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Silicon Enhancement of the Compound Layer for Tribological Application of Nitrided Hot-Work Steel

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Abstract

The enhancement of tribological surface properties and thermal stability of nitrided layers is possible when using a plasma process doped with silicon containing gasses (PEN/Plasma Enhanced Nanostructure). Treatment of small as well as large sized metal forming and stamping tools can be realized by the application of the latter. In this strategy, the low-friction thin-nanostructured surface is supported by a hard compound-zone that in turn is supported by a large diffusion-zone. The GDMS and XRD analysis were carried out on the H-13 samples subjected to this duplex plasma treatment (PEN) and revealed that the surface was enriched with silicon, carbon and nitrogen. Mechanical testing carried out on the samples revealed that the properties of the PEN are superior over the properties of the plasma nitrided or the non-treated H-13 forging steel samples. Results of the scratch test showed that the critical force at which the damage of the surface occurs in PEN sample is much larger ~425 mN than in the PN sample ~258 mN. At the same time, the residual depth of the permanent deformation in the PEN sample was smaller, ~0.52 μm as compared to the PN sample, ~0.75 μm and, ~1.28 μm for the NN sample. Results of the Pin-On-Disk wear tests showed reduction of the friction coefficient for the PEN layers sliding against the 440C stainless steel ball. The reduction in friction was also achieved with PN samples.

Introduction

Fatigue, wear and corrosion are the most important mechanisms that lead to material degradation, which eventually lead to failure of components and tools. The annual loss by material degradation owing to these mechanisms alone is assessed at 7-8% of a nation's gross national products (GNP), at least in the western world (Ref 1). Premature failure of forging or hot stamping significantly increases production costs and results in unnecessary delays of delivery. Those failures are caused by very complex wear mechanisms of the die surface subjected to plastic deformation, thermal fatigue and wear by friction as well as galling and scoring of the surface. Since the damage of the die is primarily limited to the near surface areas of about 2 mm deep, surface engineering opens up a variety of possibilities to improve their surface behavior. Nitriding of such dies has proven to be successful in particular, see Fig. 1 (Ref 1, 2).

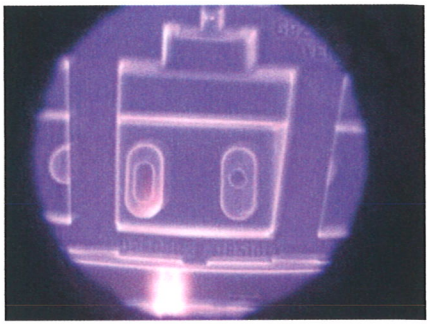


Fig. 1. Large stamping dies during plasma nitriding.

Specifically, plasma assisted nitriding offers significant benefits with good control of the structure of nitrided layer as well as the ability to mask off selected areas of the dies to protect them from the treatment (Ref 3). A nitrided layer is hard and under residual compressive stress and therefore its presence in the surface of the tool enhances wear resistance as well as thermal fatigue behavior in many applications. However, thermal stability and oxidizing resistance of the nitrided layer are detrimental factors limiting its long-term durability in forging and hot stamping applications. Typical steels used for those applications contain elevated content of such elements as chromium, molybdenum and others and therefore the major portion of the nitrided layer, or so-called diffusion layer, contains very stable nitrides formed by these elements. Solubility of nitrogen in those steels is much higher than it is in iron and may exceed 1 wt. %. The main problem of the stability of nitrided layer lies in the compound layer at the surface, which has about 6-8 wt. % of nitrogen. This is either a layer of γ'-Fe_4N or ε-$Fe_{2\text{-}3}N$ nitrides. Such layer has a very positive effect on abrasion resistance and corrosion resistance of the steel but its thermal stability is not sufficient (Ref 1). Various attempts have been undertaken to improve the thermal stability of the compound layers and the near surface areas of the nitrided tools for enhancing durability of the dies with so-called duplex or combined treatments (Ref 4-8). The treatment relied on application of the PVD and laser processing already pre-nitrided dies. The PVD coated layers such as TiN/Ti(C, N), (Ti, Cr)N and others allowed for significant minimizing of the abrasive and the thermal fatigue wear of a die (Ref 6). The disadvantages of these duplex treatments is a need for dual chamber processing, size limitations of the PVD chambers and insufficient resistance of

some of the duplex layers to oxidizing in the open forge or hot stamping applications.

