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Nitrogen and Boron Ion Implantation into Electrodeposited Hard Chrome

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ABSTRACT

Electrodeposited hard chrome has been ion implanted with nitrogen alone, boron alone, and a combination of nitrogen and boron. Separately, nitrogen and boron implantation was done at 75 keV and incident doses of 2, 4, and 8×10^{17} at/cm^2. Samples implanted with both nitrogen and boron used beam energies of 75 keV and incident dose levels of 4×10^{17} N-at/cm^2 and 4×10^{17} B-at/cm^2. All ion implantations were accomplished using a beam-line system. The retained dose was measured using ion beam analysis. Surface hardness, wear coefficient and the coefficient of friction were determined by nanohardness indentation and pin-on-disk wear testing of each sample. Ion beam analysis indicated a majority of the incident dose was retained. At a depth of 50 nm, the surface hardness increased from 18±1 GPa for unimplanted chrome, to a maximum of 23±4 GPa for boron implanted chrome and 26±1 GPa for nitrogen implanted chrome. Pin-on-disk wear testing indicated reductions in the wear coefficient by factors of 1.3x to 7.4x depending on the implantation treatment. It is shown that nitrogen implantation of chromium results in lower wear coefficients than boron implantation.

INTRODUCTION

The goal of this work is to describe the potential for using ion implantation to increase the wear resistance of electrodeposited hard chromium, or hard Cr-plating, which is commonly used as a wear resistant surface in the metal-forming and agricultural industries. Increased wear resistance of hard chromium would reduce chromium consumption in the electrodeposition industry and impact both strategic and environmental interests. Cr is considered a strategic metal because of its use in metal alloys, especially steels and other alloys [1]. Hard chromium electrodeposition processes use wet chemical baths containing the hexavalent chromium ion, Cr^{+6}, some of which is emitted into the environment as effluent or sludge. In the United States, Cr^{+6} is classified as a confirmed human carcinogen, and is thus being placed under strict emission controls. By reducing the amount of hard Cr electrodeposition, the amount of Cr^{+6} emitted into the environment can be proportionately reduced. Thus, using ion implantation to improve the wear resistance of electrodeposited hard Cr can have a positive impact on both strategic and environmental issues associated with the use of Cr.

A detailed discussion of the many estimates of chromium use in the US and Europe is beyond the scope of this work. The estimates for the US are best summarized by stating that the US consumes approximately 5.3×10^8 kg (580,000 tons) of Cr each year with about 4.1×10^6 kg/yr (4500 tons/yr) being used for hard Cr plating, about 10^6 kg/yr (1125 tons/yr) being used for decorative Cr, and the balance being used in chemicals and metal alloying. Some estimates of Cr use within the US are an order of magnitude higher. If we assume that ion implantation can increase the lifetime of hard Cr by 5x and 50% of hard Cr plated components can benefit from ion implantation, Cr consumption can be reduced by 1.8×10^6 kg/yr (1940 tons/yr). Assuming 5% of the Cr used in electrodeposition is introduced into the environment, the amount of Cr^{+6} discharged could be reduced by 8.8×10^4 kg/yr (97 tons/yr). If all the Cr was discharged in sludge (which is 24.4 wt% Cr [2]), sludge production could be reduced by 3.6×10^5 kg/yr (400 tons/yr). So by improving the wear resistance of a fraction of the Cr-plated parts by a conservative amount, a significant amount of Cr could be saved and the amount of Cr discharged into the environment could be reduced.

The increased surface hardness and wear resistance of electrodeposited hard Cr as a result of nitrogen ion implantation has been repeatedly demonstrated [1-16]. The improvements are consistently attributed to the formation of the hard chromium-nitride compounds, CrN and Cr_2N. However, relatively little work has been done on carbon [17-18], oxygen [15,17], or boron implantation. The limited amount of work [15] directly comparing carbon, oxygen and nitrogen implantation indicate nitrogen gives Cr superior wear resistance. The purpose of this work is to directly compare the effects on wear of chromium by boron implantation, which should also form hard compounds with chromium [19], and nitrogen implantation.

