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HYDROGEN EMBRITTLEMENT OF DUPLEX STEEL TESTED USING SLOW STRAIN RATE TEST

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This paper is dealing with hydrogen embrittlement of austenitic-ferritic 2205 duplex steel using the slow strain rate test (SSRT). The original material was subjected to heat treatment under 700 °C during 5 hours and following air-cooling with the aim of provoking sigma phase precipitation and embrittlement of the material. The samples of both states were electrolytic saturation with hydrogen in 0,1N solution of sulfuric acid (H_2SO_4) with addition KSCN during 24 hours. The hydrogen embrittlement appeared on fracture surfaces of tested tensile bars as a quasi-cleavage damage on their perimeter. From the established depth of hydrogen charging the diffusion coefficient of hydrogen in duplex steel with ferritic-austenitic structure and with the structure containing the sigma phase as well were estimated.

Key words: hydrogen embrittlement, duplex steel, diffusion, slow strain rate test (SSRT), sigma phase

INTRODUCTION

Duplex stainless steels (DSS), containing ferrite and austenite phases, besides their good mechanical properties offer also good resistance to corrosion. Because of their improved resistance to stress corrosion cracking and corrosion fatigue, especially in chloride-containing environments, and because of their reasonable cost compared to austenitic stainless steels, the duplex stainless steels are attractive materials for the oil and gas industry , chemical plants, marine environments and other such applications.

The steels are characterized by the two phase microstructure of ferrite (α) and austenite ().To maintain the mechanical and corrosion properties it is essential to have a dual phase structure as close to the 50/50 % distribution as possible. This can often be a challenge, especially in welds where the brittle ferritic structure tends to dominate.

Despite its general superior toughness and corrosion resistance, DSS can suffer from hydrogen embrittlement. It is a well known fact that hydrogen cracking can occur in the heat affected zone after welding. The susceptibility of hydrogen sulphide cracking in the weld root of oil and gas pipes is well documented. Over the last years also cracking incidents related to cathodic protection (CP) and hydrogen induced stress cracking (HISC) have been reported 1-3.

Lattice diffusion by interstitial jumps is the main diffusion mechanism for hydrogen in steel. A ferritic body-centered cubic (bcc) structure enables a high diffusion rate and a low solubility due to its open lattice structure. In contrast, the austenitic face-centered cubic (fcc) structure gives a lower diffusion rate and a higher solubility for hydrogen due to its close packed lattice. The hydrogen diffusivity is D_α 1 1,510^{-11} m^{2}s^{-1} for the ferrite phase and D 11,410^{-16} m^{2}s^{-1} for the austenite phase. In addition to the diffusible hydrogen atoms, hydrogen can be trapped in the structure. Trapping reduces the amount of mobile hydrogen and hence, delays the hydrogen transport. The trapping ability of austenite in two phase steels such as duplex steels are of special interest in the stainless steels. Due to its low diffusion coefficient it can be argued that austenite; in the general sense is an irreversible trap. The reported hydrogen diffusion coefficient of DSS, regardless of the charging conditions, varies from 1,810 $^{-12}$ m^{2}s^{-1} to 4,610^{-16} m^{2}s^{-1} 1-4.

During austenitic-ferritic steels annealing under temperatures between 700 °C and 1 000 °C the intermetallic sigma phase arises and it is the source of great brittleness. Therefore it is not recommended to remain within this temperature interval during industrial applications. The sigma phase occurrence cannot be however excluded in the steel welds 5-8.

EXPERIMENTAL MATERIAL

Tensile 2205 duplex steel bars of d_0 = 4 mm diameter and L_c = 35 mm length were tested in order to evaluate the material liability to hydrogen embrittlement. The original material was a bar of 16mm diameter. The chemical composition of employed steel is given in the Table 1.

