THE RESISTANCE OF MARTENSITIC STAINLESS STELL TO SULPHIDE STRESS CRACKING (SSC)

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Abstract

High-pressure steel cylinders (HPSC) are commonly used for a variety of applications like industrial gases storage and its transport, storage and transport of compressed natural gas (CNG) and many others. Especially in case of CNG storage, variety of gas purities is used worldwide. Special field of gases storage is storage and transportation of untreated CNG so called raw gas, meaning not dehumidified and desulphurized natural gas. This kind of gas causes significantly increased speed of corrosion in H_2S environment. So far, there were only two solutions.

First one was to use HPSC with very low mechanical properties, limited of tensile strength (TS) up to 950 MPa to withstand such conditions. This caused the increased weight of cylinders due to the increased wall thickness caused by the low mechanical properties of material. Second solution was for use of inner coatings of HPSC, but this solution is highly expensive and the wear processes during the gas filling caused the wear of the inner coating and its chipping. The best solution is to use a different material. In this case, the high strength martensitic stainless steel was only alternative solution to get an increased corrosion resistance and also TS up to 1099 MPa. In this paper, the basic microstructure, mechanical properties and resistance to SSC are evaluated and compared with the steel 34CrMo4, which is used as the standard material for HPSC production.

Keywords: Martensitic stainless steel, high-pressure steel cylinders, microstructure, mechanical properties, sulphide stress cracking

1. INTRODUCTION

High-pressure steel cylinders are commonly used in a variety of compressed gases applications. Nowadays, the compressed natural gas transportation and storage takes place. The great emphasis is placed on the safety of all cylinders. In dependency on the rig, the natural gas can contain high volumes of humidity, chlorides and H_2S. Basic sulphide stress cracking principles are based on the generation of hydrogen ions by reaction between the wet hydrogen sulphide and the exposed steel. This type of contaminated natural gas so called raw gas is used for certain applications, such as storage of CNG for cogeneration units for subsequent heating. The mechanics of the SSC initiation and propagation is a caused by ions of hydrogen and its reaction between the humid environment, hydrogen sulphide and the exposed steel [1-3].

The resistance of most commonly used steel type 34CrMo4 to SSC is not sufficient if the tensile strength (TS) exceeds 950 MP and other methods, such as inner coatings, to prevent SSC process of the steel have to be applied. The most suitable solution to extend the lifetime of cylinders used for the raw gas storage and transportation is the usage of martensitic stainless steel, which brings highly increased corrosion resistance compared to the 34CrMo4 steel together with high achievable values of TS and other mechanical properties.

Presented paper deals with the achieved mechanical properties of martensitic stainless steel and compares its SSC resistance with steel 34CrMo4, which were applied for high pressure steel cylinders. Part of solution is also dedicated to an analysis of observed fracture features.

2. EXPERIMENTAL PROCEDURES AND RESULTS

The experimental investigation started with the verification of chemical composition of an input material - hot forged bar and results are presented in **Table 1**.

Table 1 Chemical composition of investigated steel [wt. %]

C	Si	Mn	Cr	Ni	Mo	N	S	P
0.06	0.71	0.43	14.91	3.93	0.78	0.018	0.009	0.037

Further production steps have followed, such as all hot forming processes (reverse extrusion from billet, reversed broaching and neck forming) and finally the heat treatment based on the austenitization at 1130 °C together with the tempering at 580 °C with subsequent water mist cooling were carried out. After all mentioned processes second chemical analysis (of final product) was carried out, see **Table 2**.

Table 2 Chemical composition of investigated steel [wt. %]

C	Si	Mn	Cr	Ni	Mo	N	S	P
0.05	0.69	0.46	14.99	3.97	0.79	0.019	0.011	0.039

The evaluation of mechanical properties was the next step of an experimental investigation and was focused on the achieved yield strength (YS) and tensile strength (TS), elongation (El.), CVN and Brinell hardness (HBW) evaluation. Testing of tensile properties was carried out by use of Zwick / Roell Z 250 machine according to the EN ISO 6892-1. Hardness measurement was realized by use of hardness testing machine M4U750 according to the EN ISO 6506-1 standard. The testing of notch toughness was carried out using RKP 450 Charpy Impact Testing Machine according to the ISO 148-1. Results of all found mechanical properties are summarized in **Table 3**.

