

*Title:* **ADVANCES IN PSII TECHNIQUES FOR SURFACE  
MODIFICATION**

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## **ADVANCES IN PSII TECHNIQUES FOR SURFACE MODIFICATION**

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### **ABSTRACT**

Recent activities in plasma source ion implantation (PSII) technology include scale-up demonstrations for industry and development of variations on the original PSII concept for surface modification. This paper presents an overview of the continued growth of PSII research facilities world-wide and the industrial demonstrations within the U.S. In order to expand the applicability of PSII, Los Alamos is actively researching a PSII-related technique called plasma immersion ion processing (PIIP). In one case, a pulsed-biased target can be combined with cathodic arc sources to perform ion implantation and coating deposition using metal plasmas. Erbium plasmas have been combined with oxygen to deposit erbia ( $\text{Er}_2\text{O}_3$ ) coatings that are useful for containment of molten metals. In a second case, hydrocarbon, inorganic, and organometallic gases are utilized to create a graded interface between the substrate and the coating that is subsequently deposited using pulsed-bias techniques. PIIP represents a significant advance since it allows coating deposition with all the strengths of the original PSII approach. Diamond-like carbon (DLC) and boron-carbide are two such coatings that will be highlighted here tribological applications.

## **Introduction**

Since development of plasma source ion implantation (PSII) began at the University of Wisconsin-Madison in 1986 [1], interest in this versatile surface modification technique has continued to increase. The total number of operational PSII facilities (Fig. 1) has been doubling every two years and is now approaching 50, with some locations having more than one operational system. Between 1986 and 1993, a majority of operational PSII systems were in the United States. The period of 1991 to 1994 saw the initial operation of almost all of the known systems in Asia. More recently a few European countries, especially Germany, have increased their research efforts in PSII. The number of variations on the original PSII theme, which was limited to ion implantation, have also grown to include coating deposition and interface engineering.

PSII research initially concentrated on nitrogen implantation to improve the wear resistance of metals [2], but later evolved to include research on increasing the wear and corrosion resistance of Ti-6Al-4V [3] and other ion implantation processes for the semiconductor industry [4-5]. Despite promising laboratory results in the tribological and corrosion fields, potential applications of PSII were still limited by the inherent shallowness of ion implanted surface layers (<200 nm). In response, PSII research began to combine ion implantation with coating deposition [6]. It was also noted that hydrocarbon gases could be utilized in a PSII process to produce hydrogenated diamond-like carbon (DLC) coatings [7]. In an effort to improve the adhesion of DLC coatings on metals, PSII has been utilized to create a compositionally graded interface [8] between DLC and many different metals [9]. The successful use of PSII to coat ~3 m<sup>2</sup> with DLC and implant ~4 m<sup>2</sup> with nitrogen has been demonstrated [10]. This paper will highlight some of the recent efforts to use PSII to improve the wear resistance of electrodeposited hard Cr coatings and S7 tool steel through nitrogen implantation, for DLC deposition [9], for the deposition of adherent coatings of erbia onto stainless steel [11], and for the use of diborane and acetylene to deposit boron-carbide coatings.

## **Experimental**

### N implantation of Cr and S7

Coupons of 304 stainless steel were polished and then Cr-plated by a commercial vendor. The Cr-plated surface had a maximum  $R_a$  of 0.05  $\mu\text{m}$  and an average peak-to-valley height of 0.2  $\mu\text{m}$ . 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. Coupons, approximately 2 x 2 x 0.1 cm, were PSII treated with nitrogen using ammonia ( $\text{NH}_3$ ) as the nitrogen source, a 45 kV bias, and a retained nitrogen dose to  $2.9 \times 10^{17}$  N-at/ $\text{cm}^2$ . The retained N-dose was measured using ion beam analysis and the reaction  $^{14}\text{N}(\alpha, \alpha)^{14}\text{N}$  at 8.86 MeV. The distribution of nitrogen in the Cr surface was inferred by measuring the decrease in the Rutherford Backscattering Spectrometry (RBS) spectra for Cr. All ion beam analysis was performed using a 3 MV tandem accelerator, an  $\alpha$  particle beam, a scattering angle of  $167^\circ$ , and collected charges from 6 to 20  $\mu\text{C}$ . The hardness and modulus of the unimplanted and implanted surfaces were measured at multiple locations using a NanoIndenter<sup>®</sup> II operated in the continuous stiffness mode. The reported values are averaged from multiple measurements. Pin-on-disk wear tests were performed using a smooth, single crystal 6 mm diameter ruby ( $\text{Al}_2\text{O}_3:\text{Cr}$ ) 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 one hour. The coefficient of friction was calculated by measuring the tangential force on the pin through a load cell. Multiple wear tests were performed on each sample. The cross-sectional area of the wear track, at four equidistant locations around the track, was measured using a surface profilometer. The wear coefficient [12],  $K=(\text{track volume})/(\text{load} \cdot \text{wear distance})$ , was calculated for each location on each track. The results are compared to beamline implanted Cr that is discussed in detail elsewhere [13].

Nitrogen was implanted into an AISI-S7 forming tool using  $\text{N}_2$  gas and a PSII process. The implantation bias was 50 kV and the incident dose was  $3 \times 10^{17}$  N-at/ $\text{cm}^2$  at ambient temperature. The tools were provided and tested by A.O. Smith Corporation (Milwaukee, Wisconsin, USA). The unimplanted and implanted tools were used for the production of a low carbon steel part.

