

# **In Situ Oxidation of Steels as an Effective and Economical Pretreatment for Uniform and Consistent Vacuum Gas Nitriding Results**

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## **Abstract**

A vacuum-purge gas nitriding furnace was modified to develop a process and a furnace enhancement to produce a controlled in situ oxide layer on the surfaces of steel parts using various oxidation techniques. The process is an effective alternative to conventional grit blasting of materials as a means of surface preparation for uniform and consistent nitriding results. Pre-oxidation is known to enhance receptivity of steel part surfaces to the effects of nitriding, and in situ oxidation is inherently efficient and economical. Topics discussed include the type of oxidizing carrier used in the furnace, practical methods used to control the oxidation, and a gas delivery system developed to inject gases with an elevated dew point for the purpose of providing a controlled oxidizing atmosphere. Comparative tests with other activation techniques, and results with no activation, will be discussed along with approaches to technical process difficulties encountered.

## **Introduction**

Nitriding is a thermochemical process where nascent nitrogen (N) is diffused into the surface of steel for the purpose of increasing wear resistance. The process is performed by heating steel parts in a controlled atmosphere to a temperature range of approximately 750°F to 1150°F. Because of the absence of a quenching requirement, the attendant volume changes, and comparatively low temperatures employed in this process, nitriding of steels produces less distortion and deformation than either carburizing or conventional hardening [1]. Ammonia gas (NH<sub>3</sub>) is introduced into the furnace atmosphere and catalytically reacts on the hot steel parts. The nascent nitrogen from the dissociated ammonia diffuses into the steel in accordance with the chemical reaction:



Some of the nascent nitrogen formed is adsorbed by the steel and dissolves into alpha iron or forms nitrides with alloying elements in the steel. The atomic nitrogen and hydrogen components shown in equation 1 are unstable and unite with other like atoms to form molecules [2]. Methods of controlling the nitriding potential in the furnace include the use of an external ammonia dissociator and/or dilution of ammonia with other gases such as hydrogen and/or nitrogen.

Traditionally, a hot-walled metal retort furnace with substantial mass is used for containing the parts and atmosphere during the nitriding process. Prior to heating the part in the metal retort, nitrogen gas is used to purge air from the furnace to remove residual oxygen for safety. The amount of nitrogen gas required to purge the vessel is substantial and the purging process is time consuming. After the retort is purged of air, the furnace is heated to the nitriding temperature. The metal retort is inefficient in terms of the amount of thermal energy required to heat to the nitriding temperature. At the end of the nitriding process, the metal retort is again at a disadvantage due to the time to cool down to ambient temperature for unloading parts. The furnace also has to be purged of ammonia with large quantities of nitrogen gas during cooling and prior to unloading.

A vacuum furnace was designed to have the capability of performing the nitriding process [3]. The furnace incorporates a lightweight graphite-lined zone receiving the parts to be processed. The graphite-lined interior of the

furnace is non-reactive with ammonia gas, requiring lower ammonia flow rates compared to metal retort designs which may catalytically react with ammonia. The exterior furnace walls are cooled by means of a water jacket, providing safe working conditions. In lieu of purging the furnace with nitrogen, a vacuum pumping system is utilized to quickly, safely, and effectively purge the vessel of air followed by backfilling with nitrogen gas. The furnace is heated convectively by means of graphite heating elements coupled with re-circulation fans and baffling system. The nitriding process is initiated by pumping out a portion of the nitrogen gas and backfilling with ammonia gas to the desired nitrogen/ammonia composition. The process is controlled by analyzing the hydrogen gas generated from the reaction in the furnace in the effluent of the furnace. The amount of hydrogen generated, combined with ammonia and nitrogen mass flow controllers are used as inputs to an algorithm and feedback loop to automatically maintain a nitriding potential in the furnace atmosphere. At the commencement of the nitriding process, the furnace atmosphere is purged by means of the vacuum pumping system, then backfilled with nitrogen gas. A water-cooled stainless steel fin and tube heat exchanger and cooling fan are then used to rapidly cool the furnace and parts for unloading.

