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CARBON, NITROGEN, AND OXYGEN ION IMPLANTATION OF STAINLESS STEEL

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ABSTRACT

Ion implantation experiments of C, N and O into stainless steel have been performed, with beam-line and plasma source ion implantation methods. Acceleration voltages are varied between 27 and 50 kV, with pulsed ion current densities between 1 and 10 mA/cm². Implanted doses range from 0.5 to 3×10^{18} cm⁻², while workpiece temperatures are maintained between 25 and 800°C. The implant concentration profiles, microstructure and surface mechanical properties of the implanted materials are reported.

INTRODUCTION

Ion implantation of light elements has proven to be an effective technique to improve the tribological properties of metals. Stainless steel is a particularly interesting material to study since many of the constituent atoms such as chromium readily form covalently bonded compounds with the implanted ions, resulting in increased surface hardness, reduced friction, and altered microstructure. [1-5] In addition, implantation at elevated temperature often results in deeper modified surface layers which exceed the ballistic range of the implanted ions by an order of magnitude or more. Nitrogen implantation into stainless steel at elevated temperature is a hybrid implantation-nitriding process which results in a nitrogen-enriched outer surface with increased hardness due to higher N concentrations (20-30% at) in solid solution when compared with traditional ion and gas nitriding. [1-2] Carbon implantation is of interest since it readily forms carbides with iron which are often amorphous when there is a sufficient implant dose. [4,5] There is little data published on carbon implants at elevated temperature, and on oxygen implantation of stainless steel. In this paper we report preliminary experimental results to study the effect of C, N, and O implantation into stainless steel. Both beam implantation and plasma source ion implantation methods have been used.

EXPERIMENT

Implantation experiments were performed on two devices, a high-current-density, pulsed beam-line ion implanter at the Institute of Electrophysics (IEP) [6], and a plasma source ion implantation device (PSII) at Los Alamos National Laboratory (LANL) [7]. Neither apparatus utilized mass analysis or selection of the implanted ions. The IEP implanter used a magnetically-confined, hollow-cathode glow discharge ion source, created from a C₃H₈, N₂, or O₂ background gas. Ions were accelerated to 30 keV and extracted at current densities between 1 and 10 mA/cm² over 1 ms pulses at a repetition rate between 0 and 50 Hz. Base pressures of order 10⁻⁵ torr were obtained with an oil diffusion pump. During implantation, a pressure of 3 to 6×10⁻⁴ torr was measured near the workpiece (located 0.20 m from the accelerator grids)

due to diffusion of gas from the ion source. High temperature implants were achieved by employing the ion beam itself to heat the workpiece.

The LANL device was operated at 27-50 kV, $j = 1-4 \text{ mA/cm}^2$ at the workpiece over a 20- μs pulsewidth and 500-2000 Hz pulse repetition rate. Workpiece temperatures were controlled by adjusting the repetition rate. Gas sources included N_2 , NH_3 , or CH_4 introduced at $3-5 \times 10^{-4}$ torr. Plasmas were created with a 500-900 W, 13.56 MHz, capacitively-coupled rf source.

Workpieces consisted of cold-rolled stainless steel coupons, type 12Kh18N10T (comparable to AISI 321), composed of 0.12% (wt) C, 18% Cr, 10% Ni, 0.7% Ti, 1-2% Mn. They were polished with diamond paste to a surface roughness of 150 nm or less. X-ray diffraction (XRD) of unimplanted samples revealed primarily a FCC γ phase with lattice parameter of 0.359 nm, with relatively small concentrations ($< 3\%$) of α phase. Implanted doses ranged between 0.5 to $3 \times 10^{18} \text{ cm}^{-2}$. Workpiece temperatures were maintained between 25 and 800°C .

The composition and microstructure of the implanted materials were examined with XRD, Rutherford backscattering (RBS), and nuclear reaction analyses (NRA) of the $^{12}\text{C(d,p)}^{13}\text{C}$, $^{14}\text{N(d,\alpha)}^{12}\text{C}$, and $^{16}\text{O(d,p)}^{17}\text{O}$ reactions with a 0.9-MeV deuteron beam, and with a 8.9 MeV alpha particle beam. Depth profiles of the implanted nitrogen were calculated after comparing the measured NRA spectrum with that produced by a $\text{TiN}_{0.82}$ reference specimen. X-ray photoelectron spectroscopy (XPS) was also used to infer depth profiles. Carbon and oxygen profiles were similarly determined with U8 steel and Ta_2O_5 reference materials, respectively. Vickers microhardness was measured at both 50 and 200 g loads, with indent depths ranging between a few tenths to several microns, depending on microhardness. More sensitive surface nanohardness and modulus measurements at depths between 20 to 800 nm from the surface were made with a Nano-Indenter[®] II [8]. Wear properties were investigated with pin-on-disk test with a 6-mm diameter ruby pin, a sliding speed of 0.94 m/min, a wear track diameter of 3 mm, and in a 10% relative humidity atmosphere. Samples were tested with a load of 27 g and contact stress of 533 MPa. The yield strength of the untreated stainless steel is 200 MPa, so the conditions chosen resulted in highly accelerated wear.

