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Fluidized Bed CrN Coating Formation on Prenitrocarburized Plain Carbon Steel

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CrN coatings were formed on plain carbon steel by prenitrocarburizing, followed by thermoreactive deposition and diffusion (TRD) in a fluidized bed furnace at 570 °C. During TRD, Cr was transferred from Cr powder in the fluidized bed to the nitrocarburized substrates by gas-phase reactions initiated by reaction of HCl gas with the Cr. The microstructural processes occurring in the white layer, caused by N diffusion toward the surface during this stage were studied. This study compares TRD atmospheres employing inert gas and HCl or inert gas, H_2, and HCl. Surface characterization was performed by scanning electron microscopy (SEM), x-ray diffraction (XRD), and glow-discharge optical-emission spectroscopy (GDOES).

Keywords fluidized bed, glow-discharge optical-emission spectroscopy, nitrocarburizing, plain carbon steel, thermoreactive deposition and diffusion

1. Introduction

Thermoreactive deposition and diffusion (TRD) is a hard-coating process whereby a metallic element [i.e., a transition metal carbide- or nitride-former-chromium (Cr), vanadium (V), titanium (Ti), or aluminum (Al)] is thermochemically deposited on the surface of a substrate, and that metallic element reacts with an interstitial element [i.e., carbon (C), nitrogen (N), or boron (B)] that diffuses to the surface from the substrate. The driving force for diffusion of the interstitial element is the thermodynamic stability of the surface compound(s) formed.

The Toyota Diffusion (TD) Process, developed by the Toyota Central Research Institute, is one example of TRD.[1] In the TD process, a V carbide layer is formed at 800-1050 °C by outward diffusion of C from a steel substrate. The thickness of the layer formed under identical processing conditions is limited by the C content of the substrate being treated.[2]

It has been shown that V carbide/carbonitride/nitride coatings grow at a faster rate by pretreating with carburizing, nitrocarburizing, or nitriding.[3] Pretreatment raises the concentration of interstitials in the surface of the substrate prior to TD treatment. Chicco et al.[3] carburized H13 tool steel, followed by TD vanadizing, to yield a V carbide coating of thickness 4.6 μm. Even thicker coatings were achieved with prenitrocarburizing and prenitriding, because V has a higher affinity for N than for C. However, superior hardnesses were achieved when C was present in the coating. Similar results can be expected with other transition metals, because they generally form harder carbides than nitrides.[4]

There is some limited experimental evidence that TRD coating may be performed at lower temperatures due to the effect of interstitial surface enrichment. Vanadium carbonitride and Cr carbonitride coatings have been formed on a variety of substrate materials by nitriding, followed by TD salt-bath treatment at 530-700 °C.[5,6]

A number of patents have been filed for low-temperature TRD processes performed in a fluidized bed.[7-9] The equipment described was a fluidized bed of inert refractory powder, mixed with 10-20 wt.% of powdered Ti, V, or Cr. Ferrous substrates were suspended in the bed during treatment. The powder was activated by sublimated ammonium-halide pellets. Reaction at the surface of the metallic powder formed volatile metal halides, which subsequently transferred the coating metal to the substrate surface. In this way, the authors of Ref 9 claim to have achieved a 1 μm layer of CrN after 6 h of treatment at 570 °C and an 8 μm layer after 50 h.

Thin Cr(N,C) coatings have also been applied to H13 tool steel by nitrocarburizing, followed by TRD in a fluidized bed containing Cr metal powder. Both steps were performed at 570 °C, just below the normal tempering temperature of this steel. The Cr powder was activated by gaseous HCl in this investigation.[10]

No matter what coating method was used, the nature of the surface formed during pretreatment must have an important influence on the final coating properties. It is also vital to understand the processes whereby interstitial atoms diffuse to the surface during TRD. For example, Chicco et al.[3] reported a modification of the diffusion-zone nitride distribution after TRD treatment at 1000 °C. This finding indicates that diffusion of interstitials had occurred over large distances (several hundred microns), whereas research at lower temperatures[5,6,10] shows diffusion of a more local nature. The structural aspects of diffusion have been unexplored in the limited amount of work published so far.

Nitrided and nitrocarburized compound layers on plain carbon steel consist of one or both of the Fe carbonitrides: ε-$Fe_{2\text{-}3}(N,C)$ and γ'-$Fe_4(N,C)$. Occasionally cementite Fe_3C is

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also present. The phase diagram at 575 °C (Fig. 1) shows that of the two carbonitrides, ε-phase has a wider N and C solubility range, while the γ′-phase becomes unstable once C is present over a fraction of a percent. The ε-phase is, therefore, dominant during nitrocarburizing. It has been shown that O acts as a catalyst to the growth of the ε-phase, and hence nitrocarburizing atmospheres deliberately contain a slight O activity.[11]

Another feature of the compound layer is porosity. The fraction of the total compound layer that is porous increases as the compound layer grows.[13] However, careful choice of treatment parameters (such as temperature, N- and C-potentials) can help to limit pore formation. Porosity may hinder the formation of a defect-free coating during TRD, although this notion has yet to be thoroughly investigated. The concentration of N and C in the compound layer is significantly greater than in the diffusion zone, particularly in low- or non-alloyed steels. Therefore, as a source of interstitial atoms for TRD, a thicker compound layer is desirable. Hence, a balanced approach may be required to minimize porosity and maximize the interstitial loading of the surface.