The importance of a clean active surface for consistent and reproducible nitrogen diffusion is essential. Parts that are free from contamination will generally nitride without issues; however, some pre-nitride machining processes which result in burnished or polished surfaces will impede the nitriding process [4]. One method of overcoming machining effects is to lightly grit blast the surface of the steel and thoroughly clean off the grit media prior to nitriding.

Grit blasting has certain drawbacks, especially in terms of time and labor costs. The type of grit used, the pressure utilized, nozzle distance from the part, and operator technique must be consistent for reproducibility. As an alternative surface activation method, work pieces are preheated in a controlled oxidizing atmosphere at temperatures varying from 650°F to just below the nitriding temperature [5]. The oxidizing atmospheres are typically air, nitrous oxide, or water-saturated gas. Oxygen pretreatment is not new, however it is typically done in a separate furnace or in a dual chamber furnace in order to avoid possible mixing of the oxidizing atmosphere and the ammonia. The use of a vacuum furnace allows for a controlled oxidation step followed by nitriding in single chamber, thereby eliminating the need for two furnaces or a dual chamber vacuum furnace.

The addition of an oxide film on steel parts may be perceived as a source of contamination which would inhibit nitriding. However it has been proposed that the surface oxide actually increases the surface area of the part, which in turn facilitates nitrogen uptake, nucleation, and growth of the nitride compound layer [6]. As an added benefit, undesirable surface residues on the part surfaces are oxidized and vaporized prior to nitriding, resulting in cleaner parts and increased nitrogen diffusion. [7]

The current study looked at the use of water-saturated nitrogen ( $N_2$ ) gas and dry nitrous oxide ( $N_2O$ ) pretreatment to determine the effectiveness of pre-oxidation on the resultant nitriding properties. The material used for the experiments was ground and polished, decarb-free AISI 4140, pre-heat treated and tempered to 28-32 HRC. The resulting case hardness, case depth and white layer thickness were analyzed after the various pre-oxidation treatments and compared to the process without pre-oxidation.

The nitrogen gas was passed into a stainless steel vessel filled with de-ionized water controlled at a temperature of 90°F to 100°F. As the nitrogen gas enters the water-filled vessel through a tube extending to the bottom of the vessel and exits through the top of the vessel, the water vapor content of the nitrogen increases. The water-saturated gas exits the container directly into the preheated furnace. The oxidation temperatures used for these tests were 650°F, 750°F, and 980°F. For each trial, the exposure time of oxidation was constant at 20 minutes each.

The nitrous oxide pretreatment test used a nitrous oxide/nitrogen blend. The three different nitrous oxide blends used included 5%  $N_2O$  / 95%  $N_2$ , 25%  $N_2O$  / 75%  $N_2$  and 50%  $N_2O$  / 50%  $N_2$ . Only one oxidation temperature was

studied (980°F) and the oxidation exposure was 20 minutes for each test. A description of the test procedure for each trial is shown in Table 1 and Table 2

*Table 1 – Standard Test Procedure with No pre-oxidation*

<u>Step</u>	<u>Procedure Description</u>
1	Pump down to < 0.1 torr, backfill with nitrogen and heat to the nitriding temperature
2	Nitride at 65% dissociation for 4 hours
3	Gas quench to ambient temperature

*Table 2 – Test Procedure with Pre-oxidation Tests*

<u>Step</u>	<u>Procedure Description</u>
1	Pump down to < 0.1 torr, backfill with nitrogen and heat to the oxidizing temperature
2	Oxidize with either with wet nitrogen or dry nitrous oxide for 20 minutes.
3	Purge the oxidizing atmosphere by pumping down to < 1 torr and backfill with nitrogen and heat to the nitriding temperature
4	Nitride at 65% dissociation for 4 hours
5	Gas quench to ambient temperature

