

Andrzej Zieliński, Waldemar Serbiński

Gdańsk University of Technology,

Department of Materials Science and Engineering,

Gdańsk, Poland

RELATION BETWEEN STEEL MICROSTRUCTURE AND ITS PROPERTIES IN INERT AND AGGRESSIVE ENVIRONMENTS

ABSTRACT

Two Polish steels 26H2MF and 34HNM grade have been investigated. The steels have been subjected to different heat treatment. The microstructure examinations have shown various microstructure following heat treatment, from martensite and bainite to tempered martensite and sorbite. The degradation of fracture energy, elongation and reduction-in-area have been observed after Slow Strain Rate Tests performed in sulphuric acid solution at cathodic polarization between 0 and 100 mA/cm². The degradation has been accompanied by passage from ductile to brittle cleavage and quasi-cleavage cracking. The observed degradation has been proved to be in good accordance with microstructure of steels.

Key words: steels, mechanical properties, hydrogen degradation, brittle cracking

INTRODUCTION

The Polish 26H2MF and 34HNM steels have been used for constructing the fuel separators in the diesel ship engines. During operation of engines the cases of rapid fatigue failure, sometimes after a few weeks, have been observed [1-3].

The fuel installations operate at hard conditions which favour their sudden failure because of joint action of stresses and aggressive environment: vibration, elevated temperatures, high pressure, presence of aggressive gas and liquid media [4]. The used fuels always contain sulphur and water: first element is a constituent of hydrocarbonates and organic acids, and water is absorbed during fuel storage and transport. At 130-150°C temperature, typical of fuel separation process, electrochemical and chemical corrosion may then occur, following an appearance of sulphuric and sulphurous acids, organic acids, and possible hydrogen evolution and absorption.

Recently, the hypothesis has been put, that heavy fuel that is a mixture of aromatic hydrocarbonates may to some extent be degraded on the iron and steel surface having catalytic properties. Such reaction of fuel decomposition may in consequence lead again to a hydrogen appearance, to its adsorption and absorption, and to brittle cracking. The increased hydrogen absorption during exposure of steels to liquid hydrocarbonates and crude oil have been already observed [5].

The observed cases of fatigue failure have been attributed to improper technology of separators' construction which has remained sharp edges acting as stress raisers. However, the fuel degradation may likely result in evolution of some amount of hydrogen which could be absorbed and promote crack initiation and propagation at stress raisers. It may be result from improper construction of the fuel separators leading to sharp channell crossings and stress raisers, but it can also be enhanced by occurring chemical processes, hydrogen evolution and its entry into steel. Moreover, the improper heat treatment could also make the steels more prone to brittle cracking.

The effect could be more serious if steels applied would be prone to hydrogen degradation because of their microstructure. The present work has been aimed at careful examination of the effect of steel microstructure on susceptibility to hydrogen degradation, describing in terms of plasticity loss and change in fracture mode.

EXPERIMENTAL

Two alloy steels have been investigated: specialty alloy steel for working at elevated temperature 26H2MF and specialty alloy constructional steel for quenching and tempering. The chemical compositions of the steels are presented in Table 1.

Table 1. Chemical compositions of tested steels, wt. pct

Steel grade	C	Mn	Si	P	S	Cr	Ni	Cu	Mo	V
26H2MF	0.28	0.44	0.35	0.013	0.002	1.72	0.16	0.14	0.72	0.27
34HNM	0.329	0.534	0.234	0.016	0.001	1.442	1.621	0.181	0.176	–

Both steels were heat treated at conditions shown in Table 2. The heat treatment parameters were selected in order to obtain relatively different microstructures.

The slow strain rate tests were carried out on tensile specimens, 50 mm long and 5 mm in diameter of working part. The specimen surfaces were polished with grinding papers, the No. 800 as the last, and then carefully washed in distilled water and dried with hot air. The strain rate $1.6 \times 10^{-6} \text{ s}^{-1}$ ($8 \times 10^{-5} \text{ mm/s}$ for used specimen) was applied. The following properties were measured: tensile strength, fracture energy, relative elongation and reduction-in-area (RA). The shown results are means of 3-4 duplicates.

As environment the laboratory air and 0.01 M solution of sulphuric acid with a small addition of As_2O_3 as hydrogen recombination poison were applied. The tensile tests were performed at corrosion potential and cathodic polarization at current density: 20, 40, 60, 80 and 100 mA/cm^2 . All tests were made at ambient temperature.

