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# An industrial application of 100 keV ion beam accelerator: Studies on N ion implanted stainless steel with respect to wear resistance to mild abrasion

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## Abstract

We have built a 100 keV and 20 mA ion beam accelerator to apply for prolonged lifetime of metal parts subjected to mild abrasive environment. Studies were conducted on stainless steel which is often used for cutting blades. 70keV N ions of > 5x $10^{16}/cm^2$ were implanted into the surface polished stainless steel (SS420) with average surface roughness (Ra) of 0.04 μm. Then, wear resistance of N ion implanted specimen at the mild abrasive condition was investigated. When the beam incidence was 45° with respect to the specimen surfaces, the concentration of nitrogen in the near surface of the specimen was about 5 at% and detected up to at least 300 nm from the surface as measured with Auger electron spectroscopy. X-ray photoelectron spectroscopy analysis showed that the implanted N formed mostly $Cr_2N$ without post irradiation annealing. Hardness profiles of the specimens were obtained with nano-indentation technique as a function of distance from the surface before and after ion implantations. The peak hardness of 14 Gpa formed at approx. 50 nm depth from the N ion implanted surface was about at least 2 times higher than non-irradiated specimen. Along with the hardness measurement, ball-on-disc wear resistance test was conducted. With 500 gf alumina ball, the wear track to the onset point of abrupt increase in the frictional coefficient was about 5 m for the N implanted specimen, while wear took place for the pristine as soon as the test started. On the other hand, when 1000 gf ball was used for the wear test, the difference in the wear track between the pristine and N implanted specimen was smaller than 500 gf ball, implying that the ion implantation is not suited to severe abrasive condition. After the ion beam irradiation, the surface roughness was reduced to Ra=0.02 μm. We found the ion implantation prolonged the lifetime of the metal parts subjected to mild abrasive environment like hair clipper blades.

## Introduction

Ion implantation technique has been proved to be highly effective in the wear and corrosion resistance of meals parts and it is included in the major surface modification techniques along

with coating technique [1, 2]. However, as long as wear resistance applications are concerned, ion implanted surface is not suited to a severe abrasive condition because of limited treating depth which is a function of the ion energy [3]. Ion implantation techniques are often compared with coating technique. Coated products have been known to have obvious advantages in the severe abrasive environments, because the thickness of the coated layer is easily controllable as it is simply proportional to the coating time. In spite of sizable advances in the adhesion techniques between the coated layer and the substrate, the coated products often exhibit peeling problems during the service performance regardless of how mild or severe the abrasive condition is. That is, the abrupt interface that frequently formed in the coating products generates residual stresses in the coated layer, which cause the detachment of the coated layer from the substrate with a slight application of load. In order for the metal parts to be used in a mild abrasive condition, sometimes the ion implantation is more useful than the coating, because the implanted product does not produce an abrupt interface between the bulk and the treated layer. In general, the compressive residual stress generated in ion-implanted layer is not so significant as to peel the implanted layer off.

This work was motivated by a company for the production of the prolonged lifetime of metal parts subjected to relatively mild abrasive environment. One of the examples is the hair clipper blade, because the spring force to push the upper blade to lower blade is as low as about 500 gf, resulting in the stress of about 20 g/mm$^2$ on the surface of the blades. In this work, we have built a dedicated ion implanter for these applications and implanted N ions into Stainless Steel 420 specimen. Then, mechanical tests including nano-indentation and ball-on-disc wear tests were conducted. In order to understand the surface hardening mechanisms, Auger electron spectroscopy and X-ray photoelectron spectroscopy were employed.

## Experiments

### 1. Instrument

An industrial ion beam accelerator with 50KeV and 20mA ion source and 50keV accelerator tube was developed with 850 mm x 850 mm x 850 mm vacuum chamber, aiming at semi-mass production of ion implanted metal parts. For this purpose, higher density ion beam and larger irradiation area were required. To obtain a uniform and large irradiation area, we designed a beam extraction system with 4 holes aperture so that ion beams could be extracted from the ion source through 4 holes instead of a single hole [4]. Simulation with IGUN code [5] was followed to determine the electrode materials, number of the electrode, and distances among the electrodes to obtain the required irradiation area.

### 2. Ion beam diagnostic and irradiation

After building the implanter, SS420 plates were irradiated with N ions. Prior to ion beam irradiation, 3 cm x 3 cm samples were polished to the surface roughness of 0.04 μm. Samples

were placed in the sample holder of 200 mm x 200 mm area: one on the center and the others on the corners. Before the irradiation, the differences of ion doses during irradiation on the target were measured with a faraday cage. The faraday cage was designed to measure the ion beam current as passing the cage made of high purity copper through the beam cross section, presuming that the beam cross section is circular. The current read in the X-Y recorder was converted to the ion dose by a proper calculation.

