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Macroscopic characteristics of plasma-nitrided AISI 4340 steel

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Plasma-nitrided AISI 4340 steel, in a low-pressure abnormal glow discharge was studied. The layer formation and their characteristics, were studied as a function of the main macroscopic parameters of the gas discharge: gas flow, N_2/H_2 mixture, treatment time and sample temperature. The nitrided layers were characterized using a metallographic microscope coupled to a microhardness tester and X-ray techniques. Typical results obtained for samples which were nitrided for 2 h in a gas mixture of $0.9N_2 + 0.1H_2$ at 793 K, showed a white layer composed of ε and γ′ phases, 20 μm thick, and a 1100 HV20 microhardness.

1. Introduction

Plasma nitriding is an important surface-hardness process used for steels. The absorption of nitrogen atoms and the resulting nitride precipitation, cause physical and chemical surface modifications of the material. This fact produces substantial improvements of the mechanical and chemical properties of the surface and subsurface layers (wear, fatigue strength and corrosion resistance) [1–4].

In spite of the recent commercial application, plasma nitriding mechanisms are not yet very well understood. For example: why is plasma nitriding more effective than other processes in spite of the low nitrogen density? What is the role of different active species in the nitride layer formation? Some authors [5–7] have shown that nitrogen atoms or vibrationally excited nitrogen molecules $N_2(X, v)$ are the more important species in the nitriding process. Others have maintained that the accelerated nitriding is due to nitrogen–hydrogen molecular ion bombardment [8] or due to the sputtered iron from the cathode forming FeN in the gas, which condenses on the substrate, dissolving into stable phases ($Fe_{2-4}N$) [9]. Another proposition is based on the formation and diffusion of vacancy–nitrogen ion pairs [10]. Moreover, depending on the material structure, particularly in ferritic, austenitic or martensitic phases of stainless steel, different results have been obtained [11, 12]. The metallurgical modification of the plasma-nitrided steels shows less distortion, better wear resistance and fatigue strength than that achieved with steels nitrided by traditional methods [13]. It is important to point out that all the mechanisms discussed show that the results depend on the discharge parameters as well as on the structure and composition of the material to be nitrided. These facts make this process an interesting and important subject for experimental and theoretical studies.

The plasma-nitriding process is set up in a d.c. abnormal discharge, the steel samples being the cathode. The plasma is produced in a low-pressure (1–10 torr; 1 torr = 133.322 Pa) and low flow of a N_2/H_2 gas mixture. The samples are heated directly by ion and molecular bombardment on the cathode, during the whole treatment time, typically 2–4 h.

In this paper, we present some results of the physical and metallurgical properties of the nitrided layers of AISI 4340 steel, especially the microhardness and thickness of the nitrided layer. Metallographic and X-ray techniques were used to identify the microstructure and phases of the nitride layer.

2. Experimental procedure

The AISI 4340 steel (0.2 %–0.3 % Mo, 1.65 %–2 % Ni, 0.8 %–0.9 % Cr and 0.4 % C), has large industrial applicability which justifies our choice. The samples were constituted of 23 mm diameter and 3 mm high cylinders obtained from an AISI 4340 commercial steel. The material was analysed before being submitted to the nitriding process, presenting a microstructure characteristic of a tempered martensitic phase. The structure and microhardness (300 HV20) show that the steel was quenched and tempered at a temperature between 680 and 730 K. Prior to the plasma-nitriding process, the samples were mechanically mirror-polished, using a buffing wheel with 0.5 μm alumina slurry, and ultrasonically cleaned in petroleum ether. A supplementary cleaning was set up in the plasma reactor using a low-pressure (96 Pa) argon discharge for 30 min.