## Results

*Table 3 – Wet Nitrogen Pre-oxidation Results*

Pre-Ox Temp (°F)	Pre-ox Time (Min.)	Nitride Time (Hours)	White Layer (Inches)	Hardness 200g Vickers to Rockwell C 0.001”	Case Depth to 40 HRC (inches)
N/A	0	4	$2.6 \times 10^{-4}$	51.3	0.0058
650	20	4	$3.0 \times 10^{-4}$	52.9	0.0069
750	20	4	$3.0 \times 10^{-4}$	54.0	0.0077
980	20	4	$3.2 \times 10^{-4}$	55.0	0.0071

Table 4 – Nitrous Oxide Pre-oxidation Results

N <sub>2</sub> O Composition / Balance N <sub>2</sub>	Pre-ox Time (Min.)	Nitride Time (Hours)	White Layer (Inches)	Hardness 200g Vickers to Rockwell C 0.001"	Case Depth to 40 HRC (inches)
N/A	0	4	$2.6 \times 10^{-4}$	51.3	0.0058
5%	20	4	$3.1 \times 10^{-4}$	54.2	0.0071
25%	20	4	$3.2 \times 10^{-4}$	54.6	0.007
50%	20	4	$3.1 \times 10^{-4}$	55.4	0.007

Figure 1- Wet Nitrogen Pre-oxidation Hardness Traversal Compared to Baseline (no pre-ox) for 200g Vickers to Rockwell Hardness C

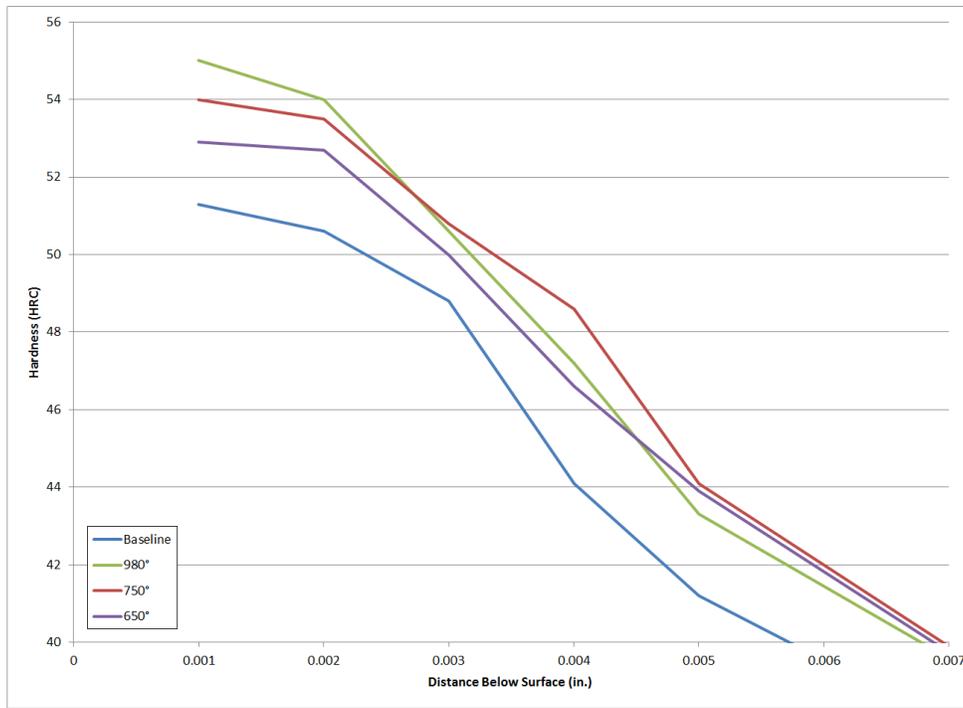


Figure 2- Nitrous Oxide Pre-oxidation Hardness Traversal Compared to Baseline (no pre-ox) 200g Vickers to Rockwell Hardness C