A process for improving the performance of the stamping dies was proposed (Ref 9). The process is a plasma duplex-type with the novel step applied after plasma nitriding for forming a nanocomposite layer, which significantly increased tribological properties of gray cast iron stamping dies. In addition to that, a proposed nanocomposite two-step process combines plasma nitriding with the plasma enhanced step carried out in a mixture of nitrogen, methane, silane and argon. Stability of the phases in Si-C-N-O system at high temperatures is very well known (Ref 10). Lower temperature reactions are also very promising for forming the ultrathin SiO_xN_y type layers (Ref 11). Application of silicon dioxide and –nitride or –carbide thin films is very broad. Processes for forming such layers have been patented many times, for example see (Ref 12). With the aid of plasma, the temperature of the nitriding process and formation of various compounds of the Si-C-N-O can be lowered to about 450^0 C (Ref 11, 13). It was also reported long ago that formation of silicon nitride layers in a deposition process from silane and nitrogen can be carried out in the glow discharge at a temperature of about 350° C (Ref 14). Similar results can be obtained using a plasma-enhanced atomic layer deposition (ALD) process for the growth of SiN_x thin films using Si_2Cl_6 and ammonia (Ref 15). The latter, however, has serious side effects to the vacuum system because of chlorides. Reactions of plasma with the steel surface will be very complex and they can be imagined as shown in Figure 2. It is likely that the vacancies formed at the surface after sputtering some of the iron atoms, will be filled with silicon atoms coming from plasma to the surface. We are hoping that the process can be easily used for the gases used for doping the surface with silicon and other gases was delivered by the specially designed perforated tubing to the plasma zone. There was a mixture of 2% silane, bal. hydrogen used for dosing the nitriding atmosphere, which contained a mixture of nitrogen and hydrogen with the addition of methane and argon. One-inch disk samples of the quenched and tempered H-13 steel were prepared for the experiments. They were run in various two-step cycles. The first nitriding step was to form the nitrided layer to establish a base for the second-step treatment, which was to form the nano-structural layer containing silicon and nitrogen. The temperature was controlled by the thermocouple which was inserted in a round steel table to hold the samples.

All the samples were located in special rings to prevent the edge effect during the plasma treatment. Voltage in the soaking portion of the cycle was about 730 V. The generated plasma allowed for maintaining a preselected cathode temperature of 520° C (978° F).

Characterization of the PEN Surfaces

Metallography

The nitrided layer formed in the first step of the process was about 0.27 mm-thick as determined from the microhardness profile, Figure.3.

larger forging dies and carried out in modified plasma nitriding equipment.

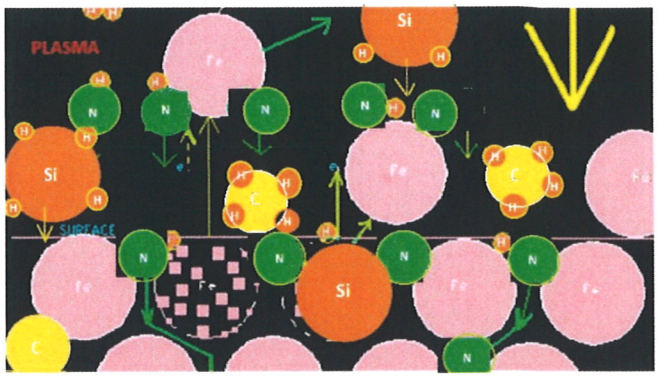


Fig. 2. Hypothetical spectrum of ions and atoms in near-cathode region of the glow discharge used for forming enhanced nanostructure in steel.

Experiments

Plasma Processing

All the processing experiments were carried out in the laboratory-type ion (or plasma) nitriding system. The system was equipped with the power supply allowing it to generate cathodic as well as anodic pulses. Such plasma characteristic with the reverse polarity were necessary for forming layers with higher content of the non-conducting phases such SiO or SiO_2. A mixture of

It should be noted that the compound layer resists etching with the nital (5% HNO_3 in alcohol) suggesting that it has a better corrosion resistance than the diffusion layer. The layer has two distinguished sublayers; the compound layer of about 0.004-0.006 mm near the surface and the diffusion layer below it, Figures 4.

