

# Investigations on the active screen plasma nitriding process

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## Abstract

This study presents the mechanism of nitrogen transfer in a large scale active screen plasma nitriding (ASPN) unit. The active screen provides a homogeneous temperature distribution within the workload as well as an arcing tendency is reduced, since the plasma is moved from the treated work pieces to the active screen. In order to study the mechanisms in detail, plasma diagnostics is necessary. The applied diagnostic methods for analyses of the excited process gas synthesised by the active screen include mass spectrometry and infrared diode laser spectroscopy (TDLAS). Together with a metallurgical characterisation of nitrided steels a better understanding of the chemical phenomena in the N<sub>2</sub>-H<sub>2</sub> plasmas is achieved. Various N<sub>2</sub>/H<sub>2</sub> gas mixtures and variable bias activation powers at the pressure of 200 Pa were investigated. It was found that even during heating up in nitrogen free process gas exited nitrogen (atomic or molecular) releases from the active screen. Infrared diode laser spectroscopy has been used as a diagnostic method to measure the concentrations of the stable NH<sub>3</sub> molecules downstream the plasma source. The ammonia production turns out to depend on the mixtures of N<sub>2</sub>-H<sub>2</sub> and the current input of the bias activation. The results are discussed with the plasma parameters measured by the electrostatic probe. Thus, a contribution to the interpretation of the mass transfer in ASPN process has been realised.

## Experimental

In the presented study a large scale active screen plasma nitriding (ASPN) unit is investigated, which are used for improving the wear, fatigue and load bearing properties of ferrous engineering components [1]. The work pieces to be treated are surrounded by large metal screen (0,8m diameter and 0,75m high) on which a cathodic potential is applied. The N<sub>2</sub>/H<sub>2</sub> glow discharge at the active screen radiates the heat and provides a reactive process gas. To supply a homogeneous temperature distribution in particular heavily loaded chamber a relative low bias voltage is subjected. Experiments were conducted to examine the influence of the process parameter on the nitride layer formation. Samples of hardened and tempered low alloy steel were nitrided at 580°C for 4 hours in 200 Pa N<sub>2</sub>/H<sub>2</sub> gases. Here the results of common engineering steels (42CrMo4, X38CrMo5.1) are present. The plasma diagnostics were carried out using mass spectroscopy (Balzers QMS 200), infrared diode laser spectroscopy (TDLAS), and an electric probe technique.

## Results

The introduction of nitrogen into the substrate surface produces a compound layer on the surface, on top of a nitrogen diffusion zone. In this work also the structure of nitride-containing cover layer on the

compound layer under consideration of the process parameters are investigated with scanning electron microscope. The results of investigations show that the bias power enhances the growth of nitride cover layer. Such processes were also observed during formation of compound layer during gas nitriding and described by a parabolic law of diffusion controlled layer growth [2]. Figure 1 shows hardness profiles and the nitrogen concentration profiles/compound layer thickness after active screen plasma nitriding with different bias power. Nitrogen content in the process gas and the bias power enhance the nitriding results. The expected nitriding case depth can be reached at bias power at the level of 5% or 15% of the active screen power. Increasing bias power produces thicker compound layers. Therefore active screen nitriding process is particularly suitable to create uniform and very thin  $\gamma'$  compound layers with a deep decarburization of the nitrogen diffusion zone.

