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John R. Conrad

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Madison, WI 53706-1687

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13. ABSTRACT *(Maximum 200 words)*

This report contains the research results to date, proposed future research on elevated-temperature PSII-IBED, a list of manuscripts submitted and abstracts of these manuscripts.

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Extension of Plasma Source Ion Implantation to Ion Beam Enhanced Deposition

FINAL REPORT

Professor John R. Conrad
College of Engineering
University of Wisconsin

October 5, 1989

U. S. Army Research Office

Contract Number: DAAL03-89-K-0048

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University of Wisconsin-Madison

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Contents

RESEARCH RESULTS TO DATE; BACKGROUND

The proposal for this Research Initiation Grant to extend Plasma Source Ion Implantation (PSII) to Ion Beam Enhanced Deposition (IBED) was submitted to the ARO in April, 1988. Although the proposal received favorable reviews, it was not funded initially due to ARO budget constraints. In December, 1988, Dr. Robert Reeber of ARO informed us that additional funds had become available; he suggested that we re-submit the proposal, and the proposal was funded on February 1, 1989. In the intervening time between April 1988 and February 1989, other sources of funding became available to the PSII group. In May, 1988, we received a Joint Materials/Manufacturing Initiative grant from NSF to develop nitrogen ion PSII for improved performance of cutting tools and dies. In October, 1988, research on the extension of PSII to IBED processing was already underway with support from the the recently established NSF Engineering Research Center in Plasma-Aided Manufacturing. Accordingly we have used the grant to accomplish what we view as the the next logical step in the development of the PSII process; namely the extension to Elevated-Temperature PSII IBED.

Through ion implantation, it is possible to inject an atom species into the surface of a material with the penetration depth determined by the ion energy and the stopping power of the bombarded substance. By this means, it is possible to produce dramatic improvements in the surface properties of a wide range of materials including metals, ceramics, and polymers.[1-12] However, in spite of the demonstrated 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.

In order to lower the cost of ion implantation, there are a number of recently emerging developments in which plasma techniques borrowed from other disciplines are being applied to ion beam surface modification applications. The MEVVA (Metal Vapor Ion Vacuum Arc) ion source which was originally developed by Brown[13,14] at Lawrence Berkeley for use in heavy ion nuclear physics research is now being employed to generate very large current metal ion beams for surface modification.[15] Wilbur and his colleagues[16,17] at Colorado State University have adopted ion thruster technology developed for spacecraft propulsion to develop a high-current density process for rapid implantation of metals. In their process, the sample temperature is allowed to rise to approximately 450°C, and enhanced diffusion at this elevated temperature leads to greater depth of implantation relative to ambient temperature processing.

The Plasma Source Ion Implantation (PSII) process for surface modification, which evolved from fusion plasma research activities, is being developed extensively, both in our laboratory[19-42] and by other groups.[43-49] PSII is a non-line-of-sight technique for surface modification of materials which is optimized for ion implantation of non-planar targets in non-semiconductor applications. In PSII, targets to be implanted are placed directly in a plasma source chamber and are then pulse-biased to high negative voltage. A thick, ion matrix sheath forms around the target, and ions accelerate through the sheath drop and bombard the target from all sides simultaneously without the necessity of target manipulation. Compared to conventional ion implantation, PSII minimizes the problems of shadowing and excessive sputtering of the target material, which can severely limit the retained dose of the implanted ion species.

