**Ultrahigh-Current-Density Metal-Ion Implantation
and Diamondlike-Hydrocarbon Films for
Tribological Applications**

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TABLE OF CONTENTS

	Page
Summary.....	1
Metal-Ion-Implantation-System Development.....	3
Introduction.....	3
Apparatus and Procedures.....	4
Operating Characteristics and Limitations.....	13
Conclusions.....	24
A One-Dimensional Model for Temperature and Thermal-Stress Histories in Materials During High-Current-Density Ion Implantation.....	25
Thermal Analysis.....	25
Thermal-Stress Analysis.....	28
Software Validation.....	29
Computed Thermal Stresses for a Ceramic Being Ion-Implanted.....	32
Comparison of Observed Failure with Model Prediction.....	37
Microstructural and Tribological Studies on Metal-Ion-Implanted Materials...	40
Titanium-Ion-Implantation Study.....	40
Boron-Implantation Study.....	46
Tribological Studies on Diamondlike-Hydrocarbon Films.....	53
Acknowledgment.....	53
References.....	54
Appendix.....	56
Rolling-contact-fatigue wear characteristics of diamond-like hydrocarbon coatings on steels.....	57
The effects of beam energy and substrate temperature on the tribological properties of hard-carbon films on aluminum.....	68
A tribological investigation of the graphite-to-diamond-like behavior of amorphous carbon films ion beam deposited on ceramic substrates.....	75

LIST OF FIGURES

Fig. No.	Title	Page
1	Metal-Ion Source Schematic Diagram.....	5
2	Power-Supply System Schematic Diagram.....	8
3	Metal-Ion-Implantation System Schematic Diagram.....	12
4	Typical Ion-Current-Density Profile at Target Location.....	15
5	Typical Correlation between Beam Current and Ion-Beam Current Density at the Target Location.....	16
6	Metal and Carbon Phase-Diagram Data Comparison.....	18
7	Typical Metal-Ion-Source Operating Data.....	21
8	Physical Arrangement for Implantation Models.....	26
9	Parabolic Temperature Profiles and Corresponding Stress Profiles.....	31
10	Silicon Carbide Temperature and Stress Histories (Moderate Implantation Conditions).....	33
11	Silicon Carbide Temperature and Stress Histories (Severe Implantation Conditions).....	34
12	Preliminary Wear-Test Data for Ti-implanted Iron.....	42
13	X-ray-Diffraction Data for Ti-implanted Iron and 304 Stainless Steel.....	43
14	Conversion-Electron-Mössbauer Spectra for Ti-implanted Iron and 304 Stainless Steel.....	44
15	X-ray-Diffraction Data for 304 Stainless Steel Implanted with Ti under Various Methane-Partial-Pressure Conditions.....	47
16	Preliminary Sliding-Wear-Test Data for B-Implanted Discs.....	49

LIST OF FIGURES (Cont.)

Fig. No.	Title	Page
17	Conversion-Electron-Mössbauer Spectra for α -Fe Implanted with B at $\sim 300^{\circ}\text{C}$	50
18	Conversion-Electron-Mössbauer Spectra for α -Fe Implanted with B at $\sim 450^{\circ}\text{C}$	51
19	X-ray Diffraction Spectra and a Typical Probability Distribution of the Mössbauer Hyperfine Field for B-Implanted α -Fe Discs....	52

LIST OF TABLES

Table No.	Title	Page
1	Beam-Current Ranges used for Processing.....	19
2	Input Conditions for Fig. 9 Test Case.....	32
3	Input Conditions for SiC-Implantation-Example Cases (Figs. 10 and 11).....	35
4	Input Conditions for PSZ-Implantation Case.....	38

ULTRAHIGH-CURRENT-DENSITY METAL-ION IMPLANTATION AND DIAMONDLIKE-HYDROCARBON FILMS FOR TRIBOLOGICAL APPLICATIONS

SUMMARY

The design features and operating characteristics of the metal-ion-implantation system that was built, tested and used to implant metals into substrates under this contract are described. The unique capabilities of a system like this that derives a broad, high-current-density beam directly from a steady, metal-plasma discharge and is simple, rugged, reliable and easy to maintain are discussed. The metal vapor required for operation is supplied by drawing sufficient electron current from the plasma discharge to an anode-potential crucible so a solid, pure metal placed in the crucible will be heated to the point of vaporization. The ion-producing, plasma discharge is initiated within a graphite-ion-source body, which operates at high temperature, by using an argon flow that is turned off once the metal vapor is present. Extraction of ion beams that are several centimeters in diameter at current densities ranging to several hundred $\mu\text{A}/\text{cm}^2$ on a target 50 cm downstream of the ion source have been demonstrated using Mg, Ag, Cr, Cu, Si, Ti, V, B and Zr. These metals were implanted into over 100 substrates (discs, pins, flats, wires) for researchers at several different laboratories in support of their research efforts.

A model that describes thermal stresses induced in materials (e.g. ceramic plates) during high-current-density implantation is presented. The tribological and

microstructural characteristics of iron and 304-stainless-steel samples that have been implanted with Ti or B are examined.

In the course of the conduct of this research, diamondlike-hydrocarbon coatings were applied to steel surfaces and found to exhibit good tribological performance. Over 200 samples and components were coated for various researchers. Papers describing the process and the tribological performance of the coatings are cited or included in the report.

METAL-ION-IMPLANTATION-SYSTEM DEVELOPMENT

Introduction

It has been known for some time that metal ions implanted into such materials as steels and ceramics can induce dramatic improvements in surface-related properties such as those related to corrosion resistance, wear resistance and friction coefficient [1-3]. A metal-ion-implantation system used to treat such surfaces typically incorporates features for 1) the production of metal atoms or metal-bearing molecules, 2) their ionization, 3) acceleration of the resulting ions, 4) the removal of undesired species from the accelerated ions and 5) delivery of the high-velocity, metal ions onto a surface of interest. A preferred system, suitable for commercialization of the technology, would accomplish these steps at low cost, could be operated on many different metals, would offer an operator good control of ion energy and current density over the ranges of interest and would be capable of treating large surfaces.

Metal-ion implanters are considerably less developed than gaseous-ion implanters [4] and it is argued that this is so primarily because it is difficult to supply metal atoms at the desired rate efficiently (item 1 above). Techniques that have been used to supply metals include 1) metal vaporization from an externally heated oven [5], 2) injection of a gaseous-metal compound (e.g. a chloride) [6,7] and 3) metal-sputtering from a discharge-chamber surface [4,8]. Each of these techniques has disadvantages. With oven vaporization, for example, only metals with modest vaporization

temperatures can be used [5]. With gaseous metal compounds, corrosion [5] and the high costs and small ion-beam diameters imposed by typical mass-separation schemes required to assure adequate beam purity [6] are drawbacks. With metal derived from sputtering, the lack of independent control of the metal supply rate, excessive metal condensation and the attendant need for frequent maintenance [4], and the ejection of metal droplets or clusters are of concern.