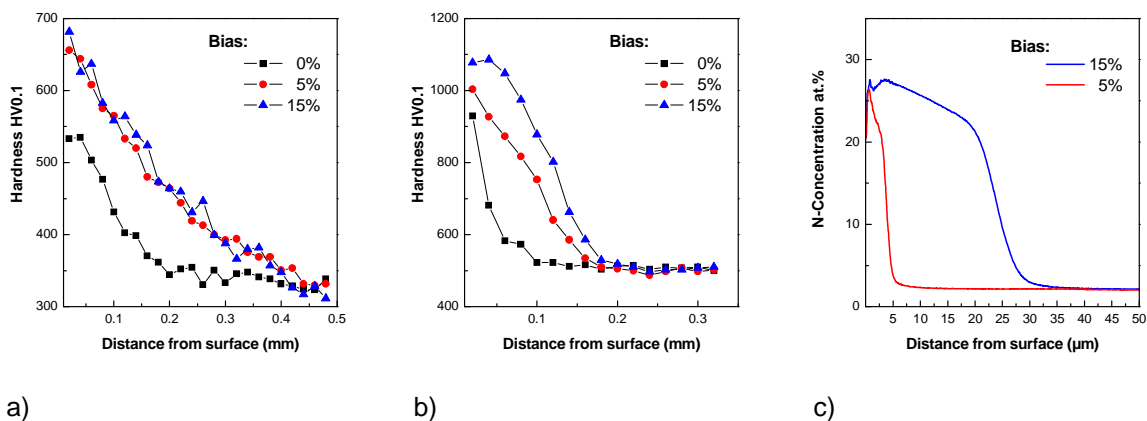


Figure 1: Influence of bias on the hardness profile of steels 42CrMo4 (a) and X38CrMoV5-1 (b) as well as the nitrogen concentration profile of the compound layer, steel 42CrMo4 (c)

The understanding of ion nitriding process, mechanism of nitrogen atom production and transfer from the media to the component surface is not complete and still in the focus of investigation of many research groups worldwide [3-6]. In the past many models have been proposed for the plasma nitriding of ferrous materials. A very common approach of “sputtering and deposition” mechanism, suggested by Kölbel cannot explain the mass transfer [7]. The high reactivity of active nitrogen species was mentioned for the first time in the literature 100 years ago. That is why R.J. Strutt designated as active nitrogen [8]. Several studies have been carried out using different plasma diagnostic methods to analyse ionized species [9] and the adsorption of neutral atoms/molecules [10]. Ricard et al [11] demonstrates that the  $\text{N}_2^+$ , the vibrational  $\text{N}_2$  and the N neutral species are most relevant.

To study the plasma processes involved in plasma nitriding at the industrial scale ASPN unit we used quadrupole mass spectrometry (QMS). The signal intensity increases compared with the measurement without discharge at the active screen. The peak intensity for  $\text{N}^+$  ( $m/z$  14) and  $\text{N}_2^+$  ( $m/z$  28) were chosen to represent the major products in a  $\text{N}_2/\text{H}_2$  process gas. The peak intensities decreased with increasing  $\text{H}_2$  composition. It was found that even during heating up in nitrogen free process gas excited nitrogen (atomic or molecular) releases from the active screen. The ion stimulated desorption of neutral gas from active screen at temperature up to 400 °C due to preceding exposures to nitrogen gas has been studied. The gas species desorbing during  $\text{Ar}^+$  ion bombardement are a result of preferential sputtering [12] and the metastability of iron nitride.

As already described above there is a mass transfer of nitrogen without a bias activation. Therefore the knowledge of the electron energy is necessary to explain the excitation processes which occur. One of the most direct ways to measure local properties of plasma is with electrostatic probes. This study used a time resolved Langmuir probe method.

