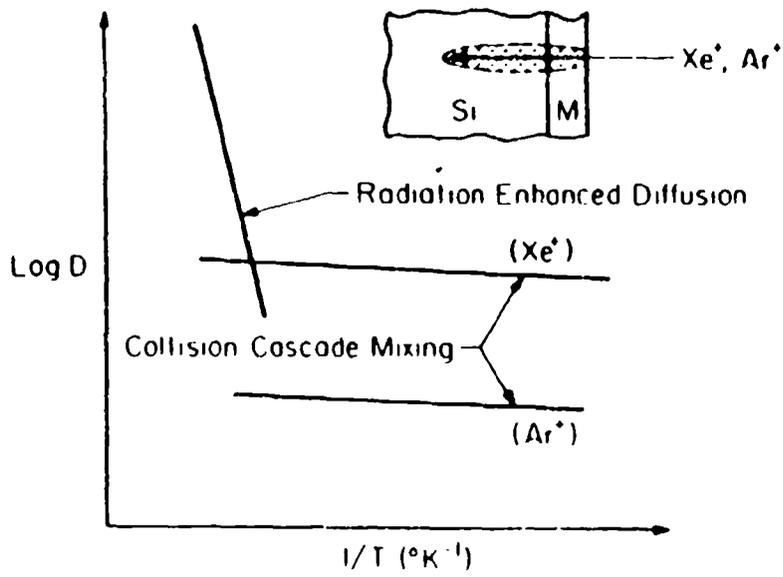


Figure 6

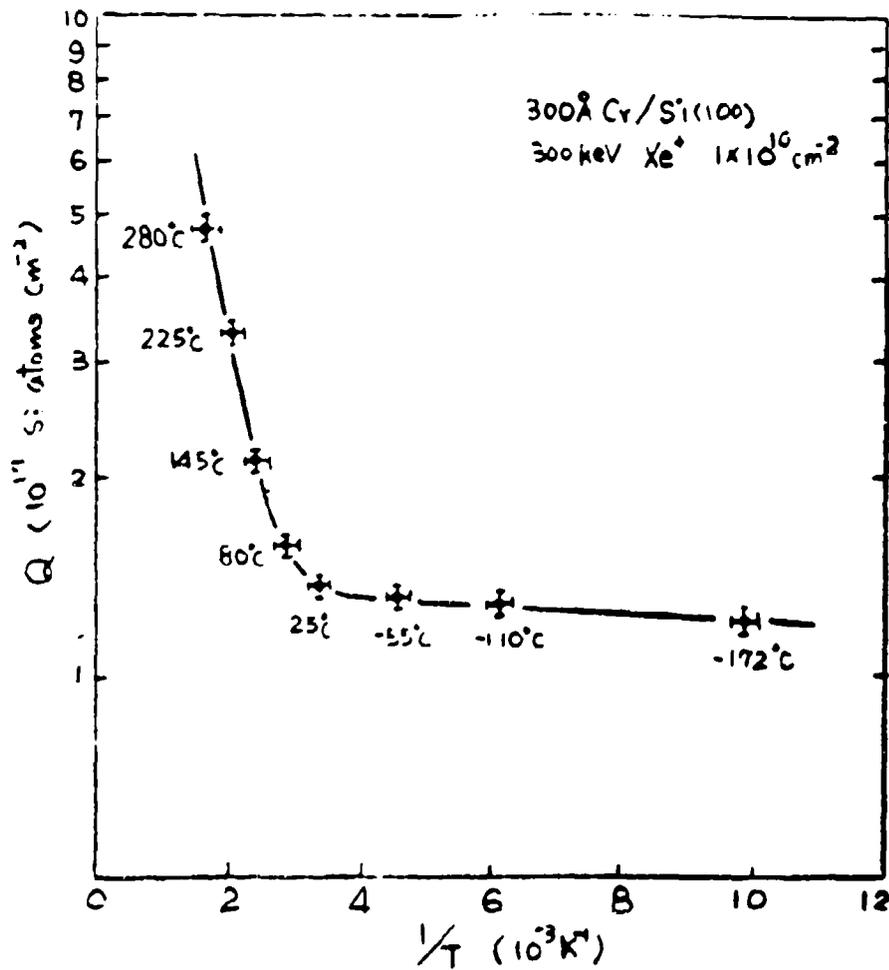


Figure 7

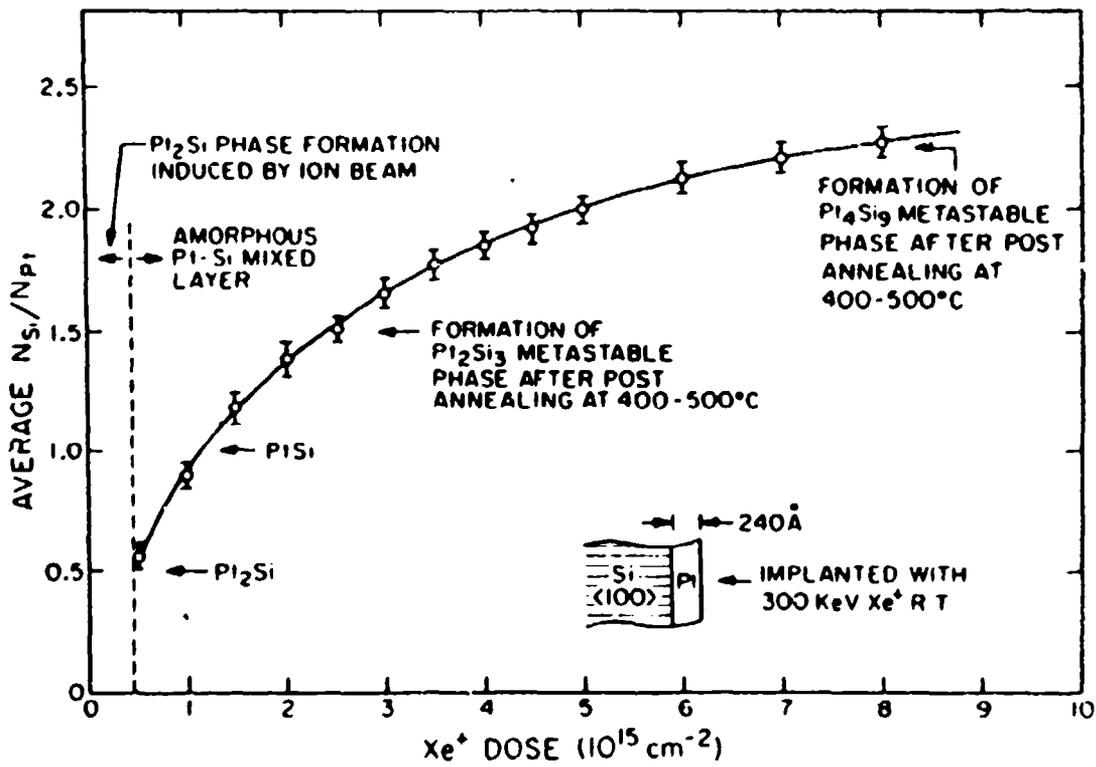


Figure 8

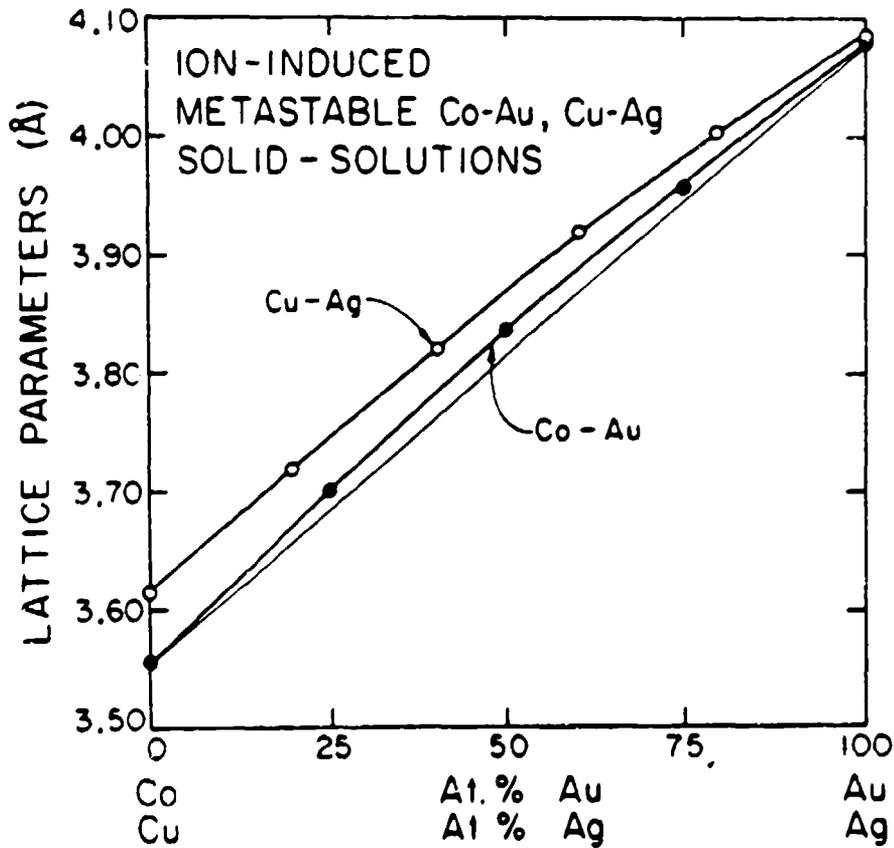


Figure 9

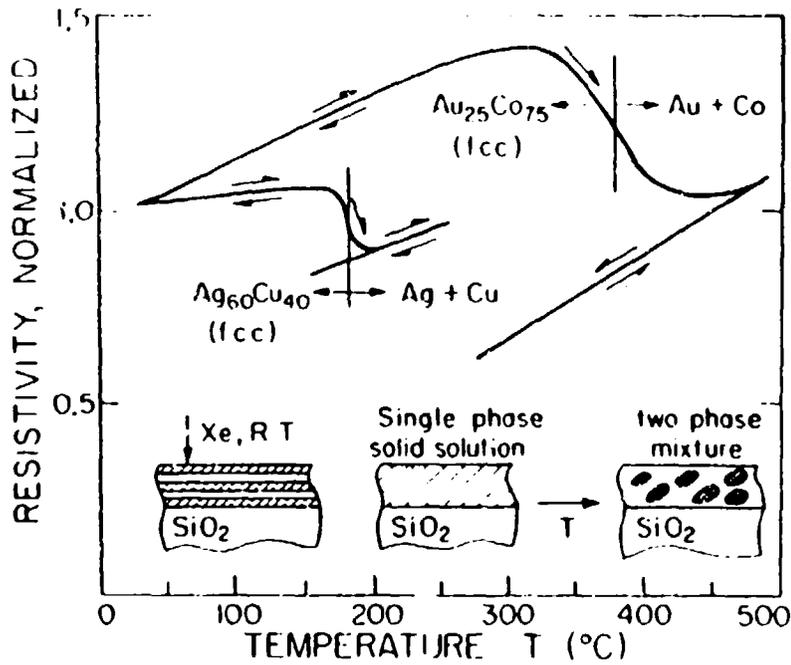


Figure 10

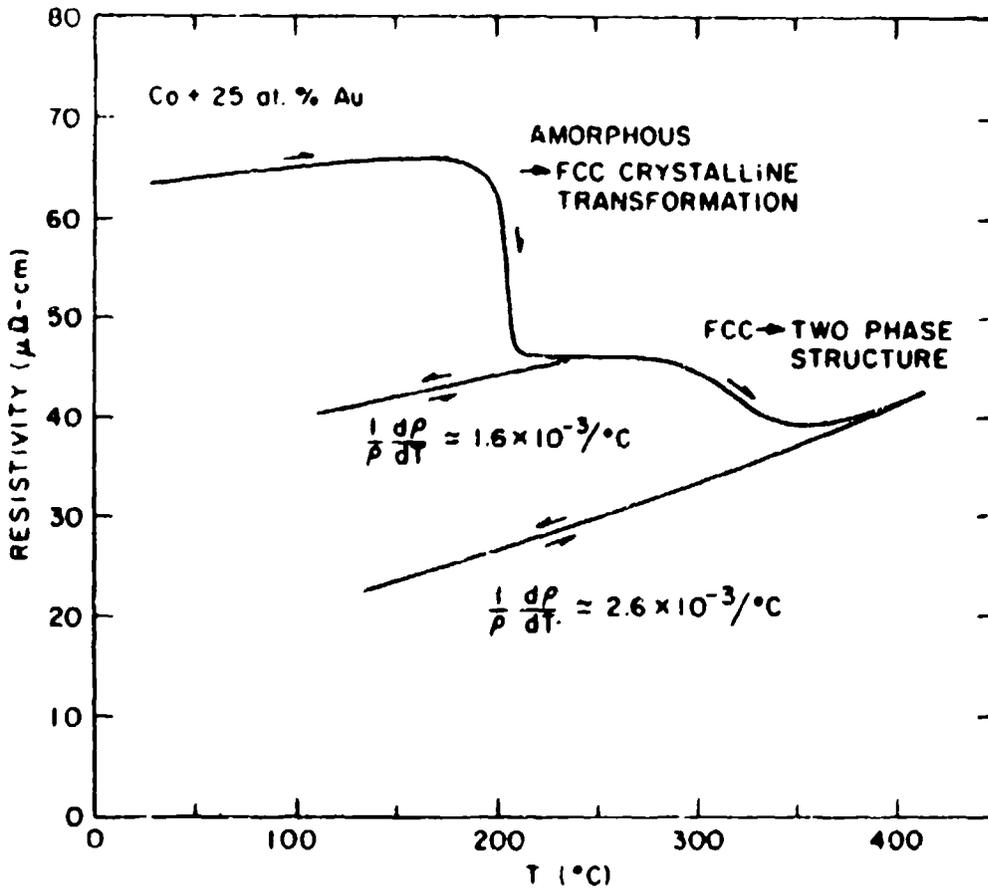


Figure 11

100-300keV Xe<sup>+</sup>  
~ 2 × 10<sup>15</sup> cm<sup>-2</sup> R T (LN<sub>2</sub>)

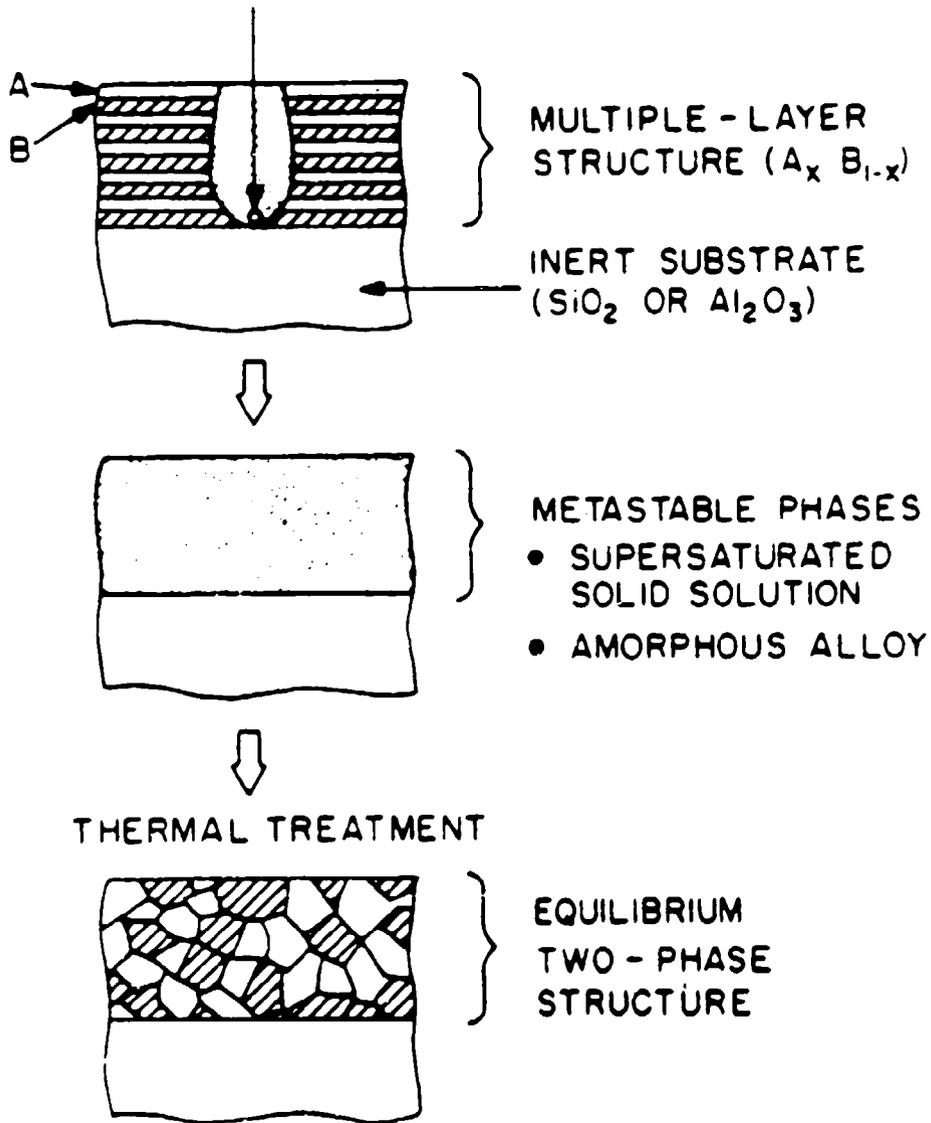


Figure 12

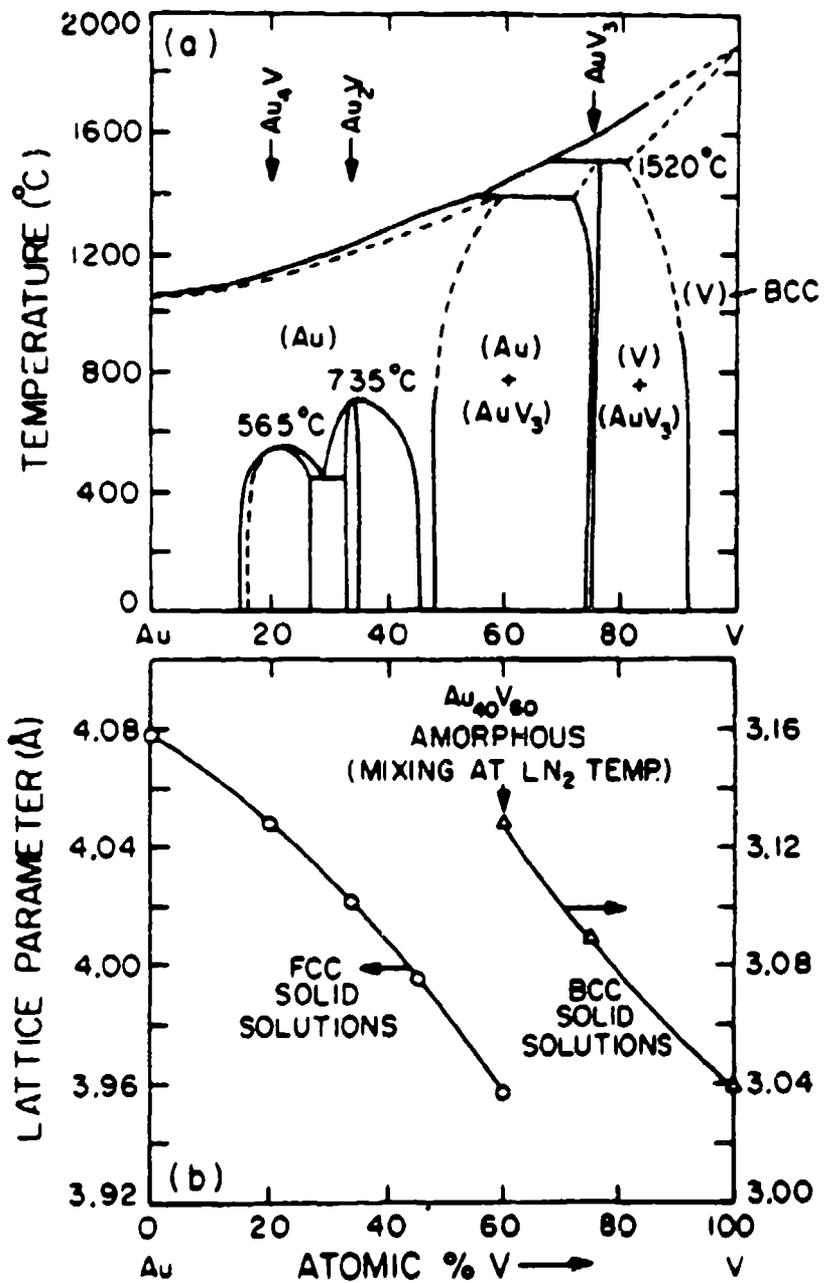


Figure 13

## QUESTIONS AND ANSWERS

R. Harrison, AMMRC: What problems might develop if ion mixing is done on a rough or oxidized surface? Does the surface have to be well prepared before ion implantation or mixing is used or will there be shadowing or interferous problems?

J. Mayer: I'm not sure this is known. My guess is that oxide layers would take part in the mixing and that rough surfaces would change the result.

S. Cytron, ARRADCOM: In your ion mixing mode, you introduced a third species--the inert beam gas for the mixing mode. In many cases it might be extraneous to the intent. Do you go through an additional treatment to completely eliminate it or can you completely eliminate it?

J. Mayer: In principle, one should not use these extraneous ions for mixing. You have quickly identified a problem. We should use one of the components as the ion beam. At this point in research, however, Xe ion beams are convenient to use.

A. Niiler, Ballistic Research Lab.: You showed the results of some backscattering analyses. How much will your apparent concentration profile be affected by the beams you are using to characterize the results?

J. Mayer: That is an area of concern. Does backscattering analysis destroy the spectra you are looking at? Relatively speaking, there are so few particles in the characterizing beam and so little energy deposited that it does not change the profile significantly. Characterization beams, however, can relieve vacancies and interstitials. This happens with arsenic and silicon. But in terms of concentration profile modification, backscattering analysis doesn't do it. On the other hand if you are sputter profiling - (removing layers by sputtering) - this ion beam penetrates deeper and the very act of sputtering removal as you get near the interface will distort the composition. So if you are characterizing with Auger or SIMS and sputtering to analyze the composition in depth, you have to be pretty careful.

N. Bulloch, TSARCOM: I am a material engineer involved in maintenance problems. We have a problem with dirty parts that need to be cleaned. Because of OSHA and EPA regulations, we have had to ban common phenolic strippers. Do you think that ion implantation could be used to modify the surface or that adhesion would be reduced? Can this technique make it easier to clean parts with common solvents, that are not carcinogenic or of phenolic type?

J. Mayer: I think that is an interesting question. We have been looking hard to see how to make layers stick and you are suggesting that we study the reverse effect.

N. Bulloch: I don't know how feasible it would be, but it would be a very exciting advantage for the Army because of the fact that we have to comply with EPA and OSHA regulations. Sometimes we have to use poor quality strippers. In addition, some aircraft parts have an oxidized layer that forms an adherent film that must be removed.

J. Mayer: I don't know that an answer to your question exists. Those in the semi-conductor business do worry about removing layers in a controlled way so it is possible that related technology exists. This sounds like an area for further investigation.

THIRD SESSION:  
CURRENT PRACTICE

# CHARACTERISTICS OF ION IMPLANTERS FOR FABRICATION OF ELECTRONIC DEVICES

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AD P 03949

During the last decade, Electronics Research and Development Command at Fort Monmouth, NJ, was among the first of the services to examine the feasibility of establishing an ion implant facility for fabrication of integrated circuits. This came about as a need for a faster more precise and controllable technology for doping semiconductor materials at room temperatures to compliment high temperature processes as diffusion and epitaxy. Reports for Bell Labs, Hughes, RCA and other semiconductor houses indicated that ion implant showed promising potential for high yield, fast throughput and more accurate control of depth and dose requirements at reduced costs and minimum time cycles for processing electronic circuits of complex design.

Ideally, an ion implant machine would be one that could drive any specie in the atomic spectrum uniformly to shallow depths a few angstroms below the semiconductor wafer surface or to multi-micron depths. Unfortunately, no such machine is practical or available without accompanying technical problems and high costs.

It took approximately a decade for the perfection of ion implant equipment to reach the reliability presently inherent in commercial machines. With the joint cooperation of manufacturers of particle accelerators and the electronics industry during the late 60's and throughtout the 70's, three types of implanters found their way into the semiconductor market.

Initially, dedicated implanters found favor with semiconductor houses for implantation of a single specie only, as for example, boron. These were low voltage machines typically used at 60 keV for shallow implants.

As requirements changed, new high dose machines were developed. These have been standardized with top voltages of 200 keV but able to generate beam currents as high as 350  $\mu$ a at voltages as low as 25-35 keV. Maximum beam currents can be in the milli-ampere range depending on the particular manufacturer. Doses of  $10^{16}$  and above can be implanted in minutes which formerly took hours. These implanters find application in high production semiconductor fabrication environments.

Lastly, high voltage implanters are designed for implanting ions deeper into the bulk of the semiconductor materials. Now standardized at 400 keV, they supercede the earlier 300 keV models. They have become the standard work horses for research facilities in government laboratories and universities. But beam currents are sacrificed. Typical scanned beam currents are below 30  $\mu$ a for most high voltage implanters. Therefore, implant times may increase to hours if doses over  $10^{15}$  or  $10^{16}$  are required. The more recent application for 400 keV machines is implantation of gallium arsenide for microwave fabrication.

Table I shows average beam currents for boron, phosphorous, arsenic, and antimony. For the first three species listed, 150  $\mu$ a may be typical scan currents. A decrease for antimony to about 90  $\mu$ a. With increasing voltages, as shown, beam currents may double or triple. Different species ionize more readily than others, which accounts for the differences in beam currents an ion source can generate.

Table II includes the beam currents for a 300 keV implanter. These are what we typically get on our 300 keV machine. However, we never have implanted at voltage below 50 keV. Again, as previously shown in Table I, the beam currents rise as the voltage is increased through the range of 150 keV to 300 keV when deeper implants are required for the three species, boron phosphorous, and arsenic.

The depth to which an ionized atom can be implanted is governed by the impressed voltage, the atomic mass, and the nature of the substrate material.

Figure 1 shows profiles of boron implanted at 50 and 100 keV similar to Dr. Mayer's profiles of nitrogen. At 100 keV, the projected range is about 0.5 micron. At 50 keV the projected range is seen to be about 0.25 microns implanted into silicon.

To implant a given dose amounts to finding Q, or the total number of coulombs/ square centimeters required:

$$Q = \frac{\text{Dose} \times \text{Col/ion} \times \text{carousel area} \times \text{charge of ion}}{\text{F.S.*}}$$

- Substituting values -

$$Q = \frac{5 \times 10^{14} \times 1.6 \times 10^{-19} \times 36.39 \times 1}{6 \times 10^{-5} \text{ ua}} = 48.5 \text{ sec}$$

Now as in the example, if we are implanting with a beam current of 60  $\mu\text{a}$ , it would take approximately 50 seconds for the implant. As can be seen, the larger the dose, or a reduced beam current, would increase the implant time from seconds to hours.

There are two basic types of implanters:

- A. Preanalysis - post acceleration
- B. Postanalysis - preacceleration

In the first type the beam is analyzed before acceleration. In the second type the beam is analyzed after acceleration.

Advantages of preanalysis machines are:

- 1. Cost less.
- 2. Generate high beam currents.
- 3. Take less room.
- 4. Only the selected ions to be implanted are accelerated versus the acceleration of the entire beam.
- 5. X-rays virtually eliminated.
- 6. Better energy and mass resolution.

Disadvantages:

- 1. Analyzing magnet at high potential.
- 2. Arcing and corona problems.

\*Full scale value of integrator current range used.

3. Greater probability to form neutrals and other "funny species" during travel to target.

4. Safety problems, since electronics not at ground potential when trouble shooting.

Advantages of postanalysis machines are:

1. Clean beam.
2. High voltage at ground potential.
3. High versatility.
4. Can be used as a research tool.
5. The postanalyzed beam containing atomic and molecular ionized species can be switched to different targets.
6. Voltages to 400 keV for deep implants.

Disadvantages:

1. More costly.
2. Large size equipment.
3. Larger more costly magnet to analyze (bend) the multi-specie beam.
4. Radiation hazards high.
5. Need large facilities.
6. Need longer distance within analyzer for adequate dispersion.

The basic steps for implanting are shown in Figure 2. For example, for all implants, a gaseous compound is used that contains the specie to be implanted. If the substance doesn't have a gaseous compound, i.e., titanium, tantalum, etc., then the solid substance has to be vaporized by a high temperature oven. It is easier to disassociate the molecules containing the specie to be implanted as boron, phosphorus and arsenic contained in  $\text{BF}_3$ ,  $\text{PF}_5$ , and  $\text{AsF}_5$  then to directly vaporize these solids to their high vapor temperatures.

First, a few tenths of a cc of the gas is leaked into an ion source where it is stripped of electrons leaving positively charged ions. The positive ions are extracted from the ion source and accelerated by a voltage corresponding to the depth of implant required. The accelerated ions which make up the beam are focused and reach the magnet chamber for analysis. Since no gaseous compound breaks up ideally into just its ionized atomic form it must be separated from the rest of the charged particles in the beam. For example:  $^{11}\text{B}^+$  from  $^{10}\text{B}^+$ ,  $\text{F}^+$ ,  $\text{BF}^+$ ,  $\text{BF}_2^+$ , etc. all which form when the  $\text{BF}_3$  molecule is ionized. The beam is deflected by the magnetic field through  $30^\circ$  or  $90^\circ$  for this separation. As the field strength or gauss is increased, each ionized specie is correspondingly bent to a degree depending on its mass. The field is increased until the desired ionized specie comes down the center of the beam line and on target. However, since the diameter of the beam may be approximately  $1/2''$  in diameter, the beam is oscillated 1000 Hz in the vertical and 100 Hz in the horizontal directions to uniformly implant 3", 4", etc., diameter substrates. In effect, we paint the surface of the substrate as it faces the oscillating ion beam until the prescribed dose is completed.

Figure 3 shows a schematic of a  $90^\circ$  implanter just described in more detail. It shows the ion source at the terminus of the accelerator column which incorporates a gap lens, focus lens, and accelerating electrodes. The gap lens being negatively charged attracts the positively charged ions from the ion source and down the accelerating column. The focus lens electrodes are positively charged for converging the

spread out beam as it emerges from the source. As shown, the beam is separated into its components by the magnet. The lighter ions are bent first, as mentioned earlier, and deposited as a film on the walls of the magnet chamber. Likewise, the heavier charged molecules or atoms also are deposited inside the magnet chamber. The specie to be implanted of course is focused down the center of the beam line. To remove any interfering specie of mass near that of the specie being implanted, a variable mass selector slit is used to narrow the beam diameter. The beam is again focused by electrostatic quadruple lenses and on through the beam scanner. There is also a 70 neutral trap to prevent the ions that have lost their charge from reaching the wafer.

Figure 4 is a spectrum of  $\text{BF}_3$  upon ionization into its component parts. The height of the peaks indicate the beam current in microamps. We also see a small current of beryllium. The beam is extracted through a beryllium orifice and some erosion takes place. The eroded beryllium particles ionize in the process accounting for a few microamps of beryllium.

Figure 5 is a schematic of the carousel used in our 300 keV implanter. It is used in either hybrid or step wise mode. It holds 25 two-inch silicon wafers. This type incidentally has been superceded by more modern designs for high production requirements. The wafermatic end stations can handle up to, or in excess of, three hundred wafers per hour.

The foremost question for buyers of implanters is the degree of reliability of a particular manufactured machine. It turns out however, regardless of make, that reliability is the biggest problem. We get arcing in the high voltage terminal causing failures of electronic components. With high current machines, the internal areas get crudded with deposits of the dopants as boron, arsenic, and phosphorous used for implanting. Tungsten filaments used for ionizing the gas dopants have short lifetimes. In addition, we have mechanical problems with compressors, and pumps. Constant monitoring must be maintained to prevent leakage of extremely poison gases. Radiation levels must be within safety limits.

As for the problems of making devices, it depends on the degree of control we want. For MOS, we need to control concentration very closely. For bipolar devices we need to closely control position of the junction. The point is to get the implants done fast enough and cheap enough.

Since the implant process can be so closely controlled for depth and dose uniformity, it finds innumerable applications in the fabrication of electronic components and circuits.

Here are listed ten applications:

1. CMOS-NMOS (for source-drain-wells)
2. Microwave and high frequency transistors
3. Monolithic resistors
4. Bipolar devices (collector-base-emitter)
5. Tailored profiles
6. Deposit gates and interconnects
7. Optical guided waves
8. Solar cells
9. Charged couple devices (storage and transfer gates)
10. Threshold voltage adjust (FET devices)

Figure 6 illustrates a self aligned gate structure done by implanting phosphorus through windows of an oxide mask covering the surface of a silicon substrate surface. By alternate masking steps we form the source, gate and drain regions.

Table I. TYPICAL CURRENT DENSITIES FOR A 200 keV HIGH DOSE IMPLANTER

Specie	25 to 35 kV	35 to 100 kV	100 to 200 kV
$^{11}\text{B}^+$	150 $\mu\text{a}$	240 $\mu\text{a}$	300 $\mu\text{a}$
$^{31}\text{P}^+$	150 $\mu\text{a}$	350 $\mu\text{a}$	500 $\mu\text{a}^+$
$^{75}\text{As}^+$	150 $\mu\text{a}$	350 $\mu\text{a}$	500 $\mu\text{a}^+$
$^{121}\text{Sb}^+$	90 $\mu\text{a}$	175 $\mu\text{a}$	225 $\mu\text{a}^+$

Table II. TYPICAL CURRENT DENSITIES FOR A 300 keV IMPLANTER

Specie	30 kV	150 kV	300 kV
$^{11}\text{B}^+$	10 $\mu\text{a}$	35 $\mu\text{a}$	70 $\mu\text{a}$
$^{31}\text{P}^+$	5 $\mu\text{a}$	20 $\mu\text{a}$	40 $\mu\text{a}$
$^{75}\text{As}^+$	5 $\mu\text{a}$	15 $\mu\text{a}$	30 $\mu\text{a}$

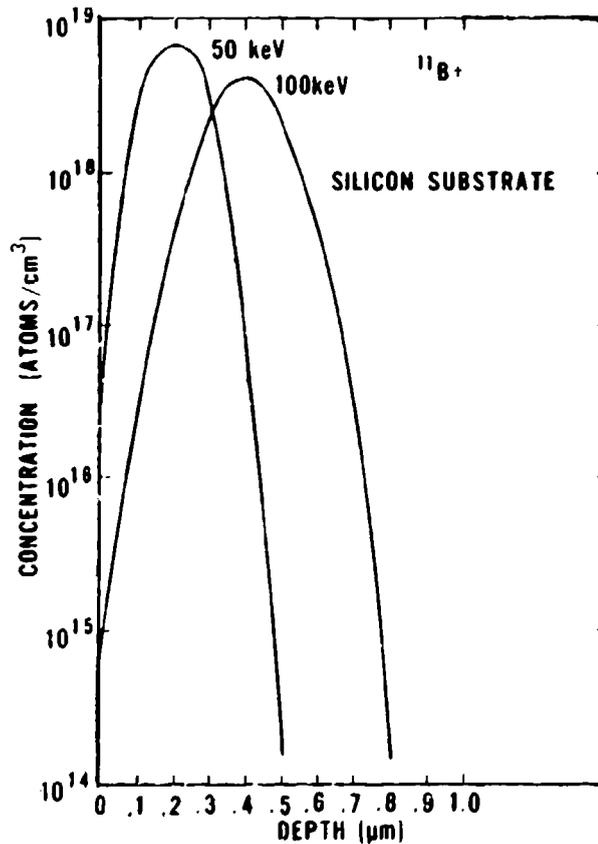


Figure 1

BASIC STEPS FOR IMPLANTING

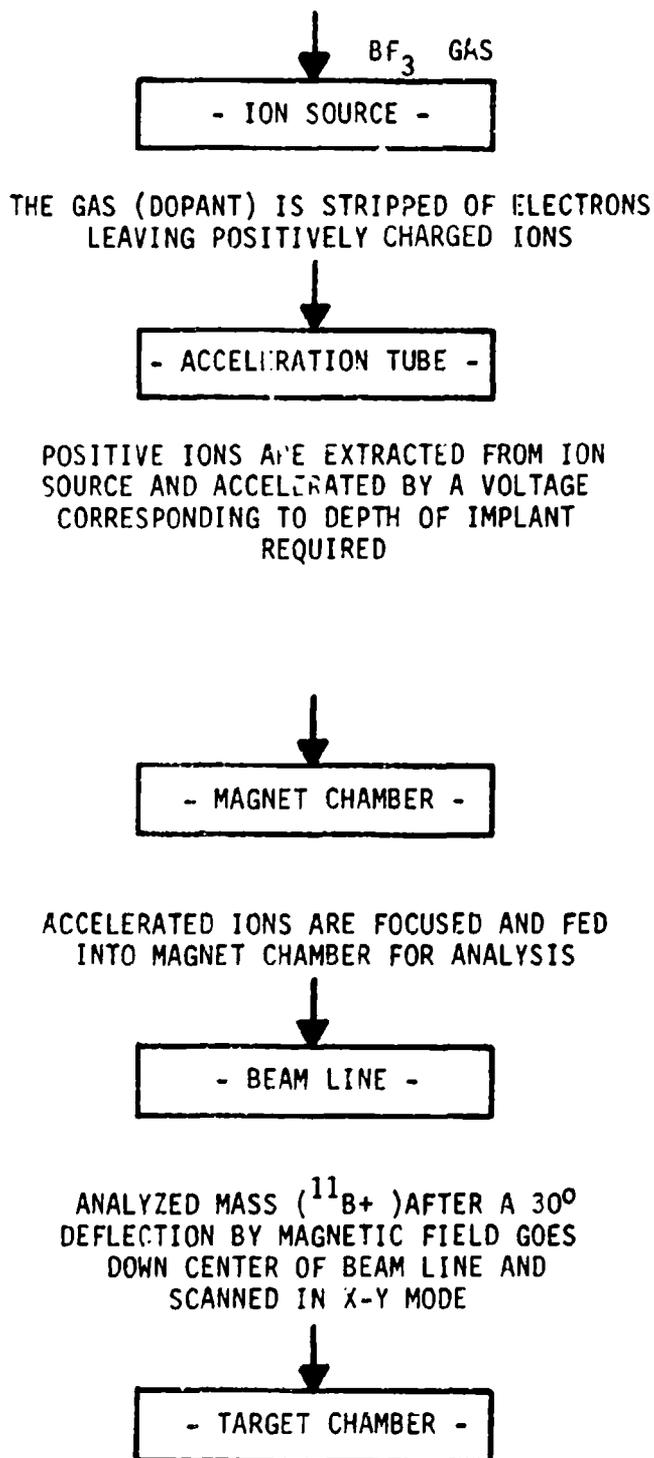
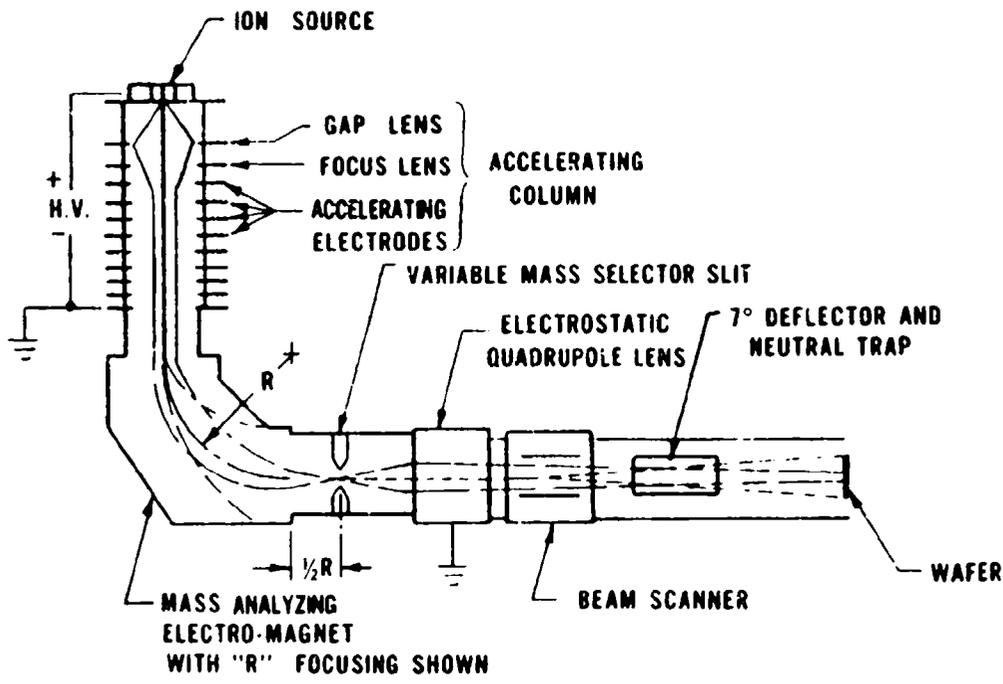


Figure 2



### BEAMLINE OPTICS

Figure 3

300keV IMPLANTER, FORT MONMOUTH, N.J.

$\frac{1}{2}$  SLITS 300keV

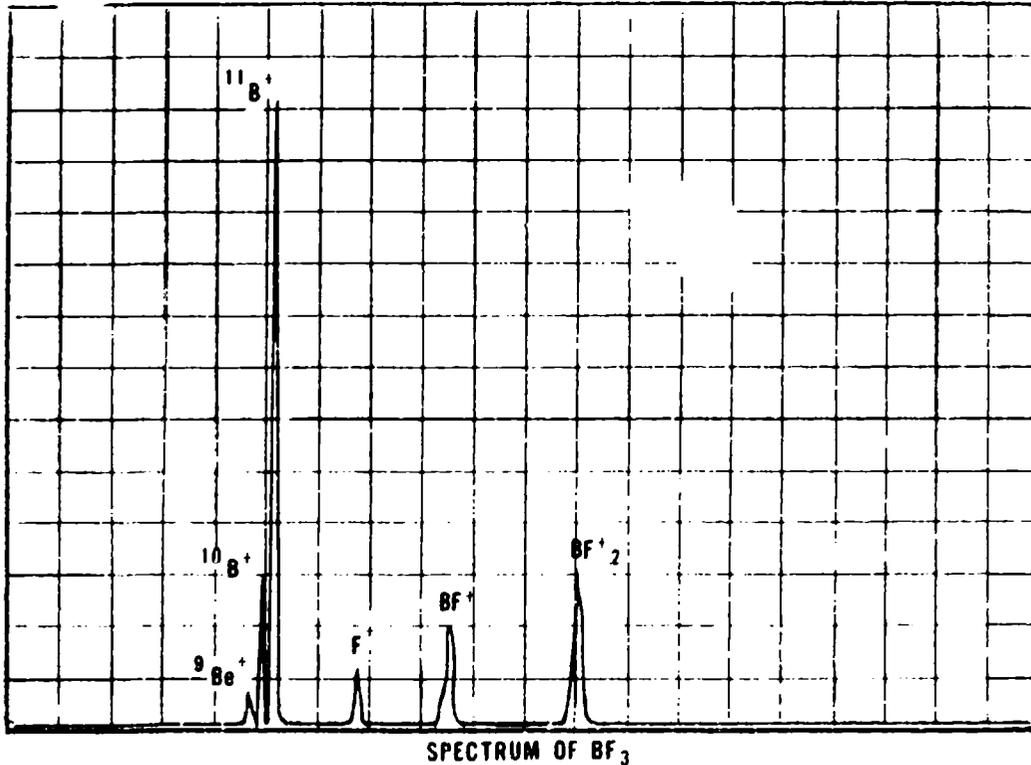


Figure 4

## HYBRID SCANNING TECHNIQUE

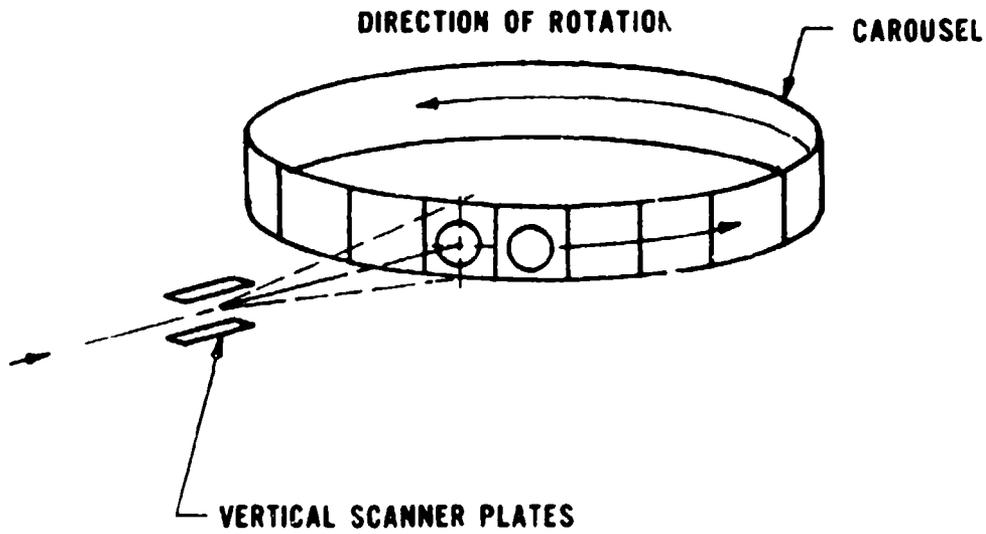


Figure 5

## SELF ALIGNED GATE STRUCTURE

### ION IMPLANT FOR SELF ALIGNED NMOS

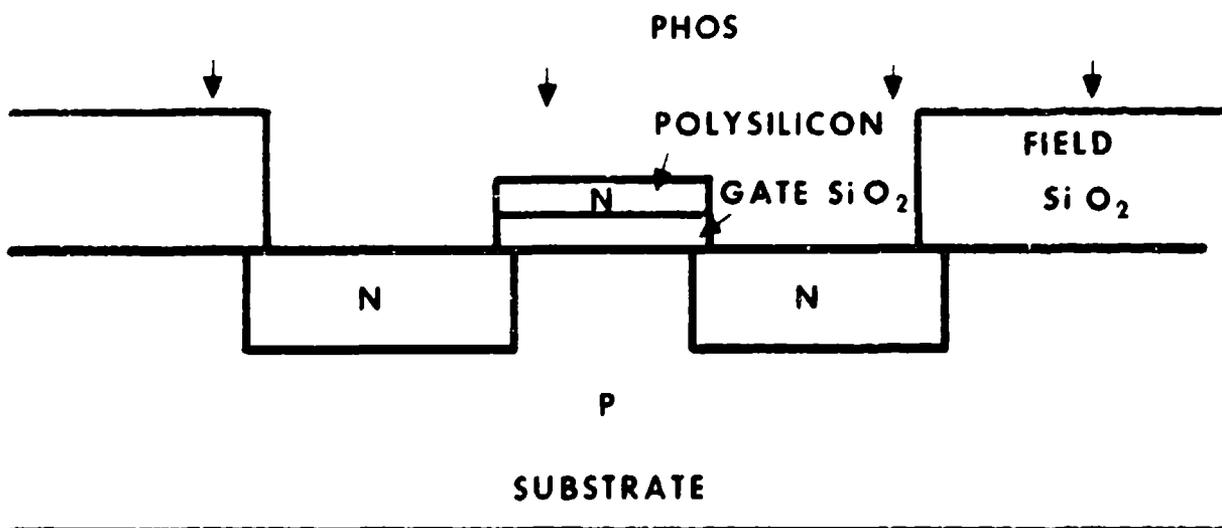


Figure 6

## QUESTIONS AND ANSWERS

C. Levy: You have given a little more practical look at ion implantation and I, for one, would like another view of your ion implantation apparatus.

A. Mark: Certainly (Figure 3). The console contains all the instrumentation for remotely controlling all the electronics of the terminal inside the lead room. Voltages for gap lenses, focus, and probe power supplies are in the 10 to 30 keV range. We have three independent vacuum sections; terminal, beam line, and target chamber. A 6" diffusion pump pulls a vacuum on the high volt terminal, accelerator tube, and magnet chamber. A 4" diffusion pump evacuates the beam line which is isolated each end by 4" and 6" gate valves respectively. An ion pump is located under the target chamber. In addition to pumping below  $10^{-8}$ , contamination from diffusion pump oils on the wafer surfaces is avoided. The other section pull down to a static pressure of approximately  $2 \times 10^{-7}$  torr. During implants, average pressure go up to  $2 \times 10^{-6}$  torr.

This drift tube contains the quadrupoles. It contains horizontal plates through which the beam passes. By impressing positive and negative voltages on these plates we shape the beam diameter to about a half inch before it reaches the target. It is not cylindrical and at best star shaped.

Two sections of the beam line are for future channeling work. When in use, instead of the beam being scanned from a fulcrum point, it is moved in horizontal and vertical planes as the beam scans the wafer surface. Channeling requires expensive supplementary equipment inside the target chamber, for example, a goniometer. There is no requirement at present for doing channeling research in our division, but the capability is there if needed. It would take another \$10,000 or more for the setup.

We have a large magnet with a mass energy product of 38, or at 300 keV for example,  $M = 38/0.300 = 126$ . Therefore, we can analyze at 300 keV, a mass with an atomic weight no higher than 126. If we use a lower voltage say, 150 keV than  $M = 38/0.150 = 253$ , or we can analyze up to a mass of 253.

The chopping slits are used to reduce the beam current when we have more than we need. That happens when  $10^{12} - 10^{13}$  implants are made. Otherwise, the wafer could be implanted in less time than the machine could handle the implant cycle. Also, if we have a mass interfering with the one being implanted, the chopping slits are run in to block it from the beam.

The choice of the machine was based on the availability in 1972-1973. Close to a year was spent in gathering implant information and making a decision on which would best fit ERADCOM needs. There was no standard machine available. Companies such as KEV, Extrion, and Accelerators were making initial custom built prototypes. We settled on a 300 keV Accelerators Inc. machine which was designed for multipurpose use. In response to cost, at that time prices ranged from \$70,000 to \$125,000 depending on the options. Present costs are from \$300,000 to over \$600,000.

Most of our implants are boron and phosphorous. Voltages used are from 50 to 100 keV and doses from  $1 \times 10^{13}$  to  $10^{15}$  are common. Since our implanter is not a high current machine, doses in the  $10^{15}$  to  $10^{16}$  range require over an hour for an implant. Lower doses, as little time as 1 to 2 minutes.

We have a number of accessories: Beam Profile Monitor, Magnet Tracking Control, Video Camera (for monitoring meters mounted in the high volt terminal), and an Oscilloscope for display of the scanned beam during implants. Most useful is a Mass Identifier. This displays the atomic weight of the specie being implanted via LED's.

A. Kant, AMMRC: To what sort of resolution do you get mass separation?

A. Mark: The ability to separate one mass from another is expressed by:

$$\frac{M}{\Delta M} = C \quad \text{where: } M = \text{mass of dopant} \\ \Delta M = \text{change of mass}$$

C in commercial implanters is a function of the manufacturers design and in most cases equal to 100.

