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PLASMA NITRIDING AS A PREVENTION METHOD AGAINST HYDROGEN DEGRADATION OF STEEL

ABSTRACT

Aim of this paper is evaluation of susceptibility of plasma nitrided structural steel to hydrogen absorption and degradation. Structural steel, nitrided at glow discharge in the gas mixture of various N_2, H_2, Ar content was subjected to cathodic hydrogen charging in acid solution simulating the aged engine oil. The effect of the nitrided layers on the hydrogen transport and on the irreversible trapping was evaluated by the measurements of the hydrogen permeation rate and by the vacuum extraction, respectively. Surfaces with modified layers were examined with the use of a scanning electron microscope (SEM) before and after hydrogen permeation tests. In the presence of the not defected compact nitride layer, no hydrogen permeation through the steel has been stated under the experimental conditions. Absorbed hydrogen was accumulated within this layer.
Using the atmosphere of the higher nitrogen to hydrogen ratio at plasma assisted nitriding provides the formation of thin compact nitride zone, highly protective against corrosion and hydrogen degradation.

Keywords: *plasma nitriding, nitride layer, hydrogen permeation, hydrogen degradation*

INTRODUCTION

Nitriding is one of the most elaborated surface modifications improving the mechanical properties and the corrosion resistance. Nitriding of steel has been used in order to prevent the hydrogen charging of industrial installations, exploited under the conditions enabling their hydrogen induced deterioration [1]. Formation of nitrided layer has been shown to improve the susceptibility to stress corrosion cracking of the structural steel [2]. At hydrogen charging of nitrided metal, the hydrogen accumulation within the nitrided layer in iron [3] and steels [4, 5] and the retardation of hydrogen transport by nitrided layer into the bulk material [3] have been observed. Additional oxidizing of nitrided layer has been shown to decrease the hydrogen entry in iron [6]. The impediment of hydrogen transport (barrier effect) results from the low hydrogen diffusivities in the modified layers; the diffusivities in compound layers are much lower than in diffusion layers. The surface effect is strongly enhanced when the plasma treatment also includes the implantation of oxygen and sulphur [6].

Although the nitriding has been widely used and the phases formed at nitriding of steel have been thoroughly recognized and standardized, still the great effort has being done to modernize the treatment [7]. Since the parameters of nitrided layer (thickness, phase composition, microstructure, and porosity) affecting the layer properties strongly depend on the conditions of the treatment [8] at any modification of the nitriding

process the phase composition and the properties of the modified layer have to be checked.

The recently developing plasma assisted nitriding of steel, allows intensify the treatment, avoid deterioration of the steel structure and modify the structure and stress distribution within the nitrided layer [9]. Application of the plasma treatment to improve properties of the low-alloy structural steels of increased strength exploited in aggressive environments should be proceeded by the thorough examinations. It is especially important in the case of possible hydrogen charging of exploited steel, since hydrogen behavior strongly depends on the chemical and phase composition and on the microstructure of the structural steels [10, 11]. In [12] the possibility to improve the resistance to hydrogen embrittlement and to stress corrosion cracking of low-alloy steels containing 0.3% C by plasma nitriding has being considered and studied. The aim of the present work, being the part of the project, was to check the effect of the γ' nitride compact zone formed at the glow discharge assisted nitriding of 34CrAlNi7-10 steel on the hydrogen transport and trapping.

Engine oil can absorb moisture and become acidic, so that hydrogen could be generated at crack tips and facilitate crack growth. A number of failures of the connecting-rod bolts in certain car engines occurred after very short times in service. Examinations of the fracture surfaces revealed intergranular fatigue crack propagation, thus suggests that the engine-oil environment was not inert for bolts made of quenched and tempered low-alloy steels [13].

