COMPARISON OF RESISTANCE OF QUENCHED AND TEMPERED STEELS TO SULPHIDE STRESS CRACKING

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SROVNÁNÍ ODOLNOSTI ZUŠLECHTĚNÝCH OCELÍ VŮČI SULFIDICKÉMU PRASKÁNÍ POD NAPĚTÍM

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Abstrakt

Předložený příspěvek se zabývá srovnáním odolnosti vybraných typů zušlechtěných ocelí vůči sulfidickému praskání pod napětím. Ke zkoušení byly použity mikrolegované oceli X52 a X60 dle API a super-martensitická ocel 13Cr6Ni2.5Mo. Zušlechtění bylo provedeno v laboratorních podmínkách a spočívalo v kalení a vysokoteplotním popuštění zkušebních kusů. Testování vzorků bylo provedeno pomocí tahových zkoušek, při kterých byly vzorky zatíženy napětím, které odpovídalo určitému podílu meze kluzu, a sledoval se čas do lomu jednotlivých vzorků ocelí. Detailní popis zkušební metody je uveden v práci [1]. Lomové plochy vzorků pak byly detailně prozkoumány pomocí řádkovací elektronové mikroskopie, konkrétně na řádkovacím elektronovém mikroskopu firmy JEOL s označením JSM 50-A.

Ze vzájemného srovnání odolnosti ocelí vůči sulfidickému praskání pod napětím se jako nejhorší jevila super-martensitická ocel 13Cr6Ni2.5Mo, a to i přesto, že pokud jde o strukturu, má velkou přednost, kterou je vysoký podíl reverzního austenitu, který činil v hodnoceném případě cca 30 %. Určitou roli v případě nízké odolnosti této oceli vůči sulfidickému praskání pod napětím by mohlo hrát i chemické složení, a to obsah niklu, o kterém se obecně soudí, že zhoršuje odolnost ocelí vůči vodíkové křehkosti.

Zušlechtěné oceli X52 a X60 jsou strukturně závislé, co se týče odolnosti vůči sulfidickému praskání pod napětím a i přes zvýšení pevnostních charakteristik, kdy by odolnost ocelí podle obvyklých kritérií měla klesat naopak vzrůstá, a to díky příznivým mikrostrukturním charakteristikám.

Abstract

Presented paper compares resistance of selected types of quenched and tempered steels to sulphide stress cracking (SSC). Experiments were made with use of micro-alloyed steel grades X52 and X60 according to API and super-martensitic steel 13Cr6Ni2.5Mo. Heat treatment was realised in laboratory conditions. The samples were subjected to tensile tests, during which the samples were exposed to stress corresponding to a certain degree of yield strength and time to rupture of individual samples of steels was measured. Detailed description of the testing method is given in [1]. Fractures areas of the samples were then investigated in detail with use of scanning electron microscopy, namely of the scanning electron microscope JEOL JSM 50-A.

Mutual comparison of resistance of steels to sulphide stress cracking showed that the worst was super-martensitic steel 13Cr6Ni2.5Mo, in spite of the fact that it has great structural advantage, since it contains high portion of reverse austenite (approx. 30 %). Chemical composition could have also played certain role in influencing this low resistance to SSC, particularly nickel contents, which is generally considered as a factor deteriorating resistance of steels to hydrogen embrittlement.

Quenched and tempered steels X52 and X60 are structurally dependent what concerns their resistance to sulphide stress cracking, and in spite of increase of strength characteristics, when resistance of steel should decrease according to usual criteria, it contrariwise increases due to favourable micro-structural characteristics.

Keywords: sulphide stress cracking, heat treatment, microstructure, mechanical properties

1. Introduction

Selection of materials for use in petrochemical industry depends usually on two basic aspects. The first one – good mechanical properties of the given material. The second one - very good resistance to corrosion, particularly to hydrogen embrittlement in hydrogen sulphide containing media, for which we recognise two basic types of damage of material. The first one is hydrogen induced cracking (HIC) and the second one is sulphide stress cracking (SSC). In case of SSC there were obtained results [2], which show that similarly as in case of HIC, it is necessary at evaluation of material's resistance to take into account not only its strength characteristics, but it is also necessary to give appropriate attention to the influence of microstructure. A question remains, however, whether this "rule" is valid generally or just for certain types of materials. Presented article therefore deals with comparison of resistance of two micro-alloyed steels after heat treatment and also super-martensitic steel, also after heat treatment.