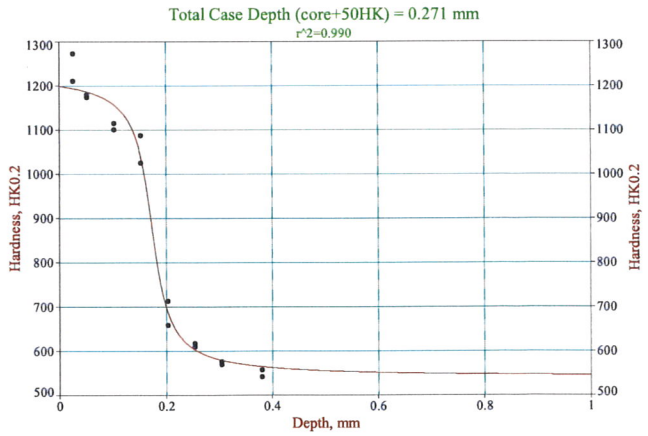


Fig. 3. A typical hardness profile in H-13 sample subjected to the duplex PEN treatment.

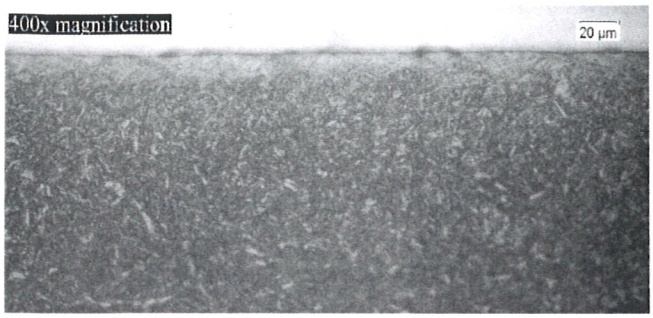


Fig. 4. Photo micrographs of the H-13 sample after duplex, nitrided and PEN plasma treatment, 400 X Etched with 5% nital solution.

Surface Analysis

The analysis was carried out on the H-13 samples subjected to the PEN treatment (Ref 16 and 17). Analysis revealed that the roughness of "as received" surface, *pa* was about 0.41 µm. However, the difference from the upper portion of the roughness, peaks to of the valleys was about 3 µm. This may affect the accuracy of depth analysis near the surface. Analysis with SEM also confirmed that the surface was enriched with silicon, carbon and nitrogen, Table 1 and Fig. 5. Two typical locations of the sample were selected for the modulated fast-flow Glow Discharge Mass Spectrometry (GDMS) analysis. It was shown that penetration depth of silicon, carbon and nitrogen in the steel reached about 3-6 µm, Figure 6 a and b.

Table 1. Top surface composition of the PEN sample tested with XDS Bruker Quantax 70 (Ref. 16 and 17).

Element	AN	Series	Unn C wt%	Norm C wt%	Atom C wt%
Iron	26	K	75.56	78.56	52.49
Carbon	6	K	8.70	9.05	28.11
Silicon	14	K	5.22	5.43	7.21
Nitrogen	7	K	3.44	3.58	9.53
Chromium	24	K	2.94	3.05	2.19

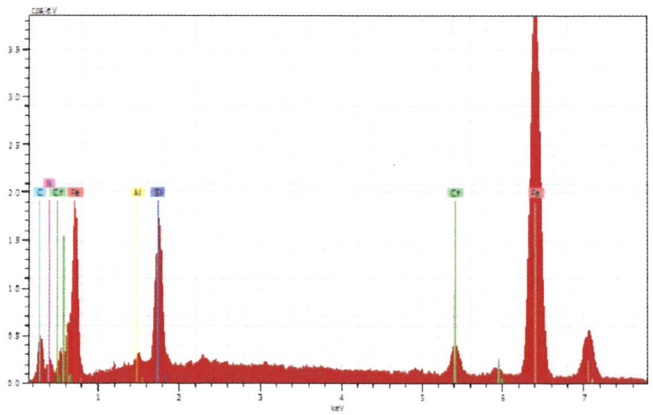


Fig. 5. Elemental spectrum of the PEN surface tested with EDS: Bruker Quantax 70 (Ref. 16 and 17).

It should be noted that this is approximately the same depth as a depth of the compound layer revealed by the metallography. It is also interesting to note that the near surface area of the sample contains an elevated level of oxygen. It is very likely that this was caused by the elevated presence of silicon, which having a high affinity to oxygen worked as a getter collecting impurities from the system. The level of nitrogen below this first compound layer (zone) stays at 230-240 ppm, which is consistent with the level of the solid solution of this element in alloyed ferrite (diffusion zone). *XRD analysis of the layers* was carried out on two samples; the H-13 samples were subjected to the plasma nitriding and the duplex plasma treatment (Ref 19). Diffraction patterns were obtained using graphite monochromatic copper K-alpha radiation on a computer-controlled Bragg-Brentano focusing geometry horizontal diffractometer.

