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IONITRIFICATION KINETICS OF TWO COMMERCIAL STEELS

TECHNICAL REPORT

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ABSTRACT

The penetration of nitrogen into two commercial steels (Nitralloy 135M and AISI 4140) has been studied under glow-discharge conditions. Comparisons are made with those steels conventionally nitrided. With the use of identical conditions of temperature and time, the depth of penetration was observed to be consistently higher for ion-nitrided samples than for gas-nitrided samples. Further, the thickness of the white layer (Fe_4N) is substantially less for ion-nitrided specimens than for those specimens commercially nitrided. The dual role of hydrogen ions in cleansing the work surface and in inhibiting the growth of the surface-layer nitrides has been established.

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INTRODUCTION

The study of techniques to improve the material service performance of military hardware is one of the missions of the Science and Technology Laboratory, U. S. Army Weapons Command. As a result, a program was undertaken to evaluate nitriding treatments under glow-discharge conditions.

Ion nitriding is a relatively new process whereby nitriding is accomplished by glow discharge in a reduced pressure environment. The materials to be treated are placed at the cathodic electrode, and a potential is applied to initiate the glow discharge. Positive ions accelerated to the cathodic workpiece promote heating as well as nitrogen penetration. Although the literature cites examples of the application of ion nitriding to ferrous alloys[1,2] as well as to certain refractory alloys,[3] the factors that promote increased penetration depths under glow-discharge conditions are still not understood.

The purpose of this work is to evaluate the ion nitriding of two commercial steels: Nitralloy 135M, an alloy designed specifically for nitriding, and AISI 4140. Comparisons are made with a typical industrial nitriding process in which dissociated ammonia gas is used. Ion-nitriding variables such as gas composition, time, and temperature are studied with relation to their effect on the case depth and the amount of white layer (Fe_4N) formed.

PROCEDURE

The materials nitrided were of the typical compositions listed below:

Material	Elements (Wt. %) C	Mn	Si	Cr	Al	Mo
135M	0.41	0.55	0.30	1.60	1.00	0.35
4140	0.40	0.90	0.30	0.95	-	0.20

The materials were quenched and tempered to a core hardness of 30-34 Rc. Test specimens, 1-inch diameter by 3/8-inch thick, were degreased and glass shot-blasted prior to surface treatment.

The glow-discharge equipment was essentially that described in an earlier paper.[1] The samples were placed on a steel pedestal which served as the cathodic electrode, the steel dome acting as the anode. The treatment temperature was controlled by a protected chromel-alumel thermocouple embedded in the steel pedestal. After the chamber was evacuated, the desired gas mixture was introduced at a reduced pressure of approximately 0.5mm Hg. A potential difference of 400 volts D.C. was maintained between the cathodic samples and the anodic grounded container. As the material was heated to the nitriding temperature, the chamber pressure was increased to a total pressure of 7mm Hg. This pressure was maintained throughout the treatment period.

The ion nitriding was accomplished at 975°F and at 1050°F with treatment times varying from 2 to 55 hours. Gas mixtures of 25 per cent and 75 per cent H_2 were used throughout the study except in those instances mentioned in the following text.

The gas nitriding was accomplished with the use of a typical industrial process of 30 per cent dissociated ammonia and 975°F treatment temperature. Nitriding times were varied from 12 to 72 hours.

After the surface-treatment operations, sections orthogonal to the treated surface were mounted and subjected to microhardness surveys and metallographic examinations. Microhardness traverses were made with a Knoop indenter (500 gram load) and a Sonodur ultrasonic microhardness tester.

RESULTS AND DISCUSSION

Hardness versus penetration distance plots have been used extensively in this study. The total case depths were sometimes difficult to define. When these conditions were encountered, the total case depth was taken to be that distance in which the slope of hardness versus distance curve was minimum or zero. In most situations, the total case depth measurements corresponded to those observed metallographically on etched specimens.

Case depths of specimens ion nitrided at 975°F in 75 per cent H_2 and 25 per cent N_2 gas mixtures were compared with those conventionally nitrided in a 30 per cent dissociated ammonia atmosphere at 975°F. The results for Nitralloy 135M are presented in Figure 1. The observed ion-nitrided samples show a larger total case for equivalent treatment-times up to 60 hours. Similar results are observed for AISI alloy 4140 as shown in Figure 2.