### Coating deposition for liquid metal containment

A cathodic arc source can be used to make a plasma out of a metal that can then be utilized in a PIIP process [11]. An erbium cathode was used to make an erbium plasma consisting of  $\text{Er}^{+2}$  and  $\text{Er}^{+3}$  ions. Pulse-biasing the 304L stainless steel target at -20 kV, resulted in an effective implantation bias of -40 to -60 kV and produces a compositionally graded interface. Adding 0.2 mTorr of oxygen ( $\text{O}_2$ ) into the vacuum chamber allows deposition of a  $\text{Er}_2\text{O}_3$  coating. X-ray Photoelectron Spectroscopy (XPS) depth profiles were obtained by intermittently sputtering the surface of the sample with argon and taking spectra for specified elements in between the sputtering steps. The spectra were combined, using established data analysis techniques and tabulated sensitivity factors, to produce a concentration depth profile. The adhesion of the erbia coating to 304L was tested by depositing the coating into a shallow cup and using a Charpy impact tester to dent the cup inside out, putting the coating in tension. Scanning electron microscopy (SEM) was used to determine the microstructure of the coating on the dented surface.

Ceramic coatings can also be deposited by a hybrid PSII/IBAD process [6]. Ceramic coatings deposited onto H13 can be used to reduce the heat checking, erosion, and soldering that occurs during die-casting of aluminum. Proprietary coatings were deposited onto core pins for testing in an Al die-casting operation.

### Adherent DLC coatings on metals

A PIIP process that has been described in detail elsewhere [8-9] has been used to deposit adherent DLC coatings on many metals ranging from Mg to W. The importance of the ion implantation step in promoting DLC adhesion was measured by depositing identical coatings on two samples, one with an ion implantation treatment, and one without. The ion implantation step utilized a PSII process, 0.07 Pa (0.5 mTorr) of methane ( $\text{CH}_4$ ) gas, a 50 kV pulse bias, and a incident dose of  $\sim 5 \times 10^{17}$  ions/cm<sup>2</sup>. After implantation, the surface was briefly sputter cleaned

to remove any graphitic C-layer that could interfere with coating adhesion. The adhesion strength of coatings was measured in tension using the Sebastian<sup>®</sup> II stud pull test.

### Deposition of boron-carbide coatings

A PIIP process using a mixture of 15% diborane ( $B_2H_6$ ) diluted in helium (He) and acetylene ( $C_2H_2$ ) has been used to deposit boron-carbide coatings. A plasma was generated from the gas mixture by applying a pulsed voltage to the sample stage. A plasma is generated spontaneously during the pulse. The pulsed bias magnitude was 4 kilovolts, the pulse duration was 30 microseconds, and the pulse frequency was 4 kilohertz. Silicon (Si) and molybdenum (Mo) substrates were coated at room temperature. Ion beam analysis techniques were used to determine the coating composition. The hardness and modulus of the coatings were measured at ten locations using a NanoIndenter<sup>®</sup> II operated in the continuous stiffness mode. The reported values are averaged from the multiple measurement. Pin-on-disk wear tests were performed on the coated Si substrates using a smooth, 6 mm diameter 52100 ball, 50% relative humidity, loads from 0.2 to 0.4 N, a Hertzian contact stress from 360 to 460 MPa, 120 rpm, and a track diameter of 3 mm. The coefficient of friction was calculated by measuring the tangential force on the pin through a load cell.

## **Results**

### N implantation of Cr and S7

The hardness of the PSII treated sample is shown in Fig. 2. The hardness at 50 nm increases from 17 GPa for the unimplanted Cr to 21 GPa after N implantation using PSII. The surface is softer than beamline implanted Cr, which has a hardness of 26 GPa at 50 nm. Note also that the hardness increase for the beamline implanted sample extends to a greater depth than the PSII implanted sample because the implantation energy was 75 keV [13]. The coefficient of friction measurements are shown in Fig. 3. Note that the PSII N-implanted sample has the lowest coefficient of friction. The ratio of the wear coefficients are plotted in Fig. 4. The wear coefficient for unimplanted Cr was  $2.4 \pm 0.5 \times 10^{-6}$  mm<sup>3</sup>/Nm. Both N-implanted samples have

approximately equivalent reductions in the wear coefficient and show increased wear resistance by factors of 7-10x. Fig. 5 shows the N-depth profiles as indicated by the reduction in the Cr signal intensity, the implications of which are described fully in the Discussion section.

Unimplanted S7 tools normally stamped 50 low carbon steel parts before exhibiting galling. The PSII treated tool stamped 480 parts before exhibiting galling. This represents an improvement of ~10x.

#### Coating deposition for liquid metal containment

The XPS depth profile for erbia coated 304L is shown in Fig. 6. The XPS spectra for erbium (not shown) indicated the element is completely bound as  $\text{Er}_2\text{O}_3$  and the complete absence of erbium metal. There was ~12at% carbon at the interface (not shown in the profile for clarity) that resulted from insufficient sputter cleaning. The profile indicates diffusion of iron and chromium into the erbia coating. No diffusion of nickel is indicated. Although nickel and iron form intermetallics with erbium, it is speculated that the higher enthalpies of formation for the iron and chromium-oxides drive the transport of iron and chromium, but not nickel. The profile also indicates the presence of erbium and oxygen beneath the steel surface and is indicative of the high voltage implantation of these elements. The implantation depths of 40 keV and 60 keV erbium ions into iron are about 10 and 12 nm, respectively. The implantation depth of 10 keV  $\text{O}_2^+$  in iron is about 11 nm. These depths are consistent with the depths observed in Fig. 6. The combined effects of the implantation of erbium and oxygen into 304L, and the transport of iron and chromium into the oxide coating result in an interface ~20 nm in width.

An example of the high adherence achievable with the PIIP process can be seen in Fig. 7, which shows an SEM image of a 3  $\mu\text{m}$  erbia coating implanted and deposited upon the inside of a shallow 304L stainless steel cup. The cup was subsequently dented inside out with a 16 mm diameter Charpy Impactor. The erbia coating has cracked, due to the tensile stresses imposed

by substrate deformation, but has not delaminated. Such a cracked coating is still useful for containing reactive molten metals if the coating is not wetted by the molten metal.