Our preliminary testing has demonstrated that ion implantation by PSII can substantially improve the properties of certain materials in certain environments. However until quite recently, the PSII process has been limited to the implantation of ion species which are gaseous at room temperature; in particular most of our PSII work to date has been done with nitrogen. This limits the applicability, for example, to steels with high chromium content and to wear applications at low to moderate temperatures. While some of the materials problems of interest to the Army can be solved by nitrogen implantation, others such as corrosion and wear phenomena at elevated temperatures can not. For these broader applications, ion species such as titanium, carbon, chromium, etc. will be required. In order to address this problem, we are beginning to extend the PSII process to operate in modes similar to the IBED (Ion Beam Enhanced Deposition) or ion mixing techniques which have been developed using conventional technology[50,51]. In these techniques, a thin layer of a desired non-gaseous implant species such as titanium is deposited onto the target. In direct ion implantation, sputtering limits the maximum achievable concentration of implanted species to atomic percentages ranging from 10 - 50% depending on the ion energy and sputtering coefficient. Also, practically achievable ion energies limit the implanted layer thickness to values of less than, or on the order of a micron. IBED overcomes both these limitations of direct implantation. In IBED, thicker, more uniform layers can be produced at lower implantation energies than are required in direct ion implantation. These films provide excellent wear and corrosion resistance, while exhibiting good adherence. Similarly, TiN coatings, which had been bombarded with nitrogen, exhibited improved wear corrosion and frictional properties, when compared to unimplanted coatings. IBED of coatings has an important additional advantage relative to more standard coating techniques (such as chemical vapor deposition), in that it does not require high temperatures for the production of highly adherent coatings.

It is the ultimate intent of this ARO research program to combine the best aspects of the PSII process with the best aspects of the IBED and elevated-temperature processes described above. There are recent examples in the literature of thick coatings produced by reacting nitrogen and vanadium in a salt bath. Japanese researchers[1] have recently described a process called Thermo-Reactive Deposition and Diffusion. In this process, a steel substrate was first ion nitrided and then placed in a salt bath containing vanadium atoms. After reacting for 8 hours at 550-650°C, a continuous, adherent vanadium nitride layer was formed. The thickness of this layer varied between 2 and 20 μm, depending on bath temperature and time. The friction and wear characteristics were superior to most other surface modification processes. The major problems with the process are long treatment times, high treatment temperatures, and environmental aspects of salt bath treatment and disposal. Our research suggests that similar coatings can be obtained by the elevated-temperature PSII-IBED technique, in shorter times and at somewhat lower temperatures.

ELEVATED-TEMPERATURE PSII RESEARCH RESULTS TO DATE

We have already demonstrated the ability of PSII to operate in IBED mode. In this section, we describe our first experiments on elevated-temperature PSII. The ultimate goal will be to combine these two processes.

With PSII it is possible to attain elevated target temperatures by controlling the ion current and the duty cycle. By using PSII at temperatures in the range of 400-525°C, hardened layers having thicknesses ranging from 10 to 50 μm have been formed on steel substrates. We have obtained surface Knoop hardnesses as high as 580, 990 and 860 (at 100 gram load) on 4340, 410 stainless steel and LOW EX 43PH steel respectively through nitrogen ion implantation. The thick, hard layers which forms on these steel substrates derive from the enhanced diffusion resulting from the combination of thermal and irradiation effects.

In the temperature range of 450-550°C, nitrogen diffusion in steel is quite high. The generation of vacancies in the ion cascade collision process further enhances the diffusion process. In addition, the ability to deposit nitrogen ions below the surface eliminates the formation of surface iron nitrides, which significantly decrease nitrogen diffusion. The experimental results of characterization of modified layers by optical metallography, microhardness, x-ray diffraction and pin on disc wear tests on a variety of steels, nickel base alloys and Tribocor (niobium base alloy) described in the succeeding paragraphs reveal the unique features of the high temperature implantation of nitrogen by the PSII process.

Although similar hardness profiles and layer thicknesses can be obtained by other processes, such as gas and ion nitriding, the times required are as high as 18 to 24 hours and an undesirable compound layer of iron nitrides often forms on the surface.

A comparison of surface Knoop hardness of PSII-nitrided and ion nitrided 4340, AISI410 and LOW EX 43PH steels shown in Table 1 indicates that it is possible to achieve surface hardnesses that are comparable to ion nitriding (with compound layer) by PSII process (without forming a compound layer).