70 keV and 5 mA N ions were irradiated onto the specimens in a vacuum work chamber (base pressure: approx. $10^{-5}$ Pa, and work pressure: approx. $10^{-4}$ Pa) for about 13 minutes, which is corresponding to about $5x10^{16}$ ions/cm$^2$ as we estimated with the faraday cage measurement. That is, neutral atoms and molecules were not included in the dose estimation.

3. Characterization of the implanted specimens

After irradiation, Auger Electron Spectroscopy (AES) depth profiling analysis was performed to see the existence of the nitrogen in the specimen and to obtain elemental profiles as a function of distance from the surface. A Physical Electronics Phi Model 670 Scanning Auger Multi-probe combined with an ion sputter gun was used for the elemental depth profiling. The Auger data were acquired E*N(E), however, the display mode of Auger spectra in this experiment is in d{E*N(E)}/dE. The sputtering rate estimated in this work was about 10 nm/minute.

Using Phi-Model 5800 X-ray Photo electron spectroscopy (XPS) with an ion sputter gun, the chemical states of nitrogen residing in the sub-surface of the implanted specimen were analyzed. The analysis was conducted after sputtering the surface until the surface contaminants such as C and O species were removed.

Nano-indentation and Ball-on-disc wear resistance tests were performed on the implanted specimens. For ball-on-disc test, 1000 gf and 500gf alumina balls were used and the frictional coefficients were recorded as a function of wear distance. The distance up to abrupt increase in the frictional coefficient was measured and compared with each other.

## Experimental results and Discussions

1. Instrument and beam diagnostic

IGUN code simulation suggested that an additional 60cm tube attached to 30cm acceleration tube should produce a uniform irradiation area of 30cm in diameter on the target. A descriptive schematic of the instrument is shown in figure 1.

As measured with a faraday cage, consistent beam current of at least 5mA was obtained at the beam energy of 70keV on the surface of the target and the difference of the ion doses between the center and the corners was about 10%, which is well consistent with the IGUN simulation results.

2. N ion beam irradiation, and elemental analysis of the irradiated specimens

At 70keV and 5mA, no distortion and dimensional changes of the specimens and the specimen holding jig system were observed. This means the system can be used even without operating the target cooling system. After ion beam irradiation, the surface roughness of the samples was reduced from 0.04 to 0.02 μm as measured with a high-resolution surface roughness tester (Mitutoyo model Surftest SJ-301).

Figure 2 shows Auger depth-profiling results of the samples irradiated on the center and on the corners of the 200 mm x 200 mm specimens' holder. Figure 2(a) denotes the sample positions in the holder, and figure 2(b) is an example of the Auger spectra acquired as a function of the sputtering cycle. As can be seen in the spectra, the nitrogen is clearly incorporated in the N ion irradiated samples. As determined with software provided by Physical Electronics Co. (USA), the concentration of nitrogen determined with peak-to-peak heights and atomic sensitivity factors was about 5 at% at the near surface and then decreased slowly as going to the deeper inside, but a considerable amount of the nitrogen was still detected up to 300nm depth from the surface as shown in figure 2 -(c) and -(d). Approximate amounts of the nitrogen detected from the samples placed on the center {figure 2(c)} and on the corners {figure2 (d)} also are similar. This is well consistent with the faraday cage measurement.

As long as the concentrations are concerned, however, it turned out much more nitrogens were implanted into the specimens in this work as compared with our previous experiment. Previously, we used an ion implanter with a mass analyzer so that only $N^+$ ions could be implanted, and we could detect as much as about 3at% of nitrogen in the near surface with the same current reading as in this work. The ion implanter newly built in this work is not equipped with the mass analyzer. This means the neutrals that cannot be measured with faraday cage is considerably implanted into the specimen along with the ions. We are currently performing an experiment to decide the precise ion doses generated by the ion implanter without a mass analyzer. In order to determine the implanted dose more exactly, we are attempting to analyze different ion species such as $N^{++}$, $N_2^+$, $N_2^{++}$ etc. together with the neutrals.

## 3. Mechanical tests

As a result of nano-indentation measurement as a function of depth from the surface (figure 3), a sizable increase in the surface hardness was achieved. The peak hardness of 14 Gpa is more than two times of the base hardness of the stainless steel (about 5 Gpa). Higher hardness near the surface of the pristine seems to be resulted from the work hardening that may have occurred during mechanical polishing prior to the ion implantation. We performed N ion implantations to various stainless steels with different base hardness values. Noticeably, we found almost the same hardening effects for all stainless steels regardless of their base hardness [6].

