

August 6, 2010



CONTROLLING COMPOUND (WHITE)
LAYER FORMATION DURING
VACUUM GAS NITRIDING

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August 6, 2010

ABSTRACT

Solar Atmospheres has established a method of controlling the amount and depth of White layer resulting from Gas Nitriding. This procedure was accomplished following extensive testing using AISI 4140 Steel in a Solar Atmospheres Gas Nitriding Vacuum furnace. Various applications requiring Nitriding often require specific White layer limits which can now be provided by this process.

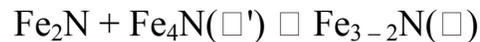
Following an initial rapid pump down to produce an Oxygen free, vacuum environment, the Nitriding cycle consisted of a pre-heat at a partial pressure of Nitrogen followed by Nitriding at a slightly positive pressure using an Ammonia/Nitrogen mixture. Many cycles were performed varying the time and gas flow parameters at temperature and the resulting White layer composition and thickness determined. The key to controlling the White layer formation was the introduction of a Boost-Diffusion technique during the Nitriding phase. Surface hardness and depth of nitride zone were then recorded from microhardness measurements and metallography. All this data was compiled to establish Nitriding procedures that provide the final desired structure in the minimum cycle time. This includes processes that produce the minimum depth or complete absence of White layer as dictated by the final application of the parts.

August 6, 2010

BACKGROUND:

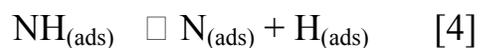
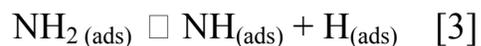
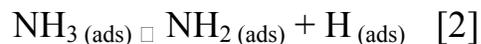
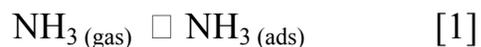
The principal phases that form during the nitriding of iron base materials (steels) are first a solid solution of alpha-iron (α), which has a maximum solid solubility of about 0.11^{w/o} nitrogen. The next phase that forms is gamma-prime (γ'). This is a phase field that has a solubility range of about 5.1 to 6.1^{w/o} nitrogen, depending on temperature, and is usually represented by the chemical formula Fe_4N . The third phase for consideration is epsilon (ϵ) Fe_{3-2}N and it may have equilibrium nitrogen contents of 7 to 8 ^{w/o} nitrogen, depending on the temperature at which it forms, Figure 1.

There may be a "white layer", that appears microscopically, on the surface of the nitrided material. This white layer is composed of α and/or γ' . It also may contain Fe_2N and various iron-nitrides. Thermodynamically, ϵ cannot form below 577°C (1070°F). Therefore, the presence of ϵ is attributed to the reaction of ^{Ref 1.}:



These phases in the white layer may have desirable and/or undesirable characteristics depending on the intended application. Therefore, it is important to be able to control the nitriding process to produce the desired structure in terms of the composition of the white layer, and if a white layer is to be present or not.

Gas nitriding usually is accomplished with an atmosphere of ammonia (NH_3) in a mixture of nitrogen (N_2), or dissociated ammonia (D-NH_3), or hydrogen (H_2). The sequence of events that occur during nitriding, according to Arabczyk, et. al. ^{Ref 2.} is as follows:



August 6, 2010

All of the above gases are adsorbed on the surface of the steel and form a gas layer. Fresh ammonia must diffuse through this layer, or the layer can be swept away. This why it is beneficial to have a dynamic, rather than a static, atmosphere to sweep away the layer. The radicals NH_2 and NH have a much higher adsorption potential than the NH_3 molecule. Therefore, the step-by-step breakdown of the NH_3 molecule accelerates the adsorption. The N and H atoms diffuse into the iron lattice, while the NH radicals diffuse along the grain boundaries. The hydrogen that goes into the metal is a reversible reaction, and diffuses out to form molecular hydrogen that is liberated.

The rate limiting reaction of the above equations depend on the partial pressure of the hydrogen. At nitriding temperatures greater than 350°C (662°F) the following situations occur:

$$P_{\text{H}_2} < 525 \text{ torr} \quad \text{equation [2] controls}$$

$$525 \text{ torr} < P_{\text{H}_2} < 750 \text{ torr} \quad \text{equation [3] controls}$$

Once the nitrogen is adsorbed, nitriding proceeds as follows:



The diffusion rate of nitrogen into the solid varies according to which phase it is diffusing through. Assigning a diffusion rate of one (1) to the rate through the alpha phase, then the diffusion rate through \square' is $1/25$, and through \square is $1/60$ ^{Ref 3}. Therefore, in order to expedite the nitriding process, the order of the development of the phases should be to maximize diffusion rates to minimize the total time.

If the nitriding reaction is permitted to proceed uncontrolled, nitrides (\square and/or \square') begin to form at the surface from the buildup of nitrogen. If permitted, this nitride layer (white layer) will become continuous, and the second stage of nitriding begins; the nitrogen coming from and through the white layer into the base metal at a much slower rate. In summary:

August 6, 2010

Stage I: N is absorbed into the alpha-ferrite.

Stage II: Solubility limit is reached in ferrite and gamma-prime starts to form.

Stage III: Solubility limit of gamma-prime is reached and epsilon starts to form.

As the reactions proceed from Stage I to Stage III, the diffusion of nitrogen into the base metal becomes progressively slower. Therefore, it seems plausible that a process that avoids Stages II & III would develop the desired depth of the alpha solid solution more quickly. This would be a process that would avoid the formation of a white layer. The avoidance of white layer can be accomplished at lower nitriding temperatures and/or lower nitriding potentials (K_n). Where:

$$K_n = \frac{P_{\text{NH}_3}}{(P_{\text{H}_2})^{3/2}} \quad \text{Ref 4.} \quad P \text{ is the partial pressure}$$

However, the diffusion coefficient decreases as both the temperature and nitriding potential decrease. Conversely, increasing both of these quantities, increases the diffusion rate while also increasing the rate at which white layer forms.

It has been found by Zinchenko, et. al.^{Ref 5.} that at 400 to 590°C (752 to 1094°F) that the solubility limit of nitrogen in alpha-ferrite forms very quickly. The gamma-prime phase starts to form within seven (7) minutes, and peaks in 25 to 30 minutes. However, these values depend on K_n and times would be significantly longer at lower K_n values. Nevertheless, it seems plausible to expedite the nitriding process using a **Boost-Diffusion** technique, whereby the white layer is not formed in short boost times. In addition, if small amounts of a discontinuous white layer are formed, then it possibly could be dissolved during the diffusion step. Using this type of process would expedite the formation of the desired nitrided depth of the base metal. If a white layer is desired, then it could be added as a second step at the end of the process rather than at the beginning.

The experiments in this study were designed to generate the information necessary to evaluate possible boost-diffuse nitriding techniques.

August 6, 2010

EXPERIMENTAL PROCEDURE:

General:

Small cylindrical specimens ($\frac{1}{2}$ " dia. x $\frac{1}{4}$ " high) were used in the experiments. The specimens were alumina sand blasted and then washed with methyl alcohol prior to nitriding. Specimens were placed in a vacuum furnace which was pumped down to $\sim 10^{-2}$ torr. The furnace was then back filled with nitrogen to 800 torr and heated to 980°F (527°C). The nitrogen was then pumped down to provide a given partial pressure. Ammonia was introduced into the furnace to a final total pressure of ~ 800 torr. A dynamic atmosphere of the ammonia–nitrogen mixture was maintained by introducing the partial pressure of each gas with mass-flow controllers. The dissociation was $\sim 65\%$.