Proprietary ceramic coatings for the H13 core pins used in die-casting of aluminum have been tested in an actual die-casting line by Harley-Davidson (Milwaukee, Wisconsin, USA). Reduced soldering of the aluminum to the pin has been observed, but more evaluation is required. The lifetime improvement for the pins has yet to be quantified. There are concerns about the ability to coat recessed areas on more complicated die surfaces using the hybrid PSII/IBAD process that may be overcome by using PIIP.

#### Adherent DLC coatings on metals

Although many metals were included in the study [6], only the results for W will be highlighted here. The adhesion strength of DLC-coated W without C-implantation before coating varied from 11 to 39 MPa. The DLC-coating on W that had been implanted with C prior to DLC deposition had an adhesion strength of 42 to 46 MPa. SEM micrographs of one test on each of the samples is shown in Fig. 8.

#### Boron-carbide coatings

The boron to carbon ratios of the coatings are shown in Fig. 9. The data indicate that small changes in the gas mixture can have a large affect on the coating composition. The hydrogen content of the coatings was between 25 and 40 at%. Oxygen content was always less than 3 at%. The deposition rate varied from 0.1 to 0.4  $\mu\text{m}/\text{hour}$ . The coating is believed to be amorphous. The hardness of the coatings is between 12 and 14 GPa and the elastic moduli ranged between 110 and 150 GPa. The mechanical properties do not vary considerably with coating composition. Fig. 10 shows the coefficient of friction for three coatings with different compositions. The tribological behavior of the coatings depends greatly on coating composition. As the coating is worn away, the coefficient of friction increases. Coatings with greater wear resistance have a lower coefficient of friction for a greater number of wear cycles. The coating



with the greatest carbon content,  $B/C = 2.2$ , has the best wear resistance. Fig. 11 shows the coefficient of friction for the coating with  $B/C=2.2$  for different contact stresses. Note the marked difference between the friction traces when changing the contact stress ~10% from 358 to 391 MPa.

## **Discussion**

### N implantation of Cr and S7

When comparing the hardness and tribological results for N-implanted Cr, it is clear that beamline implantation at 75 keV produces a harder surface, but exhibits a higher coefficient of friction and slightly higher wear coefficient than the PSII treated Cr. This can be understood as being due to the different N depth profiles inferred from Fig. 5. The reduced Cr concentration, indicated by the reduced yield in the spectra, for the N-implanted samples infers a substantial N concentration. In fact, for the PSII-treated case, the N concentration at the surface is 50 at% as would be expected if the Cr surface were converted to CrN. Note that the N concentration at the surface of the beamline implanted sample is less than 50 at% and that a significant N concentration exists well beyond the depth of the PSII treated sample (~50 nm). The N distributions for the samples can be used to explain the hardness, friction and wear results. The beamline implanted sample exhibits a higher hardness because the nanoindentation measurement is affected by material that extends ~10x farther than the indentation depth. Thus, a hard surface on top of a softer material will exhibit a lower surface hardness than a hard material on top of a harder material. Since the beamline implanted sample has a N profile that extends deeper into the Cr, the increased hardness at greater depths also manifests itself as a higher hardness value at 50 nm. The higher surface concentration in the PSII treated sample, which indicates formation of CrN, presents a different wear couple to the ruby pin than does the  $CrN_{x<1}$  surface of the beamline implanted sample. The presence of free Cr in the surface will increase the interaction between the ruby pin and the surface. Thus, the higher the N surface concentration the lower the coefficient of friction, as shown in Fig. 3. Increasing the surface hardness and decreasing the coefficient of friction will tend to decrease a material's wear

coefficient. The data show that the combinations of surface hardness and coefficient of friction give approximately equivalent wear coefficients for the implanted samples (Fig. 4).

Implantation of nitrogen into *S7* tool steel results in an increase in surface hardness due to the formation of chromium-nitride precipitates in the implanted layer [14]. Perhaps of greater importance here is the change in surface energy (friction) caused by nitrogen ion implantation, in a manner that reduces adhesion or galling of the low-carbon steel part to the die. Galling has been identified as the source of failure in forming tools used for forming the low-carbon steel part.

#### Adherent DLC coatings on metals

The adhesion results indicate that the creation of a compositionally graded interface [6] improves the adhesion of DLC coatings to W. The SEM micrographs confirm the epoxy generally forms the weakest interface for the adhesion test. Therefore, the reported adhesion strengths for the C-implanted and DLC coated W (46 MPa) can be viewed as a minimum estimate of the coating adhesion strength.

#### Boron-carbide coatings

These initial experiments prove boron-carbide coatings can be deposited by a PIIP process. As shown in Fig. 8, the coating composition is highly dependent on the diborane content in the gas. The processing window is thus very narrow and probably not amenable to any large scale use without complicated and expensive process controls. Other researchers have used other gas combinations to produce boron-carbide coatings [15-16]. This work represents the only known attempt to use diborane and acetylene mixtures to deposit boron-carbide. Secondly, the coating hardness of 12-14 GPa is higher than reported in another study [16]. In the future, research efforts will be directed at reducing the hydrogen concentration in, and improving the crystallinity of, the coatings.

## **Conclusions**

PSII is a technology that is continuing to evolve to meet the demands of the surface modification industry for improved wear resistance as well as liquid metal containment. Treatment of areas exceeding a few m<sup>2</sup> has been demonstrated for both ion implantation and coating deposition. Extensions into the use of other gases, such as diborane, will allow the deposition of tribological coatings, such as boron-carbide, over large and complicated areas with all the versatility of a PSII process.

## **Acknowledgements**

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## List of Figure Captions

Fig. 1. A world map showing the known locations of facilities actively doing PSII research in 1997.

Fig. 2. Hardness of the unimplanted and implanted Cr surfaces. The retained N doses are indicated in units of  $10^{17}$  N-at/cm<sup>2</sup>. The error bar results from averaging the multiple measurements.

