

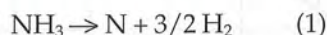
LOW TORR-RANGE VACUUM NITRIDING OF 4140 STEEL

Although the nitrided surfaces from atmospheric pressure nitriding and low-torr nitriding are similar, there are some advantages of the low-pressure nitriding including faster turn-around time, a very pure starting atmosphere, the ability to clean the surfaces of the parts using hydrogen prior to the nitriding, and uniform atmosphere.

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Nitriding of steel is accomplished by dissociating ammonia on a hot steel surface 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 remainder of the nascent nitrogen recombines to form molecular nitrogen and is exhausted from the furnace. The products in the steel resulting from the nitriding reaction could be a compound or white layer on the surface composed of gamma-prime (γ') Fe_4N and/or epsilon (ϵ) Fe_{2-3}N , with a diffusion zone of dissolved nitrogen and nitrides below the white layer.

Lehrer presented a diagram illustrating the relationship among possible phases produced in iron with respect to temperature and the nitriding potential (K_n). The diagram was developed with reference to NH_3

+ H_2 mixtures at atmospheric pressure (Fig. 1)^[1]. The nitriding potential (K_n) is defined by^[2]:

$$K_n = p(\text{NH}_3) / [p(\text{H}_2)]^{3/2} \quad (2)$$

where p is the partial pressure of the gas.

It should be emphasized that Fig. 1 represents the situation at atmospheric pressure; if other than atmospheric pressure is used for nitriding, the input nitriding gas mixture has to be modified from those indicated by Fig. 1. The purpose of this investigation was to determine the modifications needed for nitriding at pressures lower than atmospheric.

Procedure

It is common practice to mix the ammonia with hydrogen, nitrogen, or dissociated ammonia (hydrogen plus nitrogen) to facilitate control of the nitriding process. It appears that Lehrer used the mixture percentages of ammonia and hydrogen for the partial pressures in calculating the nitriding potentials at one atmos-

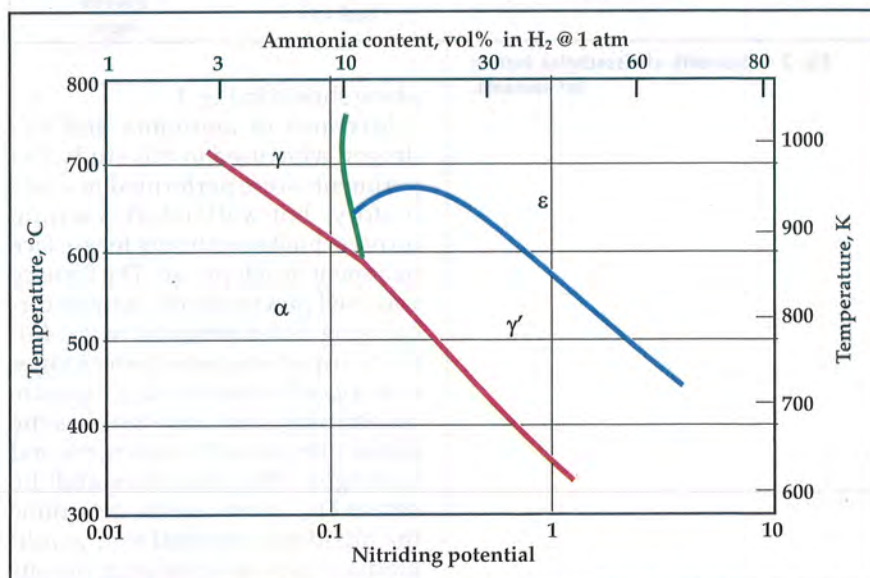


Fig. 1 — Lehrer diagram illustrates the relationship among possible phases produced in iron with respect to temperature and nitriding potential.

