Plasma source ion-implantation technique for surface modification of materials

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Plasma source ion-implantation (PSII) is a new ion-implantation technique which has been optimized for surface modification of materials such as metals, plastics, and ceramics. PSII departs radically from conventional implantation technology by circumventing the line-of-sight restriction inherent in conventional ion implantation. In PSII, targets to be implanted are placed directly in a plasma source and then pulse biased to a high negative potential. A plasma sheath forms around the target and ions bombard the entire target simultaneously. Preliminary experiments have demonstrated that PSII: (1) efficiently implants ions to concentrations and depths required for surface modification, (2) produces material with improved microhardness and wear properties, and (3) dramatically improves the life of manufacturing tools in actual industrial applications. For example, the tool life of M-2 pierce punches used to produce holes in mild steel plate has been increased by a factor of 80.

INTRODUCTION

We are developing a new, innovative and cost-effective ion-implantation technique,[1-6] plasma source ion implantation (PSII) for the surface modification of materials such as metals, plastics, and ceramics. Conventional ion implantation, as currently practiced, has been shown to be quite effective in improving the wear, corrosion, fatigue, and friction properties of materials, and in modifying the electrical and optical properties of materials.[7-10] In the ion-implantation process, ions are accelerated to high energy and are injected into a solid. Because the process is not limited by the thermodynamic constraints of more conventional techniques, ion implantation makes it possible to produce new materials with new properties. Ion implantation, whether by conventional or PSII techniques, offers a number of advantages relative to other surface modification techniques: (1) Surface properties can be changed selectively without changing desirable bulk material properties. (2) There are no problems associated with bonding failure or surface layer delamination. (3) Since ion implantation is not a "coating" process, there are no associated dimensional changes in the workpiece; cutting edges retain their sharpness. (4) The implant species concentration profile can be easily changed by changing the implantation energy. (5) Because ion implantation is a nonequilibrium process, new alloys are not limited by classical thermodynamic properties and diffusion kinetics. (6) Ion implantation is a low-temperature process; there are no (or minimal) dimensional changes due to thermal distortion; there is no (or minimal) degradation of surface finish.

The extensive literature on the application of conventional ion implantation to improve the wear properties of materials serves as a valuable data base for the development of PSII. Since most of our preliminary PSII experiments have concentrated on the implantation of nitrogen ions, we review here the literature of conventional ion implantation of nitrogen. Hutchings and Oliver[11] have shown that nitrogen implantation increases substantially the microhardness of the titanium alloy (Ti 6%-Al 4%-V) used, for example, for replacement hip joints. They also found reductions in material loss rate of over two orders of magnitude in wear tests against a ruby ball. Dearnaley[12] found a reduction in wear rate of almost three orders of magnitude using a thin layer radioactivation technique with the same titanium alloy wearing against a high-density polyethylene disk. Williams et al.[13] found that nitrogen implantation of the same titanium alloy reduced electrochemical corrosion currents by more than two orders of magnitude in corrosive wear experiments designed to simulate the *in vivo* hip joint parameters. Cemented tungsten carbide cutting tools implanted with 40-keV N^+ have shown a threefold decrease in wear rate in experiments by Fayeulle et al.[14] Yost et al.[15] implanted type 304 stainless steel with 50-keV N^+ ions and reduced the maximum wear depth for light loads (850-MPa Hertzian stress) by more than an order of magnitude. Implantation of 440-C stainless steel with 40-keV N^+ ions has increased the rolling contact fatigue lifetime by over 40% in experiments by Kustas, Misra, and Sioshanshi.[16] A 100-fold extension of the service lifetime of 440-C bearings implanted with 90-keV unanalyzed N_2^+ and N^+ ions has been demonstrated by Hirano and Miyake.[17] Extensive field testing of ion-implanted cutting tools and dies has also been favorable. A fivefold increase in the lifetime of M-2 steel taps used in phenolic resin has been reported by Hartley.[18] Tool steel fuel injectors

have shown a 100-fold improvement in experiments by Hirvonen.[19] Hartley has reported a two- to fourfold increase in the service lifetime of diamond tools for plastic cutting.[20] Dutchman and Partyka have shown that plastic extrusion die lifetime can be improved by a factor of 4.[21]