2. Experimental material

Experiments were realised on micro-alloyed steels X52 (tube 250/25) and X60 (tube 500/25) according to the API 5L, as well as on super-martensitic stainless steel 13Cr6Ni2.5Mo. Chemical composition of the steels is given in the Table 1.

Table 1 Chemical composition of steels (weight %)

Steel	C	Mn	Si	P	S	Cr	Ni	V	Nb	Ti
X52	0.09	0.92	0.28	0.007	0.010	0,02	0,01	0,004	0,03	0,01
X60	0.21	1.52	0.19	0.012	0.003	0,16	0,15	0,05	0,03	0,01
13Cr6Ni2.5Mo	0.0124	0.51	0.26	0.014	0.003	12,53	6,33	0,028	-	0,13
	Mo	**Al**	**Cu**	**N**						
	2.33	0.042	0.086	0.01						

It is obvious from the Table 1, that steels X52 and X60 are micro-alloyed by niobium, or niobium and vanadium.

Steels were subjected to the following heat treatment:

- X52 870 °C/40 min/water+ 600°C/90 min/air
- X60 870 °C/40 min/ water + 600 ^{0}C/90 min/air
- 13Cr6Ni2.5Mo 970 °C /1 h/air + 610 ^{0}C/6 h/air, $\gamma_{rev.} \approx 30$ %

Values characterising basic mechanical properties are summarised in the Table 2. Tensile tests were made on the machine INOVA TSM 50, values of hardness were determined by measurement with the measuring device made by the company EMCO test.

Strength characteristics were the lowest in case of the steel X52, but plastic properties of all steels were at almost the same level. Super-martensitic steel had the highest strength and hardness.

Table 2 Mechanical properties of steel (longitudinal direction)

Steel	$R_{p0.2}$ (MPa)	R_m (MPa)	A_5 (%)	$R_{p0.2}/R_m$	HRC
X52	486	610	22.5	0.80	11
X60	733	792	20.5	0.93	21
13Cr6Ni2.5Mo	667	897	21	0.75	27

3. Description and discussion of results

3.1 Microstructure

Structural analysis of the samples was made on the light microscope ZEISS NEOPHOT 32, fractographic analysis was realised on the scanning electron microscope JEOL JSM-50A.

Microstructures of the steels X52, X60 and 13Cr6Ni2.5Mo are presented in the Figures 1 – 3. Steel X52 show tempered bainitic structure with certain quantity of ferrite (Fig. 1). Fully hardened martensitic structure, represented the steel X60 (Fig. 2) already without occurrence of ferrite. Microstructure of super-martensitic steel 13Cr6Ni2.5Mo was fine-grained martensitic (Fig. 3) with minority content of reverse austenite, the content of which was determined by quantitative diffraction phase analysis. The structure contained unfortunately also undesirable δ-ferrite, segregated in the form of thin rows, which usually leads to deterioration of mechanical properties of these super-martensitic steels [3].

