Corrosion-enhanced fracture of the Cr-Ni-Mn steel in liquid hydrocarbons

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Abstract. The exposure of a Cr-Ni-Mn steel in boiler fuel has been investigated. Three mechanical-corrosion tests have been applied: constant load, slow strain rate and low cycle low frequency fatigue tests. Under constant load tests no negative phenomena have been observed, at slow strain rate tests sometimes the loss of plasticity and under fatigue conditions the substantial decrease in lifetime have occurred. The fracture has been shown to result from hydrocarbons degradation in presence of iron followed by its fast absorption in presence of evolved hydrogen sulfide and by brittle cracking when the plasticity has occurred.

Introduction

Hydrogen may enter steels operating in crude oil and its derivatives, the petrol gas including, following corrosion on inner surfaces of pipelines as an effect of presence of small amounts of water absorbed by crude oil as well as of corrosion of outer surfaces of pipelines [1-3]. The absorption study of the pipeline operating for 28 years showed 3 ppm of hydrogen, more than 1.6 ppm present in raw material and critical hydrogen concentration necessary in this case to develop hydrogen bubbles was estimated at only 0.3 ppm [4].

There were reports on sudden fatigue failure, even after a few weeks, of fuel separators in some ship diesel engines [5-7]. The failure was attributed to improper heat treatment resulting in microstructure susceptible to brittle cracking, and improper fabrication technology, leaving sharp passages in the crossing fuel channels. The cracking mechanism was not fully recognized; it was expressed the opinion that at these operating conditions, presence of water and sulphur in ship fuel, high pressures and stresses, hydrogen could appear as a product of fuel decomposition, and it can at least enhance brittle cracking [8].

The possibility of formation of atomic hydrogen in presence of water and hydrocarbons in heavy fuel was discussed in [3,9,10]. Relatively high sulphur content in ship fuels is allowed by present standards, and water can be also absorbed during fuel tanking and storage. At such conditions the formation of sulphurous and sulphuric acids is possible and then hydrogen evolution and absorption [11,12].

The possibility of hydrogen absorption in crude oil, fuels, oils, and greases, was suggested in a few papers [2,3,9,10,13,14]. Free hydrogen may appear in hydrocarbons following the weakening of their chains and an exchange of hydrogen atoms between hydrocarbon chains and metal surface as a result of their adsorption on the friction surface. The thermal pulses that are created during shaping and shearing of roughness peaks favour dissociation of hydrocarbons by chemisorption [15,16]. Such process is believed to be responsible for fast wear of some elements of breaks and suspension in trains [17]. The appearance of hydrogen has been observed in presence of oil as a result of

tribologic and tribothermal processes and attributed to its tribosorption by the FeN phase resulting in formation of h.c.p. hydride phase [9,18-20].

The decomposition of organic compounds results in hydrogen appearance and its entry to the metal [10]. The adsorption of formed hydrogen on the surface of metallic catalyser and formation of surface hydride is believed to occur in process of catalytic degradation of hydrocarbons [9,15]. The dehydratation may proceed also at room temperature at stresses necessary to the contact of grease with surface of refractory metals which are catalysers of decomposition of organic compounds [9,19]. In the sorbitic 38HMJ subjected to sulfonitriding and nitriding after 24 h exposure in humid air and in mineral oil at 120°C the hydrogen content increased to 14-65 ppm. The high hydrogen concentration in steels subjected to chemical-thermal treatment was attributed to hydrogen accumulation within thin surface layer, in form of iron nitrohydrides [15,16,20].

The possibility of degradation of hydrocarbons and hydrogen entry from greases and oils was the subject of a few research works on mechanical spectroscopy [9,10,21]. The presence of thin layer of hydrocarbons (grease) on the surfaces of iron and steels changed internal friction, free oscillation frequency, mechanical properties and image of slip lines in the temperature region of 160-373 K. These effects are similar to those observed after hydrogen charging, and different for steel and ceramics. This is an evidence of decomposition of hydrocarbons on the steel surface and hydrogen absorption inside the surface layer where it may interact with mobile dislocations.

The present work was aimed at determining whether in case of medium strength alloy steel its exposure in hydrocarbons may result in hydrogen-enhanced plasticity loss and brittle cracking, and under what conditions.

Materials and methods

The Polish 34HNM steel was investigated of chemical composition shown in Table 1. The applied heat treatment parameters are listed in Table 2.

