NITRIDING RESPONSE OF HIGH SPEED STEELS USING ACTIVE SCREEN PLASMA NITRIDING (ASPN)

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ABSTRACT

In the present study, an evaluation of the active screen plasma nitriding (ASPN) technique was carried out on three grades of high speed steel (HSS) substrates using a full factorial experimental design for two factors, namely, substrate bias and prior ion etch, at two levels. The results showed that the hardening response of the substrates that had been salt bath heat treated (two of the grades investigated) prior to AS plasma nitriding was highly variable. Analysis by X-ray photo-electron spectroscopy suggested that this poor response was related to contamination due to sputter/re-deposition of chloride salts from unground surfaces. The third grade of HSS was vacuum heat treated and this grade showed a consistent hardening response to the ASPN treatment. In particular, a good response was recorded for a treatment condition of of low substrate bias and prior ion etch. This results suggests that in AS plasma nitriding one should be able to avoid the problems of edge effects and hollow cathode effects so dominant in dc plasma nitriding. Finally, a preliminary study of ASPN nitrided surfaces using Focussed Ion Beam (FIB) milling revealed an acicular microstructure not evident in the more traditional metallographic techniques.

KEYWORDS

Active screen plasma nitriding (ASPN), design of experiments (DOE), microhardness, X-ray photo-electron spectroscopy, microstructure, Focussed ion beam (FIB) milling.

INTRODUCTION

The world market for cutting tools, estimated [1] to be worth of the order of $US 10 billion, is broadly divided into two groups of tool materials, namely, cemented carbide and high speed steel (HSS). Recent estimates [2] of the market share for HSS cutting tools is around 35%. There is little doubt that this figure would be much lower today if it had not been for the revolution that has taken place in Surface Engineering over the last twenty years.

For the cutting tool industry, the technology leading the way in this revolution has been the plasma-based processing technology of physical vapour deposition (PVD). This highly flexible process has developed well beyond its early promise of extended drill life through the vapour deposition of TiN [3]. Since then the market has become increasingly sophisticated with the introduction of multi-element coatings (eg. TiCN, TiAlN, TiAlCrYN, etc) further compounded with options of single layer, multi-layers and nanocomposites. It is evident that such plasma-based processing technologies are still an emerging technology with considerable scope for further innovation. One such area, in which there is considerable interest, is in the exploitation of duplex surface engineered systems. One example of such a system is plasma nitriding of a steel substrate prior to vapour depositing a hard thin film or a lubricant thin film.

Some recent results [4] of plasma nitriding of M2 HSS, followed by vapour deposition of TiN, offer the possibility of significant improvement in tool life over that of just straight PVD TiN. However, this same study advises caution due to the fact that, in some plasma nitriding systems, nitrogen mass transfer depends on the current density which can be significantly high at the lip of a cutting tool resulting in excessively deep and brittle diffusion layers and, hence, reduced service life of the duplex treated cutting tool.

The same authors also demonstrated, in machining tests using centre drills, that a combination of sand-blasted drills, plasma nitrided in a low nitrogen atmosphere, gave the lowest flank wear, while drills plasma nitrided in a high nitrogen atmosphere gave the lowest values of torque and feed force but not the lowest flank wear. Add to this the generally accepted notion that PVD coatings have much higher adhesion when deposited on bright nitrided surfaces, ie nitrided surfaces without a compound layer, it is evident that further work needs to be done on a characterising plasma nitrided HSS surfaces before duplex treated surface engineered surfaces become more widely accepted.

The aim of the present study was, therefore, one of characterising the nitriding response of different types of HSS steels when treated by the novel process of active screed plasma nitriding ASPN [5]. The latter process would seem to offer considerable benefits given the potential of ASPN for limiting the bias voltage during nitriding and hence reduce the potential for cutting edge brittleness.

1. EXPERIMENTAL METHOD

The approximate compositions of the HSS steels selected for this investigation are listed in Table 1.