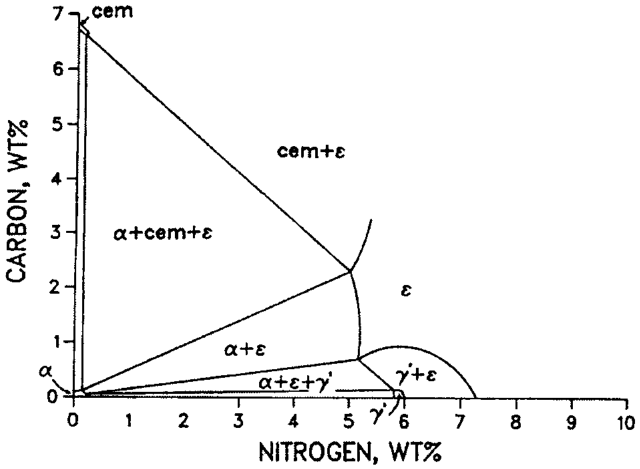


Fig. 1 The Fe-N-C phase diagram at 570-580 °C, according to Slycke et al.[12]

In Ref 3, the effect of compound layer porosity was avoided by light polishing prior to TD treatment. In Ref 10, partial reduction of the heavily oxidized surface during nitrocarburizing resulted in the formation of an extra layer of ε-nitride—the so-called cover layer. Formation of this additional layer has been shown to be dependent on the degree of porosity.[14] The layer resulted in a complex and structurally flawed pattern of coating formation during TRD. Porosity effects were not discussed in Ref 5 or 6.

The following investigation presents preliminary results into fluidized bed TRD treatment at 570 °C. Nitrocarburizing was chosen as a pretreatment due to its ability to produce thick compound layers with significant C enrichment, provided the right gas parameters are used. Chromium (Cr) was deposited by immersing the prenitrocarburized parts into a fluidized bed containing 10% Cr metal powder and activating with gaseous HCl. However, it should be noted that other metal-halide systems are available for investigation.

2 Experimental Method

2.1 Thermal Processing

Samples of plain carbon steel (see Table 1 for compositions) were polished mechanically with 1200-grit SiC paper, wiped

Table 1 Composition of Substrate Materials

	Composition, wt.%			
AISI-SAE	C	Mn	Si	Cr
1008	0.07	0.5	…	…
1018	0.15-0.18	0.7-0.8	0.2	…
1040	0.40	0.6	0.2	0.1

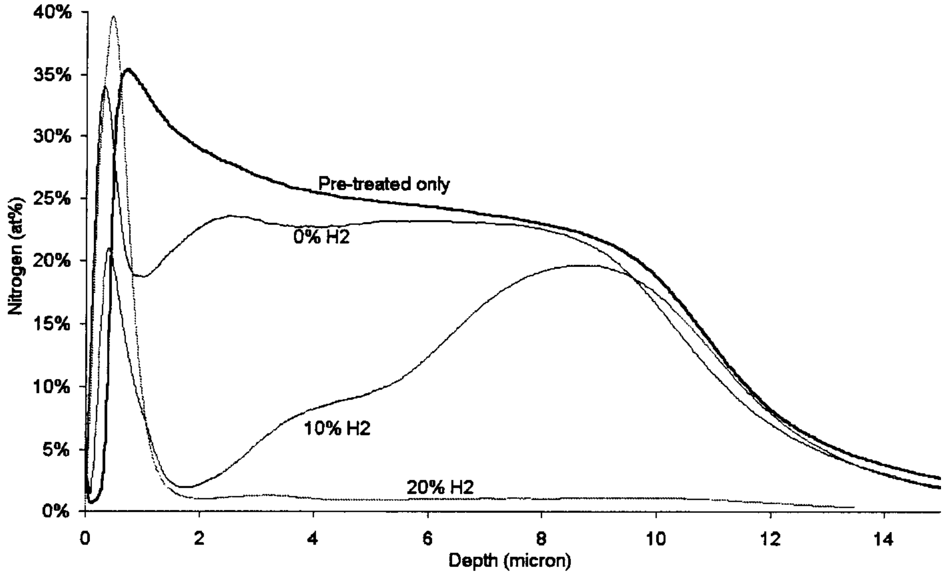


Fig. 2 GDOES nitrogen-depth profiles, showing the diffusion of nitrogen in AISI 1018 from the compound layer to the surface following TRD treatment at 570 °C for 1 h with varying hydrogen contents, 1.5%HCl/0-20%H_2/N_2

with acetone, and nitrocarburized in a fluidized bed furnace at 570 °C. The furnace consisted of an electrically heated retort filled with alumina powder, fluidized by process gases that entered the retort from the bottom, and into which the samples were lowered in a metal basket. A total gas flow of 1.5 m^3/h was required to fluidize the bed. Nitrocarburizing was performed with a gas mixture of $NH_3/CO_2/N_2$ or NH_3/natural gas/N_2. The samples were then quenched in a separate alumina bed, which was fluidized with N_2 gas at ambient temperature.

Following this process, the pretreated specimens were Cr-deposition treated in an industrial, sealed-atmosphere, fluidized bed furnace. The retort diameter was 300 mm and its effective height (the distance from the base that was covered with powder) was 600 mm, large enough for treatment of small dies and tooling. The retort itself was made of Inconel.