EXPERIMENTAL DETAILS

A 1000 cm^2 sheet of 304 stainless steel was diamond polished and then Cr-plated by a commercial vendor. The coating thickness varied from 2 to 4 μm across the sheet. The sheet was cut into smaller samples approximately 2 x 2 cm in size. The deposited Cr surface had a maximum R_a of 0.05 μm and an average peak-to-valley height of 0.2 μm. The composition of the Cr-plate, as determined by ion beam analysis, was 96.6 at% Cr, 2.5 at% O, and 0.9 at% H. Ion implantation was accomplished using a Varian CF3000 beamline implanter . Nitrogen beams were generated from N_2 gas. Boron beams were generated by flowing CCl_4 over boron powder in a crucible heated to 600°C. In both cases, a 75 keV ion energy was used. The ion range in chromium for nitrogen is 88±44 nm, and the ion range for boron is 122±57 nm. Samples were kept near 30°C during implantation. Ion beam analysis was used to measure the retained ion dose for each sample. Non-Rutherford backscattering spectrometry was utilized to take advantage of the increased nitrogen and boron cross-sections under certain conditions [20]. In all cases, ion beam analysis was done using a 3 MV tandem accelerator, an incident He^{++} beam that was normal to the sample surface, a scattering angle of 167°, and collected charges of 4 to 7 μC. The reactions $^{14}N(\alpha,\alpha)^{14}N$ at 8.86 MeV, and $^{11}B(\alpha,\alpha)^{11}B$ at 6.63 MeV were used to give 75x and 92x enhancements in the N and B cross-sections, respectively. The error in the retained dose measurements is ±10%. The hardness of the unimplanted and implanted surfaces were determined using a NanoIndentor® II operated in the continuous stiffness mode. Hardness and modulus data were collected at five to eight locations on single samples for each implantation condition. Reported values of hardness and modulus consist of average values of the multiple measurements. Pin-on-disk wear tests were performed using a smooth, single crystal 6 mm diameter ruby (Al_2O_3:Cr) ball, 50% relative humidity, 1.1 N load, a Hertzian contact stress of 955 MPa, a sliding speed of 3.1 cm/sec, a track diameter of 3 mm, and a testing time of 1 hour. The 1.1 N load was chosen so the Herztian contact stress would be much less than the estimated yield stress of hard Cr (~ 5 GPa) and plastic deformation would play a small role in the predominantly abrasive wear process. The tangential force on the pin was measured using a load cell, and the coefficient of friction was calculated and stored electronically throughout the test. Between three and six tests were conducted on multiple samples for each implantation condition. The cross-sectional area of the wear track, at four equidistant locations around the track, was measured using a surface profilometer. The depth of the wear tracks never exceeded 500 nm, but routinely exceeded the implantation depth. The wear coefficient, K=(track volume)/(load•wear distance), was calculated for each location on each track.

RESULTS AND DISCUSSION

The results of the ion beam analysis and POD wear tests are compiled in Table 1. The hardness and modulus results for unimplanted chromium, and the N and B implanted samples exhibiting the best wear resistance are shown in Fig 1a and 1b, respectively. There is a prominent peak in the near-surface region that probably corresponds to a surface oxide on the chromium. The hardness peak due to the surface oxide is smaller, and shallower, than all hardness improvements measured on the ion-implanted samples. At a depth of 50 nm, the surface hardness increased from 18±1 GPa for unimplanted chrome, to a maximum of 23±4 GPa for boron implanted chrome and 26±1 GPa for nitrogen implanted chrome. The modulus is unaffected by ion implantation.