Preliminary test runs of 5, 10, 20, 40, and 80 minutes indicated that no perceptible white layer formed until the 20 minute treatment. Figure 2 shows that the microstructure for the 10 minute nitrided specimen is void of white layer. Therefore, specimens were nitrided for 20 minutes, 40 minutes, or 80 minutes. The nitrided specimens were then given “diffuse” treatments, in nitrogen, at 980°F (527°C) for times of 0, $\frac{1}{2}$, 1, 2, or 4 hours. Specimens from each permeation were prepared for metallographic studies and photomicrographs were taken. In addition, microhardness traversals were made on cross-sections, inward from the surface. A 25 gram load, Vickers indentation was used and these values were converted to HRC hardness values.

RESULTS:

All three of the nitrided conditions produced “white layer”, as shown in Figure 3. Some details of the white layers are given in Table I below:

Table I
As – Nitrided Specimen Details

<u>Nit. Time(min.)</u>	<u>Wht. Layer</u>	<u>Depth(in.)</u>	<u>Composition</u>	<u>Continuous</u>
20	yes	$8.5-10.2 \times 10^{-5}$	$\square'+Fe_3N+\square$	No
40	yes	$8.5-13.5 \times 10^{-5}$	same	Yes
80	yes	$10.2-17.0 \times 10^{-5}$	same	Yes

August 6, 2010

The results of the tests on dissolving the white layer by diffusion treatments are given in Table II.

Table II
Diffusion Time to Dissolve White Layer

<u>Nit. Time (min.)</u>	<u>Diffusion Time to Dissolve</u>
20	½ to 1 hour
40	1 to 2 hours
80	2 to 4 hours

The metallographic evidence for the data in Table II is given in Figures 4, 5, & 6.

DISCUSSION:

The importance of a clean active surface for nitriding cannot be over emphasized. When specimens were not sand blasted, but just wiped with alcohol, there was no evidence of a white layer after a 20 minute nitriding treatment. Conversely, it can be seen in Figure 7 that when the specimens were alumina sand blasted and washed with alcohol, a white layer is starting to form after a 20 minute nitride treatment.

The effect of surface condition in a two stage nitriding cycle (1st stage 8 hrs. @ 527°C [980°F], dissociation ~35%; 2nd stage 6 hrs. @ 527°C, dissociation ~45%) is illustrated in the hardness traversal plot of Figure 8. The data reveals that the sandblasted specimen had much higher and deeper hardness penetration than the specimen that was just alcohol washed. However, sandblasting does produce a rougher surface. In order to have a smooth active surface, the specimens could have been heated up in hydrogen rather than nitrogen. Nitrogen heat up was selected for this study to simulate current commercial practice.

In order to compare continuous nitriding with a pulse boost–diffuse nitriding technique, additional test were made. The first test was to nitride for 36 hour using a continuous process. This was a “conventional” two stage cycle with “traditional” dissociation rates. Stage 1 was 7.2 hrs at 527°C (980°F), dissociation of 25%. Stage 2 was 28.8 hrs at 527°C, dissociation ~75%. The structure produced is shown in Figure 9a. Then a

August 6, 2010

series of four pulse boost-diffuse nitriding tests were made. In previous tests it was found that in order to dissolve the white layer formed after 40 minutes of nitriding, it was necessary to diffuse for between one and two hours. Therefore, pulse boost-diffuse cycles were designed to narrow down the required diffusion time to dissolve the white layer. The details of the pulse boost-diffuse tests are shown in Table III.

Table III
Pulse Boost-Diffuse Test Details

B-D Test	B(min.)	D(min.)	No. of Cyc.	Nit. Time(hr.)
1	40	80	18	12
2	40	100	15 (+60 min diff.)	10
3	40	120	13 (+80 min. diff.)	8.7
4	10	30	54	9

The extra diffuse times for tests #2 and #3 were to provide total times of 36 hours. The microstructures produced are shown in Figure 9b, c, d, & e. In addition, microhardness traversals were made for these tests and the results are shown in Figure 10.

It can be seen from Figure 9a that the conventionally nitrided material has a significant white layer composed of \square and \square' . Test B-D1 had significantly less total nitriding time (12 hours vs. 36 hours for the conventional nitrided material). In Figure 9b, B-D1 has a partially dissolved white layer. As Figures 9b, c, & d are examined, it is noteworthy that they represent decreasing total nitriding times and increasing diffusion times (see Table III). As a result, moving from B-D1 to B-D3 shows that progressively more of the white layer is dissolved, although it is not yet completely dissolved in B-D3. However, these results indicate that the pulse boost - diffuse nitriding technique can produce a nitrided structure free of a white layer.

In order to investigate this further, the B-D4 test was run (see Table III). The previous one cycle 10 minute boost test showed that no white layer forms. However, on repeated cycle testing the nitrogen layer at the surface could buildup, and after several cycles a white layer might form. Therefore, the B-D4 test was run in order to investigate this. The microstructure that resulted from this test is shown in Figure 9e. It can be seen that virtually the entire white layer is dissolved.

August 6, 2010

Nevertheless, white layer did form for the 10 minute boost cycle during repetitive pulses, indicating that the nitrogen enriched zone does buildup, and once it reaches a critical value, ϵ' forms. Since B-D3 and B-D4 had essentially the same total nitriding time (9 hours) the shorter boost time of 10 minutes used in B-D4 produced less residual white layer than the 40 minute boost time used in B-D3. Further, the 25 gram Vickers' microhardness results show that the surface hardness of B-D4 was higher than B-D3, and that B-D4 exhibited a better transition profile to core hardness, Figure 10.

Additionally, Figure 10 data shows that the conventional nitriding did produce higher hardness, but with a significant white layer. It is plausible that adjustments in the B-D technique could provide higher hardness, since only 1/3 or less total nitriding time was used in the B-D tests of this study. If a structure with no white layer is required for the conventional nitrided material, then it would require many additional hours to dissolve the white layer that was formed. In the case of the pulse boost-diffuse technique, once the desired nitrided case is produced without white layer then, if desired, a white layer could be added in a matter of minutes. Furthermore, if a white layer is added to the pulse boost-diffuse material there will be an increase in maximum hardness.

Additional work is planned in this area.