The objective of this work has been to evaluate the practicality of a simple, high-current-density, broad-beam implantation system based on the concept of arc-discharge heating to vaporize the metal from within the same discharge chamber where the atoms are ionized. System features associated with ionization, ion-beam extraction and focusing and delivery to a target surface are similar to those associated with our broad-beam, high-current-density, gaseous-ion implanter [9] and are derived from the discharge-chamber/ion-extraction technology of space-based ion thrusters [10].

Apparatus and Procedures

The essential components of the 3.7-cm-inside-diameter discharge chamber within which metal is vaporized and ionized and from which ions are extracted are shown schematically in Fig. 1. In order to operate it, current is first supplied through the solenoid to induce an essentially axial, mildly divergent magnetic field. This magnetic field differs substantially from the ring-cusp configuration [10] typically used in ion thrusters because the high operating temperature of the source precludes the use of traditional ferromagnetic materials and samarium-cobalt magnets. Further, the high

Fig. 1 Metal-Ion Source Schematic Diagram

discharge-chamber-power efficiencies realized with such magnetic fields are actually undesirable in this application where electric power is readily available and power loss to the anode is needed to heat it to a temperature where metal condensation will be impeded.

In order to initiate an electrical discharge in the source, argon gas is fed into the chamber to induce an ambient vacuum-chamber pressure in the high 10^{-5} Torr range and the graphite-chamber wall, which serves as the anode, is biased ~ 140 V positive of the cathode. The refractory-wire cathode is then heated to the point of thermionic-electron emission by increasing the current through it until the ion-source discharge ignites. The discharge is sustained for several minutes at an anode voltage and current near 140 V and 2 A, respectively, to allow the anode wall to heat up to about 1500 K. The crucible, which contains the metal to be implanted, is then biased sufficiently positive of the cathode so a substantial electron current will be drawn to it. After several minutes, the metal is typically heated to the point where it begins to vaporize. The argon flow is then turned off, the ambient vacuum-chamber pressure drops into the low 10^{-6} Torr range and the metal-vapor supply rate is maintained at the desired level by controlling the voltage applied to the crucible and/or the cathode filament (heating) current.

The metal-vapor atoms in the chamber are ionized via electron bombardment by high-energy (primary) electrons that are accelerated from the cathode through the cathode-to-anode potential difference and delivered into the bulk plasma. The current of primary electrons is controlled by adjusting the cathode-filament current. It is noted

that the solenoidal magnetic field that exists in this discharge chamber inhibits direct passage of the primary electrons to the anode, thereby increasing the distance they travel in the discharge chamber, the likelihood they will have ionizing collisions with the metal atoms and the discharge-chamber efficiency. Because the magnetic field diverges in the downstream direction, it also facilitates ion transport downstream toward the screen plate and primary-electron focusing upstream onto the center of the crucible. The power transported by these high-energy electrons sustains the crucible at the metal-vaporization temperature. Because this field is relatively weak, it also allows a significant fraction of the primary-electron current to reach the anode, thereby sustaining its temperature at a value where metal condensation can be maintained at an acceptably low level.

The supplies used to power the ion source are shown schematically along with the positive and negative high-voltage supplies used to bias the ion-source assembly and accelerator plate, respectively, in Fig. 2. Simplicity and reliability are the key features of the ion-source supplies. Crucible voltage and cathode-filament current are controlled manually to maintain proper discharge conditions as determined by visual observation of the discharge. During normal operation, the crucible, anode and cathode-filament voltages and currents are not sensed and, therefore, not indicated. The portion of this power system that is at positive high voltage is located on the opposite side of the feed-through flange on which the ion source is mounted. It is immediately adjacent to this flange and is immersed in transformer oil so the space it occupies can be safely minimized. Overheating of this oil as a consequence of heat transfer from the very hot

Fig. 2 Power-Supply System Schematic Diagram

ion source is prevented by making connections to the source that have relatively high thermal impedances and by circulating the oil.

Once stable operation on a metal plasma has been achieved, the graphite chamber and components in contact with it are biased to a high positive potential and the accelerator plate is simultaneously biased negative of ground using the high-voltage power supplies shown in Fig. 2. Under these conditions, surfaces take on the nominal potentials indicated near the elements shown in Fig. 1 and ions that drift toward the sheath-constraining mesh placed over the 2.9 cm-dia. screen aperture are extracted into a well-collimated, high-energy, metal-ion beam that can be directed onto a target surface. The current of the metal-ion beam, sensed by the ammeter shown in Fig. 2, is controlled under these conditions via the cathode-emission current by adjusting the cathode-filament current. It is noted that the rate of metal vaporization also increases with the cathode-emission and beam currents. This vaporization rate is controlled by adjusting the crucible voltage to maintain a constant intensity of the visible radiation from excited metal atoms exiting the source.

The focusing characteristics of the ion beamlets extracted from the source with high voltage applied are determined by the contour of the sheath-constraining mesh [9] shown in Fig. 1. This mesh concept, which has been used very successfully on our gaseous-ion implanter, is composed of orthogonal rows of 0.25 mm-dia. tungsten wires on ~ 2 mm spacings. The mesh has the contour of a spherical segment concave into the discharge chamber with a curvature radius of ~ 4 cm. It serves to control the divergence envelope of the beamlet and, therefore, its diameter at the axial location of

the target surface. In addition, it holds the ion trajectories relatively constant as the net accelerating voltage and beam-current density are varied over the demonstrated operational ranges (20-60 kV and $\sim 75\text{-}1000\ \mu\text{A}/\text{cm}^2$). The present ion source (Fig. 1) has only a single pair of ion-extraction apertures, but extrapolation to designs with many aperture pairs to produce beams that are as broad as needed for other implantation applications is considered straightforward.

