475 °C Embrittlement in a Duplex Stainless Steel UNS S31803

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The susceptibility of a duplex stainless steel UNS S31803 to thermal embrittlement at 475 °C was evaluated by means of mechanical tests (impact energy and hardness), magnetic measurements (hysteresis and thermomagnetic analysis) and scanning electron microscopy. The results show that the material undergoes severe embrittlement and hardening in the first 100 h. The corrosion resistance of the ferrite phase in a 10%HNO₃ + 0.05%HF solution deteriorated after 500 h of ageing. The Curie temperature (Tₐ) was the most sensitive magnetic property to the microstructural changes that promote embrittlement. Tₐ increases with ageing time due to the progressive reduction of chromium in the Fe-rich matrix during spinodal decomposition.

Keywords: duplex stainless steel, 475 °C embrittlement

1. Introduction

Duplex stainless steels (DSS) are widely used in chemical, petrochemical, cellulose and nuclear plants around the world. Because of their fine austenitic-ferritic microstructure they offer an excellent combination of mechanical and corrosion resistance properties.

The best performance of wrought DSS is obtained in the solution treated condition. Nevertheless, two hardening and embrittlement processes may occur when these materials are heated: (a) sigma phase (σ) precipitation in the range of 700 °C to 900 °C and (b) precipitation of a Cr-rich phase (α’) in the range of 300 °C to 600 °C. The α’ precipitation leads to a progressive hardening and reduction of the material toughness. This precipitation occurs by spinodal decomposition, a mechanism by which the ferrite phase decomposes into a Cr-rich phase (α’) and a Fe-rich phase. Because this reaction occurs more rapidly at 475 °C, this process is also known as “475 °C embrittlement”. However, this phase separation may also occur in temperatures as low as 300 °C in exposures after thousands of hours or at 600 °C in exposures for few minutes, depending on the chemical composition of the steel.

Many researchers have studied and developed methods of detection and also quantification of thermal embrittlement in DSS. Tsuchiya et al. and Evanson et al. employed magnetic measurements and found that the hysteresis loss, residual induction and coercive force increased with ageing time in cast DSS. Controversially, Maeda et al. have found experimentally that there is a decrease in the coercive force during the ageing of cast duplex stainless steels in the range of 350-450 °C. Kim et al. found an increase of the Curie temperature in ferritic stainless steels aged at 370 °C and 400 °C.

Another consequence of the spinodal decomposition of the ferrite phase is loss of corrosion resistance. If the Cr content of the Fe-rich matrix becomes lower than 14 at.% pits of corrosion may be observed by scanning electron microscopy (SEM) in the ferritic regions in samples etched with a 10%HNO₃+0.05%HF solution.

In the present research work, the susceptibility of a DSS S31803 to thermal embrittlement at 475 °C was evaluated by means of hardness and Charpy impact tests, magnetic measurements and SEM.

2. Materials and Methods

A 3 mm sheet of duplex stainless steel UNS S31803, with the composition shown in Table 1, was received in the solution treated condition, containing (43 ± 3)% of...
austenite phase. The material was heat treated at 475 °C for 20, 100, 300 and 500 h.

The age hardening was measured by Brinnel hardness tests. The embrittlement was measured by Charpy tests, using subsize (2.5 mm) V-notch specimens. The impact tests were conducted on a universal impact machine. The aged samples were etched with a 10%HNO₃ + 0.05%HF solution and observed by SEM.

The magnetic measurements (hysteresis and thermomagnetic analysis - TMA) were carried out in a Vibrating Sample Magnetometer (VSM) EGG PAR model 4500. The TMA data were obtained with a high-temperature oven in low vacuum atmosphere (0.1 mmHg) and under an applied magnetic field of 500 Oe. The heating rate was 5 °C/min. A barium ferrite was taken as standard for magnetic measurements.

The samples for magnetic measurements were disc-shaped with a diameter of about 3.5 mm and thickness between 0.05 and 0.20 mm. The obtained hysteresis curves were corrected for the demagnetization field as proposed by Chikazumi and Cullity.

3. Results and Discussion

Figure 1 shows the hardness and impact energy behaviour with ageing time at 475 °C. The \(\alpha'\) precipitation promotes strong hardening and embrittlement in the first 100 h of ageing. Figure 2 shows the backscattered electrons image of the sample aged for 500 h and etched in a 10%HNO₃+0.05%HF solution. The pits observed in the ferrite phase indicate that in this condition the Cr content of the matrix is probably lower than 14 at%. Even though a decrease of toughness had been detected in the first 20 h of ageing, it was only after 500 h of ageing that a pronounced decrease of corrosion resistance of the ferrite phase was observed by SEM. This fact shows that some chemical and electrochemical tests, based in the loss of corrosion resistance, may not be effective in predicting the embrittlement of the steel.

Table 2 shows the magnetic properties of coercive force (\(\mu H_c\)), residual induction (\(B_r\)) and saturation induction (\(B_s\)) obtained at room temperature in the different investigated conditions. As can be seen, \(B_r\) and \(B_s\) were not affected by ageing and the \(\mu H_c\) increased very slightly with ageing time. The difference between the coercive force of the sample aged by 500 h and the unaged sample was about 6%, which is very low if we consider the strong variation of mechanical properties that takes place in the same time.