August 6, 2010

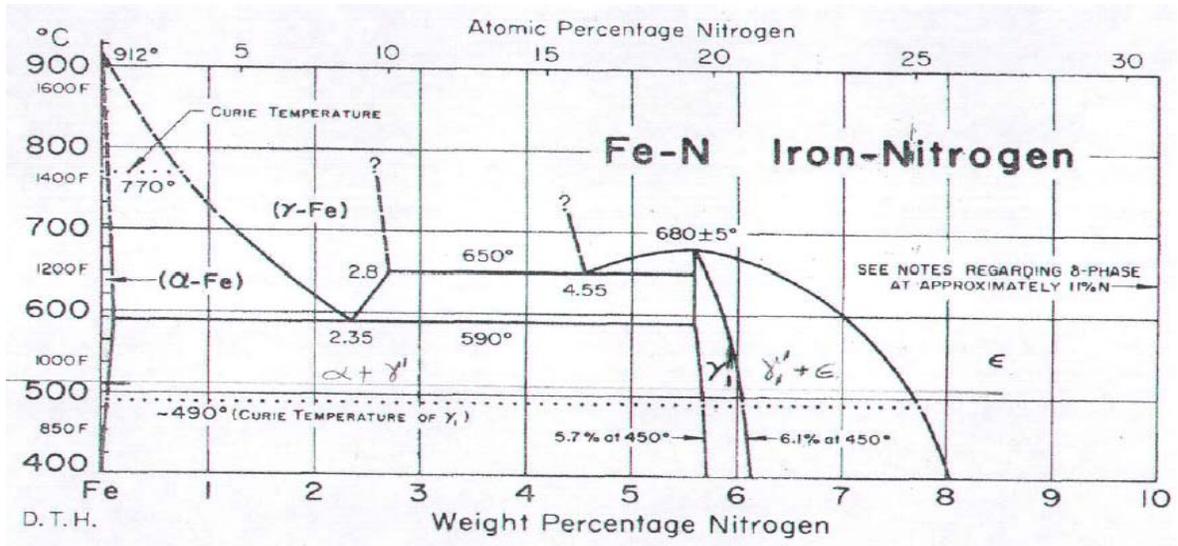


Figure 1: Iron – Nitrogen Equilibrium Phases Diagram

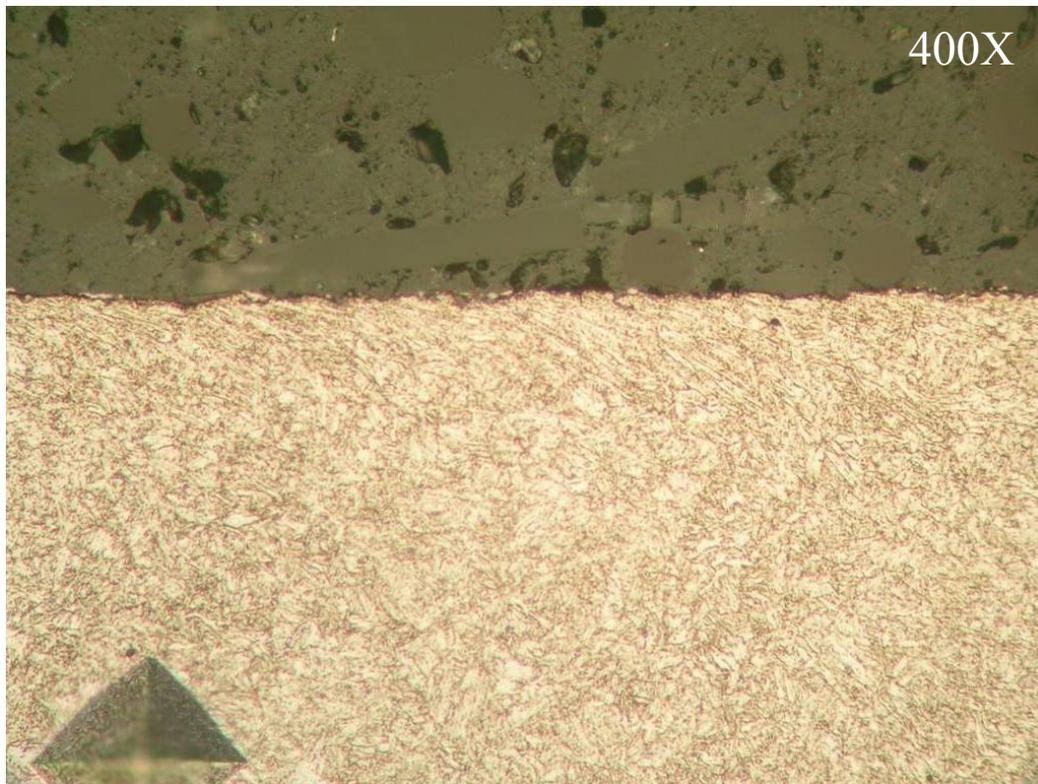


Figure 2: Microstructure after a 10 minute nitriding time (no white layer)

