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Comparison of compound layer nucleation mechanisms in plasma nitriding and nitrocarburizing: the effect of CH$_n$ species

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This article presents a new study of the mechanisms of plasma nitriding and nitrocarburizing processes, with particular emphasis on plasma diagnostics and light element detection at the treated sample surface. The results indicate that in the nitriding process neutrals, such as Fe, N and ions (such as N^+), are abundantly present near the cathode region, suggesting that the formation of iron nitrides occurs through the combination of these species. Light element detection by elastic recoil analysis (ERA) shows that hydrogen is not present on the nitrided surface, but it is abundant on the nitrocarburized surface. The latter result is discussed in view of existing nitriding models. The role of CH$_n$ radicals in plasma nitrocarburizing is also discussed. © *1999 Kluwer Academic Publishers*

1. Introduction

Plasma nitriding and nitrocarburizing are plasma-assisted thermochemical heat treatment processes that enhance the surface properties of treated components (usually ferrous materials) through the formation of a surface nitride and/or carbonitride compound layer. The nitrides or carbonitrides have superior anticorrosion, antiwear and antiscuffing properties and are commonly used for improvements in surface mechanical and chemical properties [1–3]. Such plasma-assisted thermochemical processes are now more widely used in industry due to the fact that they are environmentally harmless. Components such as gears, crankshafts, camshafts, dies, bearings, etc. [1–3] are often plasma nitrided or nitrocarburized. The two main functions of the plasma during treatment are:

1. To enhance nitrogen and/or carborn mass transfer by generating charged particles, intermediate molecules and atomic neutrals, which are ready to dissociate at the treated component surface and release nitrogen or/and carbon atoms that then diffuse into the substrate surface and form the nitriding or nitrocarburizing case at the treatment temperature.
2. To heat the treated components to the treatment temperature (500–600 °C).

Despite extensive studies of plasma treatments [4–8], the actual mechanisms controlling the processes still remain ambiguous and controversial due to complex heterogeneous reactions between plasma species and the metal surface. Most of the mechanism studies deal with plasma nitriding, whereas the mechanism for nitrocarburizing has not been fully investigated. Iron nitride formation in plasma has been proposed by Kölbel [8] according to the following reaction path

$$FeN \rightarrow Fe_2N \rightarrow Fe_3N \rightarrow Fe_4N$$

The initial "high" nitride, FeN, is formed as the result of sputtered Fe atoms combining with the incoming N atoms. Because FeN is not a thermally stable compound it then further dissociates into lower nitrides. At each dissociation stage, one atom of nitrogen is released, which becomes ready to diffuse into the lower nitrogen content region, i.e. the iron matrix. The continuous diffusion of nitrogen atoms into the material surface forms the required case. Kölbel's nitriding mechanism was supported by the studies of Edenhofer [5, 6] and Keller [9]. However, Hudis [10], based on his mass spectra studies, suggested that the prominent species that have an effect on nitriding are NH$_m$ ($m = 1$–3) neutrals. According to this model, these neutrals are readily dissociated on the surface of the component and release nitrogen atoms, which subsequently diffuse into the component at the treatment temperature and the nitriding case is formed. More recently, Szabo and Wilhelmi [11] also argued that the nitriding model proposed by Kölbel needs to be amended in view of the authors' mass spectrometric results, which showed the formation of intermediate iron–nitrogen–hydrogen products, such as Fe$_n$NH$_m$ ($m = 1$–4, $n = 1$–3) in the near-surface region (about 5 mm from the surface of the treated component). They speculated that the nitrogen

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atoms released for nitriding could be attributed to the dissociation of these intermediate phases.

In two recent publications [12, 13] a number of aspects of the nucleation and growth of the compound layer in plasma nitriding and nitrocarburizing have been presented.

The present paper aims to shed some new light on the formation mechanisms in the two processes. In particular, the role of hydrogen in plasma–surface interactions and the validity of Kölbel's nitriding model are reassessed with the aid of optical emission spectroscopy, scanning electron microscopy (SEM) and reflection high energy electron diffraction (RHEED) and elastic recoil analysis [ERA, a variation of the Rutherford backscattering (RBS) technique] [14].

2. Experimental procedure

2.1. Optical spectroscopy

The direct current (d.c.) plasma system for nitriding and nitrocarburizing was described in detail elsewhere [12].