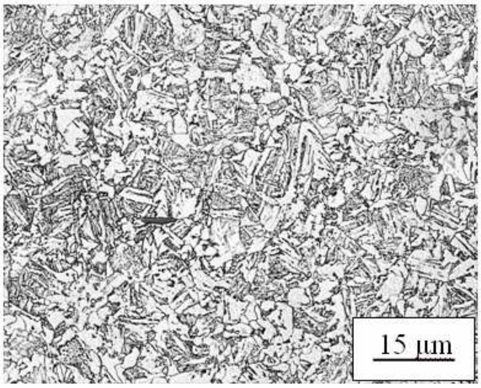


Fig.1 Microstructure of steel X52 – centre of thickness

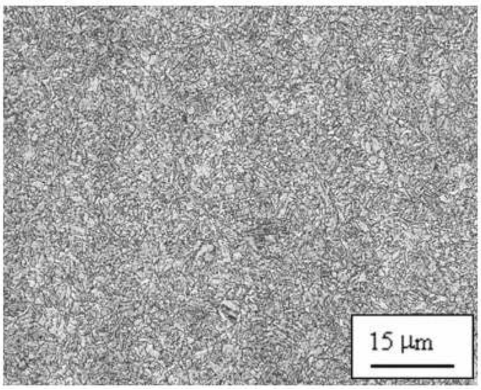


Fig.2 Microstructure of steel X60 – centre of thickness

During evaluation of cleanliness of steels X52 and X60 in principle two types of inclusions were found. There were globular oxidic inclusions and elongated manganese sulphides, which were rather numerous in the steel X52 (Fig. 4) due to higher contents of sulphur (0.01 weight %) in comparison to the steel X60. In case of super-martensitic steel 13Cr6Ni2.5Mo significant number of titanium carbides or carbo-nitrides was observed (Fig. 5). Sulphide inclusions were not found in the steel.

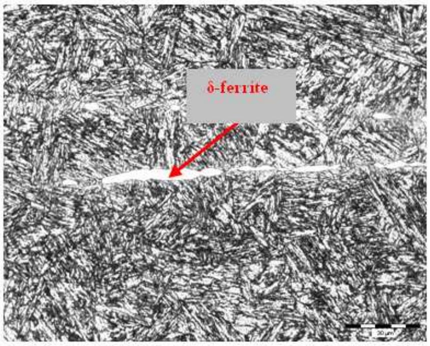


Fig.3 Microstructure of steel X60 – centre of thickness

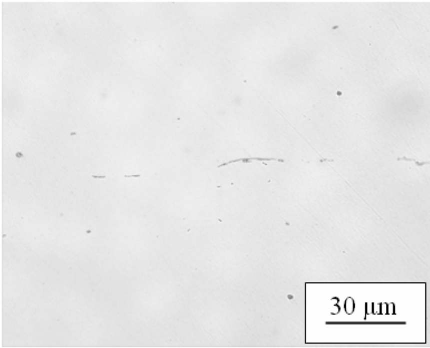


Fig.4 Sulphide inclusions in the steel X52

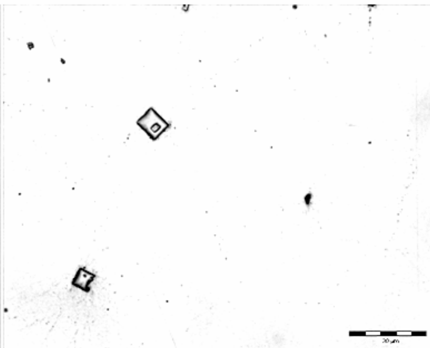


Fig.5 Titanium carbides in the steel 13Cr6Ni2.5Mo

3.2 SSC tests

Evaluation of resistance of steels to SSC was made in full respect of the directive NACE TM 0177-03, by method A. Results are summarised in the Table 3.

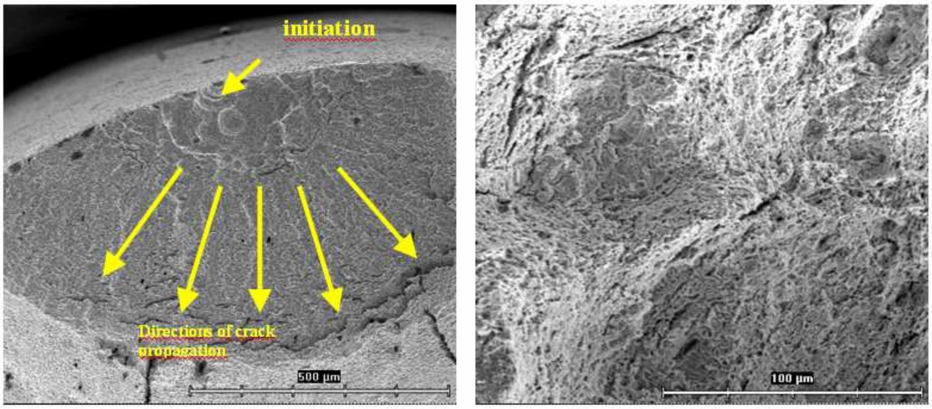
Samples from the steel X52 withstood successfully all the applied load values and therefore this steel in state after heat treatment can be labelled as resistant to SSC. Quenched and tempered steel X60 withstood only the load of 73 % $R_{p0.2}$, but absolute value of stress was 542 MPa, which is more than in case of the steel X 52 (447 MPa). In case of super-martensitic steel 13Cr6Ni2.5Mo all the samples ruptured during test. According to the directive NACE TM 0177-03 it means that the steel 13Cr6Ni2.5Mo non-conforming. Ruptured samples were subjected to a fractographic analysis. Figures 6 - 8 represent examples of fracture areas.