The wear coefficient ratio, calculated by dividing the average wear coefficients of unimplanted Cr by that of the ion implanted Cr, of all samples are shown in Fig. 2. The wear results indicate that (1) boron implantation does not produce superior wear resistance to nitrogen implantation, (2) combining boron and nitrogen implantation results in little additional benefit over nitrogen implantation alone, (3) a retained nitrogen dose of 7.3×10^{17} N-at/cm^2 is needed to improve the wear rate of chromium by 5x, and (4) the wear resistance maximizes at a retained boron dose of about 4×10^{17} at/cm^2, but increases with increasing amounts of retained nitrogen. Using the ion dose and ion straggling to estimate the peak atomic concentration for the implanted species [21], the best wear resistance for nitrogen implanted and boron implanted samples correspond to peak concentrations of 44 at%N and 24 at%B. Representative data for the coefficient of friction of unimplanted and selected implanted samples is shown in Fig. 3. Nitrogen implantation reduces the coefficient of friction slightly more than boron implantation, but the reduction is not believed to be significant.

CONCLUSIONS

The primary goal of this work was to demonstrate an ion implantation process that could increase the wear resistance of hard Cr-plate by 5x, thus reducing the amount of Cr used in hard Cr-plating and the amount of Cr^{+6} emitted into the environment. A secondary goal was to compare the effects of boron and nitrogen implantation on the wear resistance of hard Cr. Under the conditions of this study, 75 keV nitrogen implantation with a retained dose of 7.3×10^{17} at/cm^2 increased the wear resistance by a factor of 7.4±2.7x. The increased wear resistance is correlated with an increased surface hardness. Boron implantation alone did not result in comparable increases in wear resistance, although a boron dose of 3.8×10^{17} at/cm^2 reduced the wear coefficient by 2.1±0.7x. No additional improvement in wear resistance is observed if nitrogen implantation is followed by boron implantation, or vice versa.

ACKNOWLEDGMENTS

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Figure Captions.

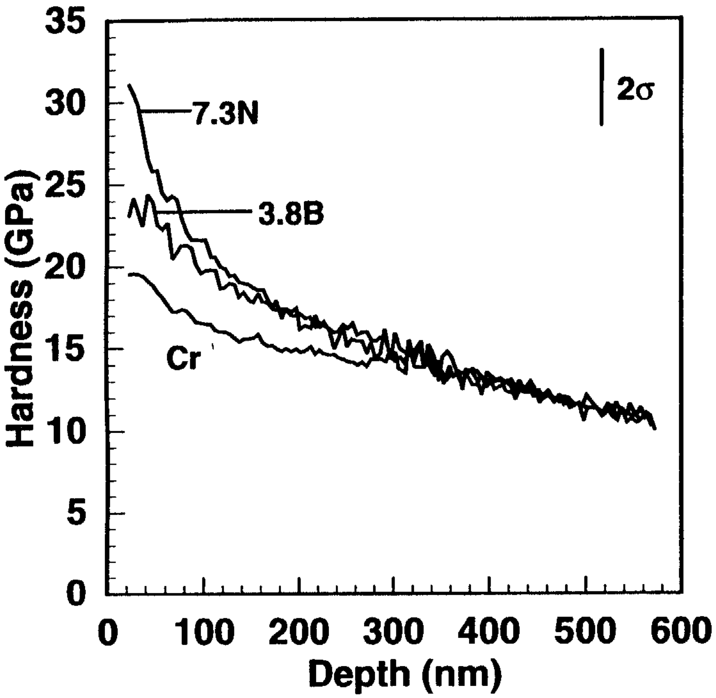
Fig. 1. Hardness (a) and elastic modulus (b) of unimplanted and selected ion implanted chromium. The hardness data for the boron (B) implanted sample with a retained dose of 3.8×10^{17} at/cm^2 and for the nitrogen (N) implanted sample with a retained dose of 7.3×10^{17} at/cm^2 are shown. The error bars result from averaging five to eight measurements. Nitrogen implantation produces a harder surface than boron implantation.

Fig. 2. Wear coefficient ratios for unimplanted and ion-implanted samples. The ratio is calculated by dividing the average wear rate for unimplanted Cr by that for the ion-implanted Cr. The labels, such as "1.8B", indicate a boron (B) implanted sample with a retained dose of 1.8×10^{17} at/cm^2. Only the 7.3N sample meets the criteria of reducing the wear coefficient by a factor of 5x, represented by the horizontal line.

