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INFLUENCE OF PHYSICAL-METALLURGICAL FACTORS ON RESISTANCE OF API CARBON STEELS TO SULPHIDE STRESS CRACKING

The paper deals with the influence of physical-metallurgical factors on resistance of the X52 and X70 steels in accordance with API 5L to sulphide stress cracking. The resistance against this kind of damage is relatively clearly claimed by usually used approach in this field by the tensile strength of steel, its hardness level, respectively. However, the experimental results had shown that the microstructural parameters are also the significant factors, which affect the resistance of steels to sulphide stress cracking. It was found that the quenching and tempering can significantly increase the resistance to sulphide cracking as in the case of hydrogen induced cracking. It would be appropriate to re-evaluate the material selection process that recommends to use the steels not exceeding approved strength limit in a case of the sulfane environments where the risk of the sulphide stress cracking exists.

Keywords: *carbon steels, microstructure, mechanical properties, heat treatment, sulphide stress cracking*

1. Introduction

Aspects of the hydrogen embrittlement are related to the steel products from their production to their long-time exploitation in working conditions containing hydrogen or in the conditions where the hydrogen release and transition in the metal matrix occur.

Environment containing sulfane, which relates with the mining industry, transport, storage and refining of petroleum and natural gas, belongs to a group of the working conditions, where the hydrogen can penetrate into the material under specific conditions and degrade it. Mechanisms of such a kind of damage are called as Hydrogen Induced Cracking (HIC), Sulphide Stress Cracking (SSC), Stress Oriented Hydrogen Induced Cracking (SOHIC). There is a generally accepted fact that the hydrogen is generated by the corrosion processes on the steel surface and that it diffuses inside the material in a form of the atoms or the protons. The theories of Hydrogen Enhanced Decohesion (HEDE) [1], [2], [3], Hydrogen Enhanced Localized Plasticity (HELP) [4], [5], [6] and Adsorption Induced Dislocation Emission (AIDE) [7], [8] are quoted today.

Increasing the share of the steel products with higher added value is one of the priority interests of the Czech steel industry. One of the possible ways is to increase the production of thermo-mechanically rolled sheets used for welded the pipelines for transportation of petroleum and natural gas to long distances. Those sheets are made of C-Mn steels with carbon content within 0.05 to 0.1 wt. % and micro-alloyed by Niobium, Titanium and Vanadium. In combination with controlled rolling and accelerated cooling is then possible to obtain the steels with high yield strength and good ductility, which are known as the High Strength Low Alloy Steels (HSLA). These steel grades are sorted in petrochemical industry in accordance with API 5L standard, e.g. X52, X60, X70, X80 etc., where the number expresses the yield strength value in imperial units ksi. Due to increased global demand for energy consumption and building of the pipelines for severe climatic working conditions a pressure in the pipelines increases and thus it makes higher requests for mechanical properties and resistance to the corrosion cracking of the HSLA steels [9], [10], [11].

Resistance of the materials to the degradation in conditions containing sulphane is related to various physical-metallurgical factors, which are of different importance. It is a matter of chemical composition, tensile strength level and microstructural parameters. According to the worldwide accepted standard NACE MR0175/ISO 15156 [12] the strength and the hardness of the steel, respectively, one can regard as a reference parameters. Limit values, valid for carbon and low alloyed steels (above them the steel is susceptible to the SCC) are set at 690 MPa and 22 HRC, respectively. The microstructure is taken into account only indirectly - within the limits given by the heat treatment process - although the steels mentioned above are normally available as-rolled, as-normalized or as-quenched. The aspects of segregation phenomenon, amount, distribution and shape of the non-metallic inclusions, are not explicitly reflected. The usually applied approach for selection of material being resistant against the SSC based on only strength or hardness criterion could not be sufficient in some cases; that is documented by various research works [13], [14], [15] and this paper also reflects this fact.

