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Plasma nitriding as a prevention method against hydrogen degradation of steel

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Properties

ABSTRACT

Purpose: of this paper is evaluation of susceptibility to hydrogen degradation of structural low-alloy steel, plasma nitrided in the atmosphere with various contents of N_2 and H_2.

Design/methodology/approach: Susceptibility of 34CrAlNi7-10 steel and samples with various plasma nitrided layers have been evaluated under monotonically increasing load in 0.005 M H_2SO_4 solution. The nitrided layers were investigated with the use of an X-ray Photoelectron Spectroscopy (XPS) and Auger Electrons Spectroscopy (AES). Slow-Strain Rate Tensile (SSRT) test was carried out under cathodic polarisation. Elongation, reduction in area, fracture energy and tensile strength were chosen as measures of susceptibility to hydrogen embrittlement. Fracture modes of failed samples were examined with the use of Scanning Electron Microscope (SEM).

Findings: All tested samples revealed susceptibility to hydrogen degradation under hydrogenation. Samples with nitrided layer have lower lost of reduction in area than base metal samples. The nitrided layer established in standard atmosphere 30% H_2 and 70% N_2 has the highest resistance to hydrogen degradation.

Research limitations/implications: Further research should be taken to reveal the exact mechanism of increased plasticity of nitrided layer with absorbed hydrogen.

Practical implications: Plasma nitriding may prevent hydrogen charging of machines and vehicles parts in hydrogen generating environments, and thus decreasing susceptibility to hydrogen embrittlement.

Originality/value: Under the increasing load and hydrogen generating environments plasma nitrided layers are effective barriers to hydrogen entry into a bulk of steel, and additionally increased plasticity of nitrided layers with absorbed hydrogen has been observed.

Keywords: Crack resistance; Plasma assisted nitriding; Hydrogen embrittlement

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1. Introduction

Steels having a tensile strength greater than 1000 MPa are susceptible to hydrogen embrittlement manifesting in lost of plasticity and may fail at stress much below their yield strength. This behavior is termed hydrogen embrittlement or delayed cracking.

Synergic action of stress and environment may result in various types of degradation of metallic materials, including hydrogen-enhanced degradation. Harmful influence of hydrogen at temperatures below 200°C is termed as low temperature hydrogen attack (LTHA). Hydrogen degrades properties of steels mainly by delayed cracking at stress below the yield strength and by the loss of ductility in a tensile test as reflected by a decreased reduction in area which is generally called hydrogen embrittlement (HE). When local hydrogen concentration is high enough (reaches critical concentration) it may cause hydrogen induced cracking (HIC) or may manifest as advancement of crack propagation (crack has been initiated by mechanical damage or corrosion).

Hydrogen effect is greater near room temperature and decreases with increasing strain rate. Hydrogen degradation is more pronounced with increasing hydrogen content or charging rate and with increasing strength of steel [1-4].

A number of failures due to hydrogen have been reported, e.g. of car engines parts, and ship engines. Engine oils can absorb moisture and become acidic, so that hydrogen could be generated at crack tip and facilitate crack growth. Martensitic steels with are known to be highly susceptible to hydrogen degradation [5-6].

Plasma or ion nitriding is a thermo-chemical process operating in the glow-discharge regime for the production of case hardened surface layers on ferrous or nonferrous alloys. Plasma assisted nitriding is now widely applied for improving hardness, wear resistance, and corrosion resistance of machines and vehicles parts. Introduction of nitrogen into surface layers of iron and steel strongly affects the ingress of hydrogen into the metal.

Hydrogen can enter a metal during fabrication, technological processes, corrosion processes including cathodic reaction, cathodic protection, and also as a result of friction and wear. The latter sources of hydrogen may be of particular importance for nitrided and other modified surfaces, because they are designed for exploitation under friction and wear.

The phenomenon of hydrogen tribosorption from the contact zone into surface layers of machine and vehicles parts has been confirmed. The effective way to protect against the hydrogen wear is to use materials that do not absorb hydrogen or to apply thermo-chemical treatment to make nitrided or nitrided-like layers. Due to specific structure and residual stresses these layers make an effective barrier for diffusion of hydrogen into a bulk of metal. Additionally, hydrogen can probably escape from a surface layers into the friction contact zone and in this way decrease the friction coefficient.