MATERIALS AND EXPERIMENTAL PROCEDURE

The constructional nitriding steel grade 34CrAlNi7-10 according to PN-EN 10085:2003 [14] was used. The round bar was heat treated at the mill with the following parameters: quenched at 880°C with oil cooling, tempered at 650°C with air cooling, and stress relief annealing at 600°C for 6 hrs. with furnace cooling. The chemical composition of the tested steel is given in Table 1. Microstructure of the steel composed of sorbite.

Nitriding was done in the gas atmosphere (Table 2), at the glow discharge at temperature 560°C for 6 hrs. The obtained modified layers consisted of the zone of compact γ' nitrides and the diffusion zone (Fig. 1), of the thicknesses given in Table 2.

The Vickers hardness was measured on a cross-section of tested bar with load of 294 N (30 kG), and on surfaces with modified layers using 4.9 and 9.8 N loads (0.5 and 1 kG respectively). Results of hardness tests are presented in Table 3.

Some specimens were subjected to the additional oxidizing after nitriding by blowing the air through the chamber at temperature 520°C for 0.5 hr.

Studied steel has been used for the engine parts. The aggressive environment in such case is the aged and oxidized engine oil, containing some acids [15]. To simulate this environment, the nondeaerated 0.005M H_2SO_4 solution has been selected as the test electrolyte.

Corrosion resistance of the studied materials was estimated in electrochemical measurements, using the minicell placed on the studied modified surfaces. The values of the open circuit potential (E_{OC}) and of the corrosion current density (i_{Corr}) evaluated

from the polarization curves, were compared with the steels in as received state and the steel with the modified surface (Table 4).

Electrochemical measurements of the hydrogen permeation rate [16] through the membranes (0.4 mm in thickness) were done using the double cell. The modified layer served as the ingress side of the membrane, galvanostatically polarized in the test electrolyte. Two modes of the application of cathodic polarization were used: (1) step by step increase in the cathodic current density within the range of 0.1 to 10 mA/cm^2 (Fig. 2a) and (2) single cathodic polarization by the current density 10 mA/cm^2 (Fig. 2b).
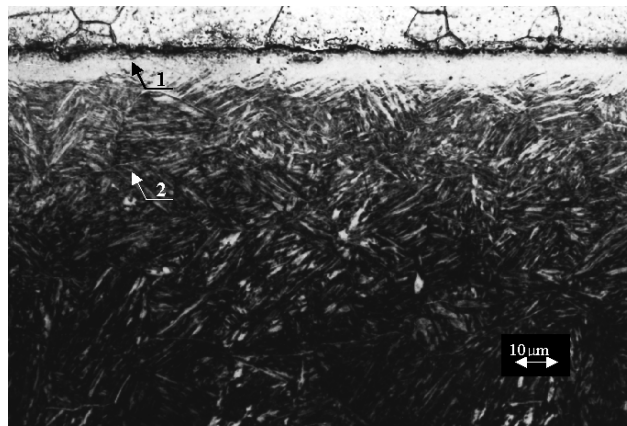

Fig. 1. Microstructure of plasma nitrided layer on 34CrAlNi7-10 steel. Sample 34A1.
1 – compact nitride zone; 2 – diffusion zone. Nital etched

Constant polarization (i_C) was kept until recorded permeation current in the egress cell (filled with 0.1M NaOH) attained the steady state value or for 100 hrs. At the end of the test, polarization was switched off. The build-up (at application of polarization in ingress cell) and decay (at cessation of polarization) hydrogen permeation transients were recorded in the egress cell.

After completing the permeation tests according to the single mode, the hydrogen content (V_H) left in the membrane was measured by the vacuum extraction at 450°C. Since the extraction was done after the removing all the permeable hydrogen from the membranes, the measured values of V_H corresponded to the mean values of irreversibly trapped hydrogen. Surfaces with modified layers were examined with the use of a scanning electron microscope (SEM) before and after hydrogen permeation tests.