For example - for boron, its mass is 11 and solving for  $\Delta M$ .

then  $\Delta M = 11/100 = 0.11$  (+ and -)

and we get mass resolution from plus and minus 0.11, i.e. 11.11 to 10.89. Since carbon is 12, we would miss it if in the ion beam. (We look for carbon contamination from our oil diffusion pumps.) Another way of looking at this is purity of beam will contain no more than 1% of adjacent mass; i.e. will resolve to 1 part in 100. Machines to be used in separating radioactive isotopes are manufactured with constants set to 2000 and over.

A. Kant: Can heavier masses, such as arsenic, be separated without difficulty from the beam?

A. Mark: Actually, if we examine the spectrum of the gaseous compound  $\text{AsF}_5$ , we find upon its dissociation into  $^{75}\text{As}^+$  and other ionic compounds, the charged arsenic ion is sitting far enough away from the other ionized species in the beam so there is no interference from these.

N. Bullock, TSARCOM: How do you calibrate your slits so that you can separate your boron isotopes 10 and 11?

A. Mark: We actually do not. Any boron 10 that would be implanted would not affect the electrical properties of the final product. It is not an interfering specie. For an isotope that is overlapping the one being implanted, the chopping slits would be adjusted by trial and error. We can judge by examining the x-y spectra of the beam and the ions proximity to each other. Moving in the slits until the beam current is reduced a few microamps generally is sufficient to eliminate an adjacent charged atom (ion).

S. Cytron, ARRADCOM: Could you give us an idea how this technique compares with the old thermal diffusion technique in terms of the number of wafers you can make?

A. Mark: It takes three to four hours for certain diffusion steps, compared to nine hours for deep drives into a substrate surface. However we are not talking about individual wafers, since a diffusion tube may hold a few dozen wafers per run. As mentioned earlier, the new high dose machines can run over 300 implants per hours.

The advantage of implanting techniques over diffusion or epitaxy beside high throughput, is room temperature processing and high uniformity. For example, we recently implanted 15 wafers in 30 minutes. The dose was  $1 \times 10^{14}$  at 100 keV.

S. Cytron: Do you also get a corresponding improvement in the number of good chips per wafer?

A. Mark: Yes. We can duplicate implant runs which were made months before. At least my colleagues so claim. Otherwise, the electrical characteristics would not be the same from run to run. The modern commercial machines do uniform implants on 3" and 4" wafers to within 1% over the entire surface.

C. Levy: What about the size of the targets that you use in relationship to what is practical and what is not practical?

A. Mark: We are upgrading our facilities from processing 2 inch silicon substrate wafers to 3 inch wafers. The industrial electronic firms are routinely processing 4" wafers. As size of wafer is increased so must all the corresponding processing equipment be increased. To implant large areas uniformly, say to six inch diameters or greater, would require implanters that could scan a high current beam through that distance at 1000 hz in the horizontal direction. Electrostatic scanning is limited to about 600  $\mu$ a beam currents. Beyond that the beam is held stationary and the target is mechanically oscillated. Therefore, for applications other than the electronics field, where large areas would have to be implanted would require monstrous size implanters. This would not be practical from a cost and engineering viewpoint.

NOTE: I would like to acknowledge the use of some of the data and diagrams supplied by Veeco Inc., Austin, Texas. (Formally Accelerators Inc.)



REVIEW OF THE UNIVERSITY OF  
MANCHESTER ION IMPLANTATION CONFERENCE

Dr. Paul Sagalyn  
Army Materials and Mechanics Research Center

Before getting started on the subject of the talk I thought I would make a few preliminary remarks that might help people in the audience who are completely new to ion implantation. First a historical note that may be of some value - the technique of ion implantation started at IBM and Bell at least 15 years ago and initially was applied to semi-conductors. It has been a production line technique for semi-conductors for at least ten years. What is new from the point of view of this installation is the application to non-semi-conductor materials. And it is the advent of such applications that got me interested in the field and really led to this workshop. It is not completely clear why it took so long for people to get interested in the applications to non-semi-conductors. From what I can see it was due to some fortuitous discoveries at Harwell in England. Naively, if you want to improve the lifetime of some metallic component, some moving part in a machine, by ion implantation, you would think that it would be of very little use because, although you can make a very hard surface layer, these layers are so thin that they would wear off very quickly and then you are back to where you started. The question is then would it be worth the trouble. At Harwell they discovered about fifteen years ago that there are certain enhancement effects. In the case of wear, for example, you can reduce the wear rate for steel dramatically by implantation with nitrogen. This reduction in wear rate lasts long after the original layer--that is long after a layer of the thickness of the original layer--is worn off the metal. The reason for the wear reduction seems to be that there is enough nitrogen to harden the surface by tying up dislocations. When the surface starts to wear, there is some heating and the nitrogen can diffuse either way, in or out. It turns out, fortunately, that most of it diffuses in, and you wear away the surface, maintaining a hard wear front. Ion implanted surfaces sometimes last 1000 times longer than one would expect just from the thickness of the original implanted layer. Similar phenomena have been found in corrosion also and apparently it was the discovery of these phenomena that started the whole interest in ion implantation for non-semi-conductor materials.

I have a few summary view graphs that go back to a Materials Advisory Board panel that Jim Hirvonen was on and for the people who are not in ion implantation, I think it would be worthwhile to pause for a moment and look at these. Figure 1 shows some of the advantages of ion implantation for metallurgical applications. We only affect the surface at no sacrifice of bulk properties. We can make metastable solutions; and you can exceed ordinary equilibrium diagrams solid solubilities. Since we are knocking ions in by brute force, diffusion constants don't enter in. A very important fact is that the concentration distribution is continuously variable in a smooth way. There are no abrupt discontinuities and therefore you don't have the adhesion problems that go with coatings. For most processes the dimensional changes are negligible, something of the order of a millionth of an inch, so no refinishing is required. You can control the depth concentration profile. That is if you implant at a single energy you will get a roughly gaussian distribution as has been shown in earlier slides but there is no reason why you can't make several implants at different energy and get a resultant distribution that will be approximately constant. There are no changes in grain sizes because it is a low temperature process. You can control the implanted area very accurately, and there are no waste products to speak of.

AD P003950

There are disadvantages. The process has to be done in vacuum. You have to buy an expensive machine, so the improvements have to be substantial. Furthermore, when you get into metallurgical applications the samples may be complex in shape. The semi-conductor applications involve the implantation of flat wafers which is about as simple a target you can find. If you want to implant a gear, then it has a more complex shape, and a new generation of target chambers is going to have to be developed.

The applications are very widespread. For metals we have corrosion inhibition, wear and friction reduction, fatigue lifetime improvements, super-conducting properties modification, catalysis and others. Ion implantation also turns out to be an invaluable research tool in metallurgy and in some places, like Cornell or Sandia Labs, very fundamental metallurgical studies are being done, using ion implantation primarily as a research tool rather than with the idea of generating a new material. It can also be used to modify the optical properties of materials. It is just amazing how many practical metallurgical properties are related to the condition of the surface of the material. It seems to me from my brief encounter with ion implantation that it is the most revolutionary metallurgical development in the last decade or two. Now before getting on to the Manchester conference I want to show some wear data (Figure 2). For knives used for cutting plastics lifetime extensions were obtained with factors of 2-10 estimates of about a 40% increase in the cost of the knife. One of the most surprising results was with the implantation of tungsten carbide tools. They got lifetime extensions as high as 100 after implantation with carbon. These are rather startling results and an awful lot of people got into non-semiconductor applications as a result of these early experiments. Now here (Figure 3) is some additional wear related data. In this particular case the third column is wear rate, which is drastically reduced; and it turns out that the lifetime extensions are nearly always very significant. Nitrogen is the most common element implanted. It is easy to make a beam of nitrogen and nitriding is a well known beneficial process in metallurgy, so it is a logical place to start. Another area of interest is fatigue. This is NRL data (Figure 4). Fatigue is a process which starts on the surface due to crack initiation or due to cracks already present on the surface and it is well known that surface treatment effects fatigue life. In this data you can see how spectacular the improvements due to implantation are. If they implanted and immediately tested there is really no statistical improvement; but when the samples were aged, either artificially or at room temperature, they got spectacular increases in fatigue life. The arrows in a couple of cases point to specimens that never did fail. So for people not involved in their developments, even this early data shows significant practical applications.

It is now time to get on to the principal subject of my talk, review of a conference on ion implantation in Manchester just last month. One reason for reviewing this particular conference is to give everyone at this Workshop a flavor of how exciting the field is, how fast it is moving, and how much interest there is in it worldwide. There were approximately 60 papers given (Figure 5). Of these, 11 were in the area of aqueous corrosion and nine were in the area of high temperature oxidation so about 20, or 1/3 of the papers, were on corrosion. I don't think this necessarily reflects the relative importance of ion implantation for corrosion. My own opinion is that in fact the best determined applications are in wear, friction and fatigue. There are some applications for corrosion; for example, NRL has an important bearing project. Corrosion is so tricky that it is going to take an extensive amount of research to find out just how to use ion implantation. It depends critically on the environment and the way the piece is used. One reason for so many papers is that it turns out however that ion implantation is a marvelous technique

for studying corrosion mechanisms; and this was a very science-oriented conference. There were 12 papers on mechanical processes, distributed over wear, micro-hardness, fatigue, adhesion and one that covered everything.

Ion implantation is applicable to all sorts of other properties like super conductivity (Figure 6). Researchers are beginning to work on polymers for the first time, affecting the surface related properties. Fundamental metallurgical mechanisms, like solute trapping, are being studied by the Sandia group. A paper on blistering and exfoliation, a big problem in fusion reactions, was given by a group from Budapest. Ion implantation can be used as a tool for studying the annealing of radiation damage. And then there were a few papers on ion beam mixing which many people think is, for practical purposes, the process of the future. There were also fundamental papers on studying the microstructure of these layers by Mossbauer techniques and papers on various characterization techniques that have come out of ion implantation work which I will not cover. Finally, there were the papers by representatives from equipment manufacturers.

I should remark at this point that I think one of the things that is holding up applications is the lack of a good commercial implanter oriented towards metallurgy. The implanters on the market today have all been designed for the semi-conductor industry. They can be used, in principle, for metallurgical applications but they have very elaborate target handling capabilities all of which were designed for handling silicon wafers. For metallurgical applications larger diameter beams will be needed because the parts are bigger, also, high beam currents, and a large target chamber there for manipulating parts that have complex shapes.

I am not attempting to cover the entire conference but just go over some highlights. In the work on aqueous corrosion I have broken it down by materials (Figures 7-9). There is a lot of work on pure iron, a lot at Heidelberg and work by various Italian groups. To someone who is not an expert in corrosion, like myself, the whole field seems somewhat disorganized. Everybody has a different implant, a different corrosive medium and different experimental conditions. The actual papers were very heavily oriented toward science. I have picked out remarks from these papers oriented toward practical applications, and these were not always easy to find. For example, at Heidelberg, they found that mercury and lead implants in iron initially reduced the rate of corrosion by quite a bit, but over long periods of time things get worse; the Italian work in water showed the same sort of thing with nitrogen implants (Figure 7). They got, with high dose implants, initial improvements in the rate of corrosion but the actual service life was reduced because, again, after long periods of immersion, the corrosion rate got worse than for untreated iron. Some very complex chemical effects are going on and it will take a lot of research to find out just what is happening. But there are some favorable results. Platinum does seem to give a more stable passivation layer. Clayton at Stony Brook found that implanting phosphorous in stainless steel produced an amorphous surface layer which greatly increased the resistance to chloride ion penetration, so that there a real improvement in the corrosion resistance.

Most of the work to date has been done on pure materials, and work on alloys is just beginning. The NRL program (Figure 8) on a bearing steel is aimed at producing a bearing which will have better corrosion resistance without affecting the mechanical properties. I gather from their abstract that titanium yields a slight improvement only but that chromium and phosphorous combined with tantalum do give some improved resistance to pitting. Again this shows one of the advantages of ion implantation

that you can alter the surface related properties but it does not effect the mechanical properties of the bulk material. There are many other examples; Phil Parrish who is in the audience has done a lot of work on ARMCO iron and has shown that the properties of a chromium implanted surface layer are approximately equivalent to those of a bulk chromium alloy. Except that at least to a first approximation apparently the oxide layer of the bulk alloy is somewhat better. Here is some Westinghouse work (Figure 8). They use a different corrosive medium; this was a 10% weight sodium hydroxide solution. They found that Boron and Neon implants had no effect but that nitrogen and phosphorous made things significantly worse. Not everything works!

One thing to keep in mind is that there are 92 elements in the periodic table and in principle with ion implantation or ion beam mixing techniques we can put any element into anything, so we have a lot of things to try. It would be overly optimistic to think that all 92 are going to help.

Again, on aqueous corrosion: two different groups have been working on titanium using platinum as the implant (Figure 9), but with slightly different, corrosive media, and the results are very optimistic. Neither group gave any numbers but the Vanderbilt group claims that a high dose of platinum gives "permanent" protection. I don't know exactly what that word means. There has also been work on aluminum and a point of interest is that the Lancaster group found there was an optimum dose that gave minimum oxidation of the surface. So you really have to do some experiments. You can't just give it a dose and say whether a particular implant is good or bad. The effect may be strongly dose dependent.

At McMaster (Figure 9) they are trying to use ion implantation to improve the electrocatalytic behavior of nickel. This is specifically to improve the efficiency with which you can produce hydrogen from aqueous solutions. They bombarded it with ruthenium, rhenium, palladium, silver and platinum. The results were not encouraging. Virtually all of them gave an initial improvement in efficiency of about 30% but in all cases it was quite temporary and not reproducible so that particular experiment has a ways to go.

Now wear is a very significant Army problem, and I think it is one of the areas where implantation is most promising from the view of practical application (Figure 10). The Westinghouse group implanted a particular stainless steel that is used in a nuclear pump and compared conventional thermal nitriding as a surface treatment and nitrogen implantation. Both of them improved the wear, but the surprising thing was that the combination of nitriding followed by nitrogen implantation was significantly better than either of them alone. This is typical of the kind of surprises that are constantly coming out of this field, because it is so new. They found that the combination treatment gave a wear rate 100 times smaller than an untreated sample.

Again, at the University of Missouri they implanted "steel" (the type wasn't specified) with nitrogen and got an order of magnitude improvement in the wear rate. All of these tests use different doses and different test conditions; this is the status of the field at the moment.

There was a paper by an engineer from a plastic molding company in England which from my point of view was the only paper of the conference that was really engineering oriented. They nitrogen implanted entire components used in plastic molding and found major increases in lifetime. These were implanted at Harwell but they were tested under production line conditions.

Fatigue (Figure 11) is another area where striking improvements have been attained. One of the things you will notice is that a lot of these papers involve the collaboration of several groups and then, if you look at the authors, each group has a number of authors. This is because no one group has all the equipment necessary to do a good job. In this business it is not enough to merely implant. There are really three work areas - you have to implant under very controlled conditions, you have to characterize the sample very carefully before and after implantation and after various processing steps, and then you have to make some sort of property measurement, such as fatigue life. The result is that often the work ends up being done at three different places. The Georgia Tech group gave two papers on pure copper which is not exactly an engineering material, but is very interesting from a scientific point of view. They found what they referred to as dramatic increases in the fatigue life of copper upon implantation with aluminum. However, they don't give a number. You will also notice on Figure 11 that SUNY/Albany found very very big increases with chlorine implantation. The common thread seems to be that they are both large atoms that put compressive residual stresses into the surface. For example, a small atom like boron implanted in copper actually decreases the fatigue life. Since there are a lot of big atoms in the periodic table it seems to me there are a lot of things to try. On the other hand at SUNY/Albany they implanted nitrogen in austenitic stainless steel and got only about a 10% increase in fatigue life which is hardly worth the trouble.

There is one particular paper from Cambridge University that caught my attention because this was a conference on metallic materials. This was the only paper at the conference devoted primarily to non-metallic materials (Figure 12) and it is of particular interest to us because we are very interested in possible applications of ion implantation to ceramics, particularly to ceramics used for structural processes. The principle measurement was microhardness and they made a rather complete analysis of the microhardness properties. They examined the indentation size effect, that is, the change and the deformation as a function of load and any changes in the fracture behavior in the vicinity of the deformation. The result that was very striking and very puzzling is that again, as in one of the other papers, they found evidence for a critical dosage of  $3-4 \times 10^{17}$  ions/cm<sup>2</sup>. There was a dramatic change in mechanical properties at this dose and there were entirely different fracture mechanisms in the vicinity of the indentation on either side. In both silicon and silicon carbide the surface was shown to soften at the critical dose. This certainly has important implications for the mechanical properties in these materials since ceramics fail typically due to cracks which are present on the surface after finishing. It would certainly be very interesting to break some samples that have had this critical dose. As far as I know nobody has done that.

Another paper (Figure 13) that I picked out for discussion because it was so practical is a paper by an engineer from Healey Mouldings Ltd. As it says here on the slide, components used for molding plastics were out surprisingly fast because of various abrasive and corrosive additives that are used for colorization and for improving the properties of the materials. The molds were implanted at Harwell and used under factory conditions. In the case of injection nozzles the lifetime was increased from six months to 18 months under standard conditions. In the case of an impression mold the number of satisfactory moldings increased by a factor of 10. On a production line basis there is no reason why the increase in cost should be anymore than 40-50% - possibly lower. So this is really a very striking advance from a practical point of view.

In conclusion, I thought I would read to you some of the results on a paper by the group from the Georgia Institute of Technology where they are working on the fatigue behavior of implanted copper, both single crystal and polycrystalline. They used four different implants. One with a positive misfit - aluminum. One with a negative misfit - boron, one with zero misfit, which is copper itself, and one that was insoluble under equilibrium conditions, namely chromium. There is one question that always comes up in implantation experiments. Are the property changes due to some chemical interaction between the impurity and the host when the ion finally comes to rest; or are the effects due to radiation damage. One standard test is to compare the effects of a particular impurity with implantation by an inert gas like helium or argon. Another standard test is self-implantation where you implant with the same material as the host so it has to be pure damage. In this case the extent of the radiation damage was actually greatest for copper ions - a lot of fancy measurement techniques were used here. Then they obtained decreasing amounts for chromium, aluminum and boron implants respectively. On the other hand the biggest increase by far in fatigue lifetime was for aluminum implants; and this sort of measurement shows clearly that damage is not the mechanism; it is chemistry. This is fortunate for the materials scientist because damage isn't all that different from one impurity to another but chemistry is very different. It turns out that the increase in fatigue life can be related to the type of deformation that you get, and the impurity that gives the most homogenous deformation is the one that gives the biggest increase in fatigue life. So this is a real metallurgical phenomenon. In the case of aluminum, they claim a drastic increase in fatigue life.

Well, as I said earlier, there were about 50 papers at the meeting and I do not have time to go over anymore of them, but I hope I have left you with the impression that the field is very exciting, that dramatic discoveries are being made all the time, there is worldwide interest in it, and that in many areas such as wear, friction, fatigue, and, in some special cases, corrosion, it is already obviously of great practical importance. Unfortunately, I do not have time to discuss the papers on high temperature oxidation. The results are summarized in Figures 14-18. Thank you.

## ADVANTAGES OF ION IMPLANTATION

NO SACRIFICE OF BULK PROPERTIES  
SOLID SOLUBILITY LIMIT CAN BE EXCEEDED  
ALLOY PREPARATION INDEPENDENT OF DIFFUSION CONSTANTS  
NO COATING ADHESION PROBLEMS SINCE THERE IS NO INTERFACE  
NO CHANGE IN DIMENSIONS  
DEPTH CONCENTRATION DISTRIBUTION CONTROLLABLE  
COMPOSITION MAY BE CHANGED WITHOUT AFFECTING GRAIN SIZES  
PRECISE LOCATION OF IMPLANTED AREA(S)  
NO WASTE PRODUCTS

Figure 1

### SELECTED EXAMPLES OF INDUSTRIAL UTILIZATION OF REDUCED WEAR BY IMPLANTATION (HARWELL)

<u>USE</u>	<u>IMPLANTED SPECIES</u>	<u>LIFE EXTENSION FACTOR</u>
CUTTING KNIVES FOR PAPER AND RUBBER	N	2X - 10X
HIGH SPEED TAPS FOR PHENOLIC PLASTICS	N	5X
CEMENTED TUNGSTEN CARBIDE TOOLS WIRE DRAWING DIES AND FORMING TOOLS	C	5X - 100X

Figure 2

WEAR

<u>MATERIAL</u>	<u>ELEMENT</u>	<u>REDUCTION OF WEAR RATE</u>	<u>REFERENCE</u>
EN40B	N, Mo	10X - 30X	HARWELL
MANY OTHER ALLOYS	MAINLY N, C	10X - 200X	HARWELL
Al, STEEL	N, C, OR Ar	10X	PAVLOV et al.
52100 STEEL	N	2X	N.R.L.
TYPES 304 AND 416 STAINLESS STEEL	N, Co	20X - 100X	N.R.L.

Figure 3

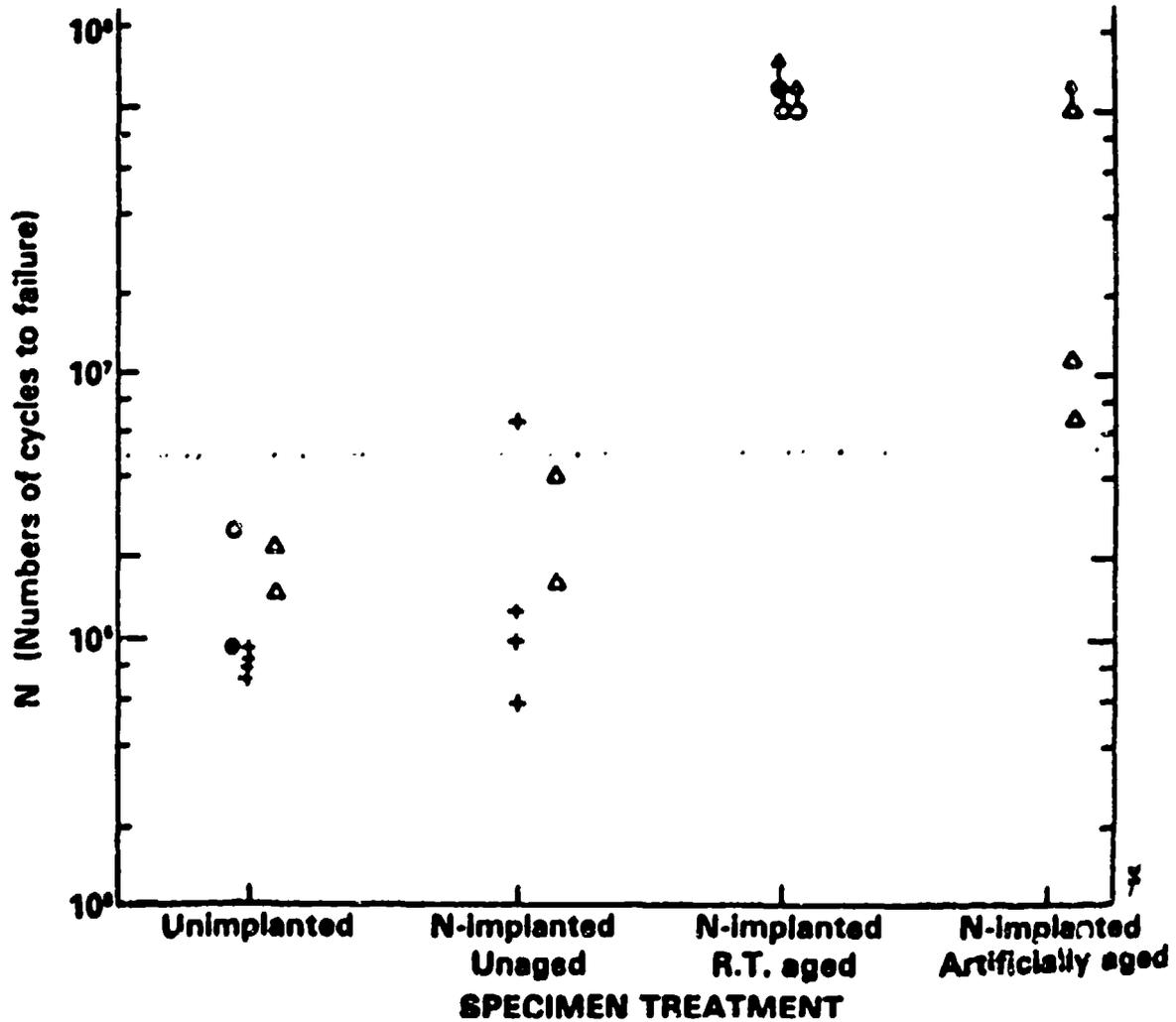


Figure 4. Fatigue lifetime (cycles-to-failure) for AISI 1018 test samples having different time-temperature histories.

## BREAKDOWN BY SUBJECT

	NUMBER OF PAPERS
AQUEOUS CORROSION AND ELECTROCHEMISTRY	11
HIGH TEMPERATURE OXIDATION	9
MECHANICAL PROPERTIES	12
WEAR	6
MICROHARDNESS TECHNIQUES	2
FATIGUE	2
ADHESION	1
GENERAL	1

Figure 5

## APPLICATIONS OF ION IMPLANTATION TO MATERIALS MODIFICATION

### SEMICONDUCTORS

DOPING

DEVICE FABRICATION

### METALS

CORROSION INHIBITION

WEAR AND FRICTION REDUCTION

FATIGUE LIFETIME IMPROVEMENT

SUPERCONDUCTING PROPERTIES MODIFICATION

CATALYSIS

FUNDAMENTAL STUDIES - METASTABLE ALLOYS

### OPTICAL MATERIALS

REFRACTIVE INDEX MODIFICATION

Figure 6

AQUEOUS CORROSION - BREAKDOWN BY MATERIAL

<u>ABSTRACT</u>	<u>MATERIAL</u>	<u>IMPLANTS</u>	<u>CORROSIVE MEDIUM</u>	<u>REMARKS</u>
60, 20 HEIDELBERG	FE	Hg PB Au Pt	SULFURIC ACID	Hg, PB - LESS CORROSION BUT ONLY TEMPORARILY PT, AU - MORE CORROSION BUT PT YIELDS MORE STABLE PASSIVATION.
9 TRENTO, PADOVA GENOA	FE	N	H <sub>2</sub> O	HIGH DOSE YIELDS INITIAL IMPROVEMENT ONLY. SERVICE LIFE REDUCED.
11 STONY BROOK BROOKHAVEN NRL	304 ss	P	DEAERATED IN H <sub>2</sub> SO <sub>4</sub> + 2% NaCl	AMORPHOUS FILM FORMED CONTAINING PHOSPHATES. RESISTS CL PENETRATION.
4 U.M.I.S.T. SALFORD	304 ss	CL	.05M H <sub>2</sub> SO <sub>4</sub>	PASSIVATION UNAFFECTED.

Figure 7

AQUEOUS CORROSION - BREAKDOWN BY MATERIAL

<u>ABSTRACT</u>	<u>MATERIAL</u>	<u>IMPLANTS</u>	<u>CORROSIVE MEDIUM</u>	<u>REMARKS</u>
28 NRL	AISI 52100 BEARING STEEL	Ti Cr, Cr + P, TA	ACIDS AND SOLNS CONTAINING CL <sup>-</sup>	Ti YIELDS SLIGHT IMPROVEMENT.  THESE DO GIVE IMPROVED RESISTANCE TO PITTING.
42 ARO	ARMCO IRON	CR	NIL CHLORIDE & .1M CHLORIDE SOLN PH 2-12	OVERALL PERFORMANCE EQUIVALENT TO BULK ALLOY. BULK OXIDE SOMEWHAT BETTER.
44 WESTINGHOUSE	INCONEL 600 (FE AND NI)	B NE  N P	10 WGT.% NaOH AT 600 F  "	B, NE YIELD NEGLIGIBLE EFFECT ON CORROSION RATE.  N, P YIELD SIGNIFICANT INCREASE IN RATE.

Figure 8

AQUEOUS CORROSION - BREAKDOWN BY MATERIAL

<u>ABSTRACT</u>	<u>MATERIAL</u>	<u>IMPLANTS</u>	<u>CORROSIVE MEDIUM</u>	<u>REMARKS</u>
60 HEIDELBERG	Ti	Pt	ACIDIC	Pt PASSIVATES Ti.
33 VANDERBILT BATTELLE OAK RIDGE	Ti	Pt	HYDROGEN SAT. IN H <sub>2</sub> SO <sub>4</sub>	HIGH FLUXES GIVE PERMANENT PROTECTION.
4 U.M.I.S.T.	AL	CL	.05M H <sub>2</sub> SO <sub>4</sub>	EXHIBITS CRACKS IN OXIDE ASSOCIATED WITH PITTING.
12 LANCASTER HARWELL	AL	MN Bi	OXIDIZING	CRITICAL DOSE = 10 <sup>-16</sup> GIVES MIN. OXIDATION
56 McMASTER UNIVERSITY	Ni (FOR ELECTRO- CATALYSIS)	Ru Rh Pd Ag Ir Pt	30% AQUEOUS KOH	INITIAL IMPROVEMENT (H <sub>2</sub> PRODUCTION) UP TO 30% BUT TRANSIENT AND NOT PRODUCIBLE.

Figure 9

WEAR

<u>ABSTRACT</u>	<u>MATERIAL</u>	<u>IMPLANT</u>	<u>MEASUREMENT</u>	<u>REMARKS</u>
18 WESTINGHOUSE	17-4 Ph SS (NUCLEAR PUMP)	N IMPLANT VS. THERMAL NITRIDING  COMBINATION OF BOTH	LUBRICATED SLIDING WEAR TEST	BOTH N IMPLANT AND T.N. IMPROVE WEAR BUT COM- BINATION BETTER THAN EITHER ALONE (100 TIMES BETTER THAN UNTREATED STEEL).
25 U. MISSOURI	"STEEL"	N	LUBRICATED WEAR, CYLINDER IN CHUCK	HIGH DOSE (2.5x10 <sup>17</sup> ) GIVES ORDER OF MAGNITUDE IMPROVEMENT.
17 HEALEY MOLDINGS LTD.	STEEL COMPONENTS FOR MOLDING PLASTICS	N	LIFETIME	MAJOR INCREASES IN COMPONENT LIFETIMES.

Figure 10

## FATIGUE LIFE

<u>ABSTRACT</u>	<u>MATERIAL</u>	<u>IMPLANT</u>	<u>REMARKS</u>
5 SUNY-ALBANY RENSSELAER CASE	POLYCRYSTALLINE <u>COPPER</u>	Ne N He Cl B Xe	Ne yields 65% INCREASE Cl yields "VERY VERY BIG INCREASE".
10 GEORGIA TECH	POLY AND SINGLE CRYSTAL <u>COPPER</u>	Cu Cr Al B	BORON YIELDS DECREASED LIFETIME Cu, Cr YIELD SOME INCREASE Al YIELDS "DRAMATIC" INCREASE.
5 SUNY-ALBANY RENSSELAER CASE	AUSTENITIC SS	N	ONLY ABOUT A 10% INCREASE IN AIR.

Figure 11

### NON-METALLIC MATERIALS

S. G. ROBERTS AND T. F. PAGE  
CAMBRIDGE UNIVERSITY, U.K.

#### MATERIALS STUDIED:

WC/Co	INORGANIC AND METALLIC GLASSES
Si	Co
SiC	LiF

WIDE VARIATION IN MECHANICAL BEHAVIOR FROM BRITTLE TO DUCTILE. MICROHARDNESS RESPONSE WAS THE PRINCIPAL MECHANICAL TEST EMPLOYED. FULL ANALYSIS OF THE LOAD VARIATION OF HARDNESS (THE INDENTATION SIZE EFFECT (ISE)) AND OBSERVATIONS OF ANY CHANGES IN INDENTATION FRACTURE BEHAVIOR WERE UTILIZED. EXAMINATION OF THE ISE, INDENTATION PLASTICITY, AND INDENTATION FRACTURE BEHAVIOR OF SiC, Si, AND Co SHOWS LARGE CHANGES IN BEHAVIOR TO OCCUR AT THE CRITICAL DOSE OF  $3-4 \times 10^{17} \text{ N}_2^+/ \text{cm}^2$ . FOR EXAMPLE, CRACKING AROUND INDENTATIONS AND SCRATCH TRACKS IN BOTH Si AND SiC IS MARKEDLY REDUCED BY IMPLANTATION, WHILE THE ISE BEHAVIOR SHOWS SURFACE SOFTENING TO OCCUR IN Si AND SiC AND SURFACE HARDENING TO OCCUR IN Co.

Figure 12

TITLE: THE USE OF ION IMPLANTATION FOR IMPROVED  
ABRASIVE WEAR-RESISTANCE

AFFILIATION: B. G. DELVES F.P.R.I.

HEALEY MOULDINGS LIMITED,  
WARLEY, WEST MIDLANDS, UK

ABSTRACT:

MANY PROBLEMS ARISE IN MOULDING PLASTICS, BECAUSE OF THE ABRASIVE NATURE OF FILLERS PRESENT IN MOULDING MATERIALS REQUIRED TO IMPROVE THERMAL AND MECHANICAL STRENGTH. IN ADDITION, ABRASIVE AND CORROSIVE ADDITIVES ARE USED IN THE PRODUCTION OF PIGMENTS FOR COLOURISATION PURPOSES. THIS COMBINATION OF FILLERS AND PIGMENTS PROVE TO BE HIGHLY ABRASIVE.

TOOLS AND MOULDS USED IN INJECTION MOULDING SUFFER ABRASIVE WEAR BECAUSE OF THESE ADDITIVES.

WE HAVE BEEN ABLE TO SHOW THAT THE ION IMPLANTATION OF NITROGEN INTO SUCH MOULDS AND TOOLS WILL BRING ABOUT SUBSTANTIAL REDUCTIONS IN WEAR RATES. THE PROCESS IS CARRIED OUT AT LOW TEMPERATURES, AND SO THERE IS NO DISTORTION, WHILE SURFACE POLISH AND DIMENSIONS ARE UNAFFECTED. EXAMPLES OF TOOLS SUCCESSFULLY TREATED INCLUDE SPRUE BUSHES, IMPRESSION MOULDS, FEED RUNNER BLOCKS, FEED WEAR PADS, INJECTION NOZZLES AND INJECTION SCREWS. MACHINES FOR CARRYING OUT THE PROCESS ON AN INDUSTRIAL SCALE HAVE BEEN DEVELOPED AND ARE NOW LICENSED FOR COMMERCIAL MANUFACTURE. THE ECONOMIC BENEFITS OF THE PROCESS APPEAR TO BE SUBSTANTIAL.

CASE (A): INJECTION NOZZLE, LIFETIME INCREASED FROM 6 MONTHS TO 18 MONTHS.

CASE (B): IMPRESSION MOULD, NUMBER OF SATISFACTORY MOULDINGS INCREASED BY FACTOR OF 10.

Figure 13

HIGH TEMPERATURE OXIDATION

ABSTRACT AUTHOR LOCATION	HOST MATERIAL	IMPLANTED SPECIES	ENVIRONMENT	REMARKS
#29 SARTWELL BUR. STDS.	IRON HIGH PURITY POLYCRYSTAL- LINE	CR Ti Si (Mo + Ta)	O <sub>2</sub> AT 300°C. 8x10 <sup>-6</sup> TORR.	Ti YIELDS BETTER PROTECTION THAN CR.
#43 PATERSON MELBOURNE	IRON STAINLESS STEEL	CR Ni	O <sub>2</sub> AT 500-800°C	PROPERTIES OF BULK STAIN- LESS STEEL AND SURFACE ALLOYS AT THE SAME COMPOSI- TION WERE FOUND TO BE ROUGHLY EQUIVALENT.
#38 HOWE BATH UNIV.	IRON	FE CR	O <sub>2</sub> AT 400°C. 0.1 TORR.	AFTER THE INITIAL 0.2 MICRON THICK CHROMIUM LAYER WAS CONSUMED (300 HRS) THE RATE OF OXIDATION WAS GREATER THAN FOR PURE, UNIMPLANTED IRON.

Figure 14

### HIGH TEMPERATURE OXIDATION

ABSTRACT AUTHOR LOCATION	HOST MATERIAL	IMPLANTED SPECIES	ENVIRONMENT	REMARKS
#21 PONS GRENOBLE	IRON	B AL	O <sub>2</sub> AT 400-700°C	THE INSOLUBLE IMPURITY, BORON, IS SUPERIOR TO THE SOLUBLE IMPURITY, ALUMINUM, FOR IMPARTING OXIDATION RESISTANCE. PROTECTION IS DUE TO THE FORMATION OF THE TERNARY OXIDES, FeAl <sub>2</sub> O <sub>4</sub> , FeB <sub>2</sub> O <sub>4</sub> .
#22 GALERIE GRENOBLE	IRON TITANIUM	SI, B IN FE CS IN TI	O <sub>2</sub> AT 600°C	AT VERY HIGH ATOMIC CONCENTRATIONS (30%) SI FORMS AN INTERMETALLIC COMPOUND WITH IRON WHICH GIVES ENHANCED OXIDATION PROTECTION.

Figure 15

### HIGH TEMPERATURE OXIDATION

ABSTRACT AUTHOR LOCATION	HOST MATERIAL	IMPLANTED SPECIES	ENVIRONMENT	REMARKS
#32 LEGG GEORGIA TECH	TITANIUM	Er	?	FOUND SIGNIFICANT DIFFERENCES BETWEEN SAMPLES IMPLANTED UNDER ORDINARY VACUUM CONDITIONS AND THOSE IMPLANTED UNDER ULTRA-HIGH VACUUM WITH IN-SITU ANALYSIS. CONCLUDE THAT THE CARBON LAYER FORMED DURING IMPLANTATION CAN SIGNIFICANTLY AFFECT OXIDATION KINETICS.

Figure 16

### HIGH TEMPERATURE OXIDATION

ABSTRACT AUTHOR LOCATION	HOST MATERIAL	IMPLANTED SPECIES	ENVIRONMENT	REMARKS
#7 BENNETT HARMELL	Fe/20%Cr/ 25%Ni/Nb STABILIZED STAINLESS	Ce Y	CO <sub>2</sub> AT 825°C	CHECKED THE EFFECTS OF CE AND Y IMPLANTS ON THE OXI- DATION RESISTANCE OF A STAIN- LESS STEEL USED IN GAS COOLED REACTORS. BOTH IMPLANTS GIVE BOTH REDUCED OXIDE THICKNESS AND IMPROVED ADHERENCE, WITH Y BEING BETTER THAN CE
#46 PIVIN U. PARIS - SUD	Fe/20%Cr/ 5% AL Ni Ni/34% Cr	Si S C Y	O <sub>2</sub> TEMPERATURE = ?	THEY WERE ABLE TO SHOW THAT YTTRIUM ENDS UP ENTIRELY IN THE OXIDE FILM.

Figure 17

### HIGH TEMPERATURE OXIDATION

ABSTRACT AUTHOR LOCATION	HOST MATERIAL	IMPLANTED SPECIES	ENVIRONMENT	REMARKS
#54 STOTT UMIST	NICKEL	Ni A C Cr Li	O <sub>2</sub> AT 1100°C	FOR SHORT TIMES (<60 MIN) CR IMPLANTS GREATLY IN- CREASED THE RATE OF OXIDA- TION; ALL OTHERS DECREASED IT. FOR LONG TIMES (>5 HRS) ALL IMPLANTS INCREASED THE RATE, PRESUMABLY BECAUSE THEY ALL CAUSED SIGNIFICANT CHANGES IN THE OXIDE GRAIN MORPHOLOGY.
#8 STOTT UMIST	Ni-20% Cr	Zr Cr Ce Ca Y Al	O <sub>2</sub> AT 1000°C	CA, CE, AND Y GIVE GREATLY IMPROVED OXIDATION RESIST- ANCE, DUE TO BOTH SLOWER GROWTH AND BETTER ADHERANCE OF THE PROTECTIVE Cr <sub>2</sub> O <sub>3</sub> SCALE.

Figure 18

## QUESTIONS AND ANSWERS

S. Cytron, ARRADCOM: Was there a concern expressed by the participants at the conference in terms of the need to fully characterize the specimens?

P. Sagalyn, AMMRC: Well, I have to say that the experts in this field are enormously characterization conscious. Every possible type of characterization method that you can think of was used by at least one group. One thing I have been saying to people here is that without characterization, implantation is of almost no value. In itself, characterization is a very active field of development.

J. Mayer, Cornell: I would like to propose that the various government agencies interested in ion implantation band together to have a common site or sites for implantation and characterization.

B. Hamill, Applied Tech Lab: What ongoing work is being done on rolling contact fatigue? Bearings, for example. Is there any independent work besides NRL?

C. Levy: Hopefully we will get to that discussion this afternoon and bring out all these questions about who is doing what, and who is going to do what.

R. Harrison, AMMRC: A question for Jim Mayer--When you say that the Government should build a big machine, are you talking about something on the scale of what Harwell has?

J. Mayer: No, but you do need a high energy machine. You also need one capable of high current with some analysis around it. I would like a center where various people can have access to do their own work.

R. Harrison: Are you saying there should be two kinds of machines--that one should be a research machine and another one should be a machine to irradiate routine specimens?

J. Mayer: Yes

R. Harrison: A question to Paul Sagalyn--Is there possibly a placebo effect in some of these improved results? That is, before someone would irradiate a die, say, they would inspect it and make sure that there were no gross defects, resulting in higher quality control of the die that is irradiated compared to the control specimens.

P. Sagalyn: Do you mean that one would irradiate their best dies? I really can't answer that question. The effects are so big that I doubt whether that is a significant factor.

**FOURTH SESSION:  
RESEARCH AND DEVELOPMENT**

RESEARCH AND DEVELOPMENT REQUIREMENTS  
FOR ION IMPLANTATION

Philip Parrish  
Army Research Office  
Research Triangle Park, NC

The field of ion implantation, as far as it relates to metallurgical applications, has created a lot of mysteries in terms of what we really understand about what's going on. A number of people here who are doing research in the area bring up the point that we certainly need to have more research on mechanisms that relate to the performance of materials that have been ion implanted. I wanted to elaborate on this point to some degree with my presentation. I wanted to point out just a few of the types of interesting phenomena that we have seen that certainly need more explanation if we are really going to take advantage of ion implantation in engineering systems. One which has already been discussed is the ion implanted metal surfaces with improved aqueous corrosion behavior (see Table I). There has been a lot of work at Harwell and the UK on ion implanted surfaces having improved oxidation resistance. A recent report from Harwell came out early this year summarizing that area. Jim Hirvonen and people at the Naval Research Lab, and also at Harwell have shown that there are certainly interesting results in the wear area; recently these results, not only in metals but in ceramics, have surfaced, and I wanted to show you some further data on the ceramics wear question. At the Manchester Conference there was a paper on using ion implantation to improve adhesion of polymeric coatings on metal fibers which I thought was quite interesting. And then there were talks on tailored catalytic behavior of metallic surfaces for either control of corrosion or any other catalytic application you have in mind where you can tailor a surface to form the type of catalyst you want. So there are a lot of opportunities, but there are also a lot of challenges in terms of understanding the mechanisms. So I think there is a lot of room for research in ion implantation. One intriguing point is the situation where you might want to form some sort of non-equilibrium condition on a surface, such as exceeding the solid solubility limit (Table II). This is a relatively simple task for ion implantation as compared to other techniques and may extend the usefulness of a limited range of commercial alloys. This might also obviate the need for developing complicated processing such as that for rapid solidification rate (RSR) powders. In the case of RSR you make the powders and then try to consolidate them while maintaining them in solid solution.

The critical and strategic materials issue really gives us a great opportunity to do research on corrosion and other mechanisms where we really do have to get a handle on how we can substitute for these materials. This will mean either substitutes or finding new processing methods, or not use the bulk compositions so much, but use the surface properties much more often than we do at the present. One of the things that I gather that is needed is greater availability of ion implantation equipment in the form that we need, not just adapting from the machines that were put together for implanting the silicon wafers and so on (Table III). Also the fellows in the universities who need to be involved in this field need to have more access to implanters. There was an overload at the Naval Research Lab. Jim Hirvonen is very generous when allowing people to get samples implanted there, but we really have to come up with more sources like that. There was talk about experimental and theoretical research into the range and distribution of implanted

AD P003951

ions and especially with the ion mixing. Now we really need to have a better handle on that. Another subject that Jim Mayer was talking about earlier, along with his plea for the better facility, was the improved ability to analyze or characterize these surfaces very carefully. We certainly need that. The aqueous corrosion research which I have been involved in and other work that I have seen from UMIST shows that the corrosion behavior on most of the surfaces that have been implanted is strongly related to the chemistry of the surface--right at the surface (Table IV). I have not found much of a strong effect of radiation damage on corrosion behavior. I thought that there may be an effect, but in my work and most of what I have read, I haven't seen that effect is really there. Now in the oxidation case, I think that there is some evidence that radiation damage is very important on the growth of the oxide. One thing that came out of some of the work I have done, some of the work Clive Clayton has done, and others, is that we really need to know what the depth profile is, and what the structure is. That has to go along with any research effort. Professor Woolf at the UMIST conference made a strong plea for determining anodic and cathodic reaction kinetics especially in terms of understanding catalytic behavior of most surfaces. In the area of oxidation, several years ago, there was quite a lot of concern about the shallow implant depth, that it would be a strong limitation in affecting the long term oxidation behavior of these surfaces (Table V). Actually, this turned out to be a bit of an opportunity because this implant depth problem seemed to worry them enough that they really took to heart the seeking of mechanisms and close characterization of the surfaces. Harwell, has studied a lot of different systems. You can see chromium has had 35 different elements implanted, mainly in Group III and rare earth elements. Out of those, 32 of them showed improved oxidation resistance. Recently there has been more work in the iron-chrome-nickel systems, nickel-chromes and now getting into the Nicraly's and the iron-nickel-chrome-aluminum. So there is a lot of research going on in oxidation, especially at Harwell. One of the things that I think is needed now is to start looking at hot salt corrosion where you have sodium sulfates and sodium chloride in the gas. This is a result from Harwell where they implanted barium into titanium, apparently forming a titanate. Figure 1 shows oxide thickness versus oxidation time for this system. As you increase the implant dose, you wind up reducing the oxide thickness quite dramatically. The figure shows about an order of magnitude and even more as you go further out in time. So it is a dramatic demonstration that there is something to this. Figure 2 shows another case with calcium implanted. The oxide actually grew faster. So you can't always rely on protection since you really don't understand completely the mechanism. We are not talking about a panacea here. We really do need to understand the mechanisms of oxidation for implanted surfaces. In wear behavior, some of the results have shown improvements in life by a factor of four (Table VI). Benefits persist even to a depth  $10^3$  times that of the implanted layer thickness.

Some results with interesting hardness and wear behavior of implanted ceramic surfaces have also been reported. Paul Sagalyn mentioned work by Trevor Page at Cambridge (Table VII) and I just wanted to point out this work on silicon, silicon carbide, single crystal silicon carbide, and reaction-bonded silicon nitride. They did several mechanical tests: microhardness, indentation fracture, single point diamond scratch test, and the microhardness test showed that the surface is actually softened at and above this critical dose level. We don't understand this at the moment. These were some of these numbers: silicon itself implanted at that dose level ( $10^{17}$ ) going from a Vickers hardness 1200 down to 900; silicon carbide 3500 down to 2500; reaction-bonded silicon nitride hardness reduced from 3500 to 2000. In the indentation test, the unimplanted surfaces showed the typical

radial and lateral fractures that you see for these ceramic materials. But above the critical dose, for silicon carbide there was no lateral fracture and the material exhibited plasticity. Silicon was pretty much the same, except there was a small amount of lateral fracture in that case. In the scratch test that they ran; the scratch track showed plasticity (Table VIII). They were similar to the ones seen on the silicon nitride. TEM studies showed that the implanted silicon carbide beneath the scratch track had transformed. It was originally hexagonal, but had transformed to a cubic structure. I am not sure whether that was ascribed to the implantation, but I assume so. The silicon was totally amorphous as implanted, but also behaved plastically. The conclusions that they came to were that for silicon in silicon, the surface compressive stresses affected the lateral fracture; for silicon carbide, this phase transformation which they said went hexagonal to amorphous to cubic seem to be the key yielding more slip planes in the cubic case. There are some unanswered questions here: what's the cause of this critical dose effect, and what happens in other ceramic materials? They were starting to look at tungsten carbide-cobalt combinations. (Question from floor: what's the evidence of plasticity? How did they determine that?) Well, just the appearance of the wear track, really I guess. I will have to show you the paper. There is an interesting paper by Professor Hale at the University of Missouri at Rolla, who is looking at the adhesion of polymer coatings on metal surfaces, the effects of ion implantation on this. Figure 3 shows the results. Here he had a polymer that was deposited on a platinum wire in a glow discharge. This was a wire for a bio-medical purpose which often fails in the body due to exposure to the saline solution, a breakdown in the coating. The implanted carbon assists in chemical bonding, and now, whereas they were getting failure in boiling water tests without implanting, they are getting survival of these coatings and are very optimistic about how they will perform in implant. There was a paper on microhardness of thin surfaces (Figure 4). We've got a little bit of information about that. The paper from Lancaster is a capacitive method, an indentation method where you are able to look at and record the elastic and plastic deformation of thin surface layers. Here is some preliminary information about the nitrogen implanted iron foils which they have been studying. This is a plot of penetration versus the force on the indenter on an unimplanted case and various levels of implantation of nitrogen at 300 keV. There is a good correlation between surface hardness and implantation.

My main message is that there are a lot of questions right now about the behavior of metal surfaces and also ceramic surfaces after they have been ion implanted. Just what are the opportunities? How far can we go with this? So, I think we're definitely in a situation where we need to strongly support research efforts in this area. We really need to use ion implantation as an applications opportunity tool and as a research tool where we can create unusual situations that are difficult to make metallurgically under conventional processing techniques, such as going past the solubility limit in corrosion studies. Thank you.

## Table I

### ION IMPLANTATION

#### Some Research Needs and Opportunities

Overview - Some promising results of recent studies (<5 years) which need further research:

1. Ion implanted metal surfaces with improved aqueous corrosion behavior.
2. Ion implanted surfaces with improved oxidation resistance.
3. Ion implanted metal surfaces with improved wear behavior.
4. Ion implanted ceramic surfaces with reduced hardness and indentation behavior indicating plastic deformation.
5. Ion implantation improved adhesion of polymeric coatings on metal fibers.
6. Tailored catalytic behavior of metallic surfaces.

Research is ongoing, but more is needed, to unravel the mechanisms underlying these beneficial effects.

## Table II

#### Some Other Opportunities:

1. Alloy additions which are difficult or impossible by conventional metallurgical techniques.
2. Possible basis for addressing some questions concerning properties RSR and other nonequilibrium materials.
3. Corrosion and wear mechanisms studies.
4. Critical and strategic materials.

## Table III

#### Some Needs:

1. Greater availability of ion implantation equipment for researchers.
2. Experimental and theoretical research to increase reliability of predictions of range and distribution of implanted ions.
3. Enhanced capability to characterize implanted surfaces.