Plasma nitriding strongly decreases the absorption of hydrogen by impending both its entry and transport in the modified layer for pure iron, low and medium carbon steels, and low-alloy steels. The effect of nitrogen is attributed to a lower solubility of hydrogen in the implanted layer, and its slower transport due to trapping at nitride precipitates. The compound zone controls the penetration of hydrogen mainly by affecting its entry. The impediment of hydrogen transport results from the lower hydrogen diffusitivities in the diffusion zone. The diffusion coefficient of hydrogen in the compound zone is much lower than in the diffusion zone, but the compound zone is not decisive in hindrace of hydrogen transport since this zone is relatively thin. The diffusion zone impedes the hydrogen transport much stronger [7-11].

2. Material and experimental procedure

The structural nitriding steel grade 34CrAlNi7-10 according to PN-EN 10085 [12] 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 annealed at 600°C for 6 hrs. with furnace cooling. The chemical composition of the tested steel is given in Table 1.

Mechanical properties obtained from a tensile test for the steel are presented in Table 2.

Hardness of base metal was measured on a cross section of the steel bar along its diameter using 98.1 N load (10 kG), and hardness of nitrided layers was measured on surface of flat nitrided samples using 4.9 and 9.8 N loads (0.5 and 1 kG respectively), both according to PN-EN 6507-1 [13].

Nitriding was done in the nitrogen-hydrogen (or argon) gas atmospheres with various hydrogen content, i. e. 0%, 30%, and 70%, at the glow discharge at temperature 560°C for 6 hrs. Various contents of hydrogen in atmospheres were chosen to obtain different initial hydrogen concentration in nitrided layer.

The nitrided layers were investigated by X-ray Photoelectron Spectroscopy (XPS), and Auger Electrons Spectroscopy (AES) methods with the use of multifunctional PHI 5700/660 electron spectrometer. The analysis was performed on cross sections of nitrided layers. The examinations were conducted in the region extending from the surface down to a depth of 400 μm.

Microstructures of the steel plate and nitrided layers were examined with the use of the optical microscope on cross sections etched with nital.

In order to estimate the degree of hydrogen degradation of tested steel and its modified layers, Slow Strain Rate Tensile (SSRT) test was conducted along with PN-EN ISO 7539-7 [14] on round smooth specimens 4 mm in diameter made according to PN-EN ISO 7539-4 [15]. The gauge length was 50 mm. Tests were performed at ambient temperature either in dry air or in 0.005 M H_2SO_4 solution. The applied strain rate was 10^{-6} s^{-1}. Tests in acid solution were conducted under cathodic polarisation with constant current density 10 mA/cm^2. During tests stress-strain curves were recorded on a personal computer. Three samples were used for each parameter.

Fracture surfaces after SSRT test were examined with Scanning Electron Microscope (SEM) to reveal a mode and mechanism of cracking.

3. Description of achieved results

The XPS investigations were performed to characterise only the diffusion zone of nitrided layers since examination was performed on a cross section of nitrided samples. Measurement points were placed along the line perpendicular to a surface with distances of about 8 μm. A step between measurement points was relatively high comparing to thickness of a compact nitride zone, and hence thin nitride zone was not analysed.

A whole XPS spectrum of diffusion zone for nitrided layers on samples 34A2 and 34A3 are presented in Figs. 1-2. The spectrum exhibits presence of Fe, Cr, Ni, Al, N, O, C, Ca, Na, Cl. Peaks of carbon and oxygen corresponds to absorbate carbon oxides, while peaks of iron and oxygen indicate that surface was covered with iron oxides. Calcium, sodium, and chlorine were from contaminations. Iron, chromium, nickel, and aluminium are components of the steel and nitrides presented in diffusion zone.

The shape of nitrogen N1s line obtained in diffusion zone of nitrided layer of sample 34A2 is given in Fig. 3. The binding energy determined for N1s line corresponds to formation of Fe_4N.

Distribution of nitrogen and iron concentration in surface layer on sample 34A2 is presented in Figs. 4-5.