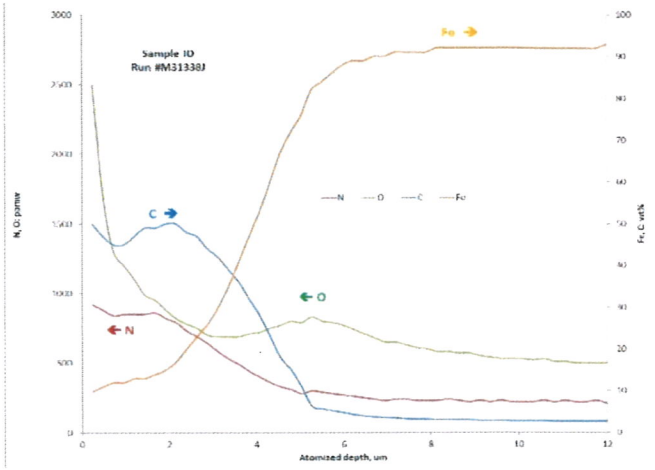


Fig. 6. Modulated fast-flow Glow Discharge Mass Spectrometry (GDMS) surface analysis of the H-13 steel sample with the PEN. Note distribution of silicon a) nitrogen, carbon and oxygen near the surface in b), (Ref. 16 and 17).

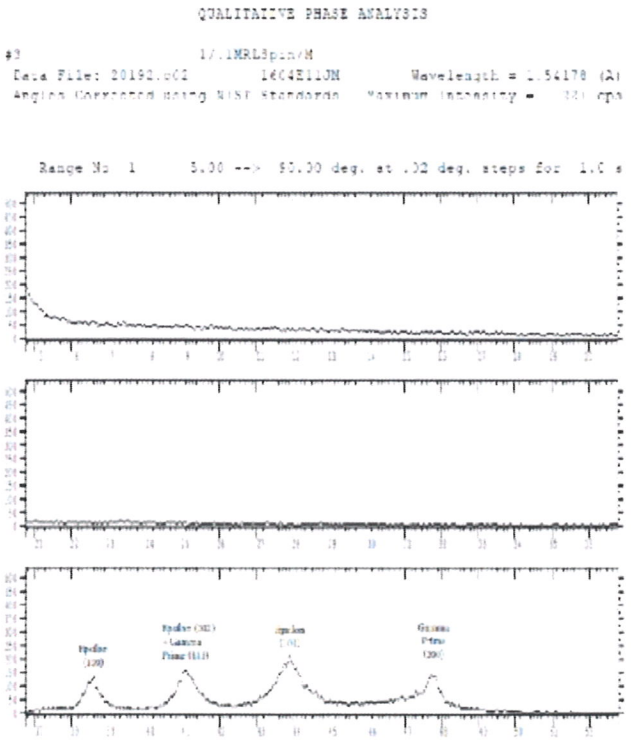
XRD analysis of the layers was carried out on two samples; the x-ray diffraction patterns were analyzed using first and second derivative algorithms, after Golay digital filter smoothing, to determine the angular positions and the absolute and relative intensities of each detectable diffraction peak. The diffraction patterns for both specimens were similar, with epsilon iron nitride, $Fe_{2\text{-}3}N$ appearing as the major phase in both. Gamma prime, Fe_4N nitride was also identified in the diffraction patterns for both specimens, see Table 2 and Figure 7 a and b.

The cell dimensions of the nitrides were: a=0.2695 nm and c=0.4362 nm for the hexagonal epsilon phase and a=0.3795 nm for cubic gamma prime phase. There may be an unidentified peak present in the patterns at about 46.5 to 47 deg. and a trace peak for the PEN sample at 63.5 deg. shown in Figure 8 b. This could be related to the presence of silicon,

but it is not possible to positively identify these peaks to any particular phase without additional information.

