THE INFLUENCE OF WELDING THERMAL CYCLES ON CORROSION RESISTANCE OF DUPLEX STAINLESS STEEL

ABSTRACT

The susceptibility of heat affected zone (HAZ) of duplex stainless steel weldments to stress corrosion cracking was investigated. Corrosion tests were performed with the use of Slow Strain Rate Test technique in the boiling MgCl₂ corrosive environment. It has been shown that high ferrite content in HAZ structure deteriorate its corrosion resistance. The metallographic and scanning electron microscopy (SEM) observations revealed various fracture propagation modes strongly dependent on austenite content in the HAZ structure.

Key words: duplex stainless steel, heat affected zone, stress corrosion cracking

INTRODUCTION

Many branches of industry have recognised the benefits of specifying duplex (austenite-ferrite) stainless steel instead of austenitic ones. The strength and the resistance in corrosive brines make these steels excellent materials for down hole piping, gathering line pipes, oil and gas separators, heat exchangers and chemical tanks [1].

Duplex stainless steels contain a fine microstructure of ferrite and austenite in roughly equal proportions. Arc welding operation gives more or less undesired heat treatment of the area close to the weld. The high-temperature area of heat affected zone (HAZ) is brought to a temperature, where the material is almost fully ferritic. At cooling, a reformation of austenite starts in the grain boundaries and then continues in the ferrite grains. The extent of ferrite to austenite transformation depends on the steel composition and welding conditions. Higher nickel and nitrogen contents and slower cooling promote this transformation. Upon too rapid cooling, high ferrite content can remain in the HAZ. Moreover, chromium nitrides can form owing to the fact that at high temperatures, the solubility of nitrogen in the ferrite is increased and during rapid cooling, when the solubility drops, chromium nitrides are formed. These particles act as initiation sites of corrosion in service. If on the other hand, the heat input is too high, precipitation of intermetallic phases can occur. This transformations in the structure can remarkable reduce corrosion properties of steel [2].

Duplex steels have been employed in welded form for a number of years in a range of media and major problems of weld stress corrosion cracking SCC have been rarely reported. However, it must be remarked that duplex steels are currently applied in more hazardous environments and therefore greater demands are expected to be placed on corrosion resistance of welds [1,2].
The aim of the present study was to reveal the effect of various HAZ structures in duplex stainless steel on the stress corrosion cracking resistance. For more accurate knowledge, tests were performed on samples subjected to simulated welding thermal cycles where homogenous structure existed.

**EXPERIMENTAL PROCEDURE**

Chemical composition of the 2205 commercial duplex stainless steel is given in table 1. The specimens were obtained from a plate 12 mm in thickness. The plate was delivered after solution annealing heat treatment.

<table>
<thead>
<tr>
<th>Metric</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt %</td>
<td>0.017</td>
<td>0.4</td>
<td>1.50</td>
<td>0.024</td>
<td>0.001</td>
<td>21.9</td>
<td>5.7</td>
<td>3.0</td>
<td>0.17</td>
</tr>
</tbody>
</table>

The welding simulation was performed on a resistance-heated weld simulator with computer-controlled temperature cycles and water cooling devices. The temperature required to ferritize the material was determined as 1350°C. Holding time at the peak temperature was 5 seconds. The different cooling rates were chosen in order to obtain various amounts of austenite fraction in the heat affected zone structures. Table 2 shows the main parameters used for welding simulation and obtained cooling rates between 1350 and 800°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Max. cycle temp. °C</th>
<th>Heating rate °C/s</th>
<th>Holding time s</th>
<th>Cooling time t_{1350-800} s</th>
<th>Cooling rate °C/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>1350</td>
<td>150</td>
<td>5</td>
<td>7</td>
<td>78</td>
</tr>
<tr>
<td>A2</td>
<td>1350</td>
<td>150</td>
<td>5</td>
<td>12</td>
<td>45</td>
</tr>
<tr>
<td>A3</td>
<td>1350</td>
<td>150</td>
<td>5</td>
<td>20</td>
<td>27</td>
</tr>
</tbody>
</table>

The susceptibility to stress corrosion cracking was determined in slow strain rate tests (SSRT) at the strain rate of $2.7 \times 10^{-6}$ s$^{-1}$ in boiling water solution of MgCl$_2$ at 125°C.

Microstructures of the specimens were examined after chemical etching in Beraha reagent (40 ml HCl, 80ml H$_2$O, 1g K$_2$S$_2$O$_3$). The MultiScan image analysis system was used to determine the amounts of various alloy phases. The fracture surfaces and the mode of crack propagation were examined on SEM.

**RESULTS AND DISCUSSION**

As demonstrated in fig.1, austenite reformation is strongly dependent on cooling rate. Obtained HAZ structures consist of ferrite and austenite at various amounts and localisation. In the A1 samples, where the highest cooling rate was applied, the acicular austenite precipitates mainly at ferrite grain boundaries (fig.1a). When lower cooling rates were applied (samples A2
and A3) the austenite precipitates at grain boundaries became thicker and considerable fraction of intergranular austenite also appeared. The greater amounts of intergranular austenite and austenite in the form of Widmannstatten structure were observed in A3 samples where cooling time $t_{1350-800}$ increased to 20 s. Austenite fraction in HAZ structures decreases with the growth of cooling rates. For the A3 samples, the amount of austenite was evaluated at 40%, 31% for A2 and 24% for A1 samples.

The precipitation of austenite during cooling duplex alloys is diffusion-controlled process. Nucleation and growth of austenite grains depends on diffusion rate of interstitial elements, particularly nitrogen [3]. Redistribution of metallic $\gamma$-stabilisation elements is slowly and requires longer time therefore nitrogen diffusion controls the phase transformation rates in modern duplex steels.