Due to the situation that the petrochemical industry represents the most demanding application from a view of a resistance against the influence of the hydrogen, it is necessary to take care of suitable precautions for the steel producers and also for the

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Table 1 The chemical composition of the steels (wt. %)

Steel	C	Mn	Si	P	S	Cr	Ni	Mo	V	Nb	Ti	Al
X52	0.09	0.92	0.28	0.007	0.01	0.02	0.01	-	0.004	0.03	0.01	-
X70	0.10	1.51	0.35	0.019	0.004	0.07	0.02	0.01	0.05	0.04	0.01	0.03

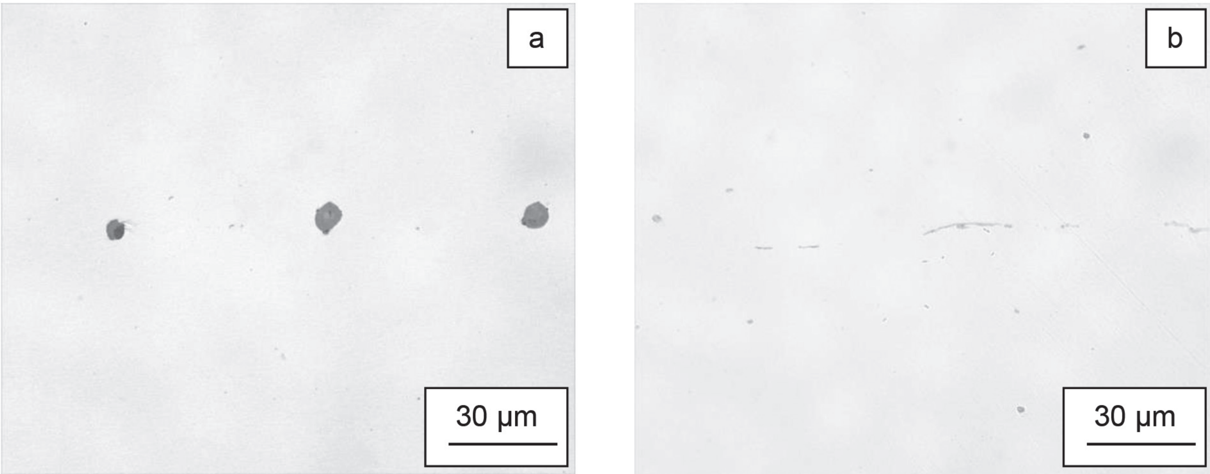


Figure 1 *Examples of non-metallic inclusions in the X52 steel*

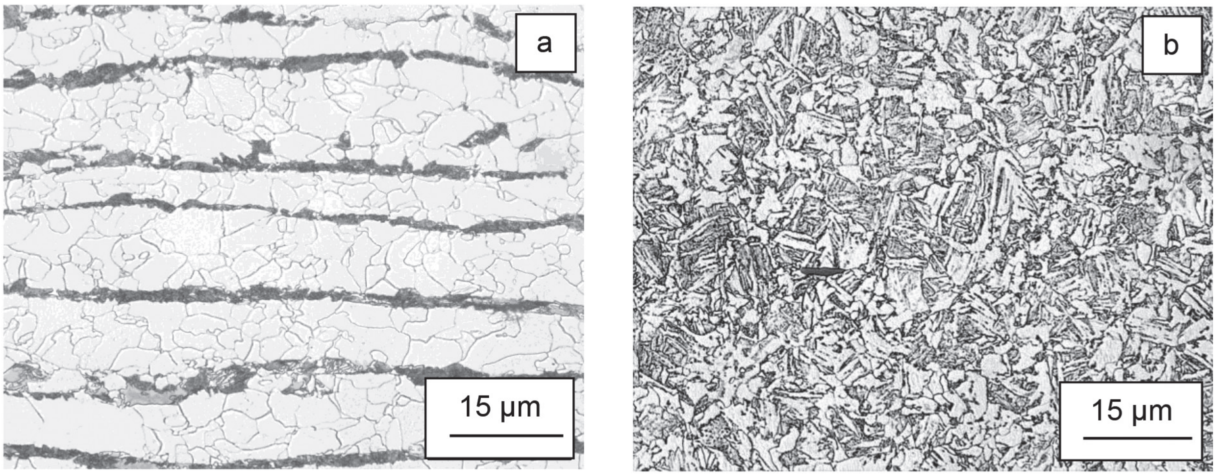


Figure 2 *Microstructure of the X52 steel in the mid-thickness*

final operators of the steel construction, to reduce the formation of the hydrogen embrittlement to a minimum.

