MICROSTRUCTURAL ASPECTS OF SULPHIDE STRESS CRACKING OF DUPLEX STAINLESS STEELS

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MIKROSTRUKTURNÍ ASPEKTY SULFIDICKÉHO PRASKÁNÍ POD NAPĚTÍM DUPLEXNÍCH KOROZIVZDORNÝCH OCELÍ

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Abstrakt

Práce je věnována hodnocení odolnosti dvou taveb duplexní korozivzdorné oceli typu 22/5 vůči sulfidickému praskání pod napětím (SSC). Oceli byly hodnoceny jednak ve výchozím stavu po rozpouštěcím žíhání a dále po žíhání v teplotním intervalu 650 až 800°C, jehož smyslem bylo vyvolat precipitaci fáze σ na rozhraní ferit – austenit. Maximální objemový zlomek σ fáze byl cca 0,04. Testy odolnosti vůči SSC, provedené v souladu s předpisem NACE TM 0177, prokázaly, že přítomnost σ fáze ve struktuře ocelí se projevila poklesem odolnosti vůči SSC. Ve výchozím stavu došlo k porušení vzorků, jen pokud bylo aplikované napětí na úrovni meze kluzu oceli. Za přítomnosti σ fáze vydržela ocel jen zatížení odpovídající cca 70% z hodnoty meze kluzu. Aby bylo možné oddělit účinek mikrostruktury a aplikovaného napětí na odolnost duplexní oceli vůči degradačním účinkům vodíku, byly provedeny i testy odolnosti vůči vodíkem indukovanému praskání (HIC). Ty ukázaly velmi dobrou odolnost oceli, a to i za přítomnosti σ fáze. Pouze při nejvyšším podílu σ fáze, po žíhání 800°C/5 hodin, byly při testech HIC nalezeny krátké trhliny na rozhraní ferit – austenit. Podíl délky trhlin CLR však nepřesáhl 0,5%.

Práce byla doplněna o stanovení koeficientu difúze vodíku v duplexní oceli metodou elektrochemické permeace. Výsledky ukázaly, že hodnota difúzního koeficientu závisela zejména na orientaci vzorků. Difúze byla snadnější, pokud probíhala podél řádků feritu ve struktuře oceli.

Abstract

Resistance of two heats of duplex stainless steels, containing 22% of Cr and 5% of Ni, to sulphide stress cracking (SSC) was studied. Steels were tested in initial state after solution annealing and after heat treatments, the aim of which was to provoke σ – phase formation. Annealing at temperatures in the range from 650 to 800°C resulted in a discontinuous σ – phase precipitation at the ferrite/austenite interface. The maximal volume fraction of σ – phase was about 0.04. SSC tests, performed in accordance to NACE TM 0177, showed that σ – phase deteriorated resistance of duplex steels to SSC considerably. In as-received state specimens failed only for stresses exceeding the yield strength of the material. If about 0.04 of σ – phase was present at the ferrite/austenite interface specimens withstood only stresses corresponding to about 70% of their yield strength. To establish the role of microstructure and applied stresses, hydrogen induced cracking (HIC) tests were performed as well. The results of HIC were different in comparison with SSC results. In the case of HIC, the presence of σ – phase did not deteriorate the resistance of duplex steels considerably.

The research was completed by hydrogen diffusion coefficient measurement in the studied duplex steels with the aid of electrochemical permeation method. Results showed that hydrogen diffusion coefficient of duplex steels depended mainly on the specimen orientation as the diffusion was easier if hydrogen diffused lengthwise of ferrite bands.

Key words: duplex stainless steels, sulphide stress cracking, hydrogen induced cracking, microstructure.

1. Introduction

Materials used in oil and gas production should meet strong requirements concerning not only mechanical properties but also a very good corrosion resistance, especially hydrogen embrittlement resistance in hydrogen sulphide containing environments. Both requirements – mechanical and corrosion resistance – can be attained together by using duplex stainless steels. That is why this material has emerged as a candidate for using in H_2S containing environments. As to microstructure, duplex stainless steels consist only of ferrite and austenite, with the proportion of these two phases less or more equal. Due to some problems in manufacturing, some other phases can appear such as σ, χ or α′. It is well known that the presence of these phases can deteriorate mechanical properties in a considerable way. On the other hand, data concerning their role in the corrosion resistance in H_2S environments are only sporadic [1,2].

The aim of this paper was to study the role of σ-phase precipitation on the duplex steel resistance to sulphide stress cracking (SSC) and also to hydrogen induced cracking (HIC). To complete this work hydrogen diffusion coefficient was measured by means of electrochemical permeation method.