Table IV

AQUEOUS CORROSION AND CATALYSIS

1. Corrosion behavior of surfaces has been related to the change in surface composition of the surface via implantation.
2. No evidence of a strong, lasting effect of radiation damage on corrosion behavior.
3. Need for careful characterization of surface composition and structure.
4. Studies needed to determine anodic and cathodic reaction kinetics to gain further understanding of corrosion mechanisms, catalytic behavior.

Table V

OXIDATION BEHAVIOR

- Early concerns about shallow implant depth and long-term oxidation protection.
- Mounting evidence that ion implantation can result in enhanced oxidation resistance.
- Some systems studied:

Cr - 35 group III and rare-earth elements

Fe - Cr, Si implantation

Ni - many ions

Fe-Cr-Ni }  
Ni-Cr } Y and Ce

Fe-Cr-Al-y

Fe-Ni-Cr-Al

Studies needed: Hot salt corrosion studies.

Table VI

WEAR BEHAVIOR

1. Improvements in life by a factor of 4 are typical.
2. Benefits may persist to a depth of  $10^3$  times that of implanted layer thickness.
3. Interesting hardness and wear behavior of implanted ceramic surfaces.

Table VII

EFFECT OF ION IMPLANTATION ON HARDNESS AND WEAR BEHAVIOR OF CERAMICS

Roberts & Page, Cambridge University

Si }  
SiC (Single crystal and RB) }  $N_2^+$ , 80 - 100 keV

Mechanical Tests: -  $\mu$  hardness  
- indentation fracture  
- single point diamond scratch test

$\mu$  Hardness

Surfaces softened at and above  $4 \times 10^{17} N_2^+/cm^2$

Si ————— 1200 —————> 900  
SiC ————— 3500 —————> 2500  
R.B. SiC ————— 3500 —————> 2000

Indentation

Unimplanted - radial and lateral fractures

Implanted (above "critical dose")

- SiC no lateral fracture; plasticity
- Si a small amount of lateral fracture

Table VIII

Scratch Tests

- SiC - scratch tracks showed plasticity
- TEM studies showed implanted SiC beneath scratch track had transformed  
HEX → CUBIC  
Dislocations
- Si - Totally amorphous as implanted
- behaved plastically

Conclusions

- Si - surface compressive stresses affect lateral fracture
- SiC - HEX → amorphous → CUBIC transformation seems to be the key - more slip planes

Unanswered Q:

1. What is the cause of the "critical dose effect?"
2. What happens in other ceramic materials?  
(WC/Co) . . . . .

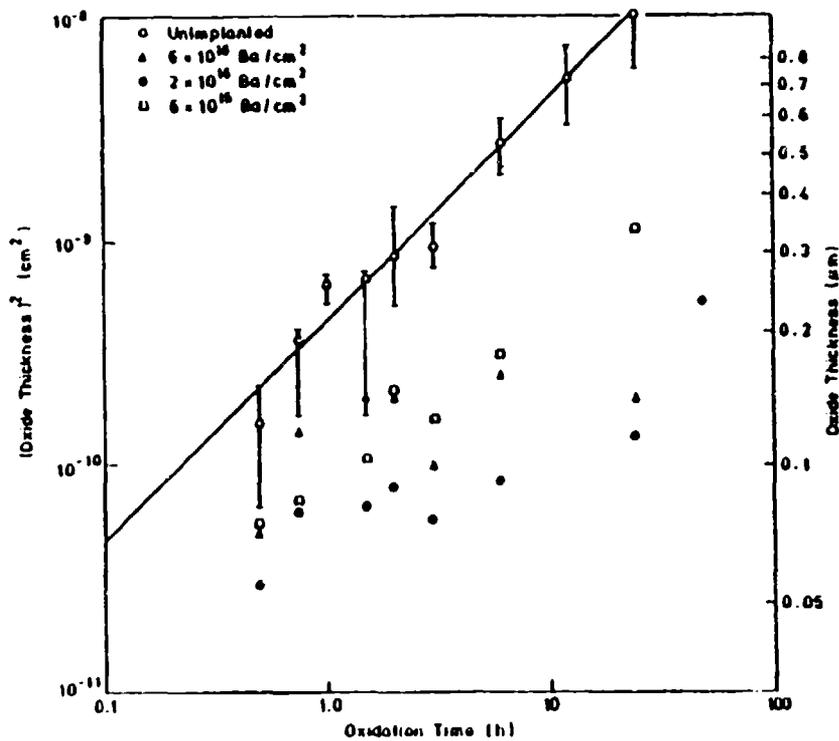


Figure 1. The influence of the implantation of barium ions upon the kinetics of oxidation of titanium in oxygen at 600°C (after Lucke et al., Ref. 6).

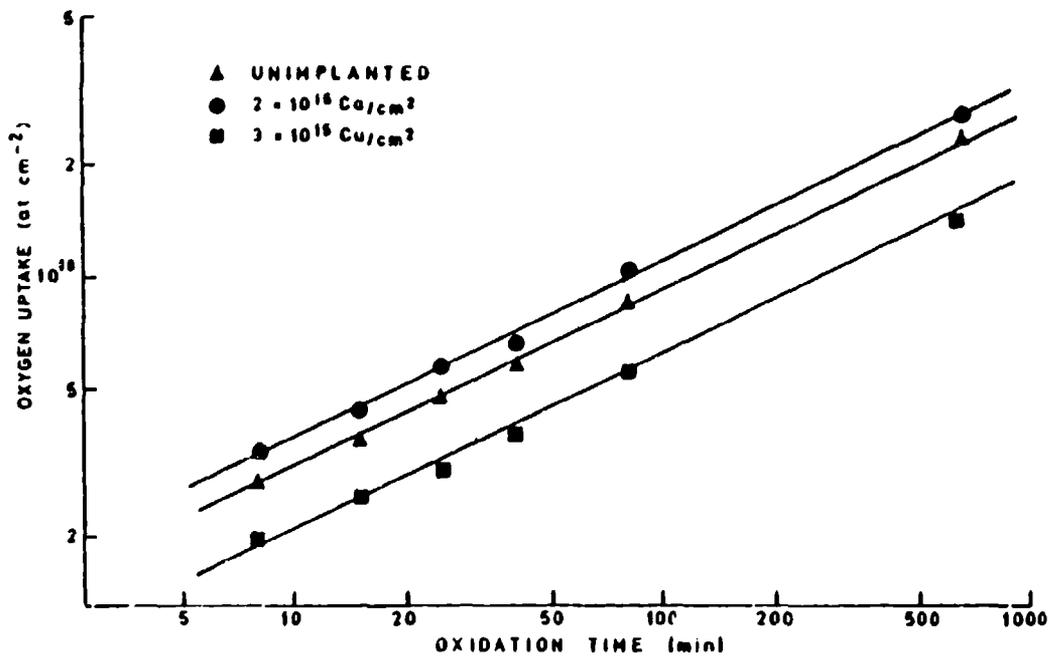
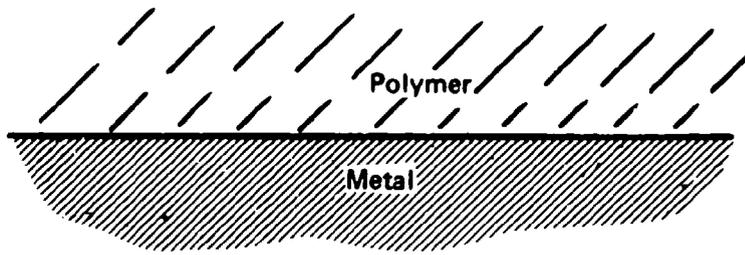
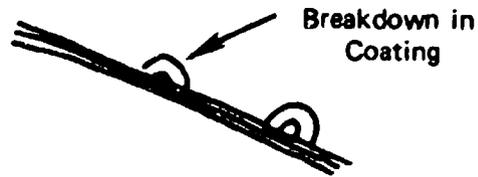


Figure 2. The influence of the implantation of copper and calcium ions upon the kinetics of oxidation of zirconium in oxygen at 450°C. The slope indicates a parabolic oxidation (after Bentini et al., Ref. 9).



(By Glow Discharge)

Polymer coating on PT wires for biomedical purposes  
- often fails in body



Implanted C ( $10^{16}/\text{cm}^2$ ) to assist chemical bonding survives boiling tests  
in 0.9% saline solution

Figure 3. Enhanced adhesion of polymer coating on metal  
surface by ion implantation treatment.  
(Prof. Hale, University of Missouri, Rolla)

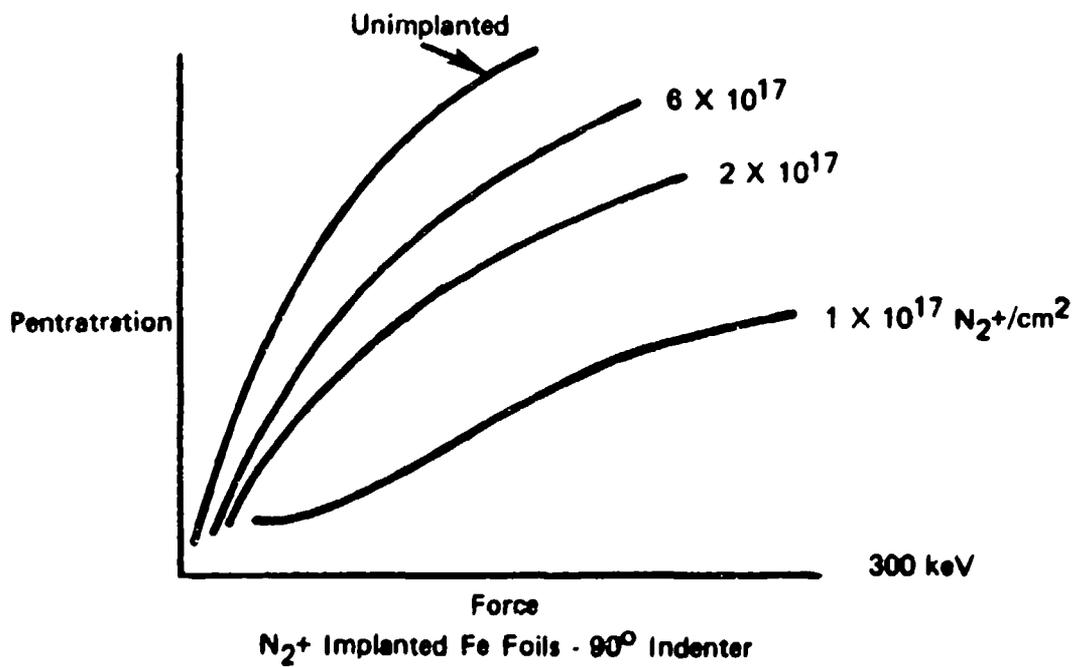
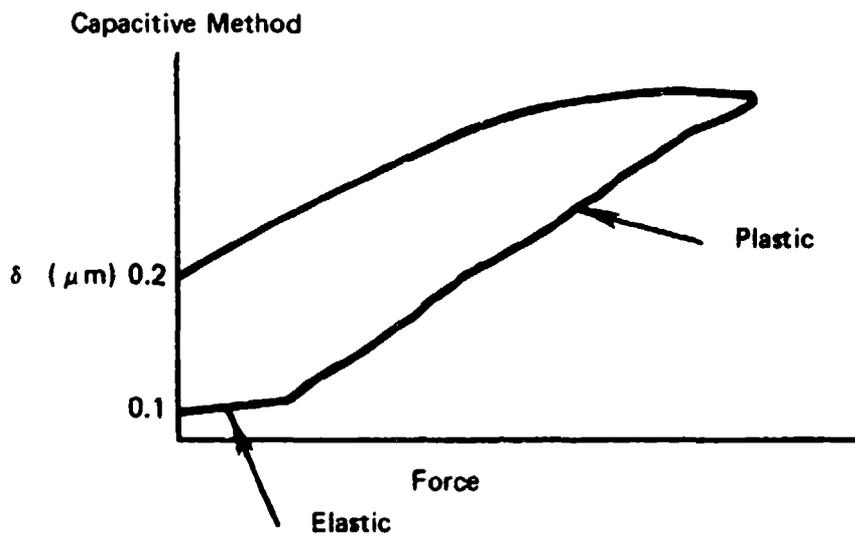


Figure 4. Ultramicrohardness measurements.  
(D. Newey, Pollack University of Lancaster)

## QUESTIONS AND ANSWERS

D. Viechnicki, AMMRC: What was the evidence for plasticity in silicon carbide and silicon dislocation studies?

P. Parrish: It was the dislocation network that they saw in the TEM studies. I will have to get you the paper.

R. Quattrone, Construction Engineering Research Labs: Phil, to go back to Trevor's work. He had done indentation hardness, of course, and was looking at the Hertzian cracks at the tip of the hardness indentation which can be related to the fractured toughness. Now I don't know whether he looked at the same sort of thing when he was doing this, but that, plus his dislocation studies, was how he was establishing the toughness or ductility changes in the system. That might supply the answer.

P. Parrish: I don't remember that he brought that up in his paper, but I do remember he talked about the dislocation structure.

J. Cox, Benet Weapons Lab: I noticed you had oxidation studies at 600° centigrade and 450° on those titanium systems. Is anybody studying the temperature stability of ion implanted materials, and, if so, what sort of results are they getting, say in terms of the melting temperature of the base materials?

P. Parrish: I can't answer but maybe you can look at that Harwell book. I'm not sure how high they are going in terms of the melting temperature. Does anybody else want to respond to that one?

J. Hirvonen, NRL: I believe that book will. I think they are going as high as about 1100° in the coatings. I don't know how that compares with the melting temperature.

AD P003952

NAVY PROGRAMS ON ION IMPLANTATION FOR MATERIALS MODIFICATION

James K. Hirvonen\*  
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Washington, DC

Today, I would like to give you an idea of some of the things that we're involved with at NRL involving ion implantation. The program started some 4-5 years ago trying to emulate the results of our English friends like Geoff Dearnaley and Nick Hartley at Harwell, and from the beginning, it was clear that there were a lot of exciting things to see. The first picture is what an ion implantation machine looks like (Figure 1). Essentially it is an isotope separator with an ion source that can provide a wide variety of species. There are about 1200 of these machines out in the world now for the production of integrated circuits. The point I will come back to is that the ion beam technology will be there once the use is established and the scientific merit and the economic merit for particular applications of metals are shown. What it consists of is 1) producing an ion beam, 2) an ion source extracting that beam then putting it through a magnetic mass filter, and picking out the isotope of interest. In most production machines, this whole terminal is raised in voltage so one can produce up to 200,000 volt ions. The beam is electrostatically scanned over the target as we will see later. In this case, the target represents a bearing race. The type of distribution that results are shown in Figure 2, a semi-gaussian type structure. This indicates the fact that an element comes to rest in a solid by losing energy to atoms in a statistical manner so you have some fluctuation in the range. The surface concentration is determined by the combination of energy and sputtering effects so one can change energies and fluences to try to produce the desired surface concentration. To be noted, obviously, are the rather shallow depths, typically less than one micron and sometimes only several hundreds or thousands of angstroms. The fact that you do not have an interface here is expected to improve the adhesion. Figures 3 and 4 show some of the particular advantages and limitations of the process. It is strictly a line-of-sight process, an intrinsic limitation. The shallow penetration is also intrinsic, but we'll see in many cases it isn't necessarily as imposing a constraint or limitation as we might initially think in terms of engineering applications. The third and fourth items I would call relative limitations. Depending on the particular application at point, they may not be too serious. Again, the critical capital costs here are relative, and I will try to address those under specific applications. Figure 5 illustrates some work in bearing materials. I will show a few examples involving bearing applications, both for wear and corrosion. We have long thought that a potential application would involve high value "real estate" items such as bearing materials and here we see the results of an experiment in which we are looking at the kinetic coefficient of friction versus distance travelled for four different cases. In each case the test involves a ball on a disc geometry in which the disc (the 52100 steel disc) has been implanted. Under dry conditions, (curve a) we see one sort of behavior. After implantation of a high dose of titanium, we see a significant reduction in that coefficient of friction. Under very poor lubrication conditions (i.e., with a very simple molecular structure fluid design to take heat away more than provide any sort of boundary lubrication), we go from a situation where we have a lot of stick-slip, which is found in the case of the unimplanted, to just a steady frictional value.

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We have also looked at the wear of these parts. This was worked on by Carosella and Singer at NRL, using a pin on disc geometry. Looking at the wear volume versus distance travelled we see for the unimplanted case a sudden increase in wear and implanting those species which are shown to reduce the wear in many other systems (e.g., boron) seems to have little or no effect. On the other hand, the system implanted with titanium shows an incubation period prior to normal wear, and micro-analysis of this system shows that the near surface layer of this disc consists of an amorphous titanium, iron and carbon layer in which the carbon is gettered from the vacuum by the titanium as it sputters away the surface. This is subsequently mixed into the surface to produce what is found to be a very thin amorphous layer, having the wear characteristics of a refractory carbide. Using abrasive wear techniques with a diamond slurry, Singer et al. found that the wear resistance relative to that of a martensitic alloy, which is already rather good, can be a factor of 4-7 times as high. We are examining potential applications for this type of treatment. Figure 6 is a result from Geoff Dearnaley and co-workers in which they looked at time to failure against percent failed. This is termed a Weibull statistic. What they claim is that they have improved the rolling contact fatigue of these lifetimes in a four-ball tester in that all the ion implanted results are above those for the unimplanted. If you read their paper carefully, they acknowledge that they don't know if it is due to the nitrogen chemical effects or to some tempering effect due to the heating by the beam. As we will see in normal fatigue, there are certainly important chemical effects present as we will see later. As a result of finding this very hard refractory titanium-carbon-iron layer we are doing some work with Professor Ramalingam at Georgia Tech in which we are implanting high speed tool steel inserts (Figure 7). He has an instrumented lathe looking at the cutting forces during wear of the machine tool bits. The results are shown in Figure 8. He tested for short amounts of time. These are very initial results but they show that there are very significant differences between the unimplanted and implanted high speed tool steels. This test was done under non-lubricated conditions on a medium carbon annealed steel but there is much more work to be done to corroborate these test results and to find under what conditions it is effective. It should be pointed out now, that nitrogen implantation of tool bits does not help this type of wear. And that should be apparent because it is known that nitrides that have been found following implantation are not thermodynamically stable at the temperatures of the cutting edge. However, this thin amorphous layer does hold up, at least to an extent. Just how prolonged that will be, or how useful, remains to be seen.

Another sort of experiment involving wear is in work done with Professors Clive Clayton, Herb Herman, and Wen Wei Hu a graduate student at Stony Brook which actually follows on some work I will describe later but it involved cavitation wear using ultrasonic horn (Figure 9). In these tests one looks at weight loss and the surface following exposure to ultrasonic cavitation waves in distilled water. This is done for 1018 steel, a low carbon steel. The results are shown in Figure 10. Here we look at the total weight loss after different times of exposure and we see again there is a steady weight loss from those samples that have been unimplanted or those which have been freshly implanted. I will go into the ramifications of this later. However, it is shown that for those samples which have been implanted and aged (which we think has to do with the redistribution of the nitrogen perhaps to dislocations) there is an incubation period before you get significant weight loss.

Another study involving bearings is some work done on beryllium gas bearings, with people at Charles Stark Draper Laboratories. These gas bearings are shown in Figure 11 and these are used in inertial guidance systems. They typically consist of beryllium bearings with a hard wear resistant coating. There are grooves machined into the hard coatings to promote the aerodynamic support for these high speed

bearings. Figure 12 shows some of the considerations needed for getting the types of materials. Beryllium, as it says, meets structural criteria, but it is not sufficiently hard or wear resistant. Ceramics might be an alternative, but they are difficult to machine. So there is usually a compromise involving coatings. Sometimes there are problems with this, in that the plasma-sprayed ceramic can be porous, a condition that affects their stability. Sputtered coatings lack good adhesion, and diffusion case hardening requires high temperatures. One thing tried is boridization of the beryllium substrate but it was found that beryllium prefers going into the boron, instead of vice versa. So they suggested that we start looking at ion implantation as a possibility for producing a hard coat.

We did several implants at different energy levels to produce a relatively uniform layer in the first micron of the surface (Figure 13). In fact we have now gone to 50-60 atomic percent in that first micron and then annealed the system so as to promote the formation of a particular boride type, BeB, which is one of the hardest known beryllium borides. This represents a case where you can implant the material (boron) you need to produce the phase you want and avoid all the diffusion problems that are present with the conventional boridization treatments.

Figure 14 shows some wear tests done by Prof. Rabinowicz at MIT and one of his students in which there was a 52100 pin riding on a disc that had been implanted. The unimplanted case is not a fair test because it hasn't had any treatment at all and shows severe erosion in the wear scar. The aluminum oxide which is conventionally used as a coating, shows a much reduced wear and, but with somewhat higher coefficient of friction. The best case shown is that for 40 atomic percent of implanted boron shows very slow wear and a much reduced coefficient of friction. There are a lot of things to be understood here. If we go to 60 atomic percent, results aren't as good.

In a moment I will show you some pictures of the objects that the Harwell people have treated. First, Figure 15 shows some of the work done by the Westinghouse group (Ram Kossowski and Bob Fromson) who have implanted a number of articles Westinghouse uses in their processings plants or production plants. One is a cobalt cemented tungsten carbide punch and die for index slottings for rotor laminations of electric motors of this particular type steel. They see a much increased lifetime (4X-6X) and because these things are so expensive (they can be thousands of dollars a pair because they are closely matched), that can be quite significant. Even after resharping the top edges they find continued improvement from the sides.

Another example is that of tungsten carbide drills used in printed circuit boards showing very similar results to the Harwell work. To show you that we are in fact honest, some high speed twist drills of theirs that we implanted for them show no improvement but, instead, a lowered lifetime. Figure 16 shows some of the cobalt cemented tungsten carbide wire drawing dies that Dearnaley and company are looking at. These are both for ferrous and non-ferrous wires, and what they find is typically a 2X-4X decrease in wear. That results in extended times between die change which can be very important in the operation in that the down-time can be expensive. Figure 17 shows what's called a sprue bushing and runner block components for plastic injection molds. This is an area which Dearnaley has been working in over the last couple of years. These are typically chrome-coated moldings which are very precise and therefore very expensive. They can be a few thousand pounds each for the big molds. Typically, they see improvements of 4X-6X. Figure 18 is an injection molding screw costing a couple of hundred dollars and they figure they can treat it for small

fraction of the price. This drives the plastic into the mold and they see most of the wear at the end because of the fillers that are in the plastics. Nitrogen implantation, again, gives a factor of at least 6X in the lifetime. Next are some mill rolls for hot rolling non-ferrous (copper) rod (Figure 19). They have also done iron and steel and again see a significant improvement, not only in the lifetime but in the surface finish of the component that goes through the rollers. Nitrogen implantation reduces the adhesion. That same observation is true for the tungsten carbide drawing dies, i.e., that quality of the drawn wire is improved using implanted dies.

Figure 20 shows a schematic for some fatigue tests that we did with Professors Herb Herman, Clive Clayton, and Wen Wei Hu, the graduate student at Stony Brook, starting a few years ago. It was initiated after reports from the Harwell group that they had seen reports of increased fatigue lifetimes up to factor of 10 in titanium, stainless steel and some maraging steels following nitrogen implantation. We looked at what was available at the time which was 1018 steel, a low carbon steel, and Figure 21 shows the results. This shows the so-called S-N curve (stress versus cycles to failure) with a logarithmic lifetime scale. For the unimplanted case, we get a broad scatter band, and the data points, which include the arrows, indicate that there was no failure of those samples. The effect of implantation was to increase the time to failure at a given stress. In the high cycle region the endurance limit, that is the stress at which you can undergo essentially indefinite flexing, is increased.

What was also noted here and isn't fully understood yet, is the fact that it was important to age these samples. Historically we implanted some samples and four months went by before testing the first one, which tested to  $10^8$  cycles without failure. Freshly implanted samples only lasted about  $10^6$  cycles. We asked ourselves what's going on? It must have to do with interstitial diffusion. So by artificially aging them we showed there is a increased tendency to extend the lifetime and some internal friction measurements which I don't have time to go into, show some very interesting effects.

Some work that Ron Vandiman at the lab did on titanium, 6% aluminum, and 4% vanadium show that nitrogen implantation helped slightly in the endurance limit, but carbon was much better (Figure 22). It was very curious because in this case it was found that many of the initiation sites for failure were sub-surface in origin and the order of microns, and yet the effect of implantation had an effect on the accumulation or the emergence of these to the surface. I do not have an explanation for that. Figure 23 shows some results that Dearnaley et al. from Harwell reported last summer at a meeting in Kingston on accelerators. He worked on the same Ti alloy trying to look at fretting fatigue in which you put fretting pads against a sample which has small oscillatory motion. One of the conjectures is that fretting fatigue is related to oxidation resistance under the oscillatory motion (Figure 24). So they looked at ion implantation. In fact, working with Rolls Royce, they have looked at between 55 and 60 different surface treatments for improvement of fretting fatigue and found that ion implantation in combination with shot peening was the third best. The others which were better were D-gun/treatment, and flame spraying. However, the others all involved a significant dimensional change. The effect of implantation of barium, an ion which has been shown to significantly reduce oxidation, used in combination with shot peening, significantly raises the endurance limit of the samples under fretting fatigue conditions.

Another area that we looked at with T. Stet at Pratt & Whitney in Florida and Dr. Fujishiro from the Air Force Materials Lab is the protection of titanium compressor blades. They have a program in the Air Force to increase the high temperature capability of titanium alloy compressor blades. They were ion plating the blades with microns of platinum to protect them against oxidation. Our adjunct study involved implanting the surface with very modest doses (monolayers) of platinum in anticipation of the ion plating to see if we could make the interface more gradual. Unfortunately, we didn't get our implantations done in time, and they had to be tested by themselves. The two highest energy, higher dose points were comparable to the ion plating, and the results were felt to be significant (Figure 25). What is thought to be happening here is that implantation is affecting the oxidation of the surface which in turn affects the crack initiation, I believe it is called alpha casing. Having done actual compressor blades, we have gone back to doing laboratory rotating fatigue samples with platinum and found that these results are also consistent. So there is reason to believe one can now try other elements, which we are doing. Barium, for instance, is a lot easier to obtain than platinum, and may improve the fatigue lifetime. It should be mentioned that it is possible under high temperature conditions to have barium inhibiting oxidation up to 50 or 60 microns in depth.

Figure 26 shows some work from Dearnaley et al. at Harwell in which they have taken the titanium 6-4 alloy and have used ion beam mixing to alloy tin deposited onto the surface. Titanium as you all know is very bad about sticking and galling. The approach used was to first deposit a layer of tin, which by itself is quite ineffective for reducing friction. Subsequently they passed a high energy nitrogen beam through it. They then characterized the distribution using back scattering. You can see that initially there is a well defined layer of tin relative to the substrate. Following implantation, or mixing, they see a peak which extends to a depth of a few microns. That is to be compared with the few thousand angstroms that the initial nitrogen beam will penetrate. What they think is happening is that tin-vacancy complexes are diffusing in a thermally activated enhanced mode. The mechanical properties, i.e., friction and wear properties of this system, are shown in Figure 27. What is found basically for the unimplanted case is that the friction is steady whereas the wear, indicated by displacement of a pin, starts going up. In the implanted case, however, they found that the friction is significantly lower and the wear stays constant and low. So they have improved the surface. There are potential applications here of technological importance. In summary, one finds in many cases unexpectedly large results or long lasting effects in both wear and fatigue (Figure 28). It is obvious we need to understand these much better, since we feel there is potential for application to small, expensive, or critical parts.

I'd now like to discuss some of the chemical changes that are affected during ion implantation. The first involves bearings. This is a program that we started, three or four years ago with people at the Naval Air Propulsion Center (Ray Valori, Dan Popgoshier). We now have a program also with the Naval Air Systems Command (Mike Valentine). The present work is being sponsored by them. Prof. Clive Clayton has been extensively involved in this program and we couldn't have done it without him to tell us what sort of corrosion properties we were obtaining. Figure 29 shows a bearing which has a corrosion problem. It is called a hinge-pin bearing and it comes from a Sikorsky helicopter. Its purpose is to give oscillatory motion to the rotor as it is going around. In order to protect the bearing the inner race has a rubber sleeve about it which is designed to hold the lubricants in and keep contaminants out. Unfortunately, the rubber seal provides a geometry which is ideal for a type of localized corrosion, called pitting corrosion, as evidenced in the photo by

a line of severe pits. These pits are aggravated by chlorine in the oil. If they start at an edge, one can and sometimes does get catastrophic failure due to fatigue. The normal procedure during rework is to machine down the corroded area, plasma spray it with tungsten carbide and then remachine it back. That gets expensive. Figure 30 gives some data on another type of bearing we are looking at, mainshaft bearings used in the F-4 plane. The average cost of the bearing has gone up from the figure shown. Aerospace bearings are very expensive because of the tight dimensional tolerances, so for this one type of bearing alone we have a very significant cost item. Figure 31 shows our approach to the problem. Prof. Clayton will be discussing more of the corrosion results tomorrow. I just want to give you an idea of what the program is about. We worked with Clive, looking and trying to develop implantation conditions for both bearings, one an M50 steel, the other 52100. We have so far implanted some 20-30 shaft bearings, all of which have been tested for rolling contact fatigue lifetime, and we have seen no degradation at all. NAPC did engine tests, and we have also done field service evaluation tests. We have implanted 12 of the rotor hinge pins. They will be installed in helicopter rotors by September and will be tracked as they come back for repair. We'll also be involved in storage tests.

We are now getting into more advanced bearing steels that have higher toughness and we feel it is very important to try to get co-op programs going with engine manufacturers so that when this new technology gets sufficiently advanced, they will be ready to pick it up. Bearing engineers are very conservative people, as they well should be. I think working together is the only way development through transfer is ever going to get done. Figure 32 shows important requirements and what we have demonstrated so far is that we have met these requirements with room temperature processing methods. We haven't lost hardness. There has been no degradation of contact fatigue, in fact there has been an improvement of the wear characteristic. There are no significant dimensional changes. Actual changes will be the order of less than a microinch which is quite within the tolerances for these large bearings.

Figure 33 mentions the types of tests that are done. Clive Clayton will talk about these since he has done them for us. I will show you one simple test that we can do in our lab. This test is depicted in Figure 34. Basically the corrosion problem with bearings in service is that engines in intermittent use experience pitting at the line of contact between the rolling element and the race. Of course the actual race would be round but a flat surface is good enough for this sort of test. We test for evidence of pits at the contact line for different conditions. This is done in a chlorine contaminated oil under cyclic temperature extremes such as you would expect in the engine. Photomicrographs show the fact that we do get a large improvement. You see here a metallographically prepared surface which is flat. Without implantation there is a line of pits and also general severe general corrosion but after implantation with a variety of species one sees there is no line of pits and only some debris from the contaminated oil. Clive will describe more of the other corrosion tests supporting these results. Figure 35 shows the ball bearings being implanted. They're 7/8 inch in diameter for the F-4, 23 of them per bearings, so we are doing two tests. What you see is a nice hue that results from the light emitted by a small number of atoms that are emitted from the surface.

The projected treatment times in Figure 36 give you an idea of what is possible. We are dealing with these sorts of fluences and you can ignore the bottom line in the

figure. We are dealing with single energy implants for this, and the data shown is for a different project. Typically we're dealing with 150 kilovolts. Beam currents that are available with our medium current machine may be a little bit better, perhaps half a milliamp. They've gone up in current with machines such as those used for integrated circuits now. There are ion sources made today that put out up to 10-25 milliamps, so for this sort of bearing area this gives you a reasonable processing time. Basically you have to worry about removing the heat, lowering the temperature so you don't lose temper on the bearing. This may mean spreading the beam out over a large area. But the technology is there to build the machine for this if it is desired.

The next example I would like to discuss is some work by McCafferty and Hubler at NRL involving a study of corrosion mechanism. What we have here are three pictures of titanium surfaces imbedded in epoxy (Figure 37). First of all, we have a metallographically flat sample before the test and we see there is no diffuse scattering so it looks dark. That is because it is very shiny. The unimplanted sample, after eight minutes of corrosion, looks very white because there is a lot of diffuse scattering and you can see it in this picture here. On the other hand, the implanted sample, continuing about ten monolayers of palladium, continues to show a rather smooth surface and lack of attack after this rather brutal treatment. Now it has been known for many years that small amounts of palladium or platinum in titanium improved the corrosion resistance. There are speculations of why, but I think this experiment showed quantitatively for the first time what is happening (Figure 38). In the case of the implanted alloy we have a buried palladium distribution with the original surface being indicated here. This was characterized by Rutherford backscattering after different amounts of exposure to the solution. The depth scale being 0 to about 1000 angstroms going from right to left in the figure. We see that the backscattering spectrum begins to sharpen and with the use of a Xe marker atom, not shown here, one can determine the distance from the original surface. As you increase the time, the distribution gets narrower, possibly as a result of palladium going to the surface in the form of islands, but with the critical concentration increasing at the surface to a point where it dominates in the corrosion behavior of the surface and shows that even a small amount of 10 monolayers can dominate the surface and stop the corrosion attack. In this case corrosion is down by 3-4 orders of magnitude from the initial rate of attack. So I would like to stress that, as this example shows, implantation can be used in very powerful way for the introduction of controlled species for the study of basic mechanisms. I think this use is probably not getting enough attention. I know certainly in DoD the emphasis is less on understanding, more on products. But it should not be overlooked.

Figure 39 shows results of some oxidation work we did a number of years ago. The figure shows the oxide thickness squared versus oxidation time for various conditions of barium implantation. Earlier work at Harwell showed that barium reduced oxidation significantly so we wanted to look at the kinetics of oxidation. We see here a parabolic behavior, represented by a 45° line on this log-log plot, to a very significantly reduced rate.

I would like to show now an example of an application where one is involving both oxidation and mechanical effects. This is Harwell work again. Figure 40 shows a burner tip from an oil burner in a power station. There are some 127 of these in the plant. I believe about a ton of fuel goes through one of these in a minute. It has a flame of about 18 feet long and particulates in the oil erode the nozzle, eventually forcing an expensive shutdown. It has been found that implantation of

elements which can form compounds having superior mechanical properties such as titanium diboride reduce the erosion rate at least an order of magnitude. Unfortunately, the power station changed the burner tip configuration in the midst of test before full results were obtained. But it is a very significant effect. There are other results that Dearnaley has reported on yttrium implantation along with nitrogen to cut down on oxidative wear and Harwell claims they are getting good results comparable to laboratory reductions in certain critical automobile components. Of course, working in the manner they do with private industry he is not at liberty to say exactly what components are being tested. But, again, for engine components with oxidative wear, it looks promising. I would like to close with a brief historical perspective of machine capabilities. In the sixties, ion implantation was evolving as a result of atomic and nuclear physics experiments with accelerators of microamp intensity. In the seventies, when the commercial prospects started coming along, industry started building machines like the isotope separators at Oak Ridge, but building them with better engineering and higher voltages. As I said, there are about 1200 of these now out in the industrial place, with a couple of companies making them. Now in the eighties, the semi-conductor machines have 10-20 milliamps beam currents at voltages up to 160 kV, and I think they are adequate for the materials work in metals.

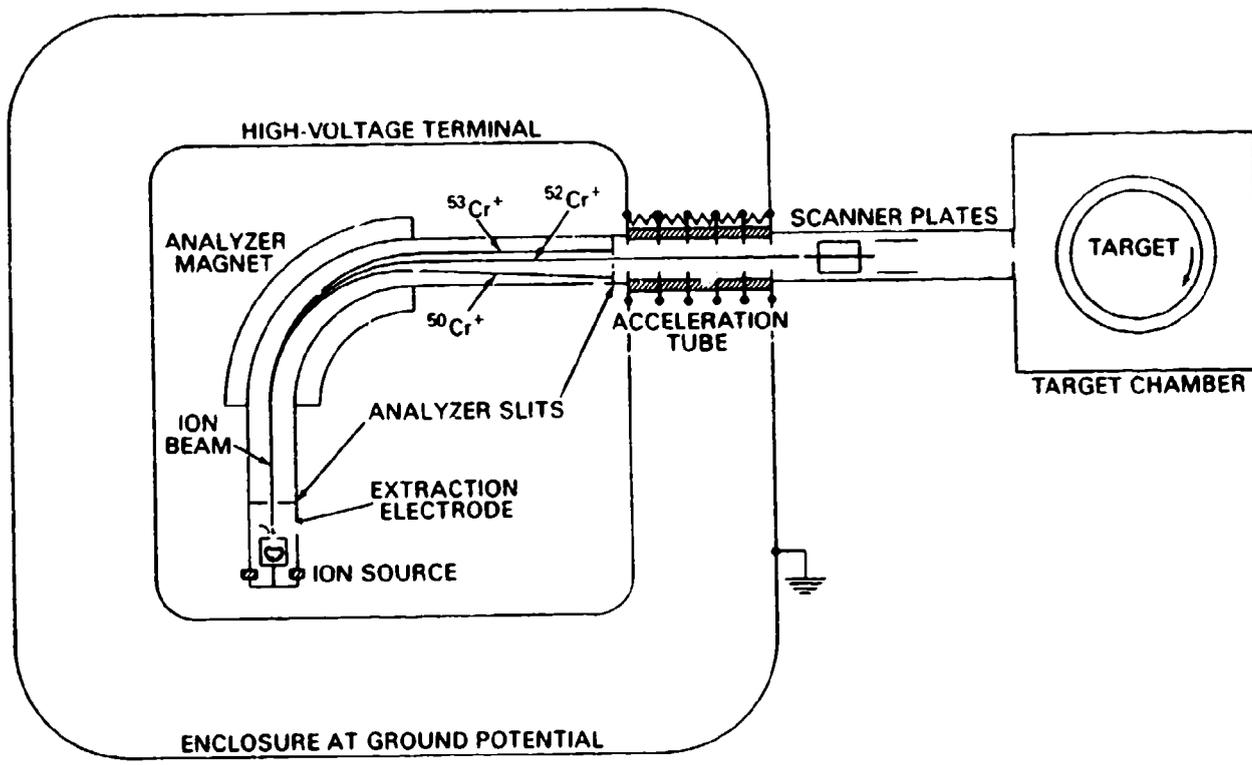


Figure 1. Schematic representation of production-type ion implantation system.

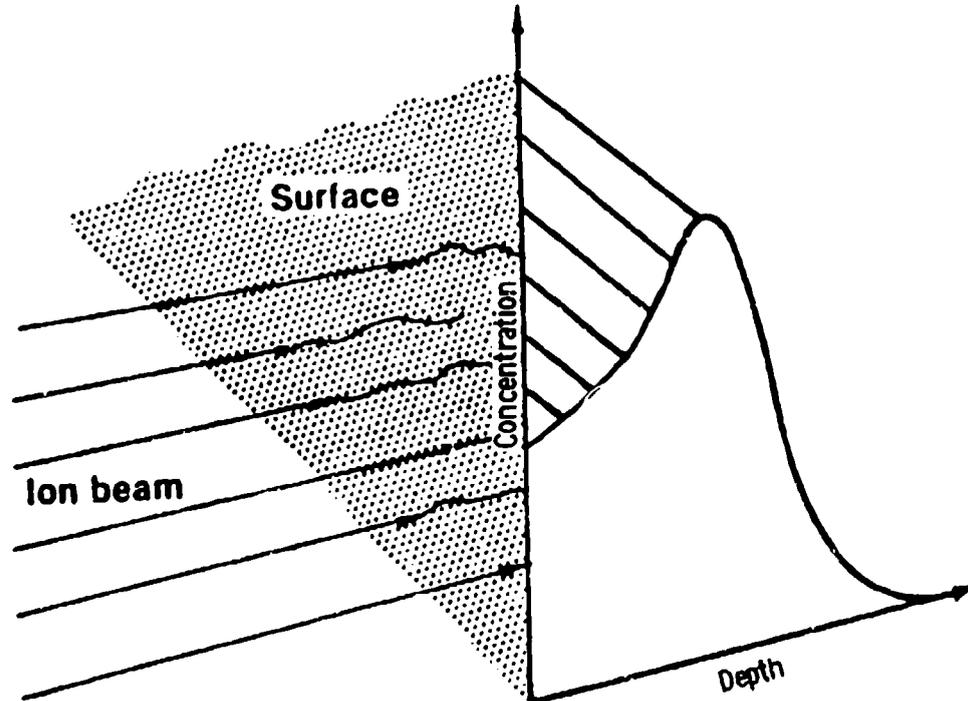


Figure 2. Gaussian sub-surface distribution of implanted ions.

### ADVANTAGES OF ION IMPLANTATION

1. NO SACRIFICE OF BULK PROPERTIES
2. SOLID SOLUBILITY LIMIT CAN BE EXCEEDED
3. ALLOY PREPARATION INDEPENDENT OF DIFFUSION CONSTANTS
4. NO COATING ADHESION PROBLEMS SINCE THERE IS NO INTERFACE
5. NO MACROSCOPIC CHANGE IN DIMENSIONS
6. DEPTH CONCENTRATION DISTRIBUTION CONTROLLABLE
7. ROOM TEMPERATURE PROCESS
8. PRECISION CONTROL
9. AUTOMATIC HANDLING POSSIBLE
10. CLEAN VACUUM PROCESS

Figure 3

### LIMITATIONS

1. LINE OF SIGHT
2. SHALLOW PENETRATION
3. HIGH TECHNOLOGY AREA (PRESENTLY)
4. RELATIVELY HIGH CAPITAL COSTS

Figure 4

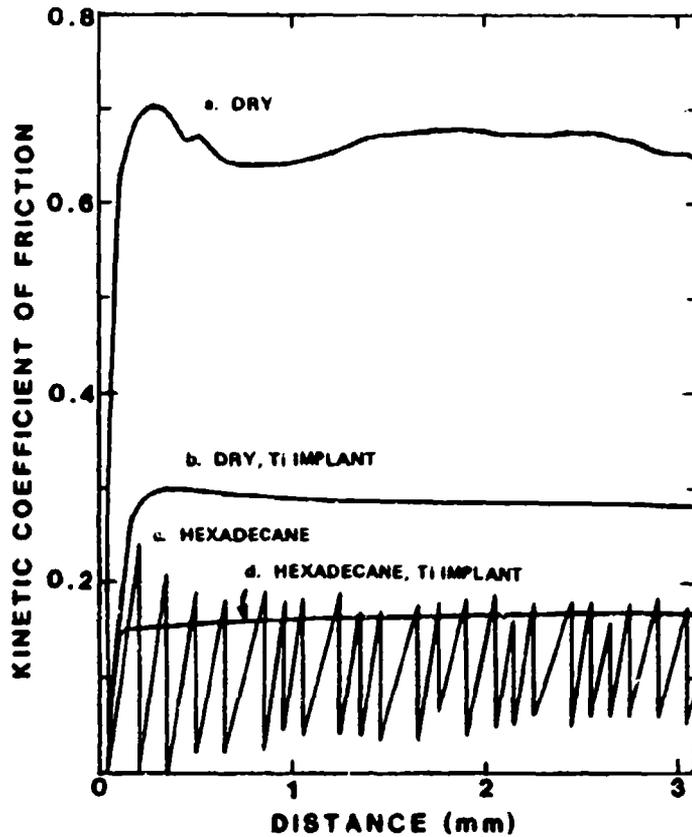


Figure 5. Kinetic coefficient of friction versus sliding distance for 52100 steel sphere on 52100 steel platen.

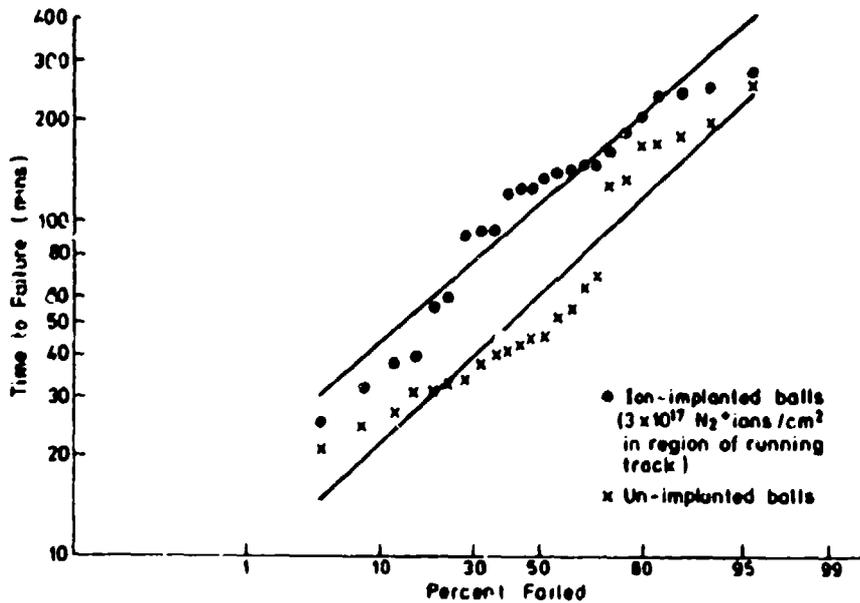
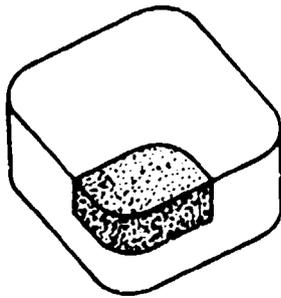
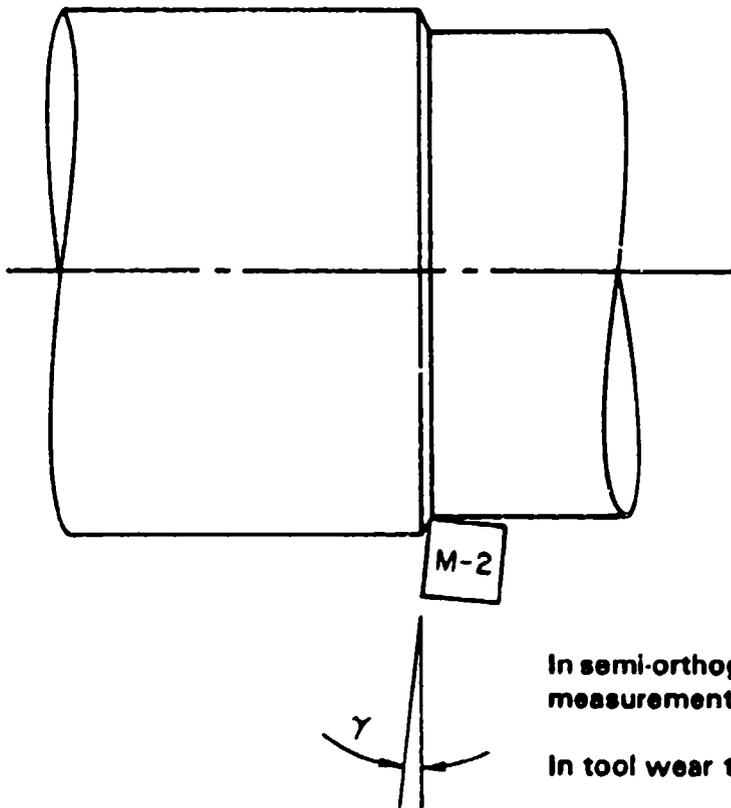


Figure 6. Times to failure of standardized steel balls run in a 4-ball tester, with and without nitrogen implantation.



Schematic illustration of ion implanted,  $1/2" \times 1/2"$  high speed steel tool inserts. Crater face and flank faces were implanted with 150 keV titanium ions. Implanted region is shaded.



In semi-orthogonal cutting tests for force measurements,  $\gamma = 5^\circ$  was used.

In tool wear tests  $\gamma = 15^\circ$  was used.

Figure 7. Geometry used for semi-orthogonal cutting tests.

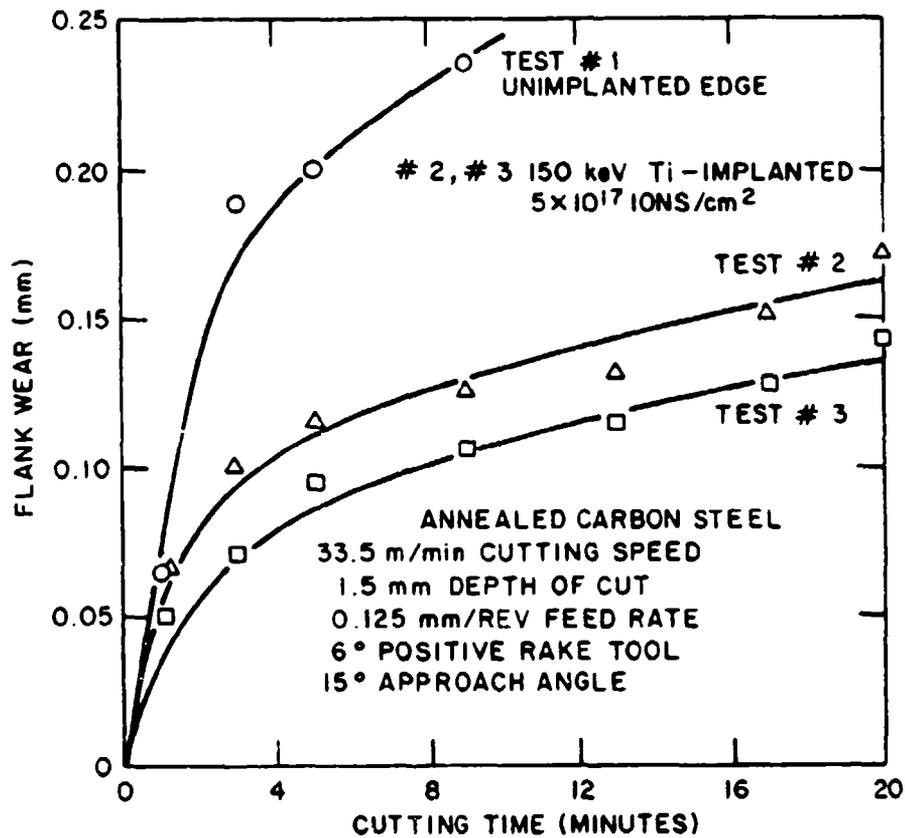


Figure 8. Comparison of tool wear characteristics of unimplanted and titanium implanted M2 high speed steel tool inserts.

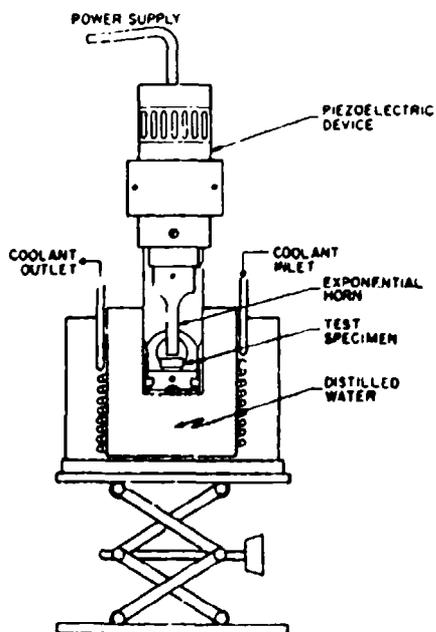


Figure 9. Cavitation erosion system employing a piezoelectric device and an exponential horn.