This paper deals with the influence of physical-metallurgical factors on resistance of the high strength micro-alloyed steels X52 and X70 to the SSC.

2. Materials and experimental procedure

Tube made of the X52 (559/30 mm) steel and sheet made of the X70 (12 mm) steel, both in accordance with API 5L standard, were used. The chemical composition of the steels is given in Table 1. The X52 steel was studied after rolling, in the as-received state (X52/AR) and after laboratory quenching and tempering at 870 °C/40 min/water + 600 °C/90 min/air (X52/QT). The X70 steel was tested after the rolling, in the as-received state (X70/AR).

Structural analysis was performed by the optical metallography. Tensile properties were determined with using of the MTS 100 kN testing machine on cylindrical specimens with a diameter of 5 mm and a gauge length 25 mm, which were taken from the mid-thickness of the materials in the longitudinal direction.

Resistance to the SSC was tested in accordance with the NACE TM 0177 Standard, Method A [16]. The testing solution was a water solution containing 5.0 wt. % NaCl and 0.5 wt. % of glacial acetic acid saturated by H_2S. The constant load tests were performed on sub-sized cylindrical specimens with a diameter of 3.81 mm and a gauge length of 25.4 mm, which were taken from the mid-thickness of the materials in the longitudinal direction. The applied load varied from 0.5 to 0.9 of the yield strength of the materials being tested. Based on the test results, a critical stress could be evaluated for each of the steels and states that were tested. The fracture surface appearance of the ruptured specimens was observed by use of the scanning electron microscopy (SEM).