Fig. 3. Coefficient of friction traces for typical wear tests of the unimplanted and N-implanted Cr surfaces. The retained N doses are indicated in units of  $10^{17}$  N-at/cm<sup>2</sup>.

Fig. 4. Wear coefficient ratios for unimplanted and N-implanted surfaces. The retained N doses are indicated in units of  $10^{17}$  N-at/cm<sup>2</sup>.

Fig. 5. RBS spectra for unimplanted and N-implanted Cr. The retained N doses are indicated in units of  $10^{17}$  N-at/cm<sup>2</sup>. The reduced Cr yield infers a N concentration in the metal surfaces. The samples were tilted 60° relative to the incident  $\alpha$  beam direction so the N profile could be measured with greater depth resolution.

Fig. 6. XPS depth profile of the erbia-steel interface.

Fig. 7. A 3  $\mu$ m erbia coating on 304L stainless steel which has been dented inside out with a Charpy Impactor. No delamination is observed.

Fig. 8. SEM micrographs of DLC coated W. (a) Without carbon implantation, the DLC coating is partially removed; (b) with carbon implantation, the DLC coating is more adherent and no area of delamination is observed.

Fig. 9. The boron to carbon ration in the boron-carbide coatings as a function of gas composition. The B/C ratio varies below and above the target of B/C=4 (for B<sub>4</sub>C) over a narrow range of gas composition.

Fig. 10. Coefficient of friction for coatings containing 12 at% carbon (B/C=4.4), 8 at% carbon (B/C=6.3), and 19 at% C (B/C=2.2).

Fig. 11. Coefficient of friction for the coating with B/C=2.2 measured for different contact stresses.