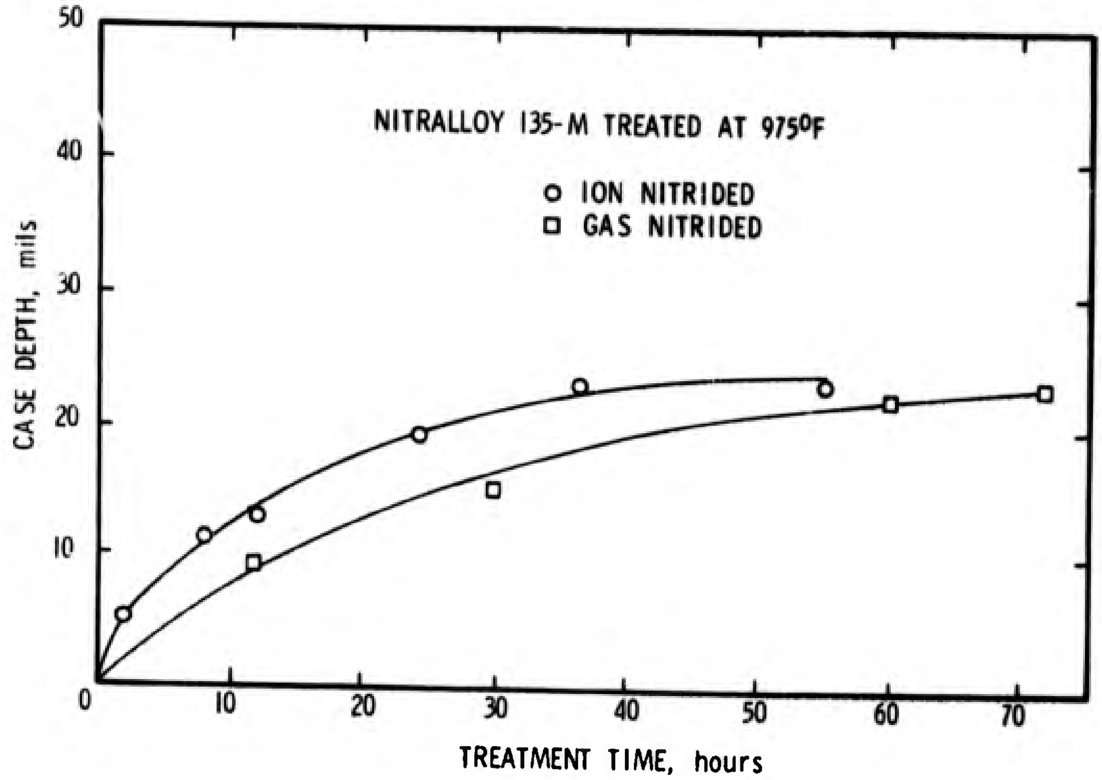


FIGURE 1 CASE DEPTH VERSUS TREATMENT TIME FOR NITRALLOY 135M

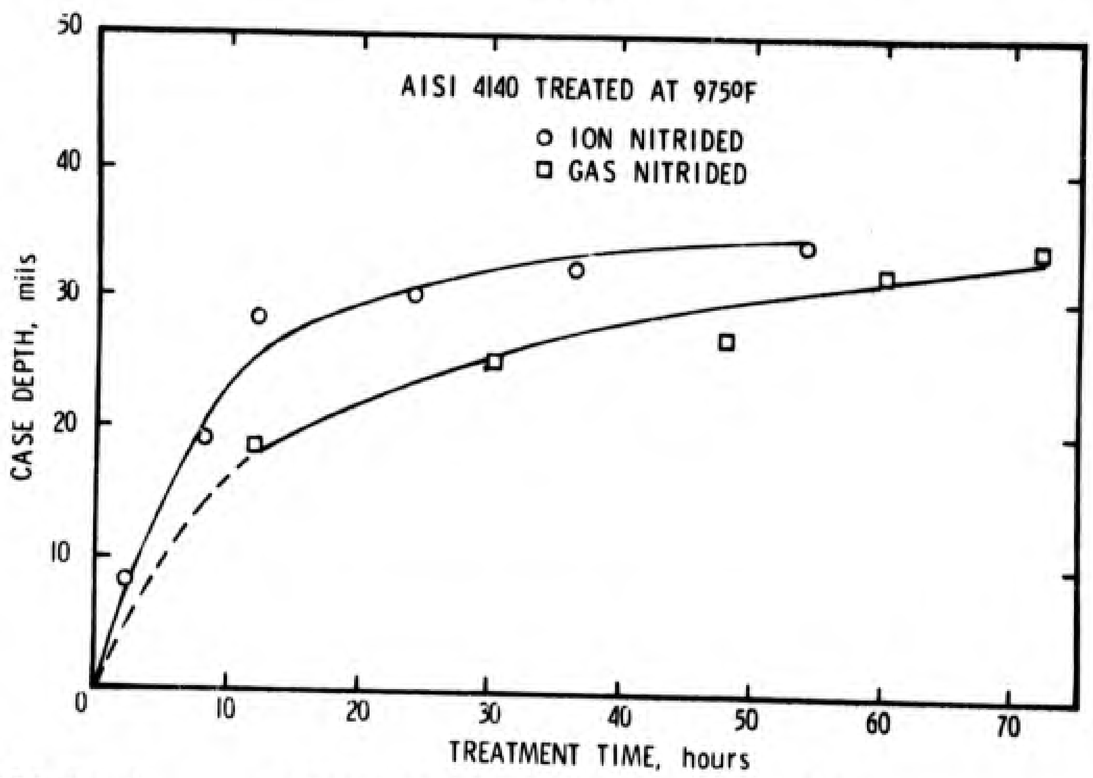


FIGURE 2 CASE DEPTH VERSUS TREATMENT TIME FOR AISI 4140

Case depth as a function of the square root of the treatment time for alloys 135M and 4140 is plotted, respectively, in Figures 3 and 4. The results of the 1050°F ion-nitriding treatments are also shown in these figures. Specimens that were glow-discharge treated clearly exhibit increased nitriding rates over those treated in the conventional manner. The parabolic rates derived from Figures 3 and 4 show that the rate constants for the ion-nitriding process are nearly twice those obtained for the conventional process. Similar results showing increased penetration of nitrogen under glow-discharge conditions were observed for a Mo-Ti alloy.[3]

