



Behaviour of nitrified layers subjected to influence of hydrogen

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ABSTRACT

Purpose: of this paper is evaluation of behaviour of plasma nitrified layers subjected to influence of internal and external hydrogen. Properties of nitrified layers like: hydrogen permeation and trapping, fracture mode, and plasticity were examined.

Design/methodology/approach: Structural low-alloy steel was nitrified at glow discharge in the gas mixture of various N₂, H₂, and Ar content. Samples with nitrified layers were subjected to cathodic hydrogen charging in acid solution simulating the aged engine oil hydrogenating environment. The effect of the nitrified 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. Slow strain rate test (SSRT) on samples with and without nitrified layers was carried out in hydrogen generating environment. After SSRT fracture mode and plasticity of nitrified layers were examined with SEM.

Findings: In the presence of the not defected compact nitride layer, no hydrogen permeation through the steel has been stated under the experimental conditions. Influence of hydrogen content in working atmosphere, i.e. internal hydrogen, was found. Absorbed hydrogen, i.e. external hydrogen, was accumulated within this layer.

Research limitations/implications: There is no possibility to perform direct observations of exact mechanism of hydrogen-assisted cracking so far. Further research should be taken to reveal the exact mechanism of increased plasticity of nitrified layer with absorbed hydrogen.

Practical implications: Plasma nitrified layers are effective barriers to hydrogen entry into structural steel utilised in aggressive environments, which is especially important in the case of possible hydrogen charging of exploited steel.

Originality/value: 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. Evidences of a likely increased plasticity of nitrified layers with absorbed hydrogen was observed.

Keywords: Corrosion; Plasma nitriding; Hydrogen permeation and uptake; Hydrogen embrittlement

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PROPERTIES

1. Introduction

High-strength steels may exhibit severe loss of ductility, toughness and strength due to hydrogen embrittlement (HE), resulting in sudden fracture or delayed failure. The susceptibility of steels to HE increases with tensile strength. The embrittlement can be caused by either external or internal hydrogen. Hydrogen can be introduced into the metal either during fabrication (e.g. cleaning, pickling, electroplating, welding) or in service (cathodic protection reactions, corrosion reactions), and also as a result of friction and wear [1].

The most common HE mechanisms are the high-pressure bubble formation, reduction in surface energy (adsorption mechanism), reduction in the lattice cohesive force (decohesion mechanism), hydrogen interaction with dislocations, and hydride formation.

In high-strength steels with yield strength over 1000 MPa, the effect of internal hydrogen supersaturation is significant. Internal HE by the mechanism of high-pressure bubble formation might be extremely severe due to the ease of cavity (microcrack) growth. Degradation is most severe under static loads or at low strain rates, where high internal hydrogen pressures can be maintained within the cavity or microcrack. Since hydrogen interacts with the high-strength martensitic structure, fractographic evidence of hydrogen degradation by internal pressure formation often exists. Isolated areas are observed of either intergranular or transgranular brittle fracture. These areas are surrounded by areas exhibiting microvoid coalescence (dimpled) or quasi-cleavage fracture modes. In principal, the presence of hydrogen may also lead to the appearance of 'hairlines' on the facets of some grains, or to a change in the size of microvoids.

Hydrogen need not be present in concentrations above the solid-solution solubility limit to embrittle martensitic and ferritic steels. Both structures can be strongly degraded by relatively low concentrations of hydrogen originating either from the bulk of the alloy or from a hydrogen-containing environment. At low concentration of hydrogen, the exact mechanism of embrittlement is often difficult to establish. The fracture surfaces of smooth and notched tensile specimens often exhibit a brittle-to-ductile transition failure. At the region in contact with hydrogen, fracture is generally intergranular, occurring by interface separation of the grain-boundaries [2].

Hydrogen degrades properties of steel under condition where cracking proceeds by all microstructural modes, including: ductile fracture, quasicleavage, transgranular cleavage, and brittle intergranular fracture [3].

Hydrogen can degrade the mechanical properties and fracture behavior of most structural alloys. Furthermore, even relatively low concentrations of hydrogen can lead to failure if hydrogen is trapped around structural defects and local concentrations exceed a critical value.

Although, hydrogen also has some positive effects on metals properties. Some beneficial effects of hydrogen on the formability, microstructure and properties of materials can be found. Several current and potential applications of hydrogen for enhancing the production and processing of materials are as follows: thermohydrogen processing (THP) and forming of refractory alloys, processing of rare earth-transition metal magnets by hydrogen decrepitation (HD) and hydrogenation-

decomposition-desorption-recombination (HDDR), hydrogen-induced amorphization (HIA) and microstructural refinement. Hydrogen is found to enhance the formability, microstructure and properties of a large variety of materials, including steels, Ti-based alloys and metal matrix composites, refractory metals and alloys, rare earth-transition metal alloys, metallic glasses.