Thermal cycles caused considerable ferrite grain growth in HAZ. In the as received steel, ferrite grains were elongated parallel to the rolling direction with mean width 40 $\mu$m. After thermal cycles equiaxal ferrite grains appeared with mean diameter 180 $\mu$m.
Slow strain rate tests results are summarised in table 3 and fig.2. The stress-strain curves in fig.3 show that structures of heat affected zones influence the stress corrosion cracking susceptibility. Tensile strength and fracture energy decreased with the growth of the sample’s cooling rate at welding simulation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Environment</th>
<th>Tensile strength, TS [MPa]</th>
<th>Elongation E [%]</th>
<th>Reduction in area, RA [%]</th>
<th>Fracture energy, En [MJ/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM</td>
<td>MgCl₂</td>
<td>700</td>
<td>22.8</td>
<td>24.3</td>
<td>124</td>
</tr>
<tr>
<td>A1</td>
<td>MgCl₂</td>
<td>398</td>
<td>7.1</td>
<td>7.8</td>
<td>22.5</td>
</tr>
<tr>
<td>A2</td>
<td>MgCl₂</td>
<td>513</td>
<td>11.6</td>
<td>22.5</td>
<td>53.3</td>
</tr>
<tr>
<td>A3</td>
<td>MgCl₂</td>
<td>546</td>
<td>14.2</td>
<td>25.1</td>
<td>58.6</td>
</tr>
<tr>
<td>PMG</td>
<td>glycerine</td>
<td>742</td>
<td>34.8</td>
<td>70.8</td>
<td>305</td>
</tr>
<tr>
<td>A1G</td>
<td>glycerine</td>
<td>661</td>
<td>33.2</td>
<td>73.9</td>
<td>247</td>
</tr>
<tr>
<td>A2G</td>
<td>glycerine</td>
<td>657</td>
<td>31.8</td>
<td>68.3</td>
<td>241</td>
</tr>
<tr>
<td>A3G</td>
<td>glycerine</td>
<td>693</td>
<td>33.7</td>
<td>74.5</td>
<td>264</td>
</tr>
</tbody>
</table>

PM – parent material

In order to estimate the loss of elongation (E), reduction of area (RA) and fracture energy (En) with reference to an inert environment, relative parameters $E_{\text{rel}}$, $RA_{\text{rel}}$, $En_{\text{rel}}$ were calculated. These parameters were obtained as a ratio of values for specimens subjected to the stress corrosion test to that of the specimens tested in glycerine. These parameters allow assessing the effect of stress corrosion cracking phenomenon in damage process of tested specimens.
As it is shown in fig. 3, A1 samples exhibited the least resistance to SCC during performed SSRT tests. There are no significant differences in SCC resistance between A2 and A3 samples. Parent material showed better resistance to SCC than HAZ structures, but when loss of reduction in area (RA\textsubscript{rel}) is considered the resistance is almost the same. The worst corrosion properties were obtained in the samples with less austenite content. The higher amounts of austenite in the structure gave better mechanical properties and SCC resistance.

Sites of crack initiation and ways of cracks propagation were investigated on cross sections where secondary cracks were present, fig.4. It was found that cracks initiate mainly on the phase ferrite/austenite interfaces. Usually cracks propagate along ferrite grain boundaries but
sometimes, mainly in A2 and A3 specimens, transgranular fractures through ferrite grains were found. These cracks often stopped inside ferrite grains at perpendicular intergranular austenite precipitates.

![Fig. 4. Crack propagation path in the A2 sample](image)

The fracture surfaces of all samples tested in glycerine were fully ductile. The samples tested in MgCl$_2$ solution showed mostly mixed - ductile-brittle - fracture, however in A1 samples almost whole brittle surfaces were found. Here, the characteristic decohesion along coarse ferrite grains was observed, fig.5.

![Fig. 5. Corrosion fractures a) transgranular in A2 sample, b) intergranular in A1 sample](image)

The differences in SCC resistance in heat affected zones should be connected with austenite fraction in the structure. The best SCC resistance was recorded for parent material where approximately equal amounts of ferrite and austenite were present. The changes in phase balance caused deterioration in corrosion resistance. According to the stress corrosion cracking models for duplex stainless steels presented in works [4,5,6] ferrite acts by promoting a combined electrochemical/mechanical coupling effect. Ferrite is cathodic relative to austenite in chloride environments causing stress corrosion and therefore cathodically protects austenite. The elastic limit of austenite is lower than that of ferrite so that applied strain is - to some degree - concentrated in the austenite. This may cause SCC but austenite is cathodically protected by the
ferrite. However at higher stress levels, deformation takes place also within the ferrite and cracking through this phase can occur. The relative electrochemical and mechanical behaviour of the two phases will depend on their compositions and amounts present. Less austenite in the structure causes higher stresses in the ferrite and development of stress corrosion cracking.

The cracks must start at local discontinuous or depassivated zones. It is believed that slip step dissolution is responsible for rupture of the passive film on the metal surface [7]. This mechanism is more effective when coarse grain structure is subjected to tensile stresses. The result of present study confirms this mechanism. The coarse HAZ structure promotes stress corrosion cracking.

CONCLUSIONS

1. Structure of HAZ of welded joints of 2205 duplex stainless steel strongly influence the stress corrosion cracking susceptibility when subjected to slow strain rate tests in the boiling MgCl₂ solution.
2. The deterioration of stress corrosion cracking resistance was observed when less than 40% of austenite existed in the HAZ structure.
3. Fracture surfaces changed from ductile for samples tested in an inert environment through mixed, ductile-brittle for HAZ structures containing over 30% of austenite to fully brittle for HAZ structure where little amount of austenite existed.
4. Cracks were propagated along ferrite/austenite interfaces or transgranularly through ferrite grains.

REFERENCES