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Table 1 — Room temperature pump-down tests(a)

NH ₃ input to furnace, parts/100	NH ₃ retained in furnace after pump-down, %	NH ₃ retained in furnace, parts/100
22	64	14
50	88	44
78	99	77
100	100	100

(a) NH₃ + H₂ mixtures at 125 torr

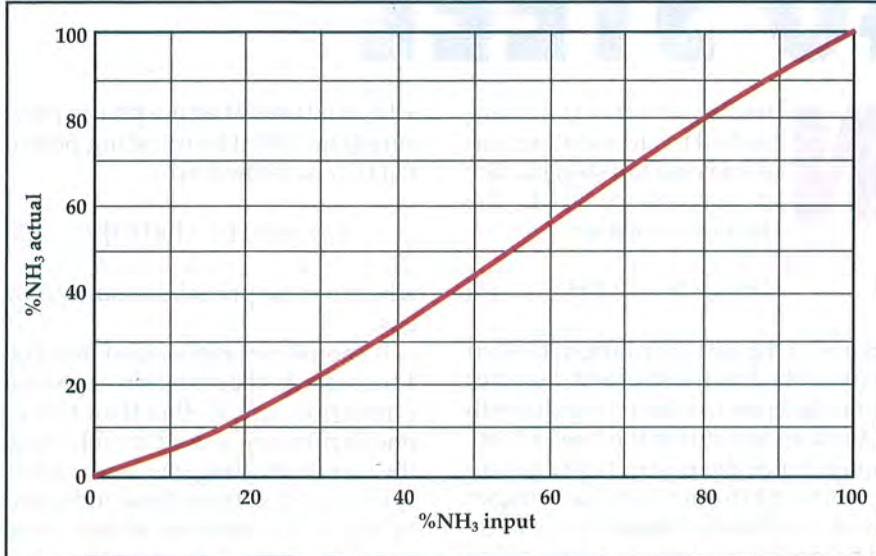


Fig. 2 — Pump-down effect on NH₃ + H₂ mixtures; %NH₃ input versus actual in furnace at 125 torr.

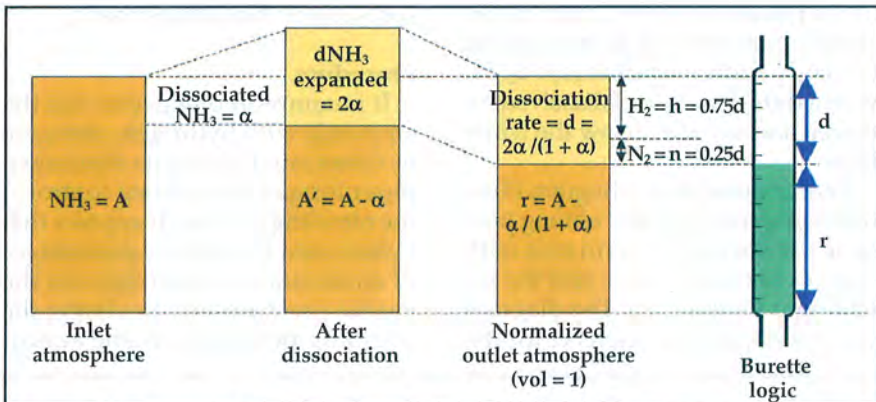


Fig. 3 — Schematic of dissociation burette for ammonia.

phere shown in Fig. 1.

Mixtures of ammonia and hydrogen were used in this study. Experiments were performed in a laboratory, hot-wall retort vacuum furnace, built specifically for surface treatment development. The furnace was used previously for vacuum carburizing developmental work. Initially, input ammonia percentages multiplied by the nitriding pressure (in atmospheres) were used as the partial pressures of the ammonia and hydrogen. This procedure and the data in Fig. 1 were used to determine the nitriding potential that would produce or avoid white layer. Results using this approach quickly indicated that the method did not work

at pressures less than one atmosphere. It appeared that much greater input nitriding potentials (K'_n) were required than those (K_n) indicated by Fig. 1. The results suggested that the input gas-nitriding potentials had to be increased as shown below:

$$\text{Calculated nitriding potentials } K'_n = \frac{(p\text{NH}_3)(P)}{[(p\text{H}_2)(P)]^{1.5}} \quad (2)$$

where $p\text{NH}_3$ and $p\text{H}_2$ are ammonia and hydrogen fractions, respectively, at 1 atm, K'_n is the input nitriding potential, and P is the reduced pressure in atmospheres⁽³⁾.

