



34CrMo4 STEEL RESISTANCE AGAINST THE SSC AFTER CONTROLLED COOLING PROCESS

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Resume

The sulphide stress cracking corrosion resistance of 34CrMo4 steel after the accelerated cooling process under the Ar₃ temperature was investigated. Two modes of heat treatment were applied to achieve homogeneous microstructure and at least partially eliminated segregation banding. First mode was based on the cooling up to the 420 °C on the air and subsequent cooling in the quenching bath. Second mode was similar except the temperature of cooling on the air, which was set up to the 460 °C. Afterward in both cases, the stress relief annealing was applied. Both modes of heat treatment resulted in the significantly banded microstructure based on the pearlite, ferrite and modified lower portion of acicular ferrite. The differences in mechanical properties of both cases of heat treatment were minimal. The SSC loading times to failure of both sets did not lead to important differences.

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1. Introduction

High pressure steel cylinders (HPSC) are commonly used products for the variety of applications. The HPSC are primarily used for the storage of technical gases. With the growing trend of eco-friendly fuels such the HPSC need as the CNG (Compressed Natural Gas) cylinders for the automotive transportation is still increasing. The CNG tanks used in automobiles, trucks, buses etc. are the best choice of the possible storage tanks, thanks to the high safety level of the reverse extruded HPSC in comparison to the LPG welded tanks, which are also used as a storage vessels for the alternative fuel. The sulphide stress cracking (SSC) resistance is one of the important parameters of high pressure steel cylinders and vessels for the CNG storage and transportation, which has been commonly produced from the 34CrMo4 steel [1, 2]. This steel type is highly suitable for the variety of

micro-alloying especially by the nitrogen, vanadium, niobium or titanium to achieve favourable mechanical properties, because those elements are able to form precipitates being potential hydrogen traps and are also able to increase strengthening as well as toughness through different refinement degree [3, 4]. Thanks to higher carbon content and presence of some other segregated elements in the steel 34CrMo4, after primary material production and especially after reverse extrusion and broaching microstructure shows strong segregation banding that is detrimental for the SSC resistance as was already formerly presented e.g. by Kawabata et al [5] on the micro-alloyed steel with vanadium, niobium and Mo addition. Partial restriction of bands would be possible by repeated normalization, however to the exclusion of a strength lost and economical expenses not representing the latest engineering solution [6].

To achieve desired parameters of mechanical properties together with simultaneously favourable corrosion resistance, combination of different heat treatment types can be used combined with accelerated cooling process. On that the presented work was focused. In frame of working possibilities, accelerated cooling under the A_{r3} temperature was chosen to achieve more homogenous microstructure with at least restricted segregation banding especially resulting from reversed extrusion and broaching [7]. The aim of presented treatment is also to obtain maximal portion of acicular ferrite during the cooling process under the A_{r3} temperature which offers chaotic, interlocking arrangement of fine displacively formed plates predominantly showing high angle misorientation supporting both strength and toughness increase [8].

For maximum efficiency, the microstructure of such heat treated products should contain the acicular ferrite in majority, supporting both strength and toughness and thereby higher hydrogen resistance, and martensite supporting strengthening ensured by higher Mo and Cr hardenability and/or low bainite and/or ferrite, pearlite in minority [9, 10]. This mixture of the phases should bring favourable results of loading times to failure, resp. of the SSC response.

2. Experimental material and procedures

Chosen steel on which procedures were carried out was the 34CrMo4 type and as a first step the chemical analysis by optical emission spectrometer Spectrolab 2000 of billet before the reversed extrusion and broaching was carried out. Results are summarised in Table 1.