For good differentiation of each phase of the austenite, delta ferrite and sigma phase microstructure, the steel microstructure was made visible by the means of electrolytic etching in 10N solution of NaOH under 6 V voltage during 7 s (Figures 1, 2). Delta ferrite content in the original state was stated with the use of picture analysis; and it was 56 %. Duplex matrix was subjected to annealing and thus modified with the aim of provoking sigma phase precipitation. The original annealing was under 750 °C tem-

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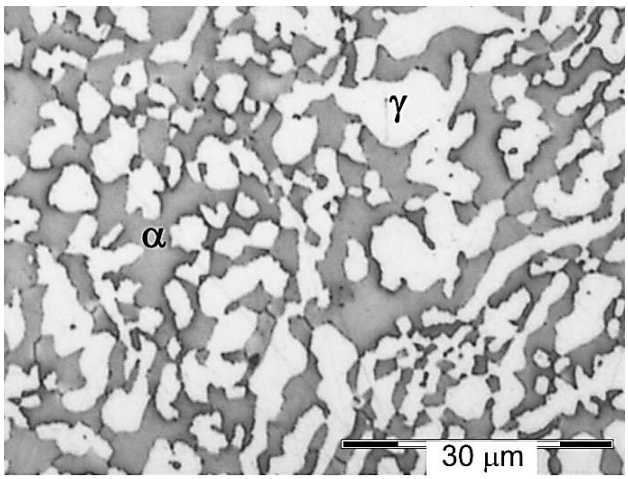

Figure 1 2205 duplex steel microstructure in cross section. Original state. Austenite (white) and delta ferrite (grey). Electrolytic etching 6 V/7 s in 10N solution of NaOH

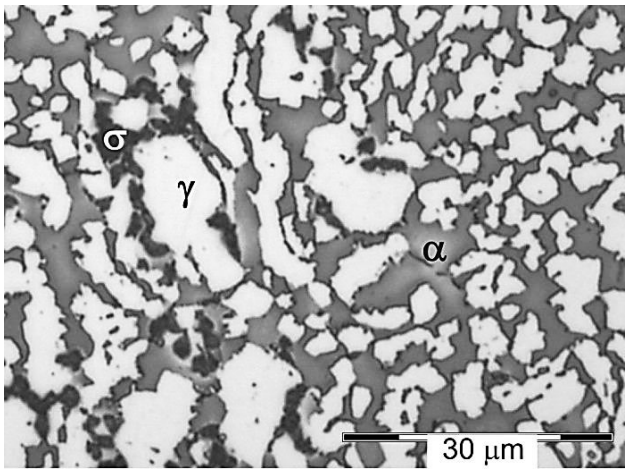

Figure 2 2205 duplex steel microstructure in cross section. State after annealing under 700 °C during 5 hours. Austenite (white), delta ferrite (grey) and sigma phase (dark grey)

perature during 5 hours and followed by air -cooling, as published in the paper [9]. In the case of this original material the whole delta ferrite was transformed into sigma phase and the material was not at all machinable.The state after annealing under 700 °C temperature during 5 hours (Figure 2) was established as the optimal one for further testing of duplex steel liability to hydrogen embrittlement. The share of sigma phase was 4,7 %.

EXPERIMENTAL PROCEDURE AND OBTAINED RESULTS

Mechanical properties were measured by tensile testing machine w+b MOD.Z/D100/EDC120. The original measured length L_0 = 20 mm was established from the original d_0 = 4 mm diameter of the tensile bars. Load rate v = 0,5 mmmin^{-1} was chosen, corresponding to = 2,0810^{-4} s^{-1} strain rate. Mechanical properties are given in the Table 2. The greatest changes after heat treatment were observed in ductility , which was almost three times lower (see Table 2, the line

Table 1 **Chemical composition of 2205 duplex steel / mas. %**

Steel	C	Si	Mn	Ni
2205	0,026	0,38	1,57	5,49
Cr	Mo	N	S	P
22,65	2,80	0,152	0,0007	0,027

without hydrogen). After the heat treatment the tensile strength increased, while the yield strength decreased.

In order to find out the participation of hydrogen in embrittlement of tested material the tensile bars were charged with hydrogen in 0,1N H_2SO_4 solution with addition of 1 g KSCN (as a promoter of hydrogen entry) for 1 litre of the solution during 24 hours. Current density of i = 1 mAcm^{-2} and 5 mAcm^{-2} was chosen. The sample was plugged into electric circuit as the cathode, tungsten grid coated with platinum was the anode.

