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Interaction between hydrogen and a nitrided layer

J. Ćwiek*
Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland
* Corresponding author: E-mail address: janusz.cwiek@polsl.pl

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Properties

ABSTRACT

Purpose: of this paper is to reveal the influence of nitrided layer on 34CrAlNi7-10 steel to its susceptibility to hydrogen degradation. Investigation was carried out with the use of slow strain tensile rate test (SSRT).

Design/methodology/approach: 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. In order to estimate the degree of hydrogen degradation SSRT test was conducted on round smooth specimens 4 mm in diameter. 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 polarization with constant current densities: 0.1; 1; 5 and 10 mA/cm^2. Fracture surfaces after SSRT test were examined with scanning electron microscope (SEM) to reveal a mode and mechanism of cracking.

Findings: Plasma nitrided layers are effective barriers to hydrogen entry into structural steel which decreases susceptibility of steel to hydrogen degradation. Hydrogen is mainly accumulated in a compact nitrides zone. Evidences of no increase in brittleness of nitrided layers with absorbed hydrogen were observed.

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 nitrided layer with absorbed hydrogen.

Practical implications: Plasma nitrided layers are effective barriers to hydrogen entry into structural steel utilized in aggressive environments, which could be potential sources of hydrogen charging of exploited steels.

Originality/value: Plasma assisted nitriding provides the formation of thin compact nitride zone which protects high-strength steels against corrosion and hydrogen degradation. Evidences of no increase in brittleness of nitrided layers with absorbed hydrogen were observed.

Keywords: Corrosion; Hydrogen degradation; Nitrided layer; Hydrogen permeation and uptake

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1. Introduction

Hydrogen is the most abundant element in the universe, and it is very important for our technical civilization. Hydrogen is believed to be a possible future energy source and it is very possible that a "hydrogen economy" will be realized soon. If so, large-scale production, storage, transportation and use of hydrogen will become necessary. Hydrogen is a safe and clean fuel gas of high calorific value. It is mainly derived from water in unlimited quantities by an electrolysis. It does not pollute environment since it produces only water as a combustion product, then it may be recovered for reuse. Another source of hydrogen are fossil-based hydrocarbons. Natural and synthetic hydrocarbon fuels are widely used and are the largest source of energy available to mankind today. Hydrogen is the lightest element with an atomic structure of one proton and a single electron and in natural state is a di-atomic molecular gas H_2. In molecular form hydrogen it is too large to diffuse into solid metals and can not easily cross the gas-metal interface. If the metal is in liquid state, molecular hydrogen can dissociate and dissolve in molten metal. Then, it can be retained as a interstitial solution under solidification. Two mechanisms of molecular hydrogen dissociation into single atoms are known - electrochemical and chemisorption [1].

Hydrogen can be introduced into metals during the making process, fabrication or service [2-4]. 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. 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” [5].

Some specific types of hydrogen induced damage to metals and alloys could be distinguished [6-8]:

- hydrogen embrittlement (HE) - the loss of ductility in a tensile test mainly reflected by a decrease of elongation (Fig. 1) and reduction in area,
- the formation of internal hydrogen blisters (Fig. 2) or blister-like cracks at internal delaminations or at sites of nonmetallic inclusions. 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,
- delayed cracking at stress below the yield strength - hydrogen stress cracking (HSC). Cold cracks in welded joints are examples of this type of hydrogen degradation (Fig. 3),
- 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),
- cracking from hydride formation,
- advancement of stress corrosion cracking and corrosion-fatigue cracking.