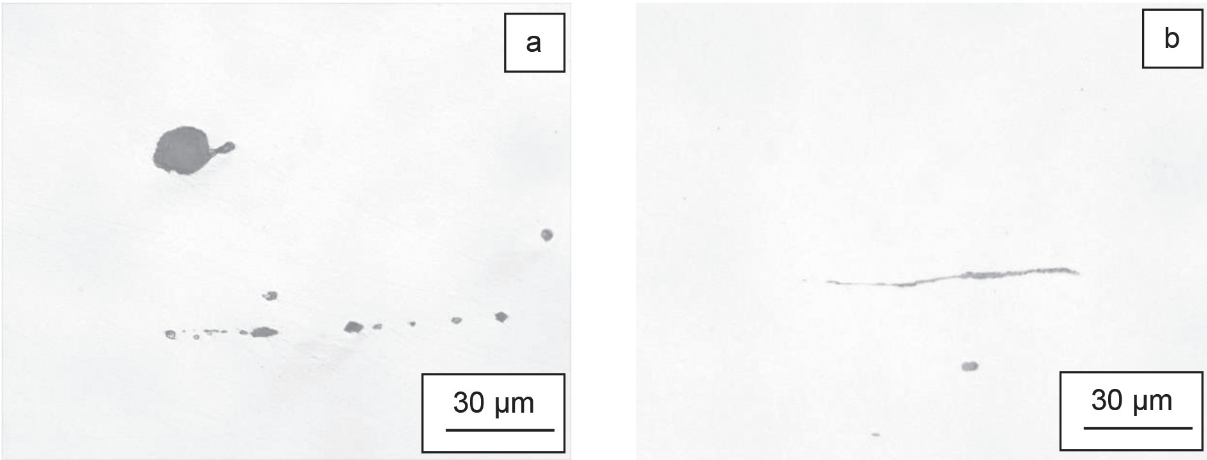


Figure 3 *Examples of non-metallic inclusions in the X70/AR steel*

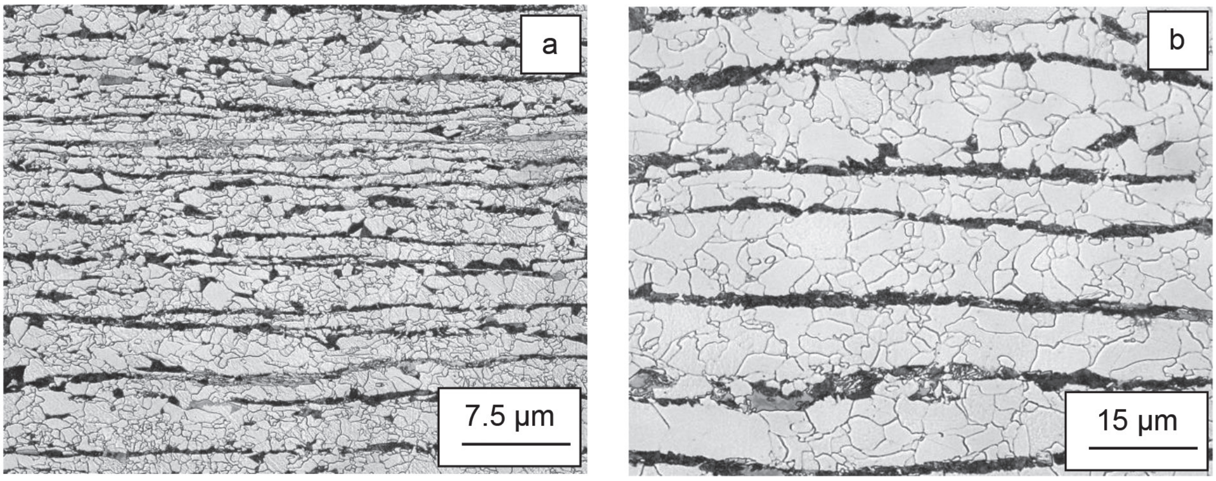


Figure 4 *Microstructure of the X70/AR steel in the mid-thickness of the sheet*

3. Results and discussion

Evaluation of a micro-cleanliness of the X52 steel relieved a presence of relatively high amount of formed manganese sulphides that relate with higher sulphur content in the steel (Figure 1b). In addition, the globular oxide inclusions were found (Figure 1a).

The microstructure of the X52/AR steel is ferritic with narrow pearlite lines where the occurrence of not-tempered martensite is observed in some areas (Figure 2a). The microstructure of the X52/QT steel consists of bainite and ferrite (Figure 2b).

The micro-cleanliness of the X70 steel being examined was very good. Mostly globular complex oxidic or oxi-sulphidic inclusions were observed. Due to the low sulphur content the formed manganese sulphidic inclusions were occasionally detected and they did not play a significant role during the initiation of the defects (Figure 3a and Figure 3b) [17].

The surface microstructure of the X70/AR steel consisted of a fine grained ferrite and narrow lines of pearlite. Between the pearlite lines the lines of not-tempered martensite in the mid-thickness of the sheet were observed (Figure 4a and Figure 4b).

The mechanical properties of the steels are summarized in Table 2. The laboratory heat treatment of the steel X52 caused a significant increasing of the yield and tensile strength (approx. about 100 MPa) with preserving of very good plastic properties.

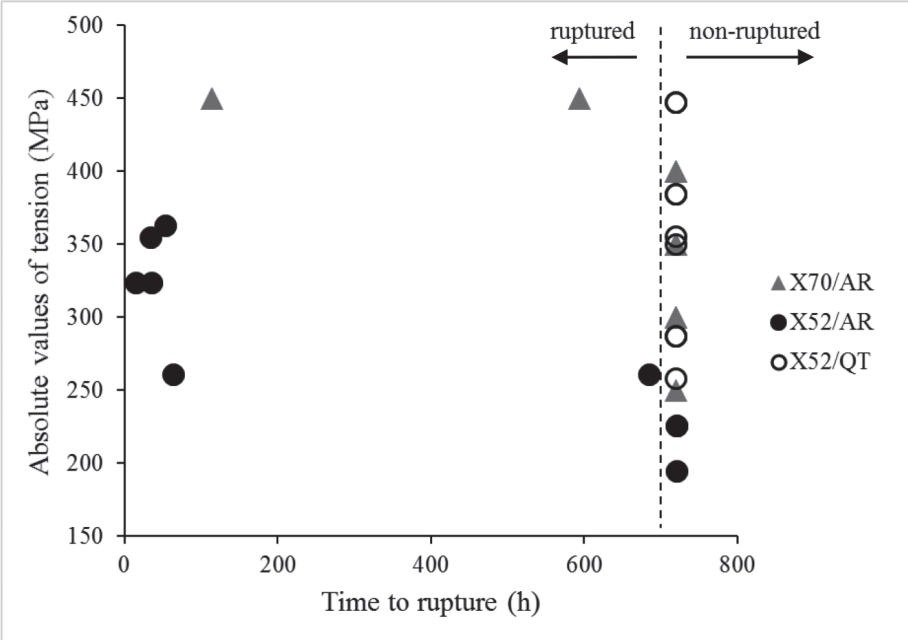
The results of the SSC tests, performed at constant loads, according to the NACE TM0177, Method A are presented in Figure 5.