In consistence with the hardness increase, wear resistance was also enhanced as measured with 500 gf alumina ball-on–disc test (figure 4). In the wear test, we paid attention to the

onset of the abrupt increase in the frictional coefficient, which implies the onset of damaging the surface layer. In the case of the pristine, wear took place as soon as the test starts {figure 4(a)}, while, in the ion implanted specimen, no increase in the frictional coefficient took place up to the wear tract of 5 m {figure 4(b)}. The ball-on-disc wear test was stopped when an abrupt increase in the frictional coefficient was observed. We consider the reason for wear resistance enhancement of the ion-implanted specimen in two ways; one is the reduced surface roughness and the other is the hardening effect. Since the surface roughness of the specimen was very low originally (average roughness: 0.04μm), it seems the enhanced wear resistance due to the roughness decrease (0.02μm) is trivial. Thus, the major mechanism of wearability increase is believed to be the surface hardening effects. However, when we used heavier balls than 1000 gf, the difference in the wearability between the pristine and the implanted surface becomes smaller {figure 4(c)}, implying that the ion implanted parts do not exhibit significant wear resistance effects under severe abrasive environment.

## 4. Chemical analysis of nitrogen in the implanted surface

In order to understand the hardening mechanism, the chemical states of the nitrogen implanted into the specimen were analyzed with x-ray photoelectron spectroscopy. As can be seen in $N_{1s}$ spectra in figure 5, most of the nitrogen residing in the near surface of the specimen formed $Cr_2N$ without post implantation annealing [7]. As results of the peak-fit, a peak exists around 398 eV, implying that small amounts of Fe-nitrides also exist along with $Cr_2N$. Binding energies of $N_{1s}$ electron from $Cr_2N$, CrN and Fe- nitrides are respectively 397.4 eV [7], 369.7 eV [8], and 398 eV [9,10]. The predominant formation of $Cr_2N$ over other possible nitrides such as CrN and $Fe_2N$ or $Fe_4N$ may be attributed to that the formation of $Cr_2N$ ($\Delta Hf$ = -30.5 cal/mol) is thermodynamically more preferential than the formation of CrN($\Delta Hf$ = -29.8 cal/mol) and Fe-N ($\Delta Hf$ = -2.5 cal/mol) [11], even though the major element in the stainless steel is iron (~80%). In our previous work, the nitride formed in SS440A was largely $Cr_2N$, but the amount of nitrogen formed to Fe-N was more than the results found in this work [12]. XPS spectrum at around 401eV seems to come from the free nitrogen and/or meta-stable nitrides that did not form the stable nitrides.

There are various hardening mechanisms of the metal parts by ion bombardment, that is, solid solution, work hardening, and precipitation hardening. etc. However, we believe that, as our XPS analysis results indicate, the formed nitrides, which are inherently very hard, plays an important role in the enhanced surface harness. The mechanisms of the formation of nitrides without post irradiation annealing can be considered in two ways: Firstly, the energy of incident ions as high as 70keV may be the driving force to form the nitrides and, secondly, the compressive residual stress formed on the implanted surface may have forced to form the nitrides as Jagielsky et. al. [13] postulated that the compressive residual stress may be one of the factors forming $C_3N_4$ compound when N+C dual ions are implanted into the copper substrate.

With the ion implanter developed in this work we have applied to hair clipper blades. The hair clipper with the implanted blades exhibited much more prolonged lifetime than the hair clipper with the non-irradiated blades. Since the hair clipper with the implanted blades is still in use, we have not concluded yet how long they will be used.

## Summary and conclusions

When 70 keV N ions of >5x $10^{16}/cm^2$ were implanted into the surface polished stainless steel, nitrogen was detected up to at least 300nm from the surface as measured with Auger depth profiling, and X-ray photoelectron spectroscopy analysis showed that the implanted N ions formed mostly $Cr_2N$ without post irradiation annealing. As measured with nano-indentation, the peak hardness of 14 GPa formed at approx. 50nm depth from the N ion implanted surface was about at least two times higher than the non-irradiated specimen. Frictional coefficients were observed as a function of wear track with 500 gf alumina ball-on-disc test; abrupt increase in the frictional coefficient took place on the pristine as soon as the test starts, while no change in the frictional coefficient took place up to the distance of 5 m in the ion implanted specimen. On the other hand, when 1000 gf alumina ball was used, the wear resistance effect was reduced.