$$\text{Because } K_n = \frac{(p\text{NH}_3)}{(p\text{H}_2)^{1.5}} \quad (3)$$

$$\text{if you let } P' = \frac{(P)}{(P)^{1.5}} \quad (4)$$

$$\text{then } K'_n = K_n P' \quad (5)$$

Equation (5) indicates that the critical nitriding potential increases with decreasing nitriding pressure. However, calculated percentages of ammonia required to produce the required critical values of K'_n were not accurate when tested experimentally, because the ratio of the input ammonia-hydrogen mixtures did not remain constant during pump-down. Therefore, tests were run by pumping down mixtures of ammonia and hydrogen at room temperature so no ammonia would be dissociated. Table 1 shows burette measurements made to determine pumped-down ratios of ammonia and hydrogen. Data in Table 1 can be represented to a reasonable degree by:

$$y = 3\text{E-}07x^4 - 0.0001x^3 + 0.0169x^2 + 0.3249x - 4\text{E-}10 \quad (6)$$

where y = % ammonia retained and x = % ammonia added.

Figure 2 shows the plot of Equation (6). Approximating the curve in Fig. 2 with a straight line leads to a simpler equation:

$$y = 0.97x - 12 \quad (7)$$

where y = parts of NH₃ retained in 100 part mix and x = parts of ammonia added. Equation (6) is accurate for the low range of $0 > x < 30$, and equation (7) is accurate for the high range of $30 > x < 100$.

Burette Readings and Corrections

A schematic for the dissociation burette used for nitriding using pure ammonia is shown in Fig. 3. The ni-

Table 2 — Lehrer and calculated critical $\alpha - \gamma'$ phase-boundary values

Temperature, °C	1 atmosphere		125 torr	
	K'_n	% NH ₃	K''_n	%HN ₃
496	0.30	21	0.70	30
524	0.23	18	0.57	26
538	0.21	16	0.50	24
566	0.16	13	0.40	21

triding potential is given by^{[4-6]:}

$$K'_n = r / h^{3/2} \quad (8)$$

where r = height of water column and $h = 0.75d$. However, for NH₃ + H₂ nitriding mixtures, the dissociation burette schematic is shown in Fig. 4. During the experimental work, furnace atmosphere samples were taken every 30 minutes for burette readings. When both the ammonia and hydrogen as a mixture is considered, and corrected for nitriding at a reduced pressure, K'_n values can be calculated directly from the burette readings using the following equation:

$$K'_n = r P (1 + \text{NH}_3)^{1.5} / [\text{NH}_3 (0.5 - r) + 1 - 0.5r]^{1.5} p^{1.5} \quad (9)$$

where P is total pressure in the furnace, r = burette reading, NH₃ = input fraction, and K'_n = corrected nitriding potential. Equation (9) does not consider the correction needed for the differential pump-down effect. Because the ammonia and the hydrogen are pumped-down in different proportions, the applicable correction yields:

$$K''_n = r P (1 + \text{NH}_3)^{1.5} / [\text{NH}_3 (0.5 - r) + 1 - 0.5r]^{1.5} [P]^{1.5} \quad (10)$$

where K''_n is corrected for pressure and pump own. The details for arriving at equation (10) are shown in Fig. 5. The pump down correction varies from one furnace system to another and must be determined for each particular furnace design.