The specimens made of the X52/AR steel passed the loading corresponding only to 58 % of the $R_{p0.2}$ that equals to 226 MPa. Thus, the X52/AR steel shown an insufficient resistance to the SSC. However, the X52/QT steel, after the quenching and tempering, passed the loading equal to 92 % of the $R_{p0.2}$ what corresponds to 447 MPa and thus it fully passed the request given for the steels being resistant to the SSC. In this particular case a favorable influence of the heat treatment was confirmed when the tempered hardened structures increased the resistance of the steel X52 to the SSC. Therefore, it was confirmed that one of the key factors, from a view of the resistance to the SSC, was the microstructure. Ruptured specimens were subjected to the fractographical analysis. The specimens were ultrasonically cleaned in a weak solution of phosphoric acid due to the high contamination of its fracture surfaces.

Most probably the lines of not-tempered martensite in the microstructure of the X52/AR steel resulted in a formation of longitudinally oriented cracks on the fracture surfaces (Figure 6). The round-shaped quasi-brittle areas looking like „fisheye", [18], were also observed on the fracture surfaces (Figure 7). The fracture surface consisted mostly of transcrystalline, brittle, quasi-cleavage character. Zones of the ductile fracture occurred to

Table 2 Mechanical properties of the steels

Steel/state	Yield Strength 0.2% offset (MPa)	Tensile Strength (MPa)	Elongation in 50 mm (%)
X52/AR	390	515	24.5
X52/QT	486	610	22.5
X70/AR	500	600	30.5