For the present study, new facilities were attached to the plasma system to conduct plasma diagnostic studies. Fig. 1 schematically shows the experimental setup of each component. The light emitted from the glow discharge enters the monochromator and a chart recorder records the light intensity versus wavelength data. The plasma species are then identified by referring to the corresponding spectra handbooks [15, 16].

2.2. Materials and sample preparation

AISI 1010 steel samples 25 mm in diameter and 5 mm thick were used in this study. The exact composition of the material was: C, 0.11; Mn, 0.73; Si, 0.01; S, 0.10; Ni, 0.01; (Cr, Mo, Ti) < 0.01 (in weight percent). In order to minimize any microstructural variations among the treated samples, the original steel rod was fully annealed at 1200 °C for 2 h and furnace cooled, after which it was sliced by an electric saw. The disc samples were polished on SiC paper to reduce surface roughness, and then further polished to $\mathrm{Ra} = 0.05\ \mu\mathrm{m}$ (mirror finish) using diamond paste. The samples were then subject to ultrasonic cleaning in a methonal bath.

2.3. Nitriding operation and experimental techniques

In the present work, the samples for all treatments were heated by plasma to the operating temperature of 600 °C. For the nitriding series of experiments, a gas mixture containing 40 vol% N_2 with a balance of hydrogen and no methane was used. The gas composition used in nitrocarburizing was: 40 vol% N_2, 58.25 vol% H_2 and 1.75 vol% CH_4. The gas flow rate, measured by Fischer and Porter tube flowmeters, was set at $2.667 \times 10^{-3}\ \mathrm{l\,s^{-1}}$ and the gas pressure (measured on a mercury manometer to avoid electrical interference from the plasma) was set at 1.3 kPa. Other parameters were kept the same.

The treatment time was controlled at 1 min, after which the samples were cooled in a sealed quartz chamber. After cooling to room temperature, samples from the two types of plasma treatment, i.e. nitriding and nitrocarburizing, were analysed by ERA to collect hydrogen spectra of the treated surface. During the analysis an aluminum filter was used instead of a Myler filter. Calibration was performed using a hydrogen implanted Si sample.

The treated samples were also examined by SEM. Phases present on the surface were identified by RHEED. The electron microscopes used were Hitachi S-520 and Jeol 100 CX for SEM and RHEED, respectively.

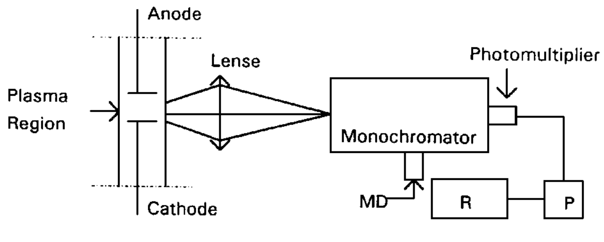

Figure 1 Experimental setup of the optical emission spectroscope.

3. Results and discussion

3.1. Optical emission spectroscopy of the nitriding process

The results of optical spectroscopy of the nitrided samples are shown in Fig. 2. The spectra show the following species present in the glow discharge (or in the cathode fall region): N, N^+, N_2, N_2^+, NH_2, Fe, H_α, H_β, H_2. No impurity spectral lines, such as those emitted by O, OH, NO or CH in contaminated plasmas, were detected in