The tubular coils (Fig. 1) conducting the current that produces the solenoidal magnetic field in the discharge chamber also carry water that removes heat radiated from the source. This and other heat-transfer considerations associated with the design are critical to proper source operation. For example, proper placement of tantalum-foil radiation insulation, insertion of junctions that induce high thermal-contact resistances between the anode and the graphite-plate structural elements, and fabrication of these elements so they will have high thermal impedances are important. The design assures the chamber walls are sufficiently hot to inhibit metal condensation while the alumina balls are kept sufficiently cool so they will have acceptably high electrical resistivities. Careful shielding of the balls is also required to prevent metal condensation on and subsequent electrical breakdown across their surfaces. Heat-transfer considerations also dictate a high thermal-contact impedance for and proper radiative shielding of the crucible to mitigate the crucible-heating-power requirement. The crucible, anode, and screen plate are all constructed of graphite so they can tolerate the high temperatures at which they operate.

The entire graphite/alumina-ball assembly that comprises the ion source is held

together by gravity in such a way that large dimensional changes associated with variations in ion-source temperature, that typically range from ambient to over 2000 K, can be accommodated. Because gravitational forces are the only ones that hold the source elements together, care had to be taken to assure the weight of the screen plate/sheath-constraining-mesh assembly exceeded the electrostatic attractive force this assembly felt from the accelerator plate. It was also necessary to isolate the source sufficiently well mechanically so vibrations would not shake it apart.

The complete implantation system with the metal-ion source at its core is shown schematically in Fig. 3. The cylindrical chamber shown in the figure represents the ground screen which encloses the actual source (Fig. 1) on all sides except the one through which the beam exits. This screen prevents electrons in the beam plasma downstream of the source from reaching high-positive-potential, ion-source surfaces. It is noteworthy that a conventional neutralizer is not required to supply electrons into the ion beam because high-energy beam ions that strike downstream metallic, vacuum-chamber surfaces induce substantial secondary-electron emission. The current of these electrons is sufficient to neutralize the beam and thereby prevent beam-divergence effects and beam-ion-induced charging of electrically insulating objects (e.g. targets) which may be placed in the beam.

Figure 3 illustrates features of the system used to support, position and control the temperature of a typical target during implantation. The graphite mask shown is located 50 cm from the accelerator plate, just upstream of the target. It functions to control transmission or interruption of the ion beam onto a prescribed region of the

Fig. 3 Metal-Ion-Implantation System Schematic Diagram

target surface. The particular fixture shown in the figure is one that holds a disc-shaped target, but other fixtures can be used to support other shapes such as rods. These fixtures, which can be rotated and translated during processing to facilitate complete coverage of the objects they support, are cooled using liquid nitrogen or chilled water. Target-temperature history during processing has been identified as important, so it is monitored using a thermocouple in good thermal contact with the object, near the surface being implanted. Temperature control based on this measurement is achieved by using various combinations of 1) films placed between the object and the mounting fixture, 2) intermittent beam interruption by the mask, 3) throttling of coolant to the mounting fixture and 4) adjustment of the beam-current density. The thermal-interface films, which are typically used to yield a gross temperature level, consist of a soft, flexible-graphite ("graf foil") layer ~ 0.4 mm thick and various numbers of thin (~ 60 μm) mica layers. The number of mica layers is increased to increase the thermal impedance of the film assembly and thereby induce a proportional increase in implantation temperature.

Operating Characteristics and Limitations

Initial system tests were conducted while operating on argon. Subsequently, the system was operated several times on copper and then much more extensively on titanium before it was used to implant samples with a relatively wide range of metals. Ion beams at currents ranging to about 25 mA at net accelerating voltages ranging to 50 kV (the nominal, positive-high-voltage-power-supply limit) were generally extracted

with each metal tested. A current-density profile measured across a typical ion beam at the location of the target surface is shown in Fig. 4. The measurements were made using a Faraday probe designed to withstand the high temperatures experienced by objects placed in a high-power ion beam [9]. The data in Fig. 4 were actually measured when the source was being operated on argon, but current-density profiles did not appear to change significantly when the operating fluid was changed from argon to the various metals that were used. This profile shows a beam-current density that is relatively uniform near $600 \mu\text{A}/\text{cm}^2$ over a region that is about 4 cm in diameter. The shape of a current-density profile like the one in Fig. 4 is determined primarily by the contour of the sheath-constraining mesh on the screen plate (Fig. 1). The flatness and diameter of the active region of the beam where the current density is relatively constant can, therefore, be adjusted by changing this contour. For the specific profile shown in Fig. 4, the spherical-segment mesh contour radius was 3.8 cm and the boundary diameter at the screen plate was equal to the plate aperture diameter (2.9 cm). The relationship between beam current and the mean beam-current density measured over a typical, active implantation zone (5 cm dia.) at the axial location of the target is shown in Fig. 5. The results in this figure suggest similar relationships between the beam current, which is measured, and the current density at the target, which is the implantation parameter of interest, for two different ions (Ar and Ti). The linear dependence between beam current and beam-current density, which would not be observed in most implantation systems, is achieved here because the sheath-constraining mesh inhibits normal de-focusing effects that accompany changes in beam current

Fig. 4 Typical Ion-Current-Density Profile at Target Location

Fig. 5 Typical Correlation between Beam Current and Ion-Beam Current Density at the Target Location

induced by changes in discharge-chamber-plasma density. The charge state of ions extracted from the source has not yet been measured, but significant fractions of multiply charged ions are expected.

The metals on which the source as presently configured can be operated is determined by whether or not sufficient crucible power can be supplied to raise them to their vaporization temperatures. Vaporization-temperature data over the pressure range from atmospheric to a relatively hard vacuum for metals on which the source has been operated to date are given in Fig. 6 along with similar data for graphite. The graphite data are important because a metal-vaporization temperature that exceeds the graphite sublimation temperature at the chamber operating pressure might be expected to result in substantial carbon vaporization, ionization and subsequent acceleration into a target surface along with the metal ions. Most of the metal-vaporization data in Fig. 6 were obtained from published information over the indicated pressure range [11]. In the case of B and Zr, however, the complete curves were estimated on the basis of published atmospheric vaporization temperatures and the behavior observed with the other metals. Although the accuracy of the graphite data in Fig. 6 is somewhat uncertain [12] they suggest there are many metals of interest for implantation applications that should vaporize well below the graphite-sublimation temperature particularly in the range of pressures where the discharge chamber is believed to operate. This operating pressure within the source (order 10^{-3} Torr) has been estimated here on the basis of measured ambient vacuum-chamber pressures (10^{-6} Torr range) and free-molecular-flow analysis of neutral atoms at typical beam current and expected

Fig. 6 Metal and Carbon Phase-Diagram Data Comparison

atomic ionization efficiencies. The data of Fig. 6 suggest graphite-vaporization temperature is ~ 2500 K at this internal pressure.