Note: 720 hours is the standard duration of the test

***Figure 5** The results of the SSC tests*

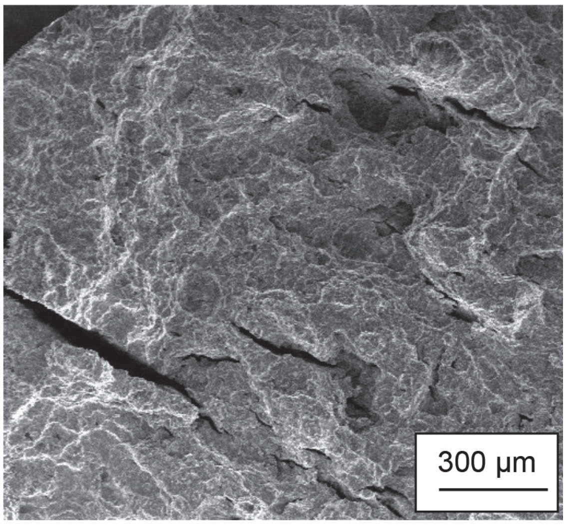


***Figure 6** Fracture surface of the X52/AR steel, 67% $R_{p0.2}$ (261 MPa), 63 hours*

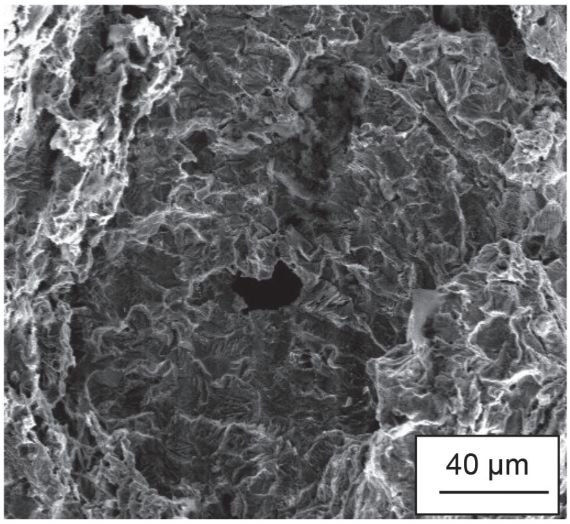


***Figure 7** Fracture surface of the X52/AR steel, 91% $R_{p0.2}$ (355 MPa), 40 hours*

a limited extent. The next example of the fracture surface is shown in Figure 8. The specimens after the laboratory quenching (X52/QT) were not subjected to the fractographic analysis because none of the specimens ruptured during the SCC test.

The specimens made of the X70/AR steel loaded by 80% of the $R_{p0.2}$ and less did not rupture after the prescribed test duration, but some longitudinal cracks were found on its surface by visual examination (Figure 9); most probably they were initiated by the lines of not-tempered martensite, which were detected in the mid-thickness of the sheet. The cracks were parallelly oriented with the applied loading force and thus its origin can be attributed to the HIC). Though the cracks did not lead to the final rupture of the specimens, it is possible to declare that the steel was not resistant to the SSC. The damaged specimens were subjected to the fractographic analysis that confirmed the key role of the not-tempered martensite lines in the microstructure when the SCC occurred (Figure 10). Similar to the case of the X52/AR steel, the

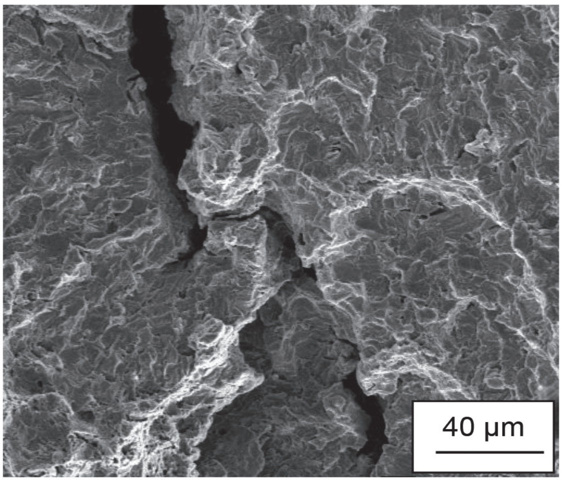


Figure 8 *Fracture surface of the X52/AR steel, 67% $R_{p0.2}$ (261 MPa), 63 hours*

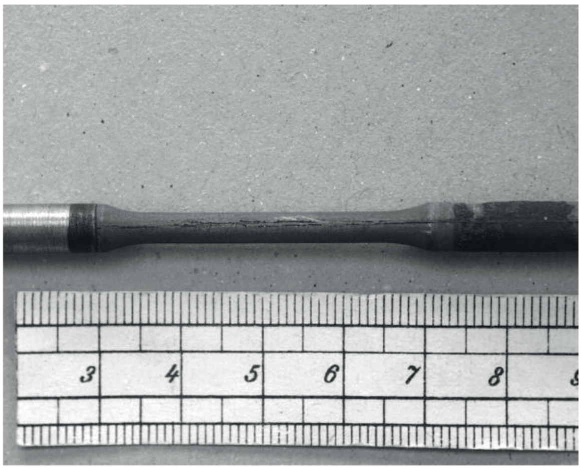


Figure 9 *Longitudinal cracks on the X52/AR steel specimen*

round-shaped zones of the quasi-cleavage damage were observed; in their centers were found the non-metallic inclusions.

Comparison of the SSC testing results between the as-rolled and the as-quenched and tempered states brings up a very important finding that the quenched and tempered state shows much higher resistance to the SSC. Even the generally applied approach, published in NACE MR0175/ISO 15156, is based on the fact that the resistance to the SSC is decreasing with increasing strength of the steel. The standard also allows to use the unalloyed (carbon) steels in as-rolled and as-quenched and tempered states, as well, if the actual hardness does not exceed 22 HRC, without any need to perform the SSC test. However, the results obtained in this paper show that the steels being regarded as the SCC resistant in accordance with NACE MR0175/ISO 15156 do not pass the tests in accordance with NACE TM 0177. It is the problem that needs to pay attention to, since the use of unsuitable material can cause a serious failure. A reference criterion about the SCC resistance of the steel is not only strength level but the microstructural properties and micro-cleanliness, as well. Due to the fact that the SCC belongs to the hydrogen embrittlement demonstration, there must be the same patterns as in the other cases, i.e. HIC or in the case of the Slow Strain Rate Test (SSRT) of hydrogen charged specimens. The presence of the not-tempered martensitic lines in the microstructure is completely