In summary, ion implantation has demonstrated diverse applicability in the improvement of material wear characteristics. However, in spite of the extensive data base which has been accumulated to document the effectiveness of ion implantation in materials processing, industrial acceptance and application of ion implantation technology has been quite limited. The principal explanation for this limited acceptance is the relatively high cost of ion implantation as compared with other surface modification techniques.[22] The relatively high cost of ion implantation is due in large part to the fact that most ion-beam materials processing facilities employ ion implanters which were optimized for the implantation of semiconductor wafers, and hence have a number of features which are not well suited to materials applications. Even the small number of facilities which were designed specifically for metallurgical and other materials applications employ implanters which do not differ fundamentally from semiconductor implanters, which in turn, evolved from low-energy nuclear physics accelerators of the 1960s.[23]

Plasma source ion implantation (PSII), which, beginning with its genesis and continuing through its subsequent embryonic developmental stages has been optimized for materials applications, represents a radical departure from conventional implantation technology. The PSII technique circumvents the line-of-sight restriction inherent in conventional ion implantation. In PSII, targets to be implanted are placed directly in a plasma source and then pulse biased to a high negative potential. A plasma sheath forms around the target and ions bombard the entire target. We believe that PSII could have a major economic impact on existing markets for ion-beam processing of industrial materials, and could allow expansion of the market to applications which are prohibitively expensive with current ion-beam technology.

PLASMA SOURCE ION IMPLANTATION CONCEPT

In Fig. 1 we compare PSII with conventional ion implantation. Conventional ion implantation is a line of sight process; ions are extracted from a plasma source, accelerated to the desired energy and then rastered across the target to uniformly implant the target. Because of the line-of-sight nature of conventional ion implantation, a manipulator stage is required to rotate the target in the beam to implant all sides of the target. The target manipulation adds complexity and reduces the size of the target which can be implanted. This target manipulation problem in conventional ion implantation is exacerbated by the need to provide adequate heat sinks at the targets to limit temperature rise during the implantation. In PSII, the target is placed directly in the plasma source and is pulse biased to a high negative potential (maximum of -40 kV at present; soon to be increased to -100 kV with a new, recently constructed pulse modulator) relative to the chamber walls. Ions are accelerated normal to the target surface, across the plasma sheath, thus eliminating not only the line-of-sight problems of conventional ion implantation, but also the "retained dose" problem. Even with target manipulation, conventional ion implantation often requires target masking (Fig. 2) in order to minimize grazing incidence of the beam which produces excessive sputtering, and thereby limits the retained dose. This masking requirement imposes a need for additional fixturing specifically tailored to each target and thus introduces additional complexity and losses in the system. Also, sputtering of the mask can coat and contaminate the workpiece. In PSII, target manipulation is not needed since the plasma completely surrounds the target; all exposed areas of the target are implanted simultaneously. The elimination of target manipulation is a particular advantage of PSII, especially for large, heavy targets. Elimination of the ion accelerator stage, raster-scan apparatus and target manipulator hardware makes PSII a much simpler and more cost-effective technology than conventional ion implantation. Because PSII is limited by neither the ion optics characteristics nor the Child–Langmuir space-charge limited flow[24] properties of conventional ion implanters, PSII can provide a much greater ion flux at low energies.

In summary, the advantages of PSII relative to conventional implantation, are: (1) Elimination of need for target manipulation and beam rastering. (2) Elimination of target masking requirement (retained dose problem). (3) The ion source hardware and controls are at near-ground potential. (4) Greater production throughput, especially for large tar-
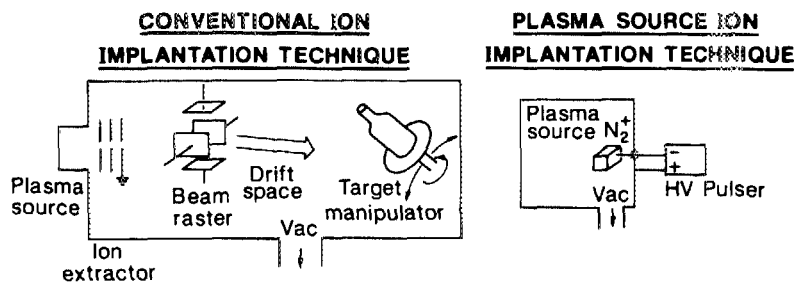

CONVENTIONAL ION IMPLANTATION TECHNIQUE

PLASMA SOURCE ION IMPLANTATION TECHNIQUE

FIG. 1. Conceptual comparison of conventional ion-implantation technique with plasma source ion implantation (PSII).