The initial bed composition was 10 wt.% Cr powder, 90% alumina powder, making a total weight of 70 kg. A fresh powder mixture was laid in the retort prior to the first treatment. Hydrogen was industrial grade, containing up to 1000 ppm O_2, 500 ppm H_2O, and 4000 ppm N_2. The inert carrier gas used was either Ar or N_2, both of which were high purity (<10 ppm O_2, <10 ppm H_2O), as was HCl (<2 ppm O_2, <0.8 ppm H_2O, <10 ppm N_2).

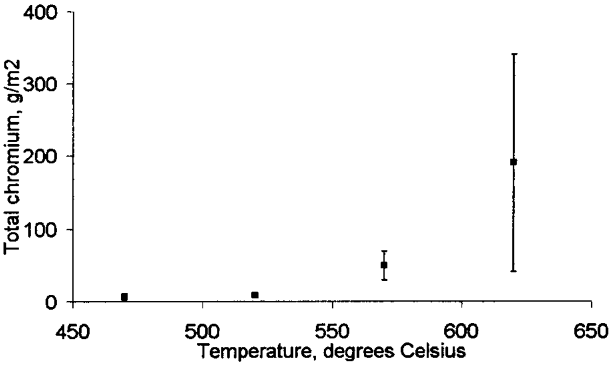


Fig. 3 Total deposited Cr on prenitrocarburized 1018, determined from the area under the GDOES Cr wt.% curve

2.2 Layer Analysis

Sputter-depth profiles were obtained by a LECO GDS-850A glow-discharge optical-emission spectrometer (GDOES) (Leco Corp., St. Joseph, MI). Ar ions, excited by a DC voltage, sputtered a 4 mm diameter area of the sample surface. The displaced matter was analyzed simultaneously by dual emission spectrometers, creating an elemental composition depth profile. The sample surfaces were not cleaned in any way prior to analysis to avoid contamination by any residual alcohol or water left within pores. The GDOES operating conditions were 700 V and 20 mA.[15-17]

Samples for metallographic analysis were cut perpendicular to the treatment surface, mounted, polished, and etched with nital, followed by a 10% solution of HCl in alcohol. Previous work has found that this etchant stains the γ'-phase darker than ε.[18] Scanning electron microscopy (SEM) was performed on the LEO 1530 FEG SEM (Carl Zeiss SMT AG, Oberkochen, Germany), operating on secondary-electron mode at 20 kV.

X-ray diffraction (XRD) was performed on the surface of treated samples using a Philips (N.V. Philips, Gloeilampenfabrieken, The Netherlands) PW 1130/90 diffractometer with a Ni filter, operating at 40 kV and 25 mA. Cu K_α radiation was used to probe the surface structure, as Cu K_α only penetrates a few microns into the most common ferrous phases. The scan rate was 1°/min and step size 0.05°.

3 Results and Discussion

3.1 General Observations Concerning Cr Deposition and N Diffusion

Figure 2 shows the decomposition of a compound layer on AISI 1018 plain carbon steel due to TRD treatment at 570 °C for 1 h. The initial compound layer contained up to 35 at.% N.

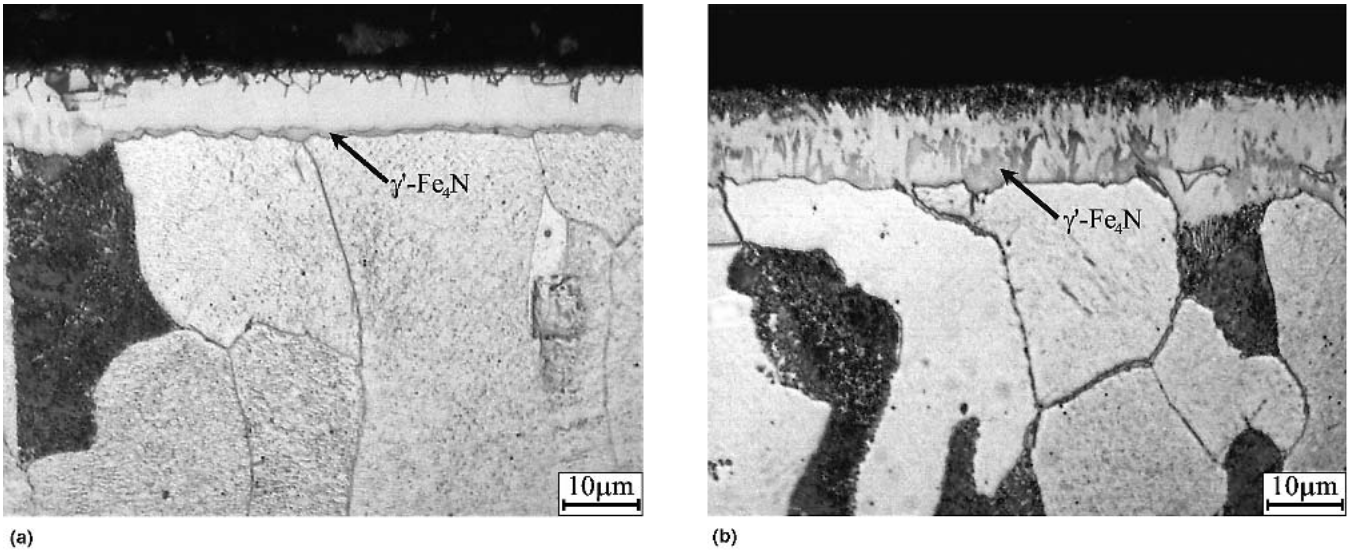


Fig. 4 Optical micrographs of prenitrocarburized specimens. The γ' regions appear dark and are marked by arrows: **(a)** AISI 1008; **(b)** AISI 1018