Fig. 1

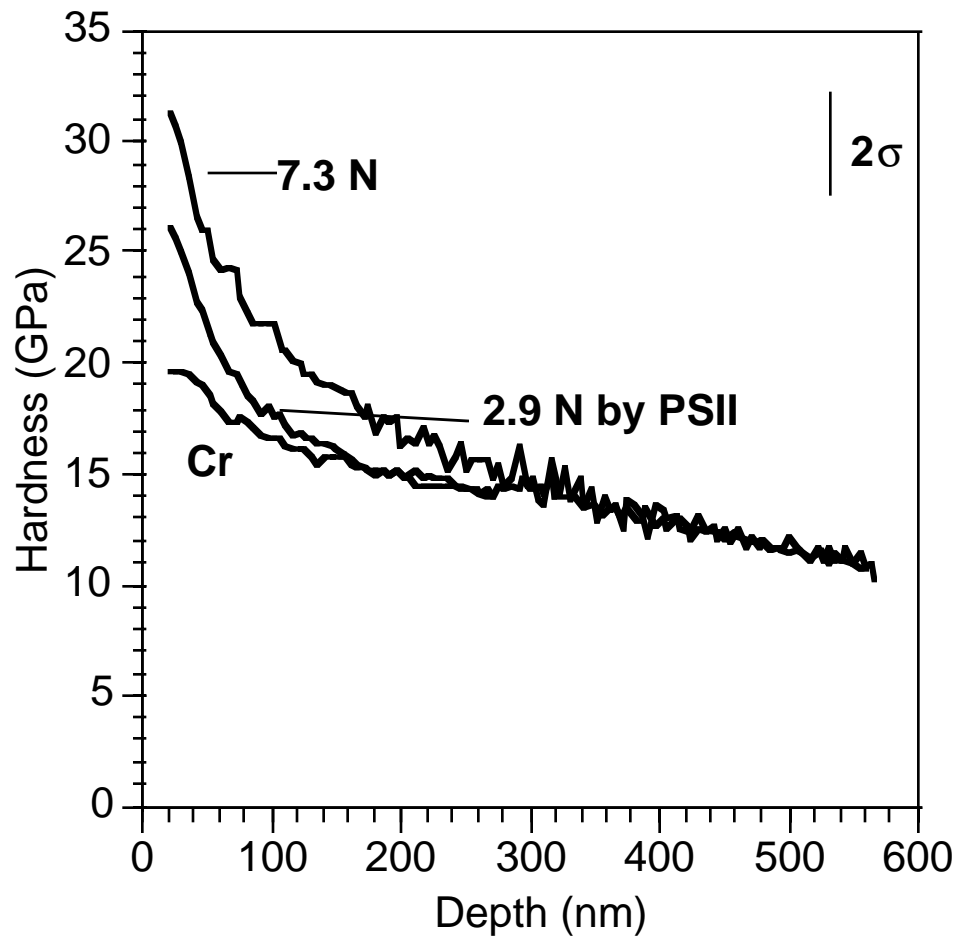


Fig. 2



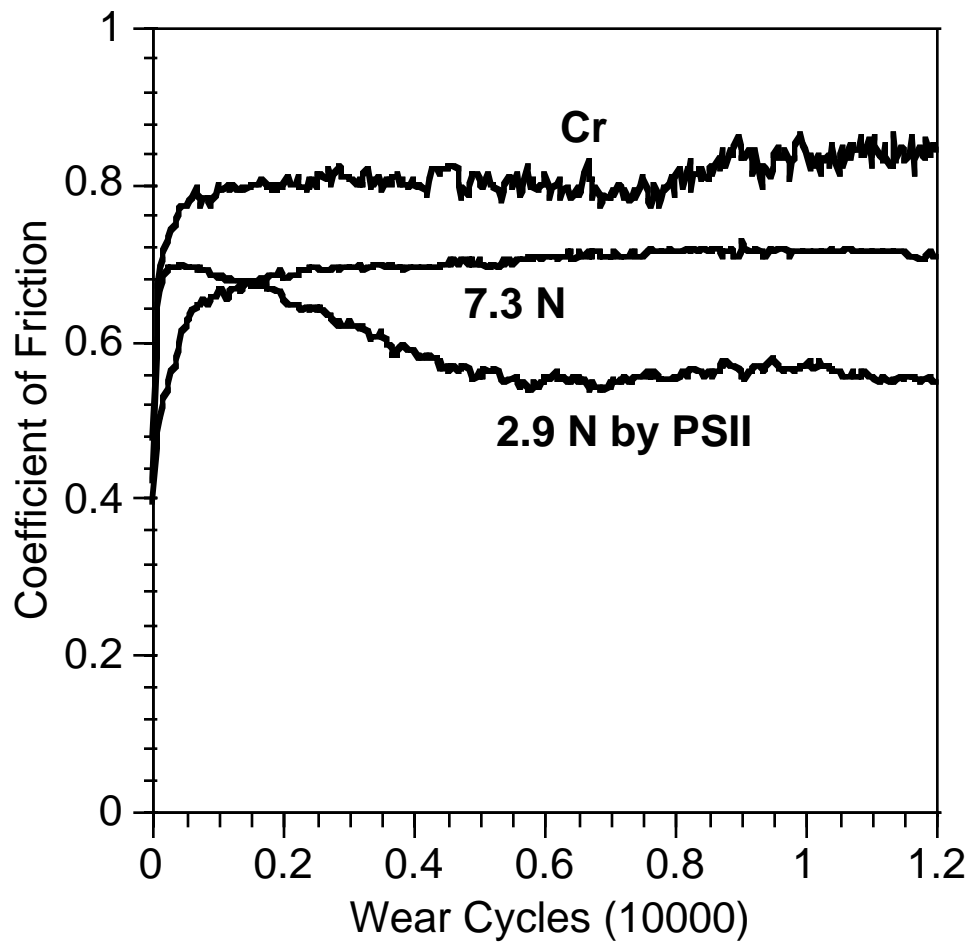


Fig. 3

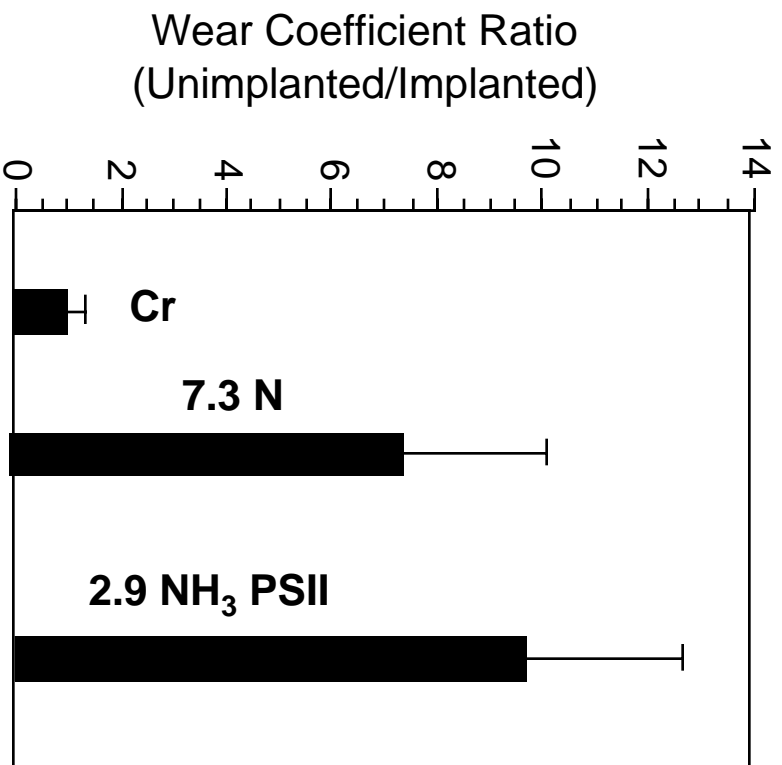
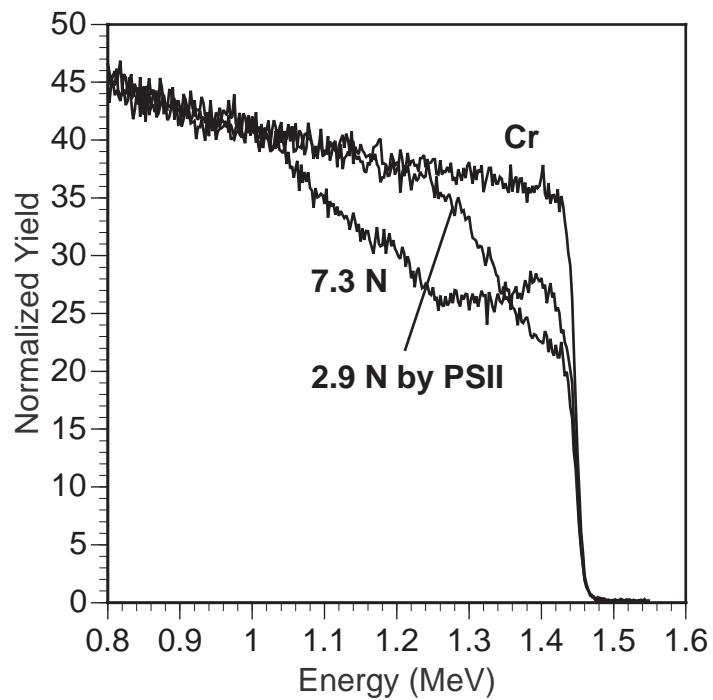


Fig. 4.