Base solutions to various hydrogen degradation forms are as follows [5]:

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 of construction and plating systems.
   - heat treatment to remove absorbed hydrogen.
3. hydrogen attack at high temperature
   - selection of material (for steels, use of low and high alloy Cr-Mo steels; selected Cu alloys; non-ferrous alloys).
   - limit temperature and partial pressure H_2 (using of the Nelson Curves).

a)

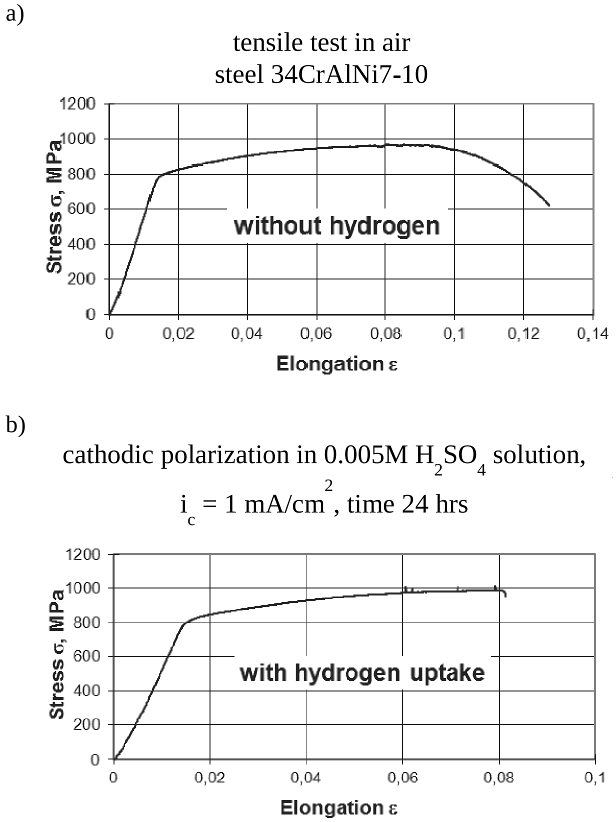


Fig. 1. Results of a tensile test for 34CrAlNi7-10 steel conducted: a) in air, b) in acid solution under cathodic polarization

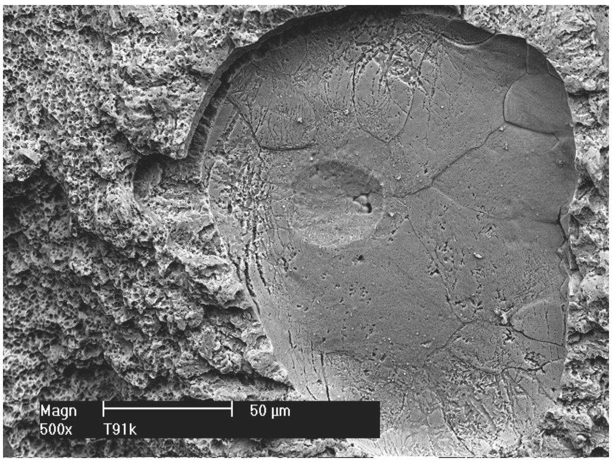


Fig. 2. The hydrogen blister in weld metal of HSLA steel S690Q

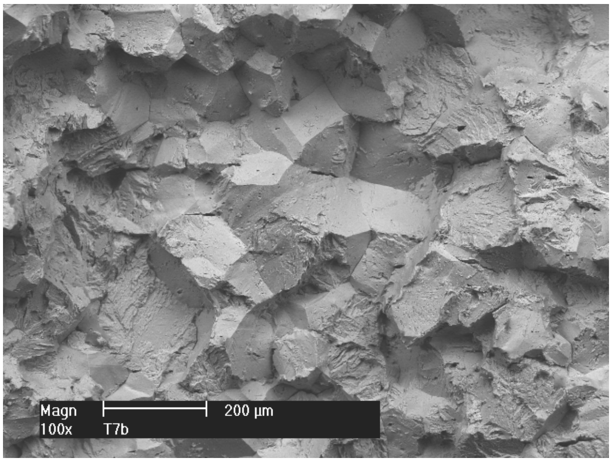


Fig. 3. Cold cracking in heat affected zone of HSLA steel S690Q

Nitrided layers strongly decrease 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 [9-12].

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 [13,14].

2. Materials

The structural nitriding steel grade 34CrAlNi7-10 according to PN-EN 10085 was used. Chemical composition of tested steel is presented in Table 1. The round bar ø 40 mm made of the steel 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.