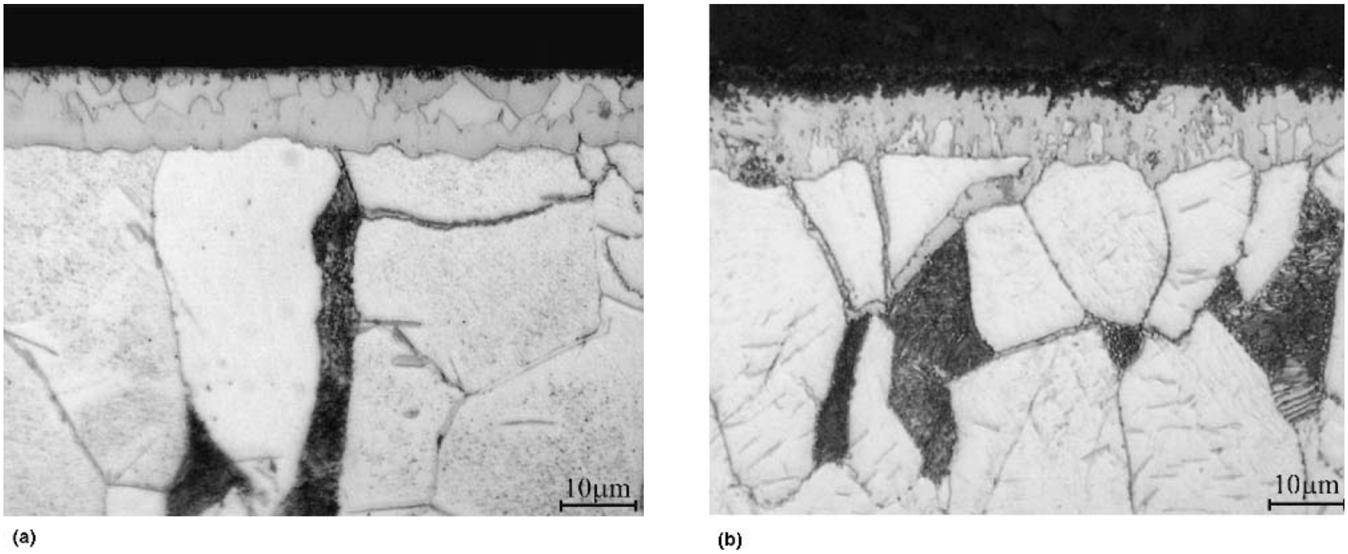


Fig. 5 Optical micrographs of specimens after 4 h of TRD treatment at 570 °C, without H_2 addition: **(a)** AISI 1008; **(b)** AISI 1018

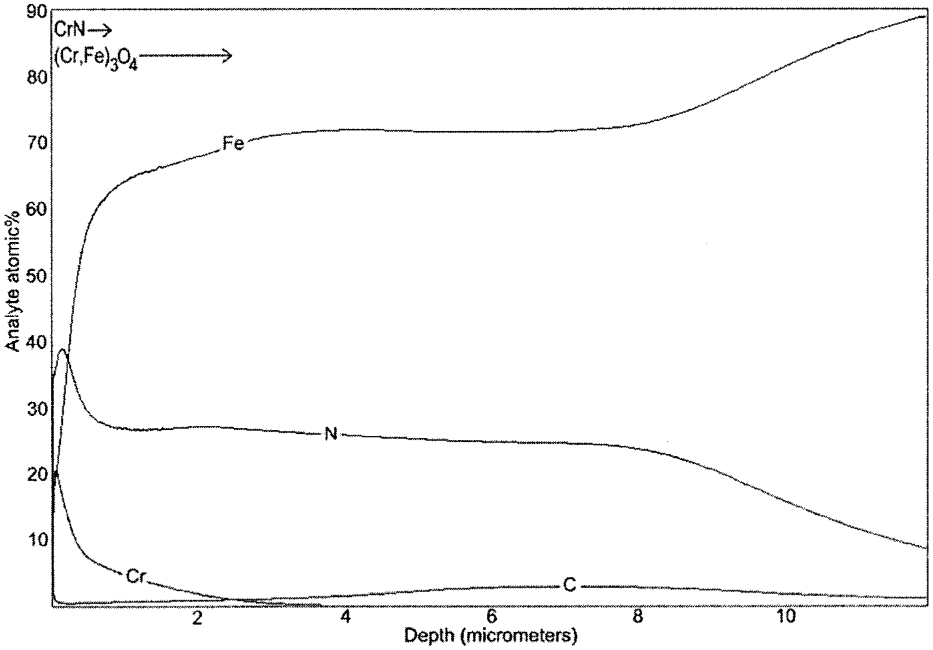


Fig. 6 Glow-discharge depth profile of AISI 1018, nitrocarburized and then TRD treated for 4 h in an atmosphere of N_2 and 1.5% HCl

By a series of transformations, as discussed in section 3.3, N was released from the compound layer and diffused to the surface. The driving force for this diffusion was a lowering of free energy through the formation of a surface layer of CrN. Thus CrN formed by a reaction of N atoms with the deposited Cr:

$$Cr + N \rightarrow CrN \quad \text{(Eq 1)}$$

The remaining N in the compound layer after 1 h in an atmosphere of 1.5% HCl/N_2 at 570 °C was traced out by the "0% H_2" curve.