The metals on which the implanter was operated and the beam-current range over which it has been operated on each of these metals to implant specimens supplied by various researchers are summarized in Table 1. Actual implantation was

Table 1 Beam-Current Ranges used for Processing

Ion	Beam Current (mA)	Current Density ($\mu\text{A}/\text{cm}^2$) (at Target)
Ag	7.5	250
B	5 - 17.5	100 - 650
Cr	10	300
Cu	7 - 15	200 - 500
Mg	8	250
Si	13 - 15	425 - 500
Ti	4 - 20	75 - 800
V	12 - 27	350 - 1000
Zr	10 - 15	300 - 500

accomplished in each case at an energy of 50 keV although operation was sustained at energies ranging from 20 to 50 keV on each of the materials during the several-minute-system-stabilization period that preceded each implantation. Thus, it is argued that operation at ion energies in the 20 to 50 keV range has been demonstrated on each material. The system has been designed so it should be possible to operate at energies ranging to ~ 80 keV, but operation at this ion energy was not demonstrated because of

the 50-keV limit on the available high-voltage power supply. Theory reveals that the ion trajectories are independent of ion mass and this is consistent with the results obtained with Ar and Ti which are shown in Fig. 5. Since, the system was operated using the same sheath-constraining mesh in all cases, the current densities, which were determined from Fig. 5, should have been relatively uniform over a diameter of ~ 4 cm. The currents and current densities in this table represent the values that were actually used to implant samples and they are not indicative of limitations. In fact, it is expected that all of the metals can be operated over the beam current range from ~ 5 to > 20 mA.

Although meters were not used to indicate crucible and anode voltages and currents during normal operation, meters were installed temporarily so the current and voltages required to sustain metal-ion-source operation could be determined. Typical results obtained from these experiments and shown in Fig. 7 suggest the relationship between required crucible voltages and vaporization temperature may be linear at a given magnet operation condition. The crucible voltages given are those required to sustain vaporization of various metals that have been ion-implanted at ion-beam currents in the range 8 - 10 mA and the vaporization temperatures of those metals are values at the approximate discharge-chamber pressure ($\sim 10^{-3}$ Torr). In the cases where error bars are shown, stable operation was achieved over the crucible-voltage ranges suggested by the bar lengths. When they are not present, operation was always accomplished at the same voltage. When the source was operated on B and Zr, it was necessary to increase the solenoid current and, as a consequence, the magnetic flux

a. Crucible-Voltage/Vaporization-Temperature Correlations

b. Magnetic-Flux-Density Profiles

Fig. 7 Typical Metal-Ion-Source Operating Data

density to their maximum values in order to achieve stable, steady-state operation. It is expected that operation on the other elements indicated in Fig. 7a could have been achieved at lower crucible voltages than those indicated if the maximum-magnet condition had been sustained although this was not demonstrated. The magnetic-flux-density profiles associated with the two magnet conditions at which the metal-ion source was generally operated are given in Fig. 7b. Typically, crucible currents increased from ~ 0.5 A when the source was operating on Mg to ~ 5 A when it was being operated on B or Zr and as a result, the crucible power increased from ~ 10 W for Mg to ~ 1 kW for B or Zr when the beam current was being held in the 8 - 10 mA range. Once the crucible power had been increased, the anode voltage would typically be reduced to 50 V, the power to the anode would drop below 50 W and essentially all of the discharge-chamber power would be supplied via the crucible power supply. It is noteworthy that increases in beam current are effected by increasing the ion-source-plasma density and this density increase causes a corresponding increase in the electron current drawn to the crucible. In order to prevent an increase in the metal-vaporization rate that would be brought on by the resulting increase in crucible power, crucible voltage was typically reduced as beam current was increased.

It was observed that the various metals on which the source was operated induced different vaporization behaviors in crucibles that were nominally a 2 cm-dia. by ~ 0.5 cm-deep cavity in a graphite block (Fig. 1). Specifically, the metals Mg and Cr both appeared to sublime as a result of electron-current flow and heating of pieces of these metals placed at any location within a crucible. On the other hand, Ag and Cu

both melted but did not wet the graphite and their post-operation appearance suggested that discharge electrons flowed directly to molten masses of these metals and probably caused them to vaporize where the electrons struck them. Metallic Ti, Si and V also melted in their crucibles, but they did wet the graphite surface. In the cases of these materials, better control of the vaporization process was realized when the crucible was constructed with a small (~ 4 mm high) dimple projecting upward at its center. It appeared then that electrons would be drawn to and heat this dimple thereby causing the metal to melt and be drawn to the top of the dimple where it would vaporize. Zirconium also melted and flowed to a central dimple where it appeared to be vaporized, but it was troublesome because it wetted the graphite so well that it also flowed up the crucible side walls and onto other discharge-chamber surfaces. The most difficult element to vaporize at a rate that would sustain discharge-chamber operation was B. It was supplied most successfully from a small (~ 1 cm-dia. by ~ 1 cm-deep) cavity in the block of graphite used to make the crucible. Because the B powder used as a feed-stock is a relatively poor electrical conductor it was compressed into pellets ~ 0.3 cm thick that were stacked in the cavity. When crucible power was supplied, it appeared that the top pellets melted and formed a puddle from which vaporization occurred. It is believed that the higher magnetic fields required to achieve operation on B and Zr (max. magnet in Fig. 7b) facilitated tighter electron focusing onto the center of the crucibles used for these two elements and that this focusing was key to proper operation with them.

Metal-implanter operation was also attempted on W, but operation could not be

sustained when the argon used to achieve start-up was turned off. It is expected that operation on W might be achieved if the power-output capability of the crucible power supply were increased. With the present system it appears that operation is practical on metals with atmospheric-pressure-vaporization temperatures to at least that of Zr (4682 K). At this and higher temperatures, however, some implanted-metal-species contamination by C might be expected.

Conclusions

Tests have shown that the basic concept of in-situ, plasma-discharge heating of a metal in a crucible to the point where it is vaporized and can then be ionized is viable. A metal-ion source utilizing the concept is simple, reliable, and easy to control and to maintain. Well-focused, metal-ion beams can be extracted from the source over a wide current-density range through a constrained-sheath-optics system. The implanter has been operated on Mg, Ag, Cu, Cr, Si, Ti, V, B and Zr at current densities in the range 75 to 1000 mA/cm² and accelerating voltages in the range 20 to 50 keV. Using the system, over 100 samples were implanted during the contract period with these elements to doses that ranged from 1×10^{17} to 1×10^{18} ions/cm². An implantation system employing the features of this one can be controlled readily and operated on many implant metals of tribological importance. The high-current-density and broad-beam features of the machine assure very rapid and therefore low-cost, metal-ion-implantation processing.