Nitriding was done in the nitrogen-argon gas atmospheres with argon content of 30% at the glow discharge at temperature 540°C for 6 hrs.

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 layer was measured on surface of flat nitrided samples using 9.8 N load (1 kG), both according to PN-EN 6507-1. Mean hardness of base metal was 317 HV10. Hardness value for modified layer by nitriding was 1190 HV1.

Microstructure of the steel composed of tempered martensite (sorbite) (Fig. 4). The obtained modified layers consisted of the zone of a compact γ' (Fe_4N) nitride, and a diffusion zone (Fig. 5). Thickness of the compound zone was 6-8 µm, and of the diffusion zone 240-250 µm.

Presence of the Fe_4N nitride was confirmed by XRD (X-Ray Diffraction) technique. The diffraction pattern for the compact nitride zone is presented in Fig. 6.

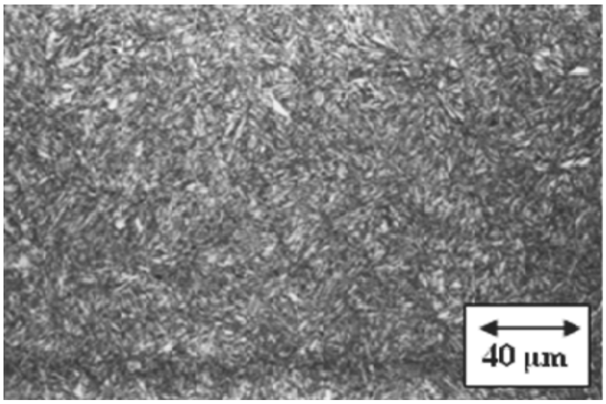
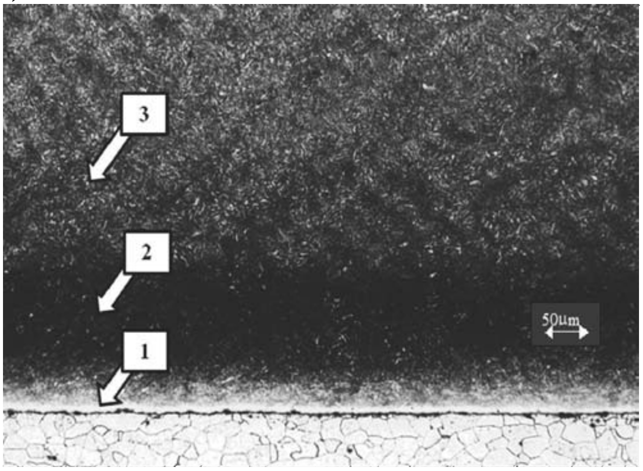


Fig. 4. Microstructure of 34CrAlNi7-10 steel. Nital etched. Light microscope

Table 1.
Results of chemical analysis of a bar ø 40 mm made of 34CrAlNi7-10 steel grade

Analysis	Elements concentration, wt.%									
	C	Si	Mn	P	S	Cr	Mo	Ni	Al	Cu
Ladle 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	0.35	0.28	0.56	0.005	0.001	1.64	0.27	0.96	1.04	0.05

a)



b)