Addition of 10% H_2 to the inlet gas mixture (i.e., 1.5%HCl/10%H_2/N_2) resulted in heavier depletion of N from the compound layer. This result was due to reduction of the compound layer. Reduction occurred according to the denitriding reaction:

$$N + H_2 = NH_3 \quad \text{(Eq 2)}$$

This reaction was studied by Clayton and Sachs in their experiments, which involved holding components under a reducing atmosphere, following nitriding.[19]

Further increments in the H_2 level resulted in not only greater loss of N, but also increased CrN coating formation, as

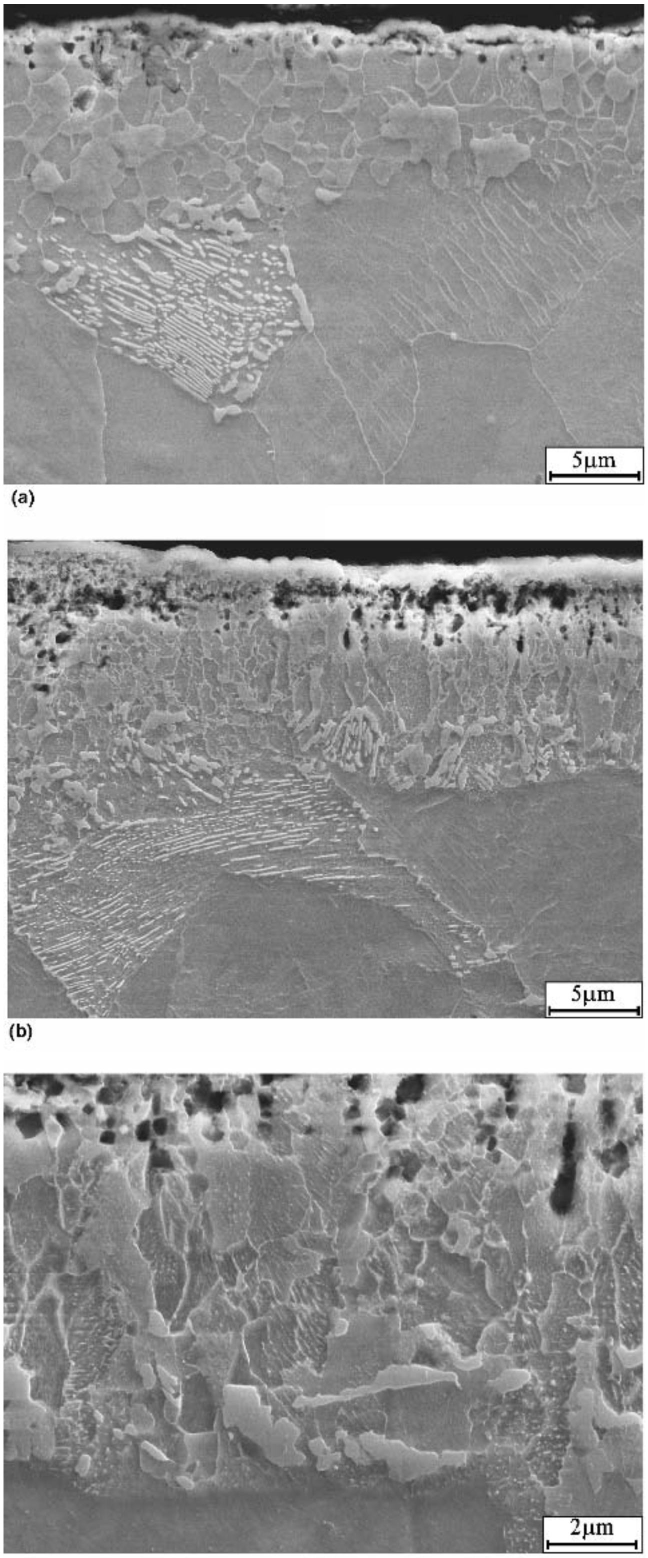


Fig. 7 SEM micrographs of specimens after TRD treatment in an atmosphere of 1.5% HCl, 30% H_2, remainder Ar: **(a)** AISI 1008, 10,000×; **(b)** AISI 1018, 10,000×; **(c)** AISI 1018, 25,000×

evident from the strength of the surface N-peaks (Fig. 2). It has not yet been determined whether the use of hydrogen may have influenced the gas-phase reactions and thus may have been responsible for an increased rate of Cr deposition. Figure 3 shows the dependence on temperature of the mass of Cr deposited during 1 h treatments.

3.2 Characterization of Prenitrocarburized 1008 and 1018

For a detailed analysis of the processes by which N is released from the compound layer, two different grades of plain carbon steel,1008 and 1018, were prenitrocarburized. The nitrocarburizing parameters used were $25\%NH_3/10\%CO_2/N_2$, with a 1 h treatment time at 570 °C.

Figure 4 shows the surface microstructures of nitrocarburized specimens. The 1018 compound layer (Fig. 4b) was significantly more porous than the 1008 layer (Fig. 4a). XRD confirmed that the near-surface region contained the ε-carbonitride only; however, etching also revealed the γ'-Fe_4N phase deeper within the white-layer. The lower carbon content of AISI 1008 enabled a continuous γ' layer to remain unbroken by the ε-phase at the interface between the compound layer and substrate (Fig. 4b, note that adjacent to pearlite, this rule was broken).