Thermohydrogen processing (THP) is the use of hydrogen as a temporary alloying element, which strongly enhance the formability and the final microstructure and properties of titanium-based alloys. In this process, hydrogen is added to the titanium alloy by holding the material at a relatively high temperature in a hydrogen environment, heat treatment or thermomechanical processing performed, and the hydrogen removed by a vacuum or inert gas anneal. The presence of the hydrogen allows the titanium alloy to be:

- a) processed at lower stresses and/or lower temperatures,
- b) heat-treated to produce novel microstructures with enhanced mechanical properties [4, 5].

Plasma or ion nitriding is a thermo-chemical process operating in the glow discharge regime for production of case hardened surface layers on ferrous and non-ferrous metals. This process is now widely used for improving hardness and wear resistance of engineering components. Apart from the beneficial mechanical properties, nitrided layers on low-alloy steels exhibit improved corrosion resistance. However, in the case of high-chromium steels, the corrosion resistance of the diffusion zones is lowered due to the precipitation of CrN and the resulting chromium depletion of the matrix.

Hydrogen can enter the metal also as a result of friction and wear, as it has been mentioned above. This sources of hydrogen may be of particular importance for nitrided and other modified surfaces, because they are designed particularly for exploitation under exposure to friction and wear [6].

Introduction of nitrogen into surface layers of iron and steel strongly affects the ingress of hydrogen into the metal. The nitriding strongly decreased the absorption of hydrogen by impeding both its entry (surface effect) and transport (barrier effect) in the modified layer on iron. Brass et al. [7] attributed the effect of nitrogen to a lower solubility of hydrogen in the implanted layer, and its slower transport due to trapping at the nitride precipitates. Fassini et al. [8] also observed a lower hydrogen diffusivity in the nitrogen implanted layer although they found the solubility of hydrogen in this layer to be considerably greater than that in the substrate. The latter finding is in contradiction to the observation of Brass et al. and Zakroczymski et al. [9].

Zakroczymski et al. [6] investigated permeation and absorption of hydrogen in Armco iron with modified layers by plasma nitriding-base treatments (nitriding, nitrocarburizing, sulphur-oxy-nitriding and oxy-nitrocarburizing). Hydrogen diffusivity and concentration were studied by the electrochemical permeation technique. The authors distinguishing a compound and a diffusion sublayers in the nitrided layer.

The mobility (diffusivity) of hydrogen in the diffusion layer is lower than that in the unchanged iron by about one order of magnitude, whereas in the compound layer it is lower by about three orders of magnitude.

In spite of the very low hydrogen diffusivity in the compound layer its participation in the hindrance of the hydrogen transport

through the nitrated layer is not decisive, because this layer is relatively thin. The diffusion layer, with higher diffusivity but also being much thicker, impede the hydrogen transport by two or three times as much. It appears that the compound layers control the penetration of hydrogen mainly by affecting its entry. This may be concluded from the results indicating that the hydrogen permeation rate is different for the various as-treated surface layers, but it is nearly the same for all the modified layers after removal of the compound layers. Moreover, the permeation rate through the modified membranes without the compound layers is only a little lower than that through the unmodified layers. This demonstrates that with respect to hydrogen entry the diffusion layers behave similarly to iron. The effect of the compound layers on hydrogen entry is manifested both in the short-term and long-term charging.

2. Iron nitrides

The storage capacity of hydrogen in metals and alloys is determined by chemical interactions between the metal and hydrogen atoms, as well as by the type, number and size of the potential interstitial sites for hydrogen. The most common materials for hydrogen storage are metals and alloys that are based on transition metals. In most of these materials hydrogen tends to occupy tetrahedral interstitial sites. Iron nitrides also have possibilities to dissolve huge amount of hydrogen.

The iron nitride γ' -Fe₄N is the iron-richest stable phase in the binary system iron-nitrogen (Fig. 1) [10]. This and other binary iron nitride phases such as ϵ -Fe₃N and ξ -Fe₂N have particular impact as hard, corrosion and wear resistant surface layers of iron and steel components.

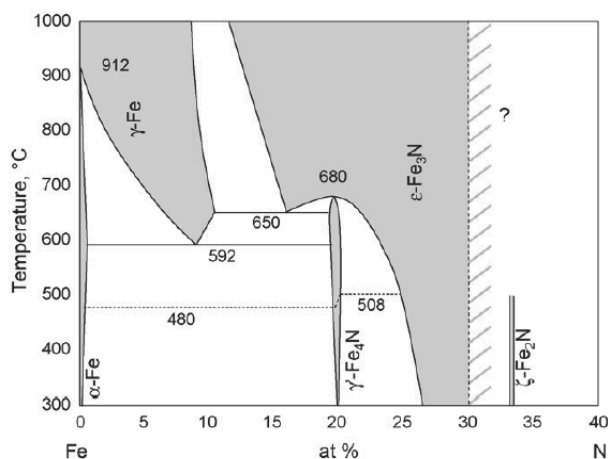


Fig. 1. Phase diagram of the binary system Fe-N [10]

The γ' -Fe₄N phase (roaldite) has cubic crystalline structure, with the Fe-sublattice arranged in a face centered cubic (fcc) structure and nitrogen atoms occupying the body-centered position one out of four (Fig. 2). As indicated in the phase diagram (Fig. 1), this phase has a narrow composition range around 20 at.% N. The lattice parameter is 3.795 Å. This nitride is

stable at temperatures below 450°C. As all the other iron nitrides, γ' -Fe₄N is a metallic conductor and is metastable with respect to decomposition in Fe+N₂. The decomposition is limited by kinetic barriers.