August 6, 2010

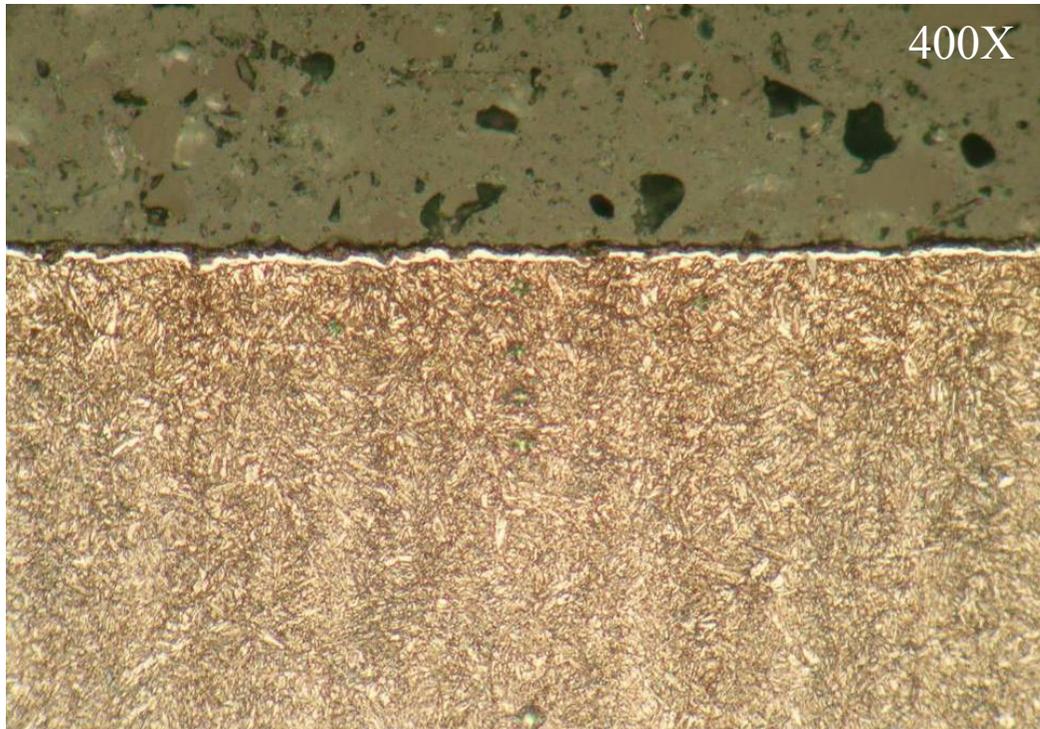


Figure 3a: White layer formation vs. nitriding time; 20 minutes

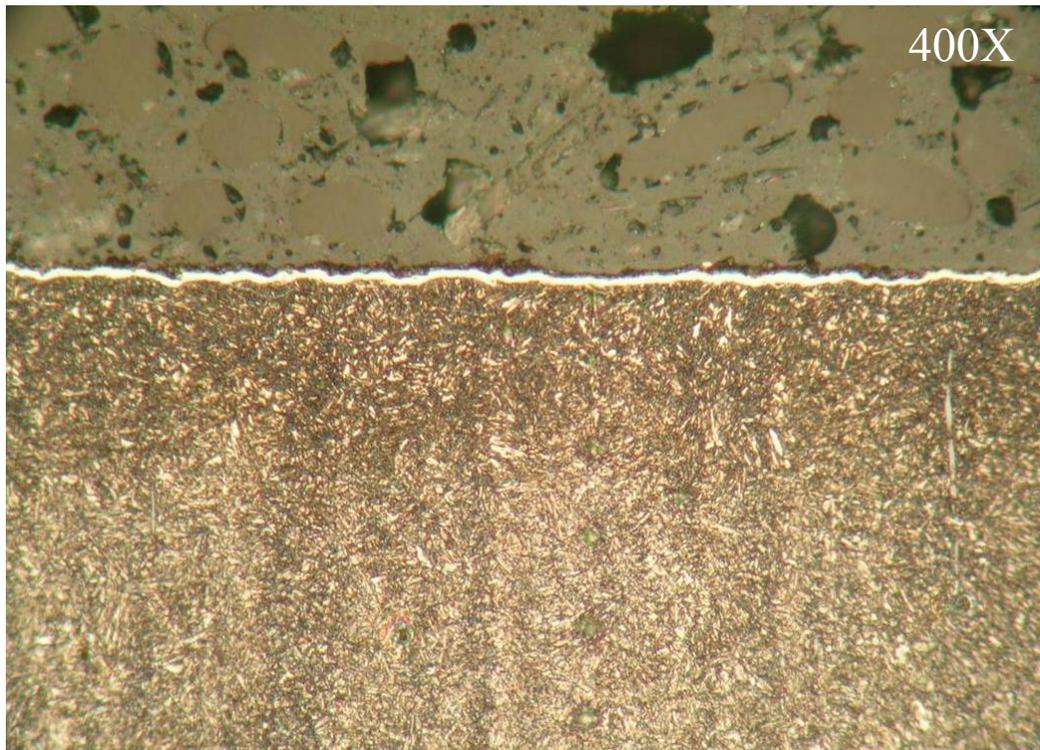


Figure 3b: White layer formation vs. nitriding time; 40 minutes

August 6, 2010

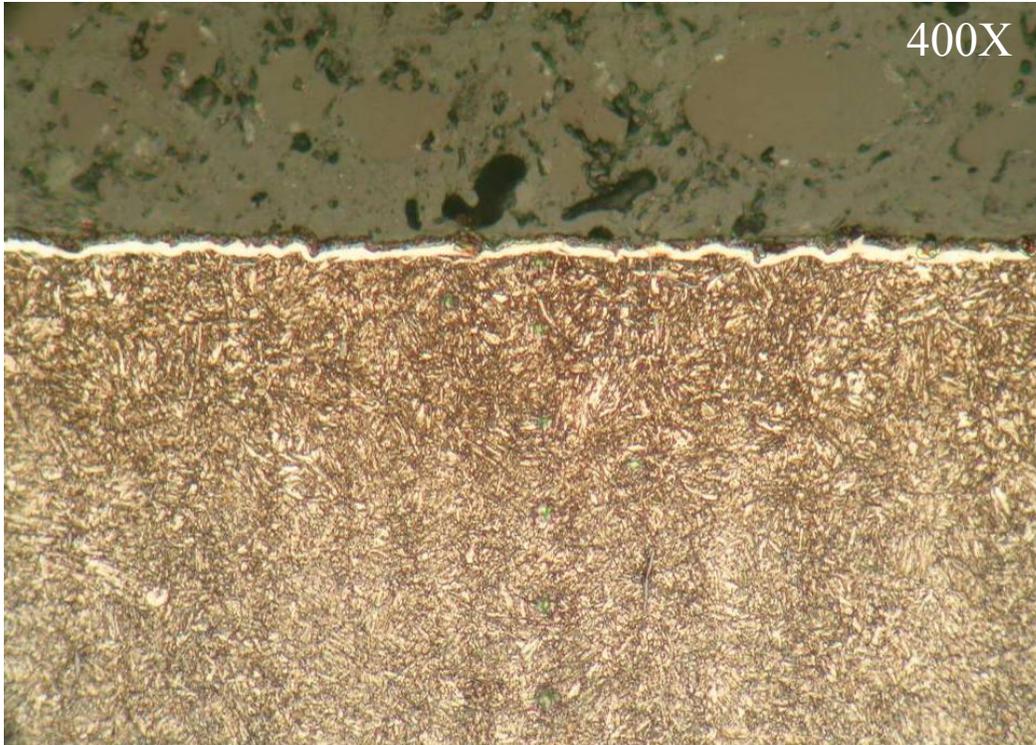


Figure 3c: White layer formation vs. nitriding time; 80 minutes

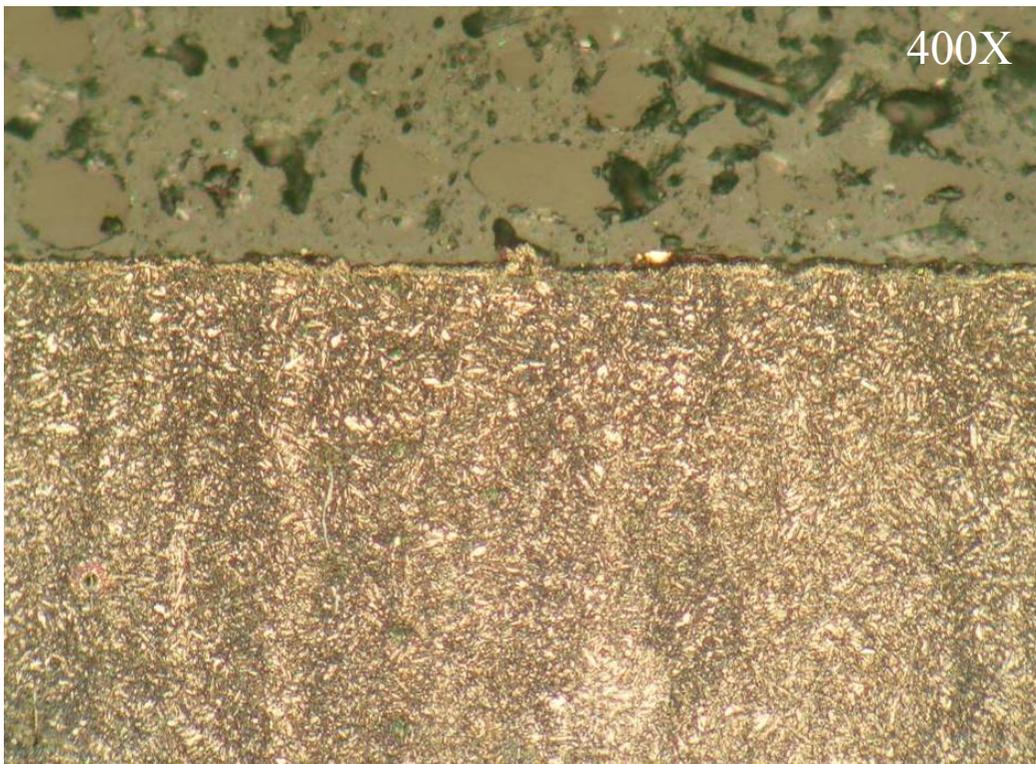