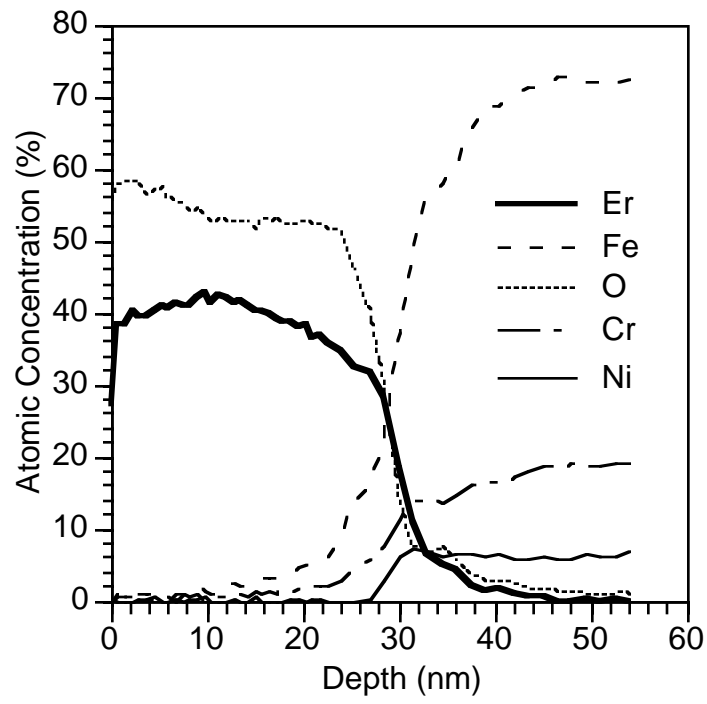


Fig. 6

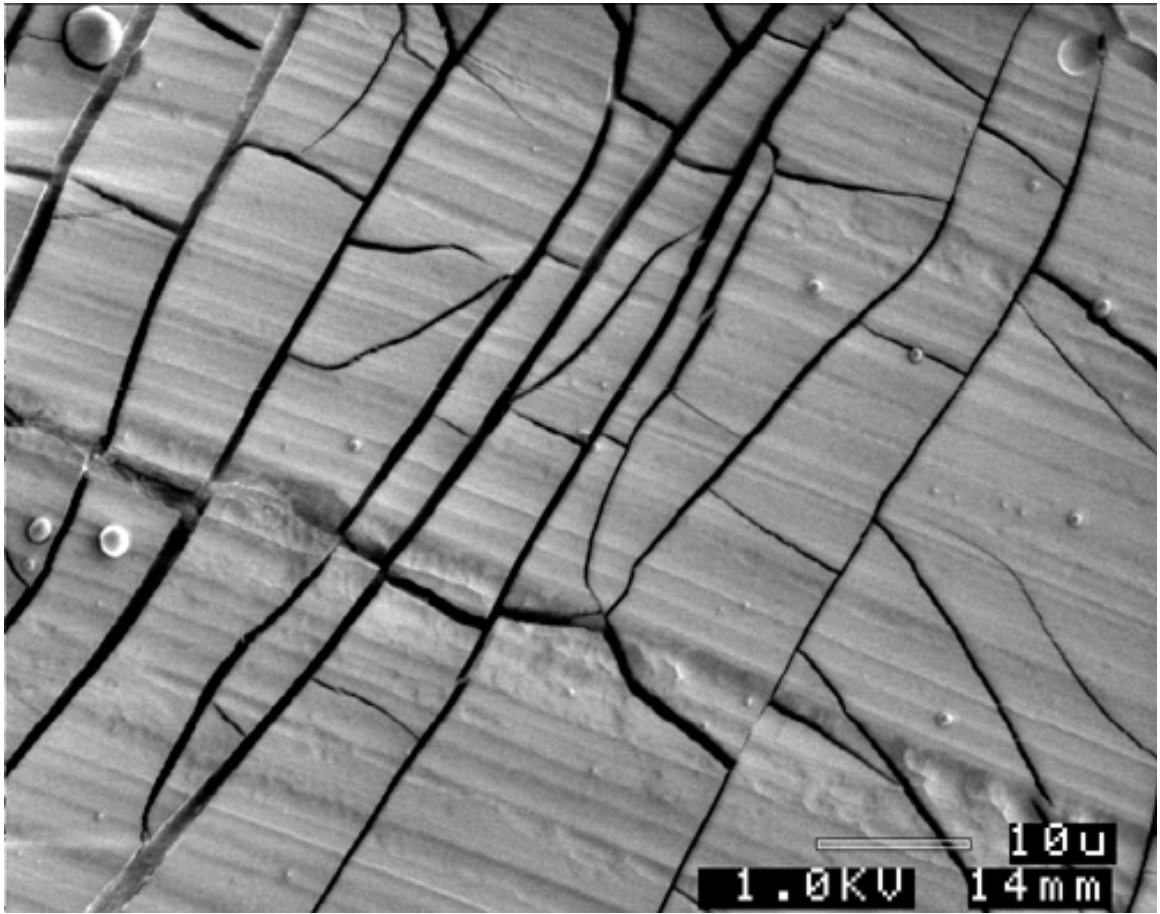


Fig. 7

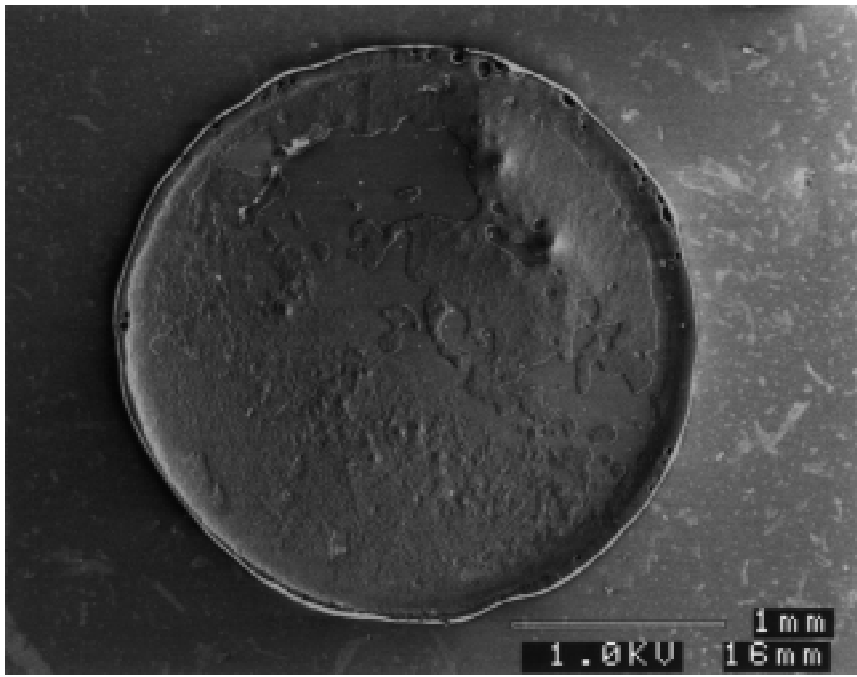


Fig. 8 b.