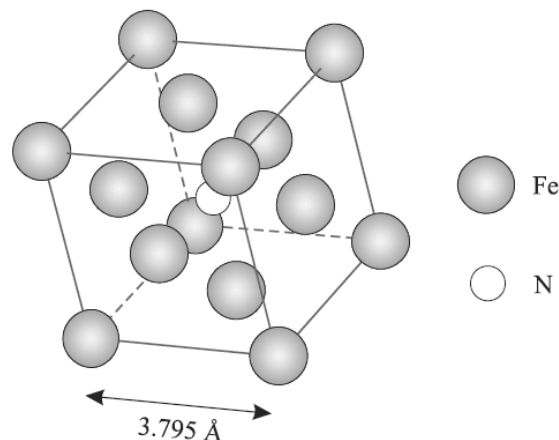


Fig. 2. Crystalline structure of γ' -Fe₄N

3. Hydrogen in metals

Hydrogen is the lightest element with an atomic structure of one proton and a single electron and is, in its natural state, a diatomic molecular gas, H₂. The diatomic hydrogen molecule is too large to enter the surface of a solid metal, and must be dissociated into single atoms to readily cross the gas/metal interface. Two mechanisms for this are known, electrochemical and chemisorption. If the metal is molten, molecular hydrogen can dissolve readily, but dissociates once in solution and can be retained as a mono-atomic solute on solidification.

The electrochemical evolution of atomic hydrogen is part of the cathode reaction in either a corrosion cell or other process. As corrosion is essentially an electrochemical mechanism, both are sufficiently similar to be considered identical for the purpose of hydrogen evolution, and take the form:



Most of the hydrogen atoms thus formed quickly combine to form diatomic gaseous hydrogen, but a portion of it enter the metal surface and remain as individual atoms in solution.

Chemisorption dissociation of hydrogen is a rather different mechanism. As a hydrogen molecule approaches a metal surface, weak van Der Waal's forces begin to act upon it, drawing it closer. An interstitial solute, hydrogen remains in the mono-atomic form and is relatively mobile, even at ambient temperatures. However, to maintain such a mobile atom as an interstitial solute presents problems in metals, although crystalline, are far from perfect, and lattice defects present areas where the lattice strain induced by the solute hydrogen atom is reduced, and thus will act as hydrogen traps.

If the trap site is a vacancy, the presence of a single hydrogen atom will lower the lattice strain due to the vacancy, and the hydrogen atom becomes a substitutional, rather than an interstitial solute.

If the trap is a line defect, there may well accumulate a string of hydrogen atoms along the defect. The presence of a string of individual hydrogen atoms would not immobilise a dislocation, although it would increase the applied stress needed for movement.

However, if two adjacent atoms on a line defect recombine to form molecular hydrogen, the applied stress required to cause movement becomes much greater, effectively pinning the dislocation at that point.

Since dislocation movement is the underlying process to plastic flow, the ductility of the material is reduced and the probability of brittle failure increased by the presence of hydrogen. In this context, interfaces such as grain boundaries or second phases should be considered as dislocation arrays, and thus are likely to accumulate solute hydrogen, quite possibly in molecular form, embrittling the interface [11, 12].

In addition to reducing the mobility of dislocations, solute hydrogen can also react, either with the solvent metal to form a hydride, or with some other solute element to form a new phase. Iron at normal pressures and temperatures does not form hydrides. Hydrogen attacks ferritic steels by two distinct and different mechanisms. One at ambient temperature is known as "hydrogen embrittlement" or low temperature hydrogen attack (LTHA). The other is a high temperature phenomenon, at temperature above 200°C, known as "high temperature hydrogen attack" [13].

4. Low temperature hydrogen attack

Hydrogen induced damage describes any of a number of forms of degradation of metals caused by exposure to environments (liquid or gas) or processes which cause absorption of hydrogen into the material.

A component or structure can pick up hydrogen in various stages of its life. This begins in the metallurgical process, because the hydrogen solubility in the molten metal is much higher than in the solid condition (Fig. 3). This hydrogen loading is reversible to a great extent, because it is caused mainly by the storage of the hydrogen in the interstitial positions of the lattice. Irreversible hydrogen degradation only occurs if the hydrogen can effuse or if it can accumulate as gas in the hollow spaces. This type of hydrogen damage is of importance in welding practice in the form of cold cracks. This type of damage is also produced during casting as fish eyes (or fakes) [13].

Low temperature hydrogen attack (LTHA) is described as a three-step process. Firstly, hydrogen is introduced into the metal, via electrochemical charging or via gaseous absorption. In some cases, hydrogen may be introduced in the lattice prior to stressing (e.g. during fabrication). This situation is commonly referred to as internal hydrogen embrittlement. Secondly, atomic hydrogen is transported through the metal lattice, increasing its concentration in the tensile-stressed surroundings of the crack tip due to gradients in the chemical-potential. In the absence of a crack, atomic hydrogen may be transported to an initiation location.