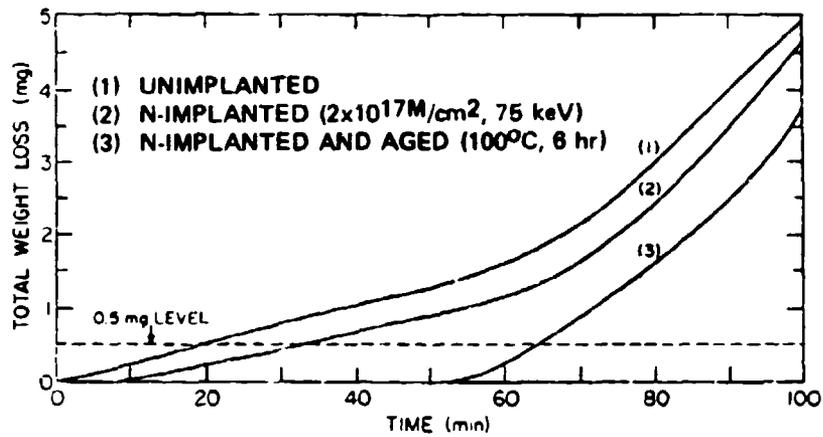
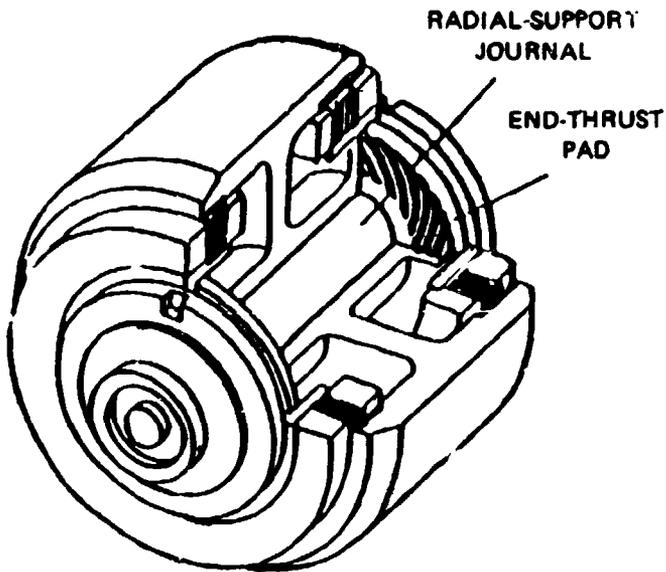


Figure 10. Weight loss during cavitation erosion of 1018 steel.

JOURNAL AND THRUST PAD TYPE



SPHERICAL TYPE

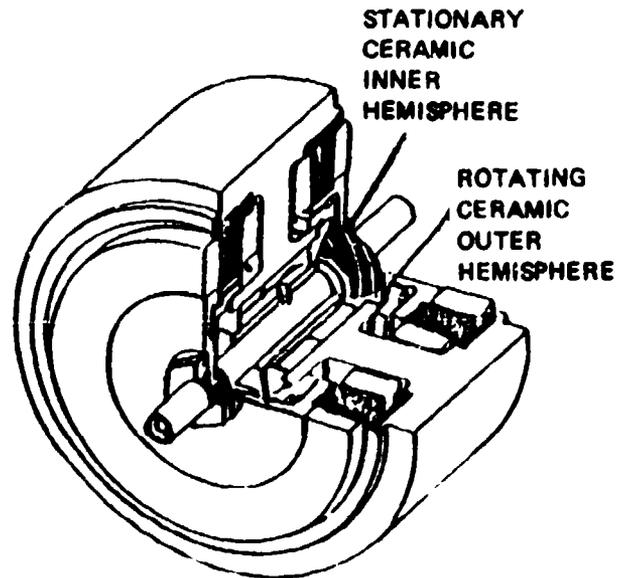


Figure 11. Typical gas bearings.

GAS-BEARING GYROSCOPES, MATERIALS SELECTION PROBLEM

BERYLLIUM MEETS STRUCTURAL CRITERIA BUT IS NOT SUFFICIENTLY HARD OR WEAR-RESISTANT

CERAMICS (e.g., BORON CARBIDE) MAY BE HARD AND WEAR-RESISTANT BUT ARE DIFFICULT TO MACHINE

HARD COATINGS ON BERYLLIUM, PROBLEM AREAS:

PLASMA-SPRAYED CERAMICS IS POROUS

SPUTTERED COATINGS HAVE LACKED GOOD ADHESION

DIFFUSED CASE-HARDENING REQUIRES HIGH TEMPERATURES, IS SUBJECT TO CONSIDERATIONS OF SOLUBILITY AND DIFFUSIVITY

Figure 12

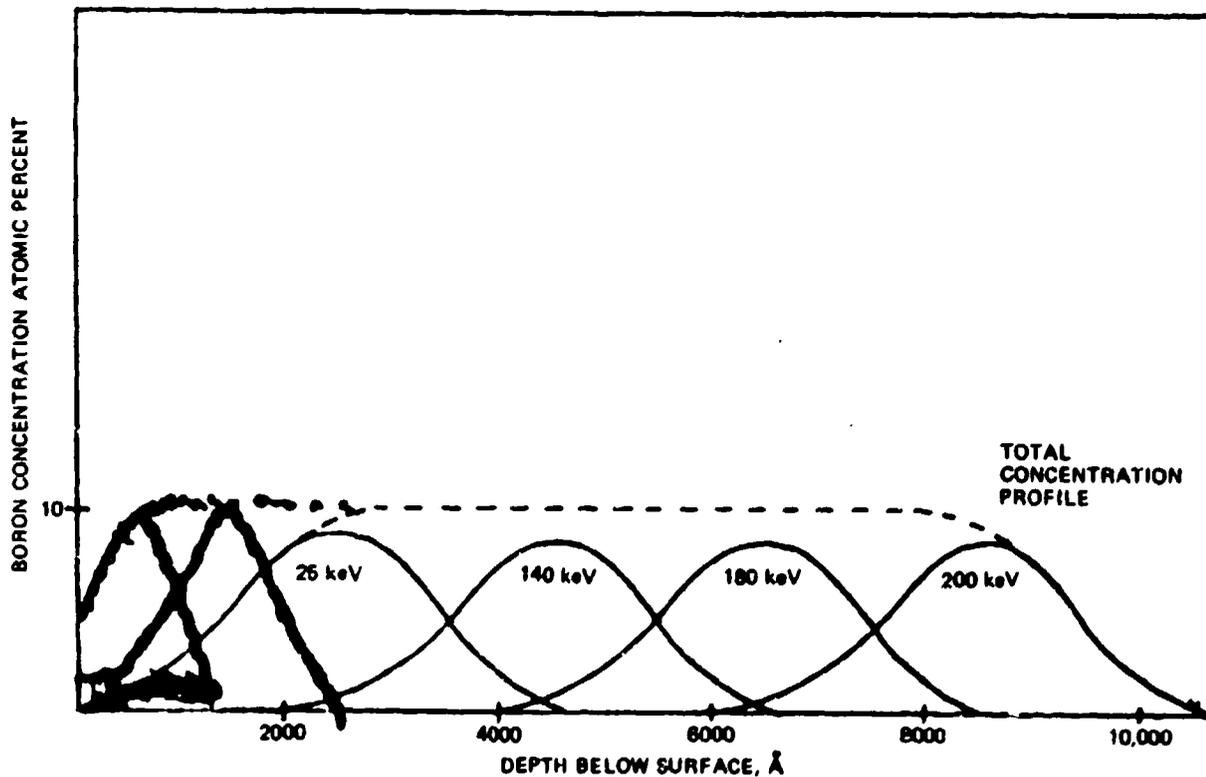


Figure 13. Nominal implantation profile,  
Sample Be/B-4-78-1.

PIN-ON-DISC WEAR TESTS  
52100 PIN - 50g LOAD

<u>DISC</u>	<u>COEFFICIENT OF FRICTION AFTER (L = 4.0M)</u>	<u>DISC WEAR VOLUME</u>	<u>REMARKS</u>
UNIMPLANTED I-400 Be ALLOY	0.30	1.1 $\mu\text{m}^3$	SEVERE EROSION
Al <sub>2</sub> O <sub>3</sub>	0.82	0.13 $\mu\text{m}^3$	SOME EROSION
40 at. % 11B	0.24	< 0.01 $\mu\text{m}^3$	NO EROSION NO PICK-UP

Figure 14

R. E. FROMSON AND R. KOSSOWSKI  
WESTINGHOUSE, PITTSBURGH

<u>APPLICATION</u>	<u>MATERIAL</u>	<u>TREATMENT</u>	<u>RESULT</u>
INDEX SLOTTING OF ROTOR LAMINATIONS IN 0.024" LOW CARBON STEEL	CO-CEMENTED WC PUNCH AND DIE	NOT GIVEN	6X LIFETIME
DRILLING FR-4 MICARTA PRINTED CIRCUIT BOARDS	WC DRILLS	NOT GIVEN	2X LIFETIME
DRILLING 405 S.S.	HS TWIST DRILLS	N, B, C IMPLAN- TATION	LOWERED LIFETIME

Figure 15

SELECTED EXAMPLES OF  
INDUSTRIAL UTILIZATION OF  
REDUCED WEAR BY IMPLANTATION  
(HARWELL)

<u>USE</u>	<u>IMPLANTED SPECIES</u>	<u>LIFE EXTENSION FACTOR</u>
1) CUTTING KNIVES	N	2X - 10X
2) HIGH SPEED TAPS	N	5X
3) CEMENTED TUNGSTEN CARBIDE TOOLS	C	5X - 100X

Figure 16

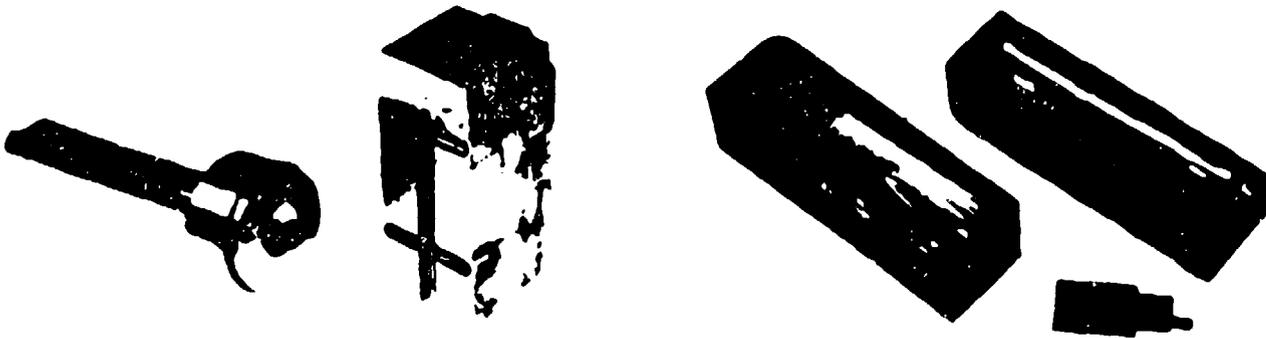
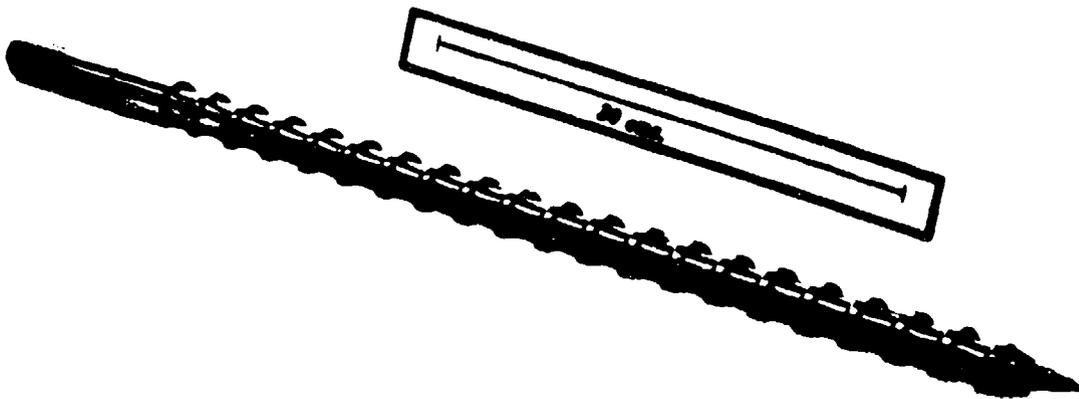


Figure 17. Sprue bush and runner block after ion implantation (left), and an impression mold (right), used for the injection molding of a thermosetting plastic. Long-lasting benefits in wear resistance have been observed.



a. Injection molding screw for plastics

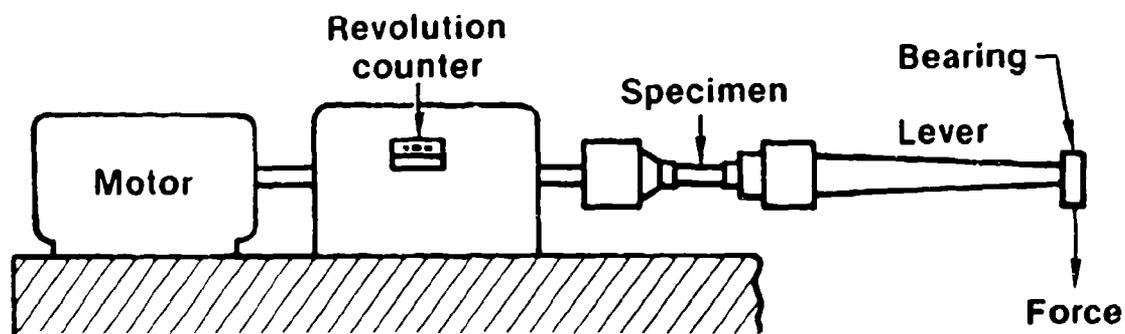


b. Injection molding screw undergoing implantation in a beam of nitrogen ions.

Figure 18



Figure 19. Hot rolling mill rolls for non-ferrous rod gave an increase in life by over a factor of 5 as a result of nitrogen ion implantation ( $4 \cdot 10^{17} \text{ N}_2^+/\text{cm}^2$  at 90 keV).



## FATIGUE — TEST SAMPLE

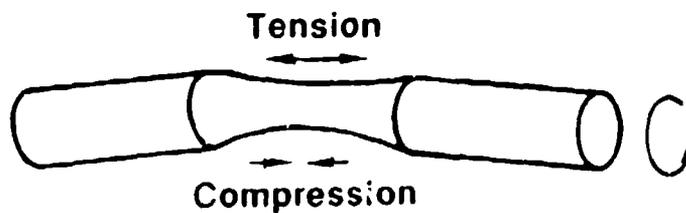


Figure 20. Fatigue test machine.

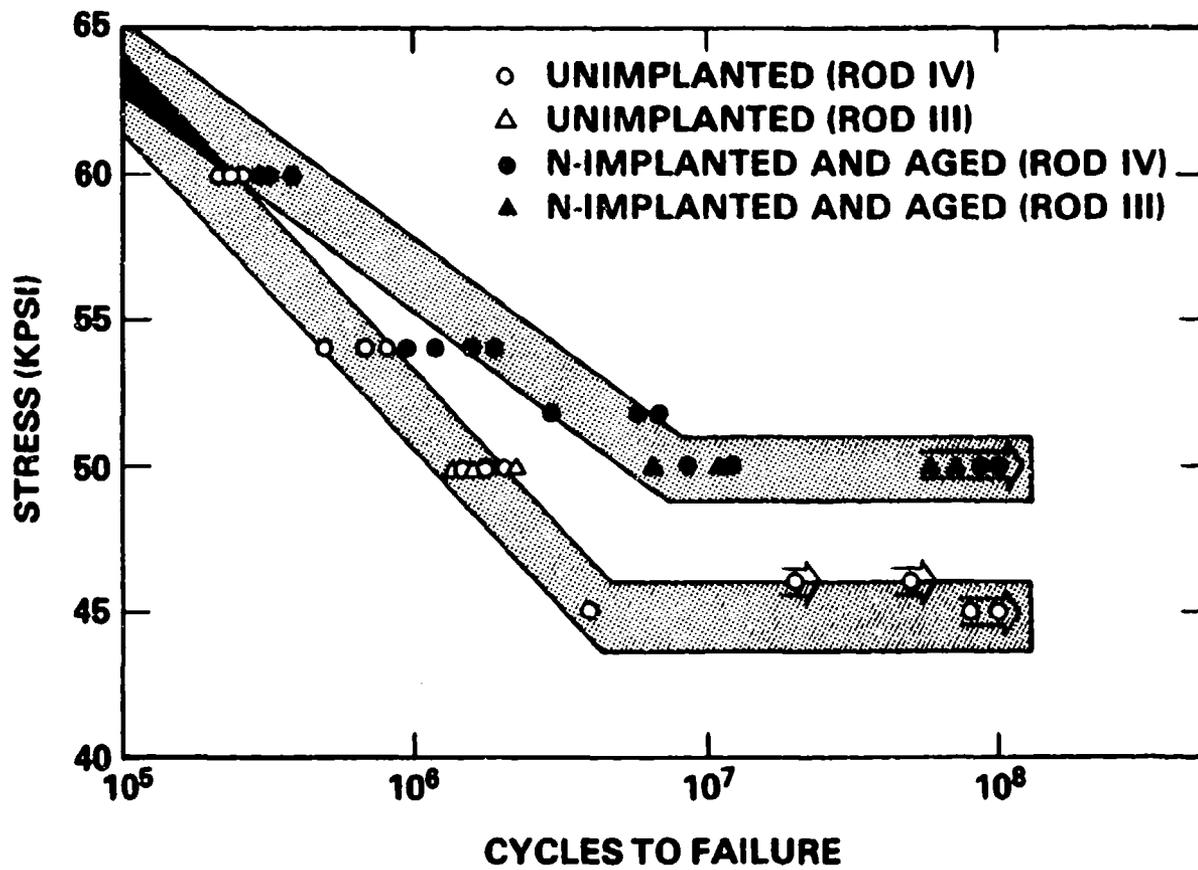


Figure 21

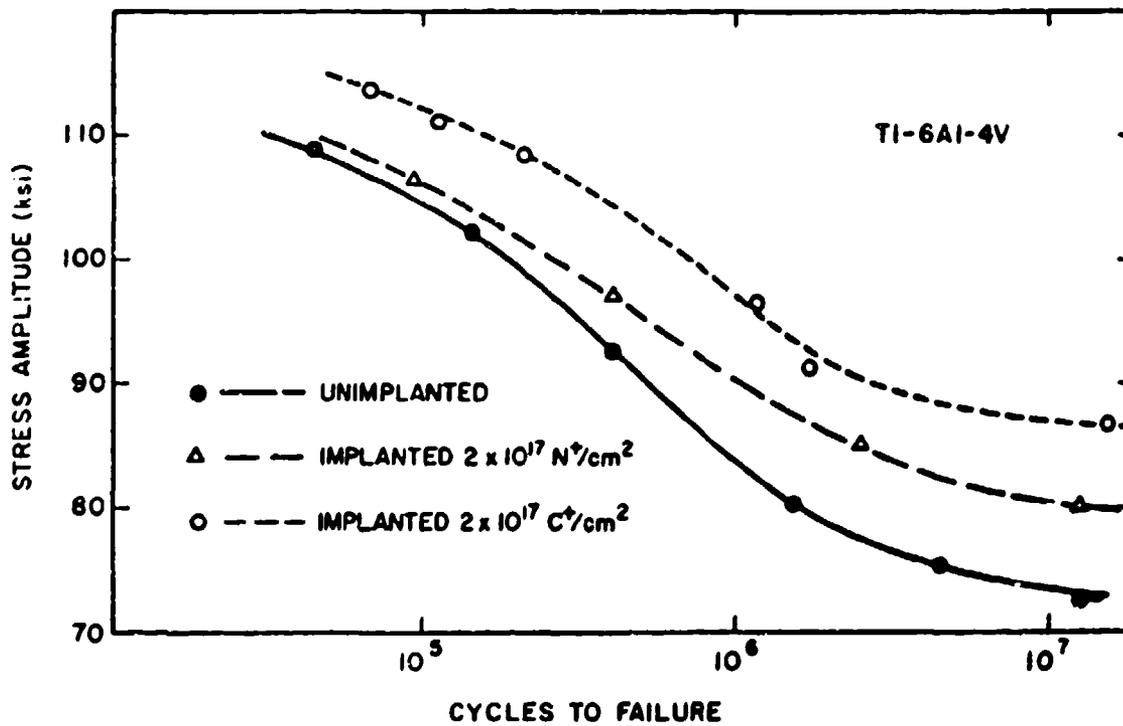


Figure 22

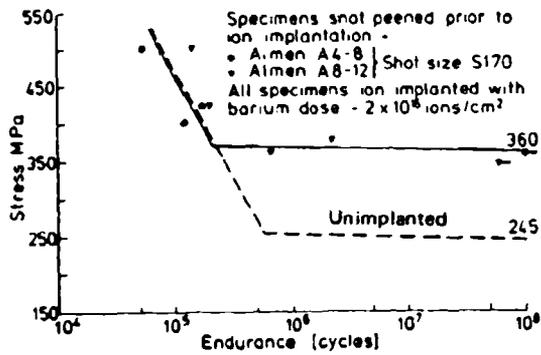


Figure 23. The room temperature fretting fatigue behavior of titanium alloy specimens.

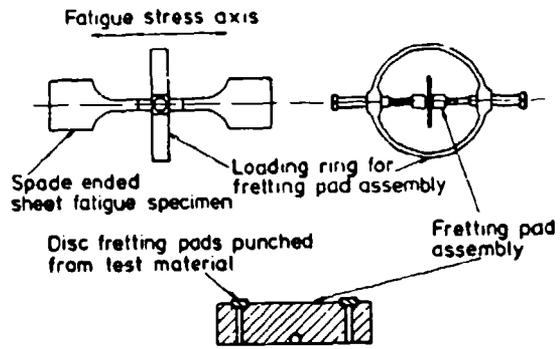


Figure 24. Specimen arrangement for a standardised fretting fatigue test on titanium alloy specimens.

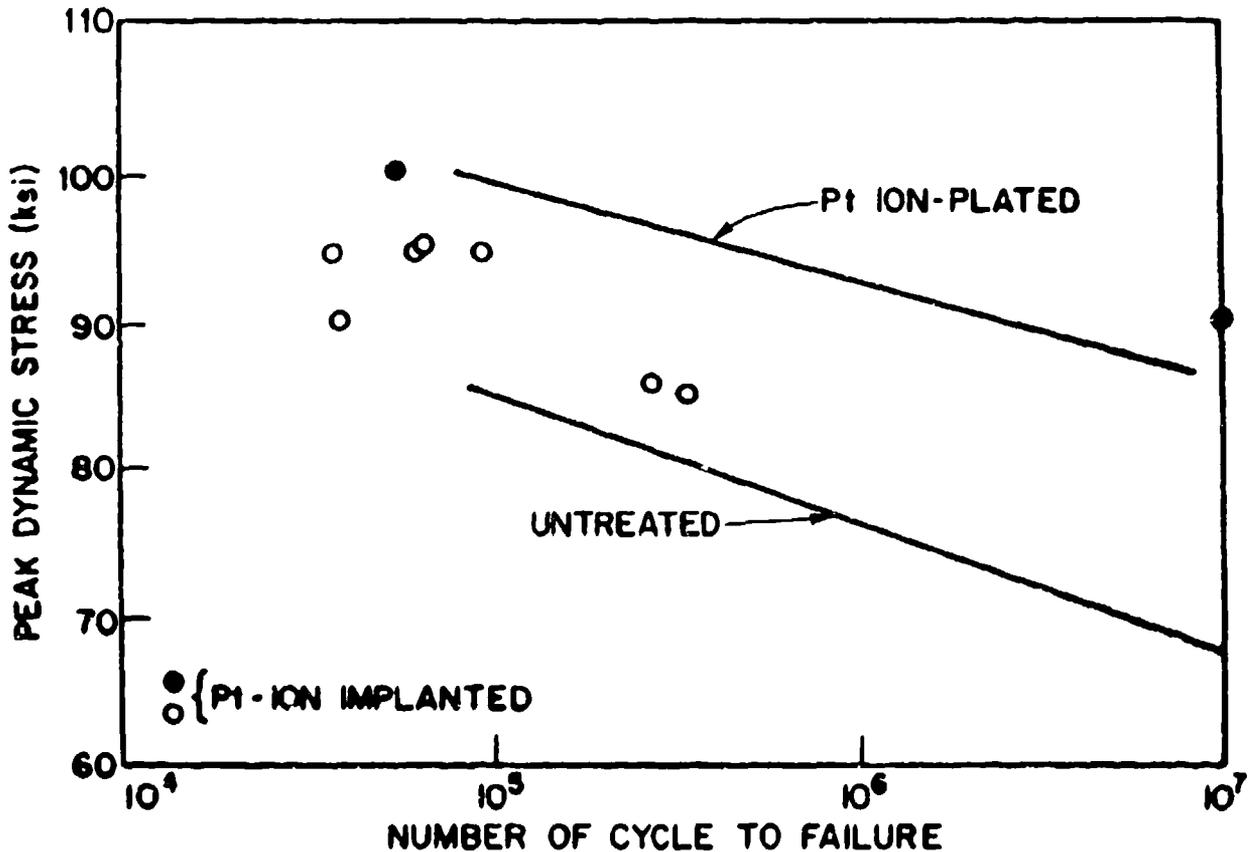


Figure 25. Fatigue test on 7<sup>th</sup> stage F100 compressor blades (Ti-6Al-2Sn-4Zr-6Mo).

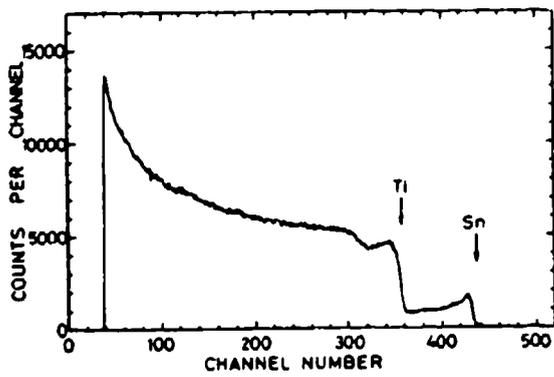


Figure 26. Ion backscattering spectrum of  $2 \text{ MeV}^4\text{He}^+$  ions from a specimen of titanium alloy (Ti-6Al-4V) into which tin has been introduced by bombardment diffusion using nitrogen ions at 100 keV energy.

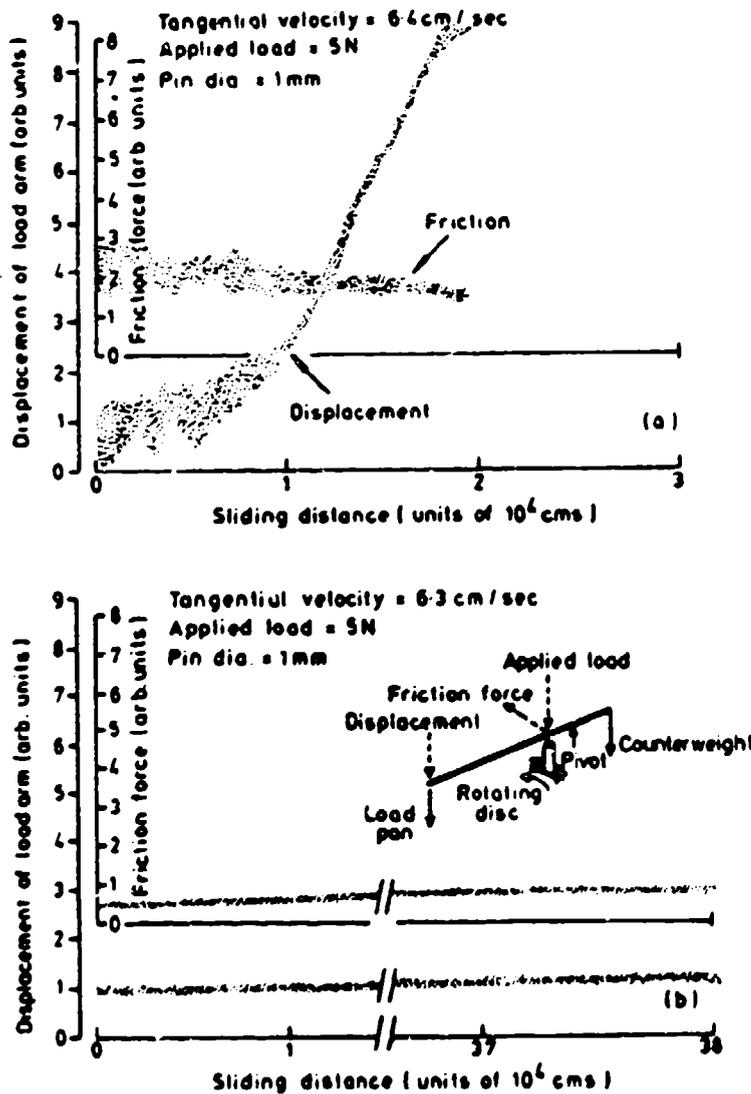


Figure 27. Reduction of friction and displacement after nitrogen implantation.

SUMMARY

MECHANICAL EFFECTS

UNEXPECTEDLY LARGE, LONGLASTING EFFECTS  
(e.g. WEAR AND FATIGUE)

BETTER UNDERSTANDING OF THESE EFFECTS  
REQUIRES THOROUGH MATERIAL (MICRO)  
CHARACTERIZATION

POTENTIAL FOR APPLICATION TO SMALL,  
EXPENSIVE, OR CRITICAL PARTS

Figure 28

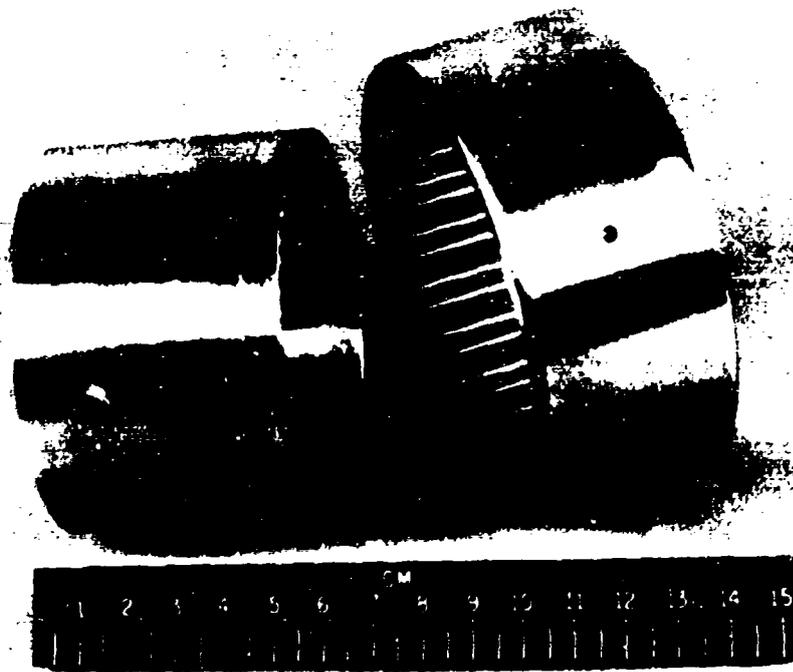


Figure 29.

MAINSHAFT BRGS. PROCESSED/YEAR AT NARFS	15,000
REJECTED BY CORROSION (30%)	4,500
AVERAGE COST PER BEARING	\$600
COST/YEAR FROM CORROSION	\$2.7M

Figure 30

APPROACH

DETERMINE BEST ION IMPLANATION CONDITIONS FOR  
M50 STEEL USING VARIOUS CORROSION TESTS

SELECT CHRONIC CORROSION PROBLEMS FOR STUDY

- DEVELOP METHODS TO IMPLANT BEARINGS
- PERFORMANCE AND ENDURANCE BENCH TESTING
- ENGINE TEST WITH CHLORIDE CONTAMINATED OIL
- FIELD SERVICE EVALUATION
- STORAGE TEST

STUDIES ON ADVANCED BEARING STEELS

CO-OP PROGRAMS WITH ENGINE MANUFACTURERS

Figure 31

REQUIREMENTS FOR TREATMENT OF BEARINGS

NO LOSS OF HARDNESS

NO DEGRADATION OF CONTACT FATIGUE,  
OR PERFORMANCE CHARACTERISTICS

NO SIGNIFICANT DIMENSION CHANGES

Figure 32

CORROSION TESTS

POTENTIOKINETIC POLARIZATION MEASUREMENTS

PITTING POTENTIAL MEASUREMENTS

SIMULATED FIELD SERVICE TESTS

Figure 33

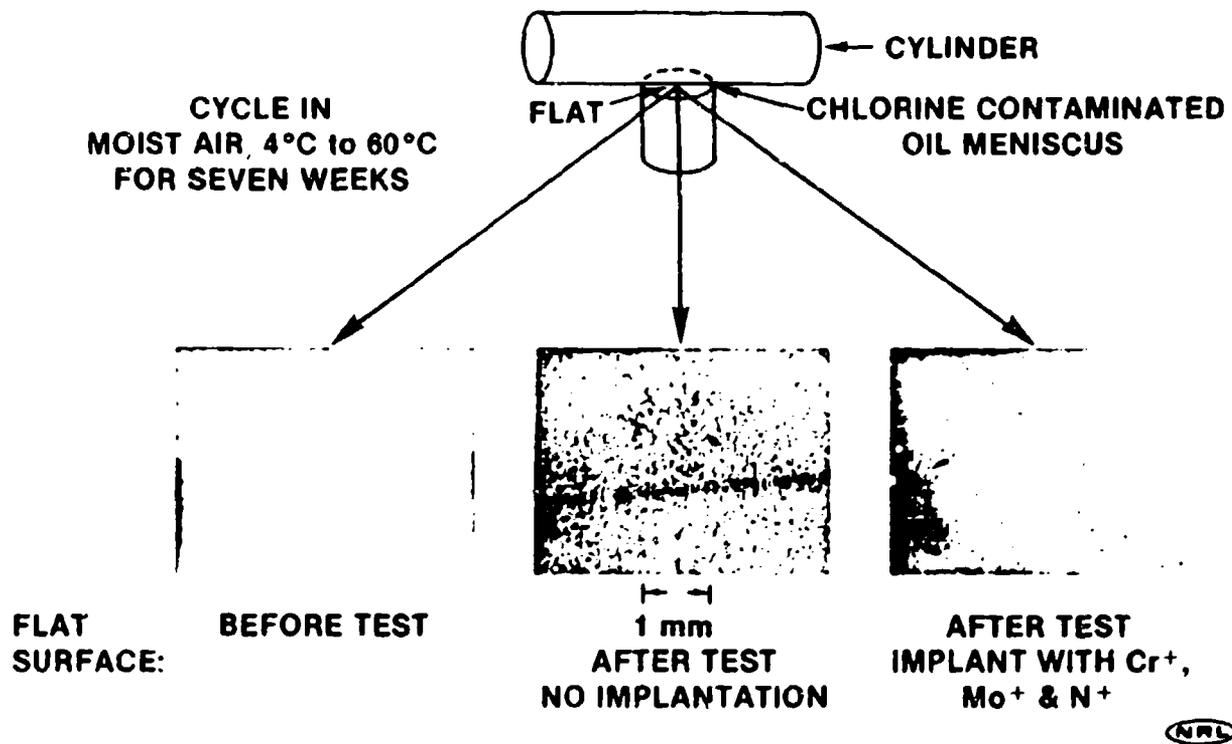


Figure 34. Simulated field service test of corrosion of M50 bearings.

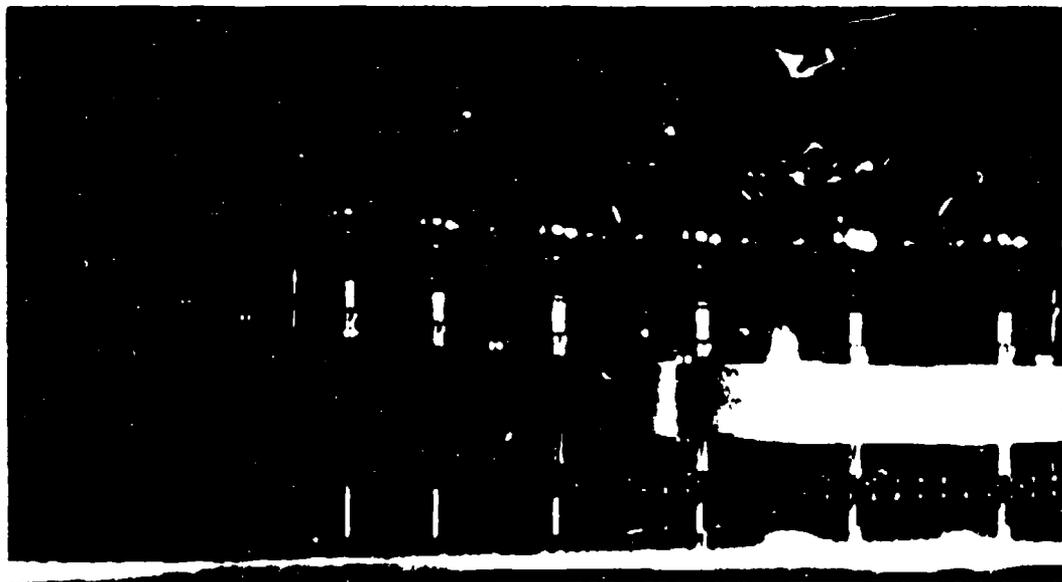


Figure 35. Carousel of M50 bearings for ion implantation.

PROJECTED TREATMENT TIMES

REQUIRED FLUENCES, ENERGIES	1-4 x 10 <sup>17</sup>
MULTIENERGY IMPLANTS	25-200 keV
BEAM CURRENTS AVAILABLE	0.5-25 MA
ESTIMATED TIME PER BEARING (~20 cm <sup>2</sup> )	2 hr - few minutes

Figure 36

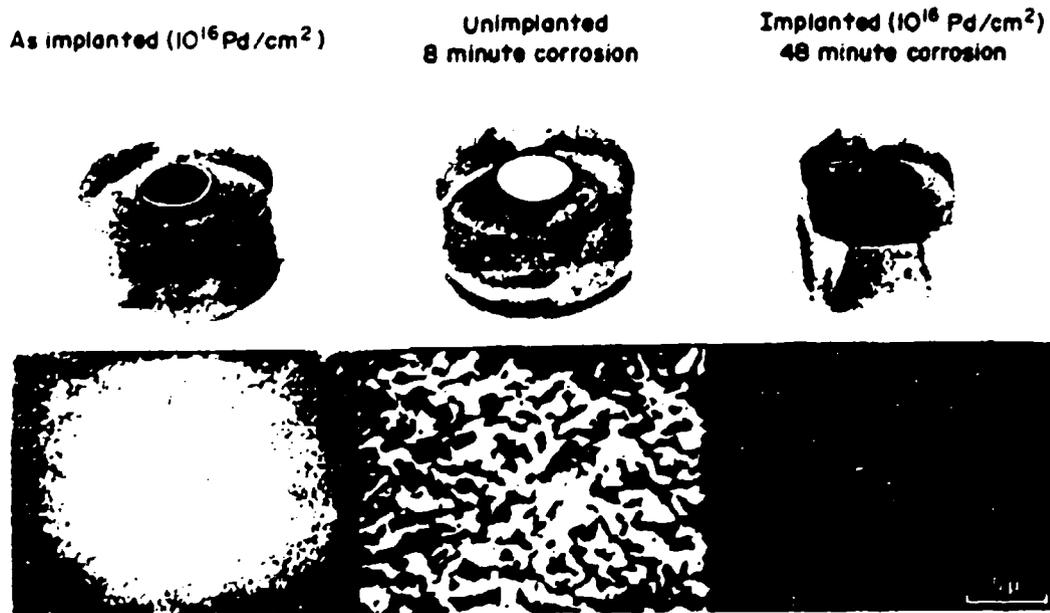


Figure 37. Corrosion of titanium in boiling 1 molar H<sub>2</sub>SO<sub>4</sub>.

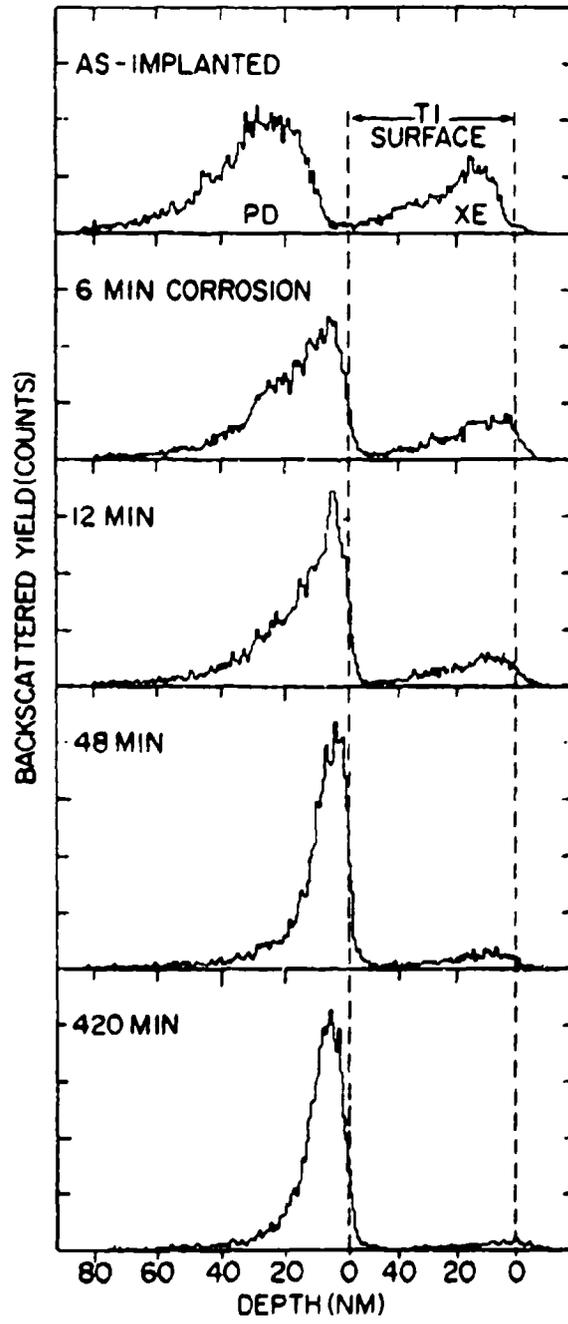


Figure 38

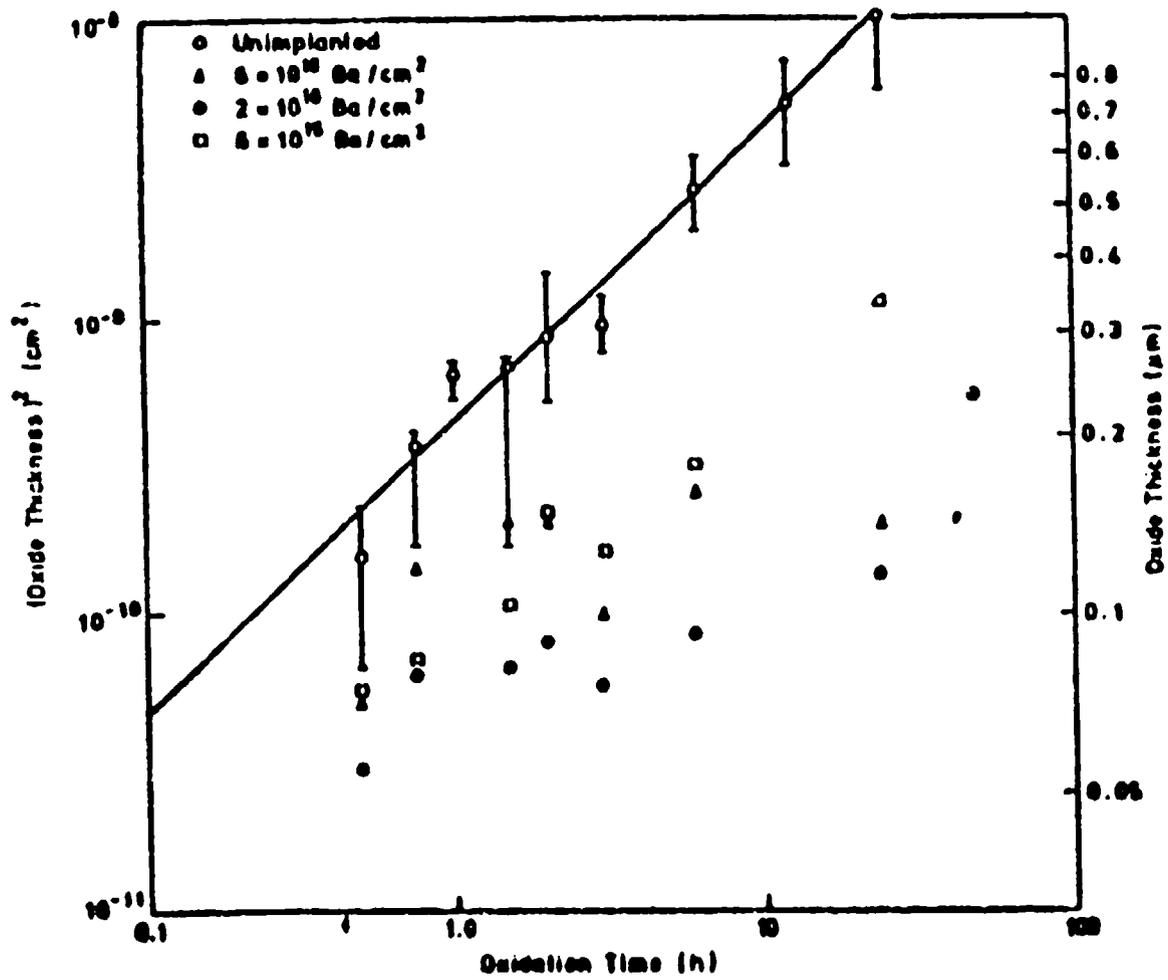


Figure 39. The influence of the implantation of barium ions upon the kinetics of oxidation of titanium in oxygen at 600°C.

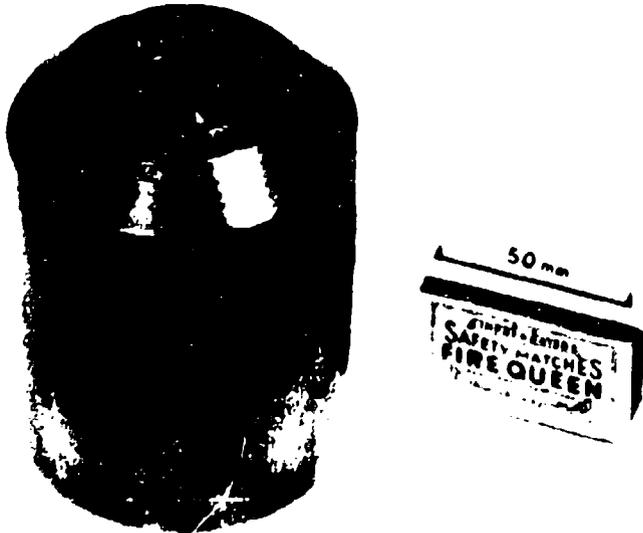


Figure 40. Burner tip for Fauley oil-fired power station. Ion implantation reduced erosion of the orifice.

## QUESTIONS AND ANSWERS

B. Sartwell, Bureau of Mines: On the high dose implant: in the vacuum system, a lot of times you get carbonaceous material deposited on the surface either as a result of hydrocarbons in the vacuum or the ion beams can be a driving force for carbon segregating toward the surface. Have you looked at whether you are getting carbon films near the surface and what effect they might have on the wear friction behavior?

J. Hirvonen: Well, they certainly are there, and we see them for the titanium implants especially where they are gettered very effectively. They are ubiquitous; I think for many wear experiments, where you are putting in nitrogen or carbon, the slight addition of more carbon by that sort of effect would not be expected to detract from it. You might expect problems, in perhaps some of the aqueous corrosion effects. Maybe Clive would like to comment on the levels of carbon found. We have a cryo-pump system which I think is something to be reasonably concerned about. If you're not careful you can have that as well as oxygen, which can come to the surface and get mixed in. If you have poor pumping, these things will come out of the woodwork to haunt you. We have not found them to have a deleterious effect on the experiments we have done for aqueous corrosion. Is that right Clive?

C. Clayton, Stony Brook: We will make a comment about contamination tomorrow. One of the points it does emphasize is the need to characterize surfaces properly. Since we have attempted to use Auger and XPS, we monitored, in each of the categories of implanted materials that we have looked at for corrosion studies, the distribution of carbon inside the alloyed surface itself from the point of view of just getting a profile. We have also been looking for chemical shifts as evidence of carbide since the majority of the corrosion work that we have been doing is to introduce passivators, elements which normally capable of forming oxides as well as carbides. We have been having to monitor their chemical states. There we have found no evidence that we're getting chromium carbide, for example, being formed as a result of any surface contamination or being recoil sputtered into the material. In fact, we don't find the level of recoil sputtered carbon to be very high at all. It could well be the background hydrocarbon from the vacuum system that we are seeing.

J. Hirvonen: You have to be very careful. If you have a oil or a dirty oil pump system, I think there would be reason to be concerned. It points back again to what several people have said, the need for good surface characterization.

P. Parrish, ARO: Jim, with the vast experience you have in implanting various materials and for the types of applications or the types of studies that we are most interested in, could you give us some kind of general feeling of what characteristics in a machine you would go after if you were designing one to do metallurgical studies?

J. Hirvonen: The type of machine we are using is an adaptation. First of all it is a machine which has an ion source capable of producing a great variety of species. There is a great deal of ion source work--it is truly ion sorcery--and there are a lot of strange things happening with the hot chemistry in an ion source, small effects which can affect your output by as much as 14 orders of magnitude in the ion beam current you are going to get. However, if done properly, these techniques for producing metal ion beams have been around for many years, since the isotope separator days, and we are adapting those old techniques to new machines even though they weren't built for those purposes. The ion source design is such that they

can be adapted, and it turns out interestingly that the ion source Harry Freeman built in England, which is used at Harwell, was built for nuclear physics targets. Subsequently most semi-conductor implanters employ variations of that source. So that is one requirement. For another, you have to start getting concerned about what energies you are going to need. Just from a machine viewpoint, it is easier to limit it to about 200 kilovolts. If you want to go to half an MV, your cost is going to start escalating. Of course, you have the option to use a multiply charged beam; but I think the machine that I would envisage for materials research, but perhaps not for production, would be an adaptation of present designs which give 10-20 milli-ampere intensity. The ion source is altered. It would be quite universal, between 150-200 kilovolts. If you have to go to 1 MV at those high currents, unless it is a very special application, I think it is going to have a very pronounced influence on the economics and may make implantation unattractive. Again, with an eye toward ion beam mixing maybe more will come along in the future. It is too early to say.

S. Cytron, ARRADCOM: Jim, you mentioned, implantation with three implanted species on the M50 bearing alloy. Were they together or separate?