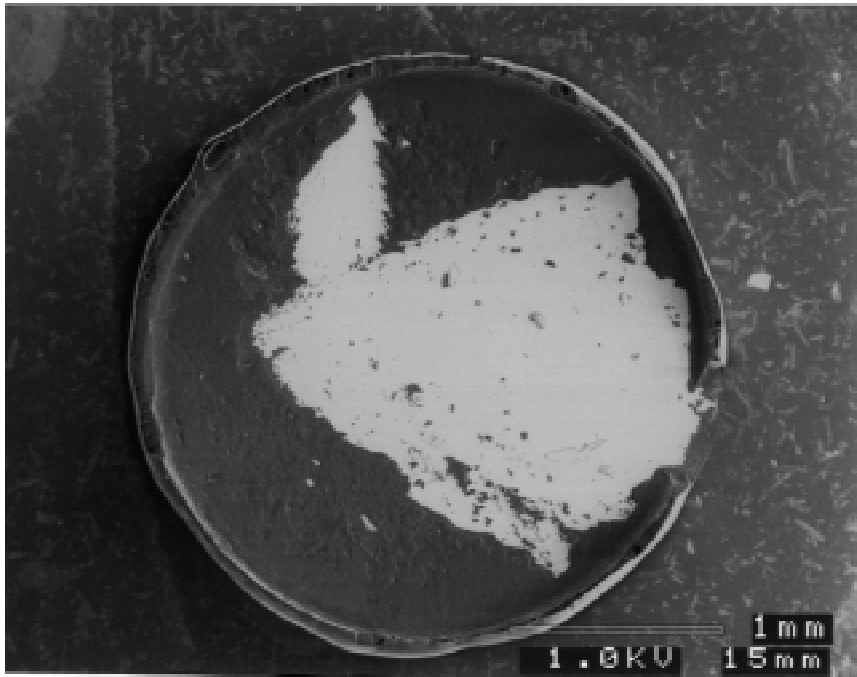


Fig. 8 a.