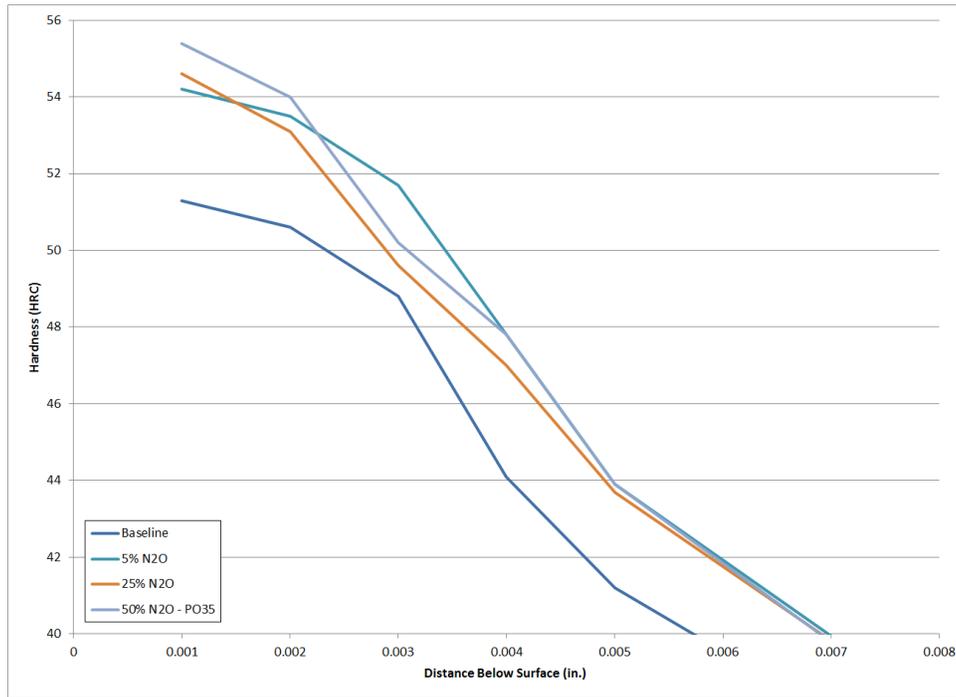
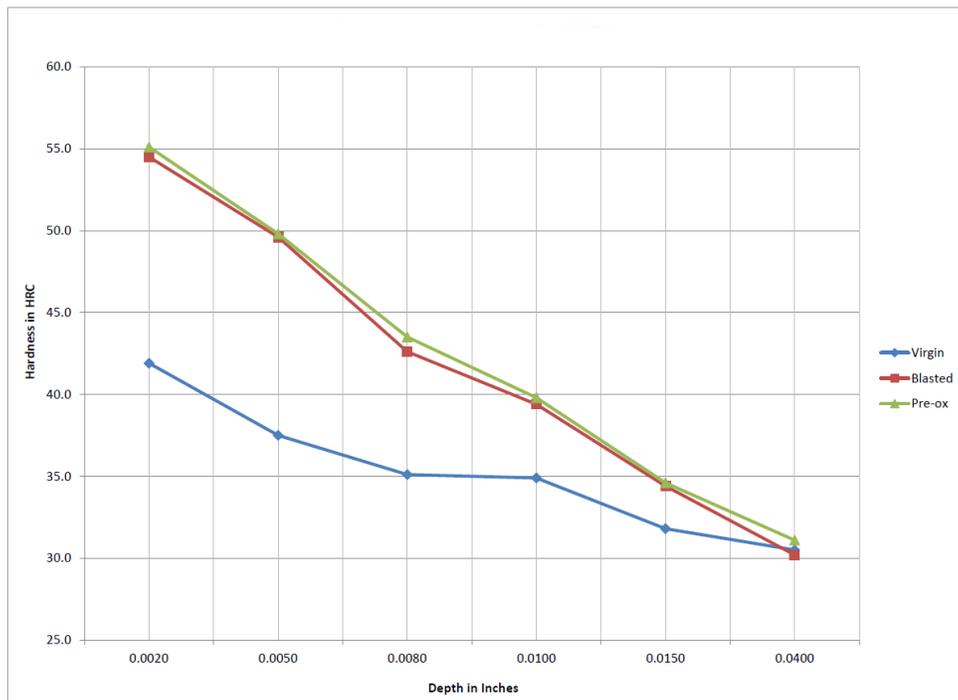


Figure 3- Comparison of nitrided case depth and case hardness of a virgin 4140, a grit blasted activated 4140 and a pre-oxidized with wet nitrogen 4140. Nitrided at 925°F for 2 hours at 80% dissociation and 1000°F for 10 hours at 95% dissociation.