2. Experimental procedure

Testing was made on duplex steels 22/05, (sheet with thickness of 12 mm). The chemical composition of the studied steels is given in Table 1.

Table 1 Chemical composition of duplex steel (mass %)

Steel	C	Cr	Ni	Mo	Mn	Si	P	S	N_2
A	0.019	22.6	5.4	3.0	1.68	0.44	0.024	0.0002	0.17
B	0.025	23.0	5.6	2.9	1.12	0.24	0.021	0.0015	0.02

Steels were studied in two different structure states:

- in initial state (after rolling and solution annealing);
- after subsequent annealing at the temperature range 675 – 800°C for 2 – 5 hours.

This subsequent annealing resulted in σ-phase precipitation at the austenite/ferrite interface.

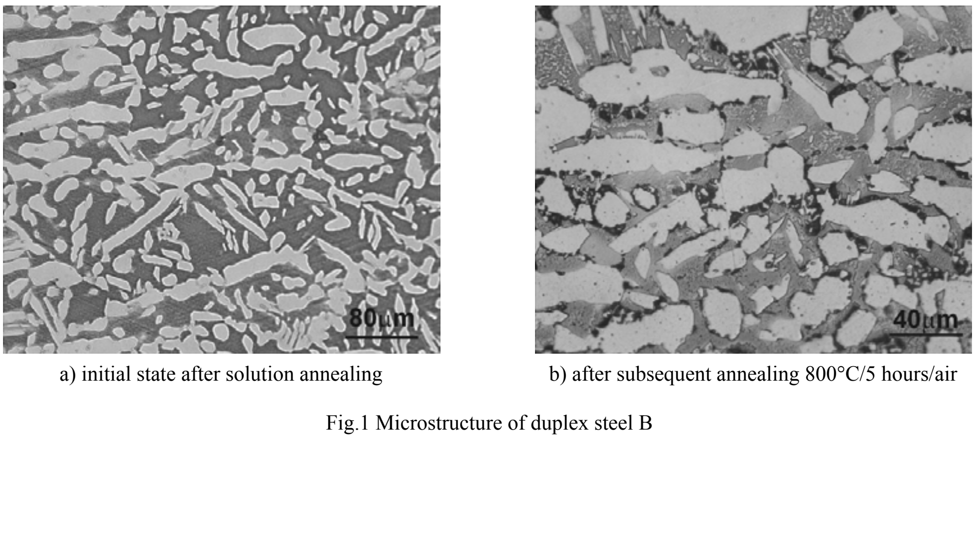
Structure analysis was performed by means of optical metallography (OM) and scanning electron microscopy (SEM). Tensile properties were determined using MTS 100 kN machine on cylindrical specimens with 10 mm in diameter and 50 mm in gauge length, taken from the mid-thickness of the materials.

Sulphide stress cracking was evaluated as required in NACE TM 0177 Standard, Method A [3]. Subsize cylindrical specimens were used with diameter of 3.81 mm and gauge length of 25.4 mm. The applied load varied from 0.6 to 1.0 of the yield strength (YS) of the tested materials. Fracture surfaces of SSC test specimens were observed carefully using SEM. Prior to the observation, they were cleaned ultrasonically in a mild solution of H_3PO_4 for 1 to 3 minutes. For comparison, HIC resistance was also tested in accordance to NACE TM 0284 Standard. The testing solution was the same as for SSC tests.

Electrochemical permeation tests were derived from the Devanathan and Stachurski method [4]. They were performed at ambient temperature in a permeation cell composed of two double wall glass compartments separated by the sample (working electrode). Only steel A was tested in both states. At the entry side, 1 M NaOH solution was used. The exit side, previously coated with a thin layer of Pd [5], was polarised in 0.1 M NaOH solution at a constant potential of 0.28 V_{NHE}. The anodic current recorded at the exit side was a measure of the permeation rate of hydrogen. Continuous argon bubbling was maintained during the whole test in both compartments. The membrane thickness was about 0.15-0.4 mm and its working area was 1.0 cm^2. After residual current density stabilisation, a first permeation was performed using a current density of –10 $mA.cm^{-2}$. The diffusion coefficient of hydrogen was calculated from the beginning of permeation transients.