Figure 4a: Microstructure of 20 minute nitrided material after 1/2 hr diffuse

August 6, 2010

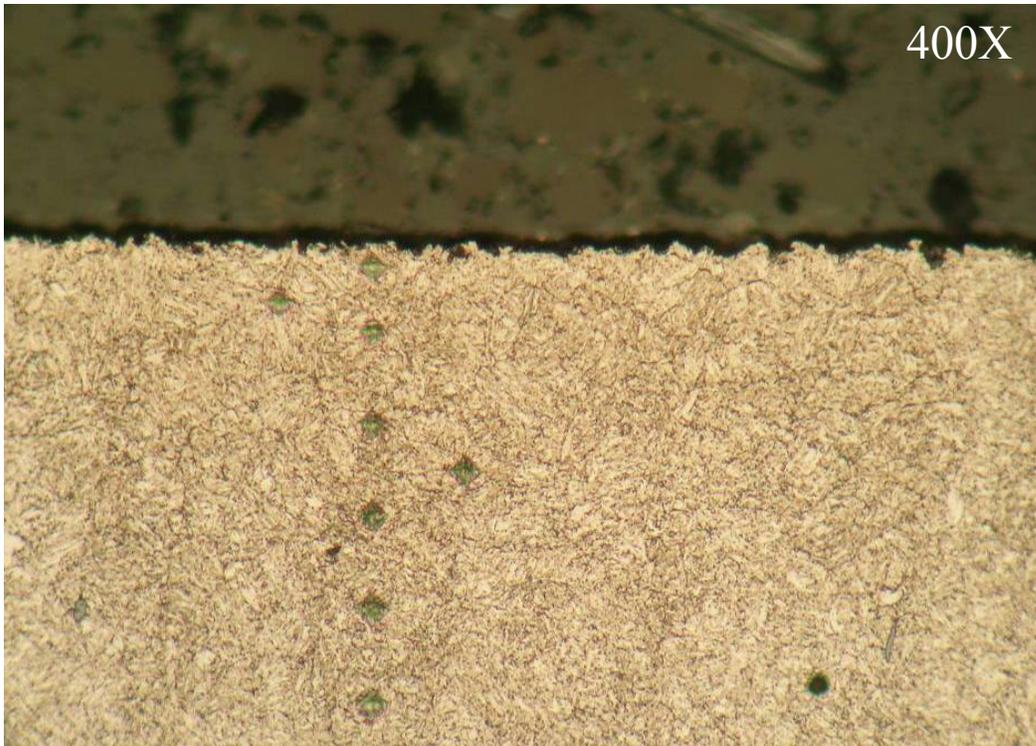


Figure 4b: Microstructure of 20 minute nitrated material after 1 hr diffuse

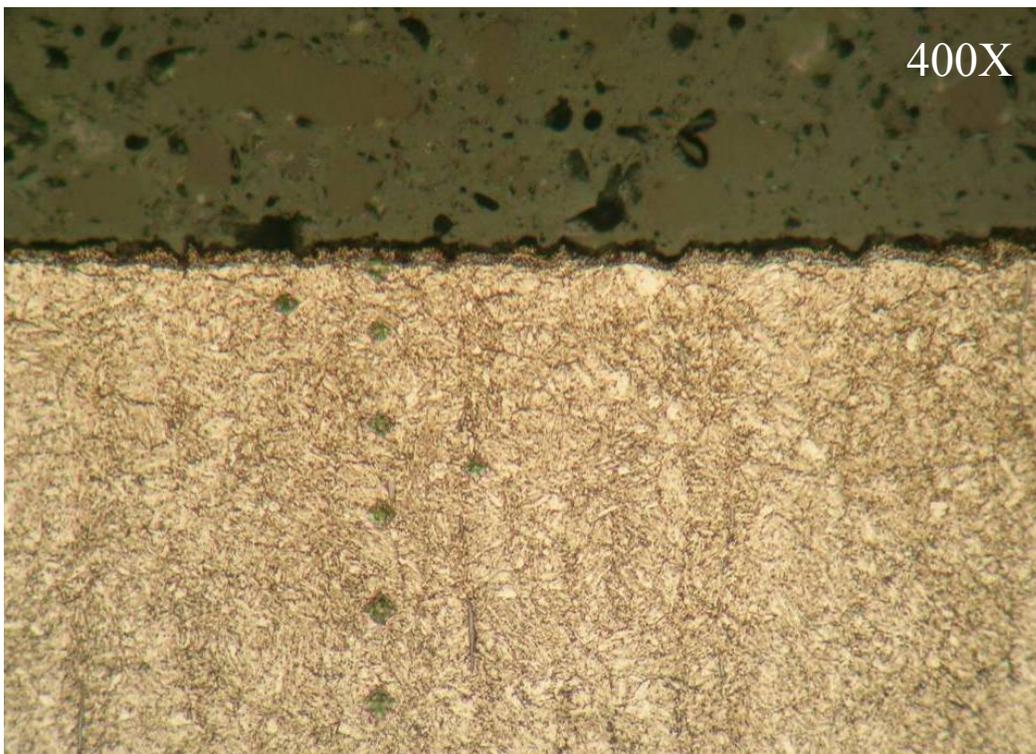


Figure 5a: Microstructure of 40 minute nitrated material after 1 hr diffuse

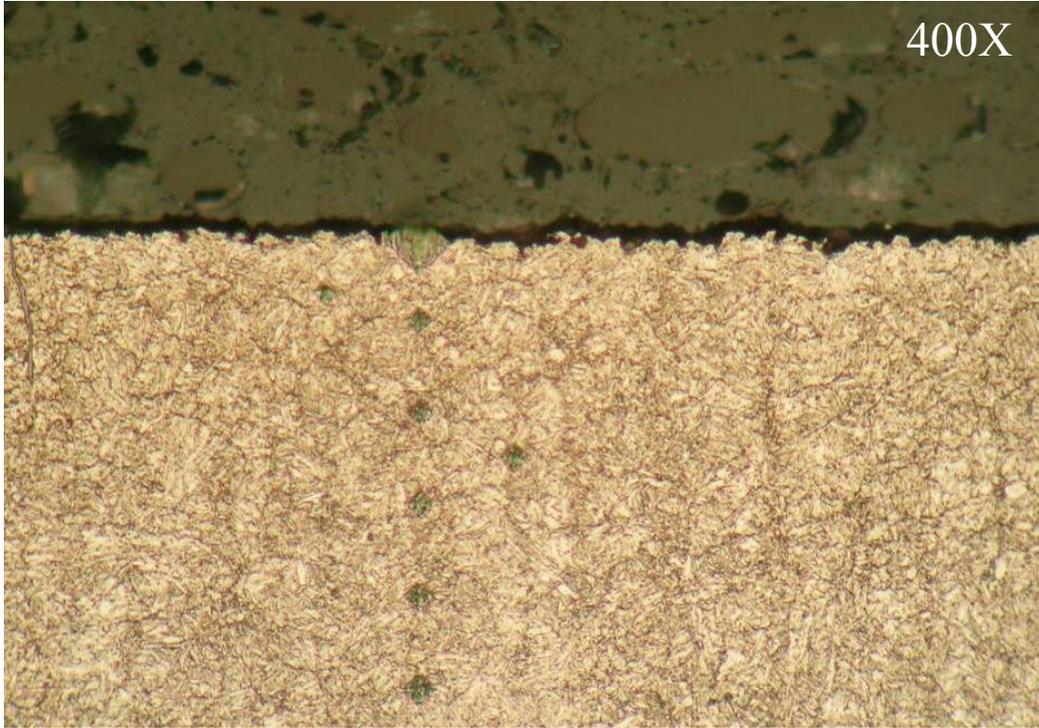


Figure 5b: Microstructure of 40 minute nitrated material after 2 hr diffuse