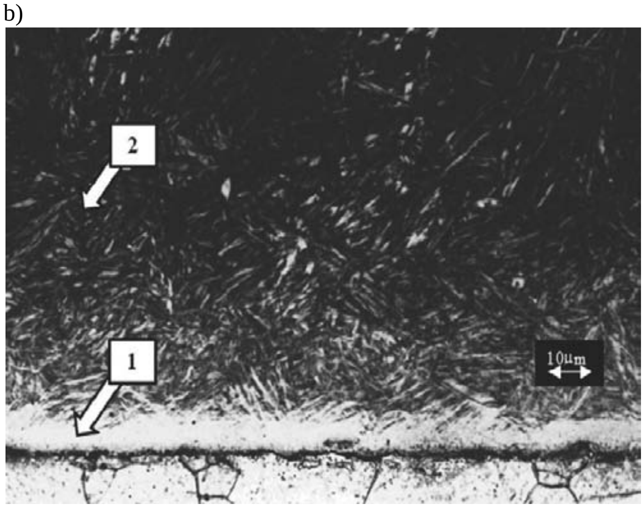


Fig. 5. Microstructure of the plasma nitrided surface layer on 34CrAlNi7-10 steel grade. Nital etched. Light microscope. a) 1-compound γ' nitride zone, 2-diffusion zone, 3-tempered martensite (sorbite), b) a part of Fig. 1a; 1-compound γ' nitride zone, 2-diffusion zone

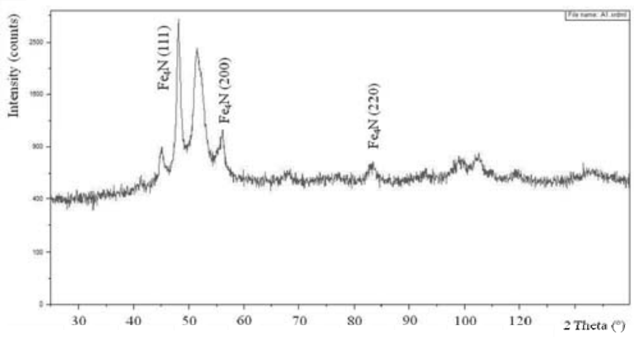


Fig. 6. The diffraction X-ray pattern for the compact nitride zone

3. Experimental procedures

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 (Fig. 7). 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 polarization with constant current densities: 0.1; 1; 5 and 10 mA/cm^2. During tests stress-strain curves were recorded on a personal computer. Three samples were used for each parameter. The SSRT machine is presented in Fig. 8.

Elongation (El), reduction in area (RA), fracture energy (E) and tensile strength (TS) obtained from SSRT were chosen as measures of hydrogen degradation. Then, relative parameters, determined as the percentage ratio of the appropriate value measured in acid solution to that measured in air, were calculated. It is known from literature that reduction in area is the most sensitive to hydrogen degradation among mechanical properties. Fracture surfaces after SSRT test were examined with scanning electron microscope (SEM) to reveal a mode and mechanism of cracking.

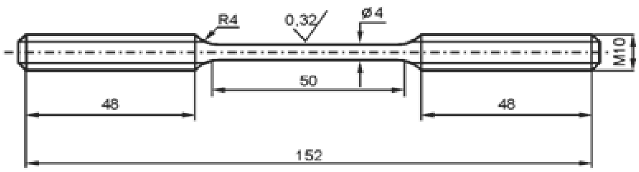


Fig. 7. The sample used for slow strain rate test

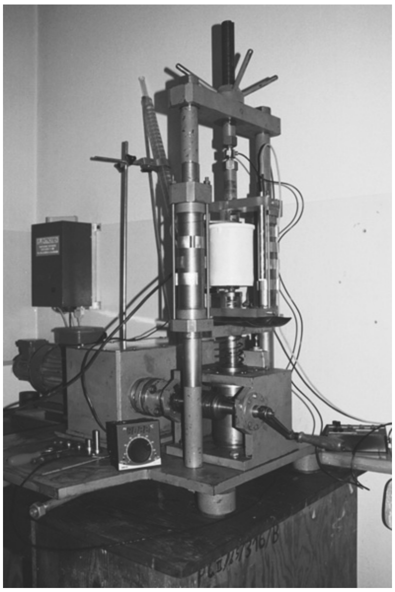


Fig. 8. The SSRT machine

4. Results and discussion

Results of the SSRT are presented in Table 2. It is seen from values obtained in air that there is loss of ductility due to presence of a nitride layer. It is obvious since nitrides are very brittle themselvs. Further decrease of ductility is due to hydrogen absorption. But the loss is lower for samples with a nitride layer, which is well seen for relative values of parameters presented in Figs. 9-11.