A ONE-DIMENSIONAL MODEL FOR TEMPERATURE AND THERMAL-STRESS HISTORIES IN MATERIALS DURING HIGH-CURRENT-DENSITY ION IMPLANTATION

During ion-implantation processing, temperature gradients develop in target materials that can induce substantial thermal stresses. As the energy flux being delivered to a target is increased, by increasing the implantation current density for example, these stresses typically become more severe. The purpose of the model described here is to compute the temperature and thermal-stress histories for relatively thin, flat samples in which simple, one-dimensional models for heat transfer and thermal-distortion-induced stresses can be applied. It is believed that analysis based on these models will yield reasonable estimates of the temperatures and stresses that develop during broad-beam, high-current-density implantation of flat, ceramic discs suitable for tribological testing.

Thermal Analysis

The essential features of the unsteady, 1-D heat-transfer problem associated with the ion-implantation process are illustrated in Fig. 8. Power from an ion beam is deposited on one surface of a sample having a cross-sectional area A and a thickness ℓ and heat is removed to a heat sink at temperature T_0 via the opposite surface. Here, it is assumed that radiation from the surface of the sample being implanted is negligible and that all heat conduction occurs and temperature differences develop in the axial (x) direction only. The thermal-power input per unit of exposed sample area ($\dot{q}$ in W/m^2) at $x = 0$ (node 1) is the product of the incident ion-beam current density (j in A/m^2)

Fig. 8 Physical Arrangement for Implantation Models

and energy (ϵ in eV).

The temperature T_i^p at any node i at time $t = (p+1)\Delta t$ can be determined using the node temperature from the previous time interval ($t = p\Delta t$) by applying the thermal-diffusion equation expressed in finite-difference form [13]. For node 1 where the beam power ($\dot{q}$) is deposited, the appropriate equation is

$$T_1^{p+1} = T_1^p (1-2F_o) + \frac{2\dot{q}}{k} \Delta x F_o + 2F_o T_2^p \quad (1)$$

The Fourier number (F_o) that appears in this equation reflects the thermal properties of the sample (k is the thermal conductivity; ρ , its density and c_p , its specific heat) as well as the time- and position-step sizes that have been selected (Δt and Δx , respectively). Specifically, it is given by $F_o = [k/\rho c_p][\Delta t/(\Delta x)^2]$. The distance step (Δx) should be selected to be large compared to the implantation depth so the assumption of surface heating remains valid but this is generally not restrictive because the implantation depth is typically small (order $0.1 \mu\text{m}$). The time-step size (Δt) must be selected to hold the Fourier number in the range where computational stability is assured [13].

At all intermediate nodes ($1 < i < N$), the appropriate, finite-difference equation is

$$T_i^{p+1} = F_o (T_{i+1}^p + T_{i-1}^p) + (1-2F_o) T_i^p \quad (2)$$

At the final node ($i = n$), the effect of heat removal through the contact conductance (h_c) to the heat sink must be reflected and the appropriate equation becomes

$$T_n^{p+1} = F_o [2 T_{n-1}^p + (\frac{1}{F_o} - 2) T_n^p + \frac{2 h_c \Delta x}{k} (T_o - T_n^p)] \quad (3)$$

The temperature history of the sample is determined by first specifying a) initial temperatures for each node, b) the energy, current density and processing time associated with the implantation process, c) the thermal properties of the sample material and d) the sample thickness. Equations 1, 2 and 3 are then solved repeatedly to determine the temperatures at each node and for each successive time increment until the time interval of interest (typically an implantation plus cool-down time) has transpired. The final result is a temperature distribution that is a function of both location, x , and time, t .

Thermal-Stress Analysis

The thermal stresses that develop in a thin-plate sample that is subject to heating and cooling can be determined from a spatial temperature profile like those determined at a prescribed time using the analysis of the preceding section. The magnitudes of these stresses are influenced greatly by the constraints imposed at the boundaries of the plate. If the plate is perfectly restrained against expansion, contraction and bending and if temperature gradients develop only the x direction (Fig. 8), the dominant thermal stresses are orthogonal to x and are given by the following expressions [14-17]:

$$\sigma_y(x,t) = \sigma_z(x,t) = - \frac{\alpha E (T(x,t) - T_0)}{1 - \nu} \quad (4)$$

In these equations, E is the modulus of elasticity of the material, α is the coefficient of

thermal expansion and ν is Poisson's ratio.

If a thin plate being subjected to thermal gradients is completely unrestrained (free to expand or contract at its boundaries and to bend) the thermal stresses are instead given by [14,15]

$$\sigma_y = \sigma_z = - \frac{\alpha E (T - T_n)}{1 - \nu} + \frac{1}{\ell (1 - \nu)} \int_0^{\ell} \alpha (T - T_n) E \, dx + \frac{6 (2x - \ell)}{\ell^3 (1 - \nu)} \int_0^{\ell} \alpha E (T - T_n) \left(x - \frac{\ell}{2}\right) dx \quad (5)$$

where ℓ is the thickness of the plate. When the plate is allowed to expand or contract, but is restrained against bending, the analysis becomes much more complex. A reasonable estimate of the thermal stresses can be obtained, however, from the following expression

$$\sigma_y = \sigma_z = - \frac{\alpha E (T - T_n)}{1 - \nu} + \frac{1}{\ell (1 - \nu)} \int_0^{\ell} \alpha (T - T_n) E \, dx \quad (6)$$

Depending on the boundary restraint(s) being applied by the fixturing that holds the samples, Eq. 4, 5 or 6 is applied in the overall analysis at the conclusion of each time interval in the thermal analysis to determine the stress distribution in the sample at that instant in time.

Software Validation

In order to verify the accuracy of the thermal-stress-analysis portion of the numerical simulation presented in the preceding pages, the program was exercised for

two cases where analytical solutions are known. In the first case, a linear temperature profile given by the following equation was imposed in the sample

$$T = T_0 + (T_1 - T_0) \frac{x}{\ell} \quad (7)$$

In this expression, T_0 and T_1 are the temperatures at $x=0$ and $x=\ell$, respectively.

When this linear temperature profile was imposed under the free-state condition (Eq. 5), negligible thermal stresses were computed throughout the sample. This result is consistent with the analytical solutions [14].