RESULTS

Implant distribution profiles as determined from RBS and NRA are plotted in Figs. 1 and 2. At elevated temperatures, relatively deep penetration (when compared to the $< 100 \text{ nm}$ ballistic ion range) of the C and N are observed. A dramatic change in the C profile is observed between $T = 390^\circ\text{C}$ and 480°C . Examination of N profiles obtained with the same implanted dose ($1 \times 10^{18} \text{ cm}^{-2}$) but with pulse ion current densities of 3 and 10 mA/cm^2 reveal different spectra (Fig. 1). A lower concentration of N is observed at 10 mA/cm^2 which was implanted at 765°C , when compared with the 3 mA/cm^2 implant which was performed at 613°C . These results suggest an increased diffusion coefficient for the 10 mA/cm^2 case, which may be attributed to the increased temperature and/or radiation induced phenomena associated with the high current density. [2]

An RBS spectrum of a nitrogen PSII implant dose of $1 \times 10^{18} \text{ cm}^{-2}$ at 325°C for 1.25 hours is shown in Fig. 2. The spectrum indicates the presence of approximately $1 \times 10^{17} \text{ atom/cm}^2$ oxygen on the surface which is probably due to surface oxidation during the high temperature implant. No evidence of oxygen implantation was detected. The retained nitrogen dose is $5.9 \times 10^{17} \text{ cm}^{-2}$ with a profile extending to a depth of about 540 nm. The profile depth exceeds the ion range at 40 keV, which is about 60 nm, and confirms the positive effect often observed with high temperature implantation for a PSII process. [1,3]

Depending on temperature, the carbon implant profiles extend several microns into the samples, well beyond the ballistic range, and appear to be deeper than the nitrogen implants performed at similar temperatures. XPS analyses of ceramic coupons placed near the workpiece reveal a thin deposited carbon layer atop the implant that is graphitic with an approximately 15% concentration of the diamond-like carbon phase.

Oxygen implants show no evidence of diffusion, but rather, are confined to a near surface of order 100 nm thick, comparable to the ion range. For a $1 \times 10^{18} \text{ cm}^{-2}$ oxygen implant, the retained dose increases from $0.19 \times 10^{18} \text{ cm}^{-2}$ at $T = 377^\circ\text{C}$ to $0.45 \times 10^{18} \text{ cm}^{-2}$ at 710°C , presumably because of increased surface oxidation at the higher T .

XRD indicates that an interstitial solid solution is formed. A lattice parameter of the FCC structure changes from an initial value of 0.359 nm to 0.367 nm with C implantation. A transformation from γ to α phase is observed, accompanied by the appearance of BCC (ferrite) and tetragonal (martensite) structures (Fig. 3), depending on temperatures. The N concentration are close to their maximum values for a solid solution of N in $\gamma\text{-Fe}$.

Vickers hardness H_v data for the beam-line implants are shown in Fig. 4. These measurements represent indent depths of order 1 μm . For the virgin samples, the 20 and 200 g loads resulted in indent depths δ of 0.7 and 7 μm , respectively, corresponding to a microhardness of about 200 kg/mm^2 .

Fig. 1: Implant concentration profiles of beamline implants determined by NRA.

Fig. 2: RBS profile of a PSII nitrogen implant at 325°C .

For hardened surfaces of 1500 kg/mm², δ was 0.5 μ m at 100 g. For low temperature carbon implants, $T < 400^\circ\text{C}$, there was no measurable change in H_v . As T was increased from 400° to 600°C , one observed an approximate doubling of H_v . The highest H_v were obtained at C_3H_8 implant doses of $3 \times 10^{18} \text{ cm}^{-2}$ and intermediate temperatures. There was no clear correlation in H_v with C ion current density the observed changes in phase microstructure, although the highest H_v was observed when there was an interstitial solid solution of carbon without precipitates (*i.e.*, when the $\gamma \rightarrow \alpha$ transformation did not occur). Changes in H_v due to the heat treatment were examined by indenting the back (untreated) sides of the implanted samples and found to be less than 10%. H_v of the N implants also increased with T to approximately a factor of two. At the highest temperatures, $T > 750^\circ\text{C}$, H_v decreased. In contrast to the C and N implants, oxygen implantation resulted in no discernible change in H_v .