Table 3 Cylinder's mechanical properties after HT

YS [MPa]	TS [MPa]	El. [%]	CVN transverse -50 °C [J.cm-2]	CVN longitudinal-50 °C [J.cm-2]	HBW (2.5 / 187.5) [-]
1011	1058	18.6	129	112	316

The next part of investigation was aimed to the SSC resistance of above-mentioned material. Specimens were exposed in the solution of distilled water buffered with 0.5 % sodium acetate tri-hydrate and continuously saturated by the hydrogen sulphide. This procedure was carried out according to ISO 11439 standard and NACE TM0177 standard, because combination of those standards is suitable and prescribed especially for the SSC testing of high-pressure steel cylinders. The applied load of samples was set up on the 0.6 of minimal prescribed YS. Starting and also finishing pH of the corrosion solution was set up exactly to 4.0 and the pressure in the testing chambers was in accord with mentioned standard. Dwell times of 6 SSC specimens until the full fracture were 12, 16, 17, 15, 10 a 12 hours. In frame of metallographic observation study of microstructure after the heat treatment, micro purity and grain size evaluation using the light microscopy (Olympus IX70) was carried out. For metallographic observation and micro-fractography investigation also the SEM (scanning electron microscopy SEM JEOL JSM-6490 LV equipped with X-ray analyser EDA) was used. Metallographic samples of the finished cylinder were prepared in transverse and longitudinal direction by the conventional methods of grinding; polishing and etching in Nital and/or in sodium hydroxide (electrolytic etching) to make the δ-ferrite presence of approximately 5 % visible in the tempered martensitic matrix, see **Figures 1**, **2.** Separately, metallographic samples of SSC cracked specimens in longitudinal direction to the specimen axis were prepared as it can be seen in **Figure 3**, in which also cracks along the grain boundaries were revealed.

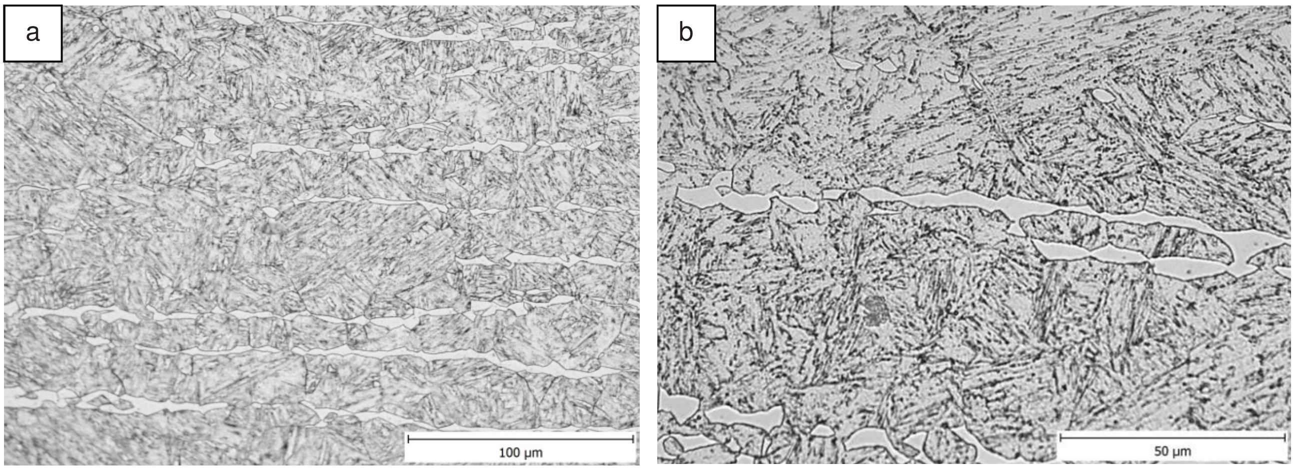

Figure 1 δ-ferrite in tempered martensite in central area of wall thickness (transversal direction)
a) general view, b) in detail