Lehrer $\alpha - \gamma'$ Boundary at 125 torr

The critical values for the $\alpha - \gamma'$ phase boundary as a function of temperature, pressure, nitriding potential, and percent ammonia input are shown in Table 2. The values given for 125 torr were determined using equation (10). The data in Table 2 are plotted as a function of ammonia input in Fig. 6, and as a function of nitriding potential in Fig. 7.

Experiments were run at different

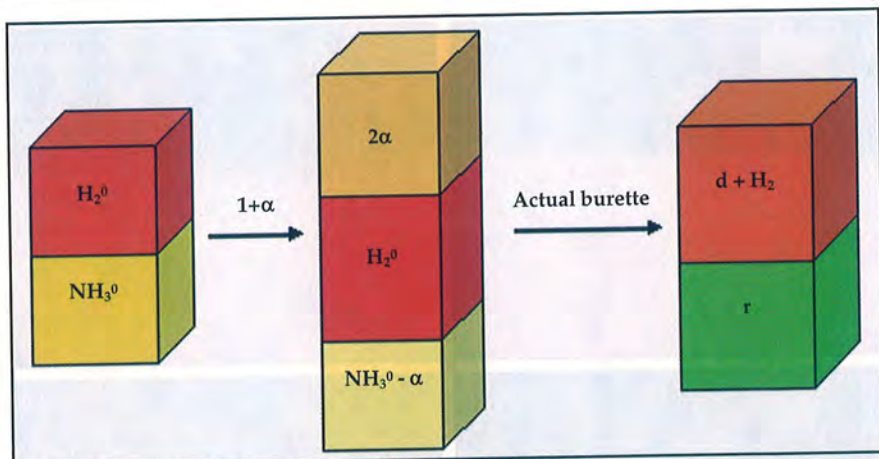


Fig. 4 — Schematic of dissociation burette for ammonia and hydrogen.

- NH₃⁰ = actual ammonia in furnace
- $r = (\text{NH}_3^0 - \alpha) / (1 + \alpha)$ and $\text{H}_2^0 = 1 - \text{NH}_3^0$
- Solve for α ; $\alpha = (\text{NH}_3^0 - r) / (1 + r)$
- Look at burette to know that gas increases by 2α and ammonia decreases by α to get $K'_n = r / [(0.75[2\alpha] + \text{H}_2^0)^{1.5}] / [(1 + \alpha)^{1.5}]$
- Substitute equations for α and H_2^0
- $K''_n = r P / [\text{NH}_3^0 (0.5 - r) + 1 - 0.5r]^{1.5} [P]^{1.5} / (1 + \text{NH}_3^0)^{1.5}$

Fig. 5 — Nitriding potential corrected; reduced pressure and pump down

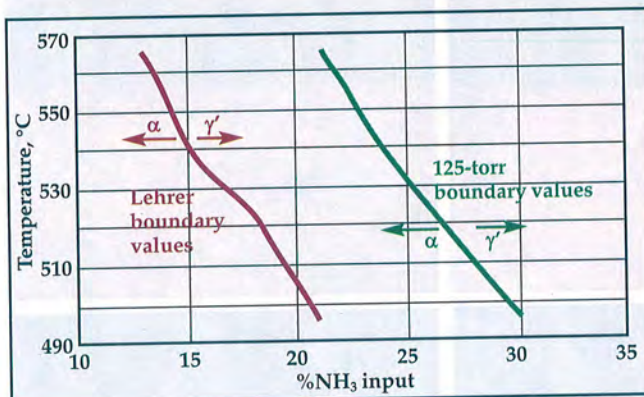


Fig. 6 — NH₃ input values for $\alpha - \gamma'$ boundary at one atmosphere and 125 torr.