The examinations of microstructure and fracture surfaces were performed by the SEM Philips XL-30.

Table 2. Heat treatment parameters of tested steels

Steel grade	Heat treatment designation	Heat treatment	Temperature °C	Heating time min	Cooling medium
26H2MF	N	Normalizing I	970	15	air
		Normalizing II	940	15	air
	NT700	Normalizing I	970	15	air
		Normalizing II	940	15	air
		Tempering	700	30	air
	NQT650	Normalizing I	970	15	air
		Normalizing II	940	15	air
		Quenching	880	30	oil
		Tempering	650	120	air
	NQT600	Normalizing I	970	15	air
		Normalizing II	940	15	air
		Quenching	880	30	oil
Tempering		600	120	air	
34HNM	N	Normalizing	870	15	air
		Normalizing	870	15	air
	NQT680	Quenching	860	12	oil
		Tempering	680	120	air
		Normalizing	870	15	air
	NQT640	Quenching	860	12	oil
		Tempering	640	120	air
		Normalizing	870	15	air

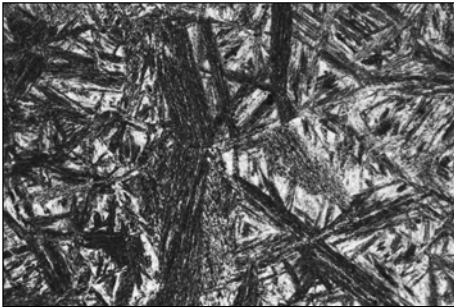
RESEARCH RESULTS

Microstructure examinations

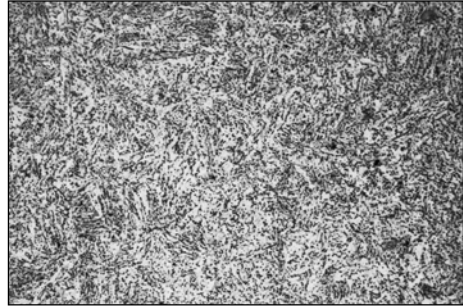
In the 26H2MF steel after normalizing (Photo 1) the structure consisted of upper and lower bainite. After normalizing and high tempering at 700°C, heat treatment that is typical of this steel, the structure consisting of ferrite and carbides appeared. After normalizing, quenching in oil and tempering at 650°C, the ferritic matrix, partly in acicular form and showing some islands of dispersed carbides, was observed. Finally, similar treatment finished with tempering at 600°C results in obvious bainitic structure.

In the 34HNM steel after normalizing the acicular martenite is observed (Photo 2). The normalizing, quenching and tempering at 680°C results in sorbitic structure with uneuqal carbides` distribution. The decrease in tempering temperature to 640°C leads to much smaller carbides, and appearance of clear ferrite areas with lower amount of carbides. The structure typical of quenching is quite visible.

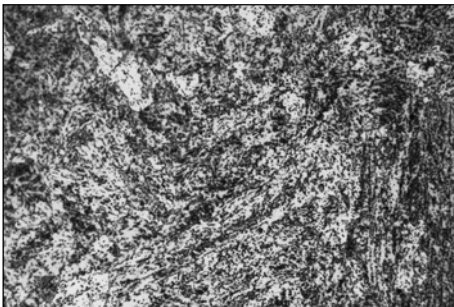
a)



b)



c)



d)

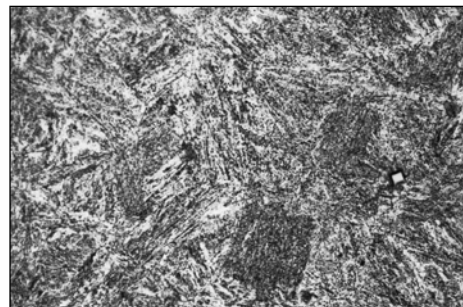


Photo 1. Microstructure of the 26H2MF steel after: (a) normalizing; (b) normalizing and tempering at 700°C; (c) normalizing, quenching and tempering at 650°C; (d) normalizing, quenching and tempering at 600°C. 1000x. Etching with $Mi1Fe$ reagent