The experimental apparatus is shown in Fig. 1. The plasma-nitriding reactor constituted a stainless steel (AISI 304) cylinder, with 250 mm inner diameter and 250 mm high. The samples were placed on a cathode discharge and polarized with a negative fully rectified wave, varying between 0 and 1 kV RMS. The temperature was measured using a chromel–alumel thermocouple. This temperature was simultaneously compared with the rotational temperature of the $N_2 + (B)$ state, which under our conditions could be correlated with the sample temperature [14]. This comparison is

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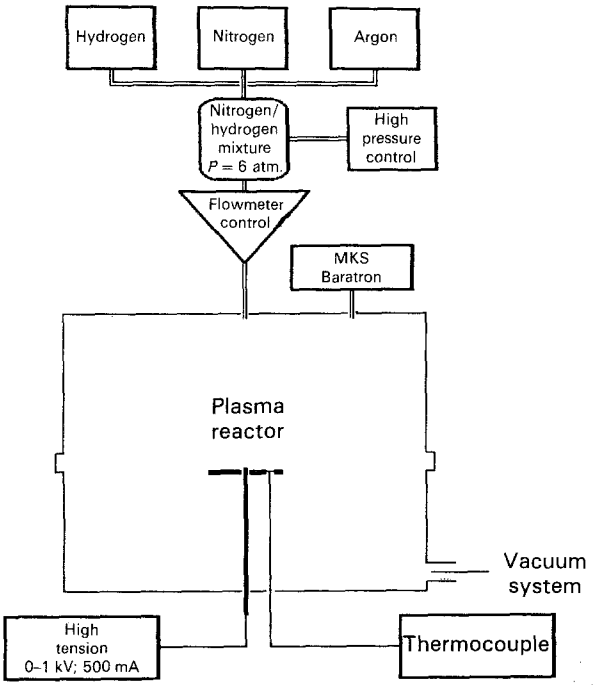

Figure 1 Experimental apparatus.

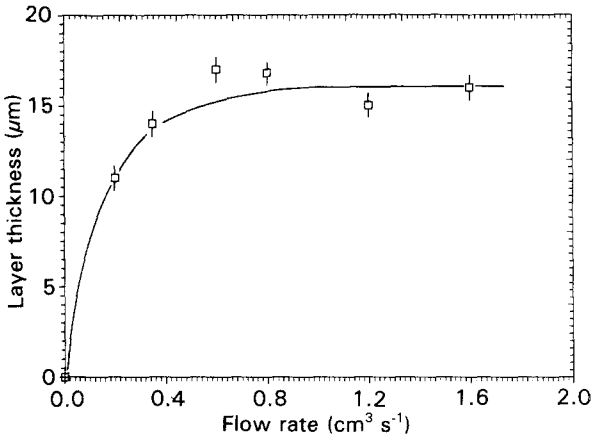

Figure 2 Variation of the layer thickness as a function of the gas mixture flow rate. See text for the experimental conditions.

important to avoid measurement errors caused by thermal coupling between sample and thermocouple during the treatment time. Before each treatment, the system was pumped by a mechanical two-stage pump until a residual pressure below 0.13 Pa (0.001 torr) was achieved. The treatment pressure, 400 Pa (3 torr) was measured using a 222 B MKS baratron absolute gauge and the gas flow was controlled by an air–liquid mass-flow controller. In our experiments, the gas flow, N_2/H_2 ratio, treatment time and sample temperature were the varying parameters.

The metallographic analyses, were made in a Carl Zeiss Neophot microscope coupled to a microhardness tester. The X-ray analyses were obtained with a Rigaku diffractometer, using a Cu$K\alpha$ radiation filtered by a nickel filter at 1.154 05 nm.

3. Results and discussion

In order to determine the influence of the plasma parameters on the layer formation and their characteristics, a set of experiments was performed. Fig. 2 shows the white layer thickness composed of ε and γ′ phases ($Fe_{2-3}N$ and Fe_4N, respectively), as a function of the gas flow. Under these experimental conditions (90 % N_2 + 10 % H_2, 3 torr, 793 K and 2 h treatment), a white layer thickness saturation was observed for a gas flow higher than 0.6 $cm^3 s^{-1}$ NTP. The thickness reduction for low flow ($\phi < 0.6$ $cm^3 s^{-1}$) is probably due to impurities desorbed from the chamber wall, mainly oxygen and water vapour. These impurities lead to surface oxidation, which make nitrogen diffusion difficult, consequently producing reduced-thickness layers. For relatively high flow, the $[O_2]$ ratio is sufficiently low, so that the impurity effects on the nitride formation can be neglected. In our experiments this ratio is evaluated to be lower than 10^{-3} for flows higher than 0.6 $cm^3 s^{-1}$ NTP, indicating that a higher impurity level will affect the nitriding layer. In fact, this evaluated value is consistent with recent results obtained by Detourbe *et al.* [15] where, for oxygen concentrations higher than 0.004, the Fe_2O_4 formation has drastically reduced the nitride layer.