Figure 6a: Microstructure of 80 minute nitrated material after 2 hr diffuse

August 6, 2010



Figure 6b: Microstructure of 80 minute nitrated material after 4 hr diffuse



Figure 7a: Nitriding for 20 minutes after surface washed with alcohol only

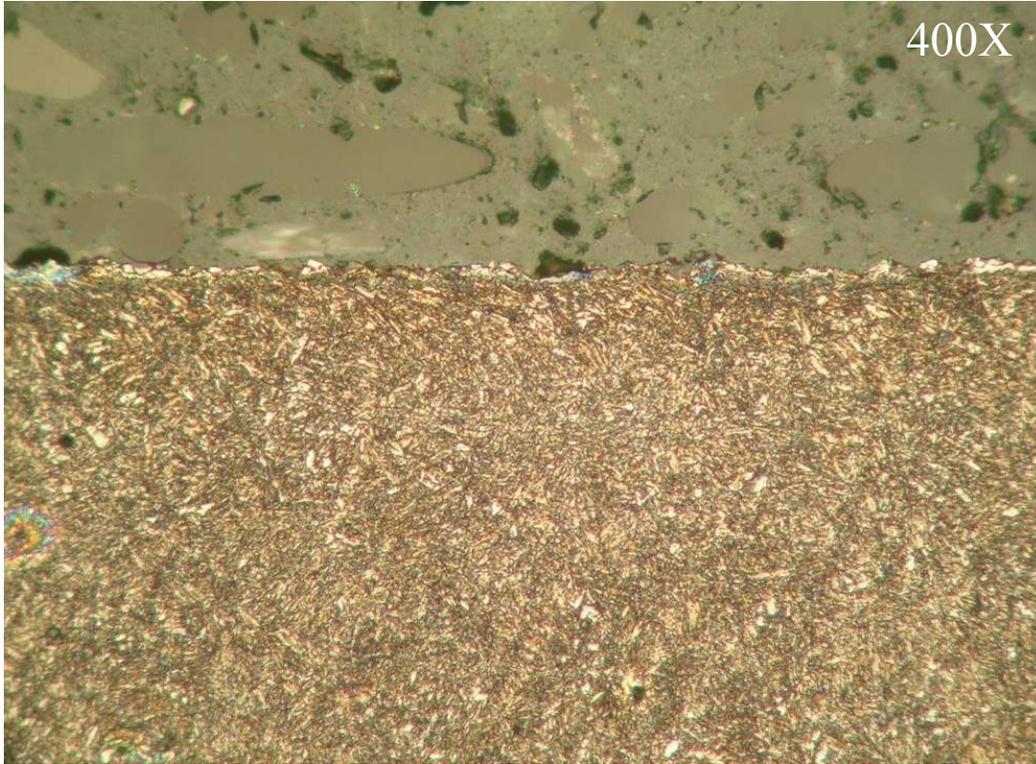


Figure 7b: Nitriding for 20 minutes after surface sand blasted then washed with alcohol