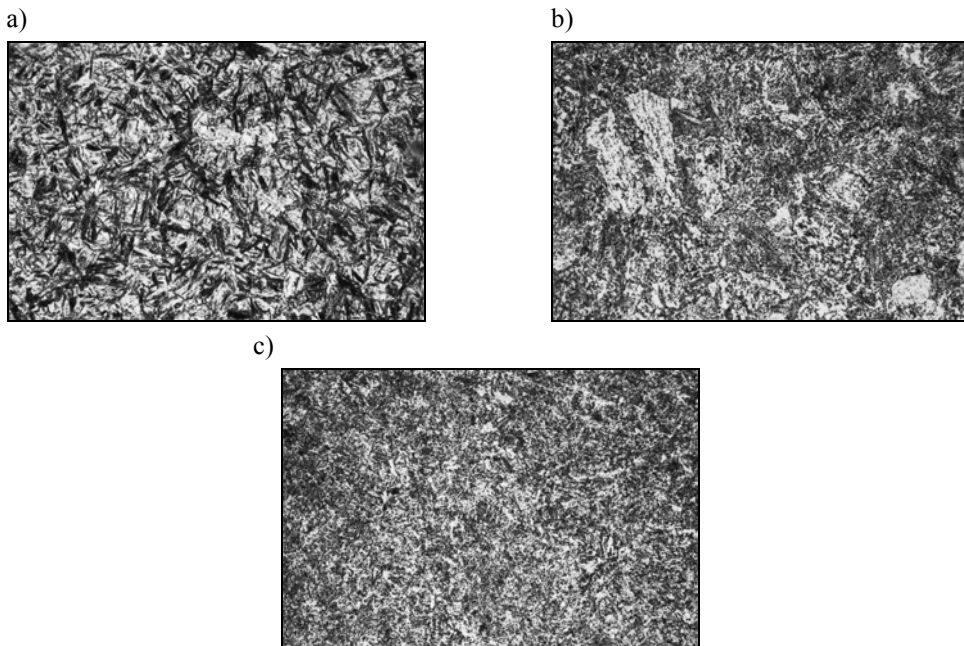


Photo 2. Mikrostruktura of the 34HNM steel: (a) after normalizing, (b) after normalizing, quenching and tempering at 680°C, (c) after normalizing, quenching and tempering 640°C. 1000x. Etching reagent Mi1Fe

Slow Strain Rate Tests

The results of Slow strain Rate Tests made in air and in acidic solution are shown in Tables 3 and 4. The obtained results disclose a distinct relation of mechanical properties on cathodic current density, qualitatively similar for all tested materials. The deep loss of some plastic properties became already at current density 20 mA/cm² and next increasing current density had much smaller effect. Almost complete loss of plasticity was often observed.

Table 3. Slow Strain Rate Test results for the 26H2MH steel

Heat treatment	Property, unit	Medium						
		Air	Acidic solution					
			Cathodic current density, mA/cm ²					
		0	20	40	60	80	100	
N	Tensile strength, MPa	1185.7	1001.0	197.40	184.7	202.4	227.7	193.1
	Fracture energy, MJ/m ³	132.30	45.90	1.58	1.40	0.91	0.74	0.71
	Elongation, %	12.60	6.70	1.05	0.88	0.55	0.35	0.49
	RA, %	41.40	38.5	1.45	0.70	0.30	0.40	0.10
NT700	Tensile strength, MPa	965.0	666	723.6	700.4	735.8	768.2	742.4
	Fracture energy, MJ/m ³	135.00	74.53	28.52	22.51	32.05	47.10	45.04
	Elongation, %	15.70	12.23	4.81	4.12	4.75	7.13	6.48
	RA, %	45.00	40.50	5.60	5.35	5.80	5.60	12.00
NQT650	Tensile strength, MPa	1071.30	794	648.7	707.5	739.3	657.7	756
	Fracture energy, MJ/m ³	106.70	79.00	17.18	16.10	14.72	18.14	16.41
	Elongation, %	12.13	11.90	1.19	2.43	2.42	3.86	2.26
	RA, %	38.90	39.00	5.80	1.00	2.30	2.30	1.80
NQT600	Tensile strength, MPa	1187.7	915.4	812.7	758.1	655.3	716.3	934.7
	Fracture energy, MJ/m ³	112.00	92.92	4.24	3.47	5.48	3.39	59.27
	Elongation, %	12.70	11.20	1.40	1.11	1.60	0.85	7.48
	RA, %	41.70	49.10	5.40	4.08	2.30	3.35	18.50