As the following step, two modes of heat treatment were chosen, as it was already mentioned. Heat treatment was based on the heating at 750 °C/70 minutes in case of both heat treatment modes and subsequent cooling process on the air down to the 420 °C in case of the first mode of heat treatment (HT1) and

cooling on the air down to the 460 °C in case of the second heat treatment (HT2) followed. The next stage of the experimental procedure was the mechanical properties testing. This part was focused on the evaluation of achieved mechanical properties such as tensile strength (TS), yield strength (YS), elongation (El.) by use of the Zwick/Roell Z 250 machine, transverse notch impact strength at -50 °C (CVN-50) using the Charpy RKP 450 device and Brinell hardness (HBW) tested by use of the M4U750 device. The SSC specimens strained on prescribed value of the yield strength, which is dependent on the product and its prescribed standard is the following key step of this full experimental procedure. In case of the high pressure steel cylinders, the standard for the SSC testing is NACE TM01777-96 (testing is adjusted to the specification in ISO/DIS 11439.2 for the high pressure cylinders testing), which prescribes the chemical composition of the solution and loading time to failure.

Subsequently, metallographic observation by the light optical microscope Neophot 21 followed. Samples were prepared by classic way (grinding, polishing and etching in Nital) in longitudinal and transverse direction from notch impact test samples. As the part of the microstructural observation the macro and micro analyses of the structure, depth of the decarburization, evaluation of the materials purity, grain size measuring and micro-hardness evaluation were carried out. Further, micro-fractographic analysis on fracture surfaces of the SSC bars using the scanning electron microscope SEM JEOL JSM-6490 equipped with X-ray analyser EDA was realized. Fracture characteristics and initiation core of the SSC rupture were the focal point of this observation.

3. Results

The resulting chemical composition of investigated steel fully corresponds to the 34CrMo4 steel type as it Table 1 demonstrates.

Table 1

<i>Chemical composition of billet (in wt. %).</i>								
C	Si	Mn	Cr	Mo	S	P	N	V
0.40	0.35	0.98	1.15	0.25	0.004	0.012	0.131	0.051

Table 2

<i>Results of mechanical properties testing of HT1 and HT2.</i>					
Heat treatment mode	YS (MPa)	TS (MPa)	El (%)	CVN₅₀ (J.cm²)	HBW (2.5/187.5) (-)
HT1	489	815	20	22	234
HT2	515	840	18	24	235

Table 3

<i>The SSC specimens loading times to failure of both heat treatment modes (h).</i>		
Heat treatment mode	Loading times to failure	Average
HT1	2, 5, 5, 6, 7, 8, 5, 5, 5, 6, 7, 7, 5, 6, 6, 6, 8, 8	6
HT2	3, 3, 5, 5, 6, 6, 3, 3, 5, 7, 11, 14, 6, 6, 6, 7, 7, 7	9

Results of the mechanical testing after both modes of heat treatment are summarized in Table 2. The reached values of mechanical properties are higher for the HT2 with exception of elongation, which was by 2 % higher in case of the HT1. Differences between both heat treatments are generally negligible and the YS, TS, hardness and CVN-50 values were 26 MPa, 25 MPa, 1 HBW and 2 J.cm⁻² (given in sequence). Loading times to failure of the SSC specimens after the HT1 and HT2 are presented in Table 3.

Generally, the SSC specimens after both HT modes did not show favourable results of loading times to failure according to minimal prescribed values. In any case the HT2 showed slightly higher SSC resistance, because the loading times were in range from 3 to 14 hours and 9 hours in average, while for the HT1 the range was from 2 to 8 hours, resp. 6 hours in average. Observed microstructure presented evidently banded structure and contained pearlite, ferrite and low bainite mixture and partially also shape modified acicular ferrite as can be seen from Figs. 1, 2 and especially from Figs. 3 and 4.

Micro-purity and the depth of decarburization evaluation revealed the minority presence of non-metallic

inclusions and the depth of the partially decarburized layer in case of both modes of the HT is presented in Table. 4. Detected inclusions were on basis of sulphides, silicates and oxides and/or their complexes. Observed inner decarburized layer was thinner by 30 µm in case of the HT2, while the outer decarburized layer of both HT showed the same thickness.