Thirdly, the combined action of stress and hydrogen concentration leads to failure of the metal in an embrittled zone.

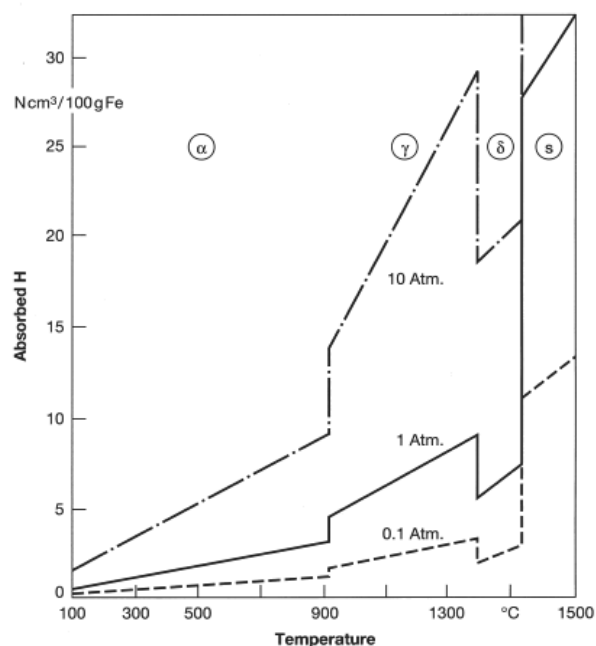


Fig. 3. Solubility of hydrogen in iron as a function of temperature and pressure [13]

When hydrogen enter a material it can affect the mechanical performance of materials in several ways [14, 15]:

1. The formation of internal hydrogen blisters or blister-like cracks at internal delaminations or at sites of nonmetallic inclusions in low strength materials. These internal cracks may propagate by a process called hydrogen-induced cracking (HIC) or hydrogen blistering. No external stress is usually required to induce this type of cracking. In some cases, however, these blister cracks may take on an alignment caused by the presence of residual or applied tensile stresses.
2. The loss of ductility in a tensile test as reflected by a decreased reduction in area which is generally called hydrogen embrittlement (HE). The process of hydrogen-assisted microvoid coalesce can occur during plastic straining. This can reduce the ductility of normally ductile engineering materials while not inducing brittle cracking.
3. Delayed cracking at stress below the yield strength - hydrogen stress cracking (HSC.)
4. An extreme case of ductility loss from hydrogen is the brittle fracture of susceptible materials under applied or residual tensile stresses. This form of cracking, which typically changes from transgranular to intergranular with increasing yield strength and other processing variables, is normally referred to as hydrogen embrittlement cracking (HEC).
5. Brittle failure by cracking under the combined action of tensile stress and corrosion in the presence of water and hydrogen sulfide - sulfide stress corrosion cracking (SSCC).

With respect to HE and HEC, most susceptible materials show a major effect of stress concentration (i.e., notches) and level of stress intensity and tend to produce failures in a relative short time (i.e., <1000 h). Therefore, tension, notched, and precracked specimens and fracture methods are widely utilized in the evaluation for HEC.

5. Mechanisms of hydrogen degradation of metals

The numerous mechanisms have been proposed to explain LTHA phenomena, which reflect the many ways in which hydrogen was observed to interact with metals [13-17].

Internal Pressure Model

Precipitation of molecular hydrogen at internal defects (nonmetallic inclusions, voids) develops high internal pressure. This pressure is added to applied stress and thus lowers the apparent fracture stress. The mechanism was initially proposed by Zapffe and Sims.

Hydrogen Induced Decohesion Model

Dissolved hydrogen (lattice hydrogen) reduces the cohesive strength of the lattice, i.e. interatomic bonds and thereby promotes decohesion. Mechanism proposed by Troiano and modified by Oriani. There is absence of direct experimental measurements supporting this mechanism. There are also a number of "open issues" relating to the observational base on which the decohesion model is founded. The most important is that fractography of transgranular fracture resulting from decohesion should be cleavage fracture, whereas most observations can be classified as quasi-cleavage.

Surface Energy Model (Adsorption Model)

Adsorption of hydrogen reduces the surface energy required to form a crack propagation and thus lowering of fracture stress. This model was first proposed by Petch. There are no direct experimental observation and reliable calculations that hydrogen can reduce surface energy

Adsorption Induced Localised Slip Model

Adsorption of environmental hydrogen atoms at crack tip results in weakening of interatomic bonds facilitating dislocation injection from a crack tip and then crack growth by slip and formation of microvoids. Mechanism proposed by Lynch.

Hydrogen Enhanced Localized Plasticity (HELP) Model

Absorption of hydrogen and its solid solution increases the ease of dislocation motion or generation, or both. Mechanism first proposed by Beachem and developed by Birnbaum et al. In many cases, the definition of hydrogen-related fracture as a "brittle fracture" is based on loss of macroscopic ductility (e.g. decrease of reduction in area and elongation). But careful fractographic examinations with high resolution technique shows, that hydrogen embrittlement of steel is associated with locally enhanced plasticity at the crack tip. Distribution of hydrogen can be highly nonuniform under an applied stress. Thus, locally the flow stress can be reduced, resulting in localized deformation that leads to

highly localized failure by ductile processes, while the macroscopic deformation remains small.