Table 4. Slow Strain Rate Test results for the 34HNM steel

Heat treatment	Property, unit	Medium						
		Air	Acidic solution					100
			Cathodic current density, mA/cm ²					
			0	20	40	60	80	
N	Tensile strength, MPa	1287.0	799.3	344.9	336.9	389.9	340.6	540.6
	Fracture energy, MJ/m ³	58.30	4.53	0.82	0.76	0.33	0.10	0.10
	Elongation, %	5.30	1.17	0.51	0.46	0.26	0.35	0.49
	RA, %	14.70	7.40	1.00	1.00	1.00	3.00	1.00
NQT680	Tensile strength, MPa	724.0	700.9	722.4	701.3	727.3	636.9	689.5
	Fracture energy, MJ/m ³	70.30	68.23	15.10	15.31	13.73	38.75	10.36
	Elongation, %	10.60	9.50	4.05	3.55	2.70	5.45	2.50
	RA, %	39.40	13.60	8.55	7.50	5.45	3.70	14.75
NQT640	Tensile strength, MPa	742.7	702.7	680.2	699.4	691.7	723.1	698.7
	Fracture energy, MJ/m ³	57.70	7.80	14.05	15.96	14.19	18.36	14.40
	Elongation, %	9.10	1.35	2.63	2.72	2.46	3.09	2.59
	RA, %	41.00	0.20	5.20	5.45	2.80	4.97	2.67

The brittle crystallographic cleavage fracture was observed for normalized steels, and quasi-cleavage for normalized, quenched and tempered steels as a rule. Some examples are shown in Photo 3.

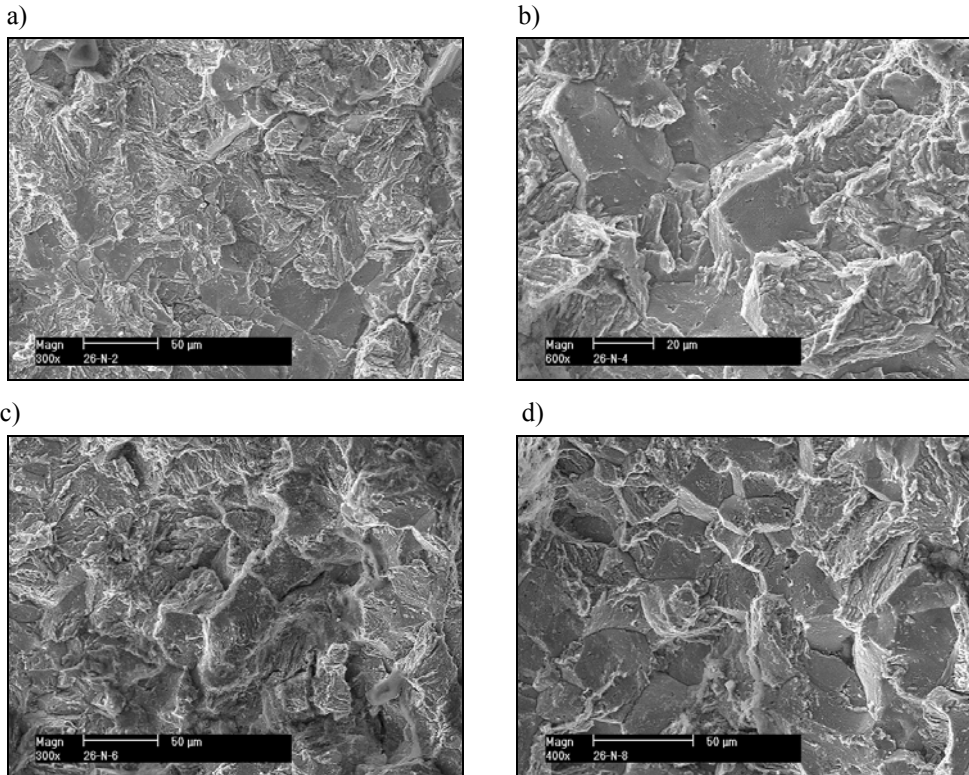


Photo 3a,b,c,d. Fracture surfaces after Slow Strain Rate Test in acidic solution at cathodic polarization: 26H2MF steel, after normalizing and cathodic polarization at (a) 20 mA/cm², (b) 40 p mA/cm², (c) 60 mA/cm², (d) 80 mA/cm², (e) 100 mA/cm²; (f) after normalizing, quenching and tempering at 650°C, 60 mA/cm²; (g) after normalizing, quenching and tempering at 600°C, 60 mA/cm²; (h) 34HNM steel after normalizing, quenching and tempering at 640°C, 60 mA/cm²