Fracture surfaces of the SSC specimens produced by application of the HT1 mode and after 6 hours exposition and subsequent crack are presented in Fig. 5, while Fig. 6 the SSC fracture surfaces of the HT2 samples after 14 hours documents. Micro-fractographic analysis revealed the typical fracture surface for the SSC fracture with numerous crack networking initiated in some cases in the vicinity of particles detected as complex oxides.

4. Analysis of results

Achieved loading times to failure of all specimens did not show long lasting resistance for this applied type of experimental heat treatment. This phenomenon can be described especially because of the presence of more noticeable segregation banding especially in case of the HT1 mode (Fig. 1), where the average loading times to failure was slightly

lower (6 h in average) unlike the 9 h in average of the HT2 mode (Table 2 and Fig. 2). This can be ascribed into the partially eliminated segregation bands and simultaneously their thinner thickness in case of the HT2 mode thanks to partially reduced time for possible diffusion process at higher temperatures during the air cooling down to 460°C.

Microstructure containing mixture of structures based on the pearlite, ferrite, bainite and partially modified acicular ferrite was obtained by the heat treatment based on the air cooling from above A_{r3} temperature by the cooling rate between $0.9 - 1.1 \text{ } ^\circ\text{C}\cdot\text{s}^{-1}$, which probably was sluggish and formed good condition for diffusion process of all segregating elements. According paper [5, 11] due to strong segregation of Mn which usually reaches up to 50 % of local increase, in different segregated areas 50°C differences of the A_{r3} temperatures can occur, which leads to dissimilar mechanical properties of matrixes in such different areas. The original aim of applied heat treatment was partial re-austenitization and subsequent partial acicular ferrite formation and segregation suppressing during cooling process so that the SSC resistance would be maximized.

The original strong segregation banding was result of the first operation (conventional reversed extrusion and broaching) and followed-up re-austenitization temperature was not effective as well as the cooling rate that was insufficient for formation of more important acicular ferrite portion being able to secure the satisfactory SSC response, even when filling among acicular ferrite plates would be martensite, bainite or pearlite as a result of faster or slower cooling from the temperature of about 500-450 °C [11]. On the contrary, the martensite microstructure could be effective for higher strength level of final matrix as it was presented in numerous works [12, 13]. In presented material was addition of Mo, which extends the acicular ferrite area and shifts the pearlite transformation to the longer times and supports higher level of hardenability as it was

presented by García De Andrés et al [8]. Moreover, investigated steel was alloyed, resp. micro-alloyed by nitrogen and vanadium predestined to form vanadium nitrides showing excellent lattice similarity with acicular ferrite, hence easy probability of acicular ferrite formation [14] formability.

Small amount of non-metallic inclusions presented in the microstructure of the studied material was result of metallurgical melting process. Main types of observed inclusions are on basis of oxides, silicates and sulphides. Oxides and silicates result from refractory or another places based on the oxides and silicates. Sulphides were formed during melting process from the presented sulphur in heat and such MnSiO_3 inclusions are suitable nucleable particles for acicular ferrite formation [15, 16]. Generally, any fine and homogeneous dispersion of inclusions represents other traps for hydrogen during the SSC exposition and consequently a reduction of hydrogen atoms accumulation in lower number of potential hydrogen traps. Favourable hydrogen response is dependent on higher number of fine and homogeneously dispersed hydrogen traps. The depth of decarburization of outer surface is caused by the austenitizing and tempering heating. The decarburization of the inner surfaces is caused by the hot air, which is trapped inside of the cylinders during the heat treatment process. In case of the HT1 unlike the HT2 the longer cooling (to the 420°C) induced higher level of decarburization as it from Table 3 follows.

Micro-fractographic analysis showed typical fracture surface after exposition in corrosion solution with hydrogen sulphide with numerous cracks, mostly revealed in vicinity of complex oxides. However, to specify crack initiation in more details was impossible, because due to ultrasonic cleaning potential particles were cleared away. Unfortunately, a searching of initiation source of cracks was also not too successful in the longitudinal section.