Table 2. Quantitative phase analysis of two plasma treated coupons of H-13 steel

Sample	Phase	Formula	Structure	Relative Abundance
Plasma Nitrided	ε	$Fe_{2-3}N$	Hexagonal	Major
	γ'	Fe_4N	Cubic	Minor
Duplex Plasma Treated	ε	$Fe_{2-3}N$	Hexagonal	Major
	γ'	Fe_4N	Cubic	Major



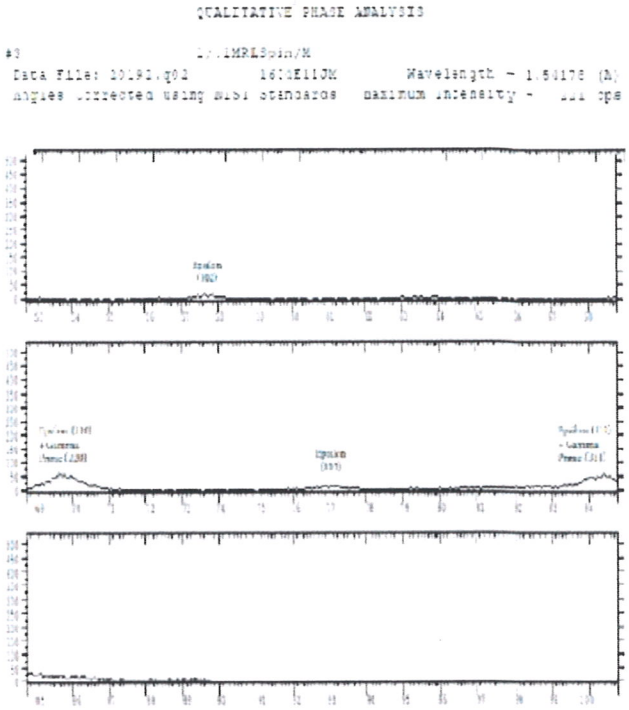


Fig. 7. XRD patterns of the PEN sample showing peaks of the epsilon and gamma prime nitrides, a) and unidentified peak at 63.5 deg., b), (Ref. 19).

Based upon the intensity of the peaks, the sample with the Plasma Enhanced Nano layer (PEN) seemed to have a larger percentage of the gamma prime phase versus the epsilon phase as compared to the plasma nitrided sample (PN). This is probably an effect of the silicon atoms present in the upper portion of the compound zone replacing iron atoms as shown in Figure 7 a. Despite minor content of carbon in the steel as well as in the plasma promoting formation of the epsilon nitride, the effect of silicon on phase composition seems to be stronger and therefore more gamma prime nitride was formed.

Mechanical evaluation of the treated surfaces

Mechanical properties of the layers formed during our experiments were assessed using a combination of the adhesion and scratch testing to determine resistance to scratching and coefficient of friction, fracture testing; nanohardness and Young's modulus of the layer; fracture toughness.

Microhardness

The microhardness profile for the PEN sample is shown in Figure 3. Areas near the surface could not be tested accurately with the Vickers or Knoop indenters therefore the nano hardness testing of the surface was carried out.

Nano hardness

Testing was performed in accordance with ASTM E2546 except for the following: the loading and unloading time was

30 s instead of 15 s (Ref 20 and 21). The measured values of indentation hardness (H_{IT}), indentation modulus (E_{IT}) and maximum indenter displacement into the sample (h_{max}) are tabulated below with their averages and standard deviations. Table 3 and 4 present a summary of the results. The following units are used: -Vickers (kG/mm2) and MPa for H_{IT}, -GPa for E_{IT}, -Microns (micrometers) for h_{max}, -The conversion for HIT in MPa is the following (modified Berkovich indenter): H_{IT} [Vickers] ~H_{IT}/10.8 [MPa]. It should be noted that despite a slightly lower hardness of the PEN sample, the penetration depth of the nano indenter was lower in it than into the PN sample. However, the samples could not be indented with multiple loads in order to monitor the influence of the surface since the surface layer was apparently very thin and also was too uneven and textured, see Figure 4 and 5.

Table 3. The measured values of indentation hardness (HIT), indentation modulus (EIT) and maximum indenter displacement into the sample (h_{max}) of the Plasma Nitrided (PN) and Plasma Enhanced Nanostructure (PEN) samples.

Sample	H_{IT} (Vickers)	H_{IT} (MPa)	E_{IT} (GPa)	h_{max} (microns)
PN	1,153 ±151	12,453 ±1,626	233.94 ±8.67	0.305 ±0.016
PEN	1,078 ±110	11,646 ±105	239.76 ±25.59	0.217 ±0.002

Table 4. Details of the nanohardness data of the two PN and PEN samples tested with 20 mN and 10 mN loads.