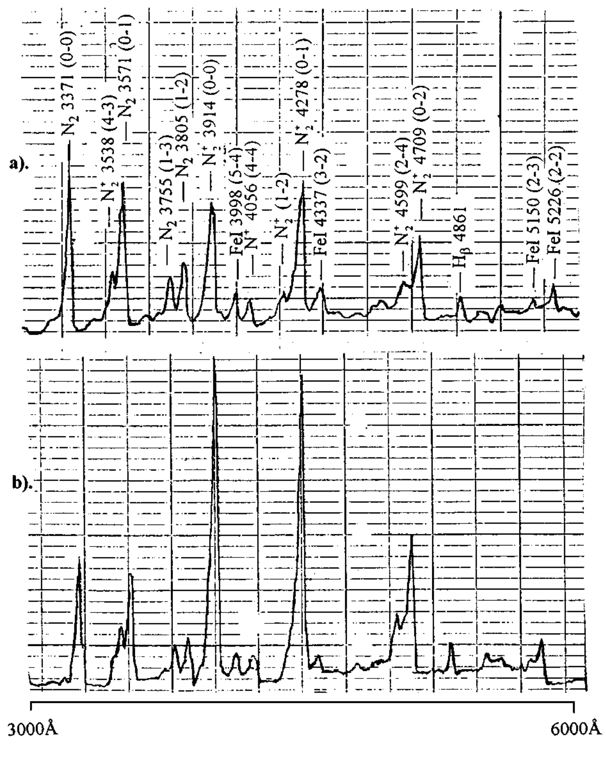

Figure 2 Spectra of nitriding plasma: (a) 40 vol% N_2 and (b) 60 vol% N_2. Showing the presence of nitride forming species, resolution 0.5 nm. Wavelength between 300 and 600 nm (3000 and 6000 Å).

any spectra. No NH 336 nm (3360 Å) line was observed in plasmas with hydrogen and nitrogen. The three types of species that show the strongest intensities are: H_β, N_2^+ and N_2.

It should be noted that the spectrum lines from the excited Fe atoms are extensively formed in the plasma around the cathode. These excited iron atoms are always ready to form any type of iron nitrides and play an important role in the mechanism of plasma nitriding or nitrocarburizing. Similar studies by Marchand *et al.* [2] indicated that there is a distribution of excited iron atoms around the cathode region. It should be noted that the Fe atoms may reach a distance of more than 3 cm away from the cathode surface. It is believed that the species that result in nitride forming are Fe and Fe ions, N and N^+. This is because these neutrals and ions are highly unstable and readily combine and form iron nitrides. In fact surface observation of the 1 min treated sample reveals that the phases formed on the surface are various forms of iron nitrides [12].

3.2. Nitrided and nitrocarburized sample surface analysis

The surface morphology of nitrocarburized samples treated at 600 °C for only 1 min with a gas mixture of 40 vol% N_2, 58.25 vol% H_2 and 1.75 vol% CH_4 is shown in Fig. 3. The sample was not repolished after treatment and therefore the micrograph is blurred. Although the surface was polished to $\mathrm{Ra} = 0.05\ \mu$m finish before treatment, the 1 min treated sample shows a much rougher surface. Examination of the structure reveals that the surface is covered with tiny deposited particles, which result in a rough surface. As discussed in detail elsewhere [12], pores have formed, which are in open contact with the plasma atmosphere and increase the contact area of the sample with the plasma, enabling faster diffusion of the active species.

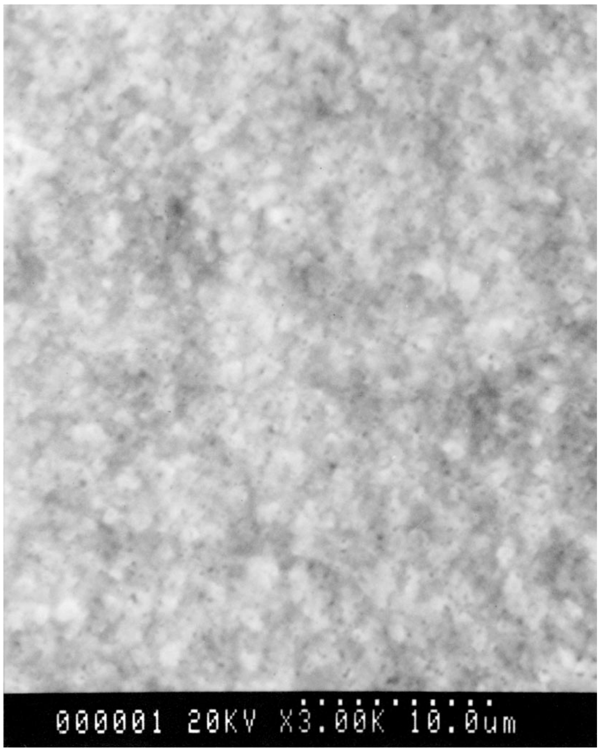

Figure 3 One minute treated sample surface appearance showing deposited nitrides (or carbonitrides).