Table 1. Chemical composition of the 34HNM steel, wt. pct

Reference	C	Mn	Si	P_{max}	S_{max}	Cr	Ni	Cu_{max}	Mo	V_{max}
Standard	0.32÷0.4	0.4÷0.7	0.17÷0.37	0.035	0.035	1.3÷1.7	1.3÷1.7	0.3	0.15÷0.25	0.05
Analysis (forging A)	0.33	0.54	0.29	0.001	0.003	1.4	1.41	0.25	0.165	0.008
Analysis (forging B)	0.27	0.37	0.21	0.003	0.02	1.53	1.50	0.34	0.15	0.007

Table 2. Heat treatment parameters of the 34HNM steel

Forging	No. of heat treatment	Heat treatment operations	Temperature [^{0}C]	Heating time [min]	Cooling medium
A	1	Normalizing	870	20	Air
		Quenching	860	20	Oil
		Tempering	680	120	Oil
	2	Normalizing	870	20	Air
		Quenching	860	20	Oil
		Tempering	560	120	Oil
B	3	Normalizing	970	20	Air
		Normalizing	940	20	Air
		Tempering	700	120	Air

The tests included: SEM examinations of microstructure and surface, constant load tests, slow strain rate tests and low cycle fatigue tests. The smooth round specimens were applied in slow strain rate tests and fatigue tests, and pre-notched round specimens in constant load tests. Specimens were cut from steel sheets in long transverse direction, then polished with abrasive papers, No. 800 as the last, washed in tap water and dried in hot air.

The boiler fuel (2.3% S) used as a component of fuels for ship diesel engines, and pure glycerin as a reference environment were used. The tests were made at temperature 135 ± 3^0C.

The slow strain rate tests were made at a strain rate 10^{-6} s^{-1} with an especially designed tensile machine. The specimen was fixed in clamps of tensile machine, and the experimental cell was filled with applied liquid and heated. When appropriate temperature was achieved and stabilized, the tension of specimen was started. The following parameters were measured: tensile strength, elongation, reduction-in-area and fracture energy.

The constant load tests were made on pre-notched specimens with imposed load between 0.90 and 0.98 F_m, where F_m the maximum force.

The fatigue tests were performed with the INSTRON tensile machine according to procedure applied in slow strain rate tests. The lowest and highest strain values (strain amplitude), strain rate, number of cycles and time to failure were recorded.

Results

Microstructure examinations

The 34HNM steel subjected to normalizing, quenching and tempering at 680^0C had sorbitic microstructure with substantial coagulation of carbides (Fig. 1). The decrease in tempering temperature to 560^0C resulted in relatively dispersed carbides. The steel subjected to double normalizing and tempering at 700^0C disclosed ferritic structure with highly coagulated carbides.
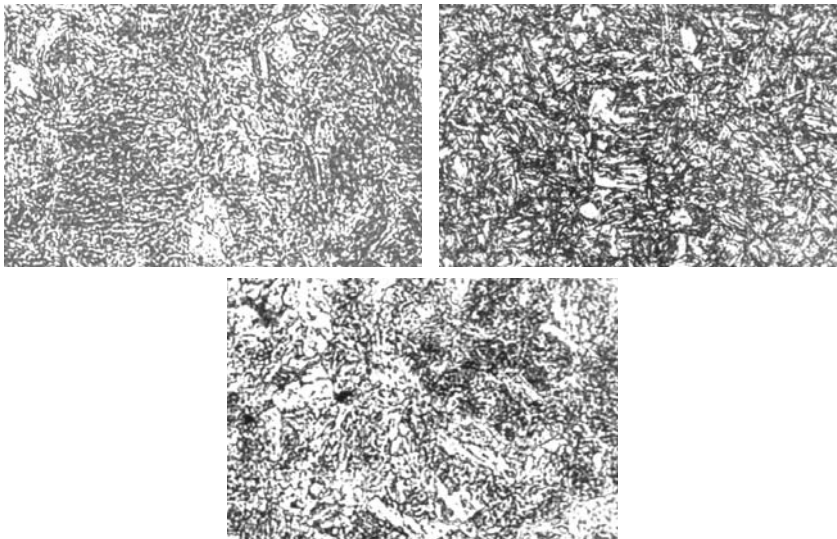
Fig. 1. The microstructure of 34HMN alloy steel: a) normalizing, quenching and tempering at 680^0C; b) normalizing, quenching and tempering at 560^0C, c) after double normalizing and tempering at 700^0C