*Table 1. Chemical composition of tested 34CrAlNi7-10 steel bar*

Analyse	Chemical composition, wt %									
	C	Si	Mn	P	S	Cr	Mo	Ni	Al	Cu
Ladle according to PN-EN 10085	0.30 0.37	max 0.40	0.40 0,70	max 0.025	max 0.035	1.50 1.80	0.15 0.25	0.85 1.15	0.80 1.20	-
Control	0.38	0.28	0.59	0.008	0.001	1.50	0.25	0.95	0.90	0.07

Table 2. Parameters of the surface treatment and the thickness of the modified layers

Codes of specimens	Parameters of nitriding	Thickness of compact nitrides zone, μm	Thickness of diffusion zone, μm
34	as received – no layer	-	-
34A1	70%N_2 + 30% Ar	10-12	200-225
34A2	70%N_2 + 30% H_2	4-8	200-225
34A3	30%N_2 + 70% H_2	10	200-225
34A1U	oxidizing in air at 520°C, 0.5 hr. after A1 nitriding process	10	200-225

Table 3. Vickers hardness test results of tested steel and modified nitrided layers

Codes of specimens	Vickers hardness		
	HV0.5	HV1	HV30
34	-	-	326
34A1	960	960	-
34A2	1080	1090	-
34A3	1080	1080	-
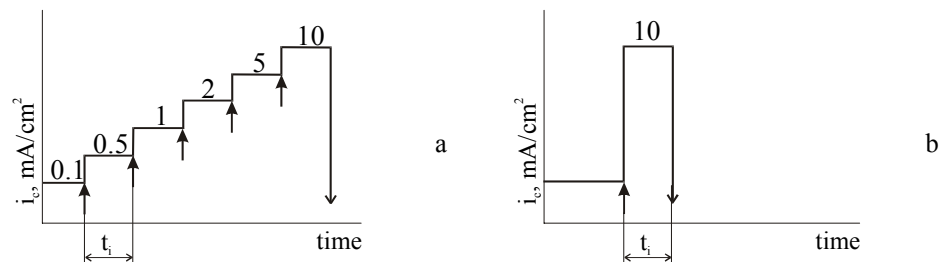
Fig. 2. Schematic presentation of application of cathodic polarization:
step by step (a) and single (b) modes

Table 4. Open circuit potential (E_{OC}) and corrosion current density (i_{Corr}) established for studied materials

Codes of specimens	34	34A1	34A1U	34A2	34A3
i_{Corr}, mA/cm^2	0.290	0.150	0.003	0.0003	0.180
E_{OC}, mV$_{Hg/HgSO4}$	-1200	-925	-280	-180	-1020

Table 5. The steady state values of hydrogen permeation current density J∞ (μA/cm^2) recorded in the egress cell at application of cathodic polarization (i_C) in the ingress cell

Polarization, i_C, mA/cm^2	Mode of i_C application	34	34A1	34A1U	34A2	34A3
0.1		2.7	0	6.8	0	0
0.2		2.8	0	7.4	0	0
0.5		3.7	0.3	9.3	0	0
1	step by step	4.3	0.32	9.7	0	0
2		4.8	0.6	8.2	0	0
5		5.3	22	8.2	0	5.9

| 10 | | 12.2 | 39 | 8.4 | 0 | 13 |
| 10 | single | 11 | 0 | 8.5 | 0 | 0 |

Table 6. Concentration of irreversibly trapped hydrogen, as measured by vacuum extraction (V_H) and as recalculatedfor compact nitride layer (V^*_H)

Codes of specimens	V_H, ppm wt	V^*_H, ppm wt
34	0.8	0.8
34A1	1.4	63
34A1U	2.8	140
34A2	1.2	120
34A3	2.6	135

RESULTS AND DISCUSSION

Surface modification increased the resistance to corrosion in acid solution. Nitrided steels revealed the open circuit potential more positive and the corrosion current density lower than those values estimated for as received material (Table 4). The additional oxidation of nitrided steel caused the further shift of open circuit potential into the anodic direction and the further substantial decrease in the corrosion current density, and thus in the corrosion rate.