- Line of sight process
- Beam rastering and target manipulation are required to achieve uniform implantation

- Plasma sheath surrounds target
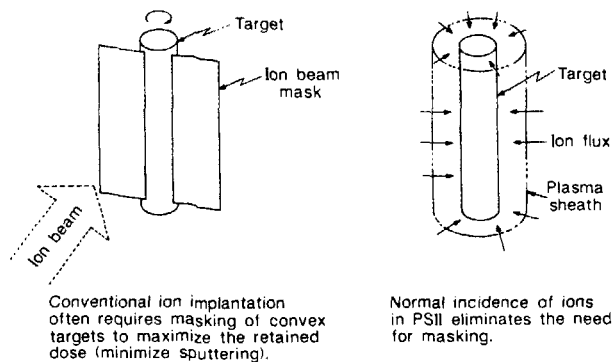- Ions bombard target on all surfaces without beam rastering or target manipulation

Conventional ion implantation often requires masking of convex targets to maximize the retained dose (minimize sputtering).

Normal incidence of ions in PSII eliminates the need for masking.

FIG. 2. Comparison of conventional ion-implantation technique with plasma source ion implantation, with respect to retained dose considerations.

FIG. 3. Ion matrix model for PSII target fluence per pulse.

gets. (5) PSII is readily scaled to large and/or heavy targets. (6) The PSII implantation facility is smaller, less expensive, simpler to maintain and operate, and more compatible with "in-house" operation as opposed to the "outside service facility" mode operation which is prevalent at present in the ion beam processing industry.

PSII can be distinguished from techniques commonly referred to as "ion plating" or "ion coating"[25] in several ways. Although ion plating devices share some features in common with our PSII device, the applied voltage in ion plating is too low to allow ions to penetrate substantially into the target surface. As the name implies, "ion plating" produces a surface layer or coating on the target. This coating is subject to scratching and delamination problems. In contrast, the voltages applied in PSII are sufficiently large to allow the accelerated ions to penetrate the target lattice, thus providing a superior surface modification. The pulsed nature of the voltage in PSII is essential for a number of reasons. First, the short duty cycle (pulse width multiplied by repetition rate) eliminates surface damage to the target from sustained high-voltage arcing. Second, the short-pulse voltage applied provides spatial uniformity and implantation depth uniformity because the pulse width is chosen to be short enough that the plasma sheath which forms around the target does not expand during the voltage pulse to contact either the vacuum chamber wall or the sheath which surrounds an adjacent target if multiple targets are being implanted. Finally, low-energy ion bombardment between high-voltage pulses provides continuous *in situ* discharge cleaning which minimizes impurity contamination.

PLASMA PHYSICS ISSUES IN PSII: MODELING

In addition to the requirement of sufficiently large potentials for implantation rather than deposition, the particular process parameters which delineate the characteristics necessary in order to achieve plasma source ion implantation (as distinguished from ion plating techniques) can be understood in terms of a model for the transient sheath characteristics. When a large negative potential pulse is applied to a target electrode immersed in a plasma, a plasma sheath forms around the target, as illustrated schematically in Fig. 3. A plasma sheath is a region between a quasi-charge neutral plasma and an electrode in which charge neutrality is
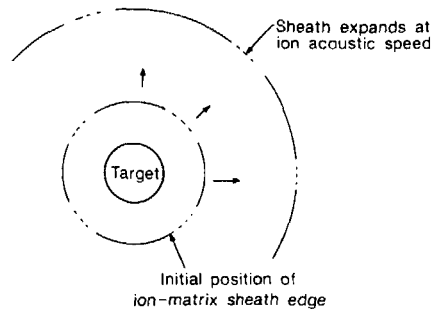
violated. Three time scales govern the response of the sheath. At time $t = 0$ the electrode is at zero potential. As the potential is established at the electrode, electrons near the electrode are expelled from the region near the electrode. This rapid expulsion occurs on a time scale of the inverse electron plasma frequency. On this time scale the ion motion is negligible so that as the electrons recede, they leave behind a region of nearly uniform ion space charge. This positive space-charge region establishes a potential profile described by the ion-matrix model. Next, on the slower time scale of the inverse ion plasma frequency, ions are accelerated toward the electrode as they fall through the ion-matrix sheath. Finally, on a still longer time scale (much greater than the inverse ion plasma frequency) the decreasing ion density inside the sheath region causes a corresponding decrease in the electron density and the sheath edge expands at approximately the plasma ion acoustic velocity. For pulse lengths greater than the inverse ion plasma frequency, but short enough that the sheath does not expand to the chamber walls, the ion energy is very nearly equal to the ion charge multiplied by the applied potential. Preliminary scaling experiments suggest that the observed target fluences (as measured by infrared pyrometry) can be accounted for by simply assuming that the fluence per pulse is equal to the plasma density multiplied by the volume of plasma between the target and the expanded sheath, divided by the area of the target.