The mechanism of hydrogen enhanced localized plasticity (HELP) appears to be a viable one of the many suggestions for an explanation of the hydrogen related failures. Arguments in support of the HELP mechanism are based on experimental observations and theoretical calculations. High-resolution fractography of hydrogen embrittled metals, such as Ni and Fe, show extensive plastic deformation localized along the fracture surfaces. In-situ transmission electron microscope (TEM) observations of deformation and fracture of samples in environmental cell gave evidence that HELP model is a viable failure mechanism.

Corrosion Enhanced Plasticity (CEP) Model

This model takes into account the generation of vacancies due to localized anodic dissolution and hydrogen evolution by cathodic reaction at the newly de-passivated crack tip. Thus, corrosion produces an enhanced localized plasticity. The activated dislocations along slip bands form pile-ups interacting with obstacles. The resulting high local stress can initiate cracking. Model was developed by Magnin et al. This model has application mainly to passive metals and alloys like stainless steels, nickel and its alloys.

Hydrogen Rich Phases Model

Formation of hydrogen rich phases - hydrides, whose mechanical properties differ from those of matrix. Cracking could proceed by the formation and cracking of brittle hydride near the crack tip. Model was generalized by Westlake. For iron it was found that no stable hydrides are formed up to hydrogen pressure of 2 GPa, so this model is not valid for steel hydrogen degradation.

6. Prevention of low temperature hydrogen attack

In order to prevent hydrogen degradation of components or structures, both the source of the hydrogen and the embrittlement mechanism must be known well. As important measures in the prevention of hydrogen damage, the following points should be taken into account [13]:

- material - selection of suitable material,
- medium (environment) - it is not easy to influence, possibly by the addition of inhibitors,
- design - avoid notches, slots and sharp transitions, avoid local plastic deformation.

Base solutions to LTHA are as follows:

1. Internal cracking or blistering:
 - use of steel with low levels of impurities (i.e. sulfur and phosphorus),
 - modifying environment to reduce hydrogen charging,
 - use of surface coatings (possible application of nitride layers) and effective inhibitors.
2. Hydrogen embrittlement:
 - use of lower strength (hardness) or high resistance alloys,
 - careful selection of materials and plating systems,
 - heat treatment to remove absorbed hydrogen.

7. Nitride layers as a prevention against hydrogen degradation

Susceptibility of 34CrAlNi7-10 steel and samples with various plasma nitrided layers have been evaluated under monotonically increasing load in 0.005 M H₂SO₄ solution. 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) [18-20].

7.1. Material and experimental procedure

The structural nitriding steel grade 34CrAlNi7-10 according to PN-EN 10085 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.

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.

Corrosion resistance of the studied materials was estimated in electrochemical measurements, using the minicell placed on the studied modified surfaces.

Electrochemical measurements of the hydrogen permeation rate through the membranes (0.4 mm in thickness) were done using the double cell with the use of Devanathan-Stachursky test. 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/cm² (Fig. 2a) and (2) single cathodic polarization by the current density 10 mA/cm².

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.

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 on round smooth specimens 4 mm in diameter made according to PN-EN ISO 7539-4. The gauge length was 50 mm. Tests were performed at ambient temperature either in dry air or in 0.005 M H₂SO₄ 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/cm². 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.

7.2. Description of achieved results

The XPS investigations were performed to characterise only the diffusion zone of nitrided layers. The shape of nitrogen N1s line obtained in diffusion zone of nitrided layer of sample 34A2 was found. The binding energy determined for N1s line corresponds to formation of Fe₄N.

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' (Fe₄N) nitride, and the diffusion zone (Fig. 4), of the thicknesses given in Table 4.

Distribution of nitrogen and iron concentration obtained by AES in surface layer on sample 34A2 is presented in Fig. 5.

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 5).

Table 6 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/cm². 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/cm² and higher,
- 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/cm² and higher.

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	

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

Codes of specimens	34	34A1	34A2	34A3
i_{Corr} , mA/cm ²	0.290	0.150	0.0003	0.180
E_{OC} , mV (Hg/HgSO ₄)	-1200	-925	-180	-1020

Table 6.
The steady state values of hydrogen permeation current density J_{∞} ($\mu\text{A}/\text{cm}^2$) 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	34A2	34A3
0.1	step by step	2.7	0	0	0
0.2		2.8	0	0	0
0.5		3.7	0.3	0	0
1		4.3	0.32	0	0
2		4.8	0.6	0	0
5	single	5.3	22	0	5.9
10		12.2	39	0	13
10		11	0	0	0

Table 7.

Concentration of irreversibly trapped hydrogen, as measured by vacuum extraction (V_H) and as recalculated for 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
34A2	1.2	120
34A3	2.6	135

Table 8.