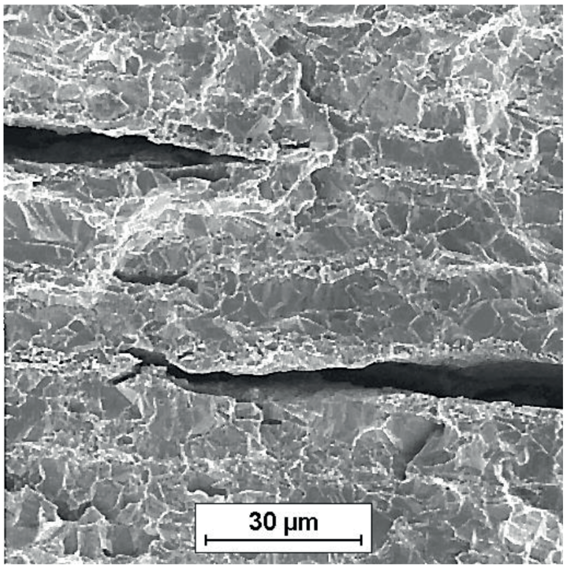


Figure 10 *Fracture surface of the X70/AR steel, 90% $R_{p0.2}$ (450 MPa), 593 hours*

unsatisfactory from a view of the SSC resistance; on the other hand, as-quenched and tempered microstructure exhibits the high resistance to the SSC, even under the test loading corresponding to 90 % of the yield strength.

4. Conclusions

Presented paper was mainly focused on the study of influence of the X52 and X70 steels microstructure on the resistance to the SSC.

The resistance of the steel against this kind of the damage was evaluated in accordance with usually used field approach from which the relationship with the tensile strength level or the hardness level, respectively, was clearly predicted. However, the experimental results have shown that the microstructural parameters are important factors too; they do have the influence on the steel resistance against the SSC. It was found that the resistance to the SSC can be significantly increased by quenching and tempering - similarly as for the HIC. In the case of the as-rolled (as-delivered) steels, the damage mechanism was a superposition of the HIC and the SSC. The cracks located in the segregation lines, caused by the HIC, led to significant reduction of time to rupture, despite the fact that they were longitudinally oriented in the direction of applied loading during the SSC test. This negative phenomenon was not observed after the quenching and tempering. Even though the quenched and tempered steel has the higher tensile strength level in comparison to the as-delivered state, a substantially higher resistance against the SSC was achieved.

It means that the steel selection process for sulfane working conditions, where the SSC risk exists - based on using the steels not exceeding the limited tensile strength level, should be re-evaluated. The influence of the microstructure should not be excluded since it could lead to selection of the material with the low resistance to the SSC that can cause a catastrophic service failure.

Acknowledgement

This paper was created at the Faculty of Metallurgy and Materials Engineering as part of the Project No. LO1203 "Regional Materials and Technology Centre – Feasibility Programme" funded by the Ministry of Education, Youth and Sports of the Czech Republic.

References

[1] RANGLOFF, R., P.: Comprehensive Structural Integrity: Hydrogen Assisted Cracking of High Strength Alloys. MILNE, I., RITCHIE, R., O., KARIHALOO, B. (Eds.), Environmentally Assisted Fracture, Elsevier, Amsterdam, 6, 31-101, 2003.

[2] GERBERICH, W. W., MARSH, P. G., HOEHN, J. W.: Hydrogen Induced Cracking Mechanisms - Are There Critical Experiments? THOMPSON, A. W., MOODY, N. R. (Eds.). Hydrogen Effects in Materials, TMS, Warrendale, PA, 539-553, 1996.

