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 (H₂SO₄) 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 (γ). 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 \( D = 1.510^{-11} \text{ m}^2\text{s}^{-1} \) for the ferrite phase and \( D = 1.1410^{-10} \text{ m}^2\text{s}^{-1} \) 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 \( 1.810^{-12} \text{ m}^2\text{s}^{-1} \) to \( 4.610^{-16} \text{ m}^2\text{s}^{-1} \) 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 \( d = 4 \text{ mm diameter} \) and \( L = 35 \text{ mm length} \) 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-
temperature 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 \( L_0 = 20 \text{ mm} \) was established from the original diameter \( d_0 = 4 \text{ mm} \) of the tensile bars. Load rate \( \nu = 0.5 \text{ mm/min} \) was chosen, corresponding to \( 2.08 \times 10^{-4} \text{ s}^{-1} \) 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 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\(_2\)SO\(_4\) 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 \( i = 1 \text{ mAcm}^{-2} \) 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 charging the tested samples were in the shortest time possible moved into tensile testing machine and they were loaded under \( \nu = 0.5 \text{ mm/min} \) 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 \( F(\%) \)

\[
F = \frac{A_0 - A_H}{A_0} \times 100 \quad (1)
\]

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 \( i = 1 \text{ mAcm}^{-2} \) current density the ductility decreased from 11.8 % to 8.8 %, which resulted into \( F = 26.3 \text{ %} \) hydrogen embrittlement. After hydrogen charging with \( i = 5 \text{ mAcm}^{-2} \) current density the ductility decreased only of 1 % and the hydrogen embrittlement index was 15.8 %. Yield strength and tensile strength de-

<table>
<thead>
<tr>
<th>Material</th>
<th>( i ) ( \text{mAcm}^{-2} )</th>
<th>( R_{y,l} ) ( \text{MPa} )</th>
<th>( R_{m} ) ( \text{MPa} )</th>
<th>( A_{20} ) /%</th>
<th>( F ) /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>without</td>
<td>-</td>
<td>792</td>
<td>947</td>
<td>32.0</td>
<td>-</td>
</tr>
<tr>
<td>HT</td>
<td>1</td>
<td>772</td>
<td>927</td>
<td>20.3</td>
<td>36.7</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>791</td>
<td>940</td>
<td>22.1</td>
<td>30.9</td>
</tr>
<tr>
<td>with</td>
<td>-</td>
<td>757</td>
<td>3 0011.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HT</td>
<td>1</td>
<td>722</td>
<td>967</td>
<td>8.8</td>
<td>26.3</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>742</td>
<td>990</td>
<td>10.0</td>
<td>15.8</td>
</tr>
</tbody>
</table>
creased after the hydrogen charging. With both materials we observed higher embrittlement and decreased breaking limit of the materials after the hydrogen charging 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 charging, preventing from further saturation of the material by hydrogen.

Fractographic analysis of fracture surfaces in the original state and after the electrolytic hydrogen charging 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 charged tensile bars the levels of quasi-cleavage damage appeared (Figures 3, 4) as in work 1, 11, 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 charging 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-cleavage 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\(^2\)s\(^{-1}\)) was established on the basis of the depths of perimeter levels with quasi-cleavage damage \( h \) (m) and of the known time of hydrogen charging \( t \) (24 hours = 86 400 s) according to the (2). The results are summed up in Table 3.

\[
D = \frac{h^2}{4t} \tag{2}
\]

The average hydrogen diffusion coefficient in duplex steel was \( 2.35 \times 10^{-14} \) m\(^2\)s\(^{-1}\) in the original state. This value corresponds on the order to values of effective diffusivity, \( D_{ef} \) (m\(^2\)s\(^{-1}\)) in [12-14] paper measured by hydrogen per...
P. VÁŇOVÁ et al.: HYDROGEN EMBRITTLEMENT OF DUPLEX STEEL TESTED USING SLOW STRAIN RATE TEST

Table 3 Depth of hydrogen charging h and diffusion coefficient D

<table>
<thead>
<tr>
<th>Material</th>
<th>i /mA/cm²</th>
<th>h /m</th>
<th>D /m²s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>without HT</td>
<td>1</td>
<td>8.4210⁻¹</td>
<td>2.0510⁻¹⁴</td>
</tr>
<tr>
<td>5</td>
<td>9.5810⁻¹</td>
<td>2.6510⁻¹⁴</td>
<td></td>
</tr>
<tr>
<td>with HT</td>
<td>1</td>
<td>3.2110⁻⁴</td>
<td>3.2410⁻¹⁵</td>
</tr>
<tr>
<td>5</td>
<td>3.2410⁻⁴</td>
<td>3.0310⁻¹⁵</td>
<td></td>
</tr>
</tbody>
</table>

CONCLUSION

This paper dealt with the hydrogen influence 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 effective hydrogen diffusion coefficient were established. Those were the hydrogen diffusion coefficient for the original state of the material 2.3510⁻¹⁴ m²s⁻¹ and for the state after heat treatment 3.1410⁻¹⁵ m²s⁻¹. The difference between these values shows us that sigma phase in duplex steel acts like irreversible hydrogen trap.

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