Mean values of hydrogen degradation parameters of 34CrAlNi7-10 steel and samples with 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

Table 9.

Relative values of plasticity hydrogen degradation parameters of 34CrAlNi7-10 steel and samples with 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

The lack of hydrogen permeation through material does not mean any hydrogen ingress into the metal. As revealed the vacuum extraction measurements (Table 7) 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. Assuming the accumulation of all the measured hydrogen (V_H) within the compact nitride zones of the mean thicknesses given in Table 4, the hydrogen concentration in those zones (V_H^*) has been recalculated.

The presented above unexpected results of the hydrogen permeation measurements (Table 6) 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.

As seen in Table 5, 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. 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.

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 deeper layers of the metals, and the hydrogen permeation started to be detected at the certain applied polarization (Table 6). 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 7), 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 6).

Elongation, reduction in area, fracture energy and tensile strength obtained from SSRT were chosen as measures of hydrogen degradation (Table 8). Then, relative parameters, determined as the ratio of the appropriate value measured in air to that measured in acid solution, were calculated (Table 9). It is known from literature that reduction in area is the most sensitive to hydrogen degradation among mechanical properties [2].

All tested samples revealed susceptibility to hydrogen degradation under hydrogenation. Samples with nitrided layer have lower lost of relative reduction in area 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.

Plasma nitriding strongly decreases the absorption of hydrogen by impeding 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 diffusivities in the diffusion zone.

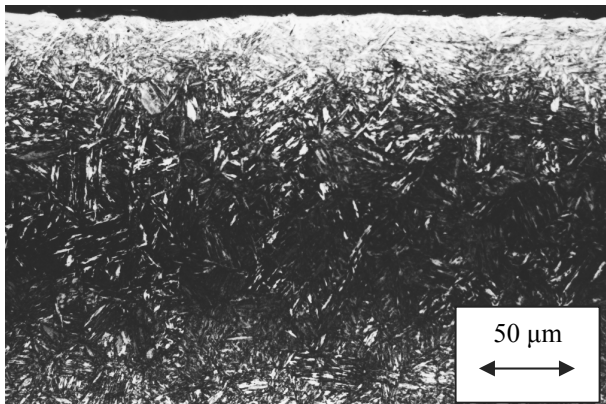


Fig. 4. Microstructure of plasma nitrided layer. Sample 34A2. Compact nitride and diffusion zones. Nital etched

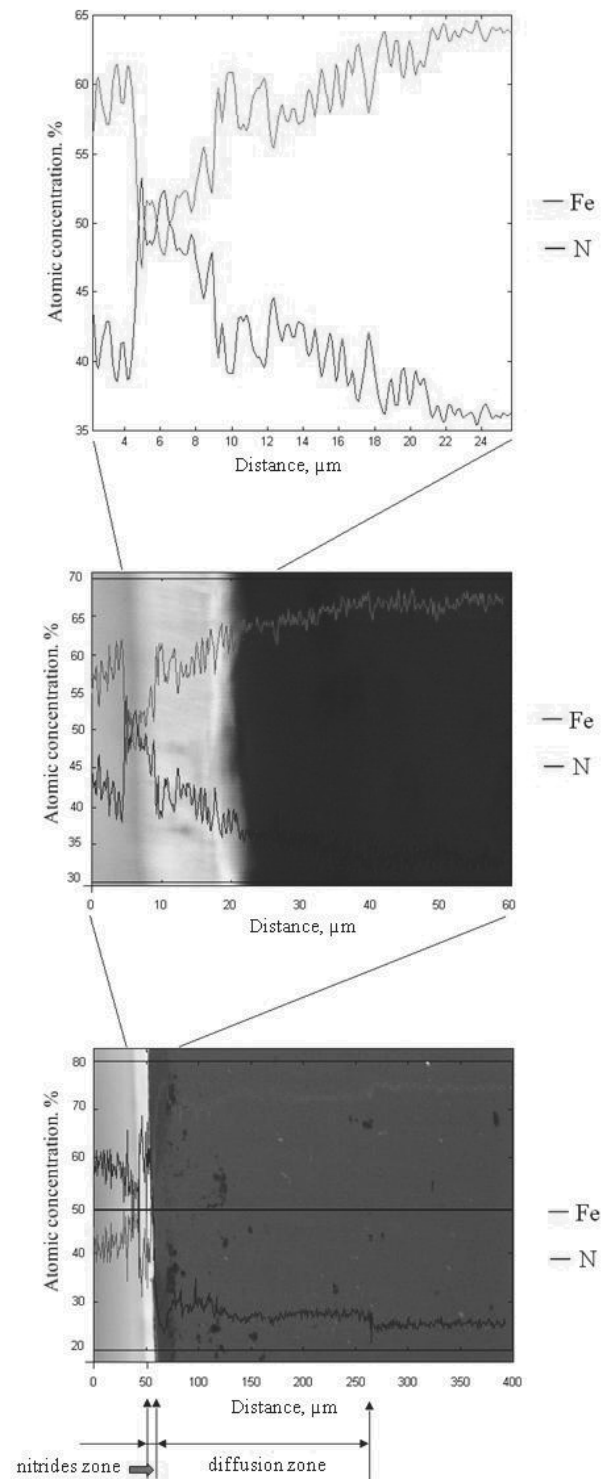


Fig. 5. AES line profiles of chemical composition (nitrogen and iron) with SEM view of nitrided layer on sample 34A2