Conclusively, the enhanced wear resistance of the stainless steel by N implantation is attributed largely to the formation of hard nitrides in the implanted volume, and the ion implantation for wear resistance is more effective under the milder abrasive conditions. We are applying these ion implantation parameters to hair clipper blades.

## Acknowledges

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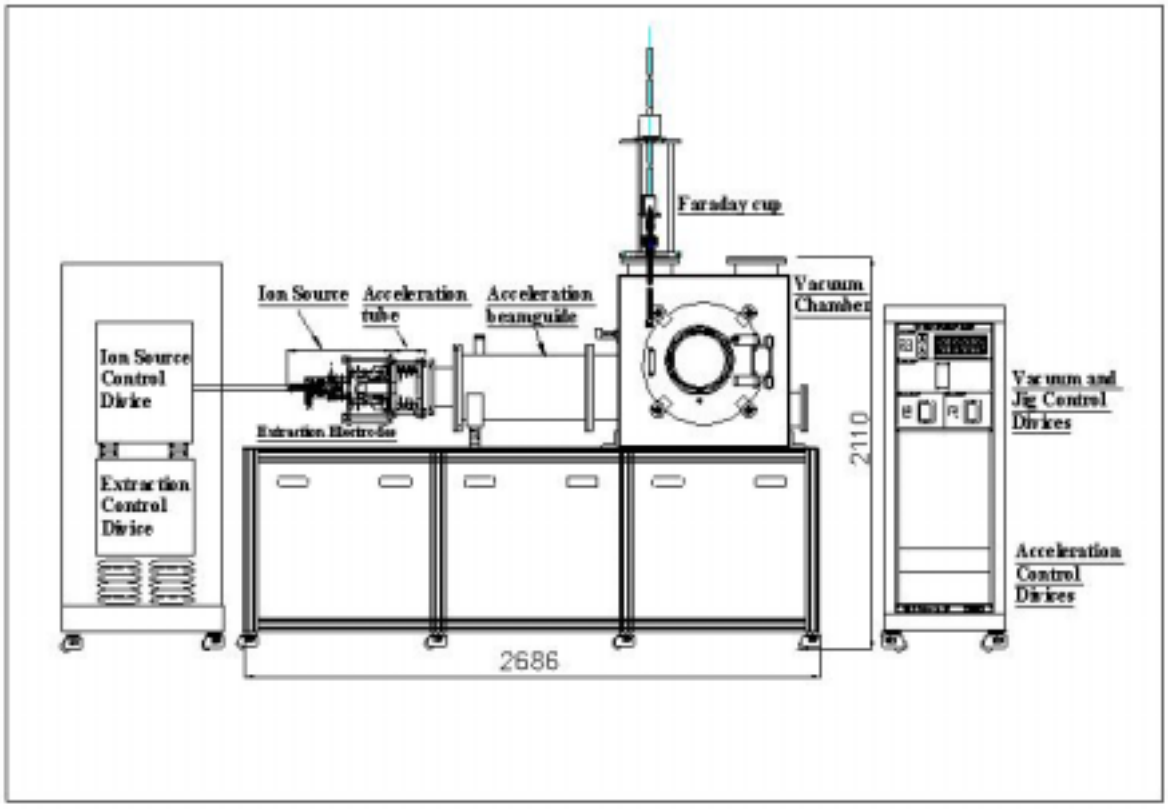
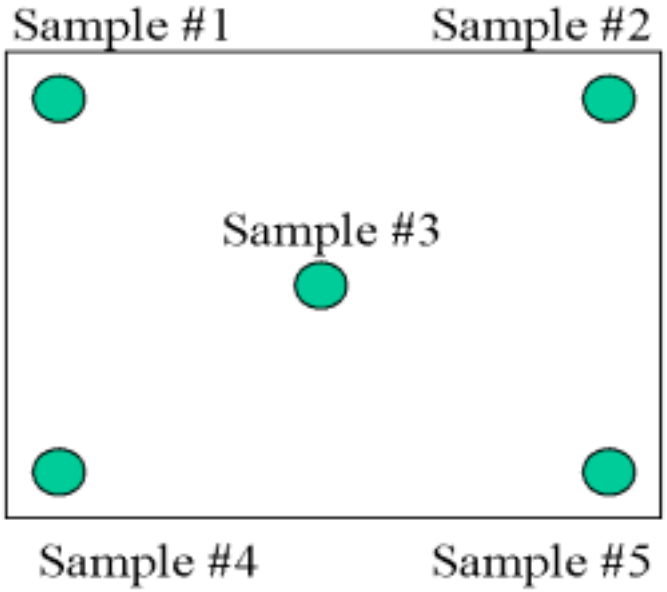
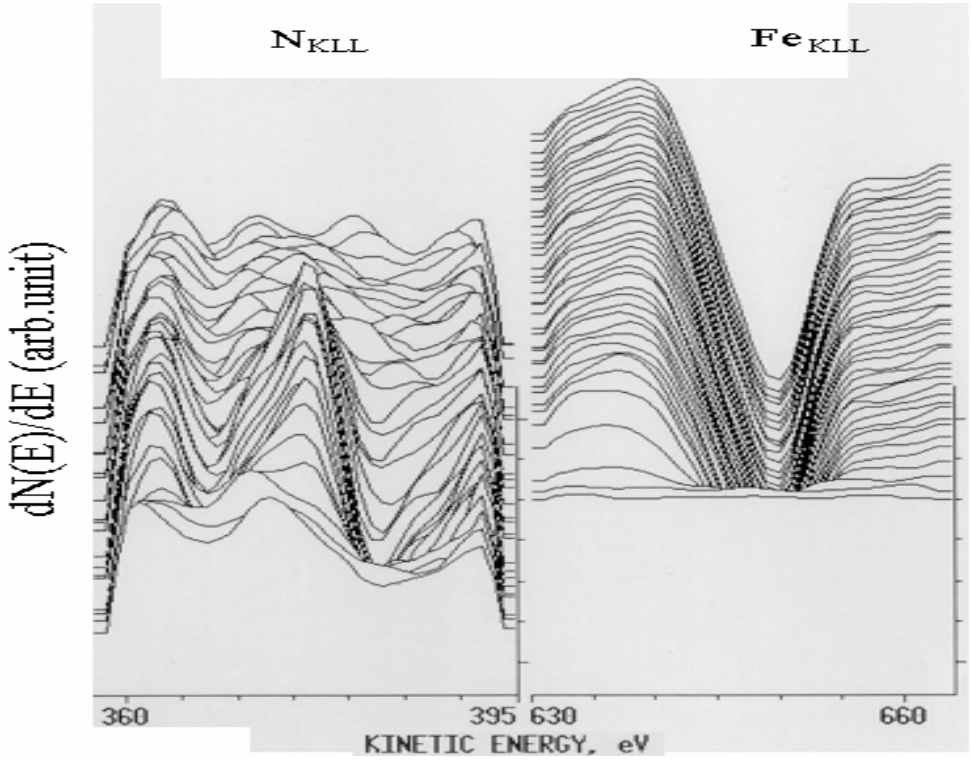