Since the acceleration of nitrogen diffusion in the steel matrix by the ionizing treatment is implausible, the arrival rates of nitrogen at the steel surfaces under the glow-discharge conditions must be greater than those for the conventional process. Since the ammonia or nitrogen molecules dissociate at the gas-specimen interface under conventional nitriding conditions, the amount of nitrogen available for diffusion may be limited by the initial contamination on the substrate. This initial contamination is removed early under the ion-nitriding conditions, thus making more sites available for nitrogen diffusion. For extended times (approximately 36 hours or greater), decreasing penetration rates are observed for even the ionizing treatments as noted in Figures 3 and 4. This may be attributed to the increased buildup of surface layer nitrides at these longer treatment times.

Thickness measurements of these surface layer nitrides (white layer) were made on samples nitrided at 975°F. The white-layer thickness as a function of treatment time in both processes for alloys 135M and 4140 is plotted, respectively, in Figures 5 and 6. In each instance, the gas-nitrided samples exhibit a thicker white layer than those treated under ionizing conditions. X-ray diffraction analysis of the white layer on the ion-nitrided specimens, treated for less than 36 hours, showed that the layer consists primarily of the $Fe_4N(\gamma')$ phase. Diffraction analysis of specimens ion nitrided for 36 hours or longer revealed both the γ' and ε (Fe_2N or Fe_3N) phases. An accelerated growth rate of the white layer for both materials after 48 hours of conventional gas-nitriding conditions is illustrated in Figures 5 and 6.

The amount of white layer present for comparable total case depths in the 135M material is shown in the photomicrographs of Figure 7. Treatment times were 48 hours at 975°F for the gas-nitriding process and 54 hours at 975°F for the ion-nitriding conditions. The nitride layers produced by both processes appear quite dense. In contrast, as shown in Figure 8, the conventionally nitrided 4140 samples exhibit porous