Fig. 3. Coefficient of friction traces for typical wear tests of unimplanted, boron-implanted, and nitrogen-implanted chromium. The coefficient of friction is not significantly reduced by ion implantation. The numbers indicate the retained ion dose in 10^{17} at/cm^2.

Table 1. Compilation of retained dose measurements and tribological testing of 75 keV nitrogen and boron implanted chromium. "K" is the wear coefficient. The row labeled "Cr" includes results for unimplanted chromium. The rows labeled "Cr", "B:N" and "N:B" includes results for unimplanted chromium, chromium implanted with boron followed by nitrogen, and chromium implanted with nitrogen followed by boron, respectively.

Ion Species	Retained Dose (10^{17} at/cm^2)	Average K (10^{-6} mm^3/Nm)	Coefficient of Friction
Cr	---	2.4±0.5	0.8
N	1.2	1.1±0.3	0.7
N	1.7	0.7±0.2	---
N	3.7	0.6±0.1	0.65
N	7.3	0.3±0.1	0.65
B	1.8	1.6±0.5	0.7
B	3.8	1.1±0.3	0.75
B	6.7	1.8±0.5	0.8
B:N	3.3 B:4.2 N	0.6±0.2	0.6
N:B	3.9 N:3.0 B	0.8±0.1	0.85



35
30
25
20
15
10
5
0
Hardness (GPa)
0
100
200
300
400
500
600
Depth (nm)
7.3N
3.8B
Cr
2σ

FIG 1A

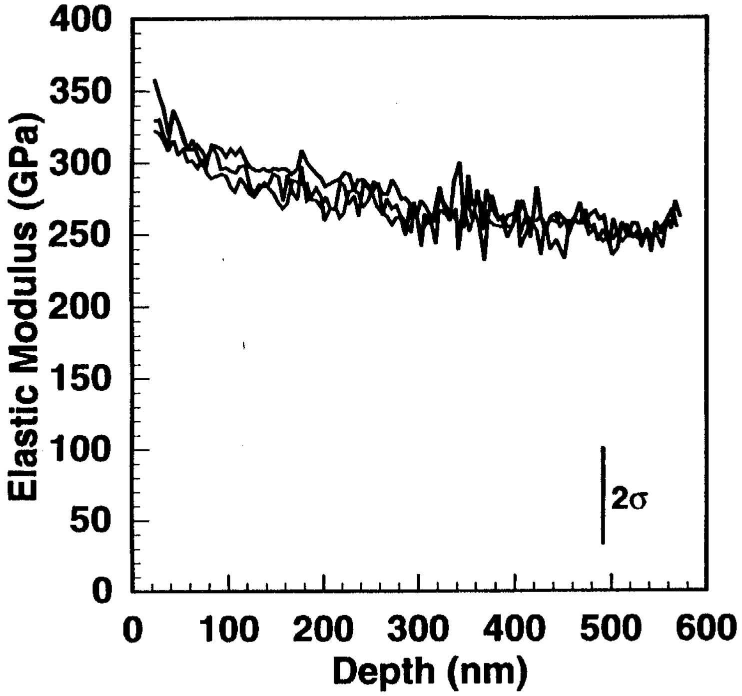
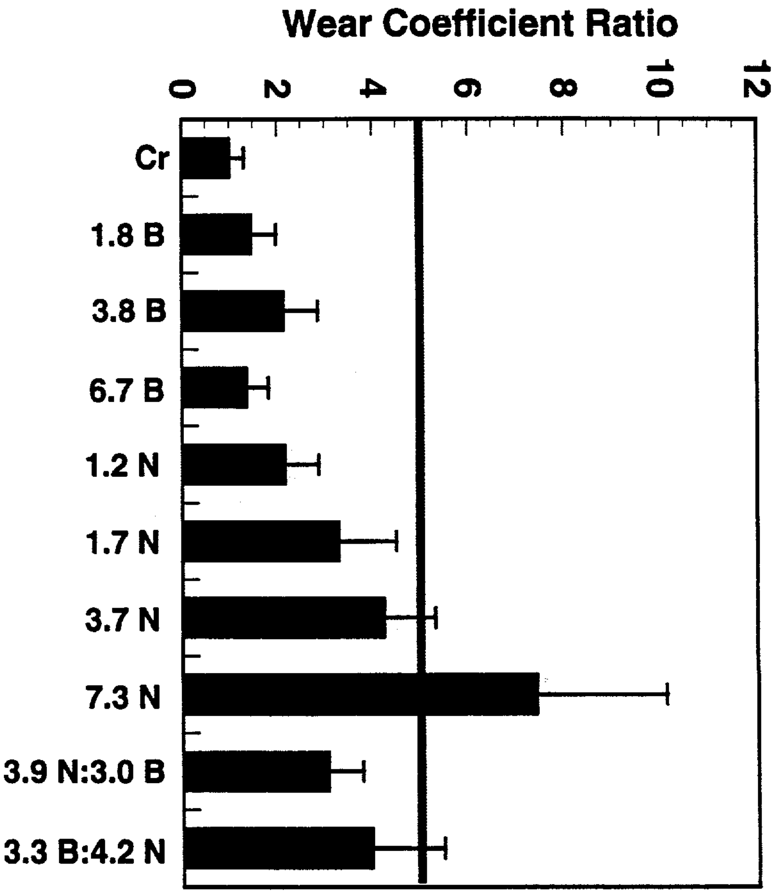