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

Analyse	Chemical composition, wt %									
	C	Si	Mn	P	S	Cr	Mo	Ni	Al	Cu
Ladle according to PN-EN 10085:2003	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 of the bar	0.37	0.28	0.59	0.008	0.001	1.50	0.25	0.95	0.90	0.07

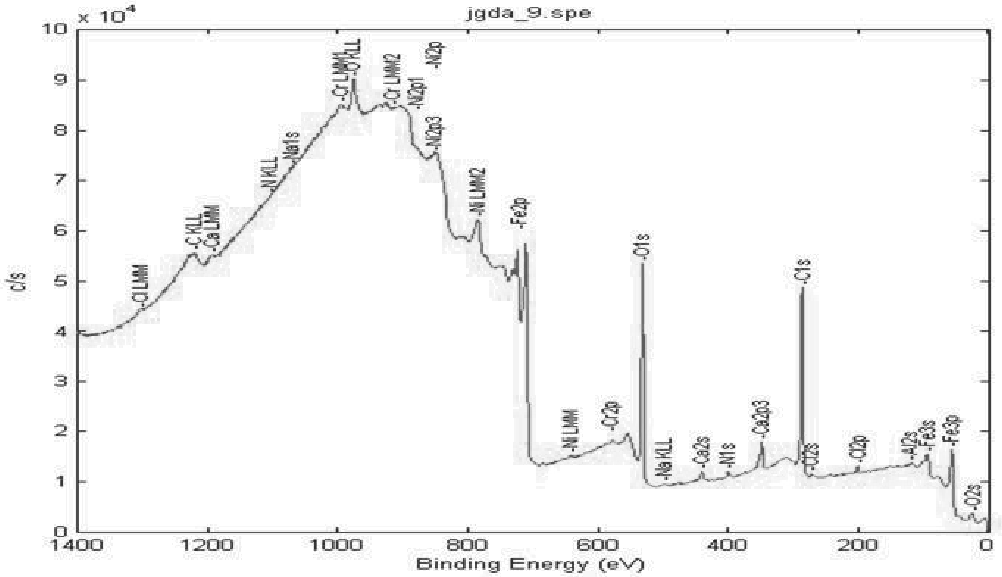


Fig. 1. The whole XPS spectrum for diffusion zone of nitrided layer on sample 34A2

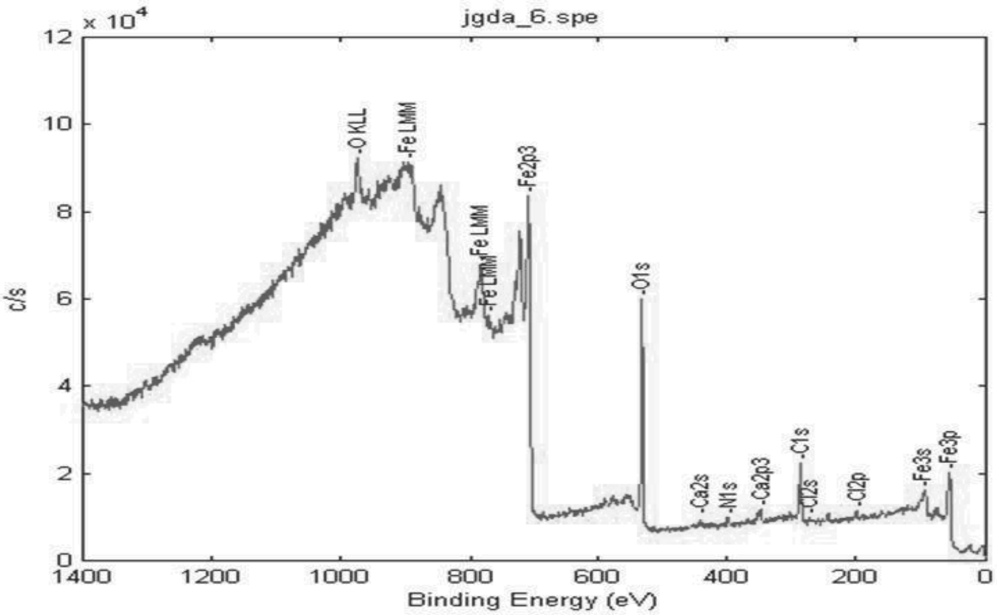


Fig. 2. The whole XPS spectrum for diffusion zone of nitrided layer on sample 34A3

Table 2.
Mechanical properties (longitudinal direction) of the bar made of 34CrAlNi7-10 steel

Samples	Yield Strength MPa	Tensile Strength MPa	Elongation %	Reduction in Area %
Base metal	842	988	19.0	59

Table 3.
Vickers hardness test results of modified nitrided layers

Codes of specimens	Vickers hardness	
	HV0.5	HV1
34A1	960	960
34A2	1080	1090
34A3	1080	1080

Table 4.
Parameters of the surface treatment and the thickness of the modified layers