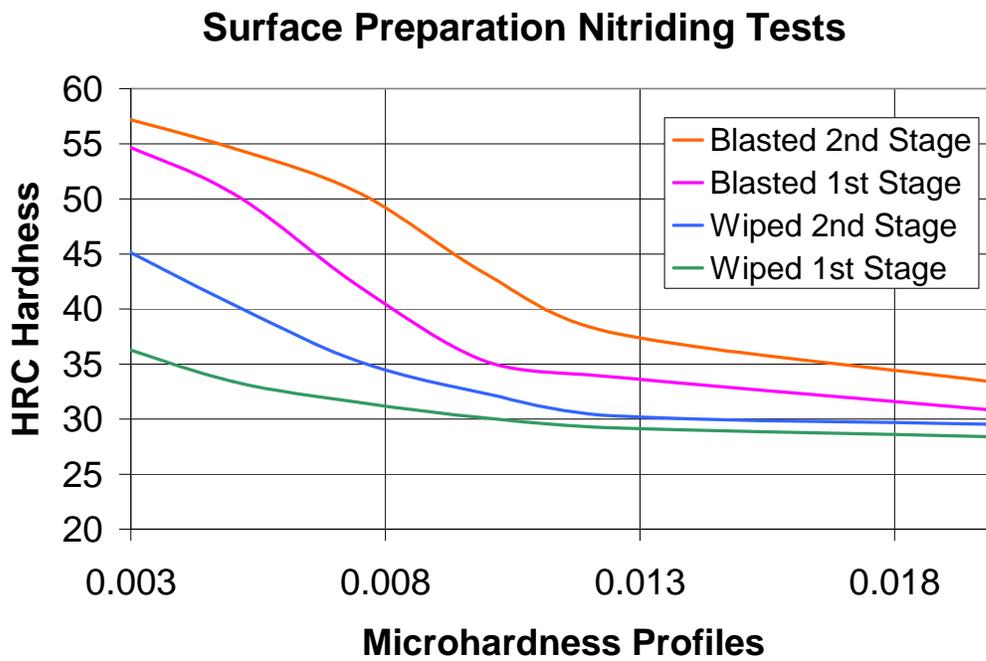


Figure 8: Hardness profile as affected by surface preparation

August 6, 2010

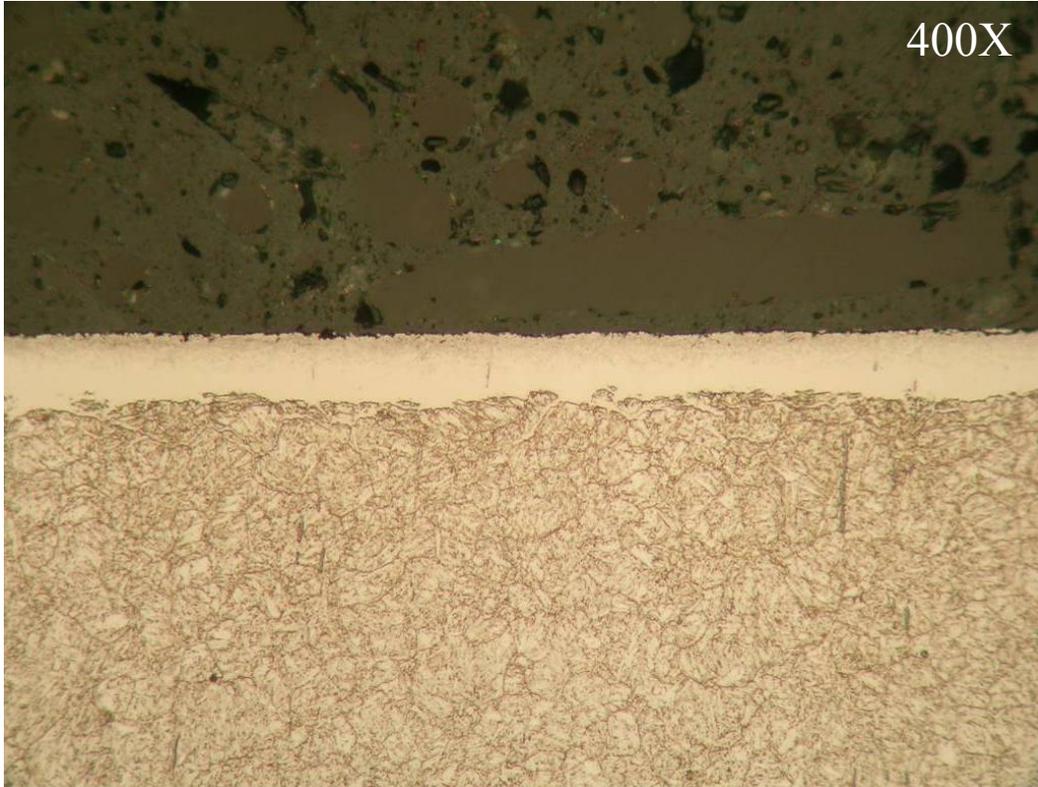


Figure 9a: Microstructure of 36 hr “conventional” two stage nitriding cycle

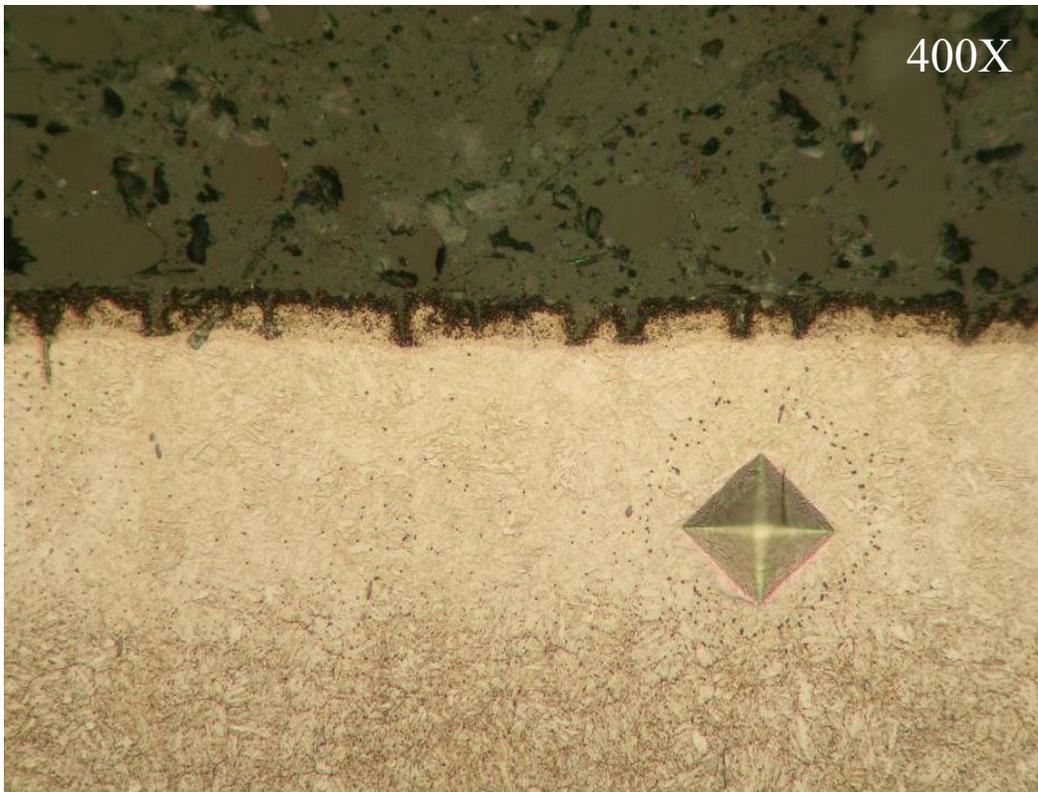


Figure 9b: Microstructure of pulse boost-diffuse test B-D1

August 6, 2010

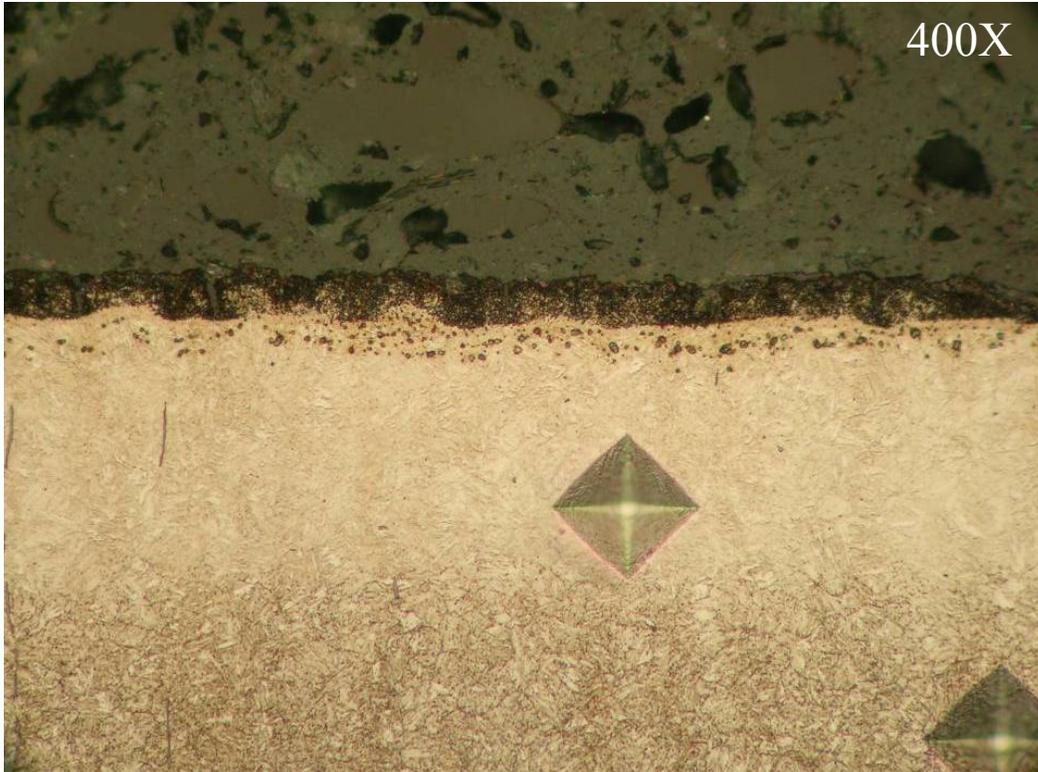


Figure 9c: Microstructure of pulse boost-diffuse test B-D2