400
350
300
250
200
150
100
50
0
Elastic Modulus (GPa)
0
100
200
300
400
500
600
Depth (nm)
2σ

FIG 1B

FIG 2



Wear Coefficient Ratio
0
2
4
6
8
10
12
Cr
1.8 B
3.8 B
6.7 B
1.2 N
1.7 N
3.7 N
7.3 N
3.9 N:3.0 B
3.3 B:4.2 N

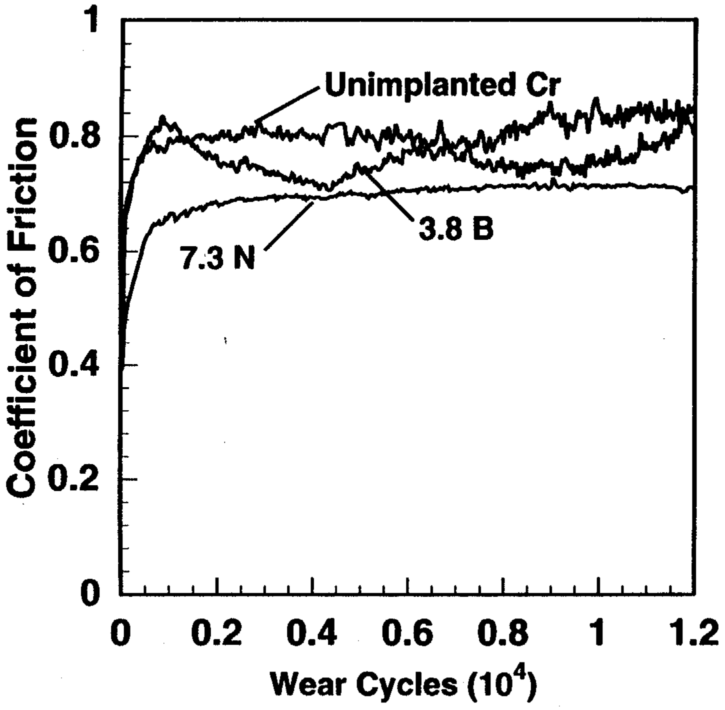

Unimplanted Cr
3.8 B
7.3 N
Coefficient of Friction
0
0.2
0.4
0.6
0.8
1
0
0.2
0.4
0.6
0.8
1
1.2
Wear Cycles (10^4)

FIG 3