Table1: Composition in wt. % of the commercial grade of HSS investigated.

HSS Commercial Grade	C	Cr	Mo	W	Co	V	Hardness Range (HVN)
M2	0.90	4.1	5.0	6.4	-	1.8	830-880
C8	1.05	4.0	6.0	5.0	7.8	1.6	920-960
M9V	1.20	4.2	8.5	3.5	-	2.7	850-900

The HSS samples were commercial blanks (ranging in diameters from 6-8 mm and lengths ranging from 60-80 mm) removed from production after the blanks had been soft machined, heat treated and partially ground.

Two blanks of each grade of HSS steel were held vertically in purpose made blocks of mild steel and placed on the work table in the nitriding chamber. The arrangement of the two blanks was such that one blank had no nearest neighbours (termed single) and the other blank was surrounded by six nearest neighbours at a distance of ~1.5 diameters (termed cluster). The objective of investigating such an arrangement was to find out if the cluster arrangement gave rise to any hollow cathode effects and thereby adversely affected the hardening response. The experiment consisted of a randomised full factorial experimental design for two factors at two levels (see Table 2). One factor involved adjustment of the substrate bias at high (25%) and low (10%) bias. These values were set via a manually operated potentiometer setting. The other factor involved the use of argon ion etching prior to the nitriding phase of the process cycle. Details of current and voltage values recorded for each treatment are shown in Table 3, while the ASPN process recipes are shown in Table 4.

Table 2: Experimental design for two factors at two levels. Factor A is bias and Factor B is etch.

No	Treatment	A	B	AB
1	(25% Bias, Etch ON)	+1	+1	+1
2	(25% Bias, Etch OFF)	+1	-1	-1
3	(10% Bias, Etch ON)	-1	+1	-1
4	(10% Bias, Etch OFF)	-1	-1	+1

Table3. Current and Voltage (Indicated values) for each treatment.

	Etch Step:				Nitride Step:			
Treatment No.	I_{screen} (A)	V_{screen} (V)	I_{work} (A)	V_{work} (V)	I_{screen} (A)	V_{screen} (V)	I_{work} (A)	V_{work} (V)
1	88	223	7.4	223	82.3	400	7.5	275.5
2	-	-	-	-	73.9	398.5	6.9	273.1
3	86	367	7	225	84	391	1.7	194.5
4	-	-	-	-	79.9	399.9	2.1	209.6

Table 4. Process Recipes. Note, step 1 is a ramp from room temperature to the set temperature which takes approximately one hour.

Process Parameter	Step 1 (Heat up)	Step 2 (Etch – OFF or ON)	Step 3 (Nitride)
Step Time (min)	1	30	30
Pressure (mbar)	0.75	1.5	2.0
Gas Mix (l/hr)	40.0 H_2	28.0 Ar, 28.0 H_2	120 N_2, 10.0 CH_4
Bias	OFF	ON	HIGH or LOW
Temp (°C)	505	505	505

In the ASPN process, the temperature in each step of the process is controlled automatically by varying the power supplied to the screen. The load and work table are heated by radiation from the glow discharge around the screen. The temperature is monitored by an isolated K type thermocouple mounted in a dummy sample on the worktable. The bias power supply is a pulsed DC unit running at 500Hz with a 75% duty cycle. During the negative pulse a higher frequency waveform is superimposed, running at ~5kHz. Process gases are supplied via mass flow controllers.

After each treatment, the nitrided blanks were sectioned and metallographically polished to 0-1 μm diamond finish. The sub-surface hardness profile was measured using a Shimadzu Microhardness Tester. The samples were than etched in 2% nital and examined metallographically. In the case of the latter examination, previous experience has shown that, although the depth of nitriding can be identified from the etching response, there is no other structural metallographic witness of the diffusion layer. We elected, therefore, to examine cross-sections of the blanks using focused ion beam milling (FIB) in an exploratory attempt to see if this new technique might reveal structural information in the top few microns of the nitrided surface layers.