Table 2.
Mean values of the results of tensile SSRT performed in air, and in 0.01N H_2SO_4 under cathodic polarization

Samples	Current density mA/cm^2	El %	RA %	TS MPa	E MJ/m^3
base metal	air	10.8	69.8	958	87
	0.1	10.2	26.2	954	85
	1	7.4	13.7	964	59
	5	9.8	17.5	976	83
	10	10.5	17.5	967	87
with nitrided layer	air	3.0	14.4	953	21
	0.1	4.0	3.7	923	28
	1	3.9	3.7	932	27
	5	3.1	3.3	920	19
	10	2.4	2.5	871	12

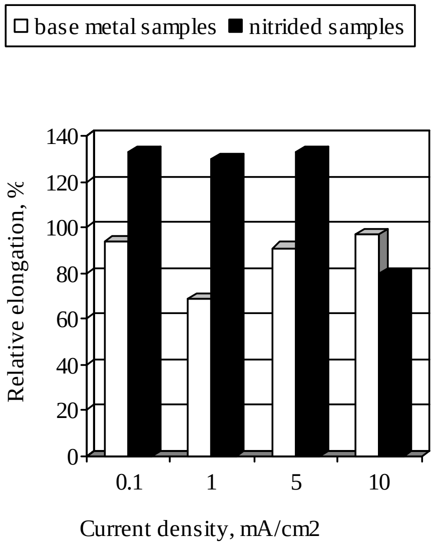


Fig. 9. Relative values of elongation vs. cathodic current density

Fractographic observations of SSRT samples are presented in Figs. 12-15. Base metal samples tested in air indicated ductile fracture mode - MVC (Micro Void Coalesced) with quasi-cleavage (Fig. 12). Observed base metal samples tested in acid solution under cathodic polarization (hydrogenated samples) revealed brittle fracture mode - intergranular with transgranular cleavage fracture (Fig. 13). Fracture of nitrided samples tested both in air, and acid solution under cathodic polarization revealed the same mode of fracture: a) trans granular cleavage in nitride layer, b) and ductile MVC with quasi-cleavage mode in the core of samples (Figs. 14-15). There is an evidence of protective action of nitrided layers against hydrogen diffusion into a bulk of steel. Susceptibility of steel to hydrogen embrittlement is reduced, and additionally no increase of brittleness of a nitrided layer was found. Compact nitride layer strongly decreases the absorption of hydrogen by impending both its entry and transport in the modified layer for low and medium carbon concentrations in low-alloy steels.

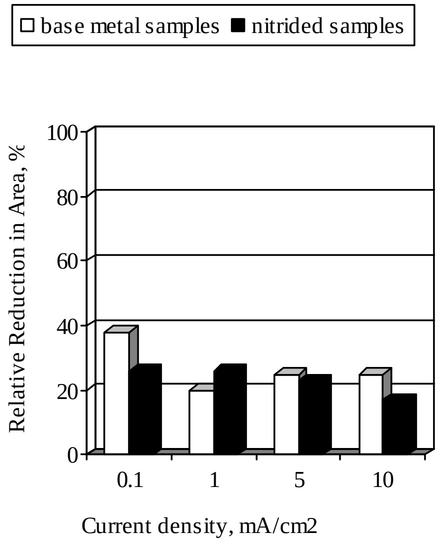


Fig. 10. Relative values of reduction in area vs. cathodic current density

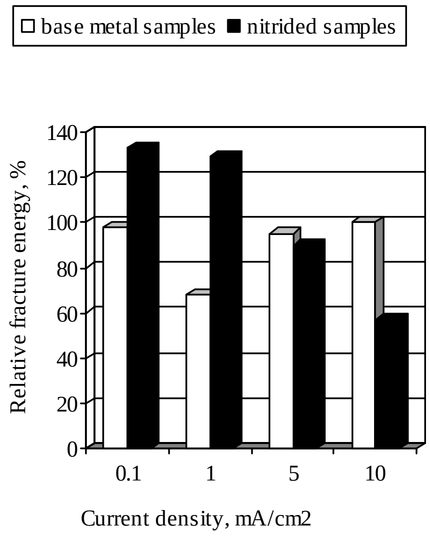


Fig. 11. Relative values of fracture energy vs. cathodic current density

a) b)