Next, the time-varying, parabolic temperature profile shown in Fig. 9a was computed from the equation

$$T = T_0 + \frac{4}{\pi} (T_1 - T_0) e^{-\lambda t} \cos \frac{\pi (x - \ell/2)}{\ell} \quad (8)$$

where λ (s^{-1}) is a thermal-decay constant, T_1 is an initial uniform temperature and T_0 is the constant temperature at which the boundaries are maintained at $x=0$ and ℓ after time zero. This equation is only approximately correct, but it is quite accurate after a time that is brief compared to the reciprocal of λ which may take on any value for purposes of this validation. The thermal-stress distribution under the free-expansion boundary condition is [13]

$$\sigma_y = \sigma_z = \frac{4 \alpha E (T_1 - T_0)}{\pi (1 - \nu)} e^{-\lambda t} \left[\frac{2}{\pi} - \cos \frac{\pi (x - \ell/2)}{\ell} \right] \quad (9)$$

Under the perfect-restraint boundary condition, the analytical expression for the thermal

a. Temperature

b. Thermal Stress (Perfect Restraint)

c. Thermal Stress (Free State)

Fig. 9 Parabolic Temperature Profiles and Corresponding Stress Profiles

stress is obtained by substituting Eq. 8 directly into Eq. 4. Numerical results showing typical spatial and temporal variations in the thermal stresses orthogonal to the x-direction for these two cases are shown in Figs. 9b and 9c. The input data used to obtain these particular results are listed in Table 2. Every stress calculated analytically agreed with the corresponding numerically computed one to within a few tenths of a percent so the results of Figs. 9b and 9c are considered correct and representative of the true physical situations. The results of Fig. 9b show the entire sample goes into a negative (compressive) stress state when it is perfectly restrained and that the peak stresses develop in the plane midway between its boundaries. When the sample is completely free, the edges of the sample are in tension (positive-stress state) and the central plane is still in compression. In both cases considered, the stresses decay to zero as the sample becomes isothermal. All of these results are physically reasonable [14].

Table 2 Input Conditions for Fig. 9 Test Case

Modulus of Elasticity (E)	= 4.06×10^5 MPa
Poisson's Ratio (ν)	= 0.142
Coefficient of Thermal Expansion (α)	= $4.3 \mu\text{m/m}/^\circ\text{K}$
Decay Constant (λ)	= 0.1 s^{-1}
Initial Temperature (T_1)	= 673°K
Boundary Temperature (T_0)	= 273°K

Computed Thermal Stresses for a Ceramic Being Ion-Implanted

Typical results showing the temperatures and stresses that would be expected to develop in a ceramic during implantation under the three ideal conditions of restraint being considered here are shown in Figs. 10 and 11. The time- and position-dependent

Ion Energy
 Current Density
 Dose
 60 keV
 500 $\mu\text{A}/\text{cm}^2$
 1x10¹⁸ ions/cm²

a. Temperature

b. Thermal Stress (Perfect Restraint)

c. Thermal Stress (Bending Restraint)

d. Thermal Stress (Free State)

Fig. 10 Silicon Carbide Temperature and Stress Histories (Moderate Implantation Conditions)

a. Temperature

Ion Energy 100 keV
 Current Density $1500 \mu\text{A}/\text{cm}^2$
 Dose $2 \times 10^{18} \text{ ions}/\text{cm}^2$

b. Thermal Stress (Perfect Restraint)

c. Thermal Stress (Bending Restraint)

d. Thermal Stress (Free State)

Fig. 11 Silicon Carbide Temperature and Stress Histories (Severe Implantation Conditions)

temperatures were calculated by solving the thermal model (Eqs. 1-3) numerically and these results were then used to solve the thermal-stress model (Eqs. 4-6) numerically. These calculations are based on the mechanical and thermal properties of silicon carbide [18] and the contact conductance given in Table 3. The value of the contact conductance is rather uncertain. It is influenced by such quantities as the finishes of the contacting surfaces (heat sink and sample back-surface), the thermal and mechanical properties of any intermediate material between these surfaces and the pressure at the interface induced by forcing the surfaces together. The value given in Table 3 was selected as reasonable on the basis of temperature measurements made of metal samples during and immediately after ion implantation.

**Table 3 Input Conditions for SiC-Implantation-Example Cases
(Figs. 10 and 11)**

Thermal Diffusivity ($k/\rho C_p$)	= $4.13 \times 10^{-5} \text{ m}^2/\text{s}$
Thermal Conductivity (k)	= $88 \text{ W/m/}^\circ\text{K}$
Modulus of Elasticity (E)	= $4.06 \times 10^5 \text{ MPa}$
Poisson's Ratio (ν)	= 0.142
Coefficient of Thermal Expansion (α)	= $4.3 \mu\text{m/m/}^\circ\text{K}$
Contact Conductance (h_c)	= $500 \text{ W/m}^2/\text{K}$
Heat Sink and Initial Temperature (T_0)	= $273 \text{ }^\circ\text{K}$
Sample Thickness (ℓ)	= 0.01 m
Depth Increment (Δx)	= $5 \times 10^{-4} \text{ m}$
Time Increment (Δt)	= $2.97 \times 10^{-3} \text{ s}$
Fourier Number (F_0)	= 0.49

In Fig. 10, the computed temperatures and stresses pertain to a 1 cm-thick SiC sample being implanted under relatively moderate conditions (namely with ions having an energy of 60 keV at a dose rate of $500 \mu\text{A/cm}^2$ to a final dose of $10^{18} \text{ ions/cm}^2$). Figure 10a shows the temperature at each point in the sample increases with time until

until it reaches 926 °K (653 °C) at 320 s (the time when the desired dose has been delivered and implantation is stopped). These data also show that the samples are relatively isothermal over their full depths and this is expected because SiC is a good thermal conductor (k is $\sim$ half the value for Cu). Small temperature gradients do develop, however, with the surface on which the beam impinges ($x=0$) being the hottest and it is these gradients that give rise to the stresses shown in Figs. 10c and 10d. As in the case of Fig. 9, perfect restraint results in compressive stresses that become increasingly greater with implantation time until they reach a maximum value of 1.29 GPa on the surface exposed to the beam at 320 s. The thermal stresses that develop during implantation of a sample that is free to deform are shown in Fig. 10d. It should be noted first that the stress levels are relatively small (3 MPa) compared to those for the perfectly restrained sample (Fig. 10b). Further, the region near the surface being implanted (i.e. at zero depth in Fig. 10d) goes into compression because it is at the highest temperature and has expanded the most. In order to hold this unrestrained sample in equilibrium under this condition, the region near the opposite face ($x=\ell$) must also go into compression and the intermediate region must go into tension. Figure 10d shows that this is indeed what happens. As the implantation proceeds and the temperature variation through the sample becomes nearly linear, the stresses decay to zero. When the implantation is stopped, the temperature profile again becomes nonlinear and stress reversals develop briefly.