Briefly, FIB milling involves the use of a finely focused beam of gallium ions to sputter very precise regions of material. Cross-sections can then be prepared according to Figure 1 using an aperture corresponding to a beam current of 2700 pA for the initial cuts, and a finer aperture corresponding to a beam current of 350pA for the final cleaning cuts. Greater detail of the

preparation of cross-sections using FIB milling can be found elsewhere [6]. Due to geometrical constraints, it is not possible to view the cross-section directly from above, consequently the FIB milled specimen is tilted with respect to the ion beam in order to image the cross-section. Charged particles emitted from the specimen surface may be collected by a detector, such that secondary electron (or ion) images can be obtained.

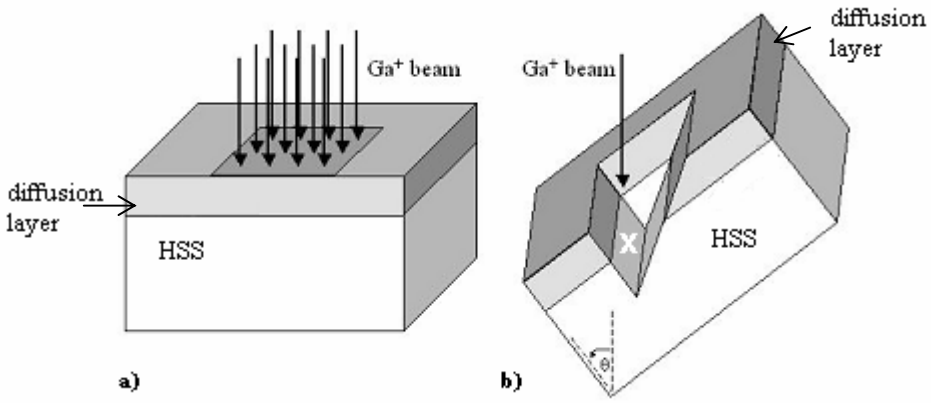


Fig 1. Schematic diagram of preparing a cross-section using the FIB. The specimen is a) milled using the ion beam and b) tilted to an angle (θ) so that the newly created surface can be imaged.

2. Results and Discussion

Sub-surface hardness profiles were measured for each HSS sample using a Shimadzu microhardness tester and the results are presented graphically in Figure 2. Also presented in Table 5 are the maximum sub-surface hardness values recorded between 10 –12 μm below the surface and the depth of nitriding response for each HSS material in the two configurations of single and cluster. In this study, the depth of nitriding response was measured at 50 hardness points above the mean substrate hardness. It is recognised that the results presented in Figure 2 are compromised to some degree because one is looking at relatively shallow depths of hardening in hardened and tempered substrates that contain large primary carbides and inevitably suffer some degree of edge rounding in preparation. We therefore sought to identify trends with respect to variation in the experimental factors. However, it should be noted that the M2 HSS treatment of high bias and prior etch for both the single and cluster configurations appears to have slightly overtempered and should therefore be excluded from further analysis. Otherwise, M2 HSS shows quite a reasonable response in sub-surface hardness and depth of hardening (Table 5).