J. Hirvonen: They were together. It turns out that was sort of an odd duck combination. Clive will say more about the combinations that we are looking at, but that was just one experiment.

S. Cytron: This leads into my more important question. In developing an ion implantation technique (and I think maybe Clive and Bruce might address this same question) do you have in mind a general scheme or approach in terms of your choice of the implanting species? Do you go back into the literature and look for what is or has been a good coating material--what has survived? Or are there any guidelines that are being developed or thought about in terms of setting up your choice of implanting species?

J. Hirvonen: I think in our oversimplified way (and I will welcome comment by Bruce or Clive later), that for the corrosion work we have been discussing the ion species like chromium or chromium plus phosphorous are analogous or derive from the conventional electrochemistry to get amorphous layers. I think, to a certain extent, things for thermal oxidation are similar--the addition of yttrium, for instance, and cerium. But you have the additional possibility of getting metastable alloys by implantation. In the wear and fatigue area, the mechanisms are less understood so it is not proper to make analogies. For example, the chemical nature of the implanted species and possible interaction of the implanted species with dislocations you are producing, is not completely analogous to just producing a hard case. So for mechanical effects, I don't think they are quite the obvious connections or the comparisons as may be for aqueous corrosion.

C. Levy: Jim, you showed us a configuration for implanting the surfaces of bearings. As a practical approach, how can we design to do this and other types of surfaces which may perhaps be slightly different configurations from those bearing surfaces? Do you have some sort of empirical approach to doing that or have you worked out a scheme of some sort?

J. Hirvonen: Well, there is certainly no universal jig for manipulating samples, as has been discussed before. One of the largest differences between semi-conductors and the metals game is that in the latter case everything is going to have a different geometry. That is a time-consuming problem for us because we only wanted a few

things with many different geometries, so a good deal of time is required to do the jiggling to hold and manipulate the sample. There are many questions to be addressed, for instance, with bearings. How do you implant them efficiently? How do you implant them uniformly, and keep them cool enough without touching them so they don't become dirty or scratched. It is a real challenge. Many people have ideas. It just takes a good clever mechanical engineer. But each application will require a considered opinion. Another large consideration is what happens with high dose rates. It is well-known that the distribution of second phase precipitates is dominated by dose rate effects. That is, how fast you implant. When you go from the laboratory scale (i.e., with microamp beams) to milliamper beam intensities, you are not necessarily assured that you are going to end up with the same structure. There has to be concern, if you are going to think about eventual production use, that you have control on all the variables. Not just temperature, but the rate at which you can have a competition between growing and dissolution of precipitates. There are basic metallurgical problems to be addressed.

R. Harrison, AMMRC: The point you just alluded to relates to my question. Suppose your bearing research were successful, that you think this is the way to go. How long will it take to get a manufacturing facility set up? Is it something that you would potentially expect one dedicated ion implanter to handle, or several of them.

J. Hirvonen: It depends on what drives the solution. One option would be for a systems command to call for the process with a specification, but it seems to me with the inertia in all systems that may not be the way it will go. I would see it more likely having engine people say "look, here is an improvement and it's cost-effective." Then maybe the specifications will change as a result. There is very much concern in the Navy now to try to think forward to Man-Tech programs where perhaps in a year or a year and a half you might have money to put a high (10 ma) current machine in some Naval facility to process meaningful numbers of hardware items so they can be field tested with enough numbers to insure good statistics. So we are looking forward to that. Of course there is always a question of money.

R. Harrison: I think you have answered the last part of my question which was the time frame. I had one other small question. You mentioned that you would predict that this irradiation of the twist drill would not work, and it didn't. How did you predict that?

J. Hirvonen: For one reason, Harwell tried it, and it didn't work. After thinking about it, it isn't reasonable. The nitrides produced won't hold up under those high temperatures. Now that is not the complete story; that is, for metal cutting. For cutting aluminum, when presumably you don't have a high temperature improvements have been found. Still, for metal cutting extremes, there have been improvements. For example, the finish of the product has been improved.

J. Perkins, AMMRC: Is there any evidence that successive ion implantation of two different ions may be helpful? Suppose you were putting on something heavy like tungsten, and it might not get in very far because of the energy involved, but then suppose you irradiate it with something like nitrogen afterward. Would that push further inward or vice-versa? If you did the light element first could you perforate your surface enough so that the heavier ion could get in more easily?

J. Hirvonen: We have considered putting in chromium and nitrogen. There the concern was not one of having a positive synergistic effect, but rather would the chromium tie up the nitrogen and thus not be available for corrosion resistance. A possible advantage of putting nitrogen in would be to improve the wear or fatigue life. It would perhaps be placed deeper than the chromium. That has not been answered. A positive effect has been seen by Dearnaley and co-workers involving the oxidative wear where they put in both nitrogen and yttrium. In that case there was a synergistic effect. Some early work that we did with Clive using molybdenum and chromium combinations looked better. So I think there are possibilities.

J. Perkins: I was thinking of something a little different. I was wondering if you could increase the penetration of one component by pushing it in subsequently with the second component.

J. Hirvonen: You will get in only a small fraction of deposited atoms by direct recoil implantation. To get a significant amount in you might have to rely on some radiation enhanced diffusion effects such as the tin-in-titanium example. Or the example that Jim (Mayer) mentioned earlier. I forgot what it was, but there was an enhancement effect. I don't think there are any cookbook recipes as yet. We still have so much to learn about what systems are compatible and under what temperature conditions will intermixing take place.

FIFTH SESSION:  
GROUP DISCUSSION

C. Levy: Thank you, Jim. In our invitation to you to participate in this workshop, we set out a number of objectives. I would like to recall these now and open discussion relating to our accomplishment of these objectives, not only for the Army but for the whole Defense Department. We are looking for your participation. What we are trying to do with this workshop is acquaint Army materials designers and development people with ion implantation for potential improvement of surface related properties. We are trying to stimulate interaction and coordination of activities. We are trying to get cross-fertilization of ideas which may be applied to end items at various depots, commands, contractors, and so forth. Anybody want to open a discussion? Talk about some problem you may have where ion implantation may serve as a mechanism of achieving an improved surface.

P. Sagalyn, AMMRC: Let's talk about the status of the field and limitations due to lack of suitable commercial equipment. Peter Rose is the president of Nova Associates and he told me that a company asked him to implant  $2\frac{1}{2}$  thousandths wire drawing dies and he simply could't do it because he is so far behind on delivery of his machines that he doesn't have a demonstrator. The question was just elementary. I was also curious when Jim Hirvonen showed a picture of a jig containing a ball bearing. How do you manipulate them in order to irradiate the entire surface uniformly?

J. Hirvonen, NRL: That certainly would not qualify for a production system. Implanting a spherical object uniformly, yet keeping it cool in a vacuum without touching it, is a interesting problem and our Mod I solution to that is what you saw. We have a few bearings to do, and in order to avoid the time necessary to make these very adroit manipulators that Charlie was talking about we simply opted to make a ferris wheel with spinning tees so the balls spin under the beam as they move in front of it. Now that of course leaves the poles unexposed and unimplanted. So, halfway through, we rotate the bearings  $90^\circ$  and that, as you recognize, will give you non-uniformities. However, one of the desirable aspects of implantation of metals is that often, especially with corrosion resistance, after you have implanted above a critical dose, or a critical concentration, excess chromium won't hurt you. So the secret is to try to get sufficient chromium even in the portions of that ball which are receiving the least amount of chromium. Other compensating factors will include the angle and sputtering effects and the fact that you will start coming to a steady state surface concentration due to sputtering. That is not what we would use for a large number, but that's how we do it for our limited number.

D. Tenney, NASA, Langley: There have been a number of instances over the last few years where people would want to put metal ions into polymeric type materials. In your knowledge, is ion implantation used anywhere to do this?

J. Hirvonen: Yes. There is a rapidly growing program at our lab on conducting polymers. Part of that involves the implantation of species to change the conduction of materials like polyacetylene and  $\text{SiN}_x$  in which it is found that implantation does give very significant doping effects, different than seen by conventional intercalation techniques which use specific chemical compounds to introduce the halogens. Fluorine looks very promising and much more so than when chemical compounds are used. In fact, it is being used as a test of a conduction mechanism in the polymers. I understand that there is quite a bit of interest at MIT in polymers as well.

D. Tenney: Who is doing that in your lab?

J. Hirvonen: Dave Weber and Pat Grant in Dave Venesky's branch. It involves several branches in our Chemistry Division. If you were to write to myself or Fred Smidt we could put you in contact with them.

S. Cytron, ARRADCOM: We have been looking at ion implantation techniques for sometime. We have the problem of justifying the use of a Cadillac technique. You have to justify that everything else has been proved inadequate and that this is, you might say, a method of last resort. At the moment it is difficult to show that justification. But we are looking at one particular area. That is corrosion protection for depleted uranium. The present technique makes use of ion vapor deposition of aluminum onto the DU and then a dip/chromate coating. It has been shown effective. There are some problems, and we are wondering whether we can use ion implantation techniques on DU. If one goes back into the literature, one sees that one of the earliest studies did indicate some protection, and we would like to amplify on this and extend that capability. One of the disadvantages that we'd have to overcome in this type of application is the line-of-sight implantation situation. The finished product of a depleted uranium penetrator has buttress grooves and these buttress grooves are extremely crucial so that we want to avoid any corrosion, or you might say any crack development, in the buttress grooves. Therefore one must insure that you are fully implanting your protective species along the entire surface. That is one consideration. Other considerations are the jiggling and an analysis to show that the process is going to be cost effective and competitive with the present techniques. One thing in favor of the ion implantation technique is that there is no dimensional change. When you go through an IVD technique you have to insure that your coating thickness meets certain tolerances so that when the penetrator is assembled, there are no problems in terms of its future performance. Implantation has that supposed advantage over the IVD technique. This is something that we are looking to experiment with. Another area relates to very highly corrosive atmospheres. That is we have materials that are subjected to very high corrosive environments. Where typical corrosion rates cannot be tolerated.

C. Levy: Could you be more specific on those, where not classified?

S. Cytron: Corrosion rates of 20 mils per year are unacceptable. We're specifically talking about CW agents and materials compatibility. Here you're dealing with an extremely corrosive environment. The impurity content of these materials seems to be the precursor for the extensive corrosion that we see. Now what do you do in terms of protecting containment materials? IVD techniques might be proved wanting in terms of undermining the coating so we're looking at ion implantation techniques. There again, since this is a totally new chemical corrosive environment, we have no experience. We have the whole spectrum of periodic table, but we can't afford to do that, so there will have to be some judicious choices in terms of what to use. We can't fall back on the literature because the previous compatibility tests have shown that we can be fooled by the guidelines in terms of what normally should be corrosion resistant. There is another possible use for implantation here, however, in the fact that implantation has a broad spectrum of potentially protective species that can be used.

C. Levy: Your remarks about the coating techniques are well taken. I see this as a prime advantage of ion implantation over coating methods where you have a distinct interface between the coating and the substrate. With ion implantation, of course, you have a material integral with the surface. This can be quite an advantage. However, your point on cost effectiveness is also well made. This is an area

that we have to work on. I'd like to ask if anyone in the audience would like to address these two areas of possible use for ion implantation: depleted uranium surface protection and for biological chemical agent protection.

P. Parrish, ARO: Regarding the first application, it seems like it would be best to implant the grooves themselves and not worry about the rest of the penetrator for the use of ion implantation. The grooves are critical, and you need a fit up without a dimensional change, so it sounds like a perfect application to me.

S. Cytron: Yes, Phil you are right. I think it still has to be demonstrated whether the grooves might be stress risers in terms of stress corrosion cracking. However, there is also a concern for coating the entire penetrator because there should be no classical corrosion after a twenty year storage. I think aluminum is going to be our first approach to a coating, but that is just a guess.

J. Cox, Benet Weapons Lab: That Ivadize process reduces the fracture toughness of the DU.

S. Cytron: There was a concern that the IVD process would somehow degrade the performance of the material, but we haven't fully demonstrated that. Nevertheless we want to have a fallback process in terms of the coating corrosion protection.

P. Sagalyn: I did learn last month at Harwell that they have a classified program in implantation of depleted uranium.

C. Levy: Paul Fopiano, I wonder if you could say something about the work of friction and wear in conjunction with what Jim Hirvonen said.

P. Fopiano, AMMRC: I think Jim can say more about that than I can. We're certainly interested, in the Army, in making both gears and bearings more corrosion resistant. If you think you have problems with bearings, try a gear. We're involved. I don't know if you want to talk about the TTCP program. Fred Smidt and Jim are very much involved with the TTCP round robin effort with the five countries. Involved are New Zealand, Australia, United States, Canada, and Great Britain. I guess he has gotten responses from Canada and New Zealand.

F. Smidt, NRL: I got to your meeting late because I have been traveling around the country with Technical Panel P-4 of TTCP that has just finished its 2-week annual meeting. One of the demonstrator projects that we have is to apply ion implantation to produce corrosion-resistant bearings. The project is one that I am sure Jim has described to you. It is the application, or more the demonstration, of something that is coming out of the laboratory and could be ready for a wider scale application. One of the mechanisms for doing this through TTCP is to get cooperative demonstrator projects in the various countries. We sent out a background statement and a proposal for some round robin testing 3 or 4 months ago to people that had been suggested as being interested. We now have a positive response from Canada from the Defense Research Establishment Pacific to follow up on some corrosion tests and fatigue tests on rolling element bearings, Paul (Fopiano) has indicated an interest, and also the Australians. So we will be conducting a round robin program over the next couple of years.

P. Sagalyn: In one review article I was reading I came across a very offhand mark by the Harwell people that sounded like sort of a trick. They have implanted

steel with molybdenum and then twice as much sulfur to, in a sense, implant moly disulfide. They then ran some friction tests and found that they had reduced the friction. No numbers are given. I am just wondering if you know any more than what I've just said about that project or whether anybody had followed up on it.

J. Hirvonen: We have tried that as well. The idea is to try to put moly in and then overlay it in the same depth with twice as much sulfur in order to promote perhaps something like moly-disulfide in micro-reservoirs. They do quote measurements in some of their earlier work on improvement where the net result of doing both is better than either alone. The result, if you look at the numbers, is not a spectacular change but I guess it is a significant. However, what they don't mention are the conditions of the implant. If you look in the literature, there is a UK patent in which they talk about that process and mentioned the desirability or necessity of doing it hot, a point which is not mentioned in any other article that I am aware of. So it is in the literature, in the patent literature of the lab.

C. Levy: Jim, when we send you your remarks for editing, could you give us that name and number for inclusion in the proceedings?

J. Hirvonen: Yes. (UK Patent No. 1, 413, 813, 11/12/75, Dearnaley and Hartley)

A. Niiler, BRL: We have, in the past, tried to use ion implantation to solve another one of the Army surface problems, namely gun tube, erosion. We have a little test device at BRL in which we can test donut shaped nozzles under essentially real firing conditions. We shoot hot propellants through the device, and, by measuring mass loss of the nozzle and wear off the surface of the nozzle by thin layer activation, we get a good measurement of erosion loss. Jim Hirvonen did some nitrogen implantation for us a few years ago, one of them to a depth of 80 kilovolt nitrogen and another one at 1 MeV nitrogen--two significantly different depths. We characterized the surface before and after each of two or three shots or until the nitrogen was gone with ion beam analysis and we found that in both cases the ion implantation had essentially no effect on the erosion or on the hot gas erosion.

S. Cytron: What was the erosion rate? Was your erosion after the first shot below the implantation layer?

A. Niiler: In the case of the 80 kilovolt implant, yes. In fact, it took off the layers thicker than the implants. In the case of the 1 MeV implant, we did two shots. The first shot took off a lot less than implant depth, but the second shot took off a lot more. We have done a lot of work with these nozzles and other types of experiments so that we know pretty well that there occur shot by shot variations greater than what we saw in the case of these implanted nozzles. So we conclude no effect.

S. Cytron: On a two shot test, did you have the opportunity of doing a profile in between the two shots (A. Niiler, yes indeed.) and what did that profile show in comparison to the initial nitrogen implant and the final?

A. Niiler: It showed most of it still there..

S. Cytron: Yes, but the profile didn't stay the same. It must have shifted or...

A. Niiler: No, not in any significant way.

S. Cytron: You got a broadening from the thermopoles. You didn't get any broadening?

A. Niiler: No. Of course now I'm remembering back two years. There may have been slight differences but not significant enough to bother with, I don't think.

C. Levy: Mr. Niiler when you send in your comments for the proceedings could you give us a reference if that has been published in a report?

A. Niiler: I have talked about it at some conferences, but that is it.

C. Levy: Okay, maybe you can give us a short write-up on it to complete our input.

A. Niiler: And now to continue. Just recently, I had another one of these nozzles implanted with yttrium by Geoff Dearnaley at Harwell. The full nozzle is implanted and I just got it this past week so we haven't had any chance to do any testing on it yet. If the erosion process is hot gas erosion, hot oxidation, then there is some hope that this rare earth element metal will help retard the erosion somewhat. Maybe if you have this workshop again next year, we can let you know what happens.

J. Hirvonen: I'd like to comment on two points. One is the experiments you are considering on the penetrator. I think I am echoing common sentiments of many people that it is necessary for every application first to be considered in a light of what's known, as you suggest, but do not plan to go directly to a end product. Everything needs some F&D in it even in today's restricted monetary situation. Regarding the hot gas erosion test, as Andy agreed when we did the implantation, there are some things which are not expected to work, like the drill bits, but you know it is worth a shot in the dark.

A. Niiler: One of the things that has been talked about has been the formation of the interface region which, from all I can see here today and some previous looking, ion implantation gives you something in the order of a 1000 angstrom interface region, roughly that. There is another process which Sheldon Cytron referred to, IVD or more specifically the ion plating, which a lot of us have gotten into. In that situation you can get a lot thicker interface regions. We have seen some which are on the order of a half a micron thick. With these you are putting on a very thin coating which may have essentially all of the advantages of the substrate for strength, etc., but the surface properties of the added plating. Possibly even some form of alloying can be done on the surface.

C. Levy: In terms of what several of our speakers said today, ion beam mixing, which is the kind of thing you are talking about, is probably one of the selected techniques that we'll use in the future in addition to the straight ion implantation. Are there any other comments? Someone mentioned hot corrosion. One of the applications that has come to our attention has been kicking around for perhaps 20, 30 years, namely turbine blades in jet engines. I was wondering whether anyone had any thoughts on applications in that area or had any comments in that area.

P. Parrish, ARO: Fred Pettit at Pratt & Whitney a few years ago did some research putting minor amounts of platinum into aluminide or  $Al_2O_3$  scales and found good hot corrosion resistance. That has been followed, to a degree, by the Australians using a coating treatment that includes platinum. I was interested in Jim's comment about the barium and whether the platinum needs to diffuse down to the metal oxide interface in order to eventually afford the protection that you wind up getting. The Australians have shown tremendous improvements in their maintenance schedules with this platinum modified coating versus normal aluminide coating from what I understand. I was wondering about implanting either platinum or barium at the point where you really want it to be, rather than waiting for diffusion to occur, to the protection you want.

F. Smidt: I can speak to that a little bit. We're just initiating a research program this year in cooperation with Fred Pettit (University of Pittsburgh). We are also getting Graham Johnson from Australia on a year exchange under TTCP. We're going to be looking at the effects of various implanted species on the performance of CoCrAlY coatings. The application is primarily the hot corrosion problem in marine gas turbine engines. But I should say that we're viewing it primarily as a research tool to understand what some of the trace elements are doing. At this point in time I am not convinced that the beneficial effects are going to persist for very long because, as the surface is oxidized, you form an oxide scale. Where it flakes off you don't have the reservoir of the bulk material to continue providing the beneficial properties. But implantation should be a tremendous research tool, and that was basically how we sold it. Pettit and his people have ONR funds and NRL has some in-house funding. I just visited Air Force Materials Lab two days ago and they've done some platinum implants on titanium turbine blades. They find improved high cycle fatigue performance. I learned just yesterday that they are also looking at implantation to retard fretting corrosion in the notch of the dovetail. The surface seems to be the point where fatigue cracks are initiating, so implantations seem to be giving quite good results. Fujishiro is the man working on the problem.

S. Cytron: I would like to clear up in my mind some general areas that came up; for example, applications at high temperatures. The implantation technique is a metastable technique. Most of the systems that we are talking about are metal species or interstitial atom species in a metal system. Hopefully you do it at room temperature and avoid any heat or thermal spots. When you put this implant material in and give it a high temperature application, if you don't develop an adherent oxide where you can actually peg that implanted species, it's going to diffuse into the bulk or diffuse out.

J. Hirvonen: Well, as Mike Bennett's review article shows, in many cases the effect of implanted species such as yttrium, stays at the metal-oxide interface where it is needed. They have also shown some years ago in niobium stabilized austenitic stainless steel that implanted yttrium was as effective as the bulk yttrium over long periods.

S. Cytron: Right. You have to establish some mechanism where the implanted species is pegged. Either it ends up at a diffusion barrier or an oxide film or precipitates out as an oxide or some other precipitate. But you'll have to somehow peg it, during or after the application process. Otherwise it is going to diffuse away, if you're dealing only with a metal ion species in a metal substrate.

J. Hirvonen: You're absolutely right. What has also been found in some cases, is that the implantation of a minor constituent in an oxide (such as alumina) is very important for its long term protective effect, presumably because of the initial cohesiveness of the oxide. That is not to say it always happens, but there are situations where you can affect the initial conditions of oxide, and that can be extremely important.

S. Cytron: If that type of mechanism is active then, are people looking at a criteria in terms of choosing an implanted species and in terms of setting up a diffusion barrier at an oxide, so that you retard the mass transfer across that metal-oxide interface? I mean the corrosion and the progressive building up of the corrosion film is a mass transport diffusion process, so are there some criteria where you can develop a diffusion barrier?

F. Smidt: There are a couple of points. Some of the mechanisms we are looking at are poisoning the short circuit diffusion paths. Pettit feels this is one of the primary mechanisms for slowing growth of the oxide film and that is one of the things that we will be looking at; what species can we use to poison or block these fast diffusion paths. The other point is, as Jim noted, if you can get a good coverage of the protective oxide film early in the oxidation stage, you don't have selective oxidation. Chromium oxides and some other things that are not as protective as alumina, will not form and break up the integrity of the protective coating.

S. Cytron: I seem to remember Jim showed a slide of the palladium in titanium after hot corrosion (or was it in hot aqueous corrosion) and the palladium profile changes pretty drastically with time. Was that in combination with the oxide on that surface or how do you account for uphill diffusion, the higher concentrations of the palladium with time?

J. Hirvonen: When you have buried palladium with the surface concentration initially a few tenths of a percent, you have rapid dissolution of the overlying titanium; that was confirmed by electrochemical data of McCafferty. As you expose more and more palladium, it remains on the surface but reaches a concentration high enough--although it is probably in the form of separated islands, but still high enough--to change the kinetics of corrosion by about three orders of magnitude. You initially have a low surface concentration but the overlying titanium gets rapidly eaten away until you reach the point where we have effectively halted corrosion by the presence of a sufficient amount of palladium at the surface.

P. Hamill, ATL: Has NASA-Lewis looked at ion implantation for their traction drives devices? Of course this application is rolling contact in power transmission, rather than the sliding contact common to gears. However, the application would seem to be almost perfect for some type of ion implantation, since you are showing increased wear resistance and improvement in fatigue life.

J. Hirvonen: Tally Spalvins of NASA Lewis had mentioned to me that NASA was doing something in that area or wanted to. You might check with him.

P. Hamill: It would be most helpful to increase the life of that traction drive. Wear is the main problem.

SIXTH SESSION:  
CORROSION STUDIES

USE OF ION IMPLANTATION TO  
MODIFY THE CORROSION BEHAVIOR OF METALS

Bruce Sartwell  
U.S. Bureau of Mines  
Avondale, Maryland

I'd first like to give you a short review of the Bureau of Mines Corrosion Research Program before going into the specific areas of the talk. I am sure that you've read somewhere recently about concern over critical and strategic minerals and the fact that we must import close to 100 percent of elements that we require such as chromium, cobalt, and platinum. Although you may be unfamiliar with the Bureau of Mines, it is the Government's principle agency for mineral resource conservation through development of efficient recovery systems for domestic reserves, and for research directed toward enhancing the use of domestic resources that might reduce some of our critical import dependency. The research has been directed toward development of a basic mineral technology, conservation of resources, extension of the span of domestic minerals, and substitution of abundant minerals for those that we have to import. It is within this latter area that our corrosion research program at Avondale is conducted.

In the presentation today, I will be discussing our application of ion implantation to the development of corrosion resistant alloys and to the understanding of corrosion phenomena. As you learned yesterday, ion implantation is a technique that permits the fabrication of micro-alloy systems of varying concentrations using essentially any element in the periodic table. In general, if you have a program where you want to determine substitute alloying elements, it is pretty costly to go out and fabricate a whole series of bulk alloys with varying concentrations of a wide range of different elements. But with ion implantation, you are modifying only the surface, and that is where you are going to do your corrosion research; in essence, how the surface interacts with an environment. You can change the surface composition at will, and you can get your whole range much cheaper than fabricating bulk alloys. As you learned yesterday, you can also form metastable alloys that can't be formed by conventional techniques. If the purpose of using ion implantation is to identify a particular corrosion resistant alloy, it is quite likely that the end process that will be used to produce these alloys on a commercial scale will not be ion implantation. But there really is little doubt as to the value of ion implantation as a research tool in a materials development program.

In studying ion implanted alloys, it is of course necessary to know what you have, and Clive is going to emphasize the value and the necessity for characterizing the implanted alloys. The technique we have used to analyze our alloys is proton induced X-ray emission (PIXE) which enables us to determine the number of atoms per square centimeter of the implanted elements remaining in the substrate after implantation and to characterize any surface impurities that might be introduced. We also use this technique to analyze the sample after corrosion testing to tell us how much of an implanted element remains. Of course, with high dose implants as you saw yesterday, you get sputtering effects which can remove previously implanted atoms. You can also get carbonaceous material on your specimen surface due to say, dirty vacuum systems, or due to the fact that you have a lot of carbon in your substrate. So, obviously it is not enough to simply measure the dose in your

implanter and state that the number of ions per square centimeter implanted is the number of atoms per square centimeter left in the substrate. That may not be true.

For those of you not familiar with proton induced X-ray emission, Figure 1 shows our PIXE facility. Behind the wall is the 300 kilovolt accelerator and it looks pretty much like the one shown yesterday for the implanter. The proton beam is mass analyzed using an electromagnet, and the beam then goes through another switching magnet where we can direct the beam into any of three target chambers. One chamber is an old Auger/LEED system so we can do simultaneous Auger/PIXE analyses. The data analysis and handling system is in the background. Figure 2 shows the schematic of the PIXE target chamber. We mount the implanted alloy on an XYZ precision manipulator. The proton beam enters the chamber, bombards the sample, and we detect the emitted characteristic X-rays using two detectors. One is a lithium-drifted silicon solid state detector. The other is a proportional counter which is used for looking at very low energy X-rays like carbon and oxygen. So it is very easy to do this analysis to get a quantitative measure of the implanted element. If you have implanted, say, chromium into iron, the proton beam is analyzed for chromium X-rays and with certain conversion factors, taking into account the X-ray production cross-section, you get a direct measurement of the number of chromium atoms per square centimeter implanted. If you have any type of surface contamination such as chlorides or hydrocarbons, you can measure exactly how many atoms per square centimeter are on the surface. You can also do depth profiling with a sputter ion gun in the chamber. A former colleague of mine, Art Campbell, developed the technique for actually getting composition depth profiles of implanted elements using the PIXE technique. We also do in situ oxidation for looking at oxide films. We can heat the sample up, backfill the chamber with high purity oxygen through a leak valve, then analyze the sample and measure oxide film thicknesses. So we can study oxidation kinetics. Emitted oxygen X-rays will pass through an X-ray filter. So we backfill this filter to about 1/10 atmosphere of oxygen. We will also have some carbon K X-rays and iron L X-rays emitted from the sample, and these will interfere with the oxygen K line because of the very poor resolution of the proportional counter. However, by putting oxygen in the filter, we selectively absorb the iron L and the carbon K X-rays. We are left with a very nice sharp oxygen peak giving sensitivity down to less than a single atomic layer of oxygen. We can even do chemi-sorption studies, so the technique is extremely valuable for looking at implanted alloys. Of course we use it for other things; analyzing corrosion films, and so forth. It is highly quantitative, and permits depth profiling. If you want to know how many atoms per square centimeter are left after the implant this is a good technique to use. One interesting fact we have found started with implanting  $2 \times 10^{16}$  lead ions into iron. If we doubled the dose in the implanter to  $4 \times 10^{16}$ , analyzed the result by PIXE, we found we haven't really doubled the amount of lead in the sample, we have only increased it by 20% because of the sputtering effect. So, by this analysis after implantation, you can get a measure of how many atoms are being sputtered off as you go to these higher doses, and you can get a measure of your absolute limit by using this technique combined with the measure of your dose coming from your implanter.

That summarizes our analysis technique. I'm now going to cover different areas of corrosion that we have examined. Figure 3 is anodic polarization. When you are going to evaluate the corrosion resistance of implanted alloys you could do the implant and then put them outdoors for a couple of years. That may be good for job security but it is not too good for rapidly evaluating corrosion resistance.

Electrochemists have developed further techniques, and one of them is anodic polarization. In this case we were using a boric acid solution containing 2400 parts per million of chloride ion so that we could also study pitting corrosion. The solution is connected to a reference electrode and you change the potential of your sample with respect to this reference electrode then measure the current. This is a measure of the corrosion rate of your metal sample. In some metals, as you increase the potential, the corrosion current will just keep on going up. But for a lot of metals, like irons or stainless steels, you get an active corrosion region. The corrosion rate will increase with potential up to a certain point. Then as you raise the potential beyond that, the corrosion rate will drop and you enter what's called the passive region. Now had we not had the chloride ion in this solution, the iron would have had a fairly long passive region through here and then it would have increased again further out here at a higher potential. But because we had the chloride ion in there, we started pitting corrosion at this potential. There were two parameters used to measure corrosion resistance. One, the current level at the peak of the active region. That is called the critical corrosion current. The other is the potential at which the corrosion accelerates after the passive region, and that is called the pitting potential. So we are looking at general corrosion and pitting corrosion resistance. As you can see, by adding chromium in the bulk iron; 5% chrome, 12% chrome, 18% chrome, we greatly reduce the active corrosion and we are shifting this pitting potential to the right. As you might guess, adding chromium to the bulk reduces the corrosion rate and increases the resistance to pitting corrosion. Therefore we wanted to see if chromium could be implanted in iron to get the same results. In this case we implanted chromium to a composition of 19 atomic percent within just the first 200 angstroms of the iron surface. Analysis showed no active corrosion whatsoever and the pitting potential has been shifted to the right, somewhat, although certainly not as much as for the bulk alloy. So in terms of general corrosion resistance, we can duplicate the bulk alloy. For pitting corrosion resistance, we can improve the situation, but certainly not as much as the bulk alloy.

Figure 4 shows some results for nickel implantation. Vascomax 250 is a maraging steel with 18% nickel in it. Type 9 nickel steel is just iron 9% nickel, and you can see by implanting iron with 25 atomic percent nickel in the first 200 angstroms, we can greatly reduce the general corrosion. We were also able to increase the pitting corrosion resistance to a point roughly equivalent to the bulk nickel alloys. So the nickel implantation was as beneficial as bulk nickel alloy additions for both general corrosion resistance and pitting corrosion resistance.

Figure 5 shows what happens when you implant chromium into a maraging steel. Implanting chromium still improves the corrosion resistance. Vic Ashworth of UMIST pointed out a possible application of this. The maraging steels are generally solution heat-treated around 1200-1250 degrees Kelvin for strengthening and toughness. If you wanted to use that alloy but increase it's normal corrosion resistance, one way might be chromizing, but that's generally done at about 1050 degrees Kelvin. So it would be difficult to get both strength and corrosion resistance with compatible heat treatments. For small precision components needing the strength and toughness of something like the Vascomax 250, but with increased corrosion resistance, you can fabricate the parts, solution heat-treat and then as a final processing step implant chromium to increase the general corrosion resistance.

So far, we have looked at chromium and nickel implants into iron. Of course, these alloys can also be fabricated in the bulk. As pointed out yesterday, one

of the advantages of implantation is forming metastable alloy structures. Since very few studies have been done, that is a wide open field. One alloy we've looked at involves implanting lead into iron. Lead normally has very low solid solubility in iron. Figure 6 shows the open circuit potentials of lead implanted iron, pure lead and pure iron. As you can see, this was in tenth normal sulfuric acid solution. We found that even over an extended period of time, the potential difference or the difference between the lead-implanted iron and pure iron remained constant. The lead was only implanted to a depth of 50 angstroms, extremely shallow. During this time period, over 300 minutes, approximately 1000 angstroms of the metal had been corroded away and PIXE analysis showed at this point we still had half the implanted lead still present. Obviously the iron is being selectively corroded away, and the lead is remaining behind. Using linear polarization to look at the corrosion resistance, the corrosion rate of the lead implanted iron was a factor of four less than pure iron. Even though we have implanted to only a 50 angstrom depth and a depth of 1000 angstroms has corroded away, there is still half of the lead remaining protecting the sample.

Eventually all the lead is going to be gone and you won't have a corrosion resistant alloy. However, we have used ion implantation to determine that a lead-iron solid solution mixture gives you a fairly corrosion resistant material. That doesn't mean that if you're ever going to form this in a commercial process, that ion implantation is going to be the technique you use. You could use laser alloying which could give you a one or two millimeters thick alloyed layer that would have long term corrosion resistance. Thus, ion implantation was a research tool that was used to prove that a solid solution mixture of iron-lead does give you a corrosion resistance surface.

We have also done a short term study on galvanic corrosion. Figure 7 shows the apparatus used. These studies were initiated by requests from an aircraft company. They were using Ti-6Al-4V rivets to hold the skin of aircraft together. The problem was that the aluminum was corroding in the vicinity of these rivets because of a galvanic couple between the rivets and the aircraft skin. For some unexplained reason coatings were never satisfactory to them. The company asked whether it would be possible to use ion implantation to change the galvanic corrosion behavior of the couple. We used a 3% sodium chloride solution, putting in a piece of titanium and a piece of aluminum at open circuit. Over here we coupled through a 100 ohm resistor, a piece of aluminum with either pure titanium or a piece of titanium that had been implanted with aluminum. We measured the potential drop across that resistor to give us the galvanic corrosion current. Figure 8 shows the results. The test ran over 6000 minutes. This is the current density giving a measure of the rate of corrosion of the aluminum in this couple. You can see it is quite high when the aluminum is coupled to pure titanium. However, when the aluminum is coupled with titanium implanted with aluminum, either 16 or 30 atomic percent in the first 200 angstroms, we get a reduction in the corrosion rate by a factor of four and it does last over the 6000 minutes. So it is possible to modify galvanic corrosion couples by increasing the surface concentration of one element. Of course you're not affecting the strength or the physical properties of the other material.

We have also looked at stress corrosion cracking, and the next slide shows the surface of 316 stainless steel exposed to a boiling magnesium chloride environment, a fairly standard environment for studying stress corrosion cracking of stainless steel. The sample was a thin cylinder about 3 or 4 millimeters in diameter,

and it was stressed to 90% of the yield strength in the boiling magnesium chloride solution. We looked at the time to failure for the sample. Figure 9 shows the formation of a series of microcracks in the surface of the sample. Obviously the boiling mag-chloride solution was very aggressive to the 316 stainless steel. We next implanted silicon ions into another 316 sample. Figure 10 shows the sample after an equivalent exposure to the boiling mag-chloride solution. We are still getting the microcracks but the density of the microcracks is obviously greatly reduced. The time to failure for the silicon implanted 316 steel was a factor of 2 higher than the time to failure for the unimplanted steel. PIXE analysis showed that the film formed on the implanted 316 was about half as thick as the film formed on the unimplanted material. It's believed that initiation of the stress corrosion crack occurs with the rupture of this passive film. For some reason, the film formed on the silicon implanted steel was perhaps more plastic, was able to withstand the stress being applied to the sample and thus at least inhibit, to a small degree, the formation of these microcracks.

On the other hand, we implanted nitrogen into the 316 steel and found that this was detrimental to the stress corrosion crack behavior. Figure 11 shows another SEM photo. These lines here are merging at slip steps at the surface and the formation of this surface topography creates the image of a small explosion occurring at these different merging slip steps. So we believe that the nitrogen is migrating to these slip steps as they emerge to the surface. When the sample is under stress there may be a high pressure build up at the slip steps that does cause a release of the gas, and these sites could serve as the initiation sites for stress corrosion cracks. We did observe that nitrogen being present was detrimental to the stress corrosion cracking resistance.

It is not only true that you're going to use ion implantation to try to improve a materials performance. You can use it to understand what happens when you put element "x" into your materials. Will it be detrimental or will it be beneficial? Thus, we are not simply looking at what ion implantation can do, we're looking at what an element can do when it's put into another material.

We have also looked at corrosion fatigue behavior. Figure 12 shows our apparatus, based on a standard R. R. Moore rotating beam fatigue testing machine. We built a little cell in which we could put a solution. The sample is a standard fatigue type sample. The necked down diameter is about 1/4 inch. Our procedure is to mask off virtually all of the steel except for the narrow portion and we do our implantation into this narrow portion. I don't have final results to show as yet. Since this is some work we just recently completed.

It is known that titanium is a fairly good material to use in a 3% sodium chloride solution. It is better than stainless steel. It forms a nice passive layer, and it's resistant to pitting attack in a sea water environment. So we thought implanting titanium into the carbon steel might be beneficial to corrosion fatigue behavior. However, suprisingly enough, not only was it not beneficial, it was slightly detrimental. As we increased the amount of titanium in the near surface region, the number of cycles to failure of the material was reduced. The reduction was about a factor of two which in fatigue experiments is not considered to be too significant. But, by also monitoring the potential of the sample during the test, we saw a significant change in the sample potential. So that, correlated with the change in cycles to failure, indicated that we were getting a different effect. We think that during implantation of titanium into steel a titanium carbide

amorphous layer is formed that can be very corrosion resistant. However, in a fatigue environment where you are subjecting this amorphous surface layer to alternating compressive and tensile stresses it can be ruptured. The site of the rupture can be a very high anodic area which will serve as a possible initiation site for fatigue cracks. So, you cannot extend the logic that a stress-free corrosion resistant surface can also be used where you have compressive or tensile stresses as well. It could actually be detrimental.

We've studied oxidation behavior of some of the implanted alloys. Figure 13 shows some results of oxidizing pure iron and iron-18 chrome bulk alloy and an iron-24 atomic percent chromium implanted alloy. The oxide thicknesses were measured by the PIXE technique and this study was done, rather than in the PIXE chamber, in a furnace that was open to atmosphere. As you can see, the rate of oxide buildup is extremely rapid for pure iron. The bulk alloy oxidizes extremely slowly. Even for a time period of 500 hours the surface alloy follows the exact same oxidation kinetics. We were able to get long term oxidation resistance by implanting the chromium into iron, but that wasn't all that surprising. Figure 14 is a photograph of the three samples after the oxidation. One is the pure iron with its oxide film. Another is the bulk alloy with the implanted chromium. The little strip across this iron is where it wasn't implanted. It oxidized, so you get the same visual appearance. We looked at the oxidation behavior of iron by implanting several different elements and that is shown in the next slide. We implanted nitrogen, silicon, titanium and magnesium into the iron. As a reference point, pure iron oxidizes at about the same rate as the silicon implant (Figure 15). You can see that nitrogen was actually a bit detrimental. We got linear oxidation kinetics for nitrogen implants. Silicon was not beneficial. We got the same kinetic of oxidation for a silicon implant. The titanium and magnesium were beneficial but not to the same extent of the chromium implant. In this particular case we were unsuccessful in finding an ion that would duplicate the oxidation resistance of the iron-chromium alloy. But negative results are results, so they are worth showing.

For the results in Figure 16, I borrowed from some of the Harwell work. There is a question on the peak temperature for heating the implant. Implanting gives a concentration gradient of the added element near the surface. So as you heat the sample one would expect that elements would diffuse inward because of this concentration gradient. In fact, when we oxidize an iron-chrome implanted alloy at 500°C, the chromium did just that. There was no oxidation resistance observed after heating to 500°C. So, one has to be concerned about this fact.

However, Antill, who was part of Dearnaley's group in 1973, looked at the oxidation behavior of a 20-25 stainless steel. They oxidized it in carbon dioxide at 800°C. One curve shows results for the basic stainless steel. The solid circles here are for yttrium implanted stainless steel. You can see over extremely long time periods, 5000 hours, the oxidation resistance of that implanted alloy stayed as good as adding yttrium in the bulk, represented by the open figures here. Where we have a yttrium composition gradient near the surface, one might expect it to diffuse in. Obviously it didn't do that. It stayed in the surface and gave oxidation protection. So, it is impossible to make any general conclusions about oxidation resistance after raising the temperature of an implanted alloy. You have to study the particular systems you are interested in. It doesn't work for iron-chromium implanted alloys. It does work for yttrium in the stainless steel.

Figure 17 came from a talk I gave in Manchester, the end of last month. Titanium seems to be extremely interesting to implant into iron. You always get strange results whether detrimental in corrosion fatigue or beneficial in other environments. These oxidation studies were done in the PIXE chamber. We heat the sample up, bleed in oxygen to a pressure of  $8 \times 10^{-6}$  Torr and then look at the rate of oxide film growth as a function of time. We implanted four iron samples with titanium to a fluence, as later measured by PIXE, of  $7.3 \times 10^{16}$  ions/cm<sup>2</sup>. We took several of those samples, and did the oxidation studies. Oxidation followed pretty much logarithmic kinetics. A second group of samples was implanted to  $8.1 \times 10^{16}$  and, to give more statistics, I did oxidation studies on that still expecting to at least come close to the curve for the lower fluence. Surprisingly enough that sample didn't oxidize at all. We kept running the oxidation test, heating it up, bleeding in the oxygen. No oxide film growth. And we're talking about a thickness here of only about 25 angstroms. The oxide film thickness stayed 25 angstroms no matter how long the sample was oxidized. I really didn't believe that this result could be simply due to this extremely small increase in the amount of titanium. We knew that if you have carbon present you can form an amorphous surface layer. We took this sample and did Auger profiling on it, and found something interesting. In Figure 18, we're just plotting Auger amplitude as a function of sputtering time. This depth represents that 25 angstroms of oxide, and, as you can see, we had a peak for the titanium in the oxide itself. So we probably had some titanium oxide as well as iron oxide. It went down again and then down at this interface here moving into the iron substrate. We got a second peak of titanium along with a peaking in carbon. So we believe that it is in this region right here that we probably have the titanium carbide amorphous layer that is somehow inhibiting the oxidation. I don't have a viewgraph to show for the Auger profile of the other sample but we did not see this carbon peak here for the other sample, it stayed fairly low going into the interface. So, for some reason, one sample had more carbon present, and it formed, or we think it formed, this amorphous layer that gave significant oxidation resistance. This is one of those studies where we got a fortuitous result just based on a little bit of additional contamination of carbon on the surface of the sample.

That covers pretty much all of the studies that we've done. I know I've run through everything very quickly but I just want to give you an idea of how valuable ion implantation is in a materials research program. We're not trying to prove that is a good commercial technique. That's not our purpose for using ion implantation. Of course, we believe it will be proven that way, but for now it is extremely valuable as a technique in a materials research program. We're not looking at what ion implantation does to materials. We're looking at what the effect of adding an element in solid solution on corrosion behavior of a material, whether it be general corrosion, pitting corrosion, stress corrosion cracking, or corrosion fatigue. I hope I have been able to convince you of its value and I hope you'll consider using it as a research tool in any type of a materials research program. Thank you.