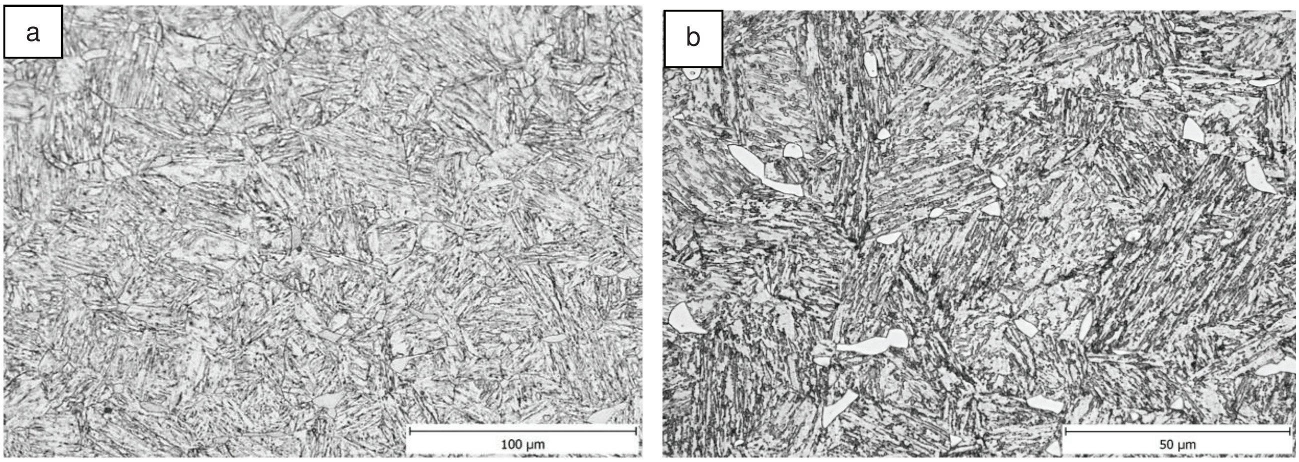

Figure 2 δ-ferrite in tempered martensite in central area of wall thickness (longitudinal direction)
a) general view, b) in detail

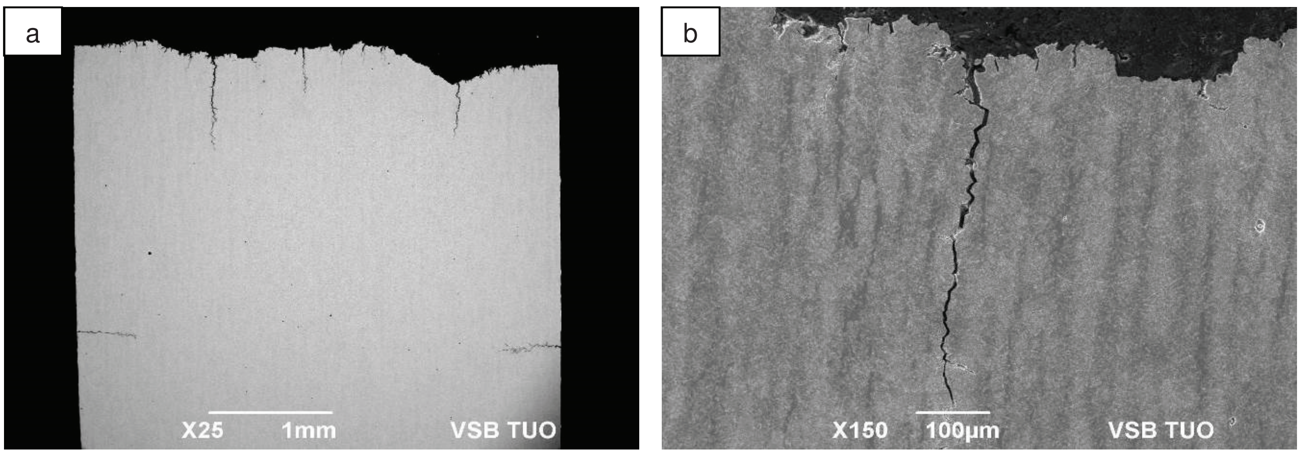

Figure 3 The longitudinal section of SSC specimen showing cracks propagating along the grain boundaries
a) general view, b) in detail

Grain size of an input material and finished cylinders according to EN ISO643 and micro purity according to ISO 4967 evaluation are shown in **Table 4**.

Table 4 Evaluation of micro purity and grain size

Sulphides fine/coarse - finished cylinder	Oxides banded fine/coarse - finished cylinder	Oxides formable fine/coarse - finished cylinder	Globular oxides fine/coarse - finished cylinder	Coarse globular oxides fine/coarse - finished cylinder	Grain size input material	Grain size finished cylinder
-	0.1 / -	- / 0.2	0.6 / 0.2	0.1	6	8