After the end of electrolytic hydrogen char ging the tested samples were in the shortest time possible moved into tensile testing machine and they were loaded under v = 0,5 mmmin^{-1} speed loading. Slow strain rate testing was allowed in order to ensure enough time for hydrogen distribution from the sample volume to those spots, where the critical concentration of hydrogen could be exceeded and where the fracture could be initiated. The SSTR method was applied for the evaluation of hydrogen influence on mechanical properties of DSS also in the paper [10].

The hydrogen embrittlement rate was established with the aid of hydrogen embrittlement index F (%)

$$F = \frac{A_0 - A_H}{A_0} \cdot 100 \quad (1)$$

where A_0 stands for the ductility value in the original state / %, A_H stands for the ductility value after hydrogen charging / % – (1).

Results of mechanical properties of the material without heat treatment achieved after electrolytic hydrogen charging are given in the Table 2. The influence of hydrogen on yield strength and tensile strength was only minimal. The ductility however decreased (20 %), comparing to the original state (32 %).

The results of mechanical properties of the heat treated material are given in the Table 2. With i = 1 mAcm^{-2} current density the ductility decreased from 11,8 % to 8,8 %, which resulted into F = 26,3 % hydrogen embrittlement. After hydrogen charging with i = 5 mAcm^{-2} current density the ductility decreased only of 1 % and the hydrogen embrittlement index was 15,8 %. Yield strength and tensile strength de-

Table 2 **Results of mechanical properties without and with heat treatment (HT)**

Material	i /mAcm^{-2}	$R_{p0.2}$ /MPa	R_m /MPa	A_{20} /%	F /%
without HT	-	792	947	32,0	-
	1	772	927	20,3	36,7
	5	791	940	22,1	30,9
with HT	-	757	1 30	011,8	-
	1	722	967	8,8	26,3
	5	742	990	10,0	15,8

creased after the hydrogen charging. With both materials we observed higher embrittlement and decreased breaking limit of the materials after the hydrogen char ging under lower current density. Possible reason for this could be the formation of thin oxide layer on the tensile bar surface during higher current density of hydrogen char ging, preventing from further saturation of the material by hydrogen.

Fractographic analysis of fracture surfaces in the original state and after the electrolytic hydrogen char ging was carried out with the aid of JEOL JSM-6490LV scanning electron microscope. In the middle of fracture surfaces there was a transgranular ductile fracture with dimple morphology. On the perimeters of hydrogen char ged tensile bars the levels of quasi-cleavage damage appeared (Figures 3, 4) as in work 1 1, 12. The morphology of transgranular ductile and quasi-cleavage fracture were different in the material without heat treatment and in the material after heat treatment, according to the microstructural change of the material. Details of the fractures on the fracture surfaces edges after hydrogen char ging representing the quasi-cleavage fracture are given in Figures 5, 6. With the aid of EDX analysis it was found that well-marked cleavage facets demonstrate higher content of Cr than surrounding parts of the fracture. In the [12] paper it was found out that cracking and cleavage damages appeared preferentially in the ferritic phase.

From the edges of hydrogen charged tensile bars in the original state without heat treatment it is clear that the quasi-cleavage fracture is distributed on the sample perimeter uniformly, while the depths of quasi-leavage damages on the sample perimeter of the tensile testing bars made of the heat treated material are quite different. The hydrogen diffusion coefficient D (m^2s^{-1}) was established on the basis of the depths of perimeter levels with quasi-cleavage damage h (m) and of the known time of hydrogen char ging t (24 hours = 86 400 s) according to the (2). The results are summed up in Table 3.

$$D = \frac{h^2}{4t} \quad (2)$$

The average hydrogen dif fusion coeffi cient in duplex steel was $2{,}3510^{-14}$ m^2s^{-1} in the original state. This value corresponds on the order to values of effective diffusivity, D_{eff} (m^2s^{-1}) in [12-14] paper measured by hydrogen per -