Figure 1. Schematic description of the ion implanter developed in this work.


Sample #1
Sample #2
Sample #3
Sample #4
Sample #5

(a)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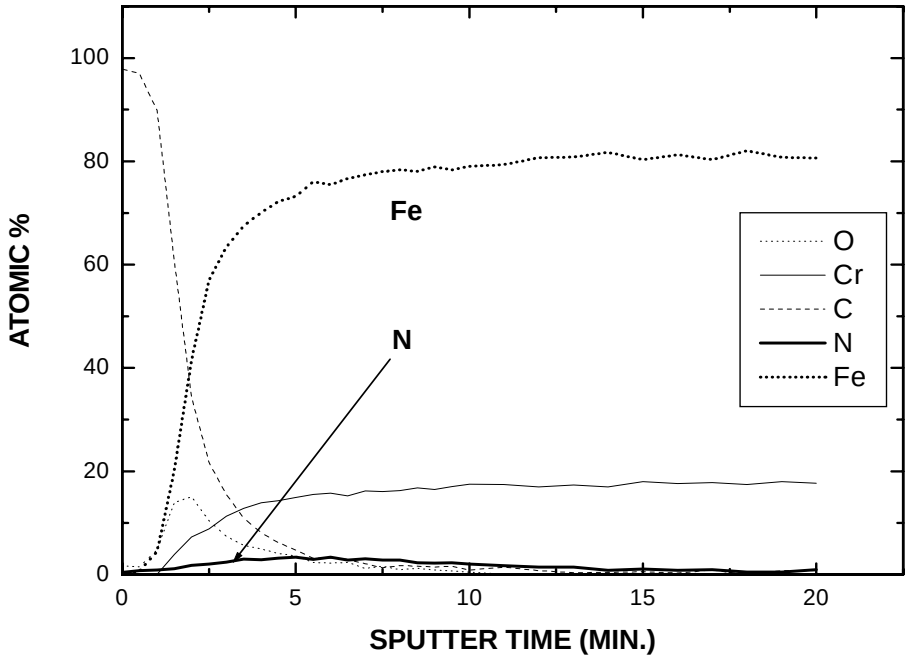
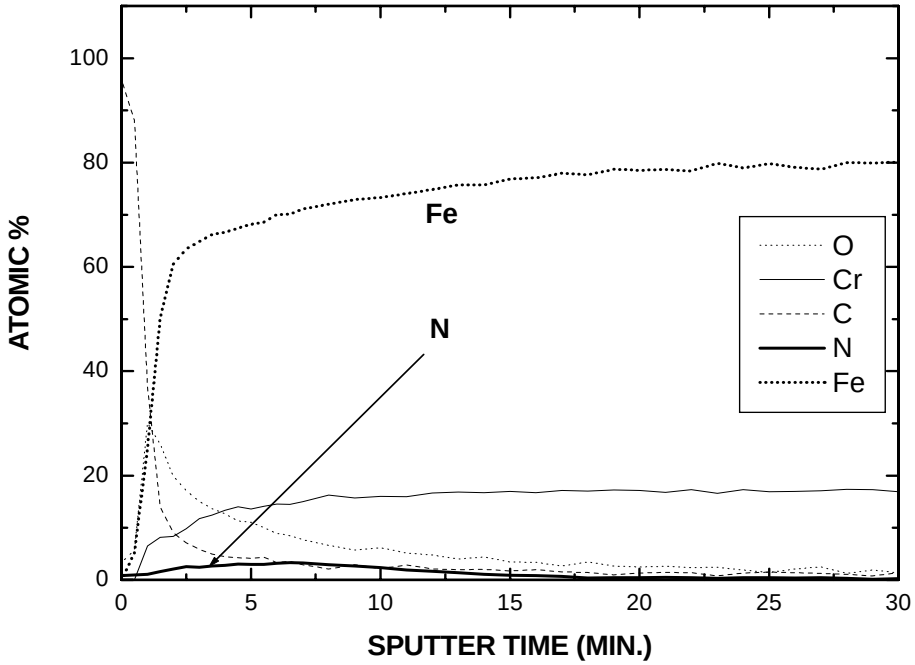
Fe KLL
dN(E)/dE (arb.unit)
360
395
630
660
KINETIC ENERGY, eV

(b)




(c)




(d)

Figure 2. Auger depth-profiling results: Figure 2(a) denotes the sample positions in the holder. Figure (b) is the Auger spectra acquired as a function of the sputtering cycle. The

concentration of nitrogen determined with peak-to-peak heights and atomic sensitivity factor was about 5 at% at the near surface and then decreased slowly as going to the deeper inside, but a considerable amount of the nitrogen was detected up to 300nm depth from the surface {figure 2 -(c) and -(d)}. Approximate amounts of the nitrogen detected from the samples placed on the center {figure 2(c)} and on the corners {figure 2(d)} are not so different.