Table 5 shows the values of the steady state hydrogen permeation current as recorded at the step by step increased polarization current density and at the single application of the current density 10 mA/cm^2. Rather unexpected results have been observed at the measurements of the hydrogen permeation:

- no permeation was detected for 34A2 material at any polarization;
- for material 34A1 no permeation was recorded at single polarization, whereas at the step by step mode, the permeation was recorded at polarization 0.5 mA/cm^2 and higher;
- material 34A1U, nitrided similarly as the 34A1 and then oxidized revealed the hydrogen permeation at all polarization applied at the step by step and at the single modes;
- for material 34A3 no permeation was recorded at single polarization, whereas at the step by step mode the permeation was recorded at polarization 5 mA/cm^2 and higher.

The lack of hydrogen permeation through material does not mean any hydrogen ingress into the metal. As revealed the vacuum extraction measurements (Table 6) materials with modified surface layer contains higher amount of irreversibly trapped hydrogen (V_H) than as received steel. Therefore, the assumption can be made that entering hydrogen is accumulated in the nitrided layer, similarly as it has been shown in [3-5]. Assuming the accumulation of all the measured hydrogen (V_H) within the compact nitride zones of the mean thicknesses given in Table 2, the hydrogen concentration in those zones (V^*_H) has been recalculated. The obtained data (Table 6) are consistent with the data given in [3-5] for nitrided iron and steels.

The presented above unexpected results of the hydrogen permeation measurements (Table 5) may be accounted for the different structure of the modified layers and for the change of the layer structure taking place during the hydrogen permeation tests [17].

As seen in Table 4, the calculated corrosion current density for materials 34A1 and 34A3 is within the range of the low cathodic current density applied to membranes. Therefore, during the long term application of the low cathodic polarization, the outer part of the nitrided layer has been subjected to corrosion degradation (Fig. 3-4). Taking into account the calculated corrosion rate and the time of the metal exposition at the low cathodic polarizations, the thickness of the corroded-off layer has been calculated to be similar to that of the compact nitride zones.

On the other hand, hydrogen charging has been shown to cause the peeling-off the ingress side of the membranes [18]. For the studied materials this also means the peeling off the outer zone of nitrided layer (Fig. 5).

Destroying the compact nitride zone due to the corrosion processes and (or) due to the hydrogen charging eliminates the obstacles for hydrogen entering into the dipper layers of the metals, and the hydrogen permeation started to be detected at the certain applied polarization (Table 5). In the case of application of single polarization of 10 mA/cm^2, no corrosion occurred and the time of hydrogen charging was not long enough to peel-off the ingress surface. Since the very high ability of the compact zone to accumulate hydrogen (Table 6), all the entered hydrogen has been concentrated in the compact nitride zone of the modified layer and no hydrogen permeation has been detected under those conditions for materials 34A1 and 34A3 (Table 5).
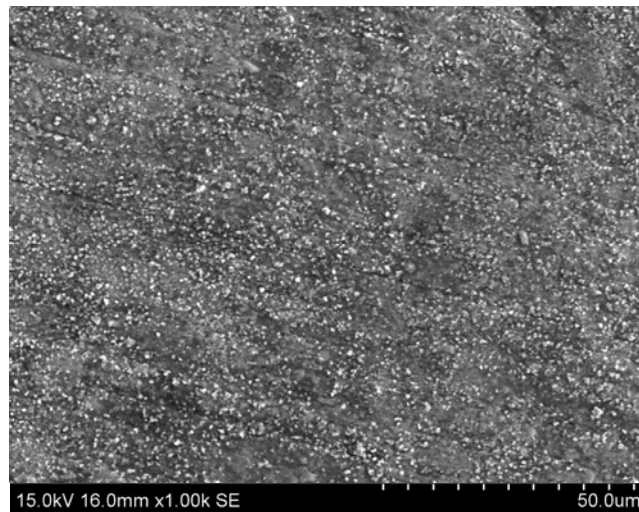