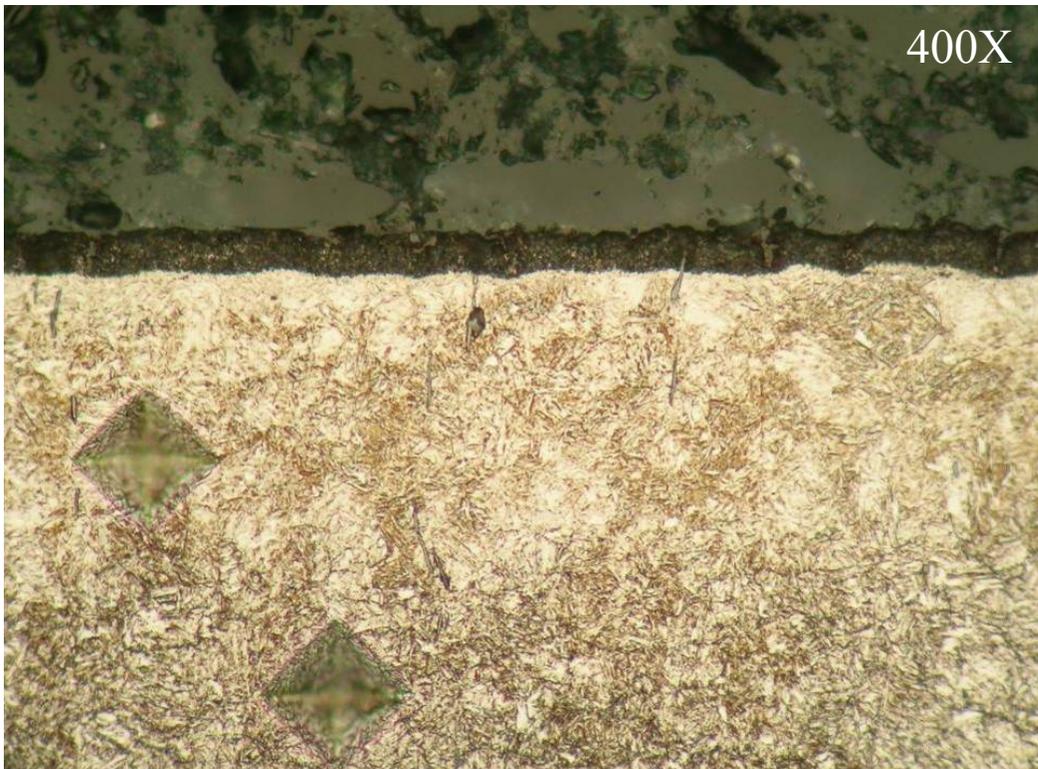


Figure 9d: Microstructure of pulse boost-diffuse test B-D3

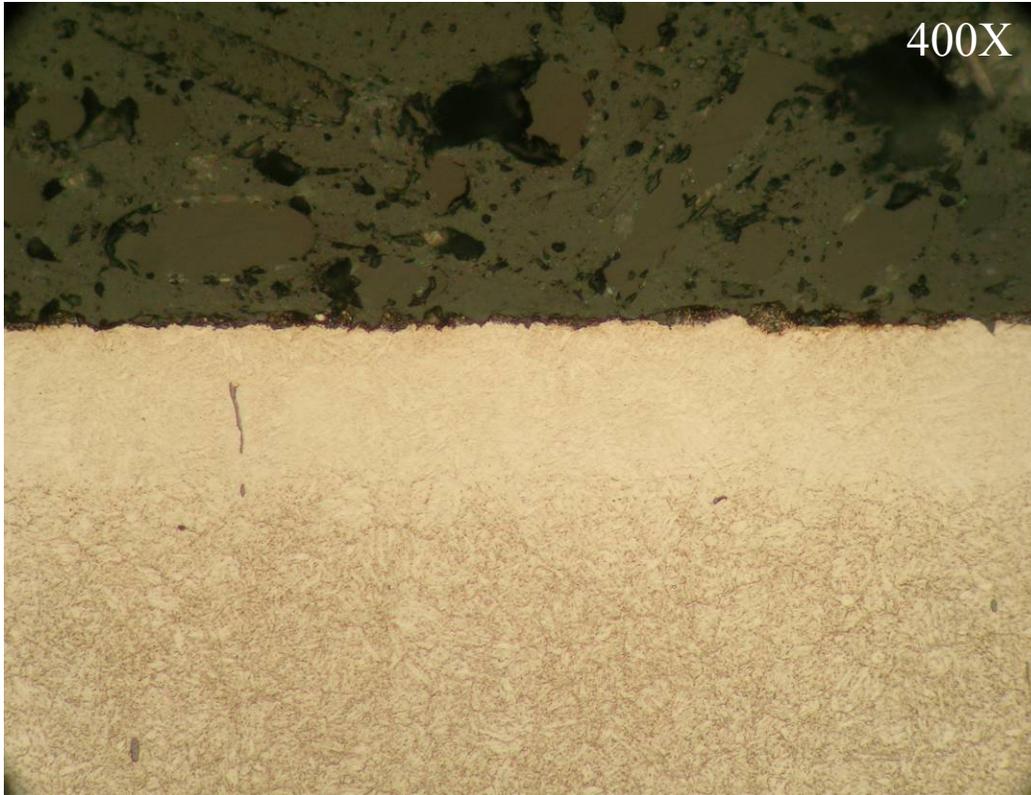


Figure 9e: Microstructure of pulse boost-diffuse test B-D4

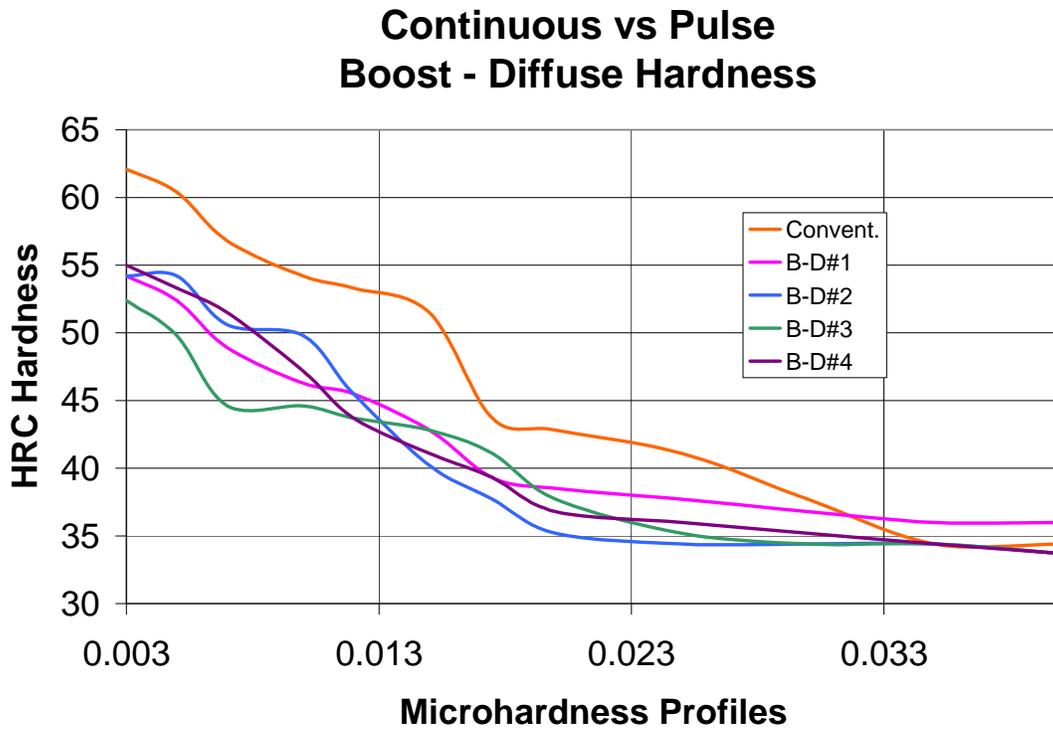


Figure 10: Hardness profiles for conventional and pulse boost-diffuse nitrided cycles

August 6, 2010

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