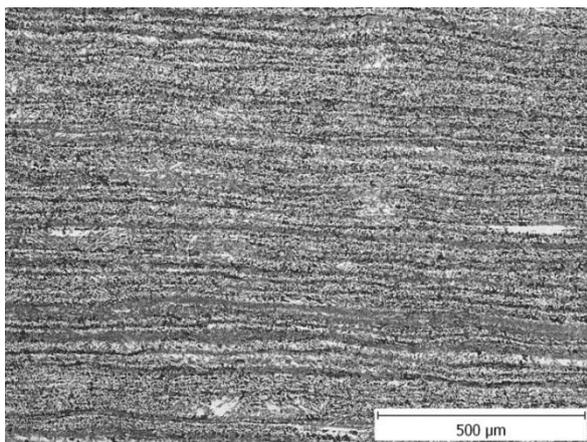


Fig. 1. Significantly banded microstructure after the HT1.

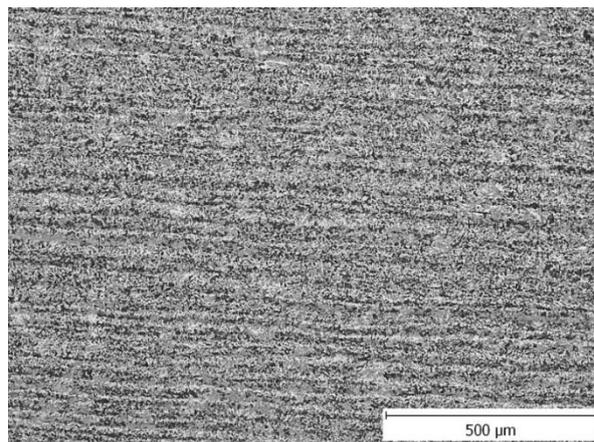
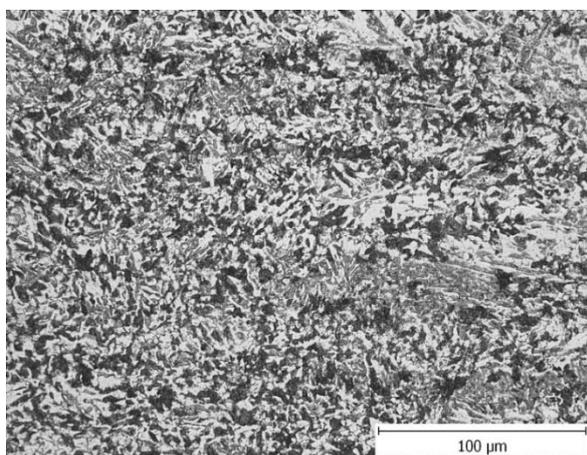
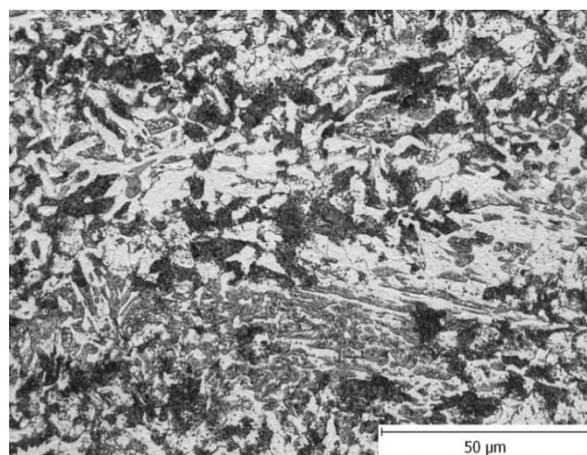


Fig. 2. Slightly eliminated banding after the HT2.