Post-exposure surface examinations

The light microscope examinations of the surfaces after 30 day exposure showed the appearance of pitting corrosion. The example is shown in Fig. 2.
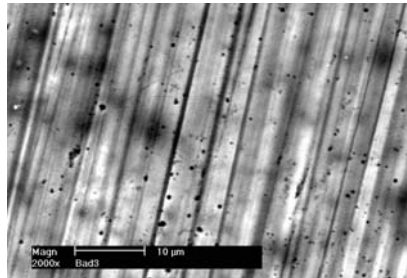

Fig. 2. View of the specimen after 30 day exposure in fuel

Constant load tests

In constant load tests no failure during 200 h was observed for specimens exposed to boiler fuel at loads: 0.90 F_m, 0.93 F_m, 0.96 F_m.

Slow strain rate tests

Fig. 3 demonstrates results of slow strain rate tests of the 34HNM steel made in boiler fuel and in glycerine. T560 means the steel normalized, quenched and tempered at 560^0C, T680- steel normalized, quenched and tempered at 680^0C; F- tests in boiler fuel, G – tests made in glycerin. In this case no effect of environment on strength properties was observed, but the RA value decreased significantly after exposure.
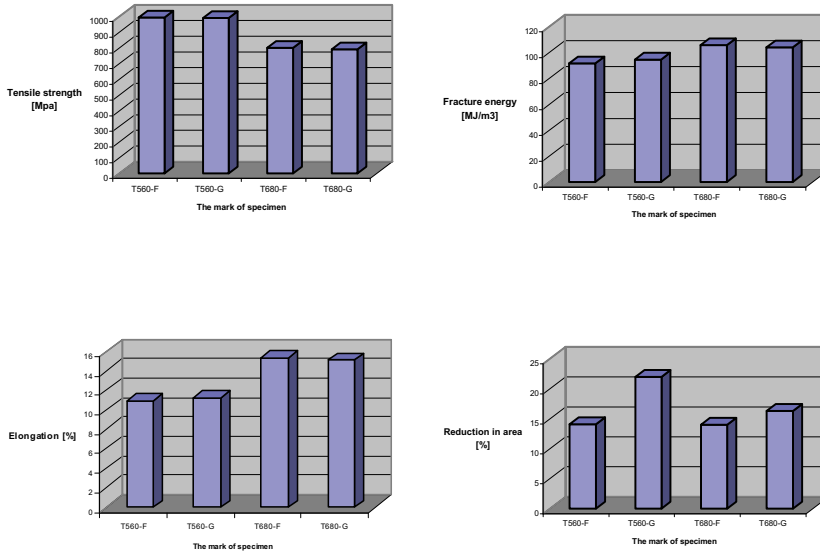
Fig. 3. The results of slow strain rate tests of the 34HNM steel made in boiler fuel (F) and in glycerine (G)

Fatigue tests

The results of tests are shown in Table 3. Because of limited number of specimens and high discrepancies, the differences in number of cycles were analysed for pairs of results obtained in tests made in fuel and in glycerin, by:

- signs` test: the signs` differences are substantial at 0.00596 level, i.e. effect of environment is substantial at the confidence level much higher than 99%,
- Wilcoxon test: differences are substantial at 0.008365 level, i.e. effect of environment is substantial at the confidence level much higher than 99%.

Table 3. The fatigue test for 34HNM alloy steel (two different forgings)

Melt	Heat treatment	Environment	The mark of specimen	The failure cycles number
A	N 870^{0}C H 860^{0}C O 560^{0}C	Fuel	34NHO560P	791
		Glycerin	34NHO560G	17171
		Fuel	34NHO560P	2871
		Glycerin	34NHO560G	16981
B	N I 970^{0}C N II 940^{0}C O 700^{0}C	Fuel	34NO700P	13911
		Glycerin	34NO700G	121541
		Fuel	34NO700P	112701
		Glycerin	34NO700G	248731