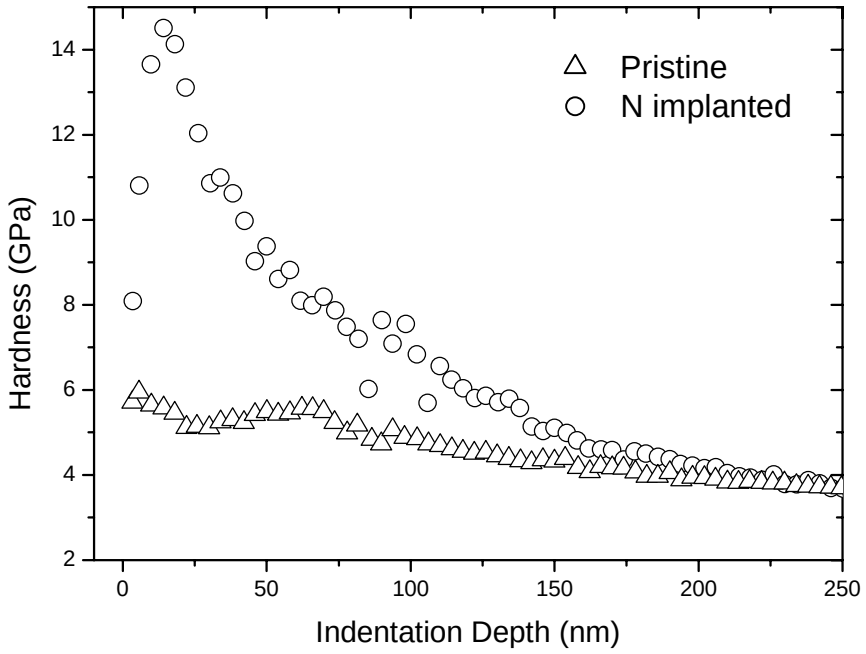
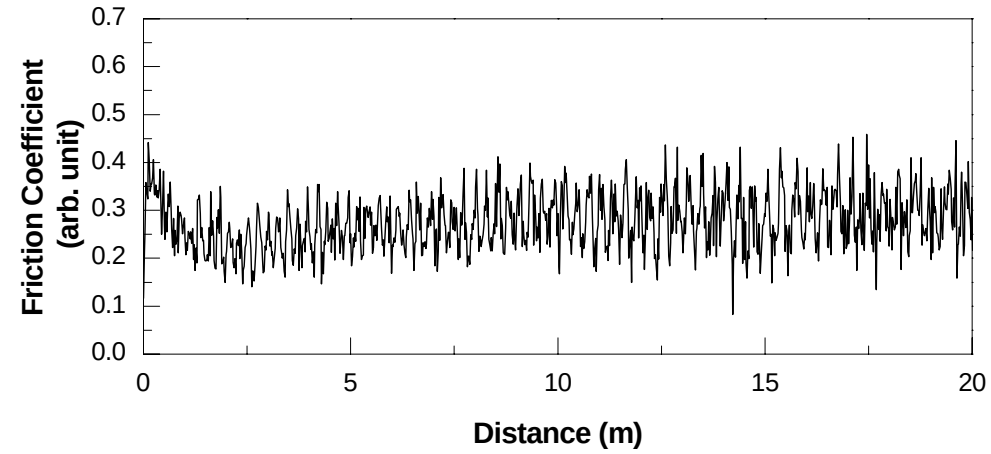
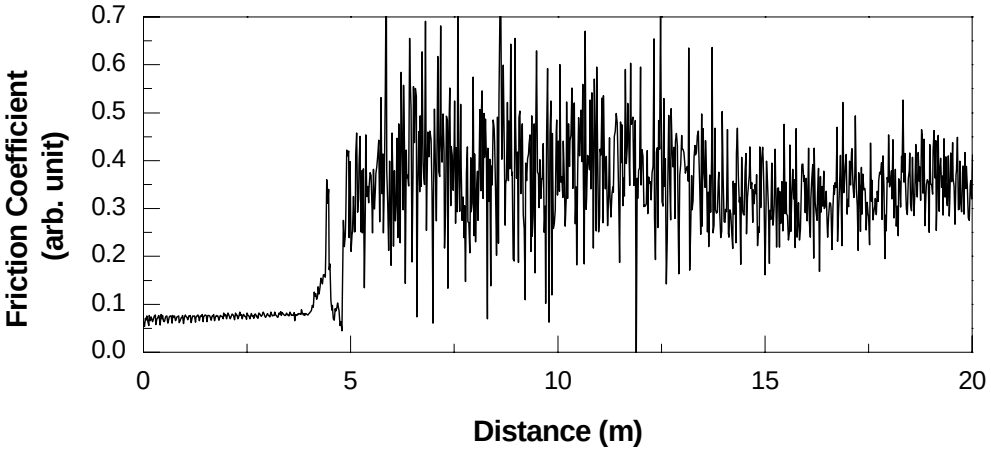


