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ABSTRACT

Martensitic Stainless Steels are a material of choice for mould and die makers because they combine high polishability with good wear and corrosion resistance. Such properties are largely controlled by heat treatment after semi-finishing. It is at this point in the manufacturing cycle that critical issues need to be resolved relating to the development of residual stress and strategies for maintaining optimum corrosion resistance. This paper summarises recent findings on the evaluation of residual stress as a function of key heat treatment parameters and presents results of effect that these parameters have on the resistance to localised corrosion in the presence of chloride ions using the potentiodynamic polarisation method.

KEYWORDS

Martensitic Stainless Steels, Residual Stress, Localised Corrosion Resistance, Potentiodynamic Polarisation, Neutron Diffraction.

1.0 INTRODUCTION

Martensitic stainless steels, based around the AISI 420 grade stainless steel (W. Nr. 1.2083), are being increasingly specified for the production of small to medium sized moulds, which are used to manufacture high value-added plastic components for use in the automotive and food packaging industries. The reason for the increasing popularity of this grade of steel lies in the fact that it combines high polishability with good wear and corrosion resistance. The latter is particularly important where tool life is compromised by the action of chemically aggressive resins and abrasive fillers. Equally important of course is the susceptibility of tooling to corrosion in storage and in the many cooling channels. However, as pointed out by Tidesten et al [1], there have been concerns regarding the toughness and ductility of the martensitic stainless steels particularly when complex and/or large moulds are to be produced. To overcome these problems steel suppliers have developed more advanced grades of martensitic stainless steels with much higher levels of hardenability than the standard grades. The increased depth of hardness ensures that sound microstructures can be developed in large cross-sections. One example of such an advance is the relatively recent innovation by Uddeholm to introduce Stavax Supreme in addition to its standard grade ESR. Chemical compositions of these grades are shown in Table 1.

Critical to achieving optimum properties in the above steels is correct heat treatment practice. Data sheets supplied by the steel manufacturer [2] recommend that in vacuum heat treatment quenching from the hardening temperature be carried out at a minimum of 4-5 bar.
overpressure while maintaining acceptable levels of distortion. This raises the issue of residual stress and the effect of the change in hardenability on the levels of residual stress generated in heat treatment. With respect to tempering, it is recommended that the best combination of hardness, toughness and corrosion resistance is obtained by tempering at 250-300°C. However, for complex or very large moulds it is recommended that a higher tempering temperature be used in order to reduce residual stresses to a minimum. This again raises the issue of residual stress and a possible adverse affect on corrosion resistance.

Table 1: Chemical compositions (supplied by Uddeholm AB) in weight percent of the modified grades of AISI 420.

<table>
<thead>
<tr>
<th>Steel Grade</th>
<th>C</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>V</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stavax ESR</td>
<td>0.39</td>
<td>13.5</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>Stavax Supreme</td>
<td>0.25</td>
<td>13.3</td>
<td>0.3</td>
<td>1.4</td>
<td>0.3</td>
<td>+N</td>
</tr>
</tbody>
</table>

The evaluation of residual stress is a non-trivial matter. Traditionally X-rays have been used but this is limited to the near surface. Recently Doyle et al [3] used thermal neutrons to evaluate residual stress in martensitic stainless steels as a function of key heat treatment parameters. In the present study, this work will be first summarised followed by potentiodynamic polarisation corrosion studies of the effect of tempering on both standard grade ESR and Stavax Supreme.

2.0 Residual Stress

Neutron diffraction measurements were performed on The Australian Strain Scanner (TASS) on the HIFAR reactor at the Australian Nuclear Science and Technology Organisation (ANSTO). A beam of thermal neutrons of wavelength 1.4 Å was selected using a Ge (115) monochromator. The (112) $\alpha$ - Fe reflection at $2\Theta \approx 73^\circ$ was chosen for investigation. A 32-wire position sensitive detector was used to record the diffraction peak with a resolution of 0.075°. Incident and diffracted beam slits measuring 3 x 3 x 8 mm$^3$ were used to define the sampling or gauge volume within the block.

In this study, strain measurements were made in steel blocks at depths of 3, 8 and 13 mm from the surface to the mid-section. Strain-free reference samples ($d_0$) were prepared by wire-cutting 2x2x2 mm cuboids from each steel and re-assembling them into 6x6x6 mm cubes.