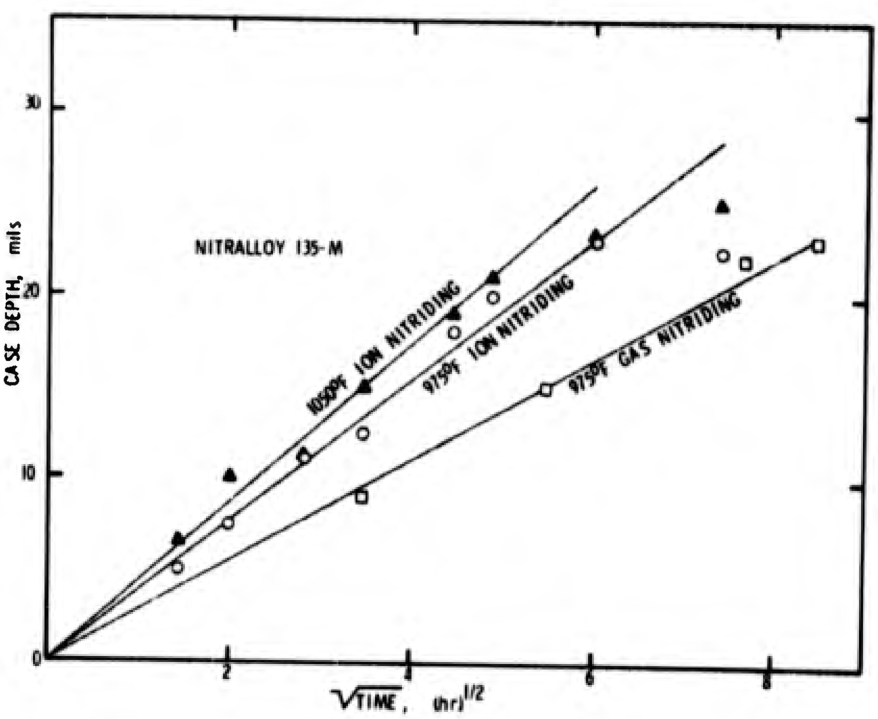


FIGURE 3 CASE DEPTH VERSUS SQUARE ROOT OF TREATMENT TIME FOR NITRALLOY 135M

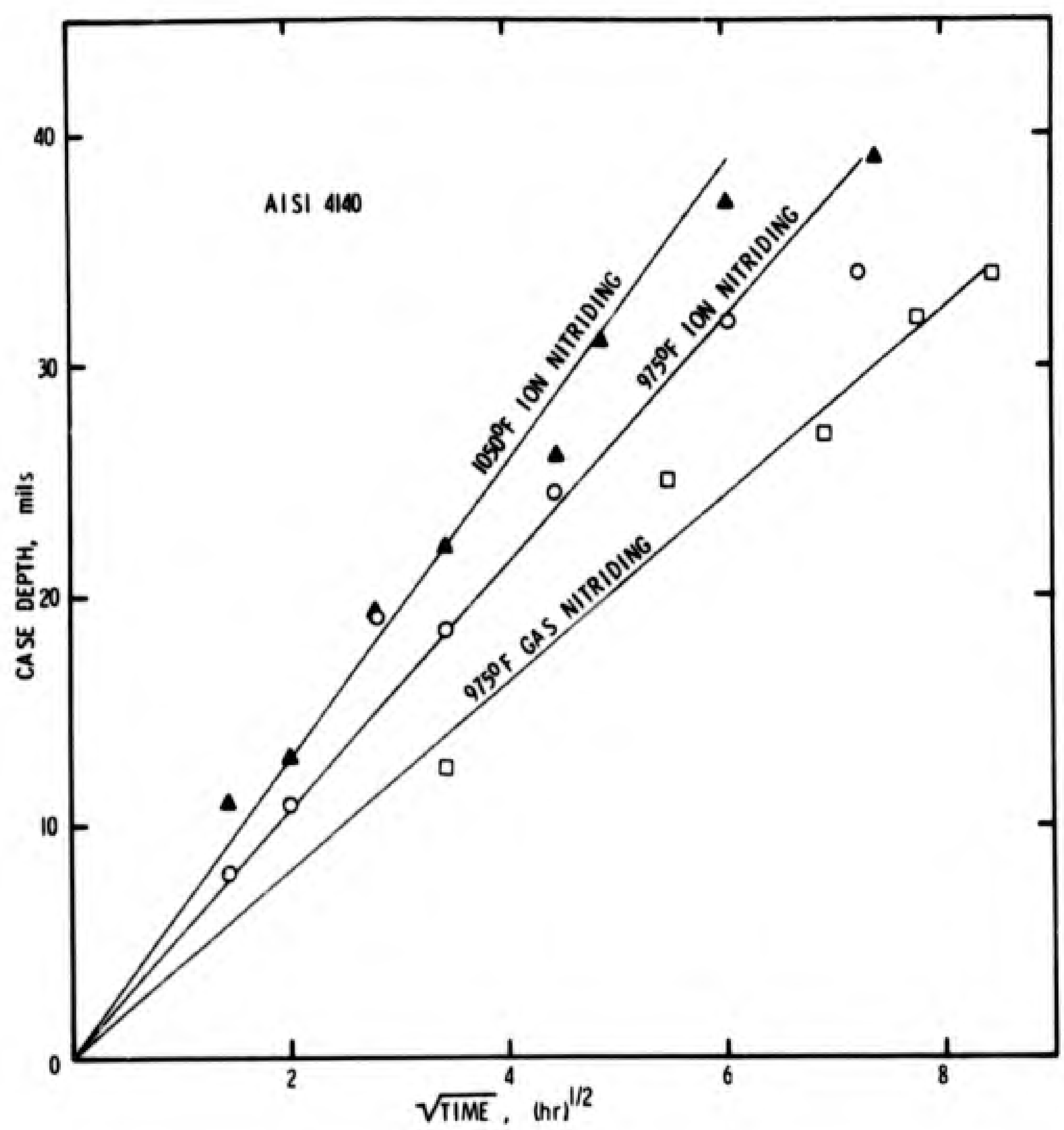


FIGURE 4 CASE DEPTH VERSUS SQUARE ROOT OF TREATMENT TIME FOR AISI 4140 ALLOY

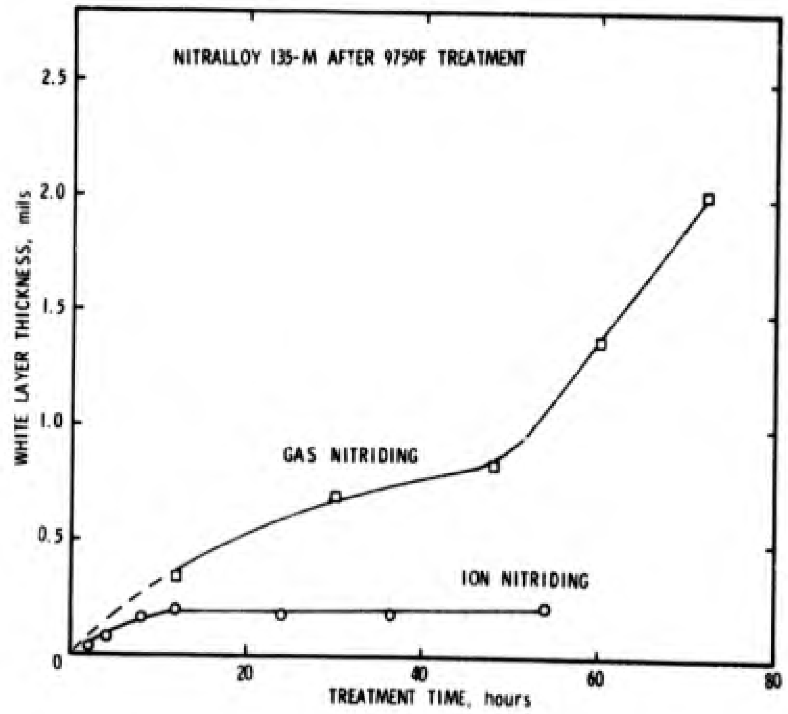


FIGURE 5 WHITE-LAYER THICKNESS AS A FUNCTION OF TREATMENT TIME FOR NITRALLOY 135M

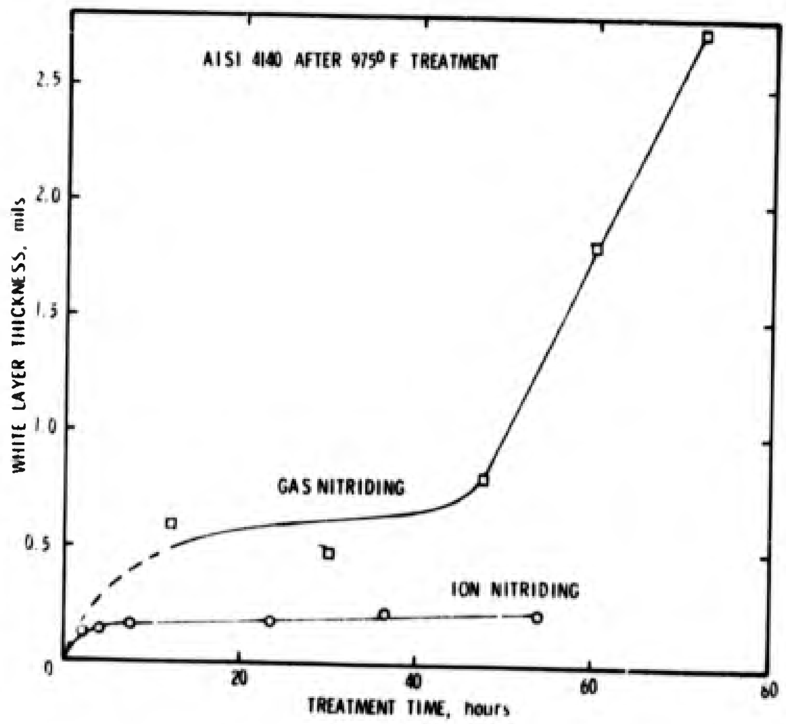
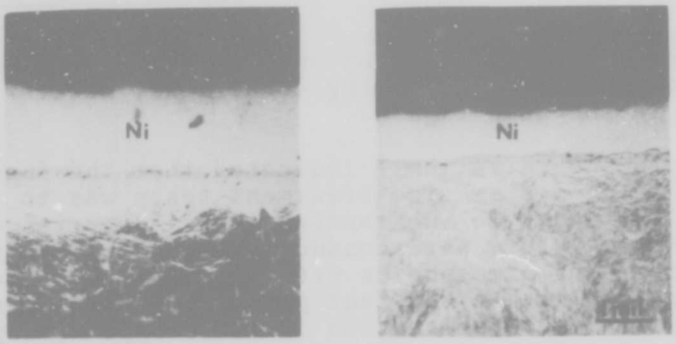


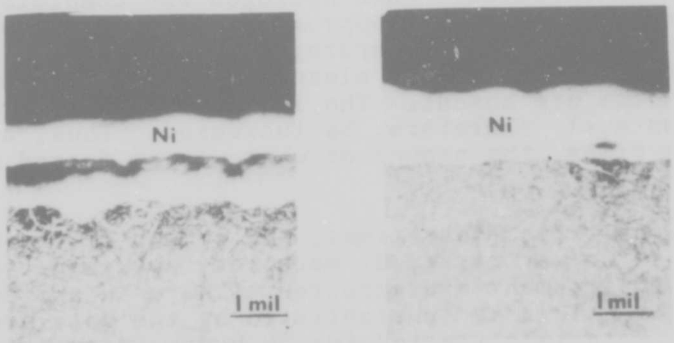
FIGURE 6 WHITE-LAYER THICKNESS AS A FUNCTION OF TREATMENT TIME FOR AISI 4140 ALLOY



(a) (b)

Nitralloy 135M

FIGURE 7 COMPARISON OF WHITE LAYER PRODUCED DURING (A) CONVENTIONAL GAS NITRIDING FOR 48 HOURS AT 975°F AND (B) ION NITRIDING FOR 54 HOURS AT 975°F



(a) (b)

AISI 4140

FIGURE 8 COMPARISON OF WHITE LAYER PRODUCED DURING (A) CONVENTIONAL GAS NITRIDING FOR 48 HOURS AT 975°F AND (B) ION NITRIDING FOR 54 HOURS AT 975°F structures in the white layer. The nitride layer formed on 4140 alloy under ion-nitriding conditions, however, is dense, as shown in the same figure.