Codes of samples	Parameters of nitriding	Thickness of compact nitrides zone, µm	Thickness of diffusion zone, µm
34R	base metal - as received	-	-
34A1	$70\%N_2 + 30\%Ar$	12	200-225
34A2	$70\%N_2 + 30\% H_2$	6	200-225
34A3	$30\%N_2 + 70\% H_2$	10	200-225

Table 5.
Mean values of hydrogen degradation parameters of 34CrAlNi7-10 steel and its various nitrided layers

Sample	Elongation %	Reduction in area, %	Fracture energy MJ/m^3	Tensile strength MPa
34A1-K	2.2	3.1	12	890
34A1-P	6.5	8.3	51	949
34A2-K	2.3	3.5	13	874
34A2-P	6.6	8.3	53	959
34A3-K	2.0	3.5	10	851
34A3-P	7.3	12.9	59	993
34R-K	8.9	12.6	72	969
34R-P	12.4	62.7	103	972

A1, A2, A3 – various surface treatments; P – tests performed in air; K – tests performed in acid solution

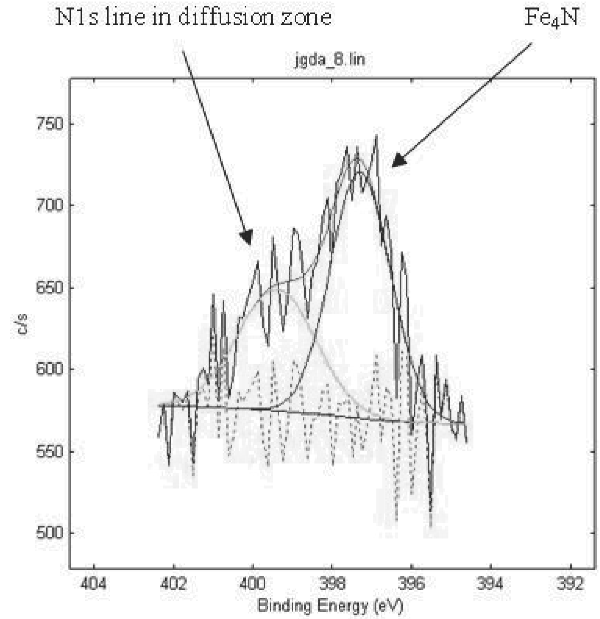


Fig. 3. The shape of nitrogen N1s line (XPS) in diffusion zone of nitrided layer on sample 34A2

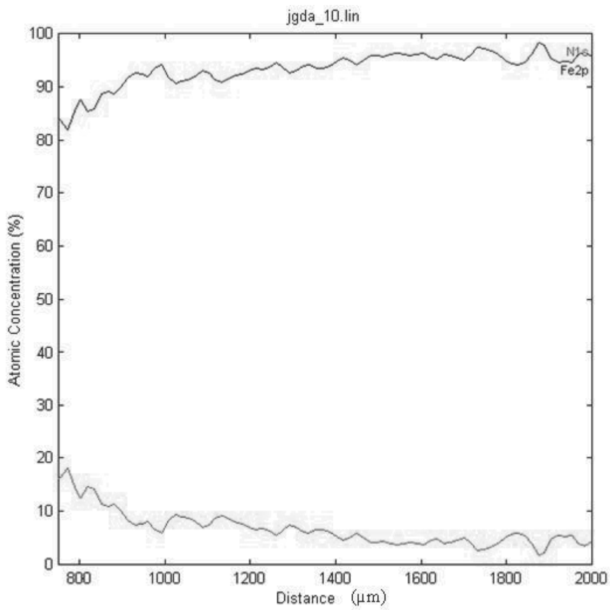


Fig. 4. The distribution of atomic concentration (XPS) of nitrogen (red) and iron (blue) in nitrided layer on sample 34A2

Mean hardness of base metal was 326 HV10. Hardness values for modified layers by nitriding are presented in Table 3.

Microstructure of the steel composed of sorbite. The obtained modified layers consisted of the zone of compact γ' (Fe_4N) nitride, and the diffusion zone (Figs. 6-8), of the thicknesses given in Table 4.