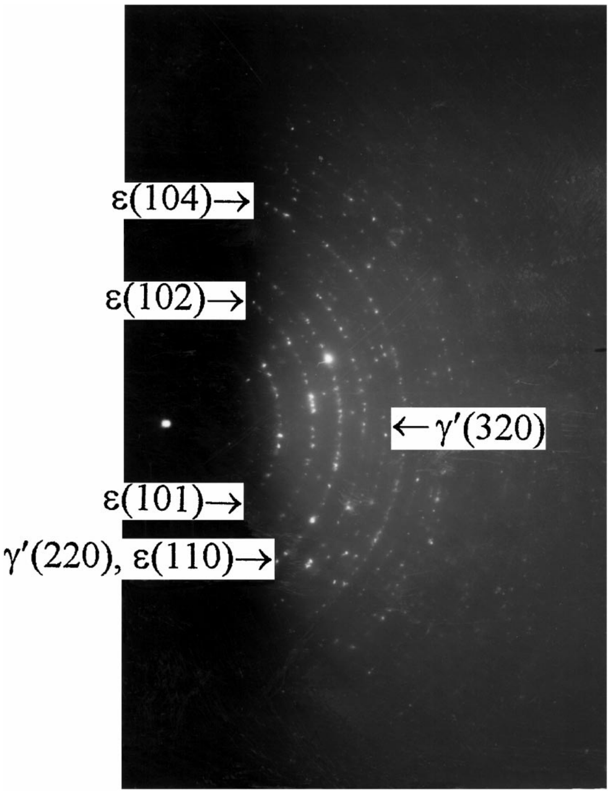

Figure 4 RHEED phase identification of Fig. 3 sample. Showing nitrides in the form of Fe_2N, Fe_3N and Fe_4N.

Phase identification by RHEED (Fig. 4) shows that the surface is mainly composed of iron nitrides (or carbonitrides, which cannot be distinguished from nitrides–see below). The identified nitrides (or carbonitrides) are ε-$Fe_{2-3}N$ [or $Fe_{2-3}(CN)_{1-x}$] and γ'-Fe_4N [or $Fe_4(CN)_{1-x}$]. It is difficult to distinguish whether the phases on the surface are iron nitrides or iron carbonitrides due to the fact that the lattice spacings between iron nitride and iron carbonitride are nearly the same [17]; it is reasonable to assume, however, that the ε and γ' phases are in the form of carbonitrides because of the presence of carbon atoms, which are easily absorbed and accommodated into interstitial positions in the iron lattice. The present results can be very well explained based on the plasma nitriding model proposed by Kölbel [8].

3.3. ERA surface analysis

Fig. 5 shows the difference in ERA results between the nitrided and nitrocarburized sample surfaces. The surface of the nitrocarburized sample shows a significant high hydrogen content, which does not appear in the nitrided sample. The results clearly show that the hydrogen atoms are at the very end of the surface region. The nitrided sample does not show a hydrogen peak at all, indicating that the freshly nitrided surface is not covered by a hydrogen containing compound.

An easy way to interpret these results is to assume that the hydrogen on the nitrocarburized sample surface