In general, to define the strain tensor at a point, measurement on six axes is required. In the present study, three normal stresses, approximately coincident with the coordinate axes of the blocks x, y and z, were calculated using the formula,

$$\sigma_x = \frac{E\varepsilon_x}{1 + \nu} + \frac{\nu E \left( \varepsilon_y + \varepsilon_z \right)}{(1 + \nu)(1 - 2\nu)}$$  \hspace{1cm} (1)

with corresponding expressions for $\sigma_y$ and $\sigma_z$. E is the elastic modulus (208 GPa) and $\nu$ is Poisson’s ratio (0.28).
Plots of the three normal stress components (longitudinal, transverse and normal) for the three positions are shown in Figure 1 (a to f) for the as quenched (2 bar), low temperature temper (320 °C) and high temperature temper (520 °C).

![Graphs](image)

Figure: 1 Plots for the longitudinal, transverse and normal directions within the steel blocks of ESR and Supreme for (a,b) as quenched at 2 bar, (c,d) low temperature temper (320°C) and (e,f) high temperature temper (520°C).

It is clear that all the blocks develop tensile stresses in the centre, with some blocks showing a trend to compressive residual stress at the 3 mm location. Given that the elastic residual stresses must balance, this implies that in some of the blocks there could potentially exist large compressive stresses close to the surface. This pattern of residual tensile stresses in the core balanced by residual compressive stresses at the surface is in agreement with published data [4].
The as-quenched results, Figure 1 (a,b) show that the Stavax Supreme has a higher levels of residual stress than the ESR. The effect of so-called low stress tempering at 320°C is effective in reducing the high levels of residual stress in both ESR and Supreme, see Figure 1 (c,d). Clearly, there is a greater reduction for ESR with the 13 mm position showing a change to compression.

The situation following the 520°C temper is somewhat obscure in the case of ESR, see Fig. 1 (e,f). It is evident that full stress relief has not occurred (as indicated in the heat treatment of Supreme) but, rather, a pattern of residual stress has developed which is different to that observed after the 320°C. Supreme, on the other hand, has clearly suffered a further reduction in residual stress to the extent that in all sections it is almost completely fully relieved. This indicates that, in this new grade of N₂ containing steel, it is possible to fully relieve the residual stress. The only issue left for resolution is to enquire if the practice of high temperature tempering in Supreme compromises too much the corrosion resistance.

3.0 Corrosion

3.1 Electrochemical Assessment of Steel Samples to Localised Corrosion

The method used to assess the effect of heat treatment on the resistance to localised corrosion of ESR and Stavax Supreme steels was the cyclic potentiodynamic polarization method. In this method, all tests were performed in a conventional, 3-electrode, water-jacketed cell (temperature controlled at 25°C) using a Pt coil counter electrode separated by a glass frit from the working electrode electrolyte. All potentials were measured and reported with respect to the Hg/Hg₂Cl₂0.5M NaCl reference electrode. All solutions were made in high purity (Mill-Q) water using AR grade chemicals. The electrolyte used was 0.35% sodium chloride solution. A flag type design for the steel electrodes was adopted as the working electrode. Electrical contact to the steel electrodes was made by using silver loaded epoxy adhesive that, in turn, was coated with non-conducting epoxy. The complete electrical contact was further sealed (epoxy) in a glass tubing to completely eliminate possible exposure of the contact to electrolyte and to provide stronger physical support to the contact. The sample was rinsed carefully in deionised water. Finally a nitrogen purge was used to prevent air access to the solution.

The sample to be tested was placed in the conducting solution, in this case 0.35% sodium chloride solution, and its potential with respect to the reference electrode was increased at a uniform rate in the positive direction from a potential, just negative of the corrosion potential of the metal sample in the conducting electrolyte. If breakdown of the passive film on the metal sample occurs during the potential scan (Vₜ), the current flowing in the external circuit between the metal sample and an auxiliary electrode (in this case platinum) will increase due to enhanced corrosion of the metal sample. While the metal remains passive very little current will flow in the external circuit. As pitting and crevice corrosion is associated with the breakdown of passivity, the technique indicates the tendency of the metal to undergo localised corrosion (crevice or pitting corrosion) or, in the absence of crevices, the tendency to pitting corrosion. At some convenient potential after the breakdown of the passive layer, the direction of the potential scan is reversed (potential of metal made more negative) and ultimately, at some potential (Vᵢ) the passive layer will reform and the current flowing decrease back to a very small value.
A typical type of current-potential response observed in this work is shown in Figure 2, where the potential of the sample was scanned positive from around -0.7V at 0.3mV s^-1.

![Graph showing current-potential response](image)

Figure 2: A graphical representation showing the effect of tempering temperature on the re-passivation potential ($V_r$).

$V_f$ is the breakdown potential and $V_r$ is the re-passivation or protection potential, i.e. the potential below which any pit formed will not propagate. $V_r$ is considered the more accurate criterion for comparing the tendency of different alloy samples to undergo pitting corrosion, as $V_f$ depends on the induction time for pitting and is thus dependent on the potential scan rate. Table 2 shows the values obtained for $V_r$ and $V_f$ as a function of tempering temperature for both ESR and Stavax Supreme.