In the nitrous oxide pre-oxidation testing the hardness and case depth increased with an increase in the nitrous oxide concentration, which was expected. Increased oxidizing concentration resulted in increased surface area of the part and enhanced nitriding. Compared with the baseline hardness of 51.3 HRC, the hardness value for 5% nitrous was 54.2 HRC, 54.6 HRC for 25% nitrous and 55.4 HRC for 50% nitrous. As can be seen, increasing the nitrous concentration by a factor of 10 gave improved hardness by only 1.2 HRC points. Such a small increase in achieved hardness compared to the cost of the nitrous oxide is questionable. The wet nitrogen value of 55 HRC at 980°F is essentially comparable to that of the 50% nitrous test and the use of wet nitrogen appears much more economical. The effect of pre-oxidation temperature and resultant hardness and case depth with the wet nitrogen runs was more significant compared to the nitrous oxide concentration testing.

An additional test was conducted to determine resultant case hardness and case depth utilizing the wet nitrogen pre-oxidation technique and comparing a grit blasted activated test part with a virgin test part with no activation. Figure 4 demonstrates the similarity of activation by grit blasting with alumina oxide (220 grit size) and pre-oxidation utilizing wet nitrogen at 925°F for 30 minutes. The case depth and case hardness values achieved with the two activation methods are comparable and significantly higher in surface hardness and deeper in case depth compared to the virgin test part.

## Conclusions

The water saturated nitrogen trials indicate that an increase in the oxidation temperature increases surface hardness and case depth when compared to the baseline test with no pre-oxidation. Increasing the oxidation temperature from 650°F to 980°F increased the surface hardness by approximately 2 HRC points; however, compared to no pre-oxidation, the surface hardness for the 980°F pre-oxidation increased by approximately 4 HRC points. Additionally, the water-saturated nitrogen pre-oxidation test showed a case depth increase of approximately 0.0015” compared to the baseline test. The thickness of the white layer also increased with wet nitrogen pre-oxidation by  $5.0 \times 10^{-5}$  inches compared to the baseline without pre-oxidation. The resultant increase in hardness and slight increase in white layer formation with increasing pre-oxidation temperature is not unexpected. A thicker oxide case forms as the temperature is increased. The oxide film increases the surface area of the part and provides more opportunity for nitrogen activity at the surface.

The nitrous oxide pre-oxidation tests also exhibited an increase in surface hardness and case depth when compared to the baseline test with no pre-oxidation. Only a minimal increase in hardness was observed when comparing the various compositions of nitrous oxide from 5% N<sub>2</sub>O to 50% N<sub>2</sub>O; however approximately 3.5 HRC points were gained when comparing pre-oxidizing with N<sub>2</sub>O to the baseline test. The case depth of the nitrous oxide pre-oxidation also increased by approximately 0.0013” compared to the baseline tests. The thickness of the white layer did increase with nitrous oxide trials compared to the baseline by  $6.0 \times 10^{-5}$  inches, similar to the wet nitrogen gas trials.

The pre-oxidation methods of water saturated nitrogen with nitrous oxide are comparable. Only a slight difference in case hardness was observed with increasing composition in nitrous oxide matching the increasing pre-oxidation temperatures with water saturated nitrogen gas. An exception may be the 650°F wet nitrogen pre-oxidation test that indicates a slightly lower surface hardness of approximately 1 HRC point when compared to the average surface hardness of all other pre-oxidation trials. Regardless of the pre-oxidation method, the white layer thicknesses were all comparable. Additionally, results obtained with pre-oxidation methods are equivalent to results obtained with activation using grit blasting.

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