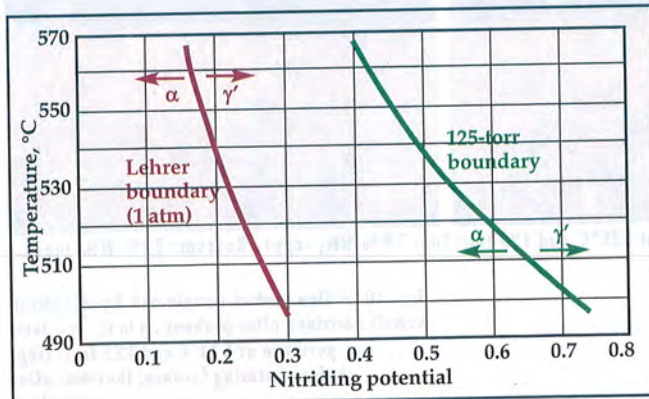


Fig. 7 — Nitriding-potential values for $\alpha - \gamma'$ boundary at one atmosphere and 125 torr.

Table 3—Conditions for oxidation prior to nitriding studies

Test	Heat-up atm.	Nitriding pressure, torr	Nitriding atm.
A	H ₂	125	NH ₃ + H ₂
B	H ₂	812	NH ₃ + H ₂
C	N ₂	812	NH ₃ + H ₂

Table 4—Statistical analysis for case depth (mm) of preoxidation tests results

Heat-up	Mean	Median	Std. deviation	Range
H ₂ at 125 torr	0.3715	0.3685	0.035445	0.023
H ₂ at 812 torr	0.357	0.3593	0.010231	0.023
N ₂ at 812 torr	0.284	0.287	0.04136	0.084

H₂ heat up produced 25-30% deeper case than N₂ heat up.

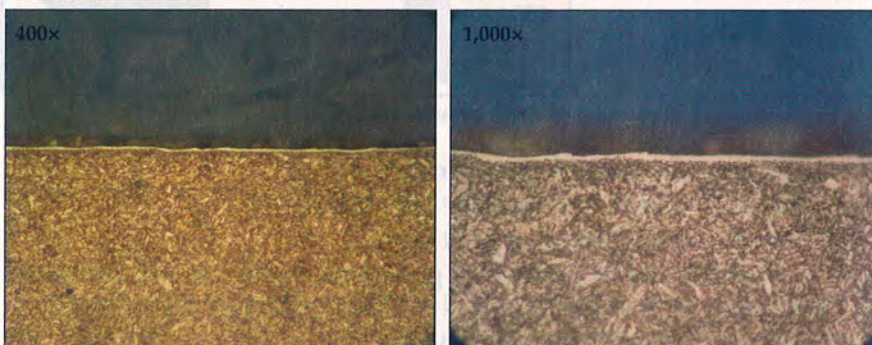
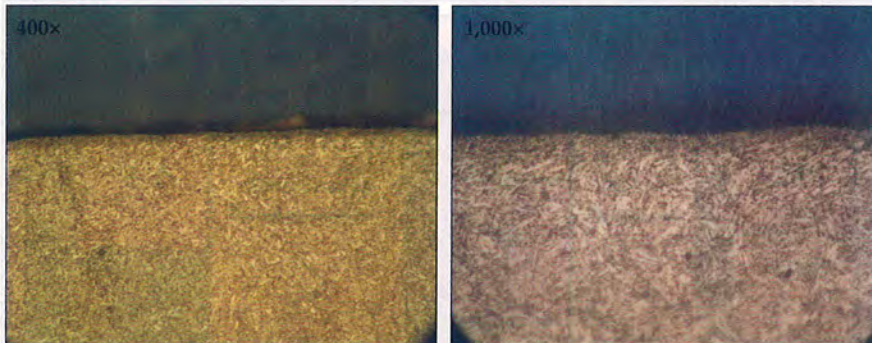


Fig. 8 — Nitriding results at 524°C and 125 torr. Top: 31% NH₃ input. Bottom: 37% NH₃ input.