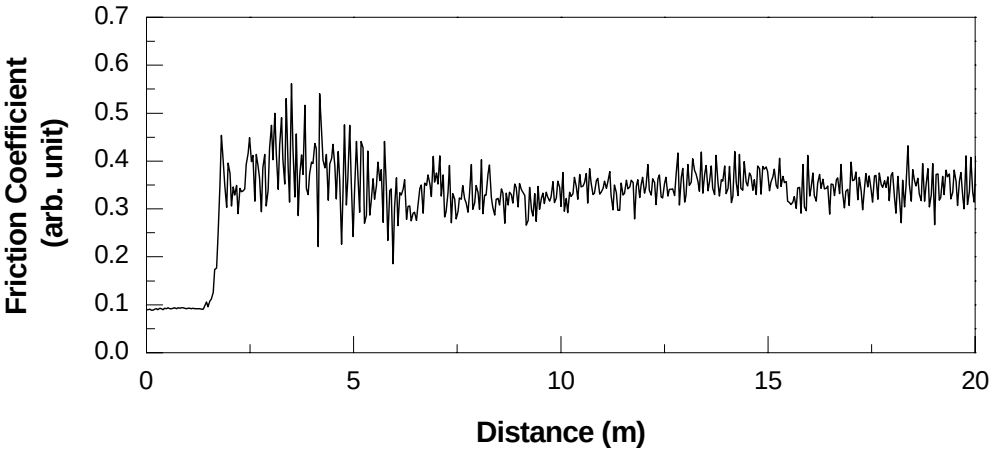

Figure 3: Hardness depth profiles obtained with nano-indentation technique: A sizable increase in the surface hardness was obtained as a result of N ion implantation. The peak hardness of 14 Gpa is more than two times of the base hardness of the stainless steel (about 5 Gpa). Higher hardness near the surface of the pristine seems to be resulted from the work hardening that may have occurred during polishing prior to the ion implantation.




(a)




(b)




(c)

Figure 4. Ball-on-disc test results: Figure 4 -(a) and -(b) are the results obtained with 500 gf alumina ball. In the case of the pristine, wear took place as soon as the test starts {figure 4 (a)}, while, in the ion implanted specimen, no wear took place up to the wear tract of 5 m

{figure 4(b)}. When heavier balls than 1000 gf were used, the difference in the wearability between the pristine and the implanted surface becomes smaller {figure 4(c)}.

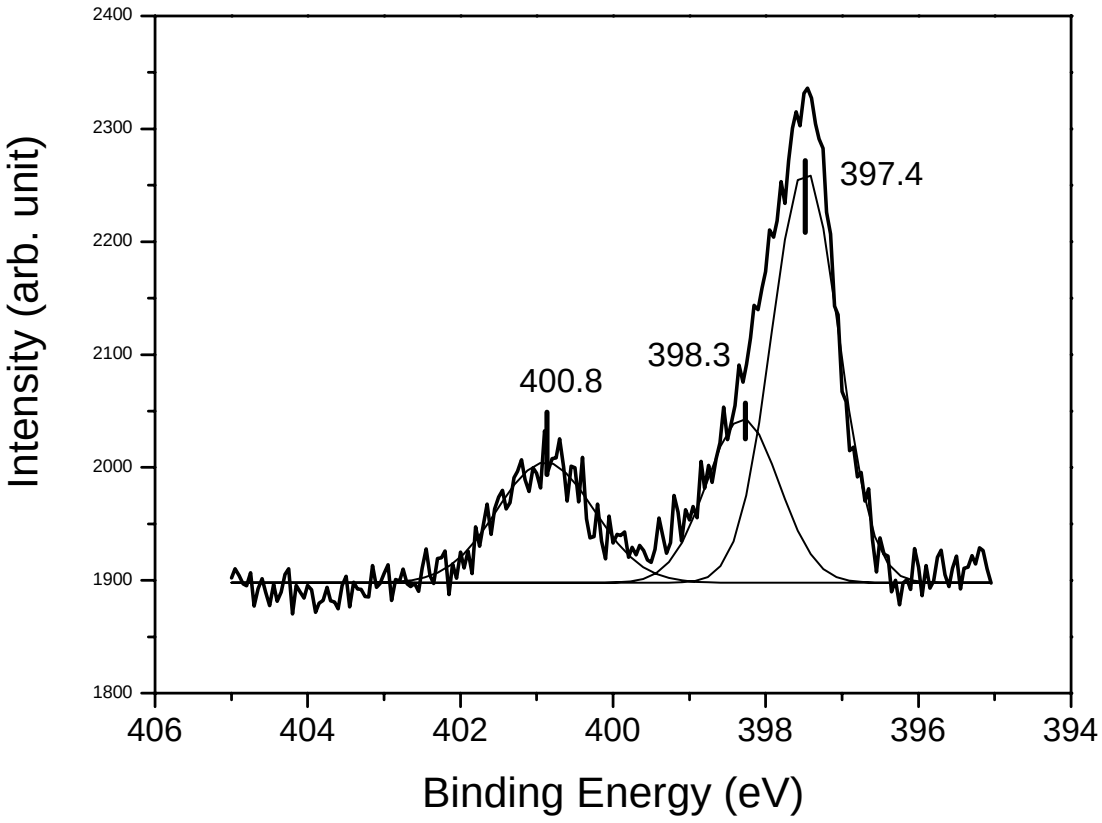



Figure 5. X-ray photoelectron spectroscopy analysis of nitrogen implanted SS420: As can be seen in $N_{1s}$ spectra , most of the nitrogen residing in the near surface of the specimen formed $Cr_2N$ without post implantation annealing.