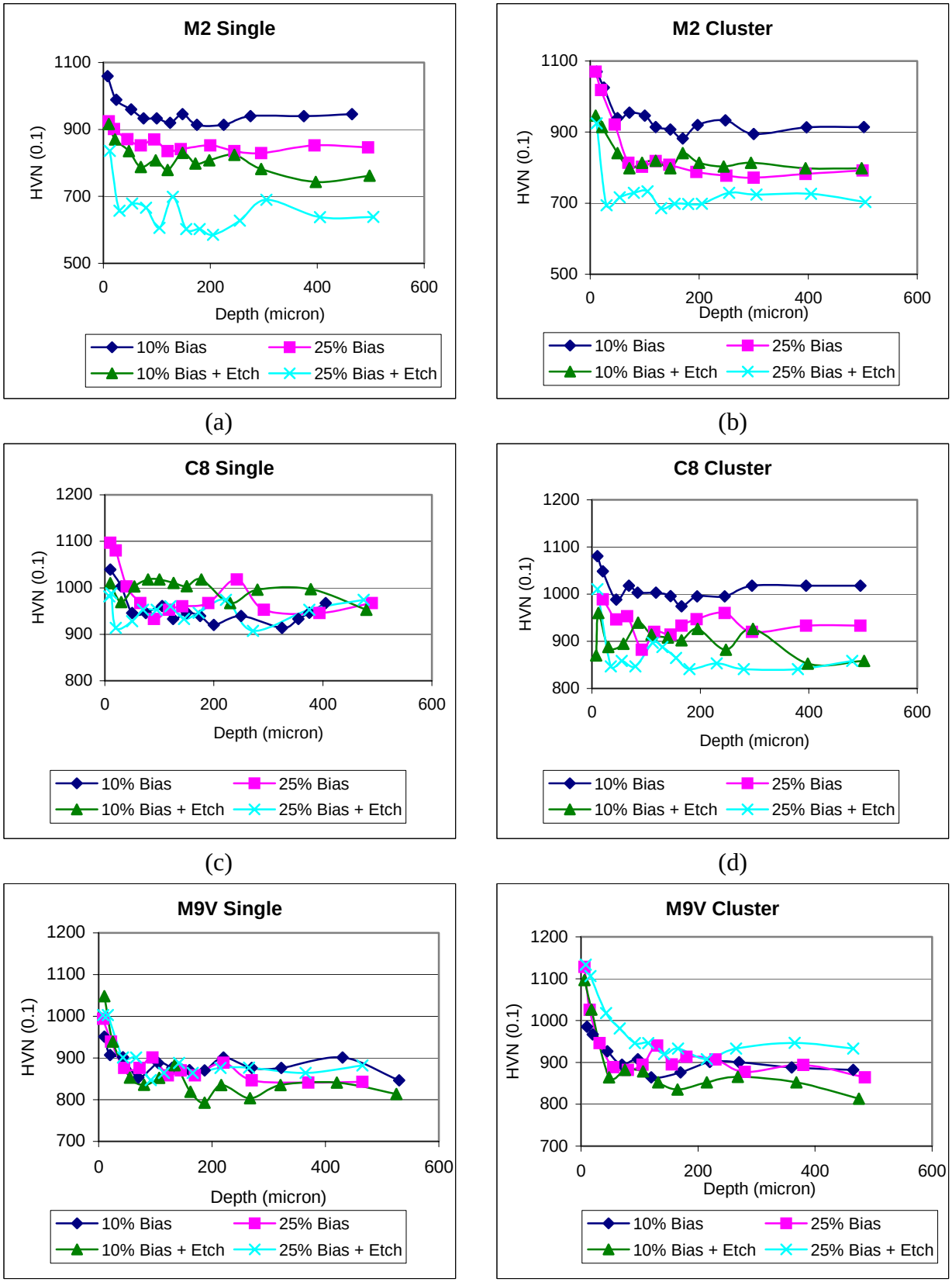


Fig. 2 Plots showing case depth hardness response for the single and cluster configurations for M2 (a,b), C8 (c,d)and M9V (e,f)steels.

The M9V results collectively showed a more uniform response across both factors on both levels. The worst response, in terms of depth of hardening, was the factor low bias only while the condition

of low bias plus prior etch showed a good sub-surface hardness and depth of hardening response for both the single and cluster configurations.

Table 5. Maximum sub-surface hardness and depth of hardening (measured at 50 points above the mean substrate hardness) for each of the three grades of HSS investigated.