3. Results and discussion

3.1 Microstructure



a) initial state after solution annealing b) after subsequent annealing 800°C/5 hours/air

Fig.1 Microstructure of duplex steel B

Examples of the microstructure are given in Fig.1a,b for the steel B. In the initial state, microstructure consisted only of ferrite and austenite (Fig.1a). Both phases were presented in the form of more or less pronounced bands. The role of subsequent annealing is demonstrated by microstructure corresponding to 5 hour anneal at 800°C (Fig. 1b). In this case, the largest portion of σ-phase appeared at the austenite/ferrite interface (about 4% measured by image analysis after electrolytic etching in 10% of NaOH solution).

3.2 Mechanical properties

Mechanical properties of the steels are summarised in Table 2 for both states.

Table 2 Mechanical properties of duplex steels (longitudinal direction)

steel /condition	$R_{p0.2}$ [MPa]	R_m [MPa]	A_5 [%]	$R_{p0.2}/R_m$
A/init. state	540	741	33.5	0.73
A/800°C/5 hours	534	714	28.5	0.75
B/init. state	485	708	30.0	0.69
B/800°C/5 hours	480	753	22.5	0.64

It is evident that steel A has a higher yield strength, very probably due to a high nitrogen content. Comparing of mechanical properties in the initial state and after subsequent annealing indicates there are no important changes for the steel A. In the case of steel B, subsequent annealing at 800°C for 5 hours resulted in increased tensile strength and in decreased elongation.

3.3 Sulphide stress cracking

The results of SSC tests performed in accordance with NACE TM 0177, Method A, are presented in Table 3.

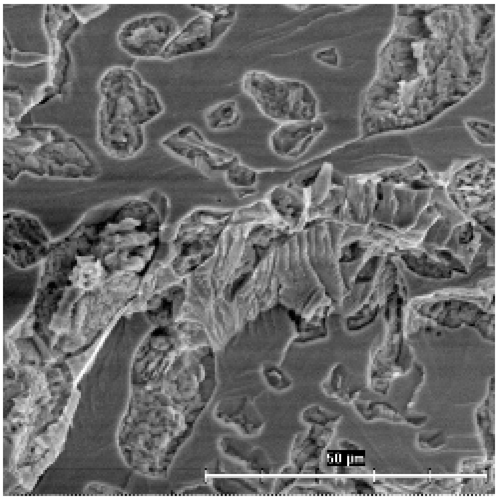
Table 3 Results of SSC tests for the steel A in two different states

initial state		**annealing at 675°C/5h/air**	
load (% $R_{p0.2}$)	**time to rupture (h)**	**load (% $R_{p0.2}$)**	**time to rupture (h)**
102	**35.1**	101	**5.2**
97	**59.7**	99	**2.3**
90	720*	93	**55.7**
91	720*	92	**19.8**
79	720*	81	**116.1**
79	720*	79	**255.4**
73	720*	72	720*
72	720*	69	720*
61	720*	61	720*

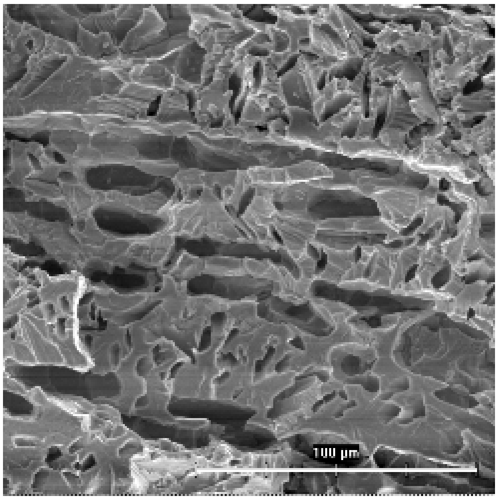
* no rupture occurred during standard duration of the test

In the initial state specimens failed only for stresses reaching or even exceeding the yield strength of the material. After subsequent annealing resulting in σ-phase precipitation at the austenite/ferrite interface specimens withstood only stresses corresponding to about 70 % of their yield strength. It is obvious that the presence of σ-phase deteriorated steel resistance to SSC. It must be pointed out that mechanical properties were not modified by the presence of σ-phase in this case. Similar results were obtained for the steel B.