The ion-matrix sheath thickness is determined by the plasma density, target radius of curvature and applied implantation potential.[26] The subsequent sheath expansion depends on the plasma electron temperature and the ion mass. For a typical case of nitrogen implantation of a cylinder of radius equal to 1 cm, at a potential of 100 kV, the initial ion-matrix sheath forms at a radius of 4 cm, and the sheath expands at an ion acoustic velocity of 0.25 cm per ms. The pulse length of the plasma source ion implantation waveform should be chosen to be short enough that the expanding sheath does not contact either the vacuum chamber wall or the sheath which surrounds an adjacent target if multiple targets are being implanted. For example, if the pulse length is chosen to be 30 ms, the sheath expands to a final radius of 11.5 cm.

PLASMA SOURCE ION IMPLANTATION DEVICE

The PSII device is shown schematically in Fig. 4. Plasma is produced in a cylindrical vacuum chamber 16 in. high and 14 in. in diameter. The chamber walls are covered with
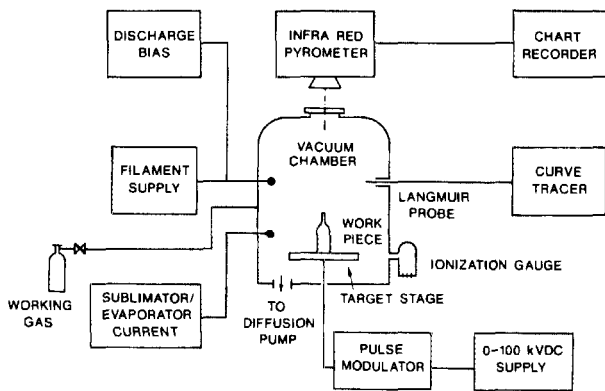
FIG. 4. Plasma source ion implantation device block diagram showing vacuum chamber, power supplies, and diagnostics.

an array of permanent magnets which enhance confinement of the plasma. Plasma is generated in the chamber by a conventional filament discharge which ionizes the working gas (most commonly nitrogen in our experiments; we have also operated the device with hydrogen, helium, and argon). The device is typically operated at a pressure of 2×10^{-4} Torr. The plasma density can be varied from 10^7 to 10^{11} cm^{-3} by adjusting the filament current and bias. A sublimator/evaporator boat provides the capability to deposit films for ion mixing implantation.[27] A pulse generator provides a bias on the target of up to $- 100$ kV. The pulse amplitude, width, and spacing are independently and continuously variable. A voltage divider and current transformer on the pulser output monitor the implantation voltage and current waveforms. An ionization gauge measures neutral density during implantation. A Langmuir probe is used to measure the plasma density and electron temperature. Target temperatures during implantation are monitored by infrared pyrometry. Targets are cooled by oil flowing through the hollow target stage.
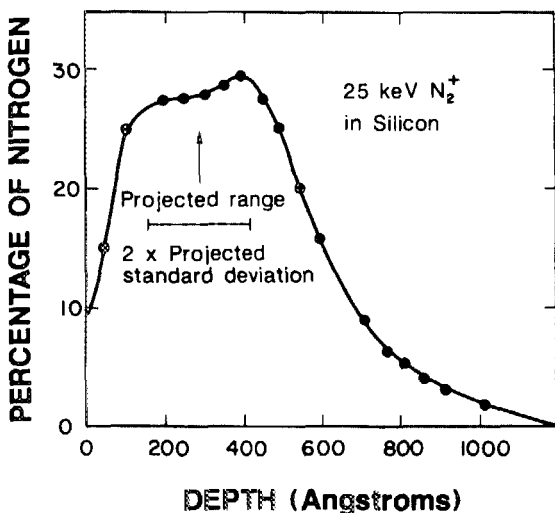
RESULTS OF PRELIMINARY EXPERIMENTS WITH PSII