3.3 Compound Layer Transformations During TRD Treatment without Hydrogen Addition

Under identical treatment conditions, more Cr was deposited on the surface of AISI 1018 than on AISI 1008. The more porous compound layer on this material meant that a greater surface area was available to the treatment atmosphere.

Figures 5, 6, and 9 show the results of prenitrocarburized specimens that were subjected to 4 h of TRD treatment at 570 °C in an N_2 + HCl (non-H_2) atmosphere. The elemental depth profile (Fig. 6) showed that Cr was deposited up to 3.5 μm into the surface of AISI 1018, through the entire porous region. It appears that paths from the surface existed for gaseous Cr chloride to penetrate deep into pore channels and deposit nascent Cr. Subsequent x-ray analysis (Fig. 9d and e) confirmed the presence of CrN in this area.

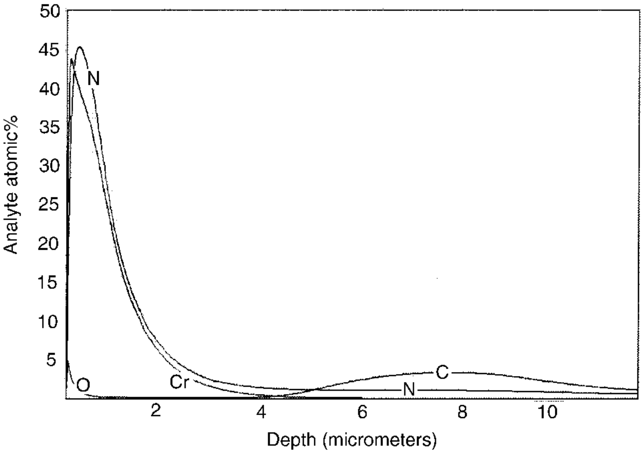
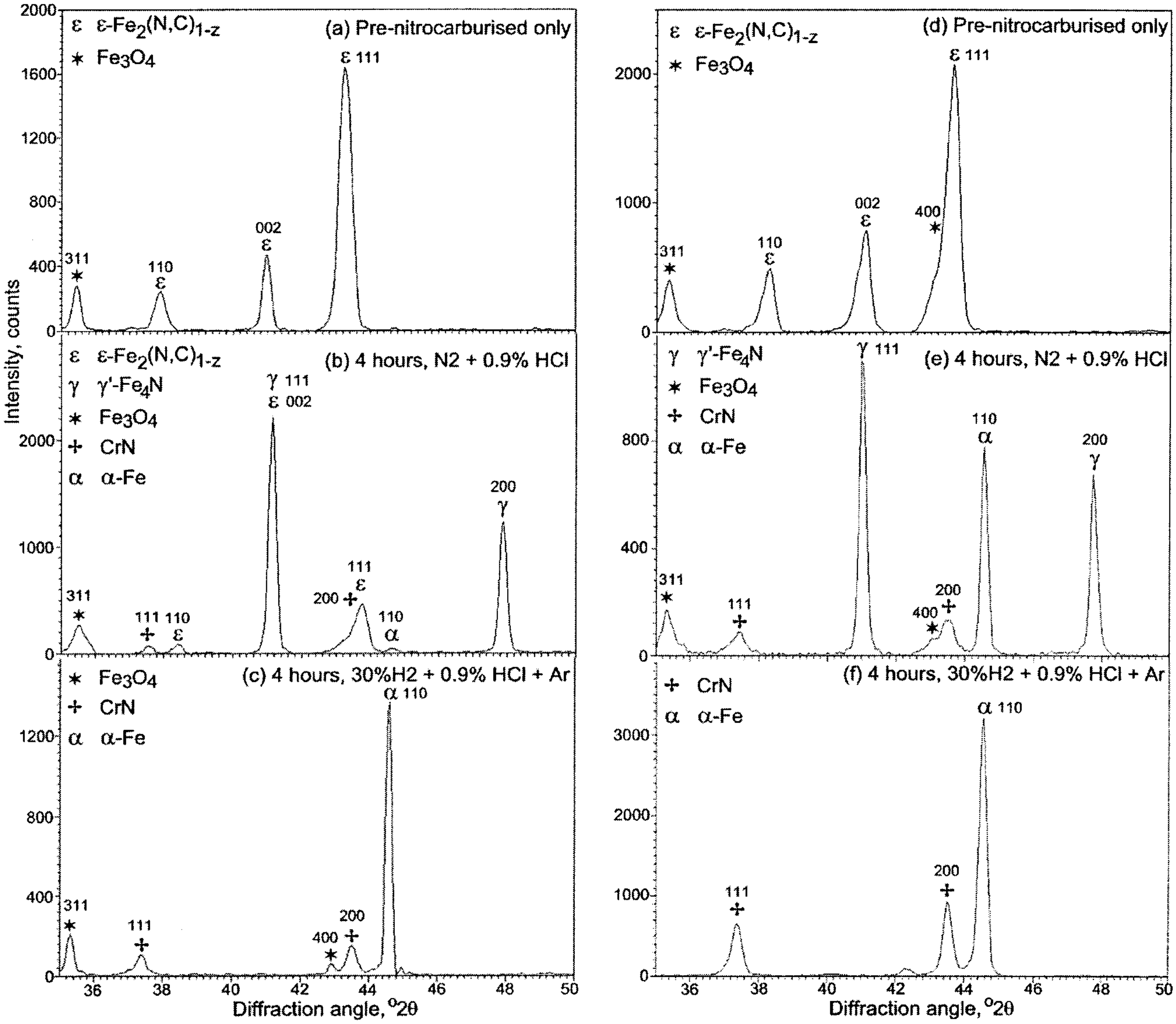