Figure 1

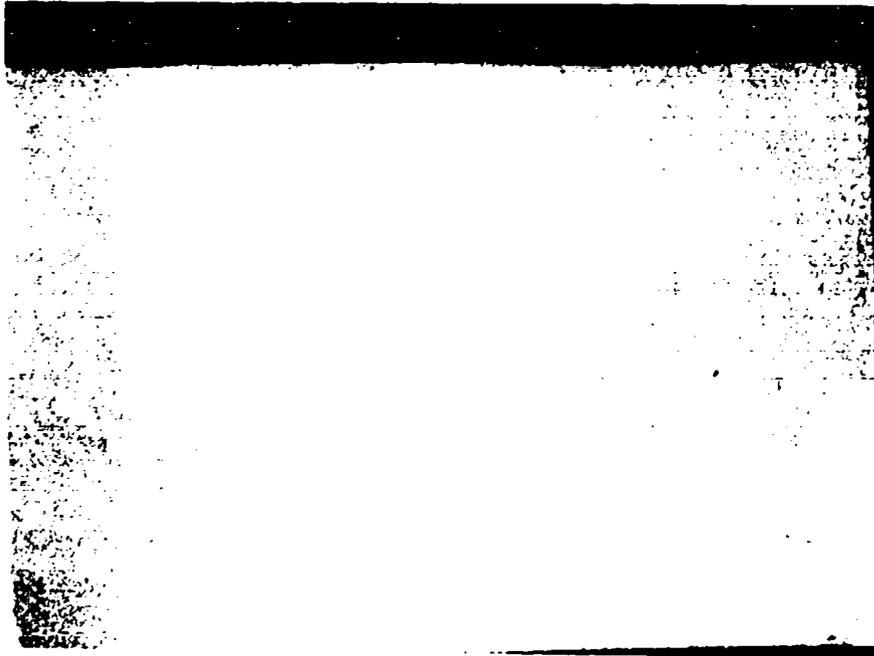


Figure 2

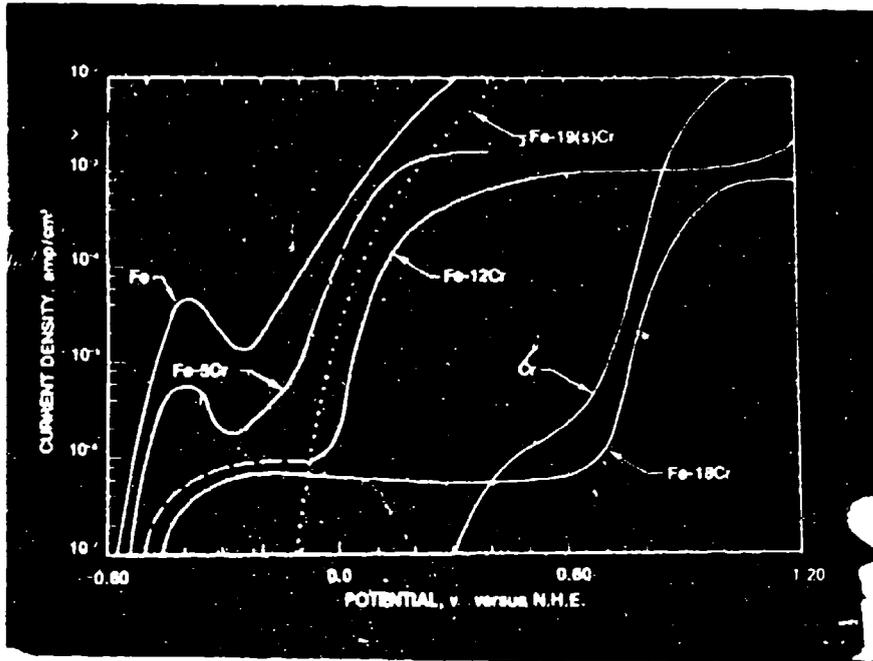


Figure 3

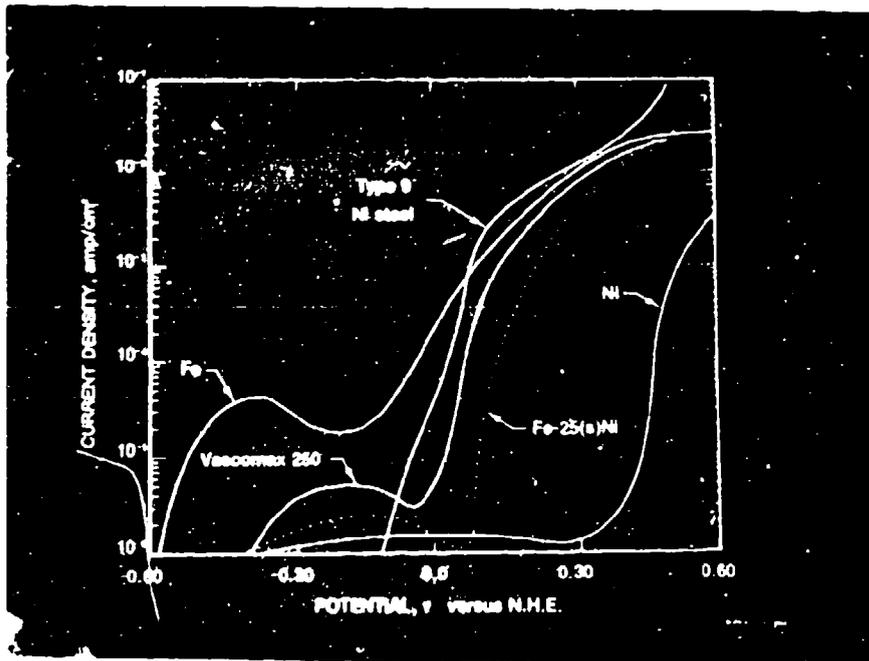


Figure 4

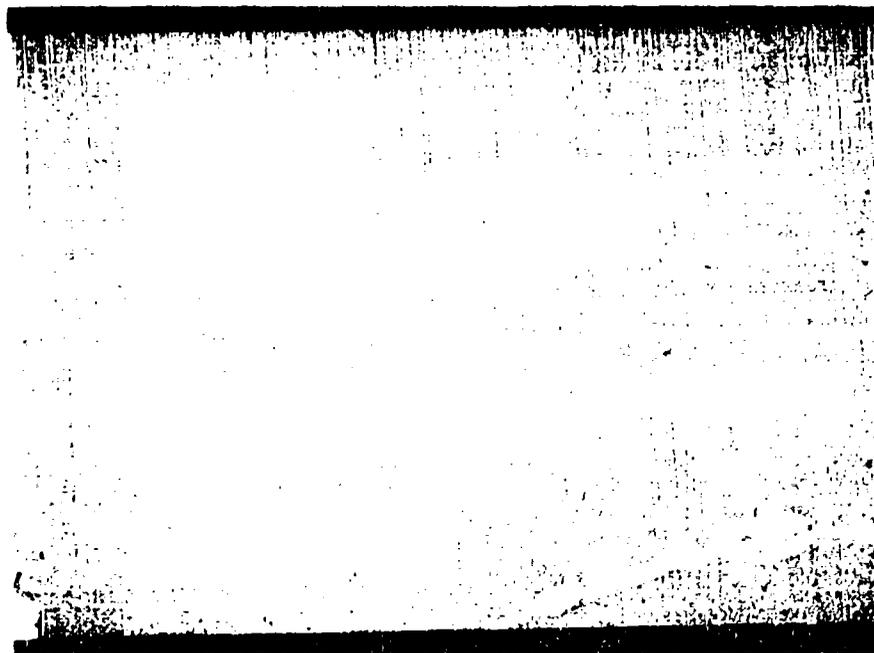


Figure 5

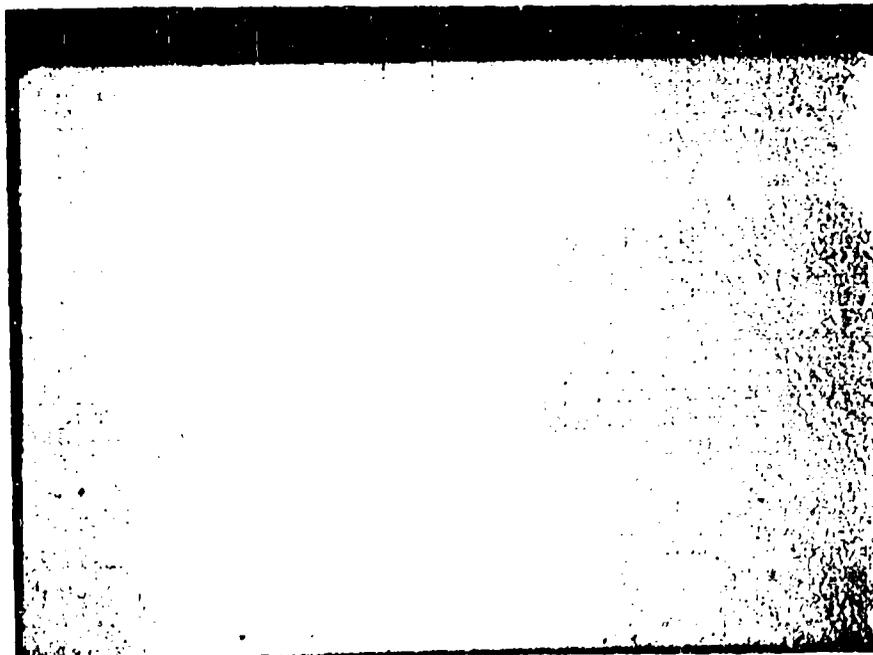


Figure 6

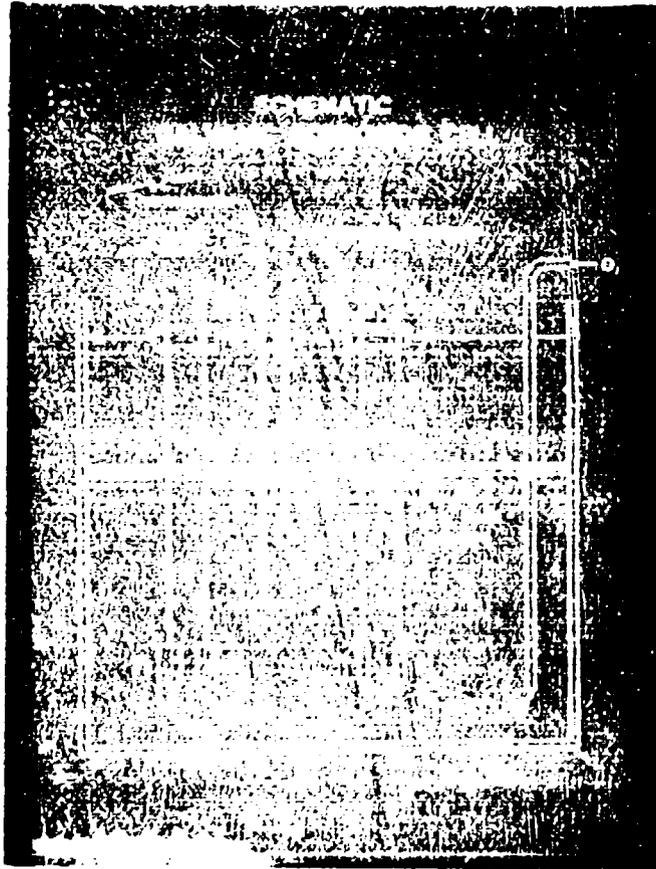


Figure 7

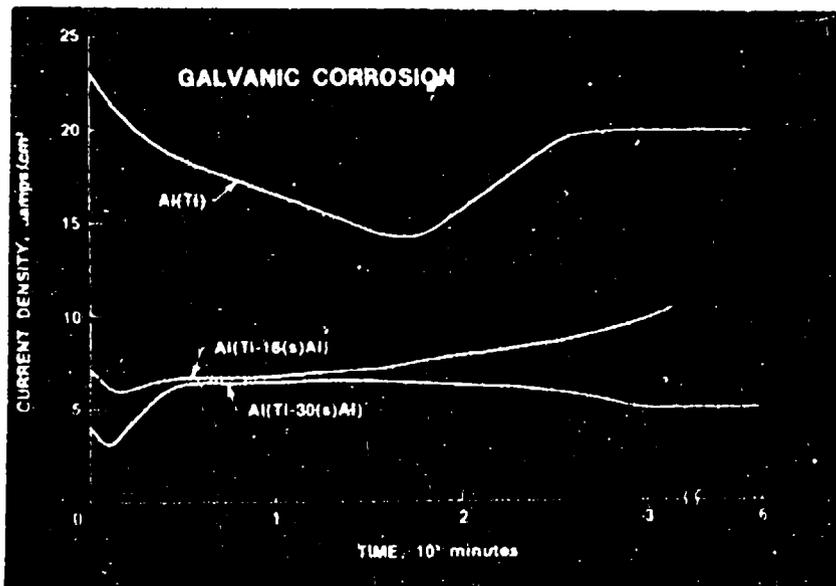


Figure 8



Figure 9



Figure 10

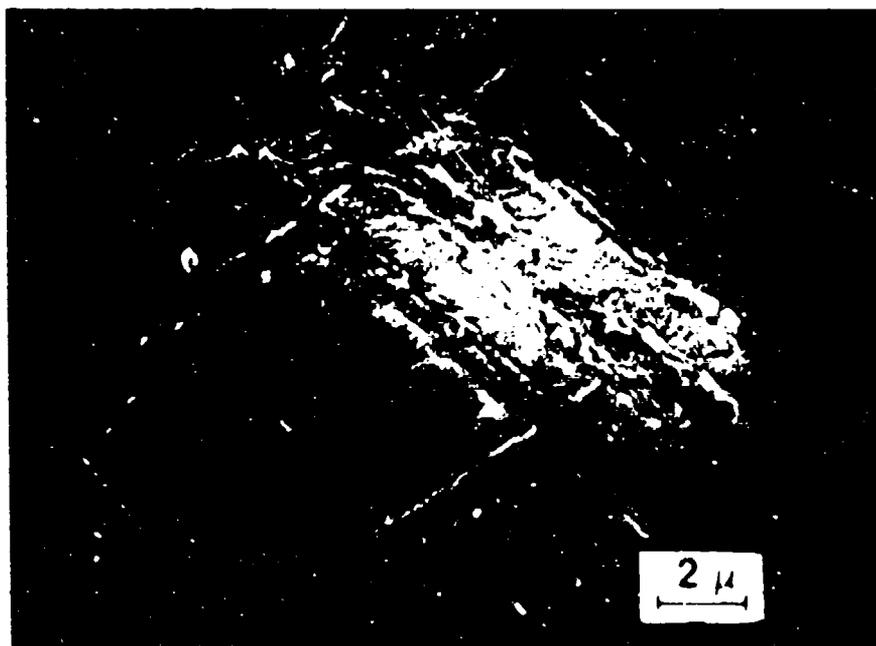


Figure 11



Figure 12

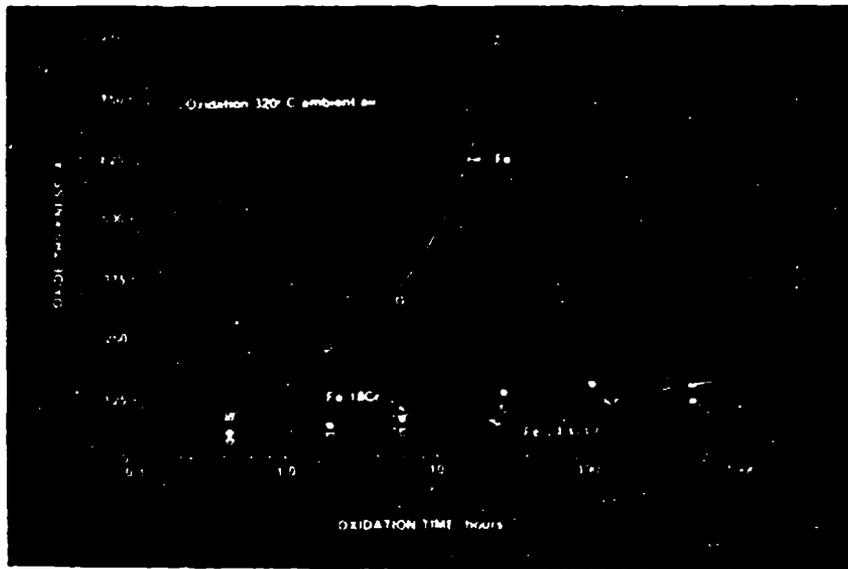


Figure 13

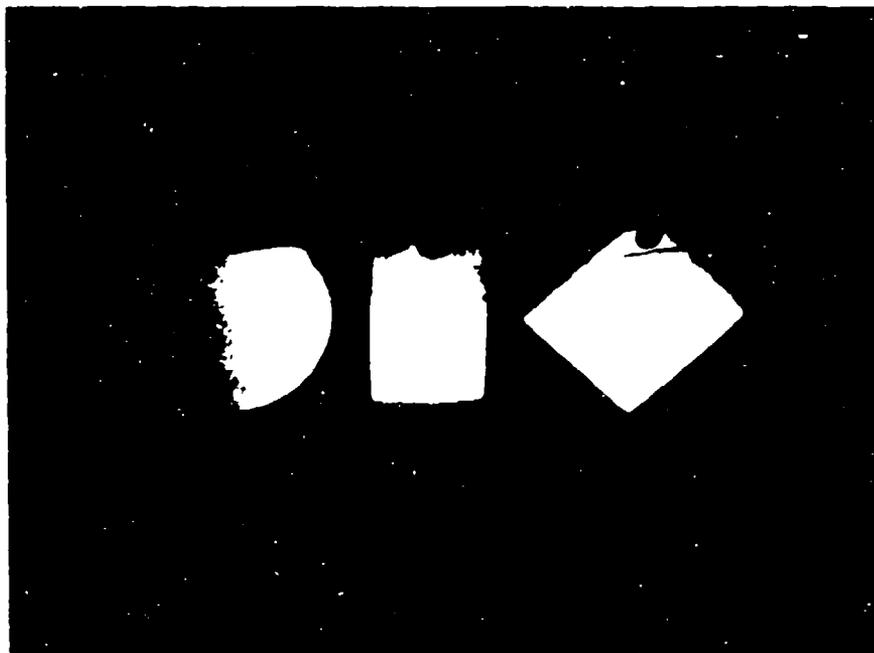


Figure 14

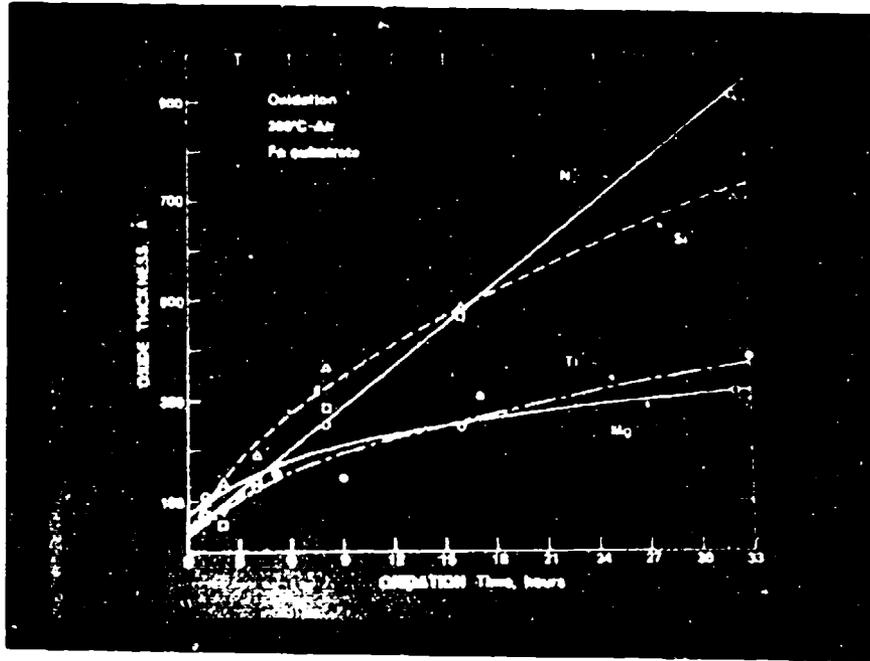


Figure 15

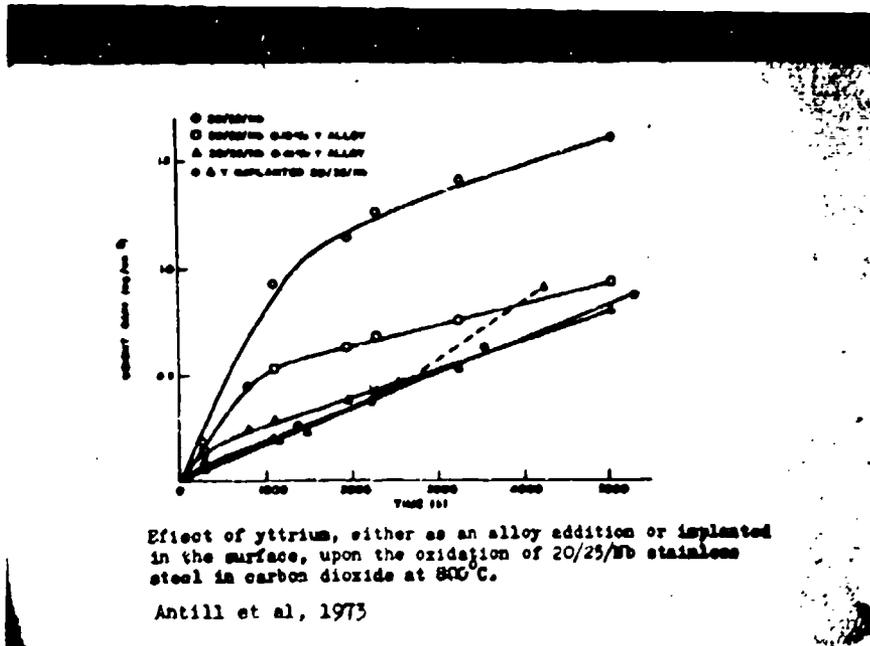


Figure 16

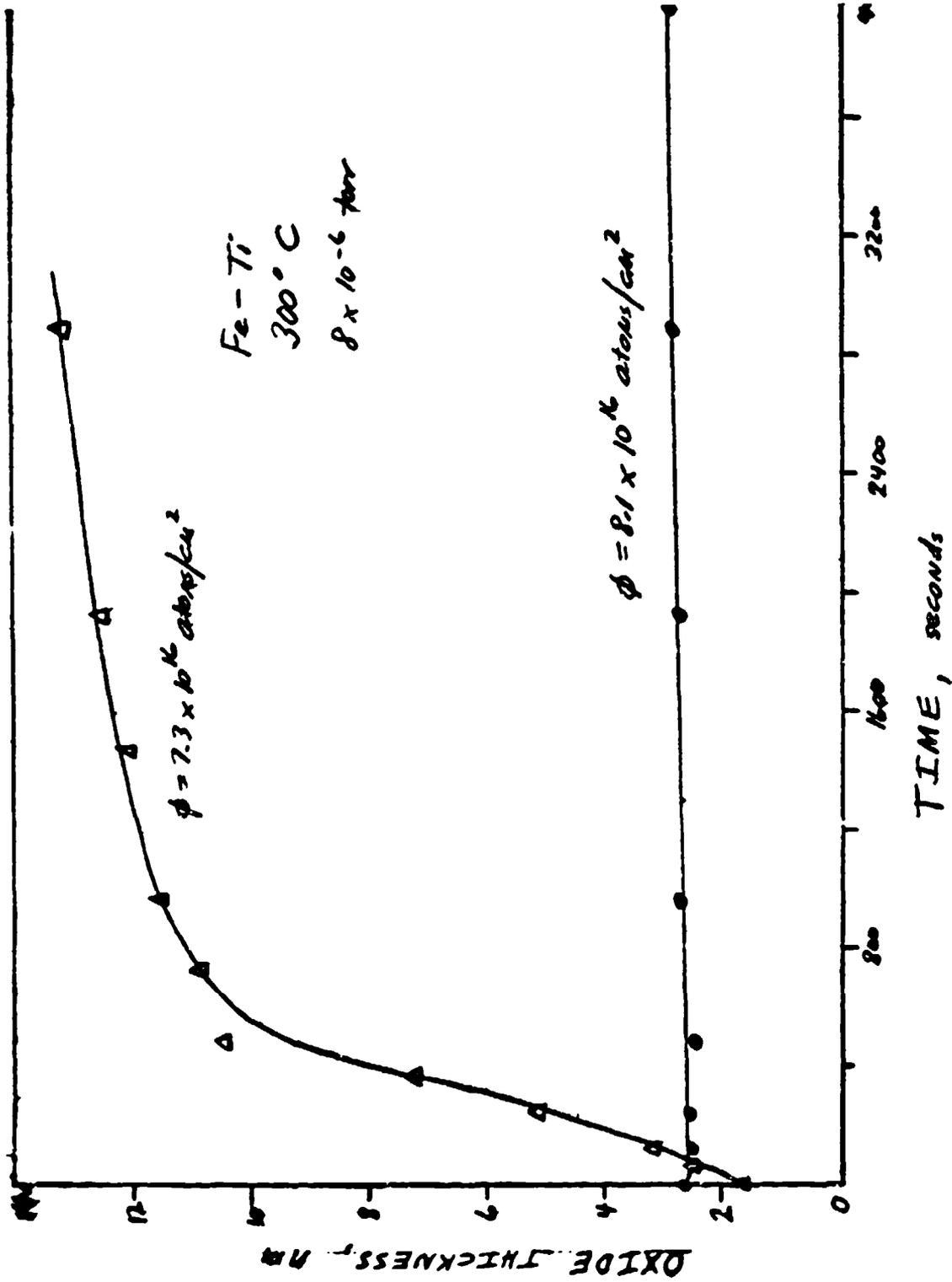


Figure 17

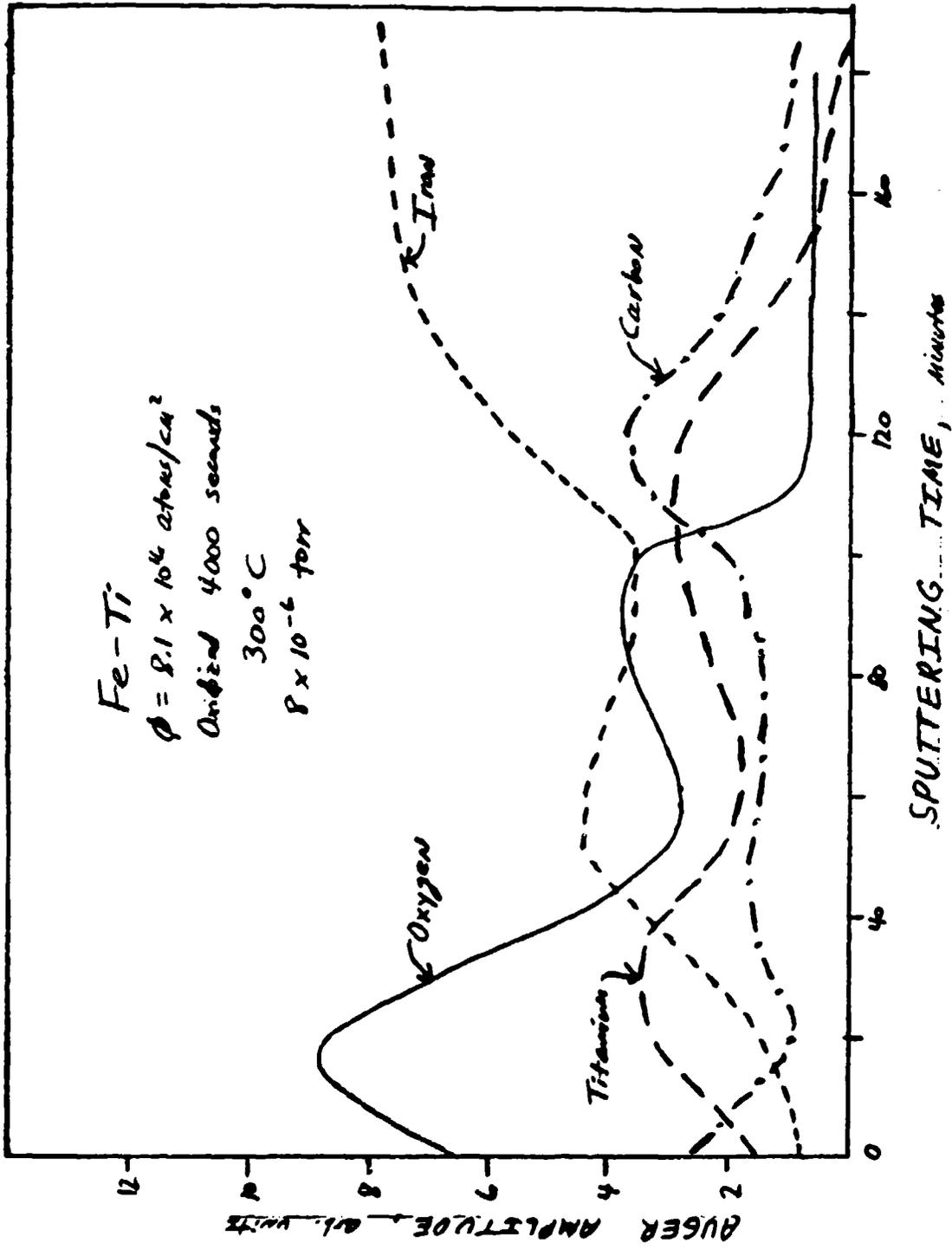


Figure 18

## QUESTIONS AND ANSWERS

P. Sagalyn, AMMRC: In the early days, Harwell reported some preliminary work: that on implanting tantalum in iron (tantalum is insoluble in the bulk). They found that it gave better corrosion protection than chromium and I was wondering if anybody followed that up in detail.

B. Sartwell: Ashworth published a series of articles in Corrosion Science. They implanted argon into iron and looked at corrosion behavior, then they implanted chromium, then they implanted tantalum and then they implanted lead. It was a series of four articles appearing in Corrosion Science. They found again that the tantalum implantation was beneficial. It gave beneficial corrosion resistance, but it certainly did not exceed the bulk iron-chromium alloy. Their studies were done using anodic polarization techniques.

R. French, AMMRC: In terms of either the point at which the ion implantation takes place or at some later stage, if we're implanting metal in metal, are we really talking about metal atoms on metal atom sites in the whole crystal or are we talking about a general mixing?

B. Sartwell: Well, generally, with the implantation, as Jim Mayer stated, you get a lot of radiation damage, but that will generally anneal out, and for most of these implants you will have the implanted metal atom occupying lattice sites in the material. It is not a random mixture. It does recrystallize into the basic structure of your substrate materials. But the implanted atoms do occupy substitutional sites.

R. French, AMMRC: Is that also true when you are in a highly metastable state that is way over the solubility limit as indicated by the phase diagram?

B. Sartwell: Generally that is true. People at Sandia have done most of the work on looking at alloy structures. They have found that you do get precipitation if you are implanting lead into iron. There is a limit where, if you keep adding more lead, you will start getting lead precipitate in the material. So you can't say that you can implant anything to any concentration and it will be in solid solution and stay metastable. You can reach a limit where you are going to start getting precipitation.

P. Sagalyn, AMMRC: I don't remember who did the work, but I believe when they implanted silver in copper where the room temperature equilibrium solubility is of the order of 1 percent they have gotten substitutional solid solutions up to 15 to 16 atomic percent silver and it is stable up to about 600°C, at which point it will start to precipitate out.

L. Jennings, AMMRC: I'd like to ask about your use of the PIXE technique. It strikes me that for quantitative analysis there's quite a bit of standardization that must have to be done for the proton exciting efficiencies and also for the X-ray getting-out-efficiency. Would you like to say a few words about how much effort there is in creating a standard for the PIXE technique?

B. Sartwell: It requires no standards. I assume you're talking about producing a standard sample that you know what's there to start with.

L. Jennings: My question is what do you have to do first to convert your X-ray counts that appear in the count totalizer to atoms per square centimeter.

B. Sartwell: Take, for example, chromium implanted into iron. You measure the number of chromium X-rays per incident microcoulomb of protons. Then you take into account your detector efficiency and the solid angle of the detector because, of course, X-rays are emitted in 4 steradians and you convert that to a yield and get the number of emitted X-rays per incident proton. So that is an absolute yield. The depth of analysis for PIXE at the energies we use is about 2000 angstroms. Since we are implanting to very shallow depths, only a couple of hundred angstroms, as the proton penetrates that layer it is not losing very much of its energy. In that regime where you have a thin layer (it could be a film or a thin implanted layer) and you are detecting an element in this thin film or thin implanted layer, take that yield that you measure, the number of X-rays emitted per incident proton, and divide it by what's called the thick target X-ray production cross-section for that element. These are tabulated for any element that you want. It becomes more complicated if your element is distributed over the full depth of your analysis region. You can't do it. So when your element is in a thin surface film, that's all there is to it. Your result is atoms per square centimeter.

L. Jennings: Does it remain true even for the lightest element X-rays that their penetration depth is large compared with the differences you're talking about?

B. Sartwell: Right, it is true. Okay, the question was is it true for the lightest element X-ray such as carbon and oxygen.

A. Niiler, BRL: Little follow up on this PIXE question. Jim Mayer mentioned yesterday that you may have some ion beam mixing when you do sputtering. In your experiments where you do the profiling with the PIXE, do you worry about, or have you seen, any effects of this ion beam mixing where in effect you would be spreading out your 50 angstrom or 200 angstrom layer of implanted species, and therefore you might have to think more in terms of what the PIXE cross-sections might be?

B. Sartwell: You're saying the mixing might be caused by the proton beam? (A. Niiler: No, by the sputtering.) Of course, sputtering is used with so many other techniques. It is possible that the sputtering is altering the profile but you know there are hundreds of people using sputtering Auger and Sims and everything else involving sputtering, and they ignore all that. They just produce their profiles and say here is our profile.

A. Niiler: I understand that concept and I'm trying to find out if you have found any discrepancies that might be attributable to this ion beam mixing that we talked about yesterday.

B. Sartwell: No, we haven't observed this but that doesn't mean that it doesn't exist.

D. Tenney, NASA Langley: I'm curious about your samples where you were talking about stress corrosion cracking. How were you able to convince yourself that in the one case where you were describing microcracks for us, and in another figure you described pitting along slip bands, that you were, in fact, actually observing microcracks and not an artifact? How were you able to really convince yourself that they were really microcracks? They didn't look any different than what you called intersecting slipbands with the surface.

B. Sartwell: Well, it could be the same thing. I guess I was a little loose with my terminology. The emergence of the slipbands at the surface can serve as a site for a crack initiation just like a grain boundary could, or a defect in the surface. So yes, I shouldn't have implied that the emerging slipbands and micro-cracks were two different things. They could be one and the same.

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THE MODIFICATION OF METALLIC CORROSION BY ION IMPLANTATION:  
ENGINEERING APPLICATIONS AND FUNDAMENTALS STUDIES

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Stony Brook, New York

A point that has been emphasised throughout this work-shop is the need to characterize as fully as possible the surface alloys formed by ion implantation. This is particularly important in corrosion studies since the activity of a metal or alloy is strongly governed by surface contamination and the presence of secondary phases. In a collaborative study between the NRL and SUNY we have attempted to use ion implantation as a means of modifying the corrosion behaviour of several important engineering alloys. Following the ion implantation treatment we have routinely characterized both the composition and, where possible, the structure of the resulting surface alloy. The corrosion behaviour of the ion implanted surfaces were in all cases evaluated by conventional polarization techniques and, where necessary, by a simulated field test.

The polarization experiments performed in this work were designed to provide us with a description of the nature and kinetics of both the anodic and cathodic reactions which constitute the corrosion of a metal in a given environment. The circuitry and apparatus used in these tests are depicted in Figures 1 and 2. As Bruce Sartwell has already explained, that polarization of the working electrode away from the open circuit potential (ocp) will result in the eventual stifling of either of the half-reactions rendering a current density measurement of the remaining reaction. Since the current density is a measure of the exchange of electrons at the metal-solution interface and, therefore, of the rate of the remaining half reaction, then the current density becomes an important measure of the kinetics of that reaction at a given applied potential. As the principles behind these measurements and the main parameters that are recorded have already been outlined, I will simply add that the applied potential also serves as a means of artificially altering the apparent oxidizing power of the solution. Hence, in Figure 3 we see that at the beginning of the anodic sweep the anodic current density is seen to increase almost linearly with the applied potential. The abrupt decrease in anodic current density which marks the end of the active region is due to the formation of a passivating layer of species which may be an adsorbed layer initially which eventually evolves into an ultra-thin film of corrosion products of several monolayers. In highly oxidizing media such films may break down due to the formation of more soluble species of a higher oxidation state. In Figure 3 this is depicted by the entry of curve A into the transpassive region. Curve B, which is the polarization of a stainless steel in an acid containing chloride ions, does not reach such high anodic potentials before the film breaks down locally under  $\text{Cl}^-$  ion attack, leading to pitting.  $E_{br}$  is the potential at which pitting is initiated. Since the anodic potential is equivalent to the oxidizing nature of the electrolyte, then the pitting potential recorded may serve as an indication of the probability that pitting may take place under freely corroding conditions. If the break down potential is very high, this would indicate that pitting would tend to occur in solutions of high oxidizing power. Since most industrial solvents and corrodents tend to be of a mildly oxidizing nature it would be reasonable to assume that the alloy in question would have good resistance in those environments to pitting. In that context we monitored the active-passive behaviour, self-passivity and the pitting potentials of some engineering alloys before and after ion implantation.

Several different approaches may be taken towards modifying the corrosion behaviour of metals by ion implantation. The following approaches are commonly adopted:-

- Promote passivity by adding elements which form highly protective ultra-thin films in an aqueous environment. EXAMPLE: -Cr, Mo, Ni added to Fe.

- Stimulate cathodic kinetics to promote passivity by shifting the open circuit potential in the noble direction into the passive range of potential. Typically an inert metal which is a catalyst for the cathodic reaction is added. EXAMPLE: -Pt, Pd, added to Ti.

- Where passivity cannot be achieved, the corrosion rate may be lowered by adding an element, such as, which tends to lower the cathodic reaction rate.

In our work we have chosen to focus on improving passivation behaviour by implanting a strong oxide former or passivator into the metal lattice. We have also explored the possibility of forming highly corrosion resistant amorphous surface alloys.

Ion implantation offers considerable scope for the design of corrosion resistant alloys. From the corrosion scientist's viewpoint, the advantages and disadvantages of ion implantation may be stated as follows:

#### Advantages of ion implantation as an alloying technique

- solubility limits may be exceeded
- single phase metastable alloys may be formed by controlling process parameters
- amorphous/microcrystalline structures may be formed
- the process leads to no significant dimensional change in the work-piece.

#### Disadvantages

- alloy thickness is limited to c.a. 1000Å
- implant reaches a saturation limit governed by sputtering characteristics.
- implantation processes may affect corrosion behaviour.

Since I shall illustrate some of the advantages of ion implantation as a corrosion protection treatment later in this presentation, I should first comment on the disadvantages. Firstly, the limited thickness of the surface alloy and the limited concentration of the implant that may be retained certainly are important disadvantages. However, both of these limitations may in principle be overcome by employing the ion beam mixing technique outlined earlier by Professor Mayer. As he indicated, more extensive solid solutions may be obtained by ion beam mixing. Furthermore, the thickness of the surface alloy layer may also in principle be extended by repeating the deposition and implantation treatments.

Now I should outline some of the potentially detrimental effects that ion implantation may have on the corrosion behaviour of a surface alloy. Several processes are listed as follows:

## Effects of the implantation process on corrosion behaviour

- surface topography: sputter damage
- surface contamination
- surface oxidation
- implant redistribution by radiation enhanced diffusion
- high defect concentrations
- second phase formation.

Sputter damage may, in engineering alloys, take the form of selective sputtering whereby second phases in the initial alloy such as carbides may stand proud of the surface leading to eventual shadowing of the nearby surface and, therefore, to uneven implantation. Figure 4a and 4b show a two-stage carbon replica taken from a Ni-implanted 430ss sample. Carbides and grain boundaries are clearly outlined (1).

The most common surface contaminant resulting from implantation is C. During the implantation of reactive elements such as Cr, C contamination, the result of hydrocarbon cracking under the ion beam, may react with the implant to form a carbide. This has been shown by Singer et al (2) in Ti-implanted 52100 steel using Auger electron spectroscopy (AES). Cr-implantation of 52100 also results in carbide formation. We have found that the carbides severely limit the maximum attainable pitting resistance probably due to disruption of the coverage of the steel by the steel by the passive film caused by the presence of the surface carbides (3). This problem may in principle be avoided by improving the vacuum conditions. Oxidation may also occur during ion implantation provided that the arrival rate of the oxygen bearing species ( $H_2O$ ,  $CO$  or  $O_2$ ) is faster than that of the implant ions. Thus at low beam currents surface oxidation will tend to consume a significant amount of the implanted passivator. This would suggest of course the need to employ higher beam currents.

The implant distribution may deviate greatly from that predicted by LSS theory due to radiation enhanced diffusion (4). An illustration of this effect is seen in an XPS profile obtained on a Ni-implanted 430ss sample (see Figures 5a and 5b). In this example a very significant redistribution of the implant Ni has taken place, migrating to the surface of the sample (Figure 5a). In addition to this the bulk Cr of the steel has migrated in the opposite direction to deeper levels (Figure 5b). This type of radiation enhanced diffusion has been observed by Okamoto and Wiedersich who have proposed a model based on the relative sizes of Fe, Cr and Ni to account for this kind of diffusion (5). Clearly such redistribution of the major passivators will influence the corrosion behaviour of the alloy in an unsystematic manner.

Since implantation results in very high concentrations of defects it is necessary to consider the possibility of defects having the following effects on corrosion:-

- enhancement of oxide growth
- increase anodic dissolution rates
- enhancement of volume diffusion during anodic dissolution leading perhaps to selective dissolution. Figures 5a and 6b shows the defect density formed when 430ss was implanted with Ni. The diffraction patterns show a supersaturated BCC ferritic structure.

Two cases have been published that indicate that surface retention of an inert species may have resulted from volume diffusion. In studies of the corrosion behaviour of Pd-implanted Ti by Hubler et al (6) RBS analysis indicated the possible diffusion of Pd into Ti during the anodic dissolution of the alloy in boiling  $H_2SO_4$ . Zamanzadeh et al (7) found similar evidence of Pt diffusion during the corrosion of Pt-implanted Fe in  $H_2SO_4$  under potential control.

#### Passivation behaviour of P-implanted 304 stainless steel

At this stage I would like to briefly review some of the corrosion properties of an amorphous surface alloy formed on 304ss following implantation at a fluence of  $10^{17}$  ions  $cm^{-1}$  and a potential of 40 keV (8). In this work the active passive behaviour of the implanted and unimplanted steel was compared by polarization studies in 0.5 M  $H_2SO_4$  (9). The pitting behaviour was compared in a solution of 0.5 M  $H_2SO_4$  + 2 wt% NaCl. Each of the solutions were deaerated. The structure and composition of the films formed in the acid solution were compared following potentiostatic formation of the film for 1 hour at several potentials. A comparison was also made of the effect of exposing these films to  $Cl^-$  ions.

It can be seen from Figure 7, which shows the polarization behavior in deaerated 0.5 M  $H_2SO_4$ , that the amorphous surface alloy exhibits a lower critical current density and passive current density. In the acid-chloride solution (Figure 8) the same parameters are again seen to be reduced by P-implantation. In addition to this, the P-implanted steel is seen to be more resistant to localized break down, as indicated by a higher break down potential. Reflection High Energy Electron Diffraction (RHEED), AES and XPS analysis of the films formed in the acid solution indicated that the implantation treatment had fundamentally modified the nature of the passive film, from a crystalline structure to an amorphous one (see Table 1). Analysis of the films after exposure to  $Cl^-$  ions resulted in no change of structure in the amorphous films and no strong evidence of  $Cl^-$  ion penetration. (See Table 2 and Figures 9 and 10.) These results were in sharp contrast to the crystalline films, which on exposure to the  $Cl^-$  ions exhibited a structural modification in the Cr and Fe compounds of the film, film thickening and significant  $Cl^-$  ion penetration. These results serve to indicate that ion implantation may be used as a research tool to improve our understanding of corrosion mechanisms and that considerable scope remains for systematic design of surface alloys to ensure the formation of the optimum type of passive film.

#### Ion implantation of M50 and AISI 52100 steel

As mentioned earlier by Dr. Hirvonen we have attempted to improve the corrosion behaviour of types M50 and 52100 steel bearings commonly used in military propulsion systems (10). Both of these steels are fully hardened martensitic steels, and are very prone to corrosion both in service in the manner discussed earlier and during normal storage. The composition of the steels are given in Tables 3 and 4.

The aim of this work was to improve the general corrosion behaviour and the resistance to  $Cl^-$  ions. As mentioned earlier by Dr. Hirvonen a simulated field corrosion test was performed initially on a high dose ( $2 \times 10^{17}$  ions  $cm^{-2}$ , 150 keV) Cr implanted sample of M50 (see Figure 11). A nuclear reaction profile indicated that a high concentration of Cr was located just below the surface of the steel (Figure 12). In the simulated field service test, the unimplanted bearing produced a considerable amount of pitting or crevicing underneath the point of contact of the

two bearings. The implanted bearing, however, maintained a clean surface (Figure 13). At SUNY we carried out electrochemical survey work on M50 steel looking at the active-passive transition in deaerated 0.5 M  $H_2SO_4$  (Figure 14b) and the pitting behaviour in deaerated 0.1 M NaCl (pH6 buffered) solution (Figure 14b). In this work we compared the behaviour of unimplanted steel with M50 implanted with a variety of passivators (see Table 5). In the top Figure 14a we have the polarization behaviour of the unimplanted and implanted M50 in the sulphuric acid solution. The unimplanted steel exhibits a large critical current density before the onset of passivity. Actually, passivity is achieved through the formation of a thick black corrosion product layer and is not so much a passive but protective film. Ti had no beneficial effect on the steel. All the other implants, however, aided in the formation of a truly passive film, so thin as to be transparent, i.e., the surface remained shiny prior to the onset of transpassivity. Both Cr and Mo lowered the critical current density. However, the combined implantation of Cr and Mo provided even greater improvements. In the  $Cl^-$  solution M50 broke down immediately upon polarization (see Figure 14b and Table 6). Self-passivity was achieved in each of the implanted steels and the break down potentials were all raised. However, again it was found that the combined implantation of Cr and Mo produced the most improvement in corrosion resistance. This result reflected the known synergistic effect of Cr and Mo in improving corrosion resistance. In general the electrochemical measurements tended to agree quite well with the later simulated field service tests.

In a second study (11) we applied the similar ideas to 52100 steel. Three implantations were considered in this work (Table 7). The AES depth profiles obtained for each of these surface alloys were determined (see Figures 15 - 17). Polarization tests were performed in deaerated 0.01M NaCl (pH6 buffered) solution. Two conditions were considered: a) polarization on immersion (Figure 18) and b) polarization following cathodic reduction of the previously formed film (Figure 19). The former condition related more closely with the "in service" surface condition. The main parameters measured during the polarization work are outlined in Table 8. In each case the implantation treatment improved the localized corrosion resistance. The most impressive results were obtained by the Ta implantation. This highly metastable surface alloy is currently undergoing TEM examination. In both sets of experiments the Ta-implanted sample raised the break down potential to c.a. 900 mV. These results certainly give strong support to the idea of using ion implantation as a corrosion protection treatment for some special applications. The use of this technique in a wear situation requires further evaluation. However, the early results have provided a solution to one important practical problem of increasing the shelf life of two types of bearings.

Now, as I mentioned earlier, ion beam mixing offers some advantages over ion implantation as a corrosion protection treatment. For this reason we have recently initiated some ion beam mixing studies in which Cr overlayers have been deposited onto 52100 steel followed by either Xe or Cr ion beam mixing. The approach we are taking is to determine whether metal ion beams are more effective in forming corrosion resistant surfaces, since it is sometimes difficult to avoid gas bubble formation following inert gas implantation. This work will also consider the use of ion beam stitching as a means of producing a well bonded, radiation homogenized, layer of a strong passivator on the surface of the substrate.

That is all I have to say.

## ACKNOWLEDGMENTS

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Table 1. Calculated Interplanar Spacings of the Passive Films Formed in 1N H<sub>2</sub>SO<sub>4</sub> at +550 mV and +250 mV for 1 Hr.

Potential	Steel	d Spacing	Phase
+550 mV SCE	304	3.23, 2.73, 2.35, 2.18 1.88, 1.69, 1.43, 1.19	$\gamma$ -FeOOH CrOOH
	304-P	2.65, 1.98, 1.44	Fe(PO <sub>3</sub> ) <sub>3</sub> CrPO <sub>4</sub>
+250 mV SCE	304	3.54, 3.21, 2.85, 2.46, 2.21 1.88, 1.70, 1.60, 1.31	Green Rust II* Fe(OH) <sub>2</sub> CrOOH
	304-P	2 diffuse Rings	—

\*Green Rust II (GR II): 2Fe(OH)<sub>2</sub> 4Fe(OH)<sub>3</sub>·FeSO<sub>4</sub>·XH<sub>2</sub>O,

Table 2. Calculated Interplanar Spacings of the Passive Films Formed in 1N H<sub>2</sub>SO<sub>4</sub> for 1 Hr. and continued passivation in 1N H<sub>2</sub>SO<sub>4</sub> + 2% NaCl for 10 Min.

Potential	Steel	d Spacing	Phase
+550 mV	304	3.33, 3.06, 2.64, 2.20, 1.80 1.75, 1.64	$\gamma$ -FeOOH Cr(OH) <sub>3</sub>
	304-P	2.65, 1.98, 1.44	Fe(PO <sub>3</sub> ) <sub>3</sub> CrPO <sub>4</sub>
+250 mV	304	3.91, 3.30, 2.97, 2.64, 2.40 2.03, 1.89, 1.76, 1.70, 1.57, 1.42	Green Rust I* Cr(OH) <sub>3</sub>
	304-P	3 Diffuse Rings 2.70, 2.16, 1.49	Fe(PO <sub>3</sub> ) <sub>3</sub> $\alpha$ -CrPO <sub>4</sub>

\*Green Rust I (GR I): Fe<sub>3.6</sub><sup>2+</sup> Fe<sub>0.9</sub><sup>3+</sup> (O, OH, Cl)<sub>9</sub>

Table 3. Percentage Composition of AISI 52100 Steel

<u>Element</u>	<u>Amount (% by wt)</u>
C	0.98-1.10
Cr	1.30-1.60
Mn	0.25-1.10
Si	0.15-0.35
P	0.025 max.
S	0.025 max.
Fe	bal.

Table 4. Percentage Composition of M50 Steel

<u>Element</u>	<u>Amount (% by wt)</u>
C	0.80-0.85
Mn	0.15-0.35
Si	0.10-0.25
P	0.15 max.
S	0.01 max.
Cr	4.00-4.25
Mo	4.00-4.50
V	0.90-1.10
Ni	0.15 max.
Co	0.25 max.
W	0.25 max.
Cu	0.10 max.
Fe	bal.

Table 5. Fluences and Energies of Ions Implanted in M50 Steel

<u>Sample</u>	<u>Ion</u>	<u>Fluence (ions cm<sup>-2</sup>)</u>	<u>Energy (keV)</u>
Cr (H <sub>2</sub> SO <sub>4</sub> )	Cr	2 X 10 <sup>17</sup>	150
Cr (Cl-sol)	Cr	1.5 X 10 <sup>17</sup>	150
Mo	Mo	5 X 10 <sup>16</sup>	100
Ti	Ti	2 X 10 <sup>17</sup>	55
Cr + Mo	Cr	1.5 X 10 <sup>17</sup>	150
	Mo	5 X 10 <sup>16</sup>	100

Table 6. Breakdown Potentials in 0.1M NaCl Solution for M50 Steel Implanted With Various Ions

Ion (s)	Fluence ( $\times 10^{17}/\text{cm}^2$ )	Energy (keV)	Sample #	$E_b$ (mV)
Cr+	1.5	150	2879	+1250
Mo	0.5	100		
Cr+	1.5	150	2879	+ 450
Mo	0.5	100		
Cr	1.5	150	2779	+ 130
Mo	0.5	100	31979	+ 60
Ti	2.0	55	111578	0
M50	---	---	-----	- 230

Table 7. Fluences and Energies of Ions Implanted Into 52100 Steel

Sample	Ion	Fluence (ions $\text{cm}^{-2}$ )	Energy (keV)
Cr	Cr	$2 \times 10^{17}$	150
Cr + Mo	Cr	$2 \times 10^{17}$	150
	Mo	$3.5 \times 10^{17}$	100
Cr + P	Cr	$2 \times 10^{17}$	150
	P	$5 \times 10^{16}$	40
Ta	Ta	$1.0 \times 10^{17}$	150
Mo	Mo	$5 \times 10^{16}$	100

Table 8. S2100 Pitting Data in 0.01 M Buffered (pH = 6) NaCl Solution

<sup>2</sup>Scan Rate: 1 mV/sec

Sample	Cathodic Treatment	Open Circuit Pot. (mV)	Breakdown Pot. (mV)	Passive Current Density ( $\mu\text{A}/\text{cm}^2$ )	Observations
S2100 Unimplanted	45 min. at 25 mA	-675	-648	23	Slightly dull, tiny pits, (similar to Mg).
2E17 Cr 150 keV	"	-764	-50	12	Surface shiny, scattered visible pits.
3.5E16 Mo 100 keV	"	-682	-612	10	Surface dull, tarnished around the metal-epoxy interface.
2E17 Cr 150 keV	"	-61	+0.0	20	Tarnished and possibly rusted islands on surface.
3.5E16 Mo 100 keV	"	-474	+225	20	Big tarnished pits visible.
2E17 Cr 150 keV	30 min. at 5 mA	-642	0	30	Small visible pits.
1E17 P 40 keV	none	-678	-608	47	Half of surface covered with tarnished rust. No visible pits seen.
S2100 Unimplanted	none	-143	+20	12	Extremely shiny. No visible pits seen.
2E17 Cr 150 keV	"	-166	+325	21	A few tarnished islands around the pits.
3.5E16 Mo 100 keV	"	-550	+75	12	Surface quite shiny.
2E17 Cr 150 keV	none	-196	+175	10	Big visible pits, surface shiny.
1E17 P 40 keV	none	-283	-205	200	Possible cervicing at sample and epoxy interface.

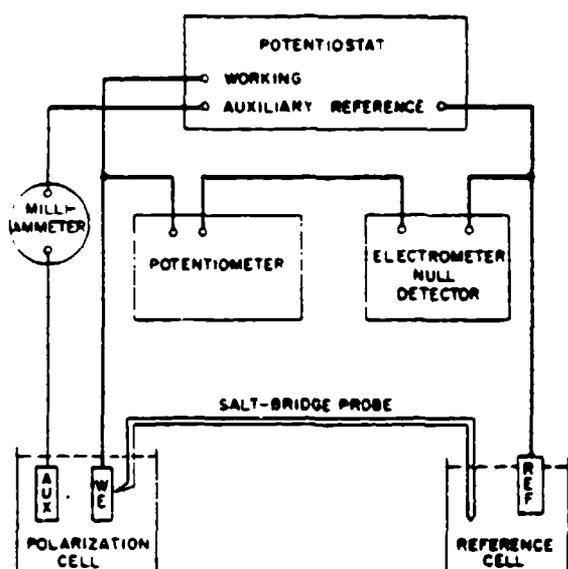


Figure 1. Block diagram of apparatus and circuitry associated with controlled potential measurements.

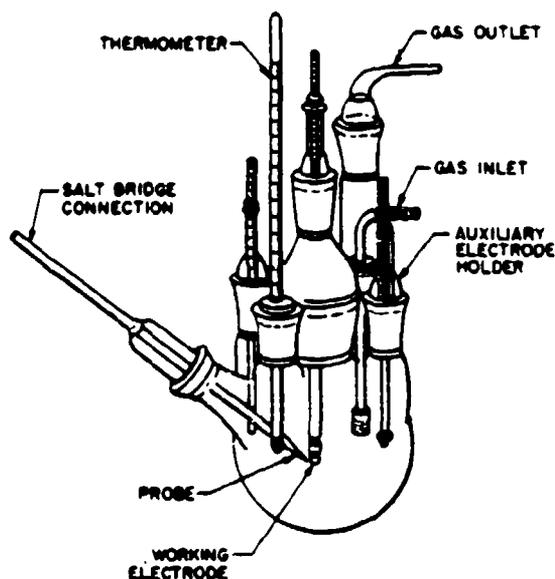


Figure 2. Standard multineck polarization cell.

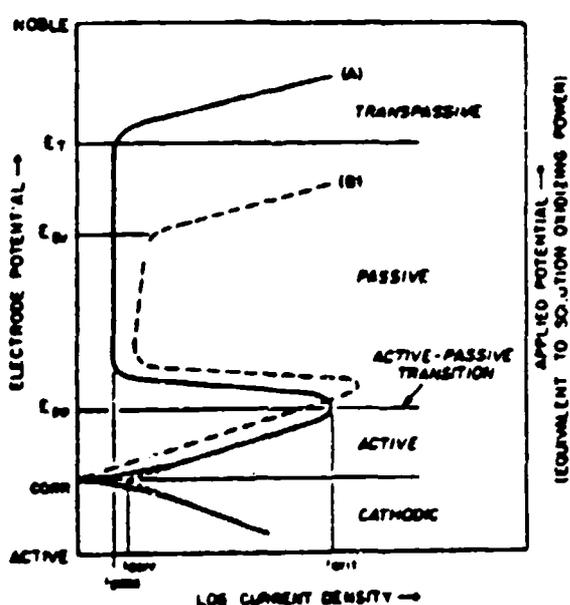


Figure 3. Polarization curves of stainless steel (a) in a mildly oxidizing deaerated acid and (b) in the same acid containing  $\text{Cl}^-$  ions.

