Effect of temperature on pitting corrosion of 316 SS in concentrated phosphoric acid containing hydrochloric acid

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Anodic polarization experiments were conducted on AISI 316 SS in 14 M H3PO4 containing 0-0.55 M of HCl at 298, 308 and 318 K. The anodic parameters i, i, Epas, En and E, were determined from the anodic polarization curves. It was found that both critical current density, i, and passivity current density, i, increased with rise in temperature. The parameters Epas, En and E, attained more active values with rise in temperature within the range of HCl concentrations investigated. Potential decay experiments were carried out to determine the characteristics of the passive films formed on 316 SS, which were found to be temperature dependent – their porosity increasing with rise in temperature. The pitting potential, E, and protection potential, En were determined for various HCl concentrations using the reverse polarization technique.

The electrochemical behaviour of austenitic stainless steels in pure phosphoric acid and in phosphoric acid containing sodium and potassium halides has been adequately investigated. As far as the effect of addition of chloride ions on the pitting of stainless steels in phosphoric acid is concerned, hydrochloric acid is found to be more deleterious than an equivalent concentration of the same ions from its salts. The corrosion behaviour of 304 SS in concentrated phosphoric acid containing varying amounts of HCl has been studied earlier at different temperatures. From these results it could be concluded that in view of the pitting and corrosion tendency of 304 SS its utilization would be rather limited in the investigated medium. Since pitting is primarily due to an imperfect state of passivity at various local points on the alloy surface, the composition of stainless steel plays a decisive role as far as pitting corrosion is concerned. The most positive effect on the resistance of stainless steels to pitting corrosion in chloride containing solutions has been observed by alloying these steels with chromium and molybdenum. In the present work an evaluation of the effect of temperature on the corrosion and pitting behaviour of AISI 316 SS in phosphoric acid containing various concentrations of HCl has been undertaken.

Experimental Procedure

The test samples for the given electrochemical experiments were obtained from M/s Goodfellow Metals Ltd., England. The composition of 316 SS was 18Cr, 8Ni, 3Mo and balance Fe. The surface preparation, actual conduct of the experiment and recording of the potentiodynamic polarization curves was very similar to the earlier studies described in detail elsewhere.

In the present study, however, potential decay measurements were also undertaken. The potential decay curves were recorded with the help of Omniscribe strip chart recorder. The specimen was initially polarized anodically till passivity was detected. Further, the applied potential was maintained at various fixed values in the passive region for different time intervals, viz. 15, 30 and 120 min. The potentiostat was then switched