Sample (Load)	H_{IT} (Vickers)	H_{IT} (MPa)	E_{IT} (GPa)	h_{max} (microns)
PN (20mN)	1,205	13,015	231.82	0.300
PN (20mN)	1,271	13,724	243.47	0.292
PN (20mN)	984	10,621	226.53	0.323
Average (PN)	1,153	12,453	233.94	0.305
Std Dev (PN)	151	1,626	8.67	0.016
PEN (10mN)	1,085	11,720	221.66	0.218
PEN (10mN)	1,072	11,572	257.85	0.215
Average (PEN)	1,078	11,646	239.76	0.217
Std Dev (PEN)	10	105	25.59	0.002

Due to the surface texture, it was difficult to get reliable readings. Not enough data could be obtained in order to extrapolate the modulus to the origin. The readings should be used for comparative purposes only. The influence of the surface substrate on the results is unknown at this point.

Scratch resistance

Scratch resistance of the Non-Treated (NT), Plasma Nitrided (PN) and Plasma Enhanced Nanostructure (PEN) samples were tested using the instrumented scratch testing method (Ref 21). The testing was performed using Nano Scratch Tester "NST" from CSM Instruments S/N 01-2767: software "Scratch" version 4.48. The guidance, recommendations and general procedure are from ASTM standards (G171, C1624 and D7187). The table below shows statistically evaluated results for all the samples tested. NST data sheets and pictures of the surface are shown in Figure 8 a, b, and c.

Table 5. Results of the scratch test performed on NN, PN and PEN samples. Where Lc is a critical force at which damage of the layer occurs and Rd is a residual depth of permanent deformation.

Sample	Settings 1 & 2 Continuous Delamination Lc (mN)	Setting 3 Mean Rd (μm)
NN	-	1.28 ± 0.20
PN	258.66 ± 47.22	0.75 ± 0.01
PEN	425.54 ± 43.76	0.52 ± 0.30

The testing data shown in Table 5 and Figure 8 strongly suggest that the sample PEN has the best scratch resistance of all the samples tested. This sample has also the least damage to the surface from the scratch indenter.

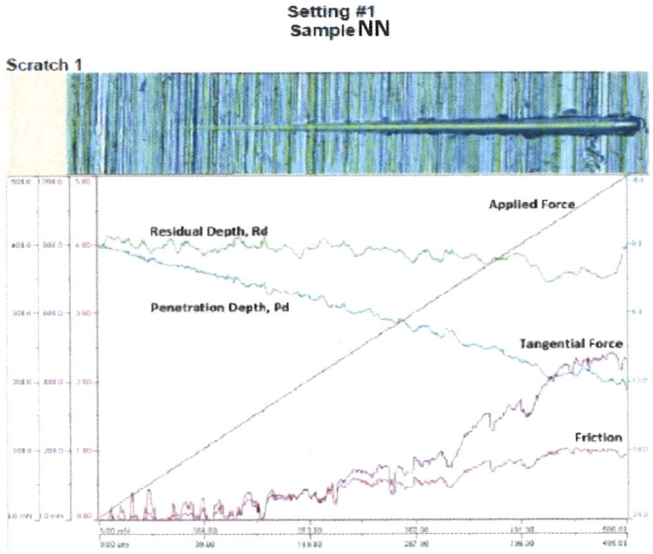


Figure 8 a. Nano scratch data (NSD) of the samples with pictures of the wear patterns. Graph shown is for a NN sample

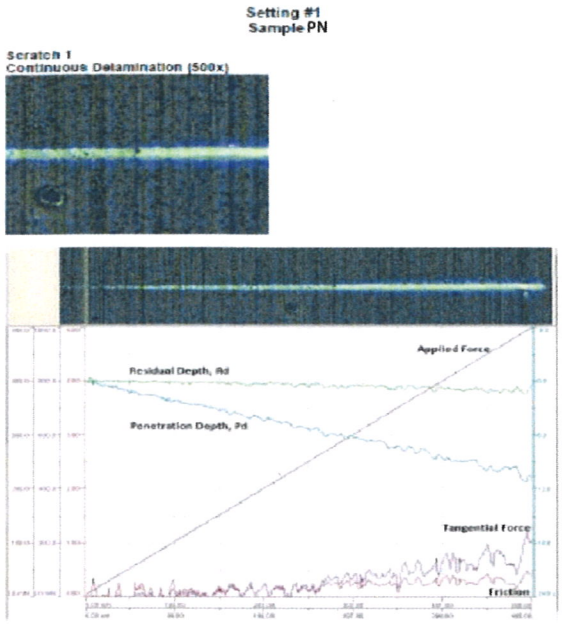


Fig. 8 b. Nano scratch data (NSD) of the samples with pictures of the wear patterns. Graph shown is for a PN sample (Plasma nitride), (Ref. 21)