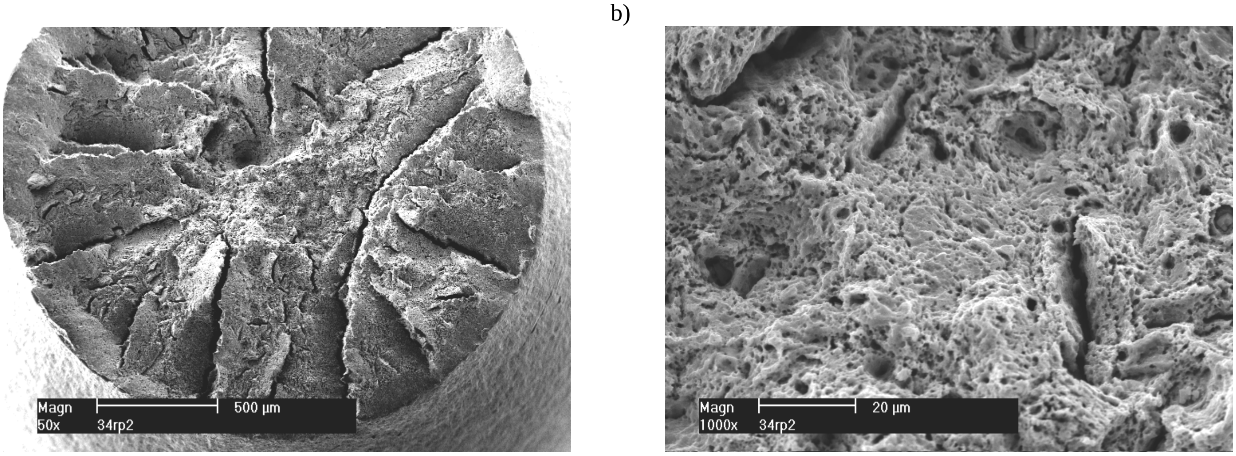


Fig. 12. SEM images of fracture surface of base metal sample after SSRT tested in air: a) macroscopic view, b) core of base metal

a) b)

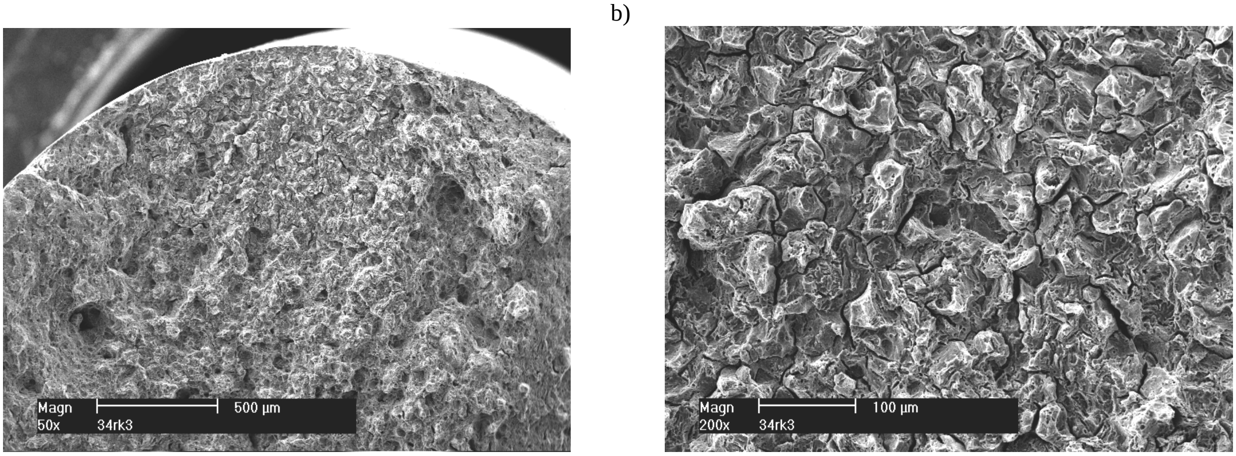


Fig. 13. SEM images of fracture surface of base metal sample after SSRT tested in acid solution under cathodic polarization: a) macroscopic view, b) core of base metal