Material	Configuration	High Bias		High Bias + Etch		Low Bias		Low Bias + Etch	
		Max $HV_{0.1}$	Depth (µm)	Max $HV_{0.1}$	Depth (µm)	Max $HV_{0.1}$	Depth (µm)	Max $HV_{0.1}$	Depth (µm)
M2	Single	924	20	835	25	1059	50	946	50
	Cluster	1070	50	925	15	1070	25	946	40
C8	Single	1097	35	982	-	1039	40	1010	-
	Cluster	989	10	1010	10	1081	10	960	-
M9V	Single	994	35	1003	35	951	15	1049	50
	Cluster	1128	40	1134	55	985	25	1097	30

The C8 HSS showed the least convincing response of all three materials investigated. Indeed, the only two significant responses, in terms of depth of hardening, were the two factors of high and low bias without prior etching.

In broad terms, the material showing the best overall response to both factors at both levels was the M9V HSS, followed by M2 HSS, while the worst material was clearly the C8 HSS. One might speculate that the high cobalt content of C8 was in some way impeding the nitriding response. However, the fact that high and low bias, without prior etching, gave a good response would seem to reject this hypothesis. At this point, it should be recalled that the three materials selected for investigation were taken directly from production. It transpired that the M9V material had been vacuum heat treated while the C8 and M2 had both been salt heat treated. Furthermore, the C8 HSS blanks had some 30% of its length still covered in a ‘black’ scale, the remaining 70% had been cylindrically ground removing up to 150 µm from the diameter. The M2 HSS blanks also had some surface scale where they had not been cylindrically ground. (The blanks were tap blanks and the region referred to is the neck of the tap, that is, the region between the pod and the shank.) It should be noted that this region on the M2 blocks was not so scale-like as in the case of the C8 blanks. The possibility of contamination due to sputter / re-deposition could explain the generally poor response of the C8 material. This was explored further by carrying out photo-electron spectroscopy (XPS) on the nitrided and scale ends of a C8 tap blank. The results are shown in Figure 3. Calcium is clearly present in both spectra but evidently more so in the black scale on the C8 blank. It is possible that this is a residue of the final step quench in salt heat treatment, since the salt bath is ~70% calcium chloride. The fact that calcium was detected on the nitrided end of the C8 blank, supports the contention that this could be due to self-sputter / re-deposition. Furthermore, the trends in hardening response for C8, as indicated in Table 5, appear to support the proposition that sputtering from contaminated surfaces is taking place resulting in re-deposition that is impeding the nitriding response. The treatments involving prior argon ion etching all suggest only limited, if any, hardening response. Treatments without a prior argon ion etch show a reasonable response for both high and low bias for the single configuration. The cluster configuration shows only a limited response which suggests that there is some plasma intensification which is giving rise to contamination from sputter/re-deposition.