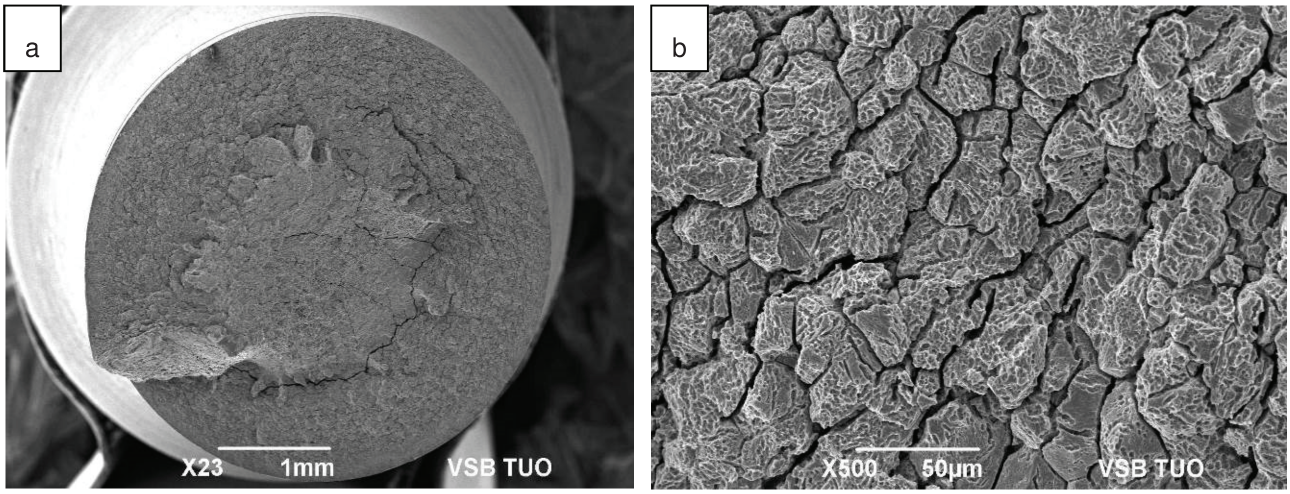

Figure 4 Fracture surface of SSC specimen a) general view, b) area close to the surface

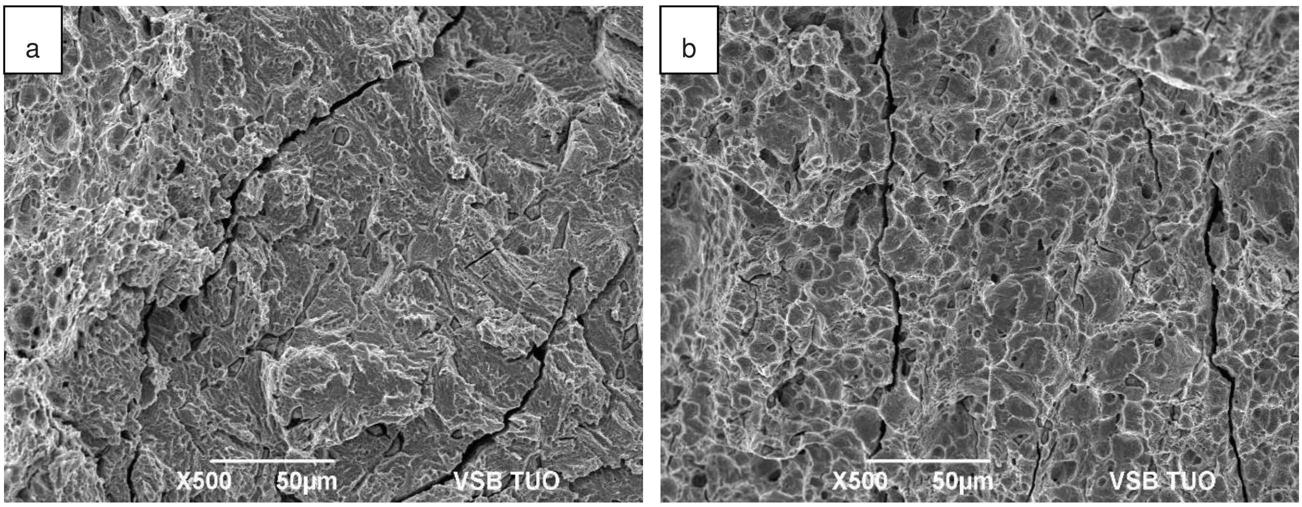

Figure 5 Fracture surface of SSC specimen a) transition area between the area close to the SSC sample surface and the central area, b) central area

The SEM analysis revealed the presence of cracks typical for SSC. The observed cracks in the SSC samples were propagated both along the grain boundaries showing inter-crystalline rupture and through the grains with trans-crystalline morphology, **Figure 5a**, which represents fracture surface of the SSC samples with three different areas. In under-surface one inter-crystalline rupture with fine dimple morphology in grains predominates (dimples were in range from 1 µm to 4 µm in diameter) as it can be seen in **Figure 4b**. Transition area (between centre and under-surface area) predominantly revealed quasi-cleavage rupture (see **Figures 5a**), which turned to ductile morphology in central area where none brittle fracture was observed. Dimples were in range from 1.5 μm to 20 μm in diameter. This finding is quite different from conclusions of paper [4] mentioning predominantly intergranular cracking in the SSC samples from steel showing yield stress higher than 700 MPa. Our steel reached 1058 MPa on average.