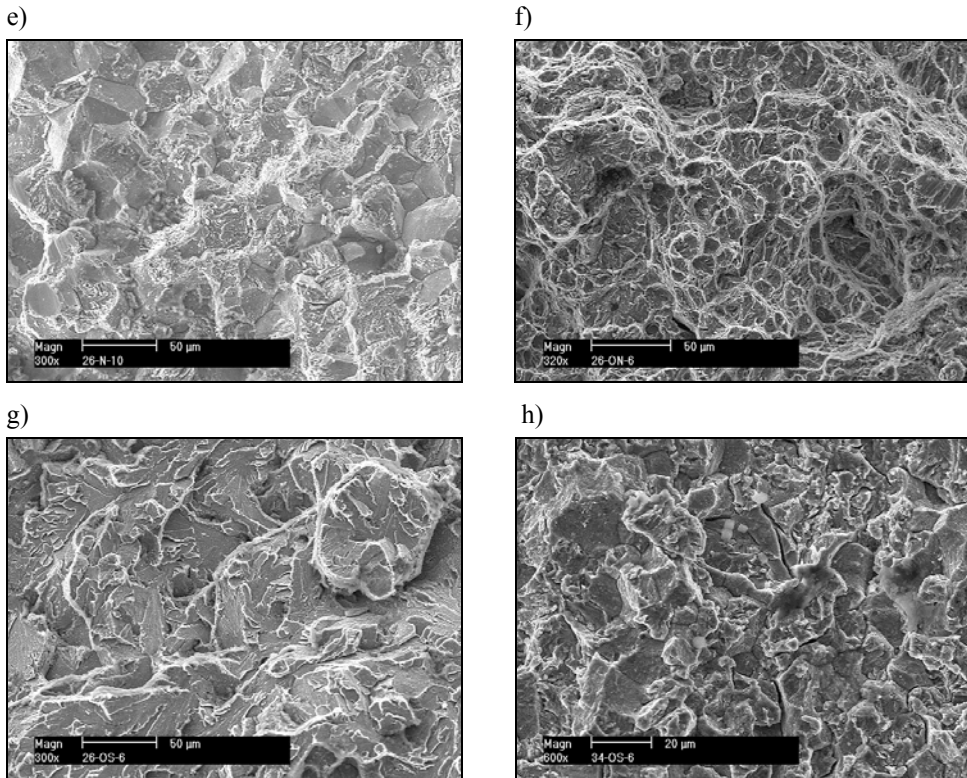


Photo 3e,f,g,h. Fracture surfaces after Slow Strain Rate Test in acidic solution at cathodic polarization: 26H2MF steel, after normalizing and cathodic polarization at (a) 20 mA/cm², (b) 40 p mA/cm², (c) 60 mA/cm², (d) 80 mA/cm², (e) 100 mA/cm²; (f) after normalizing, quenching and tempering at 650°C, 60 mA/cm²; (g) after normalizing, quenching and tempering at 600°C, 60 mA/cm²; (h) 34HNM steel after normalizing, quenching and tempering at 640°C, 60 mA/cm²

DISCUSSION

For the 26H2MF tensile strength in air was the highest after normalizing as this steel during cooling in air underwent quenching and formed bainitic structure secures high mechanical properties. Consequently, the plastic properties like RA and elongation decreased. The tempering at 700°C resulted in ferritic structure containing spheroidal coagulated carbides which then caused a distinct decrease in tensile strength, and increase in RA and elongation. Tempering at 650°C following former quenching in oil was also a source of substantial decrease in tensile strength, as compared to that of normalized steel, and increase in plasticity, mainly because of development of coagulation of carbides. The strength and plasticity measured for steel quenched and tempered at 600°C, which were close to those observed for no tempered steel, can be attributed to an appearance of highly dispersed carbides.

The high strength and low RA and elongation values of normalized 34HNM steel can be explained by an appearance of small grain acicular martensitic structure. The presence of sorbitic structure resulted in lower strength and higher plasticity of the quenched and tempered steel.

The change in tempering temperature resulted in vanishing of acicular structure and then in lowering the strength and increasing the plasticity.

The mechanical properties measured during slow straining in acidic solution gradually decreased with increasing cathodic current density. Such behaviour confirms that cathodic polarization can cause substantial hydrogen degradation of both steels.