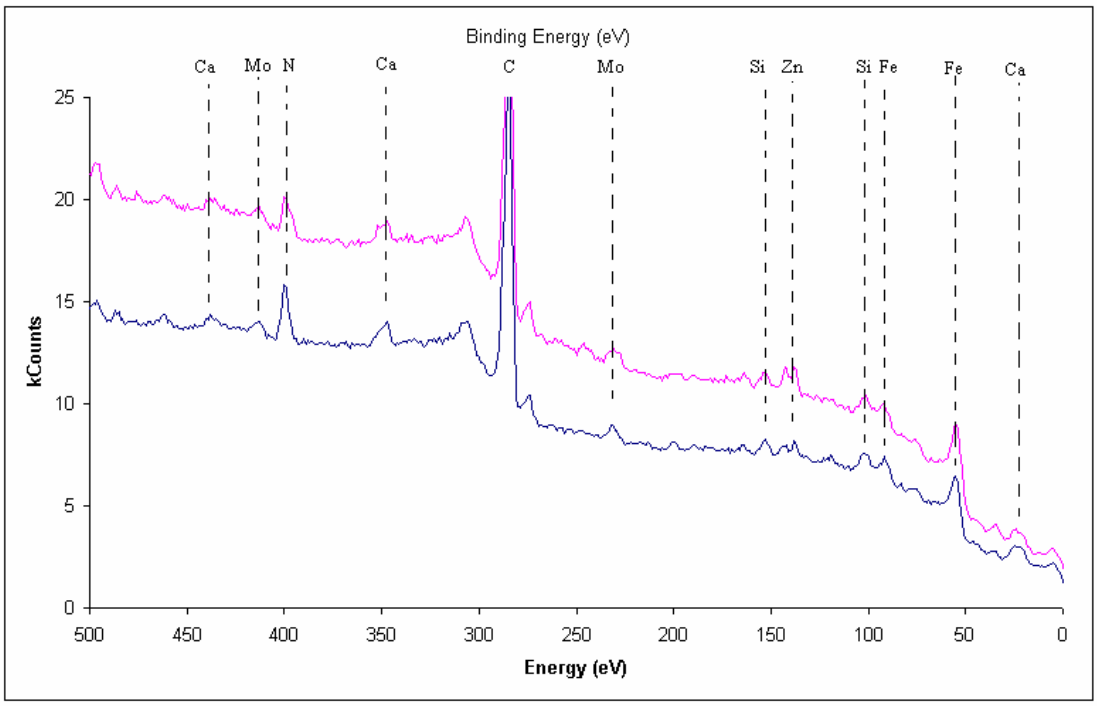
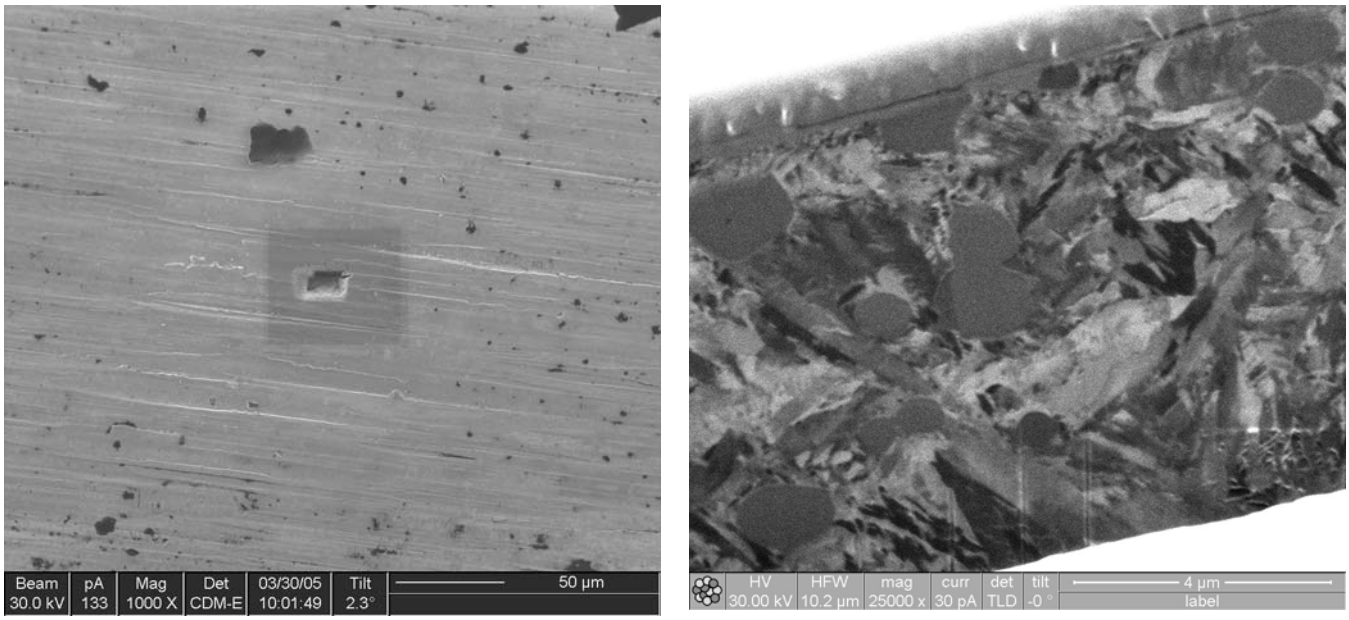