15.0kV 16.0mm x1.00k SE   50.0um

Fig. 3. SEM image of surface of 34A1 sample after nitriding

It has been shown [6] that oxidation of nitrided iron causes the further decrease in the hydrogen permeation. In the case of the nitrided and oxidized material 34A1U studied in the present work, no retardation of hydrogen permeation has been observed: for all applied polarizations, hydrogen permeation through material 34A1U is quite similar as through the received steel 34. However, the content of irreversibly trapped hydrogen within the modified layer is much higher than that in the received steel (Table 5). This may be associated with the structure of the surface layers of the nitrided steel subjected to oxidation. Indeed, the SEM observations of 34A1U steel [17] have revealed the presence of microcracks in the layer (Fig. 6). At cathodic charging hydrogen may easily enter the bulk material destroying the compact nitrided layer (Fig. 7), and the hydrogen permeation has been detected (Table 4).
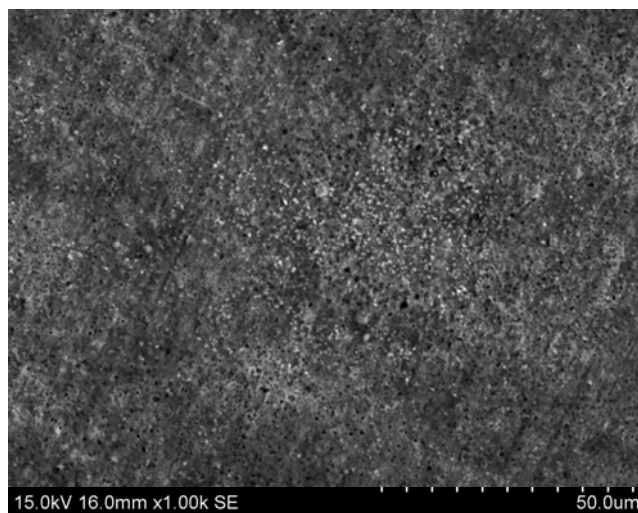
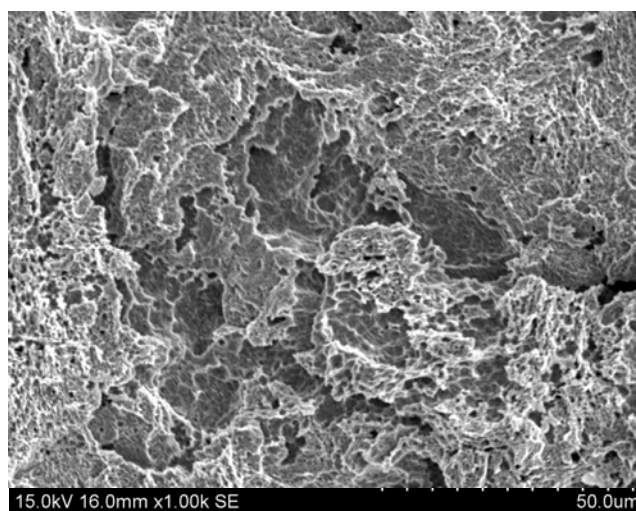**Fig. 4.** SEM image of surface of 34A1 sample after nitriding and corrosion process