The deep fall of properties observed for steels of the highest strength properties, bainitic 26H2MF and martensitic 34HNM ones, is in good accordance with previous reports [6]. According to them, the higher strength properties, the higher degradation degree expressed in terms of plasticity fall. This effect is related to steel microstructure.

For the 26H2MF steel the deepest degradation was observed for bainitic structure, obtained after normalizing treatment at these conditions; then for structure obtained after normalizing, quenching and tempering at 600°C, containing precipitated alloy carbides and cementite in matrix of bainite of decreased carbon content; next for similar structure but not showing acicular appearance, containing globular cementite; finally, for equilibrium structure containing ferrite, alloy carbides and coarse cementite. Those results are in full accordance with previous ones [6,7], which have suggested following sequence of decreasing susceptibility to hydrogen degradation: martensite, bainite, pearlite, tempered bainite and tempered martensite. The observed microstructural effects can be explained by a variety of reasons: lower length of critical crack in materials of higher strength, higher hydrogen absorption and its faster transport in quenched structures, presence of high internal stresses in martensite and bainite, a number of sites for potential crack initiation in these structures (grain boundaries, dislocations and their pile-ups and tangles). The small and globular carbide particles obtained after quenching and tempering are more coherent to matrix than any other carbide shapes, and therefore such structures are the least susceptible to hydrogen-enhanced plasticity loss and cracking.

For the 34HNM steel similar relation can be observed: the highest degradation occurred for martensitic structure, the highest one – for structure containing well tempered martensite. The susceptibility to hydrogen degradation of martensitic structure obtained in the 34HNM steel was higher than that of bainitic structure appearing in the 26H2MF steel, again in accordance with above sequence.

Considering the absolute values of degradation degree it is worthy to note a very deep fall in plasticity. According to [7], only for steels of tensile strength above 700 MPa the effect of hydrogen is substantial. In this work the quenched and tempered 34HNM steel showed high susceptibility to hydrogen embrittlement even if its tensile strength exceeded only a little this strength limit. Thus, this steel seems especially prone to hydrogen degradation.

CONCLUSIONS

The 26H2MF and 34HNM alloy steels are prone to hydrogen-enhanced degradation which manifests itself as substantial decrease in plasticity, and also fall in strength properties for no tempered steels. The drastic decrease of mechanical properties in acidic solution and at cathodic polarization, and brittle fracture form an evidence of hydrogen-enhanced degradation.

Microstructure of steels greatly influences the degradation degree. The least susceptible to hydrogen embrittlement are steels tempered at the highest temperature. The effect of microstructure may be explained by temperature related change in a number and sort of hydrogen traps at which the irreversible change of microstructure and cracking process are initiated.

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REFERENCES

1. Michalak P., Kotkowski K. et al., *Hydrogen-enhanced fatigue of fuel installations in diesel engines*, Proc. Intl. Conf. Environmental Degradation of Engineering Materials, Gdansk Univ. Techn. & Universite Bordeaux 1, Gdańsk-Jurata 1999, vol. 1, pp. 346-350.
2. Michalak P., Zieliński A., *Ocena niebezpieczeństwa kruchości wodorowej stali stopowych stosowanych na instalacje paliwowe silników okrętowych* (Assessment of risk of hydrogen degradation of alloy steels used for fuel installations of ship engines), Proc. 1st Pomorze Sci. Conf. „Materials Science and Engineering 2000”, Gdańsk Univ. Techn., Gdańsk-Sobieszewo 2000, pp. 161-166.
3. Michalak P., *Zmęczeniowe niszczenie instalacji paliwowych silników okrętowych stymulowane wodorem* (Hydrogen-enhanced fatigue failure of fuel installations of ship engines), Proc. Conf. „Mechanical Eng. 99”, Gdańsk Univ. Techn., Gdańsk 1999, pp. 43-44.
4. Piotrowski K., Witkowski K., *Okrętowe silniki spalinowe* (Ship diesel engines), Trademar, Gdynia 1996.
5. Kula P., Pietrasik R., Wendler B., Jakubowski K., *The effect of hydrogen in lubricated frictional couples*, Wear 212 (1997), 199-205.
6. Timmins P., *Solutions to hydrogen attack in steels*, ASM, Materials Park, OH, USA, 1997.
7. Coudreuse L., *Fragilisation par l'hydrogene et corrosion sous contrainte. Phenomenologie et mecanismes*. Edit. Phys., Bombannes, Francja, 1990, pp. 397-424.