The type of hardness profile that can be achieved by the high temperature PSII process is shown in Fig. 1. The modified layers obtained by the PSII process even with a low bias voltage and very low current density are relatively deep and are comparable to ion nitriding.

The elevated-temperature PSII process has yielded substantial increases in wear resistance of steel pin on disc test specimens. The profilometric traces of pin-on-disc wear tracks shown in Fig. 2 indicate the increase in adhesive wear resistance due to high temperature nitrogen implantation by the PSII process. The summary of the results of pin on disc wear tests shown in Fig. 3 also reveal a substantial improvement in sliding or adhesive wear resistance in the case of AISI410 and LOW EX 43PH materials. The wear resistance depicted by the depth of tracks follow very closely those of ion nitrided layers (with compound layers) even at loads as high as 1.0 kg.

TABLE 1. Knoop Microhardness at 100 gf Load

Material	PSII Nitrided	Ion Nitrided	%Variation w.r.t. Ion Nitriding
4340	580	688	- 15.7 %
SS410	993	1021	- 2.7 %
LOW EX 43PH	865	942	- 5.4 %

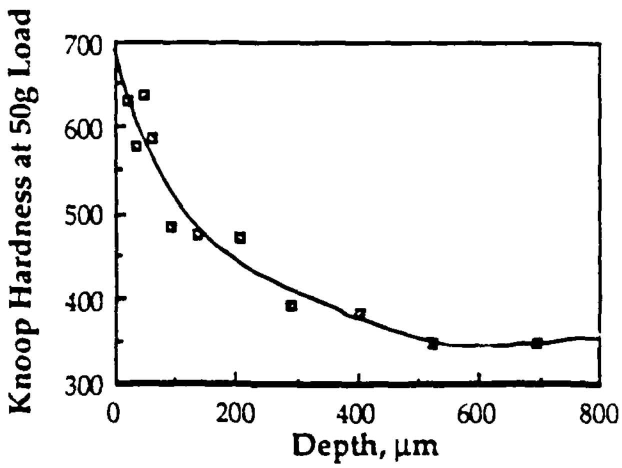

Fig. 1. Knoop microhardness vs. depth of nitrogen implanted 4340 steel. Fluence: 5×10^{18} atoms/cm^2.

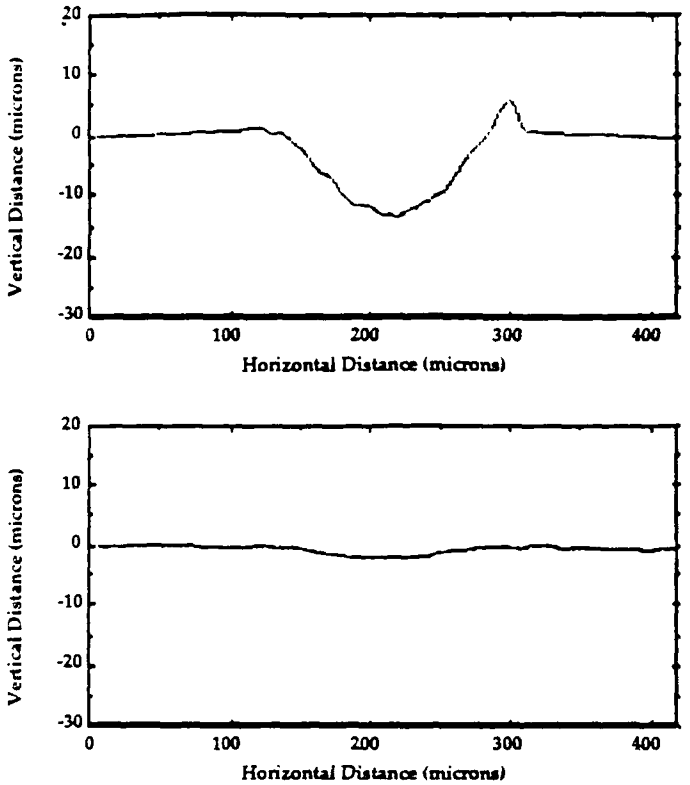

Fig. 2. Comparison of 0.5 kg load pin-on-disc wear tracks in AISI410 stainless steel; unimplanted (top), and nitrogen implanted, 3×10^{18} atoms/cm^2 (bottom).