Fig. 3 and Table I show the influence of the hydrogen relative concentration on the thickness and microhardness of the white layer. Pressure, temperature and treatment time were maintained at previously mentioned experimental values. The measured microhardness (1140 HV20) was significantly higher than that obtained by Spalvins [1] for AISI 4340 steel. This discrepancy can probably be explained by different

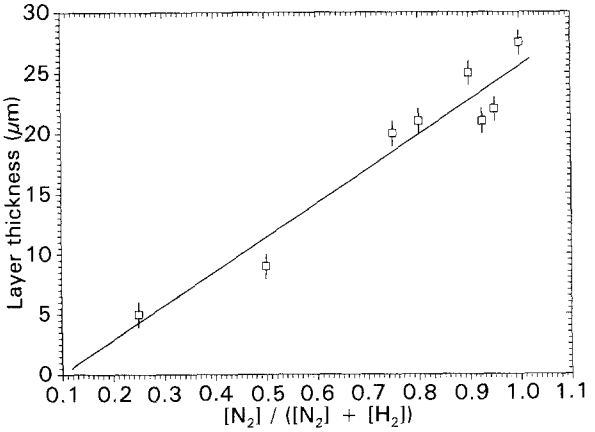

Figure 3 Layer thickness variation as a function of the gas mixture. Experimental conditions; 0.9 N_2 + 0.1 H_2, 793 K, 0.6 $cm^3 s^{-1}$ and 3 torr.

TABLE I Thickness and microhardness of the white layer as a function of the nitrogen/hydrogen mixture

	$[N_2]/([N_2]+[H_2])$						
	0.25	0.50	0.75	0.85	0.90	0.95	1.0
Microhardness (HV20)		1060	1140	1140	1140	1140	1140
Thickness (μm)	4.9	8.9	19.1	19.1	24.3	21.6	27.3

sample microstructures, before nitriding. In fact, we have observed that the white layer is a function of the tempering temperature, before ion nitriding [16].

The evolution of the white layer thickness as a function of treatment time is presented in Fig. 4. It is shown that the thickness is a linear function of the square root of time from 15 min–4 h. It is interesting to observe that the extrapolation of this curve to $t = 0$, presents a "residual" nitrided layer. This can be explained by a plasma nitriding prior to the stabilization temperature (of the order of 15 min), from which the time is considered. The thickness proportionality to the square root of time is a classical result [2, 3, 11] and can be explained by a layer formation by a diffusion-controlled process.

In Fig. 5, the white layer thickness as a function of the sample temperature is presented. The plot shows that the maximum thickness is obtained for the 793–833 K temperature interval. For temperatures higher than 873 K, no white layer was obtained. The black layer observed is characteristic of a mixture of nitride and nitroferritic phase [17].

Fig. 6 shows a typical microhardness profile. It is important to point out that these microhardnesses are higher than those obtained by Spalvins [1] for the AISI 4340 steel. For nitrided AISI 316 and 304 stainless steels, the high microhardness of 1100 HV [1, 3] is

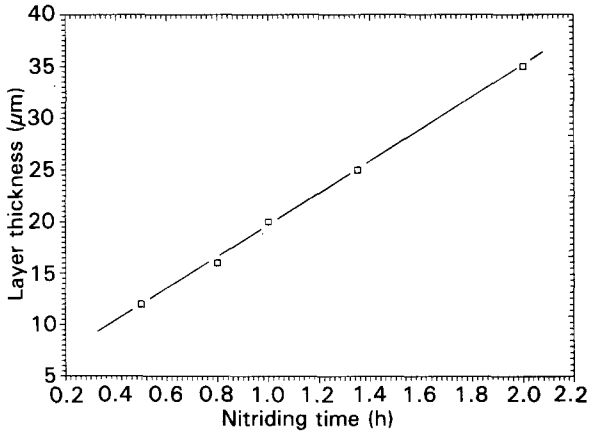

Figure 4 Thickness evolution as a function of the square root of time. The gas mixture, temperature and flow rate are 0.9 N_2 + 0.1 H_2, 793 K and 0.6 $cm^3 s^{-1}$ TPN, respectively.