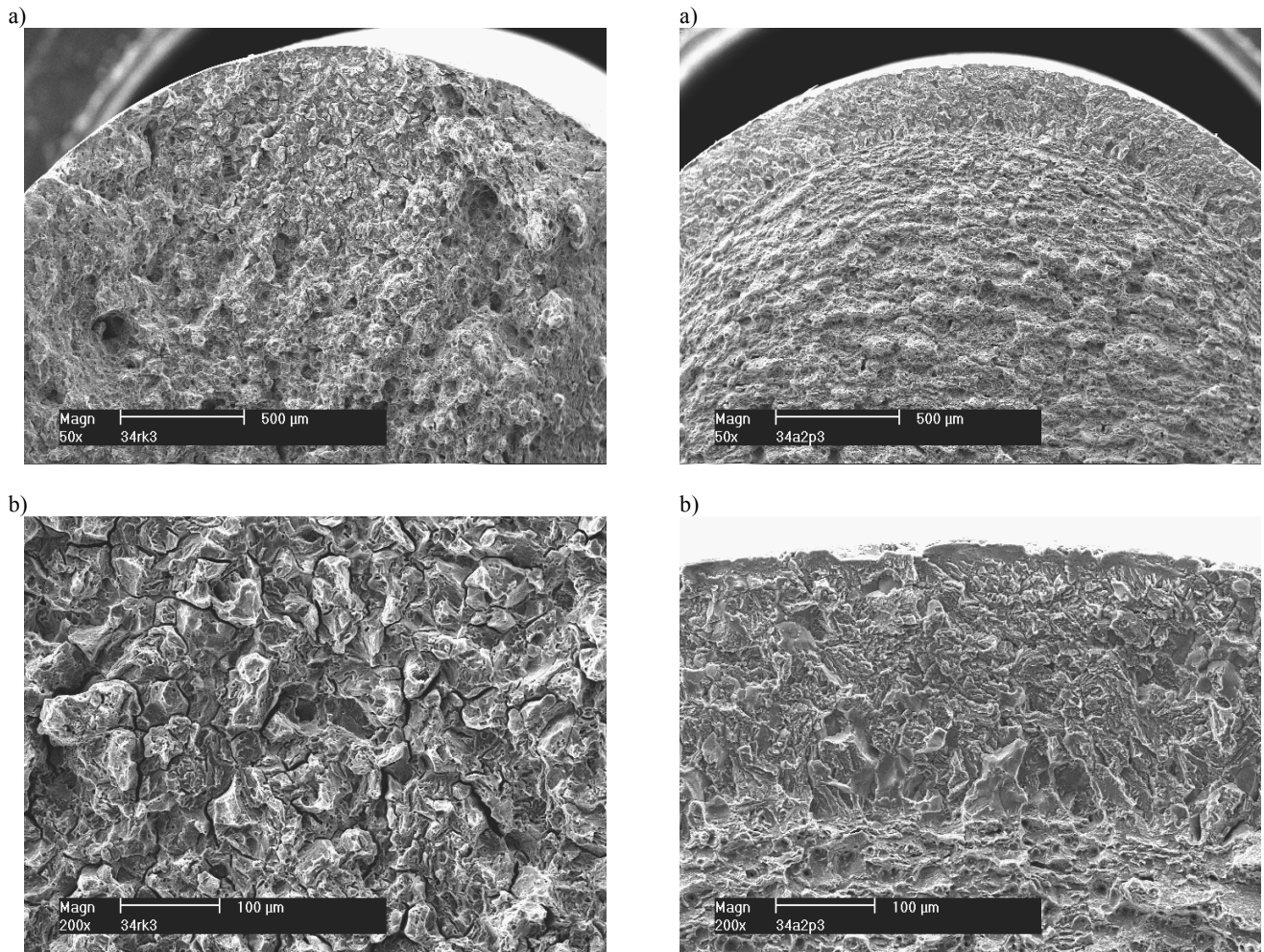


Fig. 6. SEM images of fracture surface of 34R sample after SSRT tested in acid solution under cathodic polarisation. Magnification: a) 50x b) 200x

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 behaviour of steels with the modified surface should be thoroughly recognized.