Previous observations[1] indicated that the function of hydrogen in glow-discharge treatment tests was to clean the specimen surface. To substantiate this, a series of 8-hour treatments at 1050°F were conducted. Specimens were subjected to ion-nitriding atmospheres with varying amounts of hydrogen and argon, but with a constant pressure of nitrogen. Plots of hardness versus penetration distance appear, respectively, in Figures 9 and 10, for alloys 135M and 4140. In these tests, the hydrogen content was varied from 75 per cent to 40 per cent to 0 per cent; the total pressure being 7 torr. The argon was correspondingly varied from 0 per cent to 35 per cent to 75 per cent. The plots reveal that no decrease in penetration depth was observed when the hydrogen was reduced from 75 per cent to 40 per cent. On the other hand, when hydrogen was completely eliminated, the case depth was reduced in both alloys. These observations substantiate the initial cleansing role of the hydrogen ions on the substrate.

After this initial substrate cleanup, the hydrogen ions appear to promote a reaction to form ammonia with the cathodic workpiece, resulting in the inhibition of the white-layer growth. The amount of white layer produced in the 8-hour treatments is shown in Table I. When hydrogen was reduced from 75 per cent to 40 per cent, the white-layer thickness increased as expected. When hydrogen was completely eliminated, the white layer was approximately one-half of that observed in the 75 per cent hydrogen environment. This result is not unexpected since no cleansing action is provided when hydrogen ions are absent. The incubation time for Fe_4N nucleation must, therefore, be increased. Thus, at shorter treatment times, the amount of white layer formed must be less.

At longer treatment-times, the growth of the white layer is in no way retarded; moreover, specimens treated in an argon environment are expected to have an appreciable white layer. This is substantiated by the data provided in Table I. Materials treated for 30 hours in an argon atmosphere attained more white layer than those treated for 36 hours in the hydrogen environment.

Samples of Nitralloy 135M and 4140, gas nitrided for 12 hours at 975°F, were subjected to an additional 18-hour treatment under ionizing conditions to determine the effect of the hydrogen ions on a conventionally gas-nitrided substrate. The results of this treatment are presented in Table II. Specimens gas nitrided for 30 hours are shown for