[3] McMAHON, C. J. Jr.: Hydrogen Induced Intergranular Fracture of Steels. Engineering Fracture Mechanics, 68(6), 773-788, 2001. https://doi.org/10.1016/S0013-7944(00)00124-7

[4] BIRNBAUM, H. K., SOFRONIS, P.: Hydrogen-Enhanced Localized Plasticity - A Mechanism for Hydrogen-Related Fracture. Materials Science and Engineering: A, 176(1-2), 191-202, 1994. https://doi.org/10.1016/0921-5093(94)90975-X

[5] LU, G., ZHANG, Q., KIOUSSIS, N., KAXIRAS, E.: Hydrogen Enhanced Local Plasticity in Aluminium: An Ab Initio study. Physical Review Letters 87(9), 095501, 2001. https://doi.org/10.1103/PhysRevLett.87.095501

[6] ROBERTSON, I. M.: The Effect of Hydrogen on Dislocation Dynamics. Engineering Fracture Mechanics, 68(6), 671-692, 2001. https://doi.org/10.1016/S0013-7944(01)00011-X

[7] LYNCH, S. P.: Mechanisms of Hydrogen Assisted Cracking - A Review. MOODY, N. R. et al. (Eds.), Hydrogen Effects on Material Behavior and Corrosion Deformation Interactions. TMS, Warrendale, PA, 449-466, 2003.

[8] LYNCH, S. P.: Comments on „A Unified Model of Environment-Assisted Cracking". Scripta Materialia, 61(3), 331-334, 2009. https://doi.org/10.1016/j.scriptamat.2009.02.031

[9] MAES, M. A., DANNA, M., SALAMA, M. M.: Influence of Grade on the Reliability of Corroding Pipelines. Reliab. Reliability Engineering & System Safety, 93(3), 447-455, 2008. https://doi.org/10.1016/j.ress.2006.12.009

[10] CORBETT, K. T., BOWEN, R. R., PETERSEN, C. W.: High - Strength Steel Pipeline Economics. Offshore and Polar Engineers, 14, 75-80, 2004.

[11] BRONCEK, J., JANKEJECH, P., FABIAN, P., RADEK, N.: Influence of Mechanical Anisotropy in Low Carbon Microalloyed Steel. Communications - Scientific Letters of the University of Zilina, 17(3), 25-30, 2015.

[12] NACE MR0175-2015/ISO 15156 Petroleum and Natural Gas Industries - Materials for use in H_2S-Containing Environments in Oil and Gas Production. NACE Int. Houston, Texas, USA, 2015.

[13] AL-MANSOUR, M., ALFANTAZI, A., M., EL-BOUJDAINI, M.: Sulfide Stress Cracking Resistance of API-X100 High Strength Low Alloy Steel. Materials and Design. 30(10), 4088-4094, 2009. https://doi.org/10.1016/j.matdes.2009.05.025

[14] CARNEIRO, R. A., RATNAPULI, R. C., LINS, V. F. C.: The Influence of Chemical Composition and Microstructure of API Linepipe Steels on Hydrogen Induced Cracking and Sulfide Stress Cracking. Materials Science & Engineering A, 357(1-2), 104-110, 2003. https://doi.org/10.1016/S0921-5093(03)00217-X

[15] ALBARRAN, J. L., MARTINEZ, L., LOPEZ, H. F.: Effect of Heat Treatment on the Stress Corrosion Resistance of a Microalloyed Pipeline Steel. Corrosion Science, 41(6), 1037-1049, 1999. https://doi.org/10.1016/S0010-938X(98)00139-5

[16] NACE Standard TM 0177-05 Laboratory Testing of Metals for Resistance to Sulfide Stress Cracking in H_2S Environments. NACE Int., Houston, Texas, USA, 2005.

[17] BURSAK, M., BOKUVKA, O.: Influence of Technological Factors on Fatigue Properties of Steel Sheets. Communications - Scientific Letters of the University of Zilina, 8(4), 34-37, 2006.

[18] JONSTA, P., VLCKOVA, I., JONSTA, Z., HEIDE, R.: Material Analysis of Degradated Steam Turbine Rotor. Communications - Scientific Letters of the University of Zilina, 18(3), 78-83, 2016.