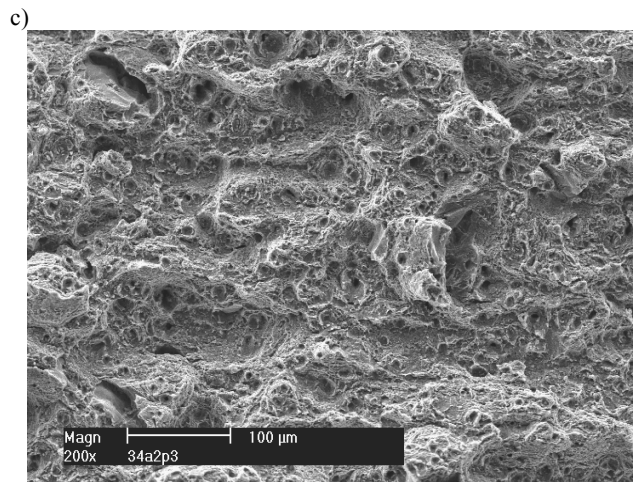


Fig. 7. SEM images of fracture surface of 34A2 sample after SSRT tested in air: a) macroscopic view b) modified layer c) core of base metal

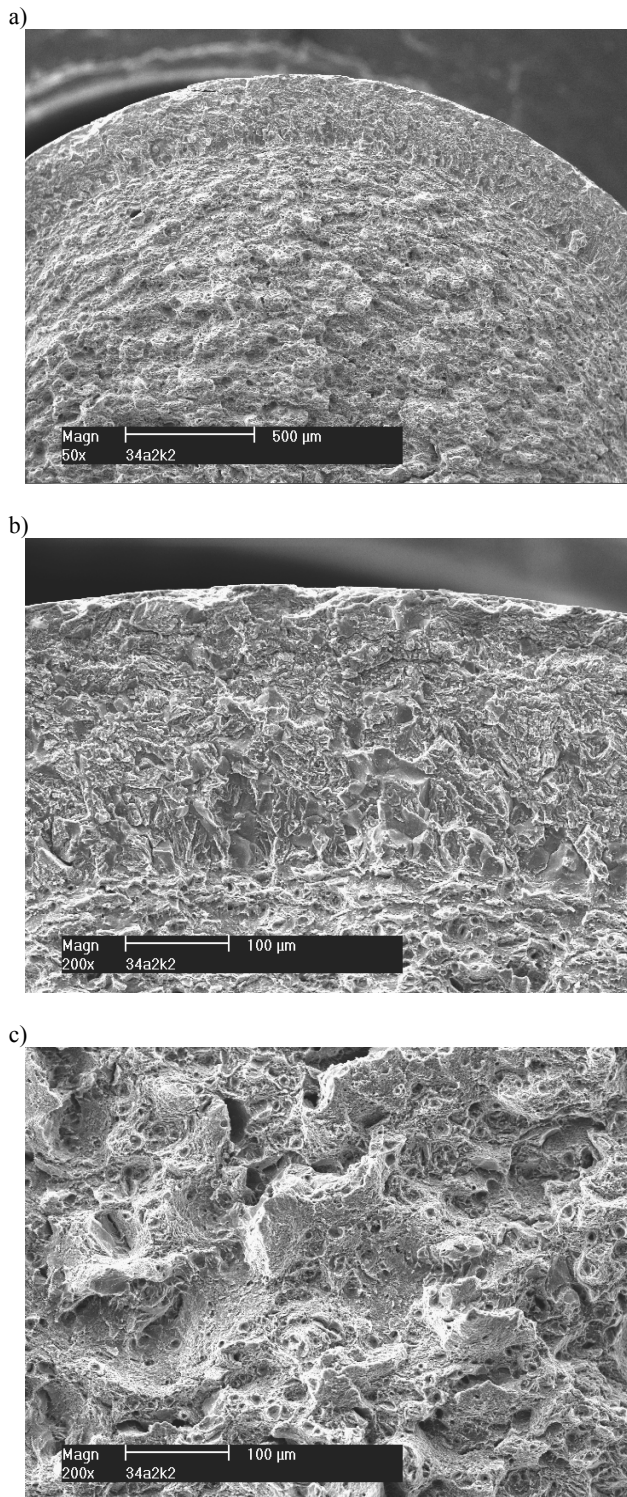


Fig. 8. SEM images of fracture surface of 34A2 sample after SSRT tested in acid solution under cathodic polarization: a) macroscopic view b) modified layer c) core of base metal

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 hindrance of hydrogen transport since this zone is relatively thin. The diffusion zone impedes the hydrogen transport much stronger.

Under the increasing load and hydrogen generating environments plasma nitrided layers are effective barriers to hydrogen entry into a bulk of steel, which was confirmed by the electrochemical permeation Devanathan-Stachursky test.

Samples with nitrided layers and absorbed external hydrogen revealed no increase of hydrogen embrittlement comparing with the same samples without dissolved hydrogen. Evidences of a likely increased plasticity of nitrided layers with absorbed hydrogen was observed. These evidences are:

- values of reduction in area at the same level,
- fractographic observations, i.e. lower percentage of cleavage fracture area.

Fractographic observations of failed base metal samples tested in acid solution under cathodic polarisation revealed intergranular and cleavage transgranular fracture mode (Fig. 6). 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. 7-8) is an evidence of protective action of nitrided layers against hydrogen diffusion into a bulk of steel.

8. 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,
- Under the increasing load and hydrogen generating environments plasma nitrided layers are effective barriers to hydrogen entry into structural steel,
- The nitrided layer established in standard atmosphere 30% H₂ and 70% N₂ has the highest resistance to hydrogen degradation evaluated in SSRT test,
- Evidences of a likely 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.

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