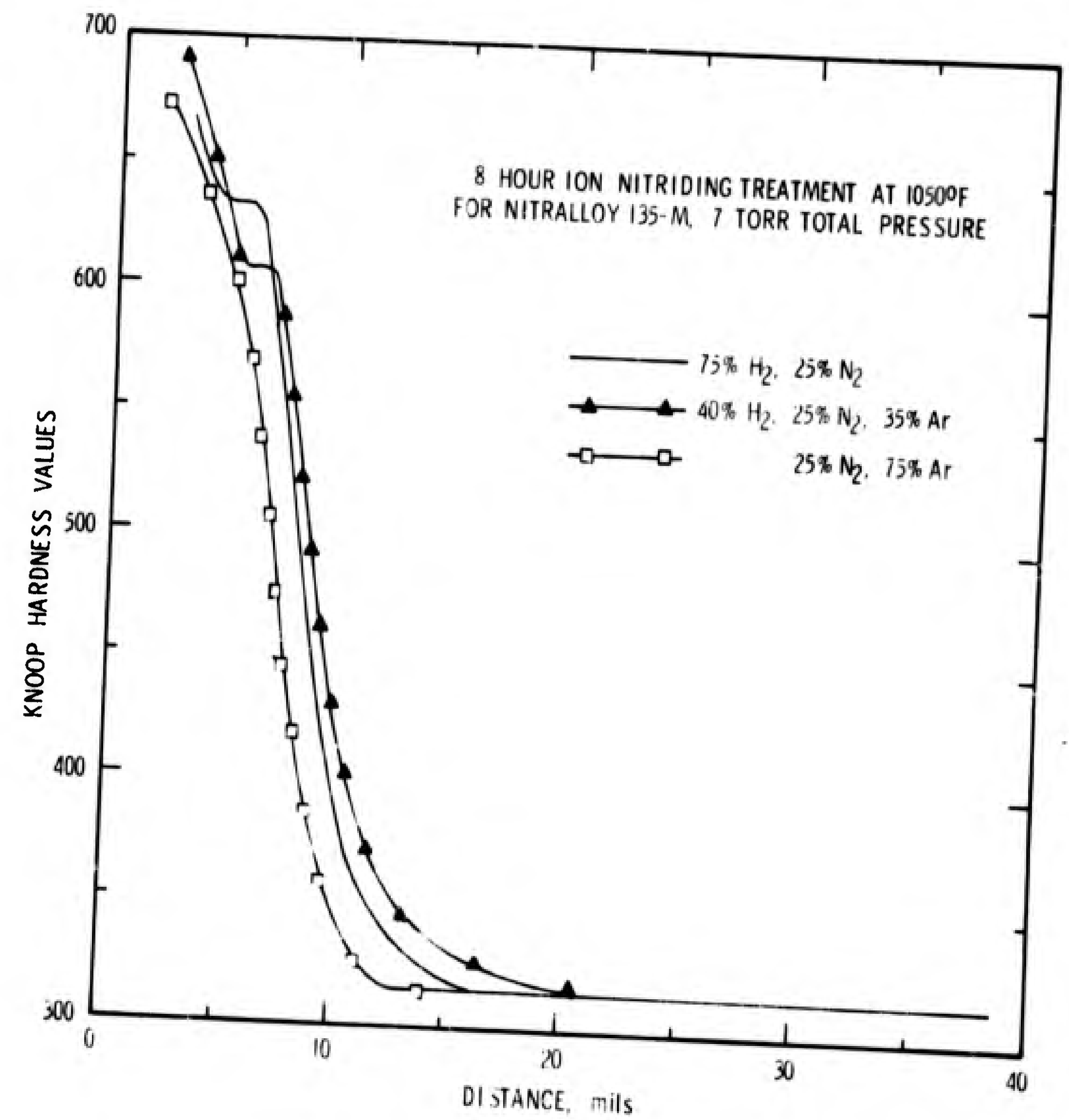


FIGURE 9 HARDNESS VERSUS PENETRATION DISTANCE FOR NITRALLOY 135M ION NITRIDED WITH VARIOUS GAS MIXTURES

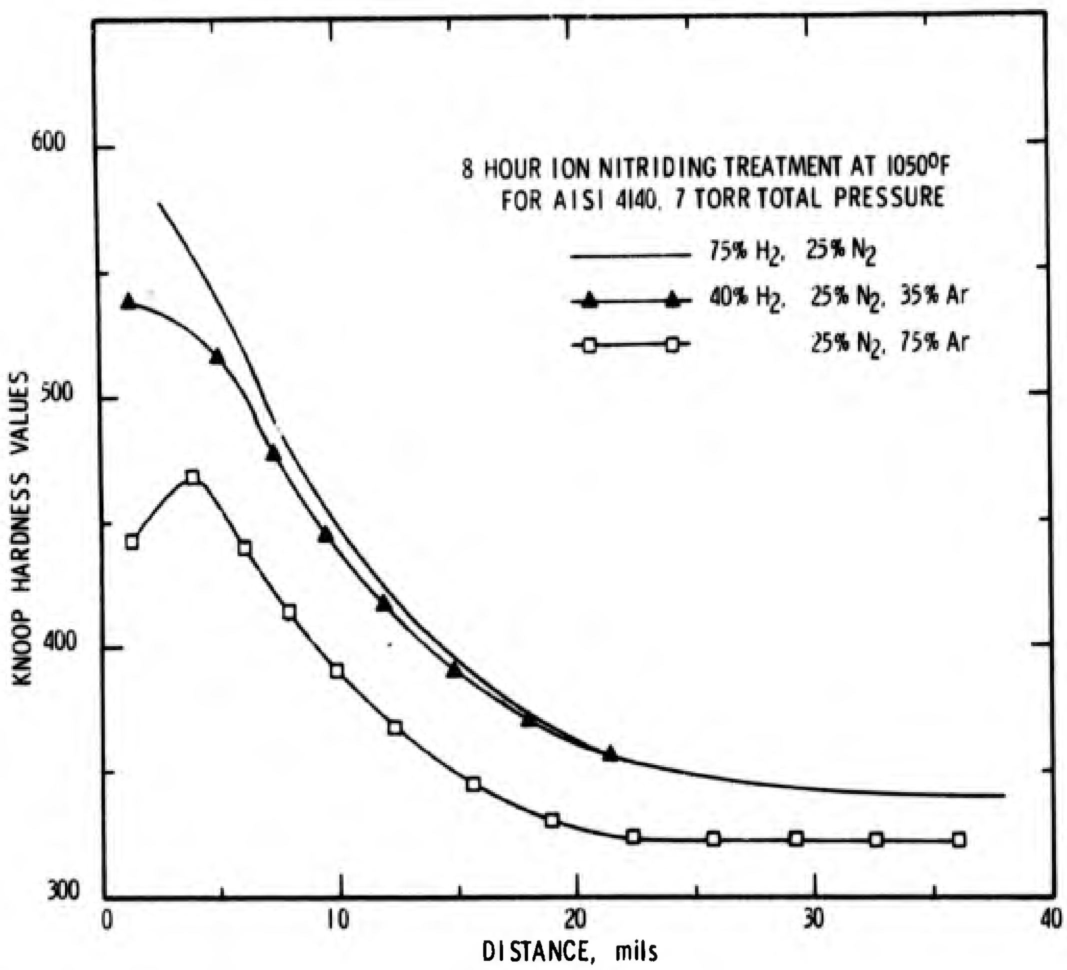


FIGURE 10 HARDNESS VERSUS PENETRATION DISTANCE
FOR AISI 4140 ALLOY
ION NITRIDED WITH VARIOUS GAS MIXTURES

TABLE I

WHITE-LAYER THICKNESS AS A FUNCTION OF GAS COMPOSITION UNDER IONIZING CONDITIONS AT 1050°F

Material	White-Layer Thickness (10^{-3}in.) 8 Hr	30 Hr	36 Hr	Gas Composition
135M	0.13	--	0.20	75% H_2, 25% N_2
135M	0.44	--	--	40% H_2, 25% N_2, 35% Ar
135M	0.08	0.50	--	25% N_2, 75% Ar
4140	0.25	--	0.63	75% H_2, 25% N_2
4140	0.39	--	--	40% H_2, 25% N_2, 35% Ar
4140	0.10	0.88	--	25% N_2, 75% Ar