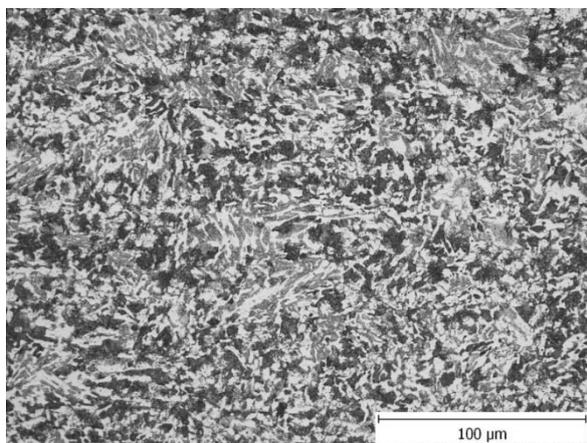


a) general view

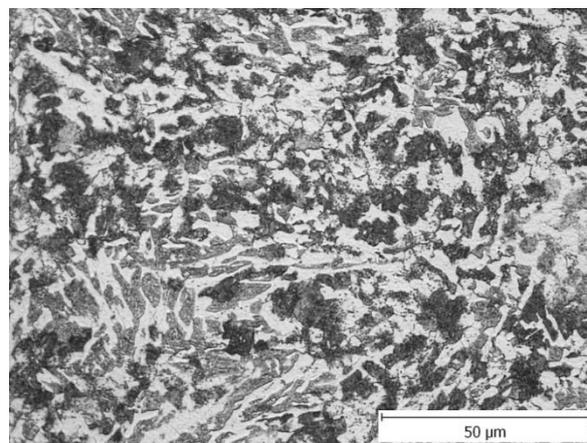


b) view in detail

Fig. 3. Image of mixed microstructure after the HT1.



a) general view

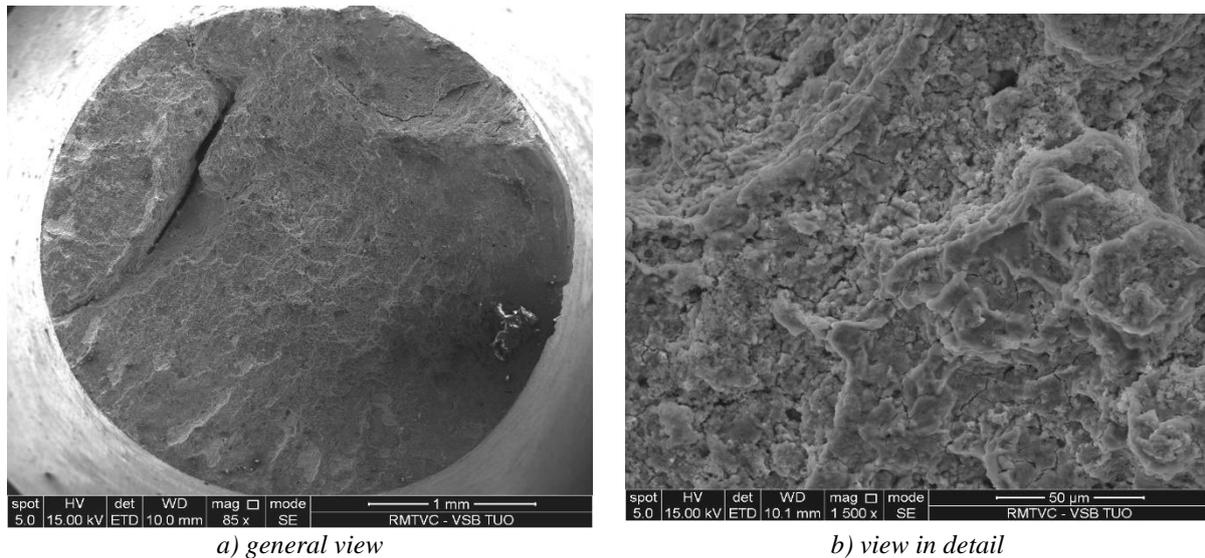


b) view in detail

Fig. 4. Image of mixed microstructure after the HT2.