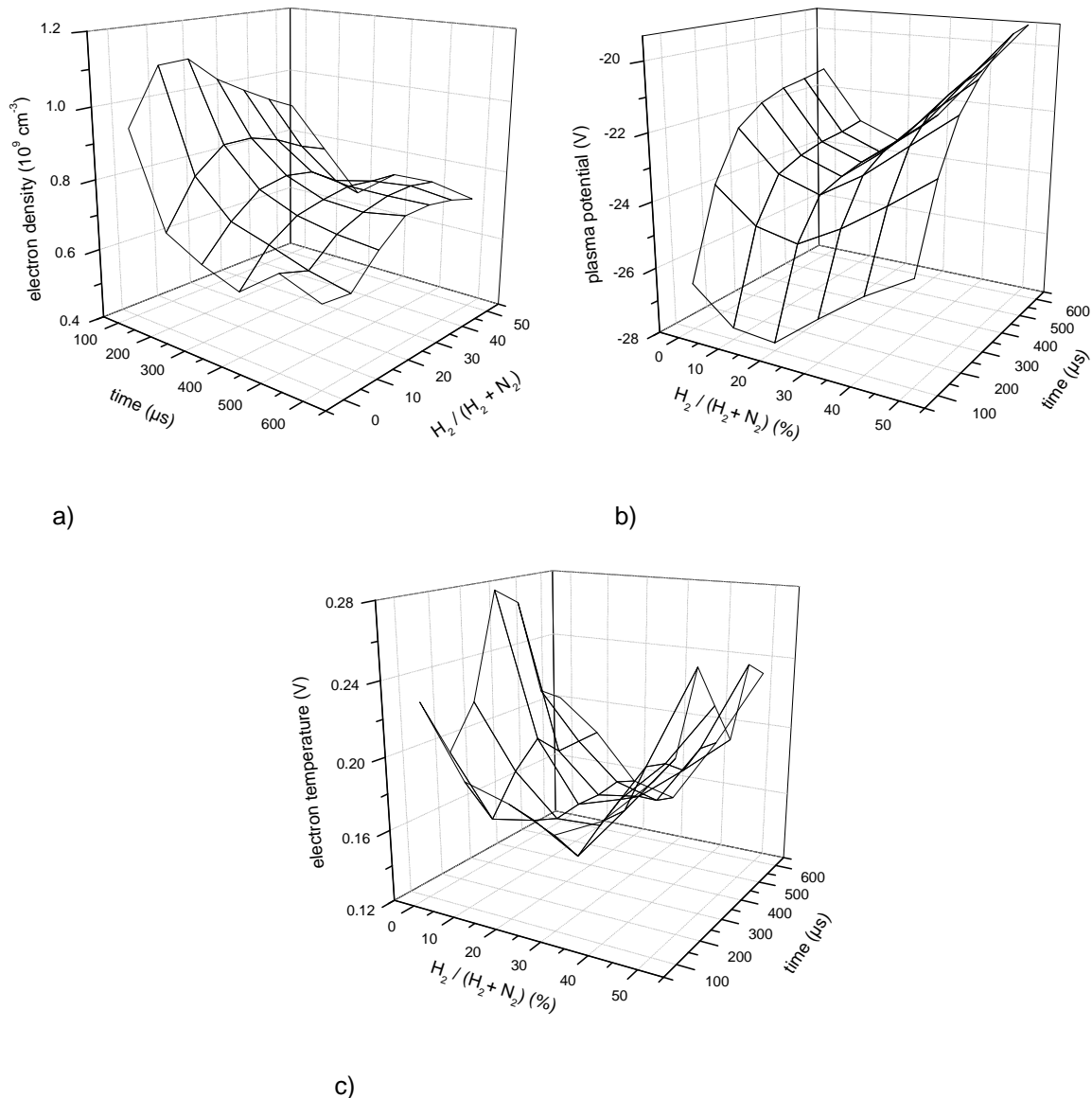


Figure 2: Temporal distribution of electron density (a) plasma potential (b) and electron temperature (c) during the on phase in dependence of the composition of the  $\text{N}_2/\text{H}_2$  process gas

A characteristic time dependence of the charge-carrier density during the pulse on time containing maximum values of almost  $1.0 \cdot 10^9 \text{ cm}^{-3}$  was found. Furthermore, the increase of the plasma parameters by varying the hydrogen content was monitored in the process gas. Floating and plasma potential indicate 20% admixture of  $\text{H}_2$  a minimum. At this proportion of hydrogen in the process gas positive ions is accelerated most strongly to the substrate. The electron density in Figure 2 a shows between 15 - 25% hydrogen content, a slight maximum, while the electron temperature (Figure 2 c) in this area has a minimum. Maximum mean electron energy is due to the quasi-neutrality in the plasma

also an ion peak, so more particles are available for charge exchange. Regardless of the process gas composition average electron temperature of  $<0.3$  V can be detected.

The qualitative measurements of quadrupole mass spectrometry (QMS) should be complemented by the possibility of determining the absolute concentrations of stable molecules through the mid infrared tunable diode laser absorption (TDLAS). Though the study of the plasma chemical reactions of active nitrogen we investigated the efficiency of ammonia generation generated from mixtures of  $N_2$  and  $H_2$  under various plasma conditions. The main result of the preliminary investigation on the reactions of the dissociated species and the  $NH_3$  - production rate is that it can be initiated depending on the gas composition, but above all as a function of bias power, a concentration of 1%  $NH_3$ . The determined maximum is at a hydrogen content of 50% and is an indicator of increased responsiveness due to adjusting glow discharge conditions.

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