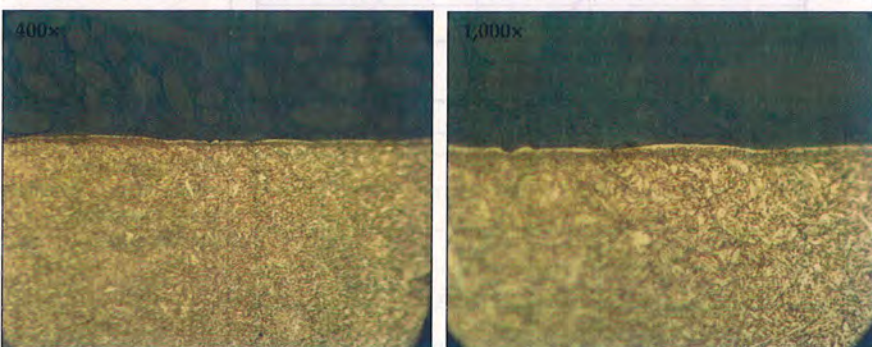
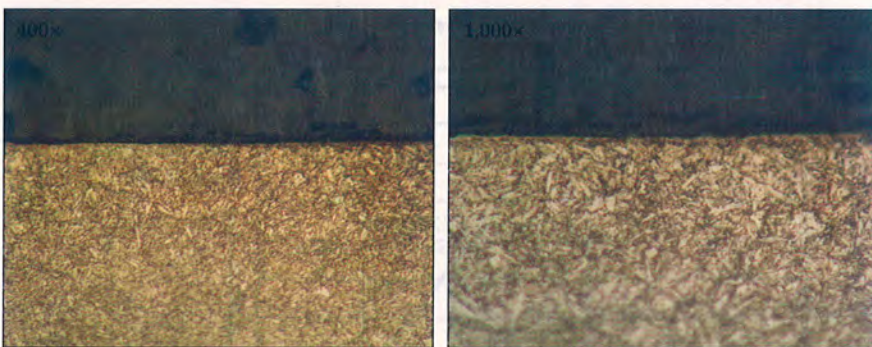


Fig. 9 — Nitriding results at 538°C and 125 torr. Top: 19% NH₃ input. Bottom: 22% NH₃ input.

Fig. 10 — One control sample and 3 preoxidized samples nitrided after preheating in H₂ to a temperature of 524°C and 125 torr; (top) before entering furnace; (bottom) after nitriding.

temperatures and ammonia input at a nitriding pressure of 125 torr as shown below

Temperature, °C	NH ₃ input, %	White layer
524	31	No
524	37	Yes
538	19	No
538	22	Yes

to determine whether the $\alpha-\gamma'$ phase boundary formed. Microstructures of the test specimens are shown in Figs. 8 and 9.

Effect of Hydrogen in Nitriding

Hydrogen was used in this study during heat up and mixed with ammonia during the nitriding cycle. During heat up, hydrogen reduces certain oxides and provides an active surface to adsorb nascent nitrogen. During the nitriding cycle, hydrogen functions as a diluting gas to control the amount of ammonia dissociation. It also provides a means of calculating the nitriding potential, where:

$$K_n = p(\text{NH}_3) / [P(\text{H}_2)]^{1.5} \quad (2)$$

To illustrate the effect of hydrogen in reducing oxides and compare low pressure nitriding with atmospheric pressure nitriding, a series of experiments were conducted after preoxidizing at temperatures of 204, 315, and 427°C as shown in Table 3. Oxidized specimens before and after nitriding are shown in Fig. 10. In each



case, a control specimen with no pre-oxidation was included with the oxidized specimens. The resulting nitrided case depth, surface hardness, and oxidation treatment for tests A, B, and C together with corresponding photomicrographs are shown in Figs. 11, 12, and 13.

These data indicate that low pressure hydrogen heat up reduces oxides produced on 4140 steel at the stated preoxidizing temperatures. Nitrided case depths and surface hardnesses were similar regardless of the preoxidizing condition. In addition, there were similar results for nitriding at reduced pressure and slightly positive pressure. Statistical data in Table 4 show that the nitrogen heat-up resulted in a 25 to 30% shallower case depth than the material that had the hydrogen heat up, indicating that the hydrogen heat up is beneficial.