Our preliminary experiments[1-6] have demonstrated that PSII is capable of implanting ions to the concentrations and depths required for surface modification. Figure 5 shows Auger data of the concentration profile of nitrogen implanted in silicon. This target was implanted by placing it in a multidipole filament discharge plasma source operating with nitrogen (primarily N_2^+) at a neutral pressure of 2×10^{-4} Torr and an ion density of approximately 2×10^8 cm^{-3}. The target was pulse biased with a peak voltage of $- 25$ kV. The resulting depth profile is approximately consistent with LSS theory[28] and our present understanding of the plasma sheath formation dynamics.[26] Since the species composition in the source is dominantly N_2^+, we have plotted in Fig. 5 the LSS theory predictions for 12.5-keV N^+. Note that the measured distribution peaks at a greater depth than the calculated range for N^+. We attribute this discrepancy to two effects: (1) Nitrogen diffusion due to heating of the sample (the target was not actively cooled in this earliest experiment), and (2) a small contribution from the minority species N^+ at full energy.

The preliminary experiments have also demonstrated improvements in the microhardness and tribological properties of targets. In Fig. 6 we show the Knoop hardness of type 5160 steel blocks which were implanted with nitrogen ions (primarily N_2^+) to a peak energy of 40 keV to a fluence of approximately 3×10^{17} cm^{-2}. The PSII-implanted specimens show an increased Knoop hardness of approximately 25% relative to the as-received material. A similar improvement is produced by heat treatment (austempering) of the as-received material. However a combination of heat treating and ion implantation results in a doubling of the Knoop hardness. It should be noted that the indenter loads in these Knoop hardness measurements are sufficiently large that the indenter penetrates well beyond the depth of the implanted zone.

The abrasive wear characteristics of an age-hardenable Invar alloy were improved significantly by PSII implantation. The alloy tested was Carpenter's Lo Ex 42 PH, a low expansivity nickel-iron alloy containing aluminum and ti-
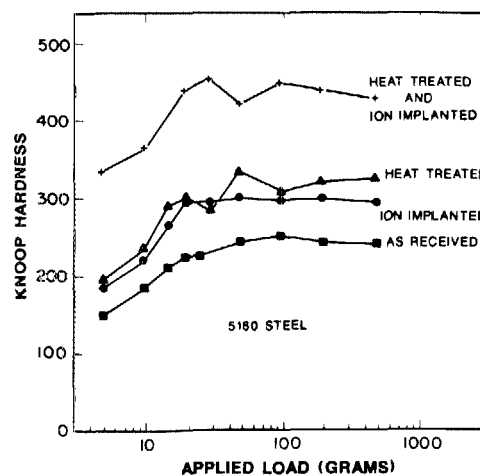

FIG. 5. Auger depth profile for PSII implantation of 25-keV nitrogen (dominantly N_2^+) in silicon. Also shown are the projected range and projected standard deviation calculated from LSS theory for 12.5-keV N^+.

FIG. 6. Knoop hardness of 5160 steel specimens.
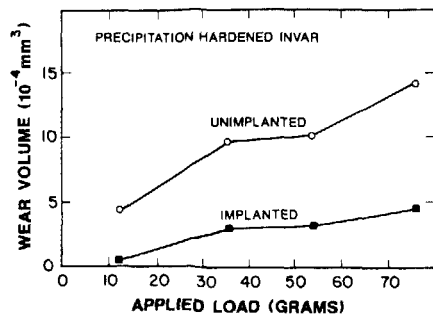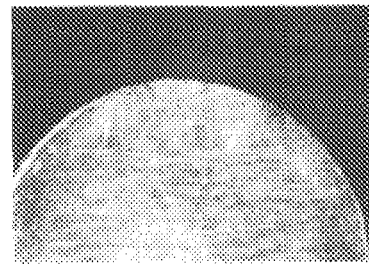
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FIG. 7. Wear test results for PSII implanted and unimplanted specimens of age hardenable Invar, Lo Ex 43 PH.