Under actual implantation conditions, samples are frequently held flat against a rigid surface by clamping at their center and periphery, but they are relatively free to

expand along the surface. Under this condition, where bending is probably constrained, the thermal stresses of Fig. 10c are computed. In this case, the figure shows the surface exposed to the beam ($x=0$) goes into compression because the temperature is greatest there. The opposite surface goes into tension and the moment induced by this condition is opposed by the external moment applied through the clamping process. The stresses generated under these conditions are seen to have magnitudes that are intermediate between those for the perfectly restrained and free-state cases.

When the same sample is implanted under more severe conditions (higher dose rate, dose and or energy) computed temperatures and stresses increase. For the case where the implantation energy is 100 keV, the dose rate is $1500 \mu\text{A}/\text{cm}^2$ and the final dose is 2×10^{18} ions/ cm^2 the results of Fig. 11 are obtained. This figure shows that higher temperatures and stresses develop, but qualitative trends are the same as those seen in Fig. 10.

Comparison of Observed Failure with Model Prediction

When an 1-cm-thick, MgO-partially-stabilized-zirconia (PSZ) disc was ion implanted with 50 keV silver ions at a relatively high current density ($250 \mu\text{A}/\text{cm}^2$), it fractured after 220 sec in the beam. Using the input data obtained from [19] and given in Table 4, the model exercised to compute the time history of thermally induced stresses in this disc.

The implantation on this particular disc was attempted with the disc mounted in

such a way that it was relatively free to expand and bend so the "free-state" thermal

Table 4 Input Conditions for PSZ-Implantation Case

Thermal Diffusivity ($k/\rho C_p$)	= $7.2 \times 10^{-7} \text{ m}^2/\text{s}$
Thermal Conductivity (k)	= $3.08 \text{ W/m/}^\circ\text{K}$
Modulus of Elasticity (E)	= $2.05 \times 10^5 \text{ MPa}$
Poisson's Ratio (ν)	= 0.31
Coefficient of Thermal Expansion (α)	= $10.3 \text{ } \mu\text{m/m/}^\circ\text{K}$
Contact Conductance (h_c)	= $500 \text{ W/m}^2/\text{K}$
Heat Sink and Initial Temperature (T_0)	= $293 \text{ }^\circ\text{K}$
Sample Thickness (ℓ)	= 0.01 m
Depth Increment (Δx)	= $5 \times 10^{-4} \text{ m}$
Time Increment (Δt)	= 0.173 s
Fourier Number (F_0)	= 0.498

stress model (Eq. 5) is considered to be the most appropriate of the three presented.

The analysis indicated maximum tensile and compressive stresses near 250 MPa should have developed on the back and front faces of the sample, respectively, at the time it failed. These tensile and compressive stresses are substantially greater and less, respectively, than the tensile and compressive strengths of the material ($\sim 50 \text{ MPa}$ and 1.9 GPa). The PSZ sample appeared to have undergone brittle fracture so the tensile stress and strength are most representative of the physical situation. The fact that the strength is 1/5 of the computed stress, suggests considerable uncertainties must exist in the numerical model, the properties of PSZ or both. The most likely sources of error are considered to be related to 1) temperature-induced variations in elastic modulus and strength that are not reflected in the model and 2) the rather great uncertainty in the contact conductance. Finally, it is noted that the stresses that are predicted in PSZ are much greater than those predicted in SiC because PSZ has a significantly greater

coefficient of thermal expansion and a much lower thermal conductivity.

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MICROSTRUCTURAL AND TRIBOLOGICAL STUDIES ON METAL-ION-IMPLANTED MATERIALS

After the metal-ion implanter was constructed, tested, modified and calibrated, over 100 samples of various sizes, shapes (rods, wires, flats and discs) and materials (metals and ceramics) were implanted with metal ions. Most of the samples were processed for researchers at other laboratories, but some were processed so they could be subjected to tribological testing and spectroscopic (Mössbauer and x-ray diffraction) investigations. The spectroscopic work was conducted under the direction of Prof. Don Williamson at Colorado School of Mines and his contribution to this work is gratefully acknowledged. This work is continuing, but a progress report describing its current status can be given.

Titanium-Ion-Implantation Study

Implanted titanium has been shown to be particularly effective as a means of improving the tribological performance of steels when carbon can be entrained with the Ti ions to form TiC [3] but widespread application appears to have been limited by the high cost of the processing. Using the metal-ion implanter developed under this contract it was possible to implant samples rapidly and therefore at a relatively low cost. Because the processing was accomplished rapidly (a few minutes), however, it was anticipated there would be insufficient time available for the C needed to form TiC to be gettered from the vacuum system during processing. The study therefore involved the implantation of iron (Fe) and AISI 304 stainless steel (S) samples with

titanium under various conditions of vacuum-chamber backfill using a carbonaceous compound (methane). Iron and 304 stainless steel were selected for this preliminary study because they are relatively simple materials that have the two crystal structures found in steels.

The specific implantation conditions used in the study are identified in Table 3. Discs FeTi-1 and 2 have been wear-tested for 10 hours in our oscillating pin-on-disc wear tester [20] against hemispherical α -Fe pins with a 0.32 cm-radius. In the boundary-lubricated environment (10% oleic acid in kerosene) where the tests were conducted the discs exhibit the behavior shown in Fig. 12. Although the wear rates for these samples are lower than the wear rate for unimplanted iron, which is also given in Fig. 12, they are generally not as good as those observed for nitrogen-implanted pure iron. The X-ray-diffraction (XRD) and conversion-electron Mössbauer spectra (CEMS) associated with the iron samples identified in Table 3 are shown in Figs. 13 and 14,

**Table 3. Implantation Parameters for Titanium-Implanted Samples
(50 keV Implantation Energy)**

Sample Designation	Dose (Ti/cm ²)	Dose Rate (μA/cm ²)	Methane Pressure (Torr)	Temperature (K)
FeTi-1	3 x 10 ¹⁷	200	0	--
FeTi-2	4 x 10 ¹⁷	175	0	500
STi-1	5 x 10 ¹⁷	175	0	550
STi-2	2 x 10 ¹⁷	175	0	400
STi-3	2 x 10 ¹⁷	175	1 x 10 ⁻⁵	430
STi-4	2 x 10 ¹⁷	175	3 x 10 ⁻⁵	410