Discussion

Processes within the surface layer

The evolution of hydrogen in these conditions may be caused by different processes: electrochemical corrosion in water phase, chemical corrosion associated with presence of organic acids and/or degradation of hydrocarbons with an appearance of free hydrogen. The last cause is the most likely origin of observed brittle cracking. As already stated, high molecular hydrocarbons may in some conditions, at elevated temperature and in presence of iron (or other heavy metals, like Ni, W, and Cu) as catalyst, undergo chemical reaction of dehydrogenation, i.e. breaking of long chains with hydrogen evolution [22]. The next hydrogenation reaction includes fresh gaseous hydrogen and complex hydrocarbons containing sulphur and results in creation of simple hydrocarbons and H_2S. It has been reported that black deposits, observed after similar exposure on the surfaces of steels, contained about 10% S [14]. The hydrogenation reaction is easier at elevated temperature and pressure, and also in presence of metallic catalytic agents, like Fe. Even if a part of hydrogen is used in hydrogenation reaction, evolved H_2S facilitates the absorption of another hydrogen part into the metal. The evidence may be an increased hydrogen content discussed elsewhere [23] and character odour during exposure in elevated fuel.

Degradation at static conditions

The tests made here on pre-notched specimens at constant load close to UTS showed no difference between steel exposed to fuel or glycerin. The relative insensitivity of some hydrogen charged steels below yield stress has been already observed [24]. However, such result can be hardly expected in pre-notched specimens in which the concentration of triaxial stresses appears, hydrogen may easily diffuse into the notch area, a local hydrogen content should then increase and crack initiate [25].

At these conditions, the low fugacity hydrogen slowly penetrates the surface layer and the metal bulk at a small hydrogen concentration gradient. Therefore the cold work is negligible or only local, on the contrary to the charging with high fugacity hydrogen, like at cathodic polarization, in acidic electrolytes and in a presence of hydrogen entry promoter. The low lattice hydrogen content even in presence of zones with high triaxial stresses may not result in a local crack initiation.

Then, in the constant-load test, at load values even approaching the yield point, the slow hydrogen absorption may neither reduce cohesive strength of the lattice nor promote the initiation and propagation of long cracks. No plastic deformation occurs, no hydrogen cracking is observed in these conditions.

Degradation at slow strain rate tension

The slow strain rate test differs much from constant load test when stress-strain state is considered. During former test the yield point is quickly achieved, the number of dislocations and local decohesions increase. Hydrogen entering the steel interacts with freshly formed defects, especially is trapped by dislocations and interfaces that may cause a local reduction of yield point. The hydrogen movement to the crack tip and plastic strain zone is easier than at constant load conditions. The cracks start from interfaces already existing, i.e. those between matrix and carbides or sulphides` precipitates, at which hydrogen is trapped. The cracks may also initiate at the bainite or residual austenite boundary [4,26].

Degradation at cycling stresses

The substantial effect of hydrogen appears at cyclic loading. The high sensitivity of fatigue strength to hydrogen deterioration of the steels has been already observed, e.g. in low-alloy steels in acidic environments [27]. The results obtained here confirm earlier reports and show that low-cycle fatigue tests performed at low strain rate and low frequency are the best tool to study the hydrogen degradation of steels [28,29].

The following explanation of the observed behaviour can be proposed. At low-cycle fatigue test the plastic deformation occurs early and hydrogen can directly interact with defects created during the test, as in slow static straining. There is, however, a fundamental difference between the slow strain rate test and low-cycle fatigue test as the number of defects, which may form during straining, is concerned. At the slow strain rate test, beginning from some limit strain value, the number of created defects may become too great to trap all hydrogen in their neighbourhood so that hydrogen influence relatively decreased with stepwise deformation. At the low-cycle fatigue test and small upper strain amplitude, the number of defects is not great. Therefore, the mobile hydrogen, even at its low concentration, could always reach the plastic deformation zone efficiently bounded by fresh structure defects.

Conclusions

1. The exposure of the Cr-Mn steel in boiler fuel at elevated temperature is associated with hydrogen evolution and absorption as a result of cracking of hydrocarbon chains.
2. Hydrogen absorbed during long term exposure in hydrocarbons does not result in hydrogen degradation of steels subjected to constant loading below the yield point. The lack of effect may be attributed to slow hydrogen entry into the metal and presence in the steel of deep hydrogen traps which bind it not allowing for further diffusion to triaxial stress sites.
3. Absorbed hydrogen affects slightly plasticity of steels subjected to tension at constant slow strain rate. Such behaviour may be explained by hydrogen interaction with freshly formed defects.
4. Hydrogen presence lowers significantly the number of cycles in the low-cycle fatigue tests. The decrease in fatigue properties may be explained by relatively small plastic deformation during the test, that allows hydrogen for its redistribution and diffusion into the whole plastic zones ahead of the crack tips.

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