Fig. 5. SEM image of surface of 34A1 sample after nitriding, and "single" cathodic polarisation
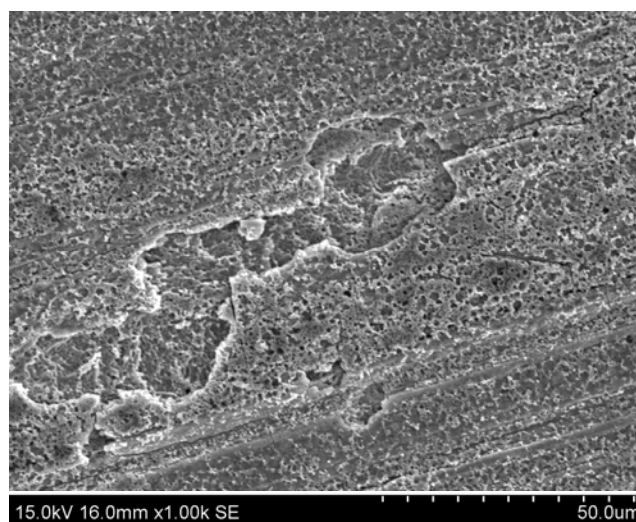with current density 10 mA/cm^2

Fig. 6. SEM image of surface of 34A1U sample after nitriding with oxidizing

From the comparison of the nitriding parameters (Table 2) and the resistance to corrosion (Table 4) and the protection for hydrogen ingress into the steel (Table 5) it might be concluded that the compact nitride zone of the low thickness but of the good protective ability has been formed at the application of the high nitrogen content in the nitrogen-hydrogen atmosphere at the plasma assisted treatment of the structural steel.
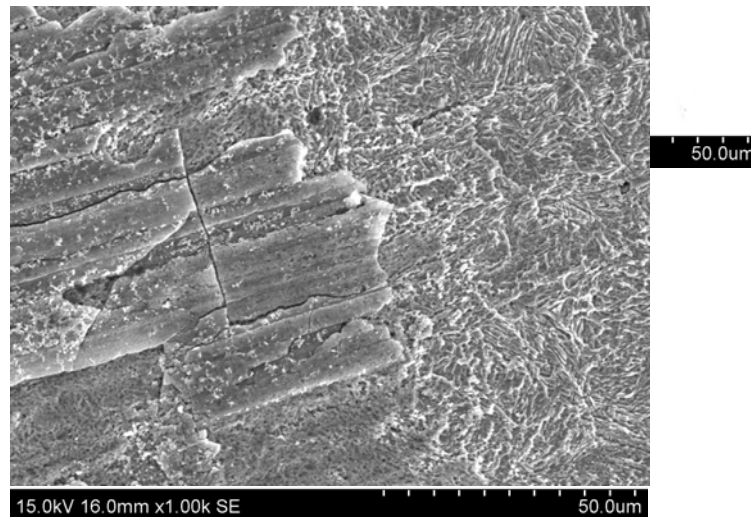

Fig. 7. SEM image of surface of 34A1U sample after nitriding with oxidizing, and "single" cathodic polarisation with current density 10 mA/cm^2

In conclusion, from the obtained results, the compact nitride zone in the nitrided layer of steel prevents the hydrogen entry into the bulk metal, providing no flaws formed during the surface treatment, and no deterioration of the layers takes place due to the corrosion processes or to the hydrogen charging. Therefore, the effect of the nitrided layer on the ability to prevent the hydrogen enter into the steel has been accounted by the corrosion rate in given environment and by the presence of flaws and cracks in the layer. Since the surface chemical thermal treatment differently affected the parameters of layers formed on iron and on the high strength steel, the results obtained for iron with the modified surface cannot be directly transferred to the steel, and the behavior of steels with the modified surface should be thoroughly recognized.

CONCLUSIONS

Using the atmosphere of the higher nitrogen to hydrogen ratio at plasma assisted nitriding provides the formation of thin compact nitride zone, highly protective against corrosion and hydrogen degradation.
Accumulation of hydrogen in nitrided layer prevents its penetration into the bulk of steel.

Flaws or cracks in the structure of nitrided layer, as well as the deterioration of the layer in the course of corrosion process or due to hydrogen action, promote the hydrogen permeation into the bulk of material.

ACKNOWLEDGEMENT

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