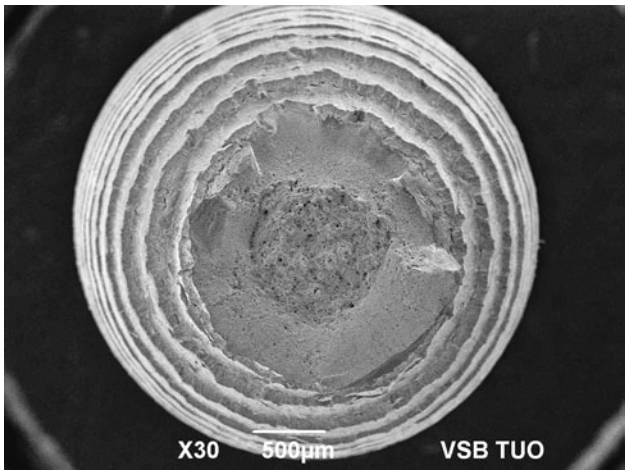

Figure 3 Fracture surface of the sample after hydrogen charging 24 h, i = 1 $mAcm^{-2}$, 0,1N H_2SO_4 with addition of 1 g KSCN for one litre of the solution. State without heat treatment

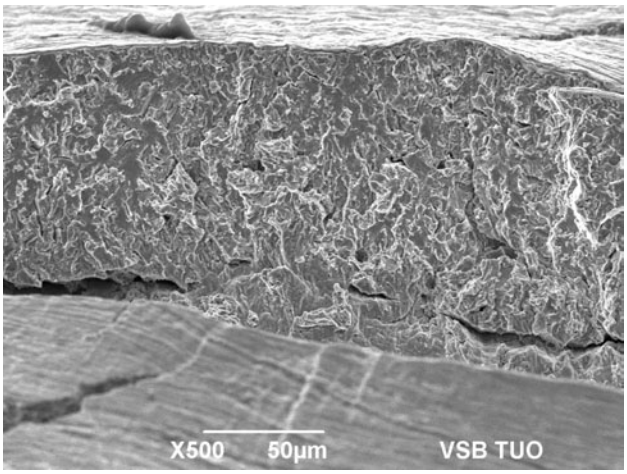

Figure 5 Detail of the fracture surface edge after hydrogen charging - quasi-cleavage fracture. State without heat treatment

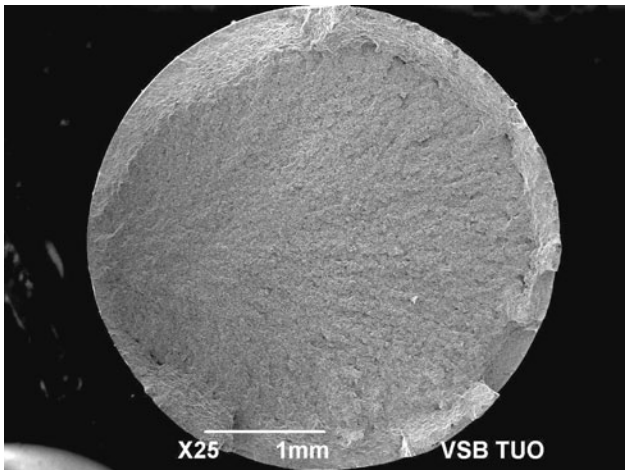

Figure 4 Fracture surface of the sample after hydrogen charging 24 h, i = 1 $mAcm^{-2}$, 0,1N H_2SO_4 with addition of 1 g KSCN for one litre of the solution. State after heat treatment

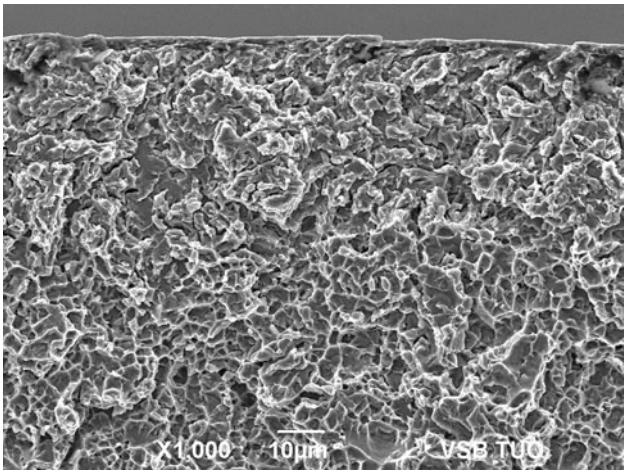

Figure 6 Detail of the fracture surface edge after hydrogen charging - quasi-cleavage fracture. State after heat treatment

