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Effect of plasma nitrided layers on low-alloy steel on its hydrogen degradation

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Properties

ABSTRACT

Purpose: 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. Slow-strain rate tensile test (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 are 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 nitided 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 was observed.

Keywords: Crack resistance; Plasma assisted nitriding; Hydrogen embrittlement

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 [1-6].

A number of failures due to hydrogen have been reported, e.g. of car engines parts [7], and ship engines [8]. 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 [7].

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 [9].

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 [10,11].

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 [9].

2. Materials and experimental procedure

The constructional nitriding steel grade 34CrAlNi7-10 according to PN-EN 10085 [12] was used. The round bar was quenched at 880°C, and tempered at 650°C with air cooling at the mill. The chemical composition of the tested steel is given in Table 1.

Mechanical properties obtained from a tensile test for the steel according to the certificate of material are presented in Table 2.

Hardness of base metal measured according to PN-EN 6507-1 [13] was 317 HV10.

Nitriding was done in the various gas atmospheres (Table 3), at the glow discharge at temperature 560°C for 6 hrs. Various contents of hydrogen in atmospheres was chosen to obtain different initial hydrogen concentration in nitrided layers.
Microstructures of the steel plate and nitrided layers were examined with the use of the optical microscope. Microstructure of the steel composed of sorbite. The obtained modified layers consisted of the zone of compact γ' nitrides, and the diffusion zone (Fig. 1), of the thicknesses given in Table 3.

In order to estimate the degree of hydrogen degradation of tested steels and its modified layers, slow strain rate test (SSRT) along with PN-EN ISO 7539-7 [14] was conducted 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.

Elongation, reduction in area, fracture energy and tensile strength were chosen as measures of hydrogen degradation (Table 4). Then, relative plasticity parameters, determined as the ratio of the appropriate value measured in air to that measured in acid solution, were calculated and presented in Table 5.

Fractographic observations of failed samples revealed mixed fracture mode composed of ductile and quasicleavage fracture in the core of nitrided samples tested in acid solution under cathodic polarisation (Fig. 2). This is a evidence of protective action of nitrided layers against hydrogen diffusion into a bulk of metal.

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	0.35	0.28	0.56	0.005	0.001	1.64	0.27	0.96	1.04	0.05

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.
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
34	base metal - as received	-	-
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

Table 4.
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]
34A1K	2.2	3.1	12	890
34A1P	6.5	8.3	51	949
34A2K	2.3	3.5	13	874
34A2P	6.6	8.3	53	959
34A3K	2.0	3.5	10	851
34A3P	7.3	12.9	59	993
34RK	8.9	12.6	72	969
34RP	12.4	62.7	103	972

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

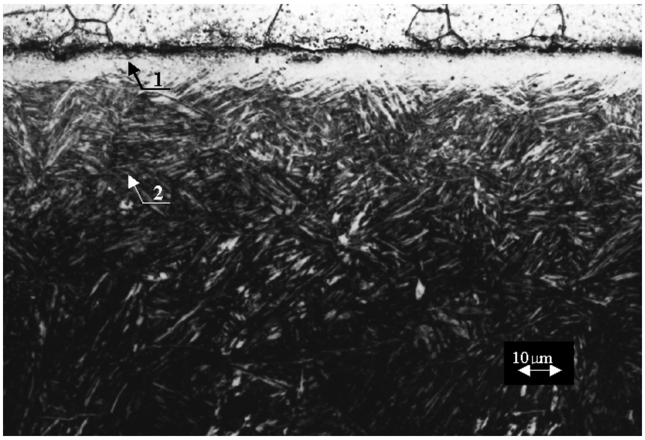


Fig. 1. Microstructure of plasma nitrided layer on 34CrAlNi7-10 steel. Sample 34A1. 1 – compact nitride zone; 2 – diffusion zone. Nital etching

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

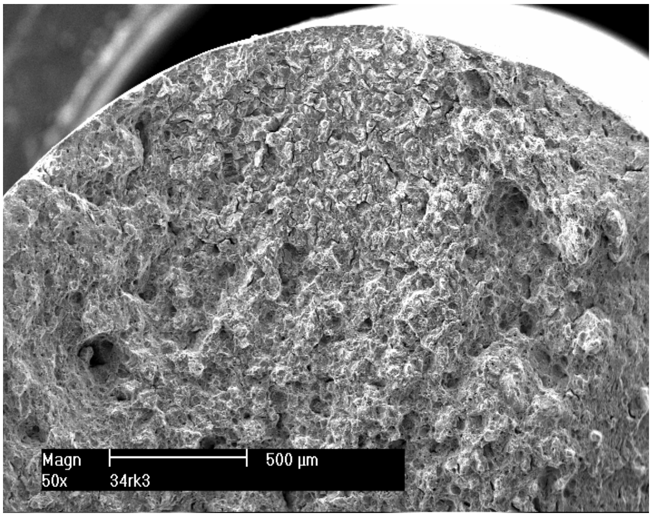
Sample	Elongation [%]	Reduction in area [%]
34A1	33.8	37.3
34A2	34.8	42.2
34A3	27.4	27.1
34R	71.8	20.1

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

3. Discussion

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.
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.

a/



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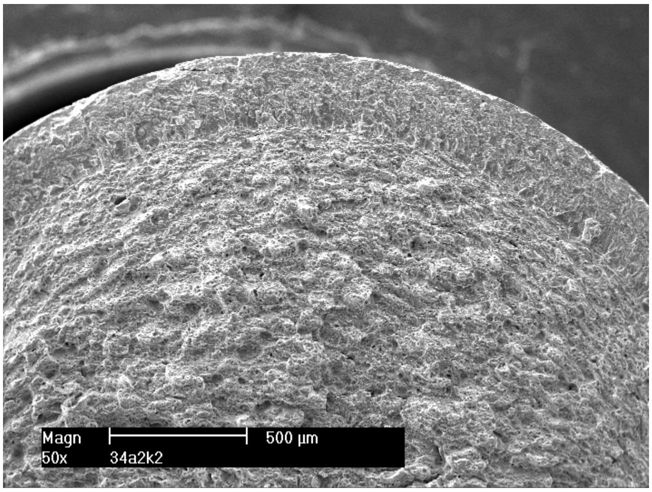

Fig. 2. SEM images of fracture surface of SSRT samples tested in acid solution under cathodic polarisation. a/ base metal b/ sample with A2 nitrided layer.

4. Conclusions

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

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