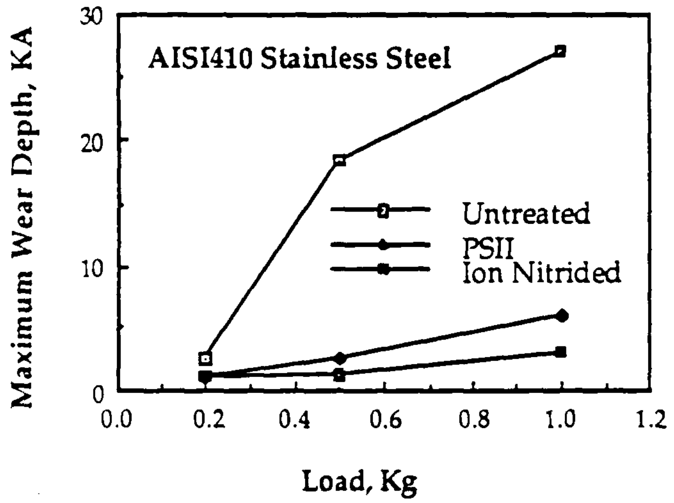

Fig. 3. Pin-on-disc wear of PSII nitrogen-implanted and ion-nitrided AISI410 stainless steel samples.

PROPOSED RESEARCH ON PSII-IBED AT ELEVATED TEMPERATURES

Based on the above results, we have submitted to ARO a renewal proposal entitled "Formation of Transition Element Nitride Coatings on Steels Using Elevated-Temperature Plasma Source Ion Implantation and Ion Beam Enhanced Deposition" The goal of this proposed research program is the development of a technique for producing transition element nitride coatings in order to improve wear, corrosion and fatigue resistance of steels used for bearings and tools. We propose to combine the beneficial effects of

- Plasma Source Ion Implantation (PSII)
- Controlled elevated-temperature implantation (400-525°C)
- Ion Beam Enhanced Deposition (IBED)

to develop thick, hard, and adherent coatings of transition element (Ti, Cr, Nb, V, and Zr) nitrides on steels used for bearings and tools for increased corrosion-resistance and wear-resistance. The desired result will be the formation of a hard and adherent nitride layer with a thickness of several microns. This process can be used on components made of materials that are resistant to tempering (for example, M-50 or AMS-5749) in the above temperature range. The process can also be used advantageously on inexpensive steels which are not very resistant to tempering (for example 52100) in the above temperature range, by pre-tempering components at a slightly higher temperature than the treatment temperature to stabilize the microstructure and then developing a hard coating of the desired type on the surface. This would result in a material with a very hard, wear- and corrosion- resistant surface and a tough core.

Surface modification of steels by elevated-temperature nitrogen PSII results in a novel microstructure (without compound layer), increased modified layer depth (greater than 50 to 100 µm), with a significant increase in hardness and wear resistance. The increased hardness of the layer produced during elevated temperature PSII can be the result of several strengthening mechanisms. The major source of hardening is the formation of stable nitrides of alloying elements present in the work piece. Elements such as V, Ti, Nb, Cr and Al are strong nitride formers which precipitate out as small particles (~50Å). These precipitates provide very strong dislocation pinning sites, which are effective even at elevated temperatures. Another hardening mechanism is Cottrell atmosphere pinning caused by high concentration of nitrogen at dislocations. Both of these mechanisms provide surface hardening and can moderately influence the coefficient of friction values and corrosion resistance. In order to improve these properties significantly, it is necessary to form a coating of the desired species on the surface which is adherent and has the requisite characteristics. This is where the IBED process can be used advantageously.