Fig. 8 Depth profile of 1018, nitrocarburized and TRD treated in an atmosphere of 1.0% HCl, 30% H_2, remainder Ar



(a) **(b)**

Fig. 9 XRD of prenitrocarburized and TRD-treated specimens: **(a)** AISI 1008; **(b)** AISI 1018

Four hours in N_2 + HCl resulted in only slight Cr deposition on AISI 1008. Epsilon carbonitride partially converted to γ' (see micrograph, Fig. 5a). Some regions of the lighter ε-phase remained, mainly near the surface. XRD (Fig. 9a and b) confirmed that both γ' and ε were present near the surface, whereas before TRD, only ε was detected. This process is represented by Eq 3:

$$2\varepsilon\text{-}Fe_2N \rightarrow \gamma'\text{-}Fe_4N + 2N \qquad \text{(Eq 3)}$$

N released from this reaction diffused to the surface and reacted with Cr, according to Eq 1.

Figure 9(e) shows that, under the same conditions, the reaction shown in Eq 3 had reached completion in the AISI 1018. This situation was due to a higher level of N diffusion, caused by more Cr deposition. Further decomposition of the compound layer resulted in conversion of γ' to ferrite:

$$\gamma'\text{-}Fe_4N \rightarrow 4\alpha\text{-}Fe + N \qquad \text{(Eq 4)}$$

3.4 Compound Layer Transformations During TRD Treatment with Hydrogen Addition

With 30% H_2 in the treatment atmosphere, the AISI 1008 compound layer completely converted to ferrite after 4 h:

$$\varepsilon\text{-}Fe_2N \rightarrow 2\alpha\text{-}Fe + N \qquad \text{(Eq 5)}$$

SEM analysis showed that the ferrite formed as equiaxed, approximately μm-sized grains (Fig. 7a).