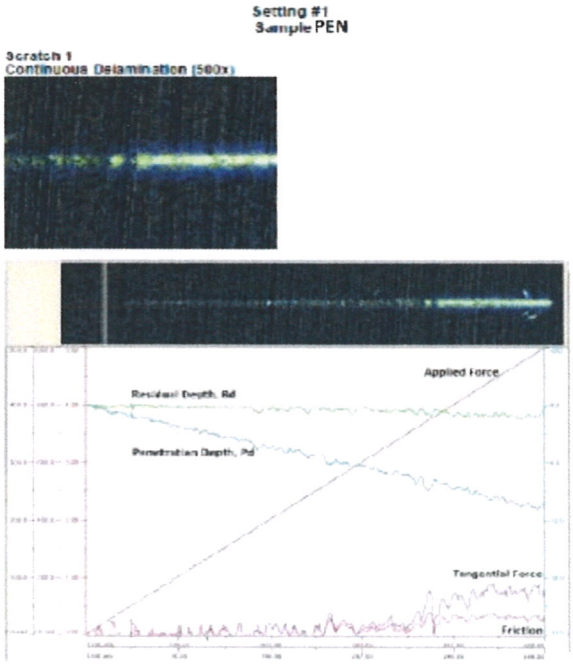


Fig. 8 c. Nano scratch data (NSD) of the samples with pictures of the wear patterns. Graph shown is for a PEN sample (Plasma Enhanced Nanostructure), (Ref. 21)

Wear Resistance

Testing was performed using the pin-on-disk method in accordance with ASTM G99 (Ref 22). Specimens tested were: Quenched and Tempered (Q&T) H-13 not nitrided (NN), Q&T H-13 plus plasma nitrided (PN), Q&T H-13 plus plasma nitrided and Plasma Enhanced Nanostructured (PEN). The counter specimen was 440C grade 25 stainless steel ball.

Results: Sample NN starts with the lowest friction and ends with the highest. Sample PEN starts with the highest friction and ends with the lowest.

Notes/observations (balls)

The most wear was observed for sample NN, the least wear was observed for sample PEN.

Note/observations (tracks): the least damage was observed for samples PN and PEN, sample PEN had the smallest/narrowest track, none of the generated tracks were clean. In all cases, material adhered in the track, making it difficult to accurately evaluate the material loss, especially for sample PN and PEN. Tables 6 and 7 and figures 9 a-c below illustrate results of the tests.

Table 6. Ball wear cap diameter after the wear test.

Setting #	Sample	Disk Cross Section Wear Track (μm^2)	Disk Volume Loss (mm^3)	Ball Wear Cap Diameter (μm)
1	NN	NR	NR	NM
1	PN	NR	NR	420
1	PEN	NR	NR	299
2	NN	NR	NR	869
2	PN	NR	NR	839
2	PEN	NR	NR	704

Table 6. Coefficient of friction recorded during the wear test.

Sample	Setting #1 (start μ)	Setting #1 (end μ)	Setting #2 (start μ)	Setting #2 (end μ)
NN	0.15	0.68	0.17	0.97
PN	0.20	0.78	0.24	0.99
PEN	0.26	0.59	0.31	0.92

Graphs demonstrating changes of the coefficient of friction versus time for the three samples are shown in Figure 9. It should be noted that the best performing sample during the wear testing was the sample with the PEN treatment. It had the lowest coefficient of friction against the 440C stainless steel ball as well as the smallest/narrowest track.