Reduced Pressure $\alpha - \gamma'$ Phase Boundary

Nitriding tests (Table 3) were run for 5 hours to establish if white layer was or was not present. Work by Sommers and Christiansen^[4] shows this should be more than adequate time to provide for the nucleation and growth of gamma prime. Comparison of data in Figs. 6 and 7 with Table 3 and Figs. 8 and 9 indicates there is not an exact correlation of the experimental data with theoretical calculated values. A principal factor that may contribute to this variance is pumping efficiency related to temperature variations. However, Fig. 14 indicates there is reasonable agreement. The horizontal lines on the theoretical 125-torr boundary represent a 20% spread band.

Conclusions

The experimental work completed thus far indicates that the calculated $\alpha - \gamma'$ phase boundary at 125 torr is within 20% of the experimental values. However, additional experimental work is required to determine whether the actual boundary at 125 torr is closer to the conditions that produced white layer, or those that did not. Nevertheless, the preliminary results indicate that the method used to calculate the boundary at 125 torr is reasonable.

Low-torr nitriding requires higher critical input ammonia content (higher input nitriding potential) as the nitriding pressure is reduced. The

Hydrogen heat up at 4.5 torr and nitriding at 125 torr

Specimen	Oxidation temp., °C	Nitrided case depth at 40 HRC, mm	Surface hardness at 0.051 mm, HRC
1	No preoxidation	0.335	52.1
2	427	0.351	52.9
3	315	0.414	52.9
4	204	0.386	51.1

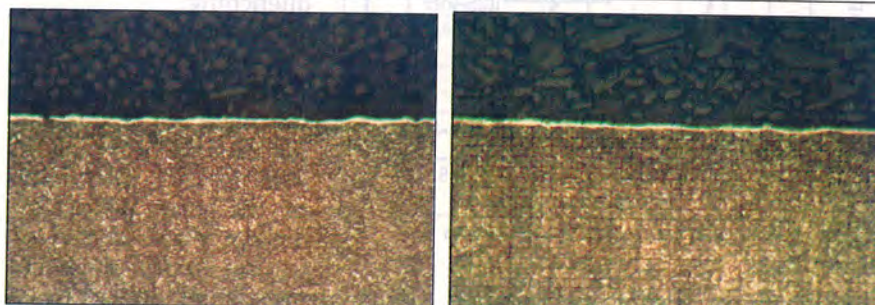


Fig. 11 — Photomicrographs of test samples nitrided at 524°C and 125 torr in preoxidation test A; (left) control: no preoxidation; (right) preoxidized at 427°C. Magnification: 200×

Hydrogen heat up at 4.5 torr and nitriding at 812 torr

Specimen	Oxidation temp., °C	Nitrided case depth at 40 HRC, mm	Surface hardness at 0.051 mm, HRC
1	No preoxidation	0.343	52.5
2	427	0.356	52.5
3	315	0.363	52.3
4	204	0.366	53.1



Fig. 12 — Photomicrographs of test samples nitrided at 524°C and 812 torr in preoxidation test B; (left) control: no preoxidation; (right) preoxidized at 427°C. Magnification: 200×

Nitrogen heat up at 4.5 torr and nitriding at 812 torr

Specimen	Oxidation temp., °C	Nitrided case depth at 40 HRC, mm	Surface hardness at 0.051 mm, HRC
1	No preoxidation	0.259	51.7
2	427	0.323	51.9
3	315	0.239	52.1
4	204	0.315	51.1