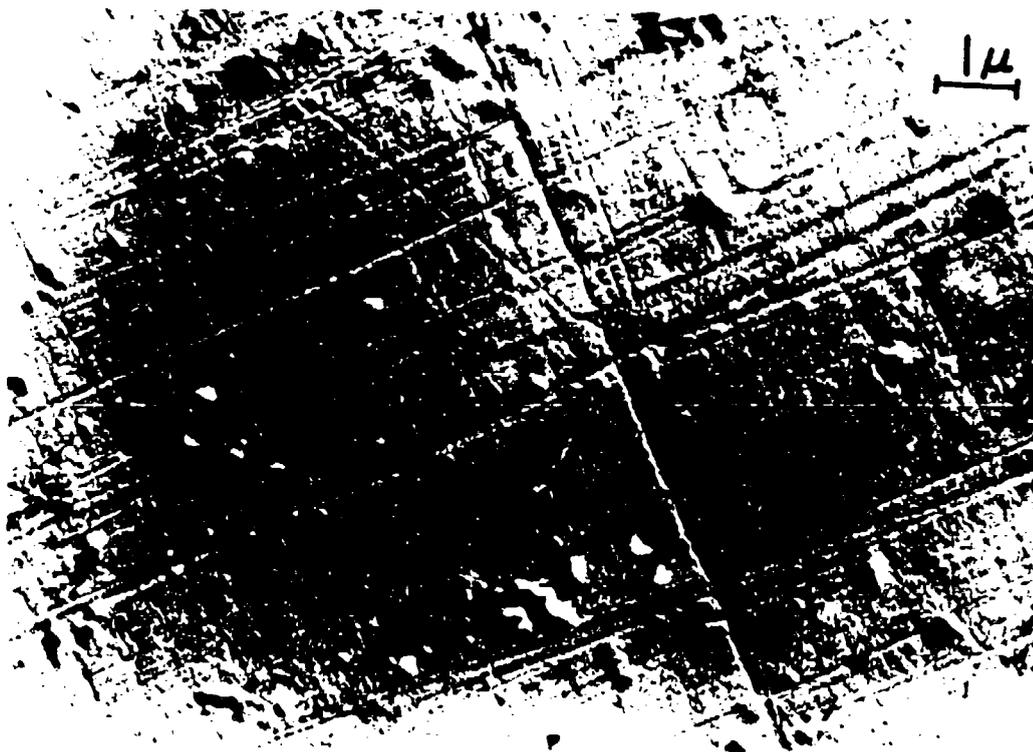
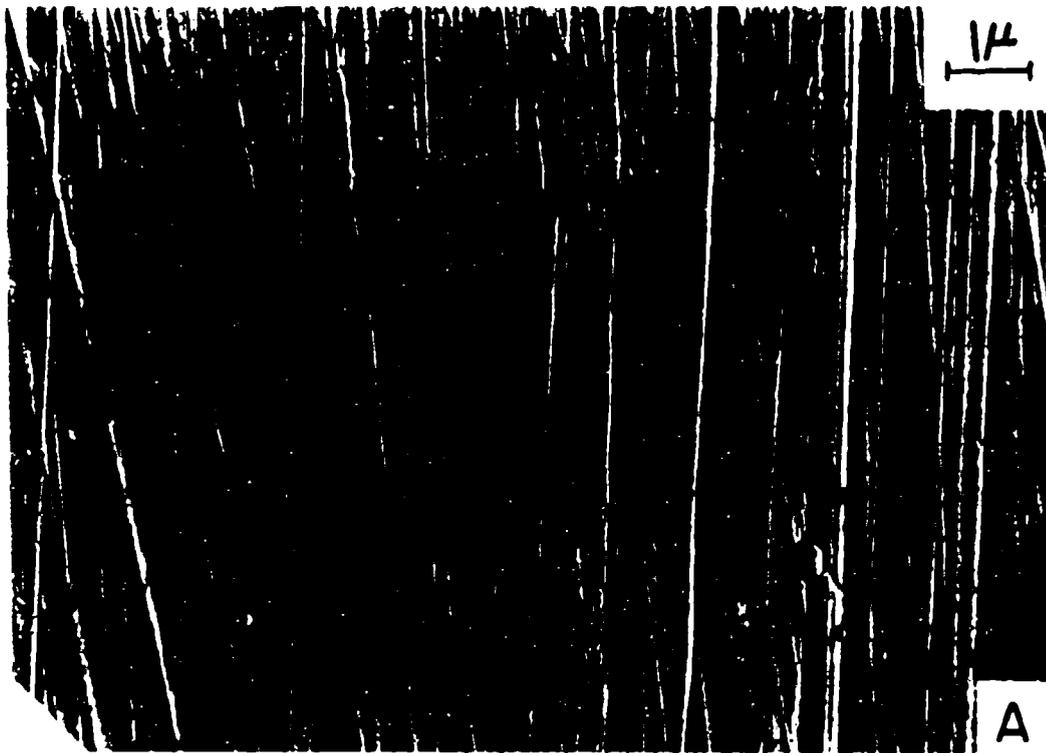


Figure 4. Replica electron micrographs of diamond polished 430 ss (a) unimplanted condition showing scratches and (b) as-implanted to  $5 \times 10^{16}$  ions  $\text{cm}^{-1}$ , 150 keV showing sputtering effects.

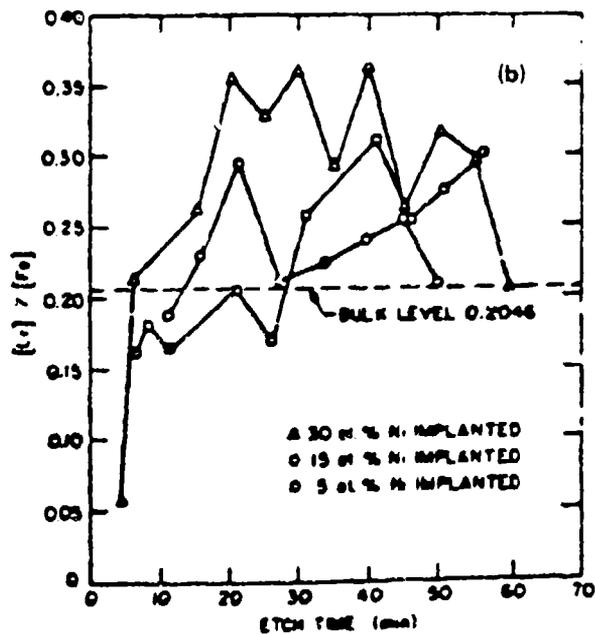
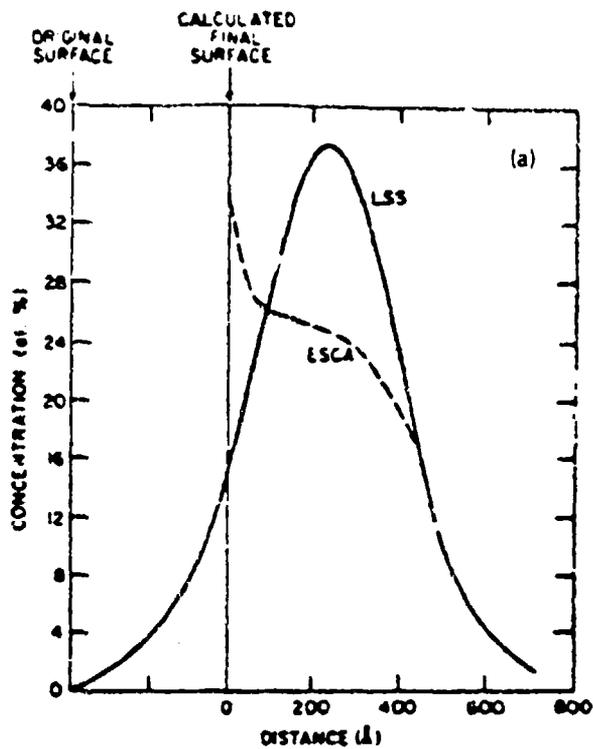
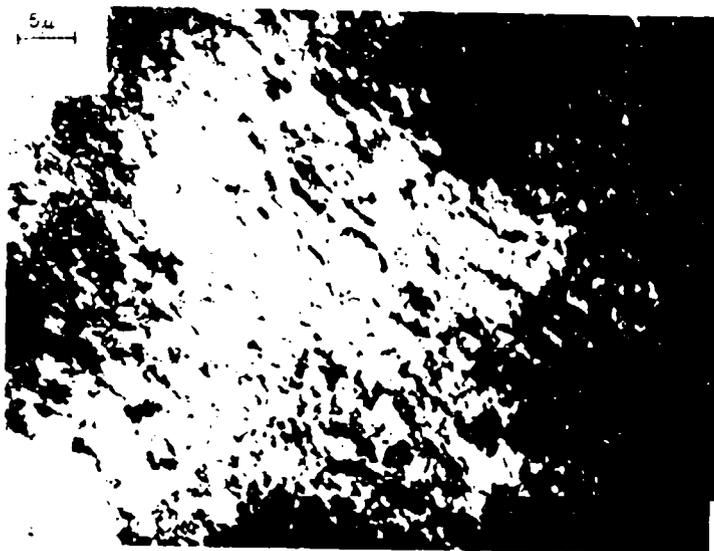
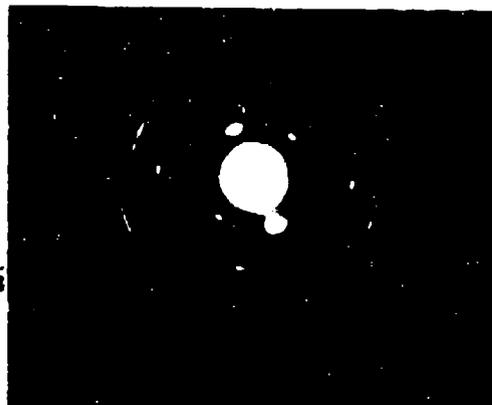


Figure 5. (a) Comparison of calculated (ISS) and XPS-derived distributions of Ni-implanted 430 ss ( $5 \times 10^{17}$  ions  $\text{cm}^{-2}$ , 150 keV) and (b) relative concentrations of Cr and Fe in the region of implantation for three Ni-implanted surface alloys formed on 430 ss.



(a)



(b)

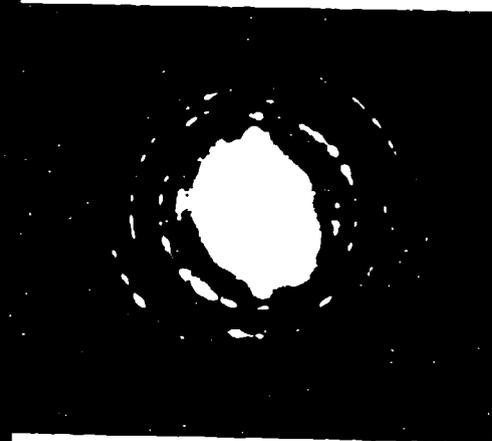


Figure 6. Electron micrograph and SAD patterns for Ni-implanted 430 ss showing radiation damage for implantations of: (a)  $5 \times 10^{16}$  ions  $\text{cm}^{-2}$ , 150 keV and (b)  $5 \times 10^{17}$  ions  $\text{cm}^{-2}$ , 150 keV.

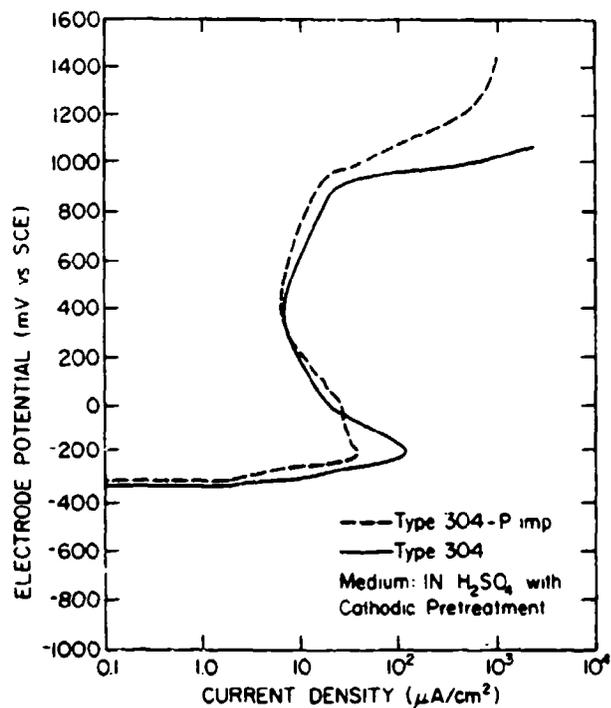


Figure 7. Potentiokinetic polarization behaviour of 304 ss and P-implanted 304 ss in deaerated 0.5 M H<sub>2</sub>SO<sub>4</sub>.

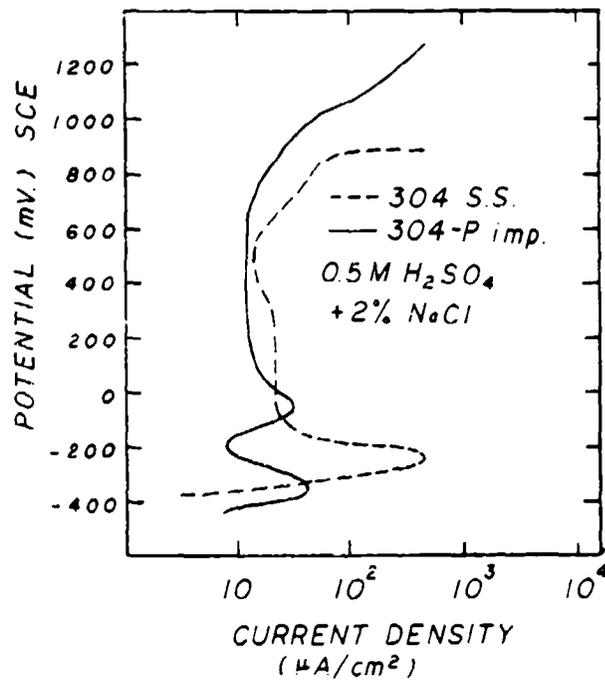


Figure 8. Potentiokinetic polarization behaviour of 304 ss and P-implanted 304 ss in deaerated 0.5 M H<sub>2</sub>SO<sub>4</sub> + 2% NaCl solution.

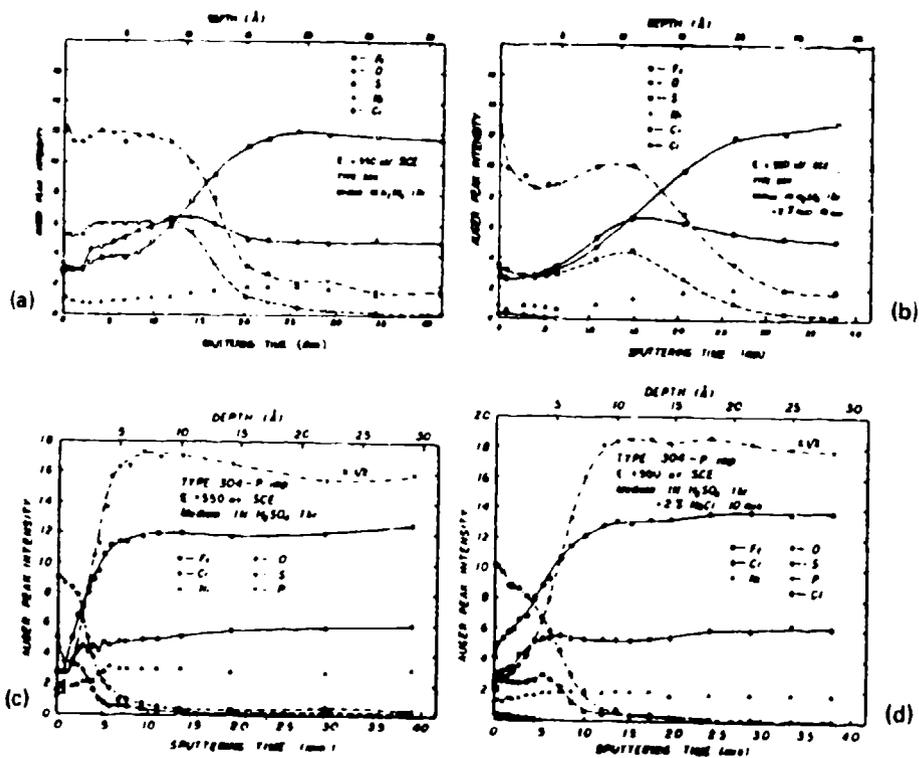


Figure 9. AES composition profiles of the anodic films formed on 304 ss and P-implanted 304 ss in 0.5 M H<sub>2</sub>SO<sub>4</sub> at +550 mV (SCE) with and without the addition of Cl<sup>-</sup> ions.

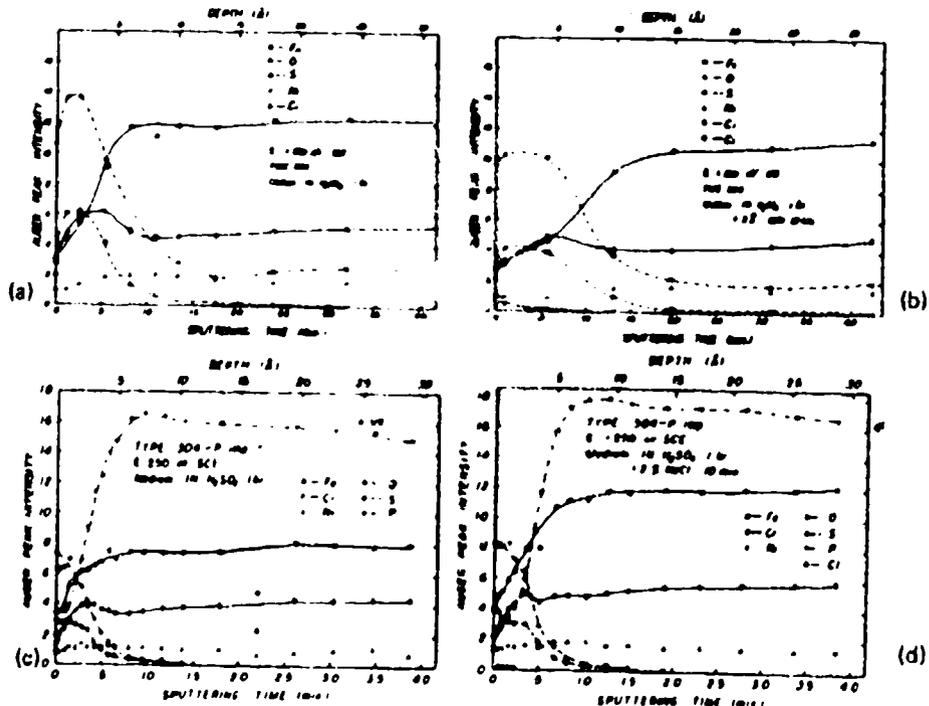
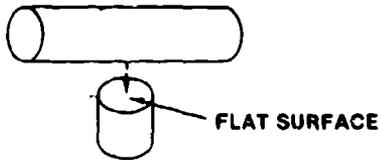
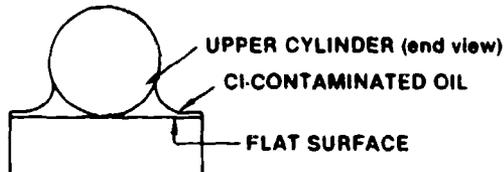


Figure 10. AES composition profiles of the anodic films formed on 304 ss and P-implanted 304 ss in 0.5 M H<sub>2</sub>SO<sub>4</sub> at +250 mV (SCE) with and without the addition of Cl<sup>-</sup> ions.

1. Test pieces (both M50 alloy steel) were placed in contact as indicated by the dotted line.



2. Both pieces in place were immersed in chloride-contaminated oil for 2 hrs., removed, and allowed to dry.
3. A meniscus of contaminated oil was retained between the two parts:



4. The above arrangement was exposed to moist air cycled between 100°F and 4°F for 2 weeks.

Figure 11. Laboratory simulated field service test of the corrosion of bearings.

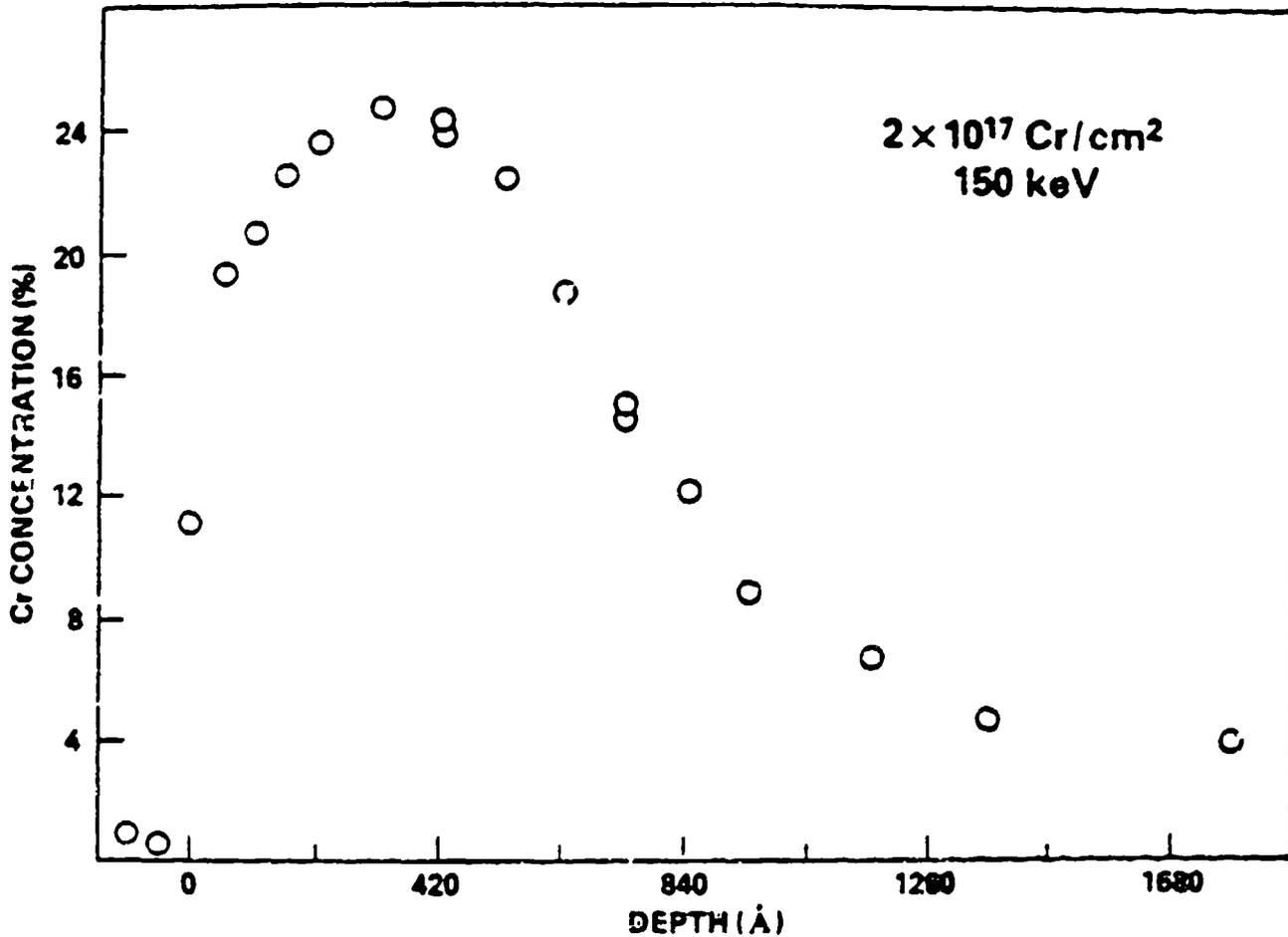
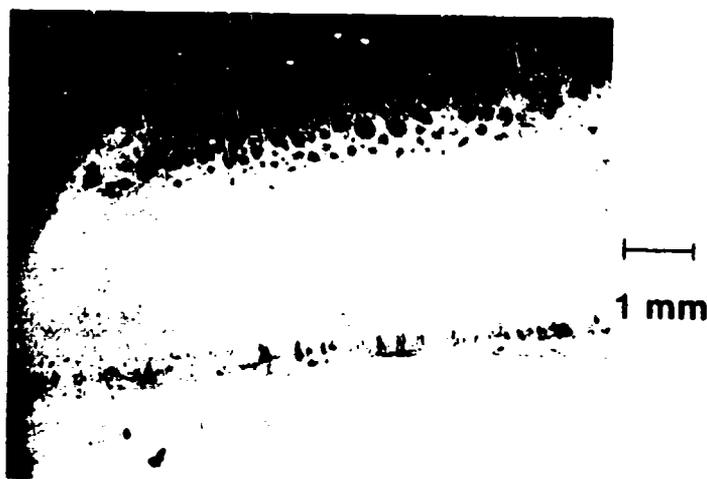


Figure 12. Nuclear (P,γ) resonance profile of Cr in M50 steel. The Cr was ion implanted with  $2 \times 10^{17}$  ions  $\text{cm}^{-2}$ , 150 keV.



UNIMPLANTED



Cr-IMPLANTED

Figure 13. Optical micrograph of the flat surfaces of M50 test samples after a simulated field test, (a) the unimplanted sample shows generalized corrosion outside the oil meniscus region and pitting under the line of contact and (b) the chromium implanted sample shows complete immunity (Mag.6X).

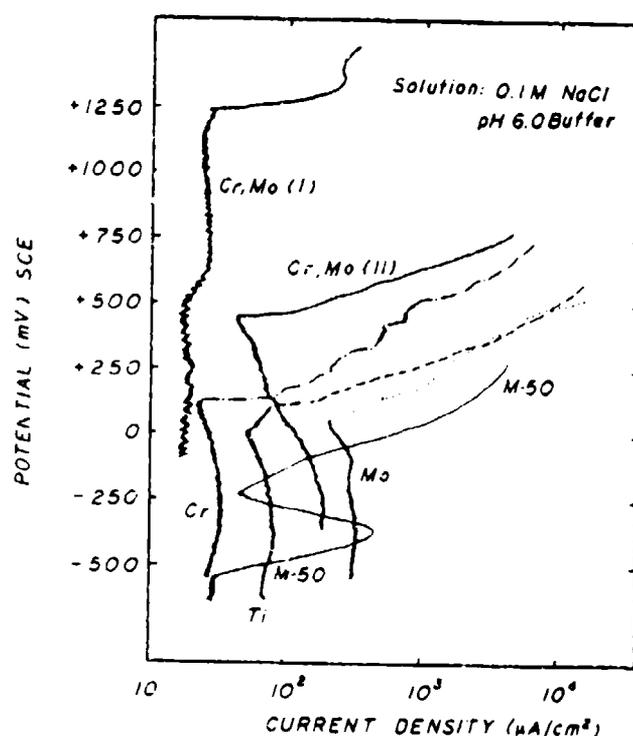
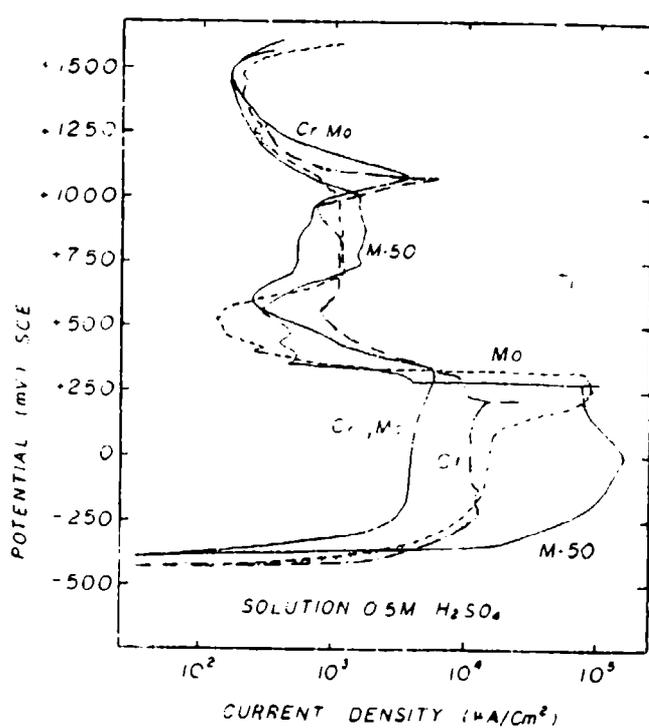


Figure 14. Potentiokinetic polarization curves produced in deaerated, (a) 0.5 M H<sub>2</sub>SO<sub>4</sub> and (b) pH6 buffered 0.1 M NaCl, for M50 steel and M50 implanted with Ti, Cr, Mo and Cr + Mo.

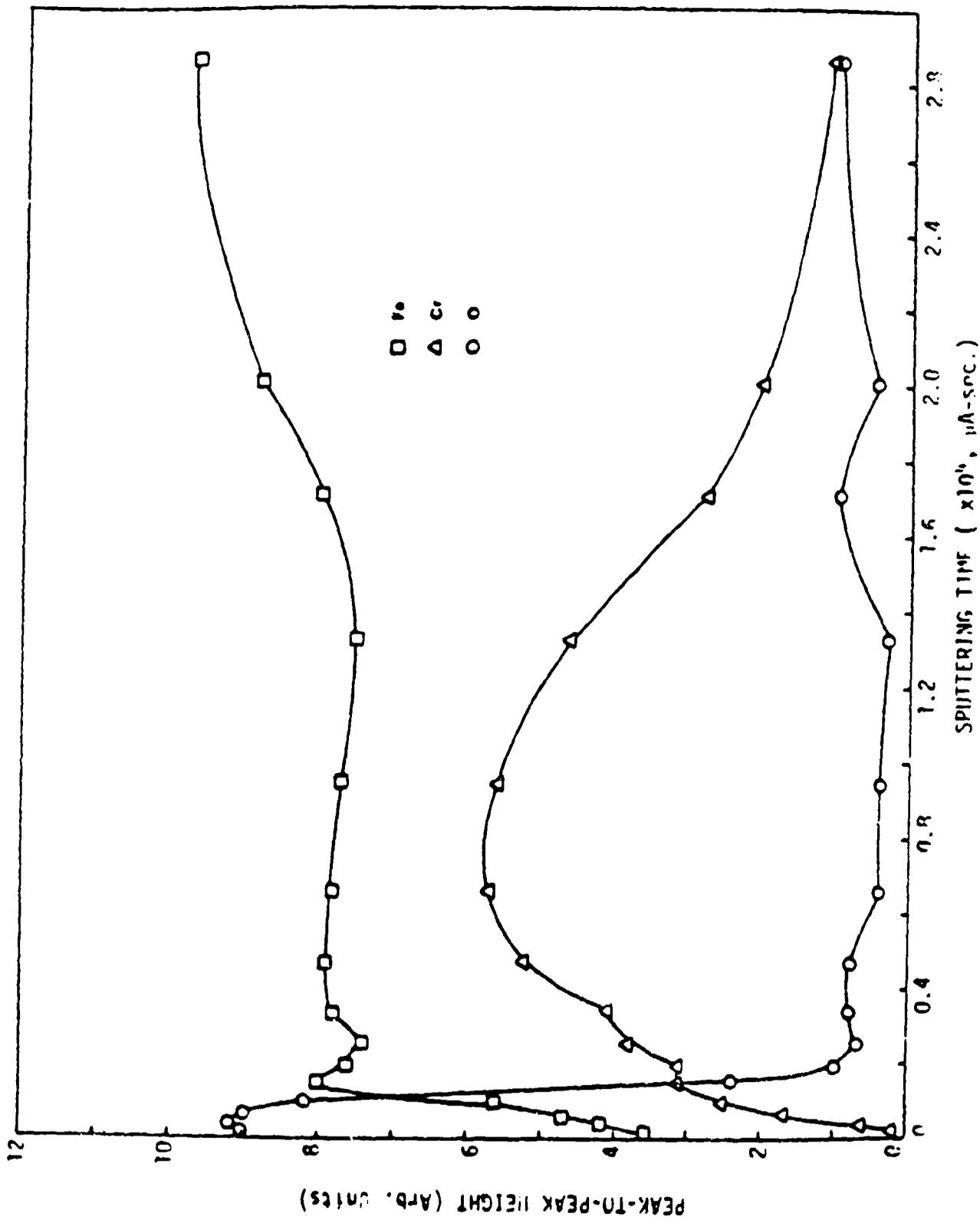


Figure 15. Auger depth profile of Fe, Cr, O for Cr implanted 52100 steel.

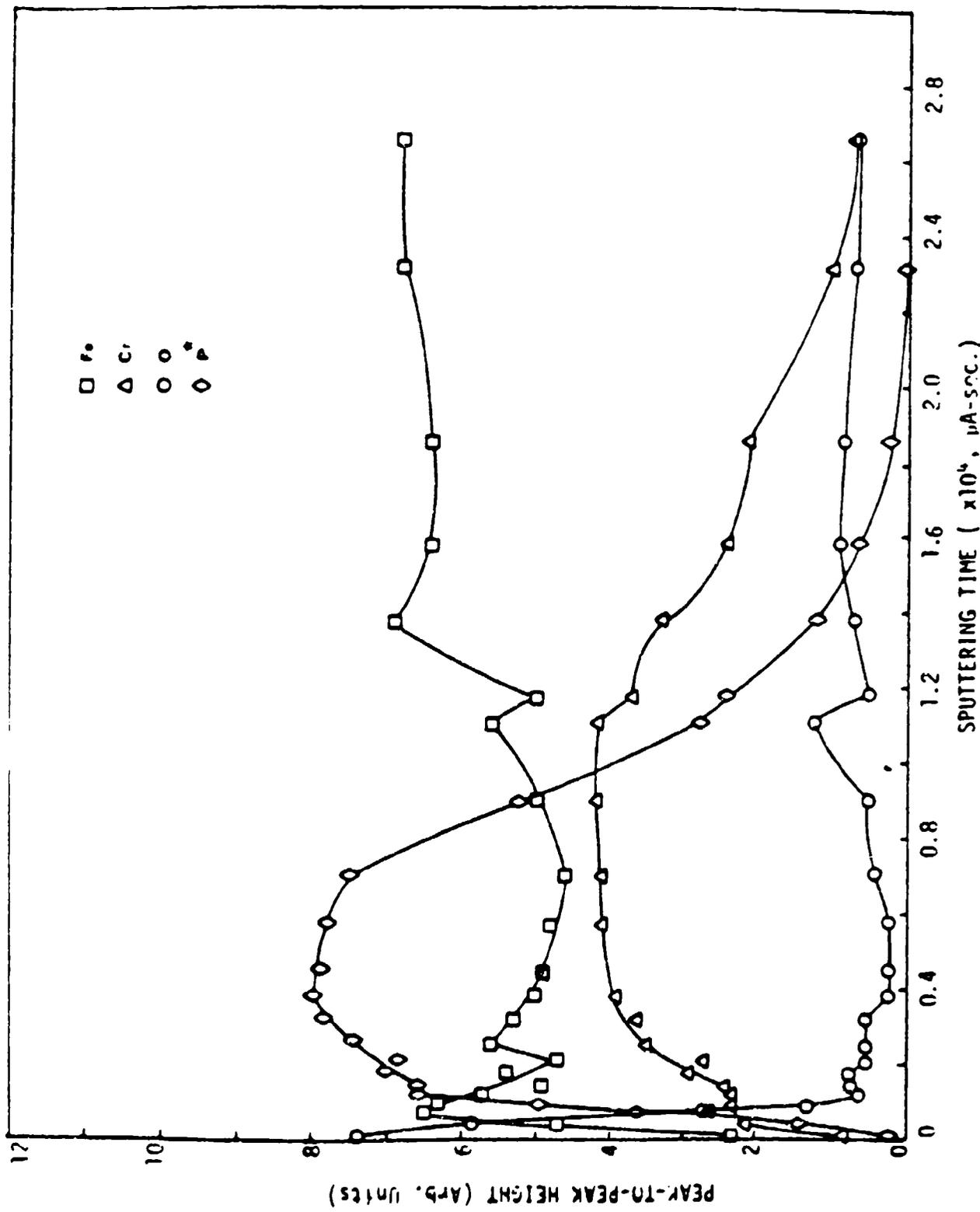


Figure 16. Auger depth profile of Fe, Cr, O and P for Cr + P implanted 52100 steel.

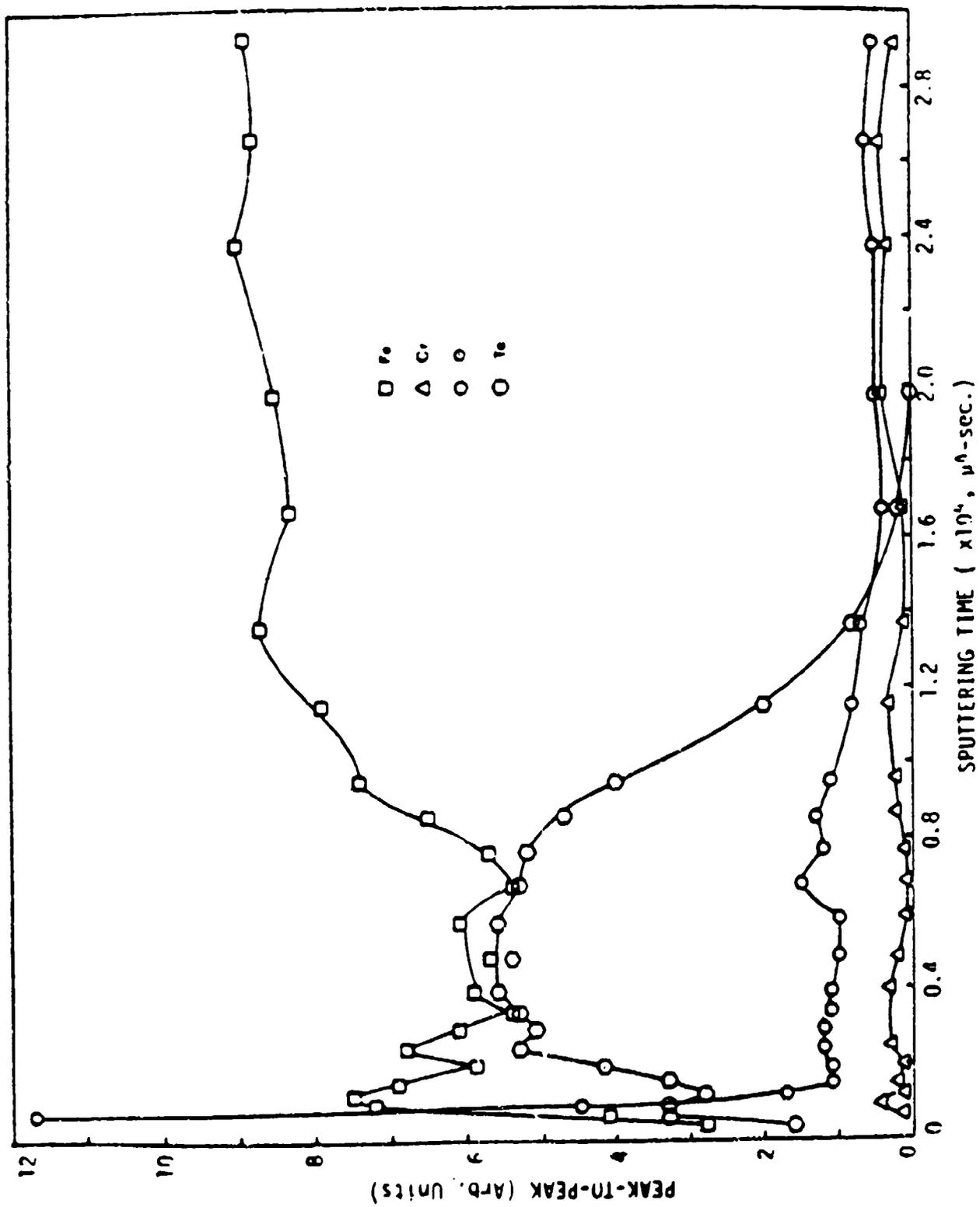


Figure 17. Auger depth profile of Fe, Cr, O and Ta for Ta implanted 52100 steel.

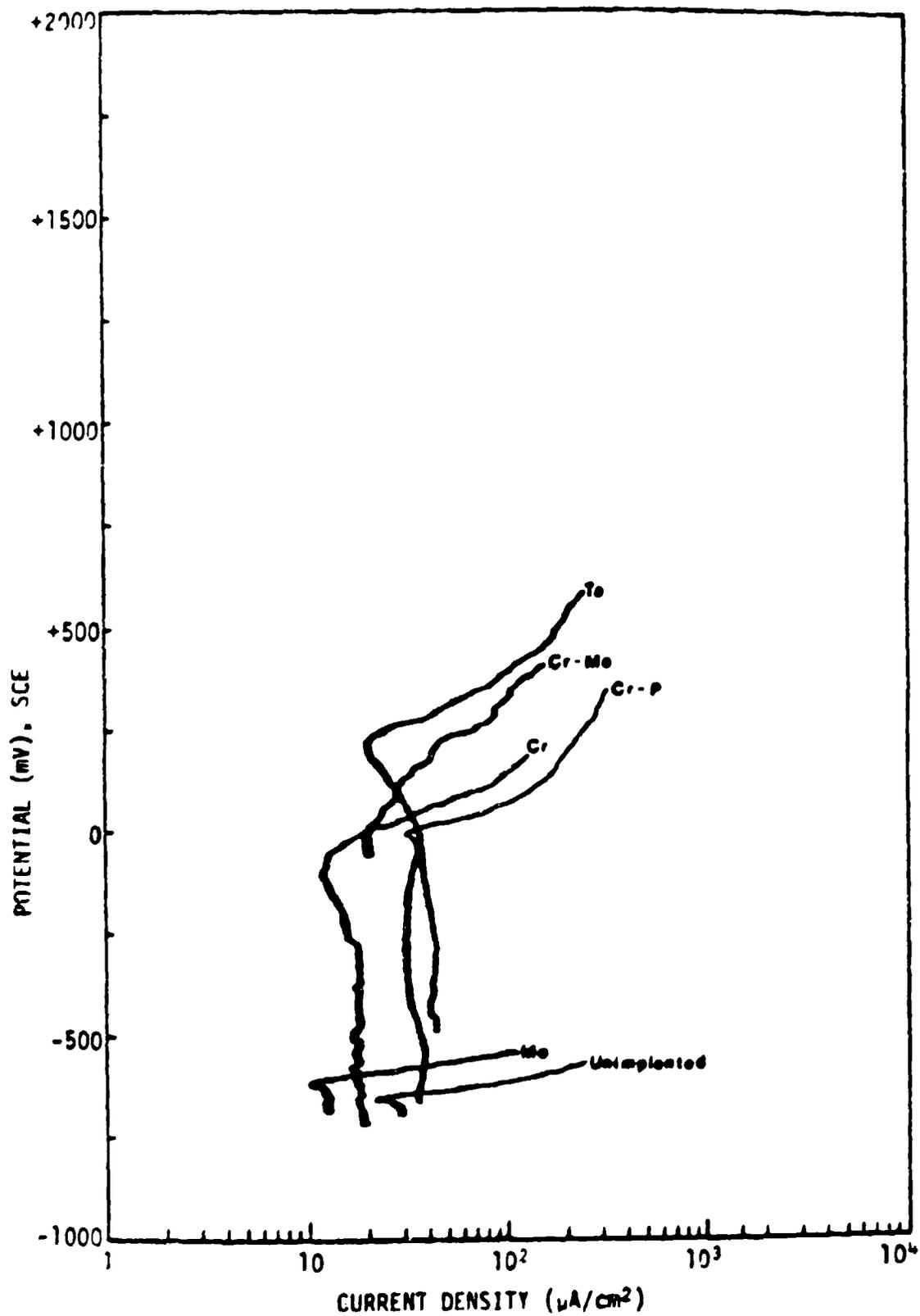


Figure 18. Anodic polarization curves of implanted 52100 steel in 0.01 M NaCl solution buffered at pH6 with cathodic pretreatment.

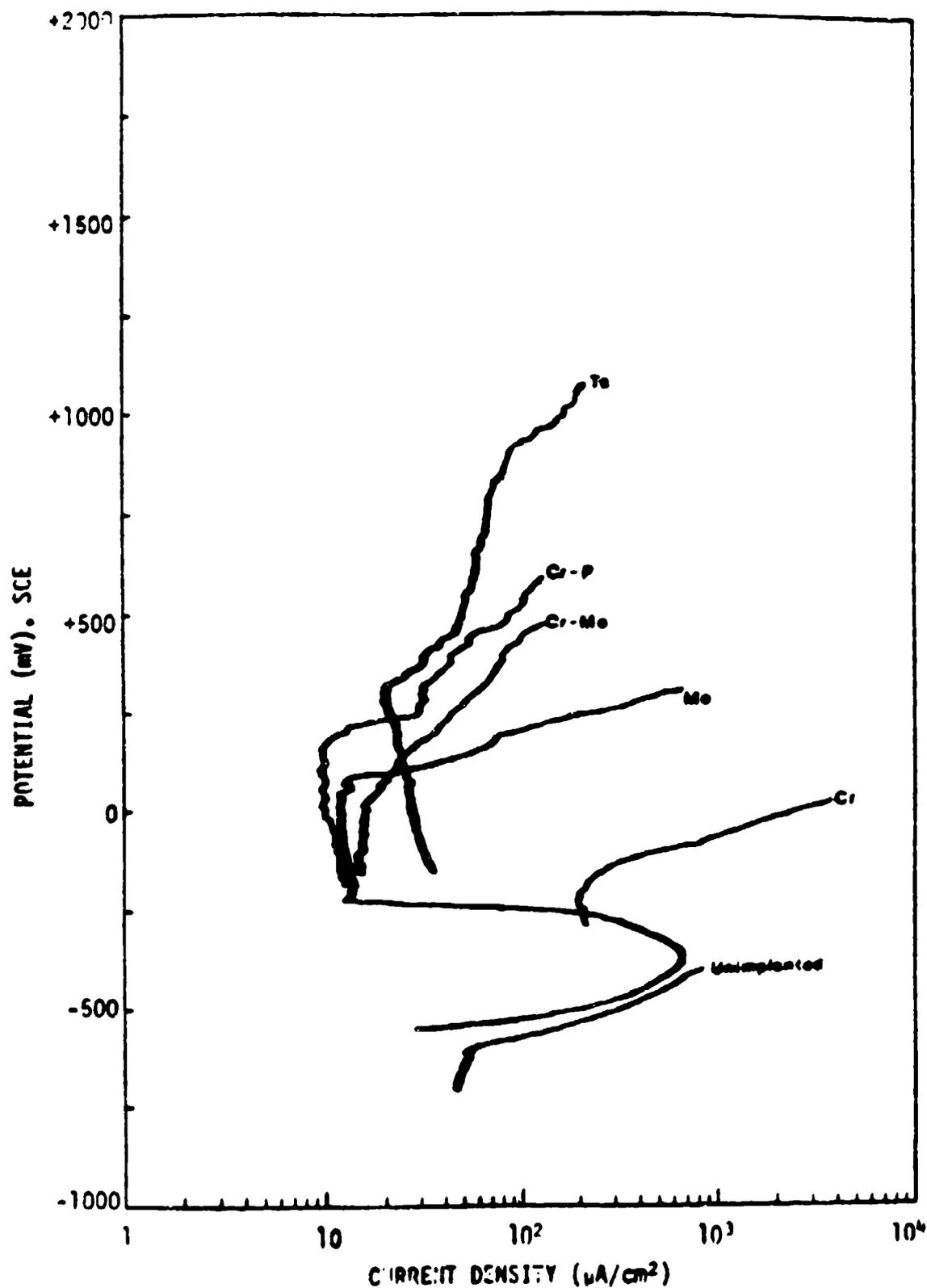


Figure 19. Anodic polarization curves of implanted 52100 steel in 0.01 M NaCl solution buffered at pH6 without cathodic pretreatment.

## QUESTIONS AND ANSWERS

S. Citron, ARRADCOM: Clive, in your double implantation experiments, do you have any general guidelines in terms of specifying or establishing the energy of the implants so that you position your implants one before the other?

C. Clayton: Well, I think as indicated by the experience we had with Ni implantation into 430 ss, it is probably dangerous to assume that the LSS calculated ion distribution in the target can be taken at face value. I think certainly that you have to characterize the system experimentally. In other words you have to find from the experience of carrying out some implantations and subsequent depth profiles what parameters to choose. However, there are some guidelines. Clearly the heavier elements will produce very significant levels of sputtering. You could, if you wanted to, use that fact not only to consider the final concentration of that element in the surface alloy but to uncover a deeper previously implanted element. The benefit of that may be that since you have to live with some degree of sputtering it might be reasonable to implant the lightest element first at a deeper level and implant last with the heavier element in order to uncover a suitable concentration of the first element.

N. Bullock, TSARCOM: As a novice I'd be interested in how you measure sputtering time.

C. Clayton: In our depth profiles we measure the landing current associated with the Ar ions. We measure the amount of charge accumulated on the sample until the profile is complete. We calibrate the etch-rates by calibrating a known thickness of the same or similar material using an independent technique such as RBS. This allows us to determine the depth scale of our profile.

F. Smidt, NRL: I'd like to make two comments, one about which ion to use first. You might recall that you get larger cascades with a heavier ion and so if you want to achieve the greatest mixing you probably want to use the heavier ion first. We are in the process of doing some intermixing studies with C and Ti and it makes a difference whether you bombard with C first and then hit it with the Ti; in that case you can get the amorphous alloys. In the other case it appears you do not. The other point I want to make is with regard to some of your defect profiles. There's been considerable literature in the radiation damage community dealing with this phenomenon. The interest started in the early 70's when they found that you can get voids formed in some of the reactor irradiations. This actually had some very serious practical applications. So there was a very large effort in DOE about this time period. Accelerators were used to simulate radiation damage, and they found a lot of peculiar things that applied to this field you are talking about. One, you can get metastable phases that you never would predict would occur in the phase diagram. Another is that some of these surface segregation reactions do take place. You mentioned Okamoto and Wiedersich, and they probably publicized their results more in the general literature than some of the other people. But, the Harwell group (Bulla) has done a lot of theoretical calculations, as have Ken Russell at MIT, Bob Johnson at the University of Virginia. Some of the effects are time dependent. You can get all kinds of weird results. You might get a transient peak where there is segregation and then it goes away at a later time. They're highly temperature dependent, i.e., temperature of the substrate. It is, in fact, an exceedingly complex field and you should avail yourself of the literature.

C. Clayton: Yes. I think that our experience of really stumbling on the literature was very fortunate. It is also a problem, that in this area of ion implantation, there seems to be little apparent concern for the effects of radiation damage itself. People do not appear to be characterizing their surfaces carefully enough to actually see if there are effects of radiation damage. It can also be used as a means of producing the final implant distribution that you are interested in looking at, and possibly this may be of value in the area of ion beam mixing.

P. Sagalyn, AMMRC: In reading the literature, one finds a variety of methods used for getting concentration profiles. Rarely, if ever have I seen any particular reason given for picking a particular method. In fact, you get the impression they use whatever they have available. I was wondering if you could make a few general comments on what are the preferred methods. For example, to me, never having done it since RBS is non-destructive, you would think it would be in most cases the method of choice but I'm not at all sure that's correct. Could you comment on that?