Table 4

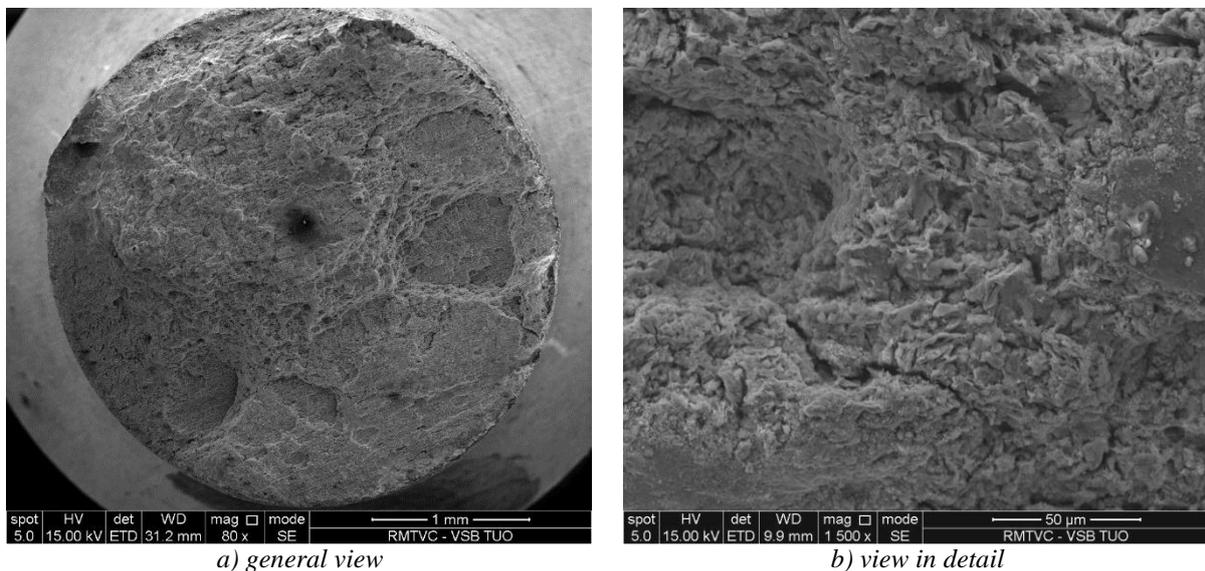
Values of the non-metallic inclusions and decarburized layer (DC).				
HT mode	A Fine/Coarse (-)	C Fine/Coarse (-)	D Fine/Coarse (-)	DC Inner/Outer surface (μm)
HT1	0.7/0	0.2/0.1	1/0.1	150/200
HT2	1/0	0.2/0.2	0.9/0.2	120/200



a) general view

b) view in detail

Fig. 5. Fracture surfaces of SSC specimens (HT1).



a) general view

b) view in detail

Fig. 6. Fracture surfaces of SSC specimens (HT2).

5. Conclusion

According to resulting microstructures after the HT1 and HT2 modes, SSC loading times to failure and mechanical properties can be said that the higher cooling rate at least in range of 15 – 20 °C in the first stage of the

experimental HT process is needed to ensure possible nucleation process of accicular ferrite and reduction of unfavourable diffusion of elements into the segregation bands.

Quenching temperature could be also slightly raised, approximately to 490 - 500 °C to

ensure the final martensitic transformation supported by the cooling rate of 25 – 35 °C. Mentioned adjustments of the HT should result in the mixed microstructure based on the presence of acicular ferrite which could bring the combination of strength and ductility and the martensite primarily present for the strengthening the matrix.

For achieving the high SSC resistance, two ways are possible. First way is to ensure the homogeneous dispersion of very fine inclusions and precipitates as the uniform hydrogen traps. And the second way is to reduce the inclusions presence to its minimal possible levels and to refine the grain-size by the more aggressive forming process to create conditions of maximal redistribution of hydrogen ions and/or atoms on numerous grain boundaries and dislocations.

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