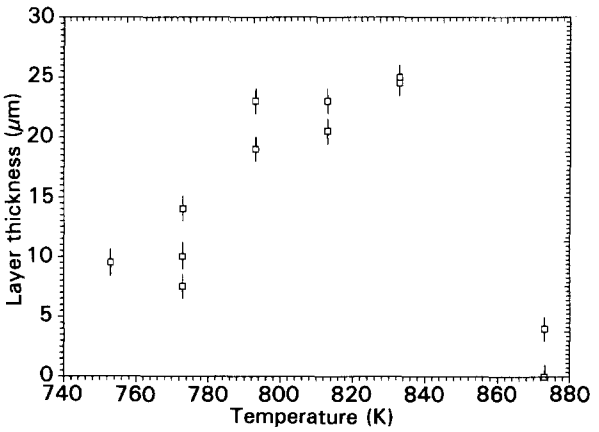

Figure 5 Evolution of the white layer thickness as a function of the sample temperature. The other experimental conditions are the same as in Fig. 4.

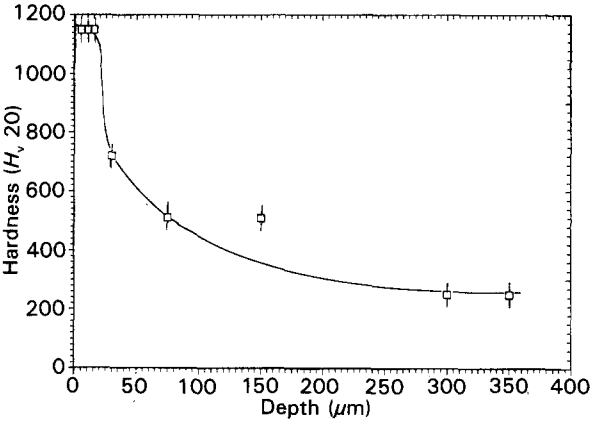

Figure 6 Depth–microhardness evolution of the nitrided layer. The experimental conditions are the same as in Fig. 3 for a 2 h treatment.

attributed to mixed nitride (γ'-Fe_4N, ε-$Fe_{2-3}N$) and possibly to CrN [18, 19] or to a non-equilibrium nitrogen supersaturated structure type (Fe, Cr, Ni, Mo)$_4$N with ε and some γ' nitride (Fe, Cr, Ni, Mo)$_{2-3}$N [12, 20]. This phase produces lattice stresses which can explain the higher microhardness. In our case, the low concentration of chromium and molybdenum, probably does not lead to the same structure. In this work the phase composition of the white layer was analysed using X-ray techniques. The spectral lines are characteristic of the ε and γ' phases. However, the observation of carbide precipitations due to the temper treatment at a temperature of about 700 K, possibly lead to the formation of mixed carbonitride during the nitriding process. This can be assumed to produce lattice stresses in the white layer, and the resulting higher microhardness.

4. Conclusion

The influence of several macroscopic parameters on the plasma nitrided layer has been demonstrated. It has been shown that the gas mixture (H_2/N_2) ratio is an important parameter for the layer-formation efficiency. In contrast with other work [8], the maximum thickness layer was obtained for pure nitrogen. The high microhardness obtained (1140 HV20) suggests new measurements are required, using other techniques, to interpret these results. The thickness–gas flow dependence was an important result, but it may be inferred that, for other N_2/H_2 ratios, the 0.6 $cm^3 s^{-1}$ limit may be different, especially for high relative hydrogen concentration, where the oxide reduction may be higher.

Finally, the results show that the AISI 4340 steel can be efficiently plasma-nitrided. The microstructure appears to be an important parameter in the mechanical properties of the plasma-nitrided steels.

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