Table 3 **Depth of hydrogen charging *h* and diffusion coefficien t *D***

Material	i /mAcm^{-2}	h /m	D /m^{2}s^{-1}
without HT	1	8,4210^{-5}	2,0510^{-14}
	5	9,5810^{-5}	2,6510^{-14}
with HT	1	3,2110^{-5}	3,2410^{-15}
	5	3,2410^{-5}	3,0310^{-15}

meation method. As for the heat treated samples, the hydrogen dif fusion coeffi cient of duplex steels in matrix without the sigma phase was lower, that is $3,14 \cdot 10^{-15}$ m^{2}s^{-1}. The hydrogen dif fusion coeffi cient decrease of one order can be considered as signifi cant. The diffusion coefficient decrease in the heat treated duplex steel with the sigma phase leads us into consideration that the sigma phase acts as an irreversible hydrogen trap and decreases ef fective hydrogen coefficient.

CONCLUSION

This paper dealt with the hydrogen infl uence on the embrittlement of 2205 duplex steels in the original state and in the state after heat treatment with sigma phase content.

- Heat treatment influenced mechanical properties. The ductility was influenced the most, while it was almost three times lower.
- The presence of higher hydrogen content in the steel appeared as material embrittlement, being more important with the materials in original state. The heat treated materials embrittlement appeared already in consequence of phase sigma exclusion and therefore the influence of hydrogen was only insignificant.
- The hydrogen presence showed as well on the fracture surfaces character that is by the presence of quasi-cleavage damages on the perimeter of tensile testing bars.
- From the depths of quasi-cleavage damages spots the values of ef fective hydrogen dif fusion coeffi cient were established. Those were the hydrogen diffusion coefficient for the original state of the material 2,3510^{-14} m^{2}s^{-1} and for the state after heat treatment 3,1410^{-15} m^{2}s^{-1}. The difference between these values shows us that sigma phase in duplex steel acts like irreversible hydrogen trap.

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REFERENCES

[1] V. Olden et al., Materials and Design, 29 (2008), 1934-1948.
[2] S. Lasek et al., Metalurgija 49 (2010) 1, 23-27.
[3] S. Brauser , Th. Kannengiesser , International journal of hydrogen energy, 35 (2010), 4368-4374.
[4] T. Zakroczymski, E. Owczarek,Acta Materialia, 50 (2002), 2701–2713.
[5] V. Číhal, Korozivzdorné oceli a slitiny . Academia, Praha, 1999, pp. 151-154.
[6] T. Borvik, H. Lange, L. A. Marken et al, Materials Science and Engineering A, 527 (2010), 6945–6955.
[7] M. Sozańska, K. Klyk-Spyra, Materials Characterization, 56 (2006), 399–404.
[8] J. R. Saithala, S. Mahajanam, H. S. Ubhi et al, Corrosion, 69 (2013) 3, 276-285.
[9] P. Jonšta, J. Sojka, K. Matocha, Z. Jonšta, Metalur gija, 52 (2013) 3, 313-316.
[10] T. Zakroczymski, A. Glowacka, W. Swiatnicki, Corrosion Science, 47 (2005), 1403-1414.
[11] A. M. Elhoud, N. C. Renton, W. F. Deans, International journal of hydrogen energy, 35 (2010), 6455-6464.
[12] W. C. Luu, P . W. Liu, J. K. Wu, Corrosion Science, 44 (2002), 1783-1791.
[13] L. Rytířová, Etude de la degradation par l'hydrogene des aciers microallies et duplex: infl uence de la microstructure, dissertation thesis, Ecole Centrale Paris, 2006, p. 170.
[14] E. Owczarek, T. Zakroczymski, Acta materialia, 48 (2000), 3059-3070.

Note: The translator for the English language is H. Marsault (independent English Language Tutor), Ostrava, Czech Republic