Besides, Fig. 3 shows that the hysteresis loops of the unaged sample and the one aged for 500 h are almost coincident. These results are in disagreement with those obtained by Tsuchiya et al. and Evanson et al. for cast duplex stainless steels. The former authors found a great

<table>
<thead>
<tr>
<th>Condition</th>
<th>(M_{Hc}) (Oe)</th>
<th>(B_r) (G)</th>
<th>(B_s) (G)</th>
<th>(T_c) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution treated</td>
<td>266</td>
<td>6590</td>
<td>7535</td>
<td>503</td>
</tr>
<tr>
<td>475 °C / 20 h</td>
<td>270</td>
<td>6800</td>
<td>7500</td>
<td>533</td>
</tr>
<tr>
<td>475 °C / 100 h</td>
<td>271</td>
<td>6776</td>
<td>7554</td>
<td>550</td>
</tr>
<tr>
<td>475 °C / 300 h</td>
<td>271</td>
<td>6740</td>
<td>7575</td>
<td>558</td>
</tr>
<tr>
<td>475 °C / 500 h</td>
<td>281</td>
<td>6882</td>
<td>7362</td>
<td>566</td>
</tr>
</tbody>
</table>

Figure 1. Impact Energy and Brinell Hardness as function of time exposure at 475 °C. (ST = Solution treated).

Figure 2. SEM composition image of the sample aged for 500 h at 475 °C, etched with 10%HNO₃+0.05%HF solution.

Table 1. Chemical analysis of the material (wt%).

<table>
<thead>
<tr>
<th>% C</th>
<th>% Cr</th>
<th>% Ni</th>
<th>% Mo</th>
<th>% N</th>
<th>% S</th>
<th>% P</th>
<th>% Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.032</td>
<td>22.38</td>
<td>5.32</td>
<td>2.55</td>
<td>0.1123</td>
<td>0.003</td>
<td>0.028</td>
<td>balance</td>
</tr>
</tbody>
</table>
change in the hysteresis loop due to ageing at 475 °C for 443 h and the latter have reported an increase in the $B_r$ values with ageing time. It's worth mentioning that in the present work, a wrought alloy was analyzed, while the authors cited above studied cast DSS, which contain phase proportions and chemical compositions different from wrought alloys. The steel analyzed by Tsuchiya et al. contained only 12.5% of ferrite phase and the steels analyzed by Evanson et al. contained 12.5 to 26.1% of this phase. These two aspects, of differences in phase proportions and chemical composition, explain the discrepancies in the of B-H curves encountered in this work, when compared with the results of the other two articles.

The output of the thermomagnetic analysis (TMA) is a curve of magnetization versus temperature. Figure 4 shows the TMA heating curves obtained for each sample. As can be seen, the magnetic transition temperature (Curie temperature - $T_c$) increases with ageing time. A precise determination of the $T_c$ can be obtained by deriving the $M(T)$ vs. $T$ curve, as shown in Fig. 5. Table 2 shows the $T_c$ values obtained by this procedure.

The increase of $T_c$ with ageing time at 475 °C is due to the influence of the chromium in the magnetic transition temperature of ferrite. As shown in the Fe-Cr phase diagrams available in the literature, when the amount of Cr is higher than 3 wt.%, $T_c$ is an inverse function of the chromium content. On the other hand, the chromium content in the Fe-rich phase is progressively reduced during the ferrite decomposition. As a consequence, $T_c$ increases with ageing time, which is in agreement with the results obtained by Kim et al. in a ferritic alloy. However, no published work on the $T_c$ behaviour in DSS during the ageing embrittlement was found by the authors.

The plot of $T_c$ against ageing time (Fig. 6) exhibits a behaviour similar to the hardness variation (see Fig. 1). In Fig. 7 the impact energy and the Brinnel hardness are plotted against $T_c/T_o$, where $T_o$ is the initial value of $T_c$ (503 °C). Although additional experiments must be performed at other temperatures, it seems to be clear that the measurement of $T_c$ may be used to detect and quantify the effects of the 475°C embrittlement on the mechanical properties of DSS. It is important to be sure, however, that the heating rate applied in the TMA is the same for all conditions investigated.
4. Conclusions

The studied duplex stainless steel UNS S31803 undergoes a reasonable hardening and embrittlement in the first 100 h of ageing, but is only after 500 h that its corrosion resistance to the 10%HNO₃ + 0.05%HF solution is deteriorated.

It was found that in ageing times up to 500 h the magnetic properties $B_r$ and $B_s$ remained nearly unaltered and the coercive force ($H_{c}$) presented a slight increase with the ageing time. There was no significant difference in the hysteresis loops of the sample unaged and the one aged at 475 °C for 500 h. On the other hand, the magnetic transition temperature (Curie temperature, $T_c$), measured by thermomagnetic analysis, increased with ageing time. This is due to the progressive reduction of Cr content in the Fe-rich phase during the ageing process. This phenomenon may be used to detect and quantify the effects of the $\alpha'$ precipitation in duplex stainless steels.

References