Samples with nitrided layers and absorbed external hydrogen revealed no increase of embrittlement comparing with the same samples without dissolved hydrogen. Evidences of a likely increased plasticity of nitrided layers with absorbed hydrogen was observed and evidences are following [15-20]:

- relative values of parameters (elongation, reduction in area, and fracture energy) for nitride samples which are mainly higher than ones for base metal samples,
- lower percentage of cleavage fracture mode for nitride samples with absorbed hydrogen.

5. Conclusions

- Plasma nitrided layers are effective barriers to hydrogen entry into structural steel, which decreases susceptibility to hydrogen degradation.
- Hydrogen is mainly accumulated in a compact nitrides zone.
- Evidences of no increase in brittleness of nitrided layers with absorbed hydrogen were observed.

To prove the thesis that: „hydrogen increases plasticity of nitrided layers" following investigations should be undertaken:

- Nanoscale indentation tests (hardness and scratch-on),
- Precise measurement of hydrogen concentration in various zones of a nitrided layer,
- Evaluation of crystalline structure modification of Fe_4N nitride due to hydrogen,
- High-resolution fractographic observations of compound nitrided layers with and without hydrogen.

Acknowledgements

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a)
b)
c)

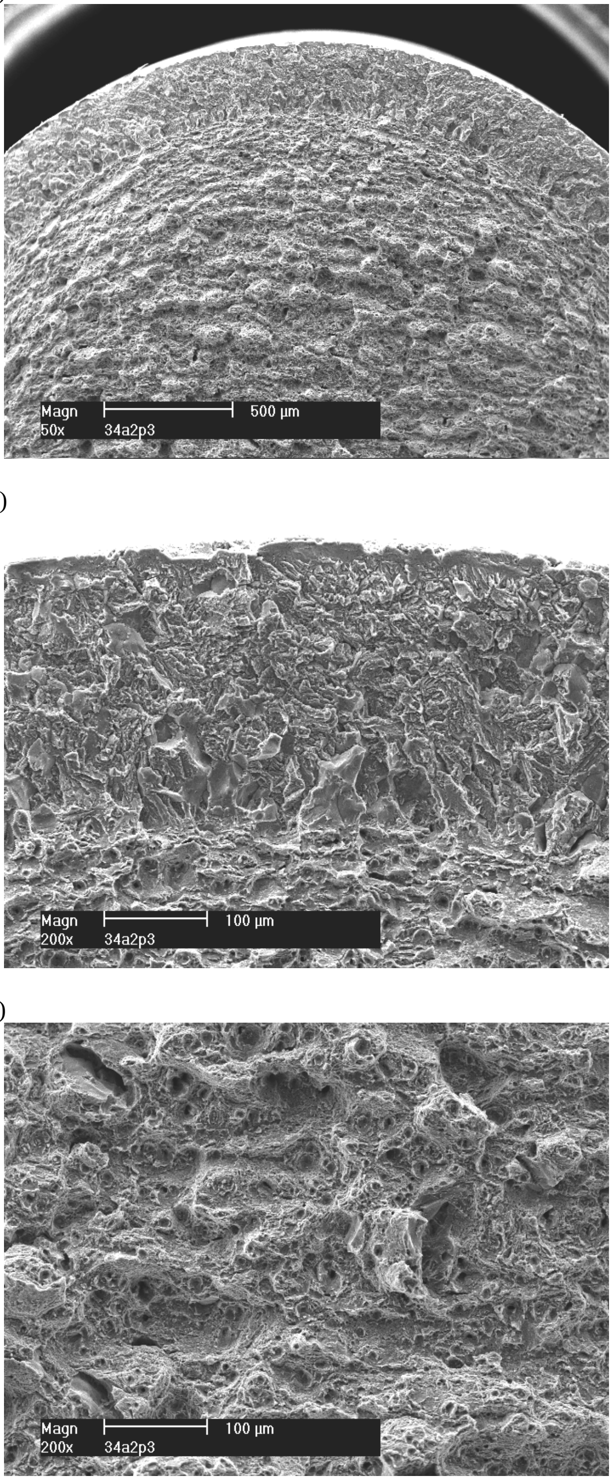

Fig. 14. SEM images of fracture surface of nitreided sample after SSRT tested in air: a) macroscopic view, b) modified layer, c) core of base metal

a)
b)
c)

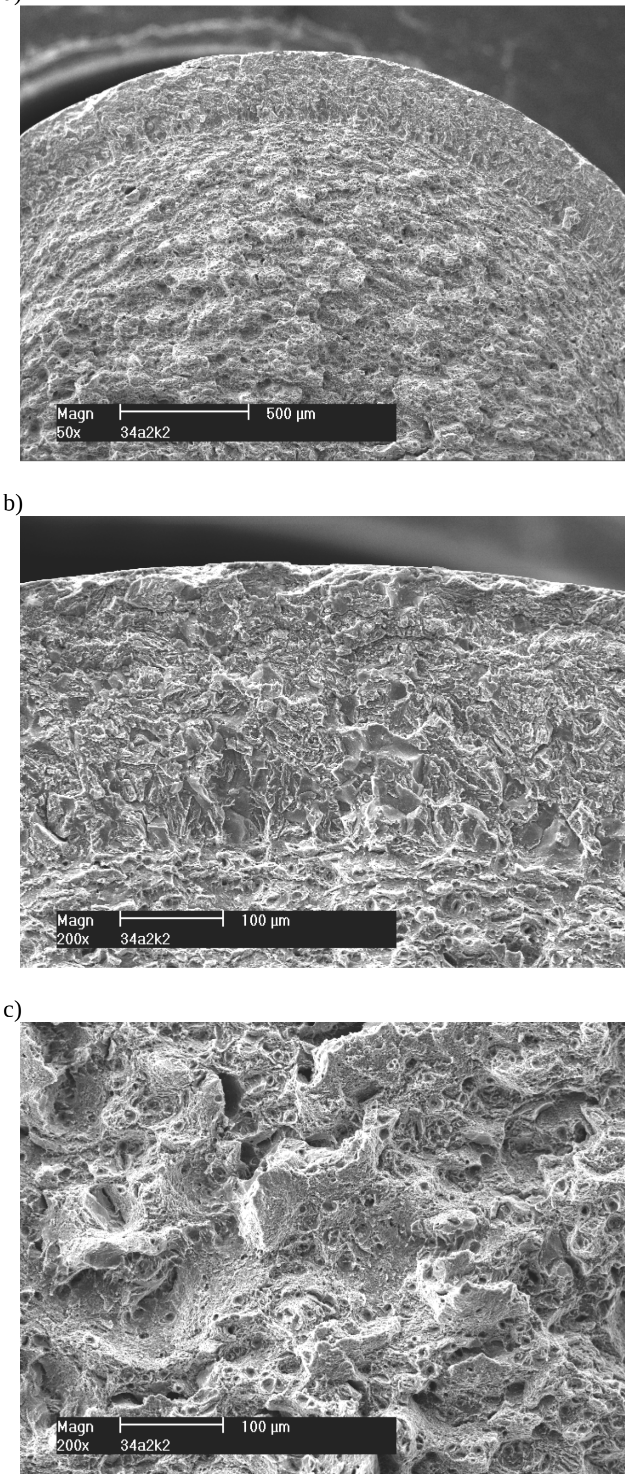

Fig. 15. SEM images of fracture surface of nitrided sample after SSRT tested in acid solution under cathodic polarization: a) macroscopic view, b) modified layer, c) core of base metal

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