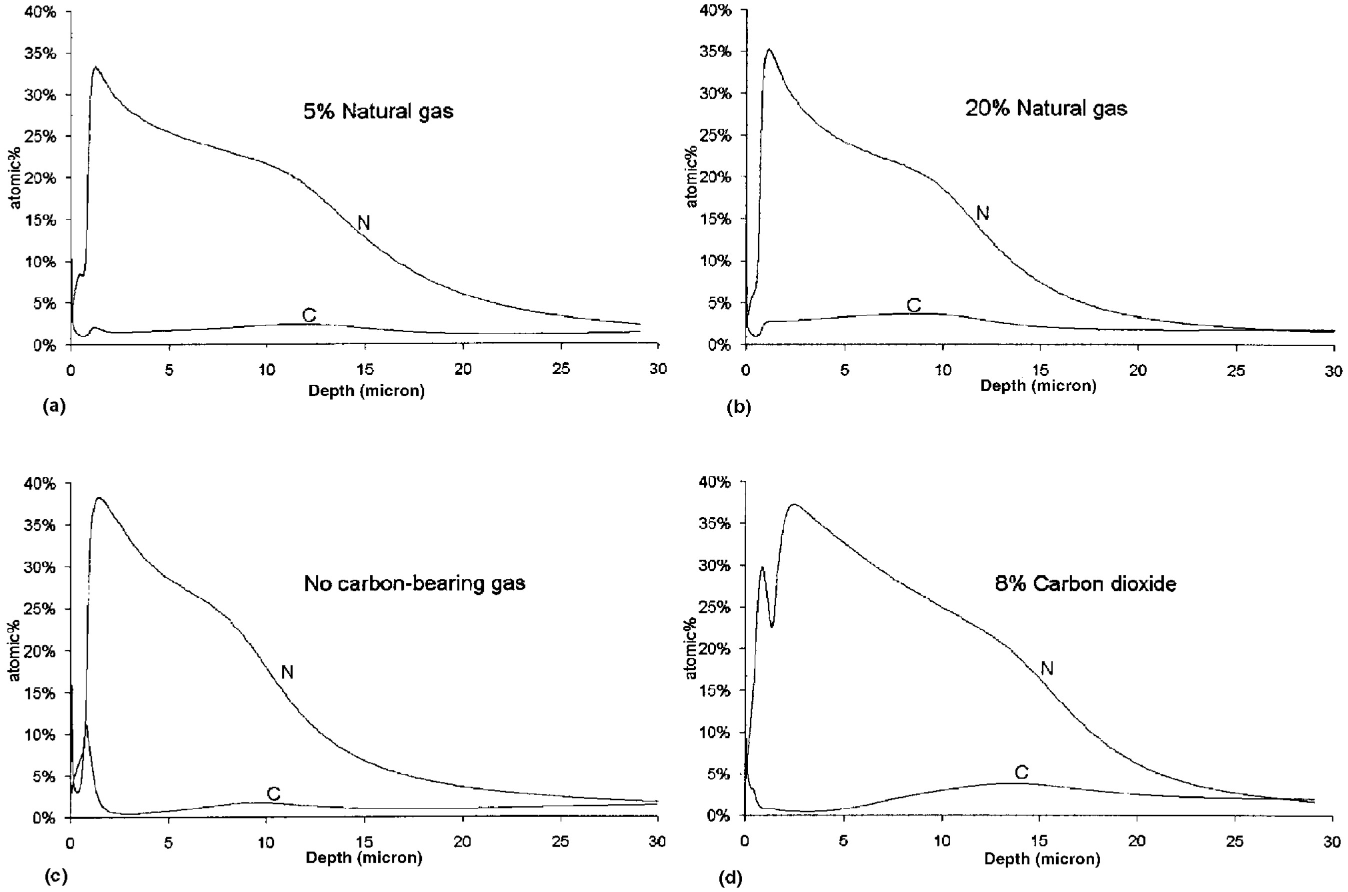


Fig. 10 GDOES curves of 1040, nitrocarburized for 3 h using various C-bearing gases

GDOES analysis revealed that in the higher-C AISI 1018 steel, C did not participate in coating formation (Fig. 8). In Fig. 7(b) and (c), the higher-C compound layer of AISI 1018 could be seen to contain a new feature—fine, submicron particles of cementite were observed within ferrite grains. The process of ε-carbonitride decomposition can be represented as Eq 6:

$$2\varepsilon\text{-Fe}_2(\text{N,C}) \rightarrow \alpha\text{-Fe} + \text{Fe}_3\text{C} + \text{N} \qquad \text{(Eq 6)}$$

3.5 Design of the Compound Layer to Suit TRD Treatment

If the amount of CrN in the highly porous compound layer on AISI 1018 is compared with that in the slightly porous compound layer on AISI 1008, it can be seen that porosity aided in the deposition of Cr. It also showed that porosity can vary dramatically under identical treatment conditions with only small differences in steel grade. It may, nevertheless, be desirable to present a fully dense compound layer to the coating treatment (i.e., if instead, a PVD coating is to be applied, underlying porosity can be detrimental to coating performance[20]). Porosity can be reduced after nitrocarburizing by mechanical or chemical means; however, this process is expensive and inaccurate. It is also possible to limit the formation of porosity by a choice of suitable nitrocarburizing parameters. Shorter nitrocarburizing times and lower nitriding potentials reduce porosity by limiting compound layer thickness.[21] In the following investigation, the choice of C-bearing gas was examined.

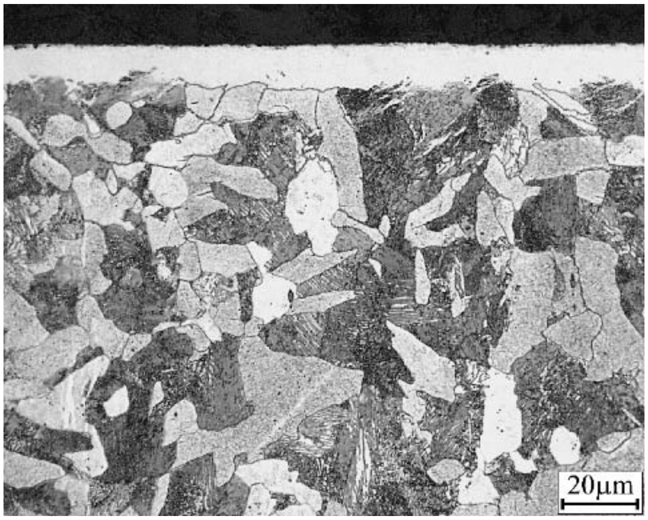


Fig. 11 Optical micrograph of AISI 1040, nitrided for 3 h

AISI 1040 plain carbon steel was nitrocarburized for 3 h at 570 °C. Experimentation with different C-bearing gases revealed that CO_2 produced the thickest compound layers. However, these layers were also more prone to porosity. Partial reduction of the thick surface scale formed during treatment resulted in a further surface sublayer of ε carbonitride, which has been shown to be detrimental[10] (see small surface N peak in Fig. 10d).

When the substrate contains sufficient C to stabilize the ε phase early on during compound layer development, pretreatment can be carried out without any C-bearing gas. The result, on AISI 1040 after 3 h, was a fully dense layer, as shown in Fig. 11.

It is feasible that under different TRD coating conditions, C may be able to participate in coating formation, creating a harder, carbonitride layer. Research into high-temperature TRD of prenitrocarburized components has certainly found that C diffuses;[3] therefore, it may be advantageous to produce a compound layer containing a higher level of C.

It was found that when natural gas was used, the compound layers contained more C. Increasing the proportion of natural gas used further raised the C content. Natural gas compound layers were generally thinner and less porous than CO_2 compound layers. Carbon dioxide also resulted in some increase in C content; however, this increase was concentrated deeper in, closer to the compound-layer/diffusion-zone interface.

4. Conclusions

- In this preliminary work, limited Cr deposition was achieved at 570 °C in up to 4 h. However, this result could be extended by longer treatments or by using higher temperatures.
- Nitrogen diffusion to the surface was affected by a series of local phase changes in the compound layer. At 570 °C, large-scale diffusion was not observed.
- Hydrogen reduction resulted in further N diffusion and seemingly more Cr deposition.
- In this study, porosity aided the Cr deposition process; however, it may not always have a desirable influence on the final coating properties.
- The compound layer can be engineered to suit the particular coating treatment to follow. However, it has also been shown that even minor changes in substrate composition can lead to large variations in the compound layer.

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