The process we envision is the sequential implantation/deposition of nitrogen and a strong nitride forming transition metal element, in such a way as to control the location and concentration of the ion species. The goal of this process is the formation of a highly adherent, hard, corrosion- and wear-resistant coating of controlled thickness on the surface of a steel substrate. A typical processing sequence for a steel component (e.g. a 52100 bearing race) would be the following:

a) Nitrogen ion implant in the temperature range 400 - 525°C to a fluence of $3x10^{18}$ atoms/cm^2. This would produce a thick and hardened layer with a thickness of approximately one micron.
b) Continue nitrogen implantation at ~100°C to a fluence of $1x10^{17}$ atoms/cm^2. This would put a high density of nitrogen atoms within ~500Å at the surface.
c) Sputter deposit ~2000Å of a strong nitride former such as vanadium, niobium or zirconium.
d) Nitrogen implant in the temperature range 400 - 525°C to a fluence of $1x10^{18}$ atoms/cm^2.

The result should be the formation of a contiguous nitride layer of about 1500-1800Å thick. With the repetition of steps b,c, and d, it should be possible to build the layer of coating to any desired thickness. There are recent examples in the literature of coatings of this type being obtained by reacting nitrogen and vanadium in a salt bath. The Japanese recently described a process they call thermo-reactive deposition and diffusion.[1] In this process, a steel substrate was ion nitrided and then placed in a salt bath containing vanadium atoms. After reacting for 8 hours at 550-650°C, a continuous, adherent vanadium nitride layer was formed. The thickness of this layer varied between 2 and 20 µm, depending on bath temperature and time in the reaction bath. The friction and wear characteristics were superior to most other coating processes. The major problems with the process are the time requirements and the environmental aspects of salt bath treatment. We propose that similar coatings with superior friction and wear characteristics can be obtained using PSII, at considerably shorter times and at moderately lower temperatures. Our specific plans consist of the following activities:

- Optimize conditions for elevated temperature PSII-IBED of nitride coatings of Ti, Cr, Nb, V, and Zr on test flats to establish the effectiveness of PSII in performing ion beam enhanced deposition.
- Characterize coatings thus developed using test procedures for evaluating the wear, friction, corrosion, and rolling contact fatigue behavior.
- Demonstrate the capability of elevated temperature PSII-IBED on a prototype component, and evaluate its performance.
- Modify and refine our existing Monte Carlo code (TAMIX, developed here) for simulating the elevated-temperature PSII-IBED process and benchmark the code to ensure its predictive capability.
- Develop a detailed plasma simulation model of PSII to generate realistic ion current and energy distribution of ions to the target (to be used as input to the TAMIX code).

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SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT

During the course of this reporting period, ARO funds were used to provide salary support for the following scientific personnel:

John R. Conrad is Wisconsin Distinguished Professor of Nuclear Engineering and Engineering Physics at the University of Wisconsin. Professor Conrad earned his Ph.D. in physics at Dartmouth College. His research has covered a broad spectrum of problems in basic plasma physics, confinement and heating of fusion plasmas, high current ion and neutral particle beams, plasma-wall interactions and ion implantation. Professor Conrad is the inventor of the Plasma Source Ion Implantation process and is the director of the PSII program.

Paul Fetherston is a research assistant with the PSII group. As chief technician for the PSII group, he is responsible for daily operation and maintenance of the PSII laboratory facilities, and for supervision of undergraduate hourly workers employed by the PSII group.

Jim Firmiss is a graduate student in the Materials Science Program. Jim received his B.S. in Physics from the University of Illinois at Chicago.