C. Clayton: I think nuclear reaction profiling and RBS are the two most commonly used techniques for determining the implant distribution. Bruce Sartwell has told us about PIXE and it's value as a destructive technique - as are XPS and AES. Now the reason why I at the present moment would prefer to use Auger depth profiling to determine an implant distribution is that I can simultaneously gather information about almost every element that could exist in that profile. And, since AES has such good sensitivity I can, for the purpose of the corrosion work at least, define quite carefully the nature of the surface alloy. It can be done very rapidly, much more rapidly, I think, than RBS. Furthermore, there are also problems with these other profiling techniques in that if they are not used in UHV, C deposits may be formed on the surface of the sample during analysis, thus having an influence on the accuracy of the profile measurement. Auger profiling has it's problems too, associated with etch-rate calibration. The comment made in the previous talk about the possibility of having an ion intermixing process going on during AES sputter profiling, is of course real, but in the energy range used commonly for sputtering, around 2.5 keV (Ar+), the intermixing depth would be around 20 angstroms. And for the grazing angles at which we sputter, we expect that such intermixing will be minimized.

P. Sagalyn: The RBS work is often done with quite energetic ions. I never thought about it before, but that, I would think, might produce considerable intermixing. Is that a well known problem?

C. Clayton: I don't think there is any evidence that I have come across that any such intermixing is observed. I've spoken with people who use these techniques and I don't think that it is a problem.

A. Niiler, BRL: We, in connection with our erosion work, have used not alpha backscattering for analysis but deuteron backscattering in combination with some deuteron induced nuclear reactions. Your comment about backscattering generally only applying to a single element is now removed. It depends on how difficult an analysis procedure you want to go through. If you've got a big computer available, you can do an analysis of as many as a dozen elements at one time and get very detailed information, not as good resolution as you can with your Auger depth sputtering, but you can get many elements at once. In fact just recently we have done some depth profiling of Cr on Fe, and most people would say you could not do it with deuteron backscattering, but you can. We've done it. It gives some very interesting results.

C. Clayton: I think one of the great limitations of sputter profiling is the fact that if one has to analyze a binary system, for example, where the atoms in that system have a vastly different mass, selective sputtering can be very important. I think in such cases it would be preferable to go to RBS because there we have the relative mass difference giving us the best resolution possible. Certainly I find encouraging the remark that systems which have very similar masses can still have reasonable resolution if the backscattering profiles are analyzed by computer.

SEVENTH SESSION:

SUMMARY REVIEW  
FOR  
PLANNING BASE

C. Levy: I'd like to ask Dr. Robert French to come up and assist in leading our discussion. Bob is the Director of our Metals and Ceramics Laboratory, which is the organization here at AMMRC involved most with the materials we've been talking about.

R. French, AMMRC: Charlie asked me to start off with perhaps what amounts to a little bit of a management perspective. Although relatively new to the business of developing ion implantation, nonetheless we at AMMRC perceived sometime back that there were definite potential applications for ion implantation within the Army systems. Like our predecessors in getting started in this business, we were seeing a scattered bench level origin of interest. It wasn't clear that any of this was really going to develop into a coherent program. Part of that concern arises from the fact that there have been findings coming out of ion implantation that rather go against the investigators original deductive reasoning. In other words, they expected a certain outcome and they didn't get it. Sometimes they got quite the opposite and then went off on a trail to explain that. If you get enough of that type of approach, you find that you have an area of research that is very intriguing to an R&D community, but from the point of view of the applications-type people you may be extensively researching the area without getting anywhere.

From the applications point of view you'd like to have an ability to establish, rather early, a broader base of information; something typically attained by an empirical approach. Implant one material with another and take a look at the results. Do that as fast as possible because then we can get the information that would tell us whether we really do have potential application without having to continually justify an endless line of research funding.

From the research point of view the purely empirical approach runs the risk of not being guided by understanding which can lead to failure and a setback of technology development. Understanding takes time.

With limited funds available,, I believe we have to do both. So, in setting up this workshop we tried to bring together a broad group of knowledgeable people from the most fundamental researcher to people who are deeply into applications. As a result you see people here from labs and repair depots. What I have seen so far indicates that we've succeeded in our goal of bringing out some new ideas. When we get down to a discussion period like this, we must try to draw out the issues to form a consensus. What are the most important issues?

I have heard references to a number of possible applications, but there is room for more. There is also room for disagreement. I was pleased to see a need appear for finding a way to discourage adhesion of a polymer. Now there may be different ways of solving that problem but I don't think anybody has heard of that kind of a potential application coming out before. Perhaps that there are other applications where we want to discourage rather than assist adhesion. So that's very interesting.

I'd like to offer a potential future application for ion implantation myself. A short time ago, while I was pulling together an Army picture on critical and strategic materials, it occurred to me that we are heading into an age when monolithic materials will less and less be able to handle the demands we place on them. Under critical and strategic materials planning, monolithic materials, usually in simple form, are the problem because the United States is so deeply dependent on imports. When you are faced with that sort of situation, the idea of creating alternatives in

the form of tailored material, engineered composites if you like, really comes into its own. We have been developing composites for performance reasons but they may just as well serve to broaden the base of alternatives in the event of a shortage of a critical material: and the success of a composite is entirely dependent on the nature of the interface between major components.

I will use one example to show you an application where ion implantation may be useful. The slide on the screen shows an engineered composite turbine blade; an iron-aluminum alloy matrix providing corrosion resistance and embedded metal filaments providing strength. This composite was created as an alternative to super-alloys containing critical elements. The slide shows how the composite was made. We have had problems with some filaments in creating a good bond between filament and matrix. Modification of the filament surface by ion implantation may be the way to solve those problems. The entire effort was a derivative of work sponsored by the Navy and by NASA, and our drive was simply to look at the technology as an alternative to critical materials.

Finally, I am noting on the board any action items that come up. The first one is our promise to publish the proceedings. If there is anything else that you would like us to do that is appropriate as an action item, we'll do our best to carry it out. So, recapping what we're looking for: issues, other potential applications, and then action items. At this point the number one issue seems to be that we have a shortage of processing facilities for research samples. Perhaps the Navy might like to comment on that.

F. Smidt, NRL: I might tell you just what my function is in the Navy. As you certainly realize, there has been a great deal of interest at NRL in utilizing ion implantation for some of the materials processing applications. Support for this program has been evident at the highest levels, namely Al Schindler who's associate director of research for materials, and the effort was going on in three different divisions. After a certain period of time there was a sort of spreading of the effort into the major areas of interest for each of the disciplines, chemistry, metallurgy and physics. To preserve an interdisciplinary effort and reverse this sort of defocusing of the effort, Dr. Schindler asked me to coordinate the program. I have a staff position half-time on his staff, and for about the last nine months I've been looking very carefully at what is being done at NRL, what the potential directions are, where we could get some payoffs and what ought to be done to try and get there. Well, one of the things that certainly needs to be done is to develop a facility that can turn out enough samples so that you can make statistical evaluations and prove to the engineers that you really have something that is reproducible and reliable and can be used for their purposes. One thrust that we are trying to exploit to get to that position is a manufacturing technology program. We have funding, at least on the books now, to start in FY 82 to put in an ion implantation facility at some Navy or industrial site. One possibility is Louisville Naval Ordnance Station. Their function is remanufacturing of some of the Navy's missile systems and ordnance application. The application of ion implantation that we are trying to exploit for them has to do with extending the wear of machine tools or machine tool bits. They would also turn out corrosion-resistant bearings for NaVAir. The project is scoped at a million and a half over a two year period and is aimed at putting in a larger scale facility and the training of the personnel to get things moving. We would anticipate that this facility could do batch processes for other DoD groups. We would like to see it reach the point where customers would come to the facility and say we want to try out this and you could turn out enough

products so that they could take it back and evaluate it. This is our hope. It is not guaranteed that all the funding will come through but this is what we have in mind and this is what we're trying to move toward.

C. Levy: Thank you Fred. Someone else like to make some general comments?

P. Sagalyn, AMMRC: I don't have any comments. I have a very elementary question. How many implanters does NRL have? Just one or two for the entire organization?

F. Smidt: Yes.

P. Sagalyn: All this cooperative work that Hirvonen and you do is done on two implanters?

F. Smidt and J. Hirvonen, NRL: Yes.

C. Levy: I might comment that we're certainly way behind the British when it comes to practical applications and we can probably take note of the progress that they have made in scaling up their equipment.

R. French: The cost of a new facility is very, very high. Unless we in the Army can develop sufficient reason to establish another facility, it makes a lot more sense, to purchase facility time from industry or the Navy.

W. Hamill, ATL: I was under the impression that all prior tries on tooling failed. What makes the Navy think that this time they're going to be able to ion implant tools for mills and bores or whatever and get a useful product, and a competitive product?

F. Smidt: I'm at a disadvantage because I don't know what Hirvonen talked about. Did he talk about the titanium carbide work? No. Well, the principle that we're trying to operate on is to produce some refractory materials that are hard on the surface. Harwell, of course, only implanted nitrogen and I don't see that that's going to be competitive with carburizing or nitriding or some of the well accepted commercial practices unless for some reason the tooling can't take the conventional heat treatment cycle. The concepts that we're operating on are to improve the surface performance of the tool. Titanium carbide is what we're currently working on and performance has been shown. We had a contract with Ramaligam at Georgia Tech in which he measured the tool forces and the flank wear on an instrumented lathe, a setup that he's developed. It showed that flank wear was half of that for an unimplanted tool, and there was about a 10 to 15 percent reduction in the power requirements. We also did some end mills which did not have the optimum implant. They didn't show any improvement, but we think we know why that didn't happen. So the answer is we're pursuing some of the more refractory compounds rather than simple nitrogen or carbon implants for the more severe wear applications.

C. Levy: It seems clear to me that one of the issues we certainly are addressing based on the papers and discussions we've heard here in the past couple of days is the need for more fundamental and applied research, R&D. So with your permission I'd like to put that on the list. We certainly need to do a lot more in those areas. Someone like to add a little bit more to that?

R. Quattrone, CERL: I don't want to add to that one but I do want to bring up one thing that is bothering me as an issue. There are several ways that you can modify the surface. You could do laser modification, for example. You can do ion plating or other approaches that can give you some relatively heavier coatings. I guess the question that's got to be asked, mainly for the Army as a whole and considering any of the bulk type applications, is there an issue with the thickness limitation of 1000 angstroms? What about if you're going to larger materials. Do we know anything about variabilities in this thickness limitation of 1000 angstroms? How much of a problem is that and how much does it say against ion implantation, rather than other techniques for surface modification?

C. Levy: Do any of our speakers want to address that question?

P. Sagalyn: I showed a slide yesterday on the work, or the experience I should say, on Healey Mouldings Ltd. in England where they got enormous factors of improvement in certain components used for molding plastics and it doesn't matter how thick or thin the layer, the net result is that they got 10 times more satisfactory molding out of an implanted mold than they got out of an unimplanted mold. Now the question of how this compares with other techniques I'm in no position to answer as a physicist but Delves, the man who gave the talk in answer to just that question, made the statement that ion implantation appeared to him to be the method of choice, relative to all other methods available for improving the lifetimes of those molds.

A. Niiler, BRL: Relative to the last two issues about the need for fundamental R&D I don't know how things work at AMMRC but I do know how they work at BRL. And the way they work there is that the application drives the work. Rather than the other way around like it does at Stony Brook and other places. The point then, is that I think that if we answered the applications column, that will answer the question as to whether our issues are big enough or strong enough to put in any of this extra money into the work or not. Certainly what Bob Quattrone mentioned on these other techniques, the competing techniques of not only modifying surfaces but protecting surfaces is important. I think we're not only talking about the modification but of really protecting bulk materials against outside influences. I think any effort that we make in terms of building facilities and so on must consider these other techniques also and not simply ion implantation.

R. Quattrone: I would like you to put it down as an issue to consider. When you're putting together your proceedings, that you do put down the thickness limitations and the comparisons with other sorts of techniques.

C. Levy: In light of the comment we just had, I'd like to just quickly run down the practical areas we talked about as possibilities for ion implantation. Aqueous corrosion?

R. French: There is one other point that came out this morning I didn't want to let go by. There are obviously problems in characterizing the implanted surface because some of the characterization techniques interfere with the measurements. That has the potential for leading to a distrust of analysis. I think there is an unresolved issue in the determination of methods to characterize an implanted surface.

C. Levy: You want to marry II with characterization. Let's just review these practical areas, and they're rather broad, that we've talked about during our workshop. Aqueous corrosion, hot corrosion, friction, wear, fatigue, stress rupture,

potential optical applications and catalytic applications. Those are the areas that we have noted so far and there may be some potential application for a high value item which is now in production or close to the production stage.

S. Cytron, ARRADCOM: In the light of the first item, access to processing facilities. Most of the facilities are setup for simple geometries and I think an issue to be concerned with here is setting up equipment that is adaptable to real structures. Are we going to face the situation where we have a complex structure configuration wise or size-wise, that is it going to be continually adapted, or are ion implantation equipment parameters to be set by manufacturers? Are they going to be amenable to providing greater flexibility in their systems to address these real structures?

C. Levy: I think Jim Hirvonen was asked a question in that regard and, once you have the basic facility, I believe what he said was that it was a matter of jiggling or arranging a configuration so that you could properly implant that part. However, I think your point is well taken and we certainly should follow it up. Want to make another comment?

Not Identified: Okay, it is mentioned that the line of sight is a problem as Jim Hirvonen also pointed out, and one that we have to keep in mind in processing parts.

A. Niiler: I never thought I would ever be up in front of any group saying what I'm going to now because basically I'm a physicist and I like doing fundamental work. But regarding the question about applications, I think you implied it but didn't say it, that what drives the Army's work in research is the need to protect XM-109 or XM-736 or any specific weapons system rather than just a general broad base of materials. So the question of aqueous corrosion or hot corrosion needs to be examined a little further. You need to say what specific cases for the Army are affected by corrosion. I'm just sort of expanding the scope of this applications column from the management point of view if we want to sell the program.

C. Levy: I think your point is well taken and we have throughout our discussions, I think, identified a large number-no I take it back, a small number-of potential end items. Somebody talked about turbine blades, which has been a continuing problem of protection against hot corrosion. That may be an area where we can justify the cost effectiveness of ion implantation processing. I'd like to hear more of the experience from the depot, from the installations. What are the real surface problems that you have that can give ion implantation a potential application?

N. Bullock, TSARCOM: As a depot engineer I would say one of the greatest problems we have is honeycomb corrosion. When the aluminum is canned, it is attached to the adhesive by bonding. In the experience we found that adhesive used later on becomes hydrophilic, attracting moisture and setting up corrosion sites. We have corrosion problems throughout the world on our honeycomb panels. Now I don't know how practical it is from a standpoint of ion implantation because the surface area is so large. I don't know if we could ever find a radiation source that could treat a honeycomb panel, as much surface area say as it occupies in a helicopter or a high speed aircraft. But that certainly would be an advantage, protecting that aluminum, if possible by ion implantation, to reduce the corrosion. For example, between the adhesive that's in the system and the skin that settled on the outside.

C. Levy: I think the point is well taken. If I may make a pun, right on the surface it doesn't appear as though ion implantation would be a potential application, but there may be some other idea that may be stimulated in our group.

N. Bullock: Well the Air Force did find out one thing. For example, we originally started out with chromic acid anodize and we thought that was the answer but we didn't know for 10-15 years until the planes and the helicopters had been in the field and came back with all these corrosion problems that wasn't the answer. So then the Air Force and other agencies found that phosphoric acid anodize seemed to be an improvement. So this chemical treatment seems to be an improvement, and I don't know how practical this ion implantation would be. If it could be adapted it would seem pretty reasonable to me.

P. Sagalyn: I was going to suggest a little earlier that you add adhesion to your list of applications. It's an area that there's been very little work on and this concept that Mayer has introduced as stitching where you really use ion implantation in a hybrid application, where you use it to improve just, say, the adhesion of a coating to a substrate might have a lot of practical applications. I'd like to make a general comment that I have spent my career on fundamental research. On the other hand I got interested in ion implantation because of the applications and when you listen to talks by people like Clayton and Hirvonen and other talks at Manchester, the thing that's striking is that ion implantation adds a whole magnitude of complexity to materials science. If you want fruitful applications in the future you're going to just have to support fundamental research at this time because there are too many parameters. I know that money is short. Everything requires a relative judgement; but, for example, there were two papers in Manchester that brought up the concept of critical dosage. Now, that means that possibly the whole dose dependence of every implantation has to be studied. Unless you do this for corrosion in particular, the whole problem is so complex and the treatment to be used is so dependent on the application that without a great body of fundamental information you're going to end up with no practical applications in my opinion.

R. French: The reason for this Workshop is to establish direction. Once that is known, we can determine affordable resources. Unfortunately, resources are scarce.

C. Levy: I think we have come up rather short on the applications kinds of things we were looking for. What I'd like to do is shift the emphasis over to actions. What is your feeling on what kind of things we can do to further investigate ion implantation for Army needs? Do you want to address that Captain Wilson?

Capt. Wilson, CADCA: First of all I've sat here for a day and a half and heard a lot of good things and Dr. French actually hit it on the nose. If you want to get a good program going then you're going to have to convince that three-star moving into that four-star slot that you're going to help the soldier in the field. I think you've got several ways you can do that. Right now the maintenance time on a tank is, running at a level of four hours of maintenance to every one hour of operation. A lot of that is changing of metal-type components. The track on a tank is going to last about 438 miles, then you have to switch out the entire track. I think through ion implantation you possibly have something that you can sell to that four-star saying that you can improve those down times. Now I'm talking on a much larger scale than anybody else here so far because I haven't heard anybody address it, doing common parts, implanting common parts, to where the life cycle of that part would

last a lot longer. I heard in one briefing, a possible 40% increase in cost. I don't know how true that is, but I know if that part is going to last me 5 or 10 times longer, then you've given me something that I can work with. Consider gun tube life on tanks. BRL and everybody else knows that if you can give me more life on that gun tube so I can fire more rounds through it, then you've got something. You got something that the user wants to hear and he'll get behind you. Yes, you need a lot more research, but don't play down what you've got so far. Look at what you've got. Put yourself together a good program, approach some of the project managers.

A big problem we had in the Bright Star exercise whenever we took the 101st Airborne over there erosion was on helicopters. Whenever helicopters started working in the sand, we got a lot of erosion on the rotors. Maybe you can do something there. Maybe you've got something that, you've got to approach the user from a selling aspect. Dr. French is more than aware of how to do that, but those are some of the ideas you can approach him with. Give him something that's going to improve what he presently has.

C. Levy: Okay, I guess that gives us an action item. Anybody have any other suggestions for action that we should take on the basis of the workshop.

W. Hamill: I was really intrigued with the increased ductility that several researchers have found with ceramics. Right now we're involved in a program where we're evaluating silicon nitride bearings in the final planetary transmission of the helicopter. I'm scared to death about the lack of ductility in the material. The material is being tried because it promises much greater rolling contact fatigue life. Also we don't have to worry about corrosion anymore with ceramics. That's fantastic.

D. Tenney, NASA Langley: I think there is another application here that hasn't really been discussed very much, that is putting metals into polymers. Metal containing polymeric films have a lot of interest for a variety of reasons. They're of interest to NASA and for the Air Force for charging effects on satellite systems or other systems that are going to be used in space. There have also been some practical uses recently in corrosion where polyimide-containing metal films have been used on well casings to greatly reduce corrosion failure in a practical application at least for the oil companies. I rather suspect that there are a lot more fruitful things that could be done in that area because of the problems of putting elements like palladium into polyimides. It is very difficult to get very much of it into the polymer structure and it just seems to me that ion implantation does offer potential, at least in that area for a variety of different applications. I think rather maybe some of the polymer chemists ought to get involved rather than just all of us metallurgists.

C. Levy: Thank you. The action items. What can we do? We're going to send you a copy of the proceedings. Anybody want to come up with something that you think we can do.

S. Cytron: I think Capt. Wilson sort of hit the nail on the head in terms of developing a mechanism where the user with the end item can relate their maintenance problems to the R&D community. There is a need to develop an interface, to make sure the problems flow both ways. The action item should be to develop sort of a group or an Ad Hoc committee or a liaison to do this job. Now that can also be

fought with problems. We don't want to end up generating paper. I think a lot of this can be done verbally, with personal contacts. I think the fact that the Captain was here bringing up his immediate concern, is something that the R&D people have missed. The contacts that we would like to establish are with the Army depots in terms of finding out their particular needs. What items are they troubled with? What items are giving them the greater problems and how amenable is this new technology toward alleviating their problems? These things have to be brought out and I say surfaced in terms of this particular ion implantation program.

C. Levy: Someone else want to make a comment on that?

P. Fopiano, AMMRC: It seems to me that the furthest that we've come has been this bearing implantation work. Everything does seem to look good in that area, but I think we have to get to understand that we're dealing with a very expensive technology. We aren't dealing with something that allows large acreage of implantation on an economic basis, and I think the cost has to be considered in any of these applications. The solution seems to be coming along very well. Now, I think we have to look at areas such as cost, and a good successful Navy program, I think could help us out. I think that program has very wide scope and I think it's been handled well. You're able to get support to the researchers based upon the same thinking of Capt. Wilson here. I think, that's the approach that we have to think about, small items, typically expensive items, where the payoff is good.

P. Sagalyn: I can't give you any numbers, but I don't think that we are limited to small acreage from talking with people that build these machines like Pete Rose at Nova Associates. When the demand is there, they are capable of turning out quite finite cost machines that will process large quantities of metallurgical type samples. It is just that, so far, there has been no demand for it. I think there will be in the future.

D. Tenney: I've heard several speakers make reference to various peoples work. I think one of the things that would be very useful would be to include a bibliography with the proceedings and what are the key papers if somebody is really interested in finding out about this. What are the 10 key or 15 key papers that they should read to get themselves up to speed. I don't know whether you can get that information from the authors here or not. I suspect if they're really the experts in the area that they should be able to provide you with that information right off. But I think that would be useful in the publication somewhere, to include a bibliography of the research papers available.

C. Levy: Could I ask if you are thinking in terms of general survey papers or application papers?

D. Tenney: I guess both. I'm not sure. I think you'd probably want to divide them into different categories, but I don't know. You might subdivide them into corrosion and wear, and I think you need to give that some thought. But the idea of including them in the proceedings would make it more useful to me at least.

A. Niiler: Supporting Cytron's comments about the need for some real items that need to be worked on, very recently I saw a list I think was generated from here at AMMRC which shows by name the various weapons systems which in fact did have some corrosion and wear type problems.

C. Levy: I have not seen this but I think that Milt Levy who is in charge of our corrosion group probably does have that available.

A. Niiler: And I think that an action item from this group, or one of the first items that should be done, is that a comprehensive list of such a nature should be drawn up, certainly including the users in it as much as possible.

F. Smidt: I apologize for salesmanship in the Army's meeting but we're publishing some reports which are a compilation of our research, semi-annually. One edition has gone out and a second one has just come off the press. If anybody wants to sign up and leave your address I'll put your name on the distribution list for it. The purpose of this publication is to disseminate as widely as possible the results of this work and hopefully interest some of the people in the user communities in solving their surface problems with ion implantation. Also, I ought to point out that the book that Hirvonen edited is probably the best single source of information on all the phenomena that people at least at this time have conceived of addressing.

C. Levy: Thank you Fred. We'll certainly put that on our bibliography list.

B. Sartwell, Bureau of Mines: I think it would be a mistake for the Army to just limit itself to ion implantation because there certainly are plenty of other techniques such as laser processing. You could even do the same types of things with electron beams. You can form metastable solid solution alloys in the near surface region. And there are many other coating techniques. So if you are just looking at ion implantation, you're really keeping your scope too limited. To sort of make a commercial announcement, I don't know how many people are familiar with the International Conference of Metallurgical Coatings. It is a conference that's directed more toward research than engineering applications but I think there would be a lot of information at that conference of interest to people here. Jim Mayer and I run a session on surface modification by all types of directed energy sources, lasers, ion implantation. There are also sessions on tribology, wear erosion, optical properties, changes by coatings, all types of coatings, thermal spraying, electrodeposition, and so on. I would recommend that some people from the Army attend that conference to get a real cross-section view of all the types of surface modification techniques. The next meeting is in April 1982, in San Diego. If you want to leave your name and address with me or write to me I'll make sure you get a copy of the call for papers that will give you all the necessary information.

C. Levy: I might follow that up in saying that the Army has lots and lots of people looking at various kinds of coatings including myself, and we do have programs in all those other areas you mentioned. However, trying to integrate those programs within the Army system is not too easy. Regarding the meeting, I'd like to expand on what Bruce Sartwell said in that there are a number of societies which are having sessions on ion beam treatment of surfaces: the Electrochemical Society, the Materials Research Society, SAMPE. I can't remember all the names off-hand but there are a lot of organizations like that are moving into this area and I think that those remarks for disseminating information are well taken.

C. Clayton, SUNY, Stony Brook: I have also to do a commercial. I think it is relevant that we have put together a one day symposium at the AIME fall meeting which is broad scale of 16 papers on the application of laser beams, electron beams and ion beams for the modification of corrosion resistance and oxidation resistance of metals. Since we already have those papers lined up, we have every intention to publish the

proceedings. I'd just like to indicate that if people are able to go to the Louisville, Kentucky meeting, they may also find that there will be some juxtaposition of papers between different techniques. The meeting may be of value to people who want to apply these techniques or are thinking of applying these techniques. In particular, there will be a paper on application of electron beams for the improvement of corrosion resistance, a paper which has never been published before.

C. Levy: Here are the summaries of the issues, actions, and applications (see Tables I, II and III). I'd like to wrap up if we have no more items you think we ought to take up or table for action from this workshop. We are going to send you a questionnaire. We've chosen not to give you your questionnaire at this time so you can go home and ruminate on these many ideas that you've heard here. We're going to give you a questionnaire which I hope will bring out some more of these points and try to accomplish some additional objectives which we have set forth for this workshop. I'd like to personally thank the speakers for their cooperation and excellent presentations and to you the participants who are helping us out in making this a worthwhile workshop. Thank you.

Table I

ISSUES

Availability of and access to processing facilities  
Need for more fundamental R&D  
Need applied R&D  
Thickness Limitations  
Marry ion implantation with surface characterization  
Setting up ion implantation equipment to address real  
structures  
Corrosion parameter problem.

Table II

ACTIONS

Publish proceedings  
Ad Hoc committee  
Bibliography of key papers dealing with ion implantation  
List of maintenance items  
Attend meetings dealing with surface treatments.

Table III

SUMMARY OF NEW IDEAS GENERATED FOR ARMY APPLICATIONS

Tank track components  
High temperature bearings  
Non-adhesion of organic coatings.

## ACKNOWLEDGMENTS

The Editor and Chairman extends his gratitude to Dr. Paul Sagalyn for his suggestions in planning the program and questionnaire; to Dr. Robert French for his support, encouragement and participation in the Workshop, as well as his editorial comments; to Bob Grubinskas of Non-Destructive Evaluation Branch for the superb acoustical quality of the microphone system and the tape recordings; to Carolann Walsh for her very efficient secretarial duties and hospitality to the attendants; Lucy Morana for her hospitality and help with Workshop arrangements; Carol Mancuso for diligent work in transcribing the tapes; Jo Ayoub for motel arrangements; and last, but not least, Jean Letterio for accurate and timely typing of the rough drafts of these proceedings.

Additional thanks go to the authors, attendants, and respondents for their excellent contributions.

## RESULTS OF POST-WORKSHOP QUESTIONNAIRE

The questionnaire sent to attendees and other interested parties is shown in Figures I and II. Fifteen of the attendees and four non-attendees responded with pertinent remarks. The following summaries of responses are identified with the respective numbers on the questionnaire.

1 and 2. Four additional surface-related properties were mentioned: (1) electromagnetic absorption and reflection; (2) fuels and lubricants; (3) high temperature oxidation (as distinct from hot corrosion); and (4) electronic properties. It should be noted that, while there was no directed effort to avoid discussion of electronic properties, emphasis of the workshop was placed on non-electronic applications, electronics being better left to the large number of engineers and technicians already working with ion implantation for electronics. Other materials mentioned in Question 2 were all for semi-conductor or dielectric materials.

3. Regarding mission areas, a wide response was received. Components with the respective problem property are listed below, in no particular order of importance.

- Integrated circuits (semi-conductors)
- Gears and bearings (friction and wear)
- Gun barrels (erosion)
- Gun recoil mechanisms (friction and wear)
- Fluidic sensors (friction and wear, high temperature oxidation)
- Optical circuits for laser and electromagnetics (optical)
- Carbon or graphite fabrics (laser hardening)
- Glass windows, canopies, optics, lenses (laser hardening)
- High strength aluminum alloys (corrosion)
- End connectors, pins and center guides for tracks (friction and wear, corrosion)
- Turbine blades (hot corrosion)
- Ductile ceramics (friction and wear)
- Depleted uranium penetrators (corrosion)
- Materials in contact with chemical warfare agents (corrosion)
- Conductive ceramic coating on titanium (corrosion)
- Helicopter compressor (hot corrosion)
- Aluminum skin materials (corrosion)
- Stainless steel substitutes (corrosion)

4. Of the relatively few people answering this question due to their non-familiarity with ion implantation, four thought the technique had high potential for Army applications, and two felt it had low potential. One person gave the opinion that it was necessary for the Army to have its own facility. Another stated that, if such a facility were built, it might have to be custom-designed.

5. Most of those attending thought the subject matter was well-covered. One commented that an economic analysis case study should have been given, while two wanted more information on implanting items of complex shapes.

6. No organizations offered financial support for an Army ion implantation facility, but several revealed that they are working with or contemplating working with ion implantation. These included Aviation Command (AVRADCOM, St. Louis), Communications Command (CEMOM, Tobyhanna), Armament Command (ARRADCOM, Dover and Aberdeen), and Electronics Command (ERADCOM, Fort Monmouth).

7. The following additional comments were offered:

a. By A. Niiler of Ballistics Research Laboratory: At the BRL we have a 2.5 MeV Van de Graff accelerator with a complete ion beam analysis setup. I would be happy to offer collaboration with other Army laboratories in the area of implant characterization by RBS and nuclear reaction methods.

b. By A. Mark, ERADCOM: It may be in the best interests of AMMRC to initially fund a program relative to alteration of material surface properties via implantation with an outside contractor, or university currently exploiting this area, before getting involved with establishing an implant facility. This comment is based on the fact that implantation equipment designed for the electronics industry may not be applicable for purposes envisioned by AMMRC. It is suggested that AMMRC first establish an internal study phase over a 1-2 year period to determine feasibility of involvement in this venture. (Editor's Note: Dr. Fred Smidt at the Naval Research Laboratory has undertaken such an effort for the U.S. Navy in the area of Ion Implantation Manufacturing Technology).

c. By F. Smidt, NRL: One of NRL's implanters is a commercial unit produced for the semiconductor industry by Varian-Extrion. NRL has installed a Freeman source and built a work piece handling chamber, but the balance of the unit is a commercially available implanter.

d. By J. Greenspan, AMMRC: At this time, there appears to be a special degree of difficulty in selecting experiments for the FY82 program that would demonstrate utility and practicality in a clear and unambiguous way. On the one hand, the existing base shows instances of outstanding effect on surface properties, but on the other hand, it also shows many gaps and uncertainties. In this symposium, for example, reference has been made to instances of uncertainty in selection of implantation species, implementation of procedures and controls, unexpected results, and methods of evaluation, among others.

Nevertheless, in FY82 the emphasis, at least in the AMMRC program, should be on one or more clear demonstrations of practicality and toward this end, high pay off. The problem is in selecting the right experiment. Perhaps consideration should be limited to cases of simplest configurations and most proven ion implantation parameters but in a high pay off area, such as compressor blade erosion, or other items of wear or erosion critical to military needs. This type of planning will require considerable search, liaison, follow-on discussion, and careful decision, but must be done in time for the FY82 submissions".

8. A list of recommended references received from respondents, authors and the Editor follows in the next section.

QUESTIONNAIRE  
ION IMPLANTATION FOR ARMY NEEDS WORKSHOP  
Army Materials & Mechanics Research Center  
Watertown, MA 02172  
30-31 July 1981

NAME \_\_\_\_\_  
TITLE \_\_\_\_\_  
ORGANIZATION \_\_\_\_\_  
STREET ADDRESS \_\_\_\_\_  
CITY \_\_\_\_\_ STATE \_\_\_\_\_ ZIP CODE \_\_\_\_\_  
TELEPHONE, AV \_\_\_\_\_ COM. \_\_\_\_\_

1. Which surface-related properties are of interest to your mission area?

- |  |  |
|--|--|
| <input type="checkbox"/> Aqueous corrosion         | <input type="checkbox"/> Hot corrosion   |
| <input type="checkbox"/> Ambient corrosion         | <input type="checkbox"/> Friction & Wear |
| <input type="checkbox"/> Erosion                   | <input type="checkbox"/> Optical         |
| <input type="checkbox"/> Fatigue                   | <input type="checkbox"/> Adhesion        |
| <input type="checkbox"/> Catalytic                 | <input type="checkbox"/> Laser Hardening |
| <input type="checkbox"/> Other, specifically _____ |  |

2. Which materials area(s) are you involved with?

- |  |   |
|--|---|
| <input type="checkbox"/> Ferrous metals            | <input type="checkbox"/> Polymers, etc. |
| <input type="checkbox"/> Non-ferrous metals        | <input type="checkbox"/> Composites     |
| <input type="checkbox"/> Ceramics                  | <input type="checkbox"/> Glasses        |
| <input type="checkbox"/> Other, specifically _____ |   |

3. In your mission area, are there any components of Army systems which might be candidates for Ion Implantation because of unsatisfactory performance, despite using conventional surface modification techniques? Please identify each component and give a brief description of the problem. If possible, relate the problem to one of the properties listed in question (1), or to other areas where Ion Implantation might be beneficial such as cost-effectiveness, component size, and configuration. Use additional paper if necessary.

4. If you are familiar with Ion Implantation techniques, we would be interested in your overall view as to its potential for Army Applications. Comments with respect to problems outside your own mission area would be welcome.

5. If you attended the Workshop at AMMRC, do you think we by-passed any aspect of Ion Implantation which should have been considered?
  
6. Would your organization support, financially, the establishment of an Army facility oriented toward the practical application of Ion Implantation for the development or processing of improved components for Army systems?
  
7. Do you want to contribute any comments to be published in the proceedings? If yes, please elaborate.
  
8. A bibliography of background reference material will be included in the proceedings. Please list any references you think might be appropriate.

PLEASE RETURN TO: Charles Levy  
Army Materials & Mechanics Research Center  
ATTN: DRXMR-KA, Building 312  
Watertown, MA 02172

## RECOMMENDED GENERAL REFERENCES

"Ion Implantation Metallurgy," edited by C. M. Preece and J. K. Hirvonen - Warrendale, PA: Metallurgical Society of AIME, 1980.

"Ion Implantation," G. Dearnaley and others, Amsterdam, North Holland Pub. Co.; New York, American Elsevier, 1973.

"New Uses of Ion Accelerators," edited by James F. Ziegler - New York: Plenum Press, 1975.

"Material Characterization Using Ion Beams," edited by J. P. Thomas and A. Cachard London; New York: Plenum Press, 1978.

"Ion Beam Handbook for Material Analysis," coordinating editors, by J. W. Mayer, E. Rimini; chapter editors, E. R. Appleton, New York: Academic Press, 1977.

"Ion Beams: With Applications to Ion Implantation," Robert G. Wilson, George R. Brewer - Reprinted with corrections - Huntington, NY, R. E. Krieger Pub. Co., 1979, c1973.

"Site Characterization and Aggregation of Implanted Atoms in Materials," - edited by A. Perez and R. Coussemant - New York - Plenum Press, 1980.

"Applications of Ion Beams to Metals," edited by S. T. Picraux, E. P. EerNisse, and F. L. Vook, New York, Plenum Press, 1974.

"Applications of Ion Beams to Materials, 1975," invited and contributed papers from the International Conference on Applications of Ion Beams to Materials held at the University of Warwick, 8-12 September 1975, edited by G. Carter, J. S. Colligon, and W. A. Grant - London, Institute of Physics, 1976.

"Ion Implantation Techniques," editors, H. Ryssel and H. Glawischnig Berlin, New York, Springer-Verlag, 1982.

"Materials Modification by Ion Implantation." J. K. Hirvonen and C. R. Clayton, in "Applications of Surface Alloying Techniques," J. M. Poate and G. Foti. N.A.T.O. Institute Series, Plenum (in press).

## SPECIALIZED REFERENCES

"Ion Implantation in Semiconductors," J. W. Mayer, J. A. Davies, and L. Eriksson, Academic Press, New York, 1970.

"Ion Implantation in Semiconductors: Science and Technology," edited by Susumu Namba - New York, Plenum Press, 1975.

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"Ion Implantation of Semiconductors," G. Carter, W. A. Grant, New York, Wiley, 1976.

"SEMICONDUCTOR Components for Monolithic Applications," E. Garmire, published Integrated Optics, T. Tamir, Editor, Springer-Verlag. New York, 1975.

"Formation of Waveguides and Modulates in  $\text{LiNbO}_3$  by Ion Implantation," G. L. Stefanis, et al, J. Appl. Phys. 50, 7898, 1979.

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"PROFILE: A general Code for Fitting Ion Beam Analysis Spectra," A. Niiler, R. Birkmire, J. Gerrits, BRL Technical Report, AR BRL-TR-02233, 1980.

"The  $^{14}\text{N}(d,p_g)^{15}\text{N}$  Cross Section, 0.23 to 1.45 MeV," A. Niiler, R. Birkmire, Nucl. Inst. & Meth., 168, 1980, 105.

"Application of Ion Beam Analysis Techniques to Ballistic Studies," A. Niiler, R. Birkmire, IEEE Transactions on Nuclear Science, NS-26, (1979) 1398, (this paper has some of our results on  $\text{N}^+$  implants on Fe).

## RESUMES OF SPEAKER'S BACKGROUNDS

James W. Mayer, Professor, Dept. of Materials Science and Engineering, Bard Hall,  
Cornell University, Ithaca, NY 14853

### I. Personal

- (a) Born: April 24, 1930; married; 5 children
- (b) U.S. citizen; address: 416 Cayuga Heights Road, Ithaca, NY 14850

### II. Academic and Industrial

- (a) B.S. (Engineering) - Purdue University, 1952
- (b) U.S. Army - Ordnance Corps, 1952-1954
- (c) Ph.D. (Physics) - Purdue University, 1960
- (d) Hughes Research Laboratories, 1959-1967
- (e) Caltech - Associate Professor, 1967-1971  
Professor of Electrical Engineering, 1971-1980  
Master of Student Houses, 1975-1980
- (f) Cornell University - Bard Professor, 1980-

III. Fellow, American Physical Society and Inst. Elect. Electr. Engr., Scientific Member, Bohmische Physical Society, SCUPA Instructor, Los Angeles County (19 UICC) and NAUI

IV. Board of Editors: Journal of Applied Physics (1971-1974)  
Thin Solid films (1975 - present)  
Diving World (1973)

V. Recipient, Von Hippel Award, 1981 (presented by the Materials Research Society).

### VI. Visiting Scientist

- (a) Technische Hochschule, Munich, Summer, 1965
- (b) Chalk River Nuclear Laboratories, Ontario, Summer & Fall, 1967
- (c) Institute of Physics, University of Modena, Spring, 1968
- (d) Research Institute for Physics, Stockholm, Summer, 1968
- (e) IBM Research Labs., Yorktown Heights, NY, Summer, 1972
- (f) Institute of Structure of Materials, University of Catania, Summer, 1973
- (g) Bell Laboratories, Murray Hills, NJ, Summer, 1977
- (h) Southern Universities Nuclear Institute, Summer, 1978

### VII. Conference Chairman

- (a) Ion Beam Surface Layer Analysis, Yorktown Heights, NY, 1973
- (b) U.S.-Italy Conference on Material Analysis, Catania, 1974
- (c) Gordon Conference on Particle-Solid Interactions, 1976
- (d) U.S.-U.S.S.R. Conference on Ion Implantation, Albany, NY, 1977

### VIII. Publications

#### A. Books

- 1. J. W. Mayer, J. A. Davis, and L. Eriksson, Ion Implantation in Semiconductors, (Academic Press, New York, 1970).
- 2. J. W. Mayer and E. Rimini, Handbook for Materials Analysis with Ion Beams, (Academic Press, New York, 1977).

3. W. K. Chu, J. W. Mayer, and M-A. Nicolet, Backscattering Spectrometry, (Academic Press, New York, 1978).
4. J. M. Poate, J. W. Mayer, and K. N. Tu, Thin Films - Interdiffusion Reactions, (Wiley and Sons, New York, 1978).
5. L. C. Feldman, J. W. Mayer, and S. T. Picraux, Materials Analysis by Ion Channeling, (Academic Press, New York, 1982).
6. J. M. Poate and J. W. Mayer, Laser and Electron Beam Processing of Semiconductor Structures, (Academic Press, New York, 1982).

B. Chapters in Edited Volumes - ten

C. Journal Publications - over 250 published papers.

ROBERT D. FRENCH

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Metals and Ceramics Laboratory  
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EDUCATION            B.S., M.S. - Mechanical Engineering, Northeastern University  
                      Ph.D. - Engineering (Materials Science), Brown University

MEMBERSHIPS        American Institute of Mining, Metallurgical and Petroleum Engineers  
                      American Society for Metals  
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EXPERIENCE         Dr. French has been involved with materials research and the development of manufacturing technology throughout his professional career. His technical accomplishments have been in the areas of thin film single crystal growth, field ion microscopy, analysis of material failures, and the characterization of new high temperature alloys. He has supervised in-house and contracted manufacturing technology developments dealing specifically with gear manufacturing, high quality cast titanium, cast refractory metals, and superalloy powders. In his present assignment he oversees the operation, planning, and coordination of four separate divisions engaged in the full spectrum of metals and ceramics development activities, from basic research through prototype production, addressing a wide variety of Army weapon and combat support system needs.

He joined the Army Materials and Mechanics Research Center in 1970 as a staff metallurgist and has since been successively appointed Group Leader of Physical Metallurgy, Branch Chief of Metals Processing, Chief of the Prototype Development Division and Director of the Metals and Ceramics Laboratory. During 1976 he was assigned to the Office of the Director of Army Research at the Pentagon. He has served as Army liaison member of National Material Advisory Board committees, Department of Defense interagency materials and manufacturing technology committees, and as a consultant to other Government agencies. He currently oversees international cooperative defense development activities pertaining to metals and ceramics.

Dr. French is a past board member of The Metallurgical Society of AIME. He is also past chairman and member of the executive committee of The Boston Section of AIME.

CHARLES LEVY, P.E.

Research Chemist  
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EDUCATION

B.S., Chemical Engineering, Massachusetts Institute of Technology  
M.S., Chemical Engineering, University of Missouri, Columbia  
Additional Graduate Level Courses at MIT in Electrochemistry and Metallurgy

Specialist Courses:

Radioisotope Techniques, Oak Ridge, TN  
Program Management, Rock Island Arsenal, IL  
Environmental Management, Fort Lee, VA

EXPERIENCE

Mr. Levy began his technical career at the Wright Air Development Center, Dayton, Ohio, in early 1951 as a Chemical Engineer engaged in studies of rocket engines. In late 1951, he transferred to Watertown Arsenal Laboratories where he served in a number of positions including Chief, Surface Chemistry Section. His projects included physical chemistry of corrosion, erosion, and electro-deposition processes. In 1959, he was employed by the Research Department, Gillette Safety Razor Company, Boston, MA, where he continued work on surface metallurgy and coatings for razor products. Mr. Levy joined Panametrics, Inc., Waltham, MA, to conduct studies of metal surface phenomena using radiochemical exchange techniques in 1964. In 1965, he became Technical Director of Swift Laboratories Inc., Waltham, MA, a consulting firm in metal finishing, chemical analysis and testing, and air and waste-water pollution control. In 1972, Mr. Levy joined AMMRC to conduct developmental programs on surface treatment and deterioration of metals. Programs have involved corrosion evaluation and surface protection of uranium alloys; encapsulation of aluminum-graphite composites; electrodeposition of titanium diboride; plasma spraying of tungsten; chemical milling; and simulated explosive experimental inert filler compositions. He also provides technical assistance in metal finishing of experimental artillery shell components, and served as the environmental control coordinator at AMMRC for 3 years.

Mr. Levy has presented numerous papers, 12 of which have been published. He has authored 15 Government reports as well as a number of patents and pending patent applications. Mr. Levy has been active in The Electrochemical Society and the American Electroplaters' Society. He is a Registered Professional Engineer in five states. He served on the Research Board of the American Electroplaters' Society for three years and as District Supervisor of a program on reverse osmosis for pollution control.

ALBERT MARK

Physical Scientist  
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EDUCATION            B.S. Physical Chemistry - Physics - English; Case Western Reserve University, Cleveland, Ohio. Graduate studies, Organic Chemistry.

EXPERIENCE            Technical career started as Research Assistant at Plastics Division of National Carbon Company. Conducted low temperature and high voltage breakdown studies on vinyl plastics. When labs were relocated, assigned to production and given charge of these activities. Transferred to Eveready Battery Division. Research on dry cells and parallel work on chlorine batteries for the Navy. Joined Strong Cobb Company early 1947 as Materials Lab Supervisor. Analysis of pharmaceutical products, essential oils, and narcotics. In 1951, hired as physical chemist by ECOM, Fort Monmouth, NJ. Studies on metal to ceramic interfaces for vacuum tubes. Established Physical Chemistry Lab for Thermionics Branch. Designed and engineered the development of a reactor for making high purity silicon. Joined Solid State group and involved on studies on jet etching and refill of silicon. Research on silicon surfaces using oxygen for surface passivation. Conducted concurrent parallel program with outside contractor. Work was forerunner of concept for isolating areas of silicon surfaces and birth of integrated circuits. Inventor of  $\text{SiCl}_4 + \text{H}_2$  process for silicon epitaxy (overgrowth). Holds basic patent in U.S. for silicon epitaxy granted in 1960 and assigned to Government. Performed advance work on epitaxial processing for fabrication of solid state devices. In 1979, established an Electron Beam facility for direct write and mask making in fabricating IC's. Member of task force in this activity. Established and presently in charge of ion implant facility for Microelectronics Division. Initial project engineer on MMT contract for development of ribbon sapphire with Tyco Inc. Initiated X-ray lithography contract with Hughes Research to determine extent of degradation of electronic properties of IC's when X-rays are used in fabrication process.

Holder of six patents singly and jointly on solid state processes and devices. Presentations and publications on epitaxial overgrowths, ion implantation, redistribution of implanted boron during annealing, etc. Four special act awards citing recognition of achievements.

PAUL L. SAGALYN

Supervisory Research Physicist  
Materials Characterization Division  
Army Materials and Mechanics Research Center  
Watertown, MA 02172

**EDUCATION**            B.S. Harvard College, 1942  
                          Ph.D. Physics, MIT, 1952

**PROFESSIONAL**        AMMRC - 1956 to present  
**EXPERIENCE**            MIT Post-Doctoral Research Associate - 1952-1956  
                          MIT Radiation Laboratory Staff Member - 1942-1945

**TECHNICAL**            Work at MIT was in the field of atomic physics, particularly double  
**SPECIALTIES**           resonance methods for measuring hyperfine structure. The work at  
                          AMMRC has been in Solid State Physics and Materials Science, with  
                          a specialty in Nuclear Magnetic Resonance in solids.

**AWARDS**                Atomic Energy Commission Fellowship, 1950-1952  
                          Sigma Xi  
                          D.A. Official Commendation, 1970  
                          Outstanding Performance Award, 1978

**PUBLICATIONS**        Approximately 32 unclassified papers, mostly in Solid State Physics.  
                          Five classified papers and reports.

PHILLIP A. FARRISH

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EDUCATION            Metallurgical Engineering - University of Florida  
                          B.S. - March 1969  
                          M.S. - June 1970  
                          Ph.D. - June 1974

EXPERIENCE            June 1975 to present: Metallurgist (GS-14), U.S. Army Research  
                          Office, Research Triangle Park, NC  
                          June 1974 to June 1975: Developmental Engineer, Fiber Industries,  
                          Inc., Charlotte, NC  
                          June 1970 to June 1974: Materials Engineer (Captain, USAF), Air  
                          Force Materials Laboratory, Wright-Patterson AFB, OH

PUBLICATIONS        P. A. Parrish, "Surface Modification for Improved Properties,"  
(partial)            Proceedings of the 1979 Sagamore Army Materials Conference,  
                          Plenum, New York, 1981.  
                          P. A. Parrish, S. Kim, and R. B. Benson, Jr., "Effect of Chromium  
                          Implantation on the Electrochemical Behavior of Iron," accepted for  
                          presentation and proceedings of Conference on Modification of the  
                          Surface Properties of Metals by Ion Implantation, Manchester, U.K.,  
                          June 23-26, 1981.

MEMBERSHIPS IN PROFESSIONAL AND SCIENTIFIC SOCIETIES

American Institute of Metallurgical, Mining, and Petroleum Engineers  
American Society for Metals  
National Association of Corrosion Engineers  
Alpha Sigma Mu (Metallurgy Honorary)  
CEBELCOR

HONORS,  
AWARDS                U.S. Air Force Scientific Achievement Award, June 1974  
                          First Place, American Institute of Metallurgical, Mining, and  
                          Petroleum Engineers National Student Paper Contest, Graduate  
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After obtaining his Ph.D. in physics in 1971 from Rutgers University, joined the Naval Research Laboratory (NRL), Washington. His research interests have been in the area of the application of high energy ion beams for near-surface materials analysis and for the modification of the surface properties of materials. He was Head of the Ion Implantation Section of the Radiation Technology Division at NRL. He has organized several symposia on the ion beam modification of materials. Has authored over 45 scientific papers and has recently edited two books on the applications of ion implantation for materials modification.

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EXPERIENCE

Following 3 years in the U.S. Navy, he began his technical career in 1973 at the Bureau of Mines' College Park, Maryland Research Center where he conducted research to determine the nature of the interactions of low and medium-energy ions with solids. This work involved the measurement of X-ray yields and ionization cross sections. Following that, he was assigned to the newly formed ion implantation project where he was the principal investigator responsible for coordinating the design and construction of small ion implantation systems and conducting several different types of corrosion tests. Mr. Sartwell also conducted experiments to measure thin film sputtering yields using proton-induced X-ray emission. In 1980, he became a Group Supervisor at the Avondale Research Center and is currently responsible for three separate projects, one with the goal of determining the effects of ion implantation and laser alloying on the corrosion of iron-based materials, the second with the goal of determining the effects of different types of nitriding on the aqueous corrosion resistance of mild steels, and the third with the goal of reducing the probability of methane-air ignitions when light metals strike rusted steel (for mining applications).

Mr. Sartwell has published over 20 papers in the technical literature and has presented numerous invited and contributed papers at conferences and symposium. He is a member of the American Vacuum Society and the American Society for Metals and is also a member of the Program Committee for the International Conference on Metallurgical Coatings where, for the past four years, he has chaired a session on Surface Modification by Directed Energy Sources.

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Dr. Clayton graduated with a B.Sc. in metallurgy and a Ph.D. in metallurgy from the University of Surrey, in 1976. In the same year he became a Research Associate at Stony Brook, where he is currently an Associate Professor in Materials Science. He is a specialist in XPS and AES, which he applies to the study of the corrosion and passivity of conventional alloys, and ion implanted and Laser treated metallic systems. Dr. Clayton has published more than 25 papers and is actively involved in the Electrochemical Society, Materials Research Society and the American Institute for Metallurgical Engineers.

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