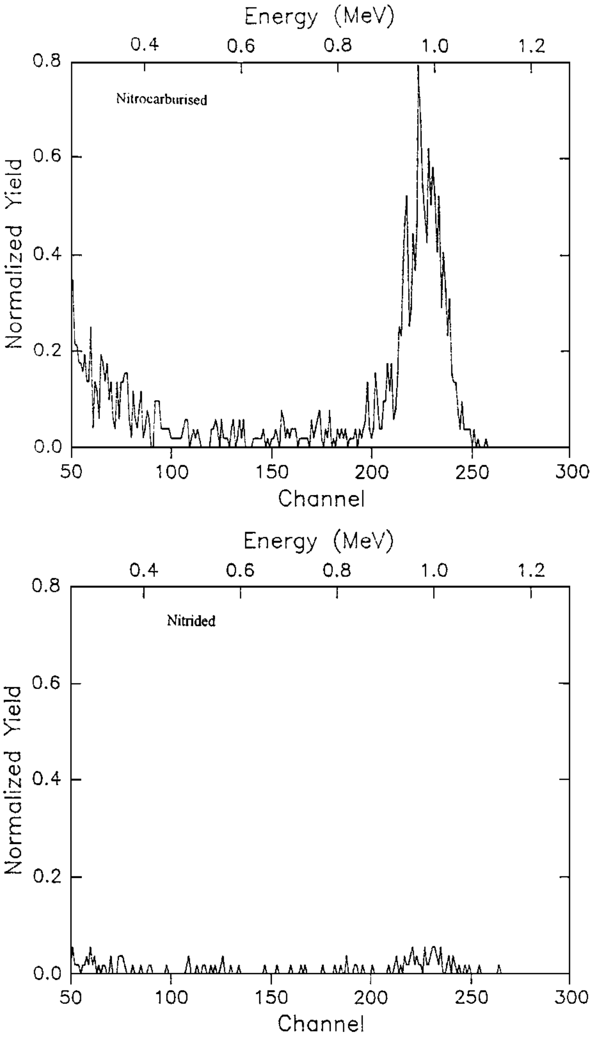

Figure 5 ERA results showing hydrogen present on the nitrocarburized surface (a) and no hydrogen being detected from nitrided sample surface (b).

results from methane radicals such as CH_2, CH_3, etc., which are attached to the surface through chemisorption. These radicals are exclusively present near the cathode region due to the lower dissociation energy required to break down the methane molecule. Compared with nitrogen and hydrogen molecules, methane is the easiest molecule to dissociate when these gases coexist in the same glow discharge chamber. In fact, the present results reinforce the plasma carburizing model proposed by Edenhofer [18], i.e. that in plasma carburizing carbon is released through dissociation of methane radicals following the path: $CH_3 \rightarrow CH_2 \rightarrow CH \rightarrow C$.

ERA results show no hydrogen on the nitrided sample surface, thus confirming that formation of surface nitride is through the dissociation of FeN and not from the dissociation of $FeNH_2$ or $FeNH_3$. Thus it can be concluded that the nitriding process follows the model proposed by Kölbel. The initial higher nitride FeN, which is redeposited on the surface, originates directly from collision between active iron atoms around the cathode region and incoming N atoms and/or N^+ ions.

However, hydrogen does exist on the nitrocarburized sample surface, indicating that the source of surface hydrogen is the CH radicals adsorbed on the nitrocarburized surface. It is very likely that the iron carbonitrides containing hydrogen are an intermediate phase, such as $Fe(CN)H_n$ ($n = 1$–4), which forms on the sample surface and works as a source for further diffusional atomic carbon and nitrogen. The ERA results also suggest that the carburizing model proposed by Edenhofer *et al.* [18] is also correct: during plasma carburizing CH radicals are absorbed on the surface supplying the required carbon diffusion by their further dissociation.

The most important finding presented here is that despite a number of similarities between the nitriding and nitrocarburizing treatments with regard to surface morphology and the appearance of the samples after 1 min treatment, there is a significant difference between these treatments, which is reflected in the abundance of hydrogen on the surface in the latter process. The above experiments and arguments suggest that without methane in the plasma, the inital nitride is formed in the form of FeN, which results from the direct combination of active Fe and N or N^+ in the plasma and is redeposited on the cathode surface. The redeposited higher nitrogen-containing nitride dissociates quickly to more stable lower nitrides, which can be identified by RHEED. On the other hand, in plasma nitrocarburizing carbon-containing radicals, such as CH^+, CH^{2+}, CH^{3+}, etc, are bound to the surface through chemisorption and most probably form intermediate phases, such as FeNCH, $FeNCH_2$, $FeNCH_3$, which dissociate into lower carbonitrides like $FeN_xC_yH_n$ ($n = 1$–4). During the dissociation process of the higher carbonitrides into the lower carbonitrides, atomic nitrogen and carbon atoms are released and diffuse into the matrix and these atoms are the sources for nitrocarburizing.

4. Conclusions

This study draws the following conclusions:

1. Optical plasma diagnostics around the cathode region in plasma nitriding revealed the presence of the following species: N, N^+, N_2, N_2^+, NH_2, Fe, H_α, H_β, H_2. No NO or NH species were identified.
2. Surface hydrogen has been found by ERA only after the nitrocarburizing treatment and its presence is attributed to the presence of CH species in the plasma. The results clearly show that the mere presence of hydrogen itself in the nitriding plasma does not create an identical presence of hydrogen on the treated surface. Nucleation during nitrocarburizing treatment starts, therefore, with the formation of iron carbonitride in the form of $Fe_{2-3}(CN)_{1-x}$ together with $Fe_4(CN)_{1-x}$, which have been identified by RHEED.
3. The results reconfirm Kölbel's nitriding model, showing that during simple plasma nitriding hydrogen does not play a part in the nucleation mechanism.

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