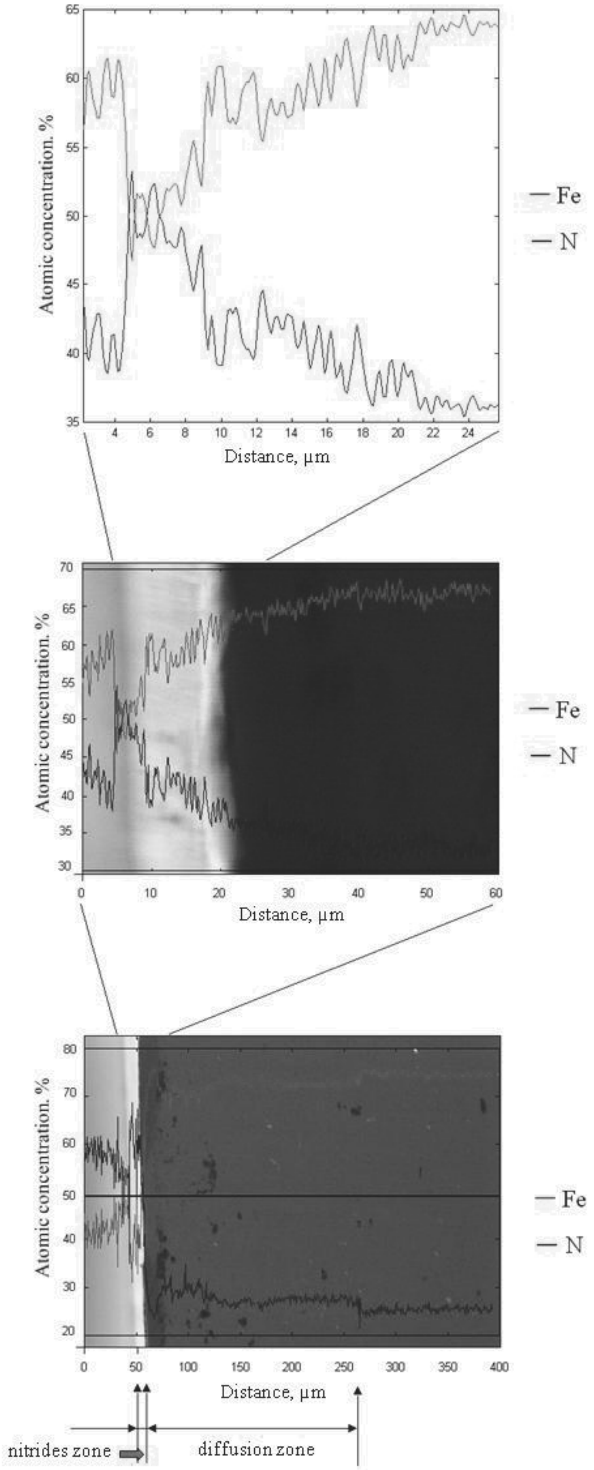


Fig. 5. AES line profiles of chemical composition (nitrogen and iron) with SEM view of nitrided layer on sample 34A2

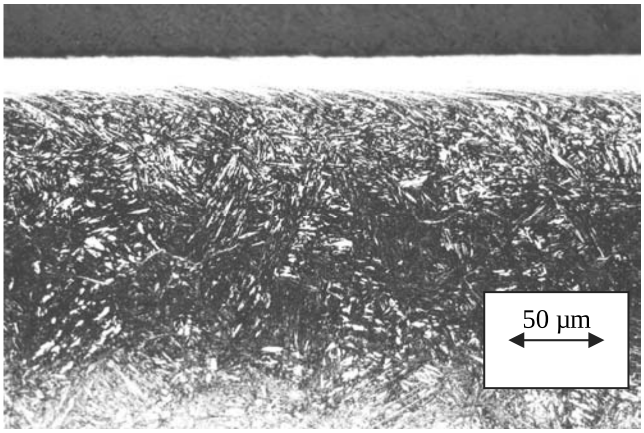


Fig. 6. Microstructure of plasma nitrided layer. Sample 34A1. Compact nitride and diffusion zones. Nital etched