Fig.3 X-ray photo-electron spectroscopy spectra taken from the C8 HSS substrate where the lower spectra was recorded from the non-ground surface and the upper spectra is from the ground nitrided surface.

If this contention is correct, one might view the results presented in Fig 2 from a different perspective. The materials that show the greatest variability to nitriding are the salt bath heat treated C8 and M2 HSS materials. Whereas, the vacuum heat treated M9V materials shows pretty much a consistent response for all materials. Indeed a closer examination of the results for M9V reveals some interesting trends. It is evident that low bias only gives the poorest hardening response (Table 5). The other three treatments are similar although there is some variation between the single and cluster configurations. The fact that these three treatments yield similar hardening responses suggests that ionic bombardment has an important role to play in governing the mass transfer of nitrogen from the plasma to the HSS substrates. However, the level of ionic bombardment to achieve a good hardening response is not that high in the ASPN treatment. Clearly, the treatment condition of low bias with prior ion etch represent good operating parameters since they are less likely to lead to cutting edge brittleness of the type reported by Kwietniewski et al [4]. Also, clustering (a commercial necessity, if plasma processing is to be cost effective) for M9V shows only a slightly shallower hardening response with an increase in surface hardness. Clearly one would need to carry out further study before being certain that such differences are real and related to material or process variables.



(a) (b)

Fig.4 FIB ion images showing (a) the ion milled trench in the as ground surface and (b) the ion milled cross-section.

As indicated in section 1 of this paper, it is generally problematic looking for fine structural detail in the diffusion layer of nitrided HSS substrate using optical or scanning electron optical microscopy techniques. As part of a preliminary study, we elected to use FIB milling to look at the cross-section of the immediate sub-surfaces of an M2 nitrided substrates. The results in the form of ion images are shown in Figure 3. Figure 3(a) is a low magnification ion image showing an ion beam milled trench on the HSS surface. Figure 3 (b) is an ion image of a FIB milled cross-section showing that the microstructure has a strong acicular appearance. The latter is no doubt related to the precipitation of alloy nitrides. The lathe-like structure is very fine, of the order of 100 nm. This possibly implies a high level of coherency with the matrix which contributes to the high level of residual stress associated with nitriding. Clearly, the FIB milling technique is one that gives far greater insight into the structural modification of the diffusion layer than the classical technologies of optical and SEM metallography and is a technique that we are continuing to exploit in an attempt to provide a much greater understanding of the ASPN process.

3. CONCLUSIONS

It is evident that High Speed Steels have the potential to show a good hardening response to nitriding using the novel process of ASPN. However, it is essential that attention be paid to the possibility of contamination arising from pre-processing activities such as salt bath heat treatment. Such contamination can impede nitriding through a process of sputter and re-deposition.
The M9V HSS showed a good collective response to all factors on both levels. Of particular note was the good response for both the single and cluster arrangements in the low bias and prior argon ion etch condition. This finding augers well for the new technology of ASPN since, under these conditions, one should be able to avoid the potential for cutting edge brittleness and hollow cathode effects when substrates are packed under high density conditions.

Examination of FIB milled cross-sections of nitrided surfaces revealed a very fine acicular structure implying a high level of coherency between the alloy nitride precipitates and matrix. Clearly, the FIB milling technique has the potential to give far greater insight into the structural modifications

taking place in the diffusion layer than the classical techniques of optical and electron optical microscopy.

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