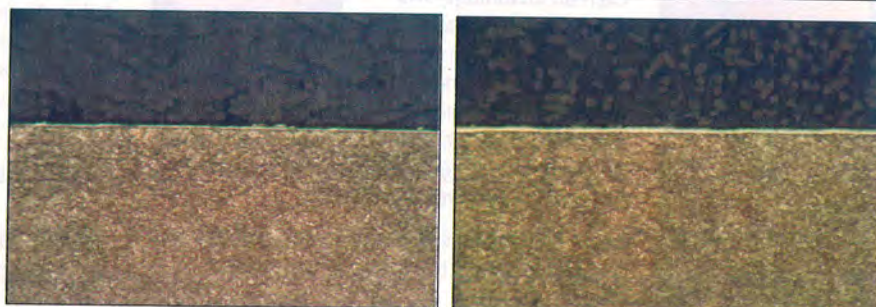


Fig. 13 — Photomicrographs of test samples nitrided at 524°C and 125 torr in preoxidation test C; (left) control: no preoxidation; (right) preoxidized at 427°C. Magnification: 200×

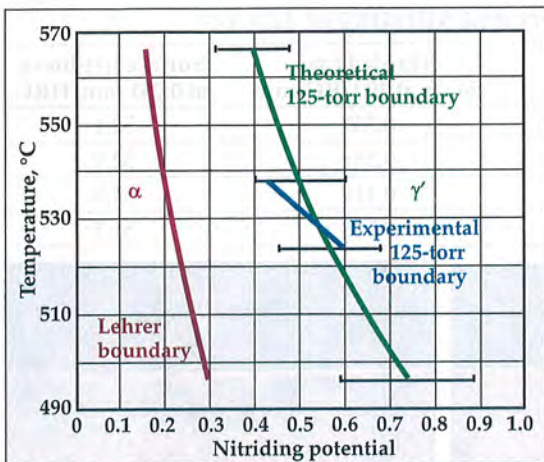


Fig. 14 - Experimental data versus theoretical data based on K_n .

modification of the input ammonia content is the result of reduced partial pressures of ammonia and hydrogen in addition to the differential pump-out of ammonia compared with hydrogen.

Although the nitrided surfaces from atmospheric pressure nitriding and low-torr nitriding are similar, there are some advantages of the low-pressure nitriding. The turn around time for a nitriding cycle is quicker owing to the fact that in a

vacuum furnace there is no retort to heat up and cool down. Further, accelerated cool-down is accomplished by circulating inert gas across a water-cooled heat exchanger, similar to typical vacuum furnace quenching.

Vacuum processing produces a very pure starting atmosphere, eliminating the need for a nitrogen purge, and provides the ability to clean the surfaces of the parts using hydrogen prior to the nitriding step of the cycle.

The hydrogen treatment can be accomplished at less than 150 torr, and this greatly minimizes any explosion risk^[7].

Low pressure processing also maintains a dynamic/uniform atmosphere in the chamber, eliminating the need for a convection fan. And of particular significance, the vacuum chamber provides an extremely tight thermally and atmospherically uniform furnace, which is ideally suited for precise functionality of modern-day instru-

mentation control of the nitriding potential. **HTP**

References

1. E. Lehrer: Z Electrochem, vol. 36, pp 383 - 392, 1930
2. E. Mittemeijer and J. Slycke: "Chemical Potentials and Activities of Nitrogen and Carbon Imposed by Gaseous Nitriding and Carburizing Atmospheres", Surface Engineering, vol. 12 No. 2, 1996
3. V. M. Zinchenko, et. al., "Nitrogen Potential: current status of knowledge", 3rd Lakhin Memorial Lecture, 21-23 September 2003, Warsaw, Poland
4. M. Sommers and T. Christiansen: "Kinetics of Microstructure Evaluation During Gaseous Thermochemical Surface Treatment", Journal of Phase Equilibria and Diffusion, vol. 23, No. 5, 2005
5. D. Herring: "Introduction to Gas Nitriding", Manuscript, Aug. 2006
5. J. Darbellay: "Gas Nitriding: An Industrial Perspective", MSE 701 Seminar, March 22, 2006.
6. T. M. Jones: "Hydrogen Reaction", Heat Treating Process, March 2002

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