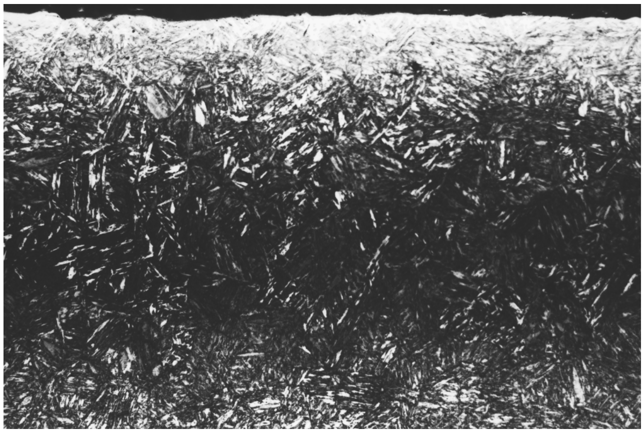


Fig. 7. Microstructure of plasma nitrided layer. Sample 34A2. Compact nitride and diffusion zones. Nital etched

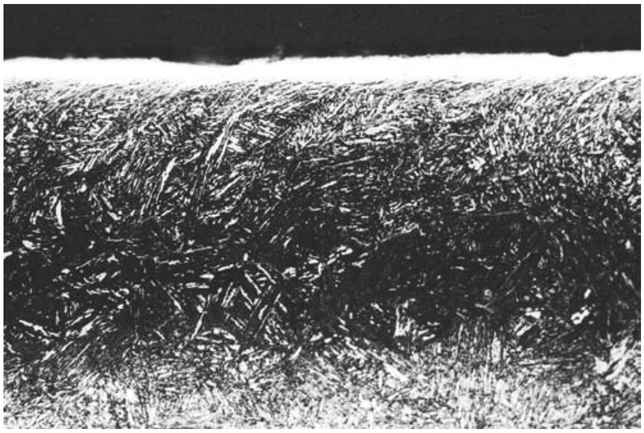
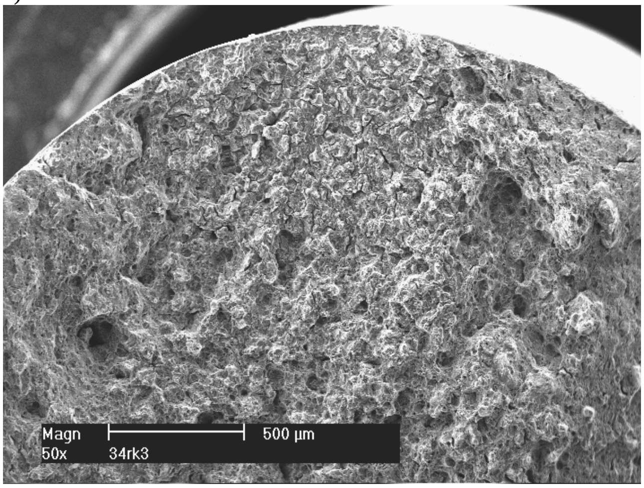


Fig. 8. Microstructure of plasma nitrided layer. Sample 34A3. Compact nitride and diffusion zones. Nital etched

a)



b)

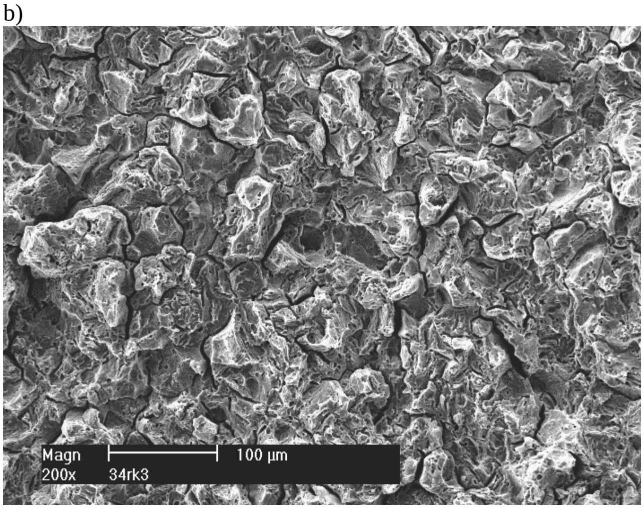


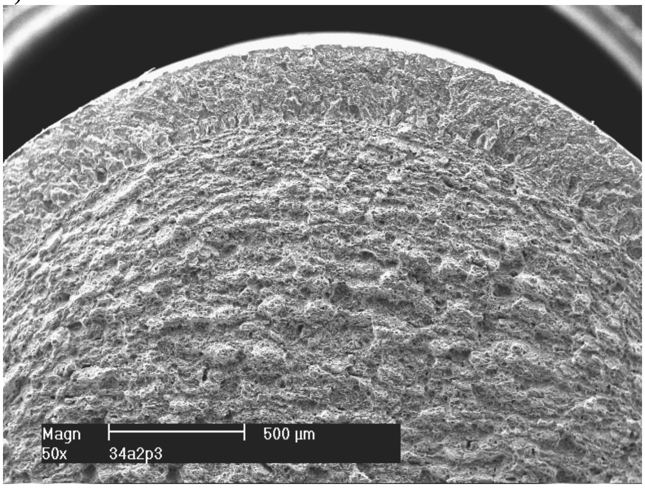
Fig.9. SEM images of fracture surface of 34R sample after SSRT tested in acid solution under cathodic polarisation. Magnification: a) 50x, b) 200x