Table 2: Values of the breakdown potential ($V_f$) and re-passivation potentials ($V_r$) for both ESR and Stavax Supreme for low and high tempering temperatures.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>ESR Low Temperature Temper</th>
<th>ESR High Temperature Temper</th>
<th>Supreme Low Temperature Temper</th>
<th>Supreme High Temperature Temper</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$V_f$</td>
<td>$V_r$</td>
<td>$V_f$</td>
<td>$V_r$</td>
</tr>
<tr>
<td>Sample 1</td>
<td>+0.380</td>
<td>+0.160</td>
<td>+0.170</td>
<td>-0.140</td>
</tr>
<tr>
<td>Sample 2</td>
<td>+0.270</td>
<td>+0.080</td>
<td>+0.080</td>
<td>-0.120</td>
</tr>
</tbody>
</table>

![Graph showing effect of tempering temperature](image)

Figure 3 is a graphical representation showing the effect of tempering temperature on the re-passivation potential ($V_r$).
In interpreting this technique, the principal is that the more positive the value of \( V_r \) (or \( V_f \)) the less prone the alloy is to localised corrosion. Regardless of which potential measurement is taken, the same conclusion is reached, that is, both grades of steel are significantly more prone to localised corrosion in 0.35% sodium chloride solution when tempered at the higher tempering temperature. While for a given tempering temperature Stavax Supreme is more prone to localised corrosion than the ESR grade.

4.0 DISCUSSION

Under the present test conditions, the results suggest that Stavax Supreme is more prone to localised corrosion than ESR particularly when tempered at the higher tempering temperature. This is a challenging result but one that was repeated in further testing. Tidesten et al [1] reported a different finding when comparing the two grades of steel tempered at a low tempering temperature only. They carried out similar potentiodynamic studies at the same scan rate to that used in the present study but in a solution of 0.05 M \( \text{H}_2\text{SO}_4 \) at a pH level of 1.2. This is a valid test but one that is very different to the one conducted in the present study. In the aggressive acid solution used by Tidestan et al [1] the surfaces of the steels are not passive whereas the steels in the present study are passive at the start of the tests. Interestingly their results do suggest that the ESR grade has less tendency to passivate than Stavax Supreme meaning that the surface oxide is probably more porous on ESR than on Supreme. Consequently, one would expect Stavax Supreme to better resist the chemically aggressive resins in plastic moulding.

In the present study, the results clearly show that both grades of steel are more prone to localised corrosion in the presence of chloride ions when tempered at the higher tempering temperature. This in itself is not surprising given that at the lower tempering temperature there will be sufficient Cr in solid solution to provide the necessary passive oxide layer while at the higher tempering temperature the matrix will be denuded of Cr due to its precipitation in the alloy carbides. One should therefore anticipate a possible loss of corrosion in cooling channels, for example, if one tempers these steels at high temperature in order to avoid issues relating to residual stress. Results from the neutron diffraction studies do show that the high temperature temper was extremely effective in reducing the residual stress to almost zero for the steel blocks treated in this study. The observed differences in residual stress generated in the two grades of steel were discussed by Doyle et al [3] and can be summarised as follows: the higher residual stress observed in the Stavax Supreme compared to the ESR on quenching is a direct consequence of its higher hardenability. This arises because higher hardenability steels have a lower \( M_s \) temperature which results in a larger volume change during transformation with less possibility for auto-tempering. One should therefore pay particular attention to stress concentration factors at the design stage of manufacture. The reduction of residual stress on tempering occurs in at least two parts. The first is due to the transformation of tetragonal martensite to cubic martensite which will occur quite quickly in these low carbon martensitic stainless steels. The second will be from recovery of highly dislocated lath martensite. Clearly, Stavax Supreme appears to be particularly effective in relieving residual stress on tempering at the high temperature, however, there would appear that a price has to be paid in terms of localised corrosion resistance in the presence of chloride ions.
5.0 CONCLUSIONS

The development of residual stress in modern tool steels is a complex phenomenon but it can be evaluated in bulk using thermal neutrons. The present findings suggest that levels of residual stress can be very high on quenching martensitic stainless steels of high hardenability, such as Stavax Supreme. However, such steels are critically important if full through hardening with sound microstructure is to be achieved in large cross-sections of moulds. Residual stress can be significantly reduced in martensitic stainless steels on tempering. There is, however, a price to be paid in terms of resistance to localised corrosion in the presence of chloride ions for the higher hardenability grades when tempered at high temperatures.

6.0 REFERENCES


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