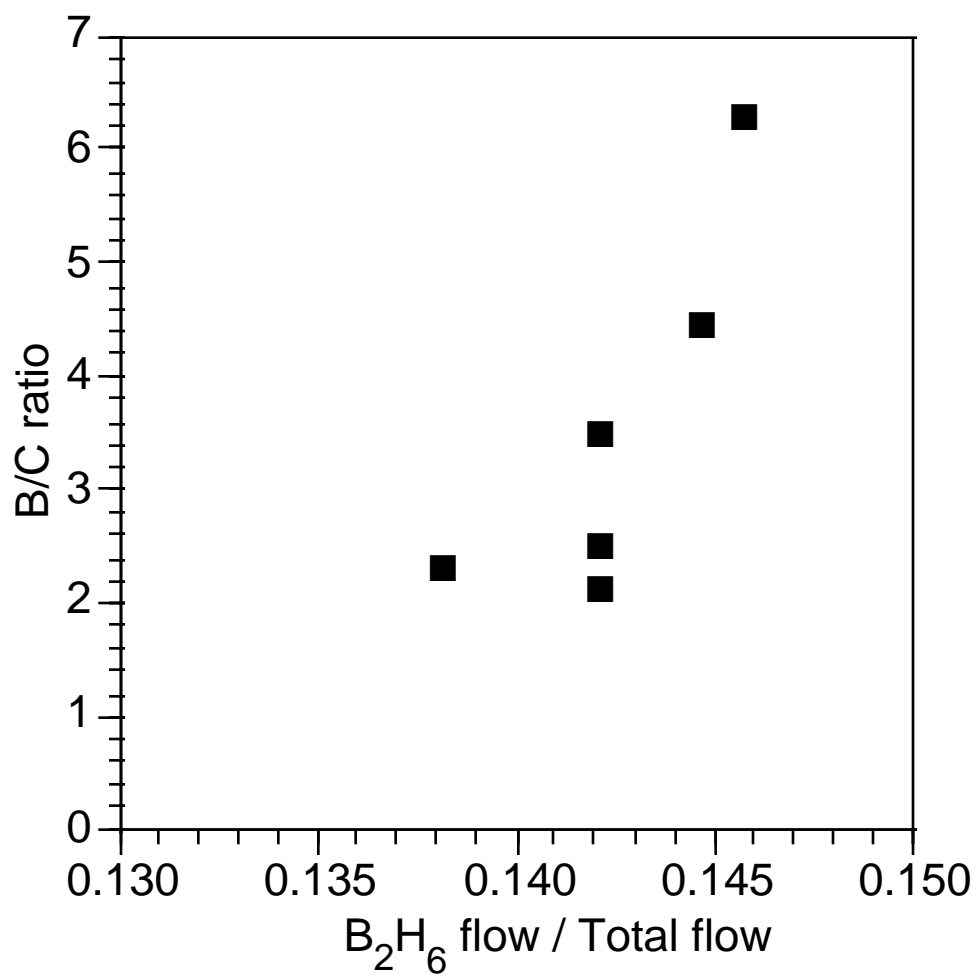


Fig. 9



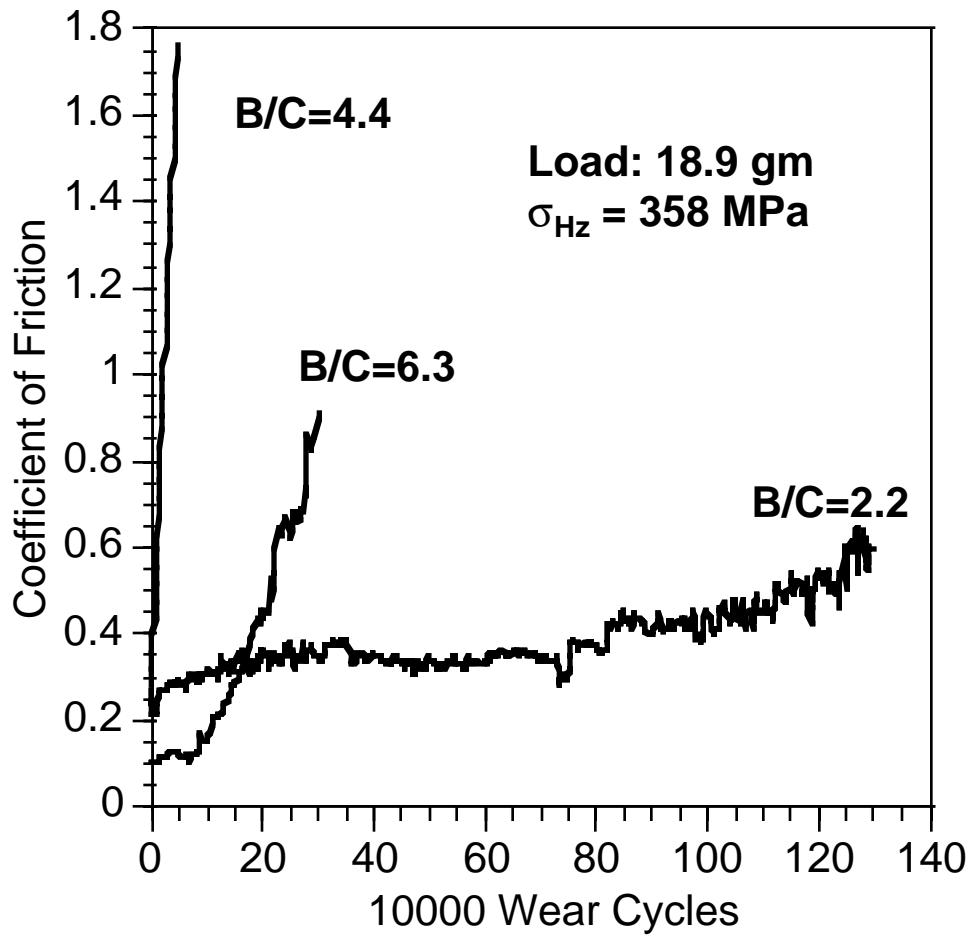


Fig. 10

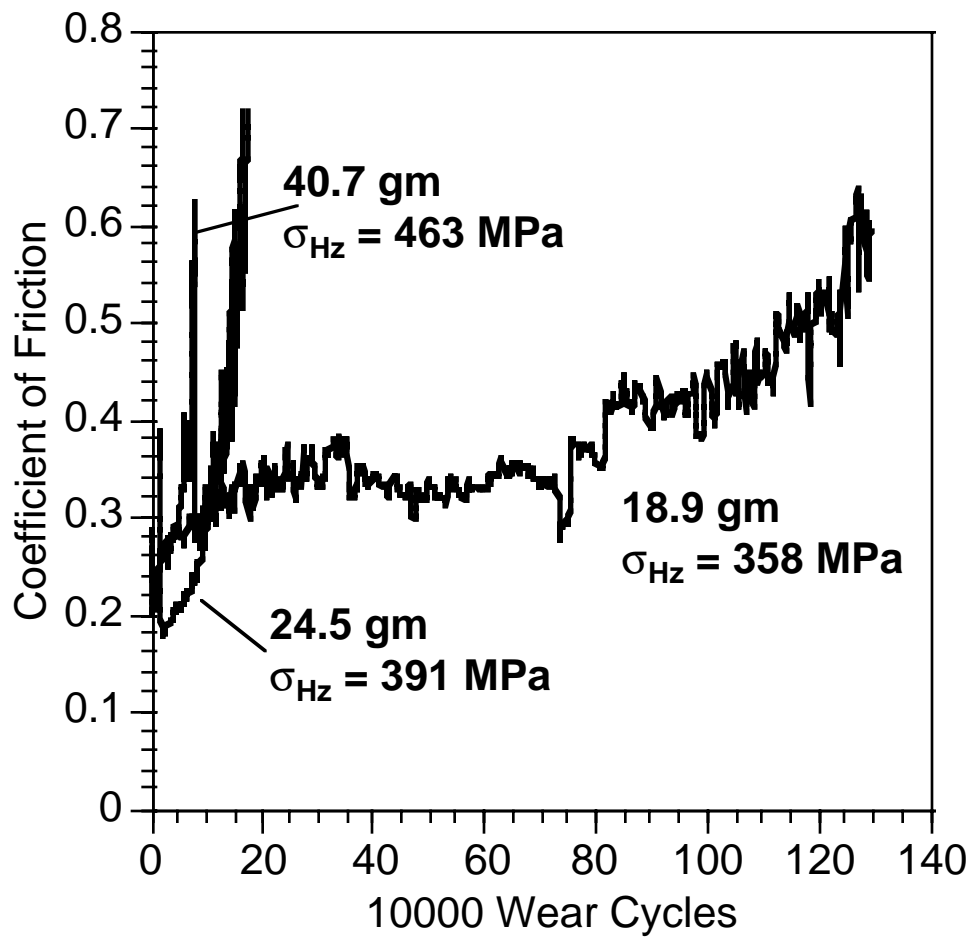


Fig. 11