Table 3 Results of evaluation of resistance of steels to SSC

X52			X60		
Load (% $R_{p0.2}$)	Absolute values of stress (MPa)	Time to rupture (h)	Load (% $R_{p0.2}$)	Absolute values of stress (MPa)	Time to rupture (h)
92	447	720*	89	652	240
92	447	720*	85	623	375
79	384	720*	81	594	451
79	384	720*	73	542	720*
73	355	720*	73	542	720*
72	350	720*	63	462	720*
59	287	720*	63	462	720*
59	287	720*	-	-	-
53	258	720*	-	-	-

13Cr6Ni2.5Mo		
Load (% $R_{p0.2}$)	Absolute values of stress (MPa)	Time to rupture (h)
89	594	7
89	594	10
80	534	28
78	520	38
73	487	43
71	474	39
59	394	53
58	387	66
49	327	163

* no rupture occurred during standard duration of the test



a) b)

Fig.6 Fracture areas of steel X60, stress 81 % $R_{p0.2}$, time to rupture 451 h

Figure 6 a) shows place of initiation of rupture of the sample and ensuing directions of crack propagation in the steel X60. Figure 6 b) shows characteristic areas of ductile damage with dimple morphology.

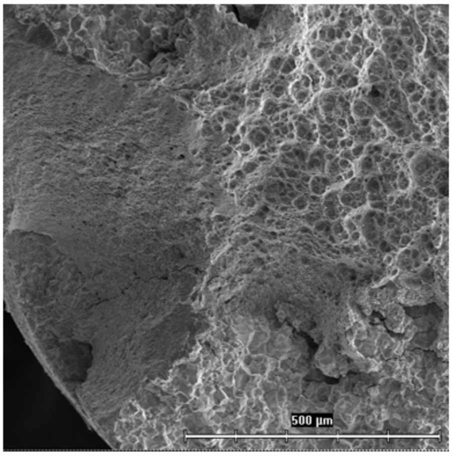


Fig.7 Fracture areas of steel 13Cr6Ni2.5Mo, 49 % $R_{p0.2}$, time to rupture 163 h

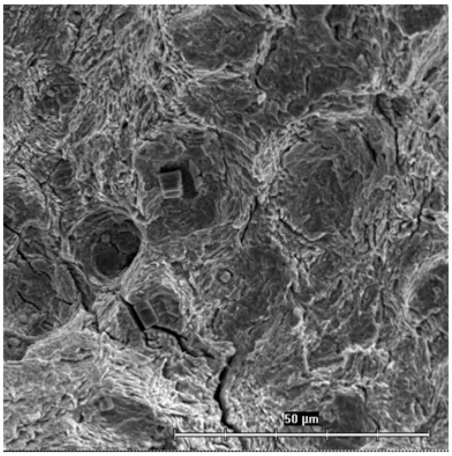


Fig.8 Fracture areas of steel 13Cr6Ni2.5Mo 73 % $R_{p0.2}$, time to rupture 43 h

Figure 7 shows overall view of the rupture area of the steel 13Cr6Ni2.5Mo. Figure 8 shows small areas of quasi-cleavage rupture, so called fish eyes. Fractographic analysis does not indicate that low resistance of steel to SSC would be supported also by δ-ferrite present in the structure, although this cannot be completely ruled out.

4. Conclusion

Objective of the presented paper consisted in comparison of resistance of various quenched and tempered steels to SSC. Experiments were made with use of micro-alloyed steel grades X52 and X60 according to API and super-martensitic steel 13Cr6Ni2.5Mo.

Mutual comparison of resistance of steels to sulphide stress cracking showed that the worst was super-martensitic steel 13Cr6Ni2.5Mo, in spite of the fact that it has great structural advantage, since it contains high portion of reverse austenite (approx. 30 %). Chemical composition could have also played a certain role in influencing this low resistance to SSC, particularly nickel contents, which is generally considered as a factor deteriorating resistance of steels to hydrogen embrittlement.

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Acknowledgements

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