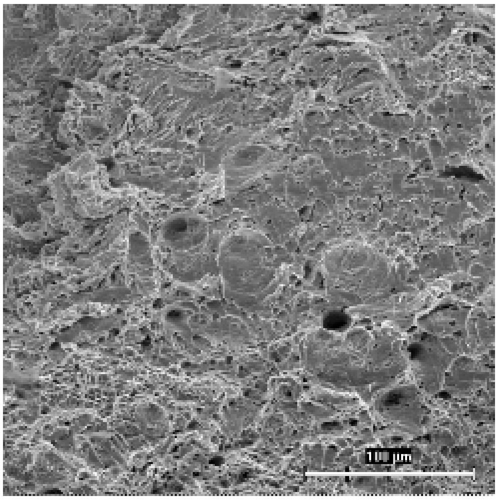
Examples of fracture surfaces of broken SSC test specimens are shown in Fig. 2a-c. In both states, fracture corresponded to rather smooth transgranular facets in ferrite while in austenite a more complicated pattern was observed. In the state corresponding to subsequent annealing at 800°C, numerous holes were observed as well (Fig.2b). These holes could correspond to regions where σ- phase particles dissolved. Some portions of transgranular ductile fracture were observed in both states (Fig.2c).



a) steel A - initial state (97% $R_{p0.2}$) – 59.7 hours



b) steel B - after annealing 800°C/5 hours (91% $R_{p0.2}$) – 22.0 hours



c) steel B - after annealing 800°C/5 hours (91% $R_{p0.2}$) – 22.0 hours

Fig.2 Examples of fracture surfaces of SSC test specimens – steel A

3.4 Hydrogen induced cracking

To be able to distinguish the role of σ -phase and the applied load, HIC tests were performed as well. The results of HIC were different in comparison to SSC results. In the case of HIC, the presence of σ -phase did not deteriorate the resistance of duplex steels considerably. Only for the highest amount of σ -phase, after 5 hour annealing at 800°C, a few short cracks were present at the austenite/ferrite interface after HIC testing. The crack length ratio CLR did not exceeded 0.5% in this case. An example of a short crack provoked by HIC is given in Fig. 3.

3.5 Electrochemical permeation tests

Tests were performed only for steel A in both states and in two orientations – longitudinal and through-thickness. An example of permeation curves is shown in Fig. 4. Hydrogen permeation curves were similar for both orientations. Apparent diffusion coefficients of hydrogen computed from permeation curves were $1.5.10^{-9}$ $cm^2.s^{-1}$ for longitudinal orientation and $2.2.10^{-10}$ $cm^2.s^{-1}$ for through-thickness orientation, the value being considerably lower in comparison with longitudinal orientation. This difference may be due to difference of the microstructure, as hydrogen diffusion is easier longwise the ferrite bands. No important difference was recorded for the initial state and the state after subsequent annealing provoking σ – phase precipitation. The values of hydrogen diffusion coefficient are in good agreement with the values found in the literature [2].

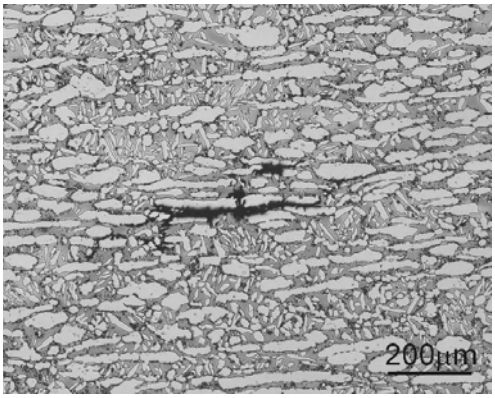


Fig.3 Example of a short crack after HIC test (800°C for 5 hours – steel B)

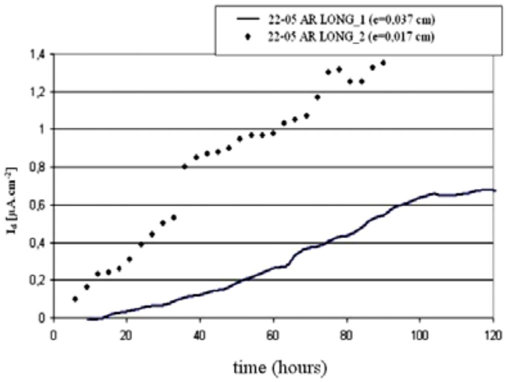


Fig.4 Example of permeation curves for steel A - initial state

4. Conclusions

The obtained results can be summarised in the following way:

- Resistance of duplex stainless steels to SSC depends strongly on their microstructure. This resistance can be deteriorated considerably by heat treatments that result in σ - phase precipitation.
- In the case of HIC, steel resistance does not seem to be influenced by the presence of σ -phase.
- Hydrogen permeation tests showed that apparent hydrogen diffusion coefficient of duplex steels depends on the specimen orientation. Hydrogen diffusion is facilitated by bands of ferrite oriented longwise the diffusion path.
- Hydrogen diffusion coefficient of duplex stainless steels is not influenced considerably by the presence of a low amount of σ – phase.

Acknowledgements

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