Table 6.
Relative values of plasticity hydrogen degradation parameters of 34CrAlNi7-10 steel and its various nitrided layers

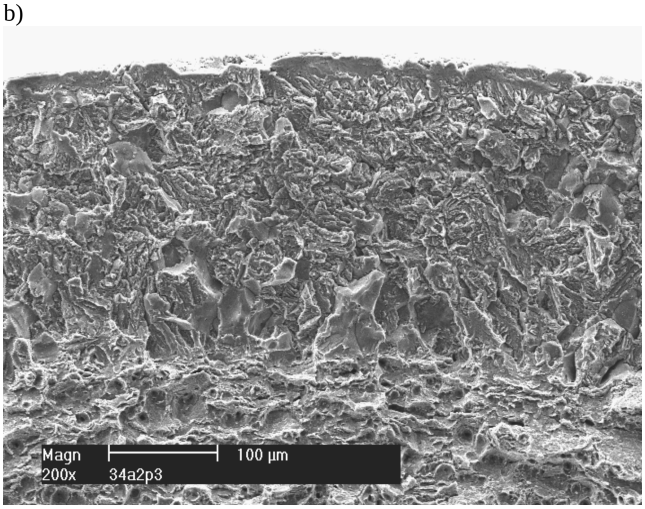
Sample	Elongation %	Reduction in area, %	Fracture energy %	Tensile strength %
34A1	33.8	37.3	23.5	93.8
34A2	34.8	42.2	24.5	91.1
34A3	27.4	27.1	16.9	85.7
34R	71.8	20.1	70.0	99.6

A1, A2, A3 – various surface treatments; 34R – base metal without nitrided layer

a)



b)



c)

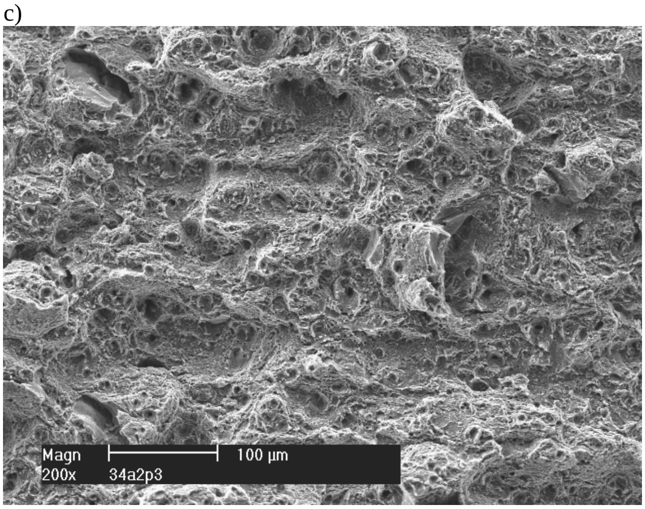


Fig. 10. SEM images of fracture surface of 34A2 sample after SSRT tested in air. a) macroscopic view, b) modified layer, c) core of base metal