(a) UN-IMPLANTED PUNCH, AFTER 500 OPERATIONS

(b) PSII-IMPLANTED PUNCH, AFTER 38,000 OPERATIONS

(c) PSII-IMPLANTED PUNCH, AFTER 43,000 OPERATIONS

FIG. 8. Optical photomicrographs $(6\times)$ of the piercing ends of 0.516-in.-diam M-2 punches, taken after field testing at a local manufacturing facility. (a) Unimplanted punch, removed from production line because of unacceptable burring of punched holes after 500 operations. Extensive back extrusion, leading to fracture and galling, is evident. (b) PSII-implanted punch, removed after 38 000 operations. (c) PSII-implanted punch, removed after 43 000 operations.

tanium for precipitation hardening. The wear test used was a nonstandard test designed to study thin-film wear characteristics.[29] It consisted of a 5-cm-diam hardened stainless-steel ball rotating against a lightly loaded test specimen. A slurry of 0.05-M diamond paste was applied to the ball to provide an abrasive wear media. The applied load, perpendicular to the coating surface, was varied between 10 and 75 g. In order to calculate the wear volume, the size of the wear scar was measured. The results of these tests are presented in Fig. 7. Here it can be seen that the PSII implanted specimens exhibited wear rates approximately one fifth of their unimplanted counterparts. It is believed that this significant improvement resulted from the formation of titanium and aluminum nitrides in the ion-implantation zone.
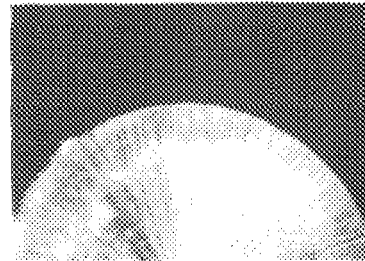
In other experiments[2,3] we have demonstrated increased wear resistance of tool steel, and ceramic cutting tool inserts (Al_2O_3 with SiC whisker crystals). We have also modified the electrical conductivity of a polymer (Kapton-H) by PSII implantation.[3]

We have observed dramatic improvements in the lifetime of PSII-implanted M-2 punches in preliminary field tests conducted at a local manufacturing facility. The hardened, 0.516-in.-diam punches were used to produce holes in mild steel plate (SAE 1008 or 1010), ranging in thickness from $\frac{1}{4}$ to $\frac{3}{8}$ in. Typically, an unimplanted punch will produce approximately 500–1000 holes, before unacceptable burring occurs around the hole circumference. Three punches were ion-implanted by PSII and tested under production conditions.
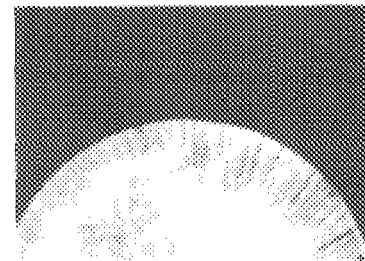
One of the three was removed after 38 000 holes had been produced, at which time unacceptable burrs were beginning to form on the workpieces. Another PSII-implanted punch was left in service for 43 000 operations, with no evidence of burring on the holes being punched. Examination of the cutting edge of the punches provided an indication of the beneficial effects of ion implantation. Representative photomicrographs are shown in Figs. 8(a), 8(b), and 8(c). The unimplanted punch exhibited a rough, jagged cutting edge, as can be seen in Fig. 8(a). This formed as a result of back extrusion of the punch material during withdrawal and subsequent fracture of the extruded lip. This fractured material became lodged between the punch and the work piece, causing severe galling and ultimately, burring of the work piece. The ion-implanted punches showed much less of this back extrusion. Figure 8(b) is a representative view of the cutting

edge after 38 000 holes had been punched. Most of the cutting edge is still sharp, with only minor indications of fracture of the extruded lip. Figure 8(c) shows the edge after 43 000 punches. Very little indication of edge fracture can be observed. A third PSII implanted punch failed after only 500 holes had been formed. Post failure examination indicated that a manufacturing flow initiated a fatigue crack which ultimately led to catastrophic failure of the punch.

The results of these field tests are in agreement with wear tests on other chromium alloy steels reported in the literature.[30,31] It is postulated that a high density of finely divided nitride compounds are being formed during ion implantation. These nitrides effectively pin dislocations near the surface at the cutting edge, thereby preventing back extrusion and subsequent fracture. We are conducting scanning transmission electron microscopy examination to determine the identity and morphology of these compounds.

CONCLUSIONS

Our preliminary experiments[1-4] have demonstrated that the new plasma source ion implantation process: (1) efficiently implants ions to concentrations and depths required for surface modification,[32] (2) produces material with im-

proved microhardness and wear properties as measured in controlled laboratory experiments,[2-4] and (3) dramatically improves the life of manufacturing tools in actual industrial applications.[5,6]

ACKNOWLEDGMENTS

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