The Vickers hardness measurements were confirmed with nanoindentation (Fig. 5). The nanohardness H_n of unimplanted sample is found to be approximately 4 GPa, with a 100-nm-thick, 8-GPa outer layer, presumably due to a surface oxide. Significant increases in H_n at low temperatures, $T < 400^\circ\text{C}$, which could not be detected in the Vickers tests because of the deep indents, are evident for both the carbon and nitrogen implants, with little change in the modulus, indicative of an increase in surface toughness. At relatively low temperatures, the carbon implanted samples may show a small increase in H_n of about 10% over a 50-100 nm surface layer. Substantial hardening is evident at $T = 375^\circ\text{C}$, with H_n values of 13 GPa, again extending over a shallow surface

Fig. 3: X-Ray diffraction (XRD) spectra.

Fig. 4: Vickers hardness H_v data obtained at 20 g load for C, N, and O implantation at a variety of pulsed ion current densities and substrate temperatures.

layer. Substantially deeper cases are observed starting at $T \approx 500^\circ\text{C}$, which is sometime accompanied by a soft outer skin (≤ 400 nm), possibly corresponding to the aforementioned graphitic surface film that occurs during the C implants. At the highest temperatures, however, of 770°C or greater, a more modest increase in H_n over a deeper case is observed. For nitrogen implants at $T \approx 100^\circ\text{C}$, a modest increase in H_n of about 10% is observed over a relatively shallow case of less than 100 nm. The highest H_n of 16 GPa is observed at the intermediate temperature $T \approx 400^\circ\text{C}$, over a somewhat deeper case depth, indicative of a modest level of diffusion induced by the elevated temperature. At the highest temperatures, $T = 670 - 860^\circ\text{C}$, up to $3\times$ increases in H_n is observed over a $1\text{ }\mu\text{m}$ depth or more, consistent with the Vickers measurements.

Virtually no changes in H_n were detected in the oxygen-implanted samples (Fig. 5). Within 100 - 200 nm from the surface, H_n decreases from about 8 GPa to 4 GPa similar to the virgin sample, and again indicative of a surface oxide. The hard surface layer does not extend into the sample at the elevated temperatures, consistent with the NRA data. A slight increase over the outer 100 nm might be discernible at $T = 455^\circ\text{C}$. The hardened outer layer disappears at the highest temperatures accompanied by a $2\times$ decrease in modulus.

The pin-on-disk wear test data for the $1\times 10^{18}\text{ cm}^{-2}$ -implanted-nitrogen-dose samples are plotted in Fig. 6. The wear rate for unimplanted steel was $31 \pm 9 \times 10^{-6}\text{ mm}^3/\text{N}\cdot\text{m}$. The implants performed at 100 and 860°C had wear rates that were 40% of that of the unimplanted material. The $T=380^\circ\text{C}$ implant had the lowest wear rate, two orders of magnitude smaller than the unimplanted material, consistent with the highest H_n data in Fig. 5. Wear testing was terminated when the implanted zone had worn through, so the quoted wear rates represent the wear resistance of the implanted zone. Wear tests of the $T=380^\circ\text{C}$ implanted sample with the 81 g load resulted in rapid wear through of the implanted region. Optical microscopy of the wear tracks indicated a predominately abrasive wear mechanism for all samples.

CONCLUSIONS

Ion implantation experiments were performed with C, N, and O ions implanted into stainless steel over a wide range of temperatures, current densities, using both beam line and plasma source ion implantation techniques. Significant increases in the surface hardness were observed in only the nitrogen and carbon implants. Highest increases occurred at intermediate temperatures of 400 to 500°C , with case depths of 5 to 10 times the ballistic ranges. Improvements in wear up to $100\times$ were observed. Deeper penetration of both C and N were found at higher temperatures, but with reduced improvement in surface hardness. In contrast, elevated temperatures did not increase the implanted oxygen depth. Moreover, oxygen implantation at any temperature did not lead to improved hardness. A more detailed account of these experiments will soon follow in a journal manuscript.

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Fig. 5: Nanohardness H_n for C, N, and O implants performed at a variety of temperatures.

Fig. 6: Pin-on-disk wear rates of the beamline nitrogen implanted samples.

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