MANUSCRIPTS SUBMITTED DURING THIS REPORTING PERIOD

During the course of this reporting period, the following manuscripts were submitted or published under ARO sponsorship:

1. S. H. Han, G. L. Kulcinski, J. R. Conrad, "Computer Simulation of Ion Beam Mixing", Ion Beam Analysis Conference, Queens University, Kingston, Ontario, June 26-30, 1989, Proceedings to be published in Nucl. Instrum. and Meth.
2. Murthy S. P. Madapura, Frank J. Worzala, and John R. Conrad, "Characterization of Ion Nitrided Layers", Second International Conference on Ion Nitriding/Carburizing, Cincinnati, Ohio, September 16-20, 1989.
3. ~~Murthy S. P. Madapura, Frank J. Worzala, R.~~ A. Do~~dd and John~~ R. Conrad, ~~"Plasma Source Ion Implantation - Nitriding Characteristics of Steels", Second International Conference on Ion Nitriding/Carburizing, Cincinnati, Ohio, September 16-20, 1989.~~ related material NSF support RRR 6/25/
4. J. R. Conrad, "Ion Beam Assisted Coating and Surface Modification with Plasma Source Ion Implantation", invited paper, 36th National Symposium of the American Vacuum Society, Boston, October 23-27, 1989, conference proceedings to be published in J. Vac. Sci. Technol.
5. S. H. Han and J. R. Conrad, "TAMIX - A Dynamic Monte Carlo Simulation Program of Ion-Solid Interaction", submitted to Applied Physics A, Solids and Surfaces, July, 1989.
6. Xiaoci Zheng, R. Arthur Dodd, John R. Conrad, and Frank Worzala, "Amorphous Metallic Alloys Formed by Plasma Ion Mixing", Conference Proceedings, 1989 Fall Meeting of the Materials Research Society, Boston, Massachusetts, Nov. 27-Dec. 2, 1989.

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Invited paper, 36th National Symposium of the American Vacuum Society, Boston, October 23-27, 1989, conference proceedings to be published in J. Vac. Sci. Technol.

ION BEAM ASSISTED COATING AND SURFACE MODIFICATION WITH PLASMA SOURCE ION IMPLANTATION* J. R. Conrad. Department of Nuclear Engineering and Engineering Physics, University of Wisconsin, 1500 Johnson Dr., Madison, Wisconsin 53706.

Plasma Source Ion Implantation (PSII) is a non-line-of-sight technique$^{1-3}$ which is being developed as an alternative to beamline accelerator technology for ion implantation. The initial development phase of PSII concentrated on implantation of ion species which are gaseous at room temperature (primarily nitrogen ions) and employed a cylindrical vacuum chamber 16 in. high and 14 in. in diameter. A second generation PSII system is being constructed to extend the PSII process to ion beam mixing and ion beam assisted coating modes of operation. The new system will feature multiple-array sources for sputter deposition concurrent with ion bombardment. Initial operation of the new cubical PSII chamber with dimensions 40 in. x 40 in. x 40 in. is expected in the fall of 1989. Preliminary results with the new system will be described.

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Ion Beam Analysis Conference, Queens University, Kingston, Ontario, June 26-30, 1989, Proceedings to be published in Nucl. Instrum. and Meth.

Computer Simulation of Ion Beam Mixing*, S.H. Han, G.L. Kulcinski, J.R. Conrad, Department of Nuclear Engineering and Engineering Physics, University of Wisconsin, 1500 Johnson Dr., Madison, Wisconsin 53706.

A highly optimized dynamic Monte Carlo program TAMIX has been developed to simulate the ion beam mixing process. In addition to the collisional features, some of the diffusional processes are taken into account in TAMIX for elevated temperature irradiation applications. TAMIX can be run in three modes, i.e. Static Mode, Collisional-Dynamic Mode, and Collisional-Diffusional-Dynamic Mode. TAMIX is a non-analogue vectorized Monte Carlo program for the full use of the capability of vector computers such as the Cray. In TAMIX, sophisticated models have been adopted to obtain both speed and accuracy, including tabulation of the scattering angles, energy-dependent mean free path for nuclear collisions, "random surface model" for sputtering, and concentration-dependent surface binding energies. The simulation results applied to a wide range of situation show good agreement with experimental data.