* 7 torr total pressure

TABLE II

EFFECT OF ION NITRIDING ON WHITE LAYER PRODUCED IN GAS NITRIDING

Material	Treatment Time (Hr)	White Layer (10^{-3}in.)
135M	12*	0.38
135M	12* + 18**	0.56
135M	30*	0.63
4140	12*	0.63
4140	12* + 18**	0.25
4140	30*	0.75

*Conventionally gas nitrided at 975°F

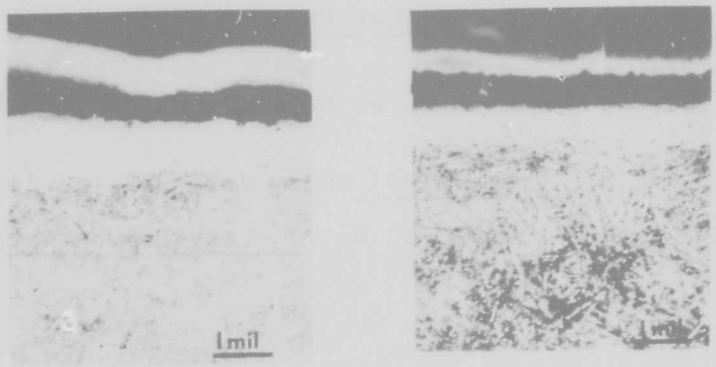
**Ion Nitrided at 975°F with 25% N_2, 75% H_2, 7 torr total pressure comparison. Although both treatments produced the same total case depth, the amount of white layer on the materials completed under ionizing conditions was less than that of a full 30-hour gas nitriding treatment; the white layer produced on the 4140 material after the 18-hour ionizing treatment was less than one-half the original amount present after 12 hours of conventional nitriding. The differences in white-layer thickness for both treatments are shown in the photomicrographs of Figures 11 and 12. These results are in accordance with the earlier observations concerning the effect of hydrogen ions in inhibiting the growth of the white layer in glow-discharge nitriding.

CONCLUSIONS

1. The ion-nitriding method, due to its high penetrative energy, produced greater case depths in two steels when compared with the gas-nitriding process for equivalent treatment times and temperature.

2. A substantially thinner white layer was formed on the steel specimens under ionizing conditions when compared with conventionally treated specimens.

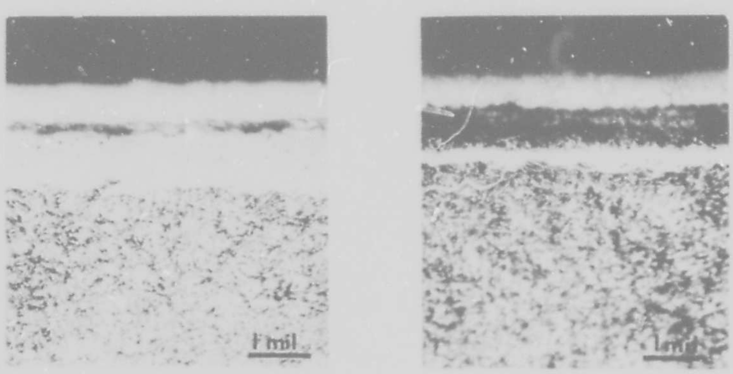
3. The hydrogen ions in the glow-discharge environment performed a dual role of cleansing the substrate surface and of inhibiting the growth of the undesirable white layer.



(a) (b)

Nitralloy 135M

FIGURE 11 COMPARISON OF WHITE LAYER PRODUCED DURING (A) CONVENTIONAL GAS NITRIDING FOR 30 HOURS AT 975°F AND (B) CONVENTIONAL GAS NITRIDING FOR 12 HOURS AT 975°F FOLLOWED BY ION NITRIDING FOR 18 HOURS AT 975°F



(a) (b)

AISI 4140

FIGURE 12 COMPARISON OF WHITE LAYER PRODUCED DURING (A) CONVENTIONAL GAS NITRIDING FOR 30 HOURS AT 975°F AND (B) CONVENTIONAL GAS NITRIDING FOR 12 HOURS AT 975°F FOLLOWED BY ION NITRIDING FOR 18 HOURS AT 975°F

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13. ABSTRACT

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2. Ion nitriding						
3. Glow discharge						
4. Diffusion						

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