3. DISCUSSION

As it is presented in **Table 3**, results of mechanical properties, mainly CVN values in transversal test direction were significantly higher than required according to the standard. This was caused by the presence of the δ-ferrite bands, which are generally more ductile than the tempered martensitic structure, as it is presented in **Figures 2** and **3** and simultaneously represent obstacles for cleavage crack propagation. Maximally around 5 % of δ-ferrite is allowable to be present in microstructure without any important impact on toughness, if exceeding 5 %, the degradation of CVN values takes place as it from work [5] follows, whereas grain boundary network of δ-ferrite results to intragranular fracture [6]. The investigated SSC resistance revealed considerably more favourable hydrogen response of 13.7 hours on average in comparison with 2.9 hours of 34CrMo4 steel type as it was formerly presented in [7, 8]. Craig and Smith reported [9] that the modified high strength steels with higher chromium content than 13 wt. % are more susceptible to hydrogen than standard 13Cr grade. However, applying a controlled quenching process with followed tempering described above, balanced mechanical properties can be reached as it **Table 2** summarizes resulting also in favourable SSC resistance [10], even in case of 13 wt. % chromium martensitic steels [11]. In paper [8] yield stress of 34CrMo4 steel type reached 515 MPa and tensile strength 840 MPa only with 4.7 times lover lifetime in the same NACE solution than the presented martensitic steel.

According to the above-mentioned findings, it is expected that the δ-ferrite banding performed in the microstructure one type of hydrogen trap due to its discontinuity, significantly low thickness and homogeneous dispersion. Also the value of grain size 8 (see **Table 4**) together with extremely low presence of sulphides inclusions type with fine and homogeneously dispersed carbides in martensitic matrix resulted to the increase of SSC resistance [12-14]. After exposition, fracture surfaces of SSC specimens showed the inter-crystalline fracture morphology, see **Figure 4b**, in the under-surface area which was continuously turning from the mentioned inter-crystalline fracture to the quasi-cleavage one as it is shown in **Figure 5a** and finally changed to the ductile character with obvious dimple morphology as it is presented in **Figure 5b**. Above mentioned findings prove that the inter-crystalline fracture was initiated on the surface and in under-surface areas of SSC specimens where the hydrogen concentration had to be the maximal during hydrogen diffusion into tested material. Similar was observed by Tawang et al [15]. The subsequent crack propagation in central areas of the SSC samples was influenced by the tensile tension rather than by the hydrogen diffusion. Observed fracture feature in central area of the SSC specimens showed finer dimple morphology anyway.

4. CONCLUSION

Paper presents mechanical properties and especially SSC response of high-pressure cylinders manufactured from martensitic anticorrosion steel with approximately 15 wt. % of Cr and 4 wt. % of Ni under operating conditions. Entire production process was controlled and was simpler than long-term heat treatment combinations in case of cylinders made from 34CrMo4 steel [8].

Paper analyses SSC samples after exposition in sour environment of NACE solution A. Investigated SSC samples showed 4.7 times higher hydrogen resistance (representing 13.7 hours of lifetime) in comparison to the 34CrMo4 steel. Under those conditions yield stress and tensile strength reached 1011 MPa and 1058 Mpa with balanced notch impact toughness values in transverse and longitudinal directions which were in range from 129 J / cm^2 - 112 J / cm^{-2}.

Fracture surfaces showed inter-crystalline rapture in under-surface area impacted by strong hydrogen diffusivity in mentioned area. Consequently, fracture character was turn into mixed fracture feature in half distance between surface and sample axis, while the central area was practically formed by ductile morphology only. It can be supposed than predominant mechanism of rapture in central area was rather controlled by tensile tension than by presence of hydrogen. In the short time (during 13.7 hours) its diffusivity had to be much lower there than in under-surface area.

Presented results represent promising way for next application of martensitic steel type in case of high-pressure steel cylinders.

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