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TAMIX - A Dynamic Monte Carlo Simulation Program of Ion-Solid Interaction* S. H. Han, J.R. Conrad, Department of Nuclear Engineering and Engineering Physics, University of Wisconsin, 1500 Johnson Dr., Madison, Wisconsin 53706.

To simulate the complicated nature of the ion beam-solid interactions, a comprehensive Monte Carlo program, TAMIX, has been developed on Cray supercomputers. Optimization of TAMIX has been achieved through variance reduction technique and the vectorized algorithm. In addition to the collisional features, some of the diffusional processes are taken into account in TAMIX for elevated temperature irradiation applications. Also, various models fro relevant physical processes have been used to obtain speed and accuracy, including tabulation of the scattering angles, energy-dependent mean free path for nuclear collisions, "random surface model" for sputtering, and concentration-dependent surface binding energies. TAMIX can be run in three modes, i.e. Static Mode, Collisional-Dynamic Mode, and Collisional-Diffusional-Dynamic Mode. The simulation results applied to a wide range of situation have shown good agreement with available experimental data.

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Second International Conference on Ion Nitriding/Carburizing, Cincinnati, Ohio, Sept. 16-20, 1989.

Characterization of Ion Nitrided Layers*, Murthy S. P. Madapura, Frank J. Worzala, and John R. Conrad, University of Wisconsin, Madison, WI 53706.

Several steels were ion nitrided to obtain compound layers of gamma prime, epsilon nitride, and a combination of gamma and epsilon nitrides by varying the process parameters. The modified surfaces were characterized by profilometry, x-ray diffraction, optical metallography, Knoop microhardness testing, pin-on-disc wear testing, and friction coefficient measurements. In selected cases, nitrogen depth profile was established by electron probe microanalysis (EPMA) and/or scanning auger microscopy (SAM).

In this paper, we will be presenting the results of the aforesaid studies highlighting (1) the relationship between modified layer depth measured by Knoop microhardness and nitrogen profile by EPMA/SAM; (2) pin-on-disc wear characteristics of gamma prime, epsilon, and diffusion layers; and (3) the microstructural features.

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Second International Conference on Ion Nitriding/Carburizing, Cincinnati, Ohio, Sept. 16-20, 1989.

Plasma Source Ion Implantation - Nitriding Characteristics of Steels*, Murthy S.P. Madapura, Frank J. Worzala, R. A. Dodd, and John R. Conrad, University of Wisconsin, Madison, WI 53706

For enhancing wear, corrosion, fatigue, and fracture resistance of engineering components, a variety of surface modification techniques are being used on a production scale. Ion (plasma) nitriding is gaining momentum and is becoming a production process for nitriding of ferrous materials/components. Plasma Source Ion Implantation (PSII) - nitriding, the newest member of surface modification processes, is very unique as it combines the advantages of conventional ion implantation and ion nitriding.

In this paper, we will present the recent progress we have made on PSII - Nitriding of several steels in order to understand the metallurgical characteristics, process kinetics, and mechanical properties of modified layers. A comparison of ion nitriding and PSII - nitriding will also be presented with examples to highlight the potential of this frontier technology.

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Conference Proceedings, 1989 Fall Meeting of Materials Research Society, Boston,, Nov. 27-Dec. 2, 1989.

AMORPHOUS METALLIC ALLOYS FORMED BY PLASMA ION MIXING.* Xiaoci Zheng, R. Arthur Dodd, John R. Conrad, and Frank Worzala, University of Wisconsin, Madison, Wisconsin.

When plasma ions interact with layered Ni-based metallic films, the structures resulting from the ion-surface reactions vary with the ion dose and ion mass. For light ions, smaller grains are formed after plasma ion mixing, but no amorphous structure is observed. For heavy ions, an amorphous phase is obtained as long as the dose is larger than a critical value. The film structures are checked by TEM and electron diffraction.

The stability of the amorphous phase has been investigated by annealing the samples at various temperatures, and recrystallization is observed when the annealing temperature is above T_R. The grain sizes of recrystallized films are dependent on the annealing time.

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