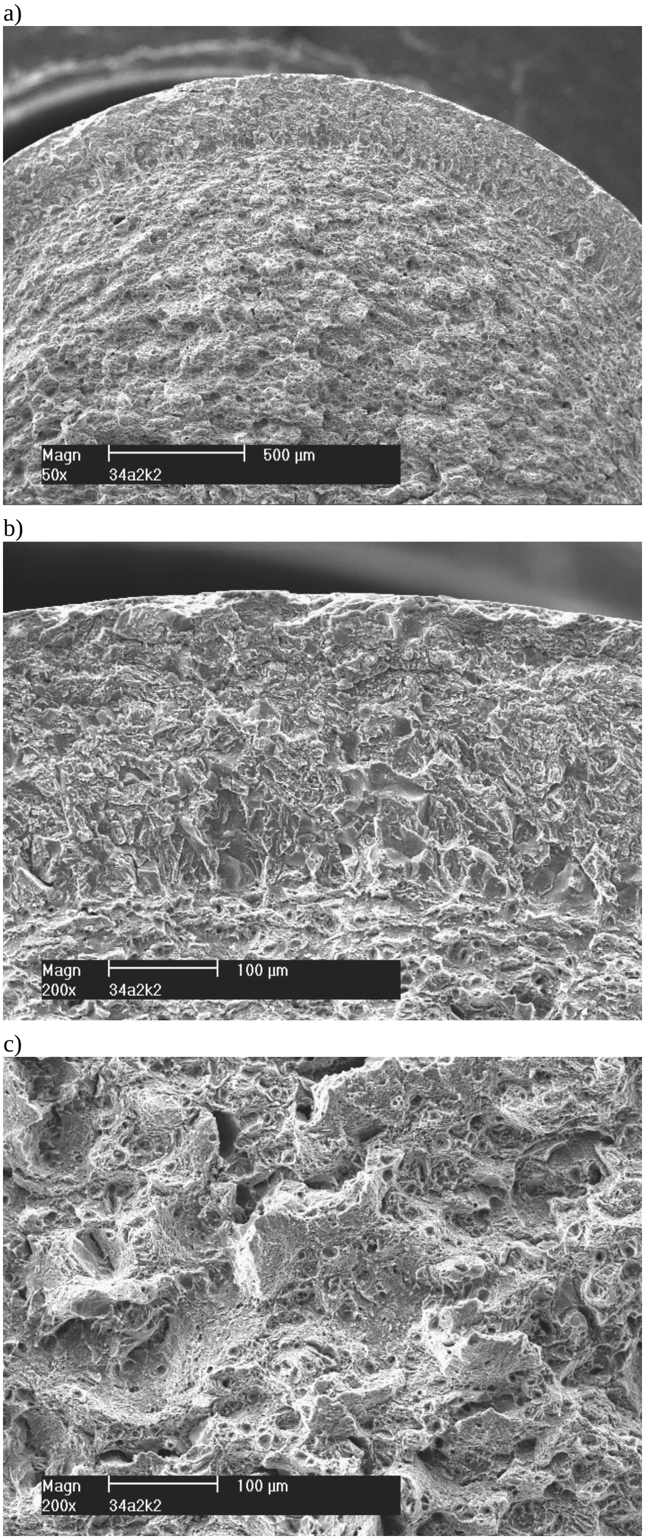


Fig. 11. SEM images of fracture surface of 34A2 sample after SSRT tested in acid solution under cathodic polarisation. a) macroscopic view, b) modified layer, c) core of base metal

Elongation, reduction in area, fracture energy and tensile strength obtained from SSRT were chosen as measures of hydrogen degradation (Table 5). Then, relative parameters, determined as the ratio of the appropriate value measured in air to that measured in acid solution, were calculated (Table 6). It is known from literature that reduction in area is the most sensitive to hydrogen degradation among mechanical properties [4].

All tested samples revealed susceptibility to hydrogen degradation under hydrogenation. Samples with nitrided layer have lower lost of reduction in are than base metal samples. In the case of elongation the base metal has lower lost of plasticity. The nitrided layer established in standard atmosphere 30% H_2 and 70% N_2 has the highest resistance to hydrogen degradation evaluated in SSRT test.

Under the increasing load and hydrogen generating environments plasma nitrided layers are effective barriers to hydrogen entry into a bulk of steel, and additionally increased plasticity of nitrided layers with absorbed hydrogen was observed.

Fractographic observations of failed base metal samples tested in acid solution under cathodic polarisation revealed intergranular and cleavage transgranular fracture mode (Fig 9). Fracture composed of ductile and quasi-cleavage mode in the core of nitrided samples tested both in air and acid solution under cathodic polarisation (Figs. 10-11) is an evidence of protective action of nitrided layers against hydrogen diffusion into a bulk of steel.

4. Conclusions

- Under the increasing load and hydrogen generating environments plasma nitrided layers are effective barriers to hydrogen entry into structural steel,
- Increased plasticity of nitrided layers with absorbed hydrogen was observed,
- Plasma nitriding may prevent hydrogen charging of machines and vehicles parts in hydrogen generating environments, and thus decreasing susceptibility to hydrogen embrittlement.

Acknowledgements

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