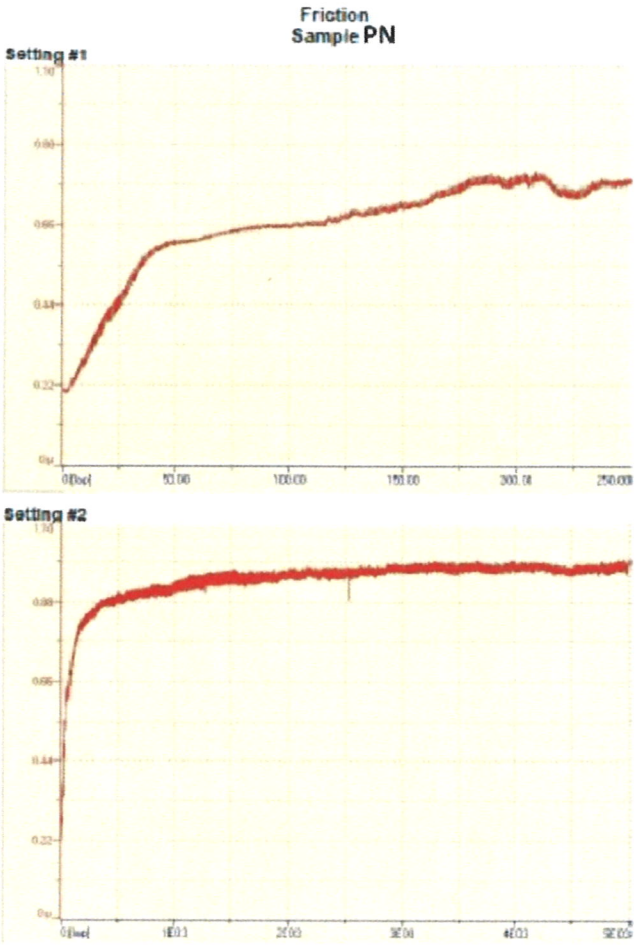


Fig. 9 a. Graphs of coefficient of friction versus time for the three samples treated with: PN.

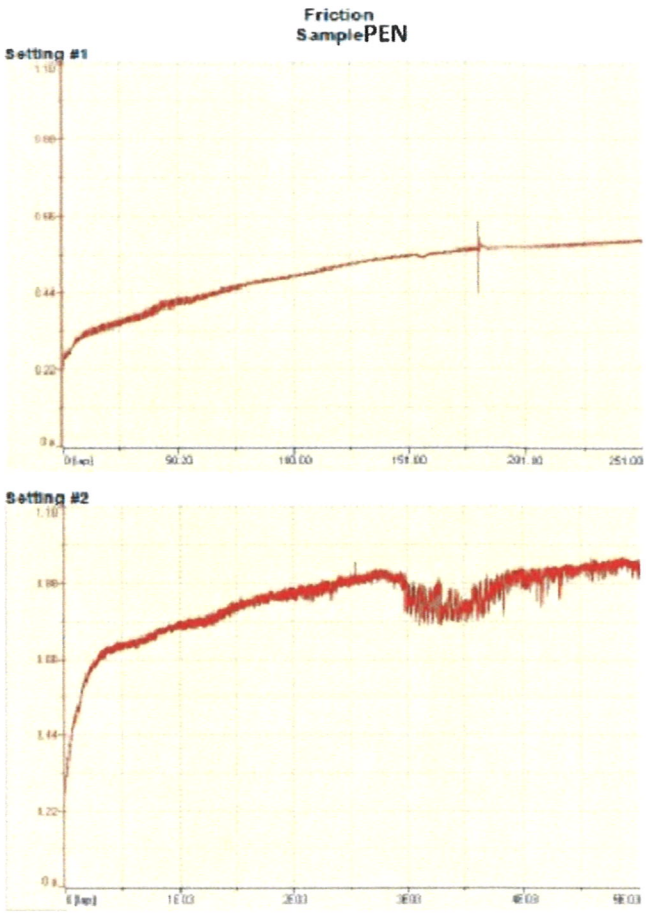


Fig. 9 b. Graphs of coefficient of friction versus time for the three samples treated with PEN

Conclusions

The GDMS analysis was carried out on samples subjected to the duplex plasma treatment (PEN). Testing revealed that the surface was enriched with silicon, carbon and nitrogen. XRD testing confirmed that the nitrided layer supporting the PEN layer had a structure containing hexagonal epsilon ($Fe_{2-3}N$) and cubic gamma prime (Fe_4N) nitrides. Presence of silicon in the surface of PEN appeared to be crucial for its mechanical properties. Mechanical testing carried out on the samples revealed that the properties of the PEN (Plasma Enhanced Nano layer) are superior over the properties of the PN (Plasma Nitrided) or the quenched and tempered steel. This finding was also confirmed by both the scratch and the wear tests. It was also observed that there is a reduction in coefficient of friction on the PEN sample as compared to the other samples. Therefore, based on the above results we can expect that the layers formed with the PEN process will have better stamping properties. The presence of silicon either in a form of silicon nitrides or carbides will very likely also enhance thermal stability of the nano layer required for forging or hot stamping application.

Acknowledgments

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