Fig. 12 Preliminary Wear-Test Data for Ti-implanted Iron

Fig. 13 X-ray-Diffraction Data for Ti-implanted Iron and 304 Stainless Steel

Fig. 14 Conversion-Electron-Mössbauer Spectra for Ti-implanted Iron and 304 Stainless Steel

respectively. The XRD data reveal the ferrite peaks [f(110) and f(200)] and Ti-implantation-induced peaks [I] that are identified in Fig. 13. A search of possible phases that could produce the "I" peaks indicates the best match occurs for TiC (Ti metal, Fe_2Ti , FeTi, FeTiO_3 , TiO and TiO_2 have been ruled out). There is also a good match for FeO but it can be ruled out on the basis of the CEMS data of Fig. 14. The CEMS data for FeTi in Fig. 14 clearly show the new components due to the Ti which are labeled as Fe(Ti) and Fe-Ti-C in the stick diagrams shown beneath the upper plot. These spectra can be interpreted as bcc Fe with Ti in solid solution and an amorphous non-magnetic phase, respectively. The data of Fig. 14 for Sample FeTi-2, on the other hand, show only the spectrum for the ferrite. This indicates that the implanted Ti is completely bound up as TiC and, as a result, it does not affect the iron atoms (elements not bound to Fe atoms are not detected using the Mössbauer effect). The conclusion that all of the Ti in FeTi-2 is bound up as TiC is supported by the fact that the signal intensity for the TiC peak (I) in the XRD data is greater for FeTi-2. Taken together these results demonstrate substantial carbon uptake by these samples even though they were being implanted very rapidly and without methane backfill. The graphite discharge-chamber is a possible source of this carbon.

Only one of the Ti-implanted stainless steel samples was wear-tested (STi-1) and because it readily underwent the transition from mild to severe adhesive (galling) wear, the test was adjusted so the critical load at which this transition occurred could be measured. The test showed that the Ti-implanted sample exhibited the same critical load as that measured for unimplanted 304 stainless steel (~ 0.1 N). Hence, it is

concluded that implanted Ti does not improve the resistance of this material to galling (implanted nitrogen in contrast induces a 1000-fold increase in the critical load [21]). The XRD and CEMS data for STi-1, which are also given in Figs. 13 and 14, show a dominant austenite phase {a(111) and a(200) in Fig. 13 and A in Fig. 14}. A strain-induced martensite phase introduced by polishing the sample {m(110) in Fig. 13 and M in Fig. 14} and strong XRD implantation-induced peaks (I) due to TiC are also present in the XRD data (Fig. 13). The appearance of the unknown and weak component "X" that is present in the CEMS data for STi-1 but not for the other samples (Fig. 14) is consistent with the fact that the implantation-induced peaks are strong for this sample.

Figure 15, which contains XRD data for samples STi-2,3 and 4, is striking because it shows implantation-induced (TiC) peaks for STi-2 and 3 but not for STi-4 which is the one processed in the highest methane partial pressure (3×10^{-5} Torr). Sample STi-4 also shows less martensite [m(110)] than STi-2 and 3. Hopefully, CEMS and eventually Auger-electron spectroscopic data will enable us to understand the reasons for these differences.

Boron-Implantation Study

A few iron (α -Fe) discs have been implanted with boron for a preliminary study that has focused on the effects of implantation temperature on tribological performance. Additional α -Fe and 304 stainless steel (S) discs are now being implanted with boron to complete the test matrix developed for the study. Preliminary sliding-wear test results obtained with the discs that have been implanted using our oscillating-pin-on-disc wear

Fig. 15 X-ray-Diffraction Data for 304 Stainless Steel Implanted with Ti under Various Methane-Partial-Pressure Conditions

obtained with the discs that have been implanted using our oscillating-pin-on-disc wear tester [20] operating at 5 N normal load, 13 cm/s mean sliding velocity with a 0.32 cm-radius, α -Fe pin under boundary-lubricated (10% oleic acid in kerosene) conditions are shown in Fig. 16. These discs, which were implanted to similar doses at different temperatures, are seen to exhibit similar wear behavior. Both of the discs exhibit initial wear rates less than that of pure iron, but generally greater than those observed in typical nitrogen-implanted discs [22]. The increase in wear rate that appears to occur at $\sim 3.6 \times 10^4$ sec is consistent with the fact that the ballistic depth of the implanted B was about $0.1 \mu\text{m}$ and this corresponds closely to the ~ 1 mg mass loss that was realized after about 3.6×10^4 sec of wear testing. Figures 17 and 18, which contain conversion-electron Mössbauer spectra (CEMS) for the two discs before and after wear-testing, all show the samples contain α -Fe and amorphous Fe/B signatures (designated by "a"), with the stronger amorphous signal from the disc implanted at the lower temperature. X-ray-diffraction spectra for the two as-implanted discs in Fig. 19 confirm the amorphous nature of the Fe/B layer in that they show evidence only of α -Fe peaks and none for any crystalline iron/boron compounds. The nature of the amorphous layer can be characterized by the probability distribution of the hyperfine field associated with the CEMS data. This distribution is given by the bottom plot in Fig. 19 for the disc implanted at the lower temperature. It shows a broad distribution that is typical of amorphous materials rather than the sharp peaks that characterize crystalline ones.

Fig. 16 Preliminary Sliding-Wear-Test Data for B-Implanted Discs

Fig. 17 Conversion-Electron Mössbauer Spectra for $\alpha\text{-Fe}$ Implanted with B at $\sim 300^\circ \text{C}$

Fig. 18 Conversion-Electron-Mössbauer Spectra for α -Fe Implanted with B at $\sim 450^\circ\text{C}$

Fig. 19 X-ray Diffraction Spectra and a Typical Probability Distribution of the Mössbauer Hyperfine Field for B-Implanted α -Fe Discs

TRIBOLOGICAL STUDIES ON DIAMONDLIKE-HYDROCARBON FILMS

During development of the metal-ion implantation system, an ion source that employed similar design features but utilized permanent magnets, a steel discharge chamber and closely spaced, multiaperture, ion-extraction grids was used to direct low-energy (< 1 keV) carbonaceous ions derived from a methane discharge onto a wide range of metallic and ceramic test samples. The process yielded hard, wear-resistant coatings that were tested extensively both locally and at various commercial and government laboratories (including Argonne National Laboratory [ANL]). Over 200 test samples (flats, rods and discs) and engineering components (e.g. pistons, bearings and shafts) were coated during the course of this work. Some of the resulting work is complete and has been described in published papers [23-28] and some is still being conducted. Papers describing some of the tribological tests conducted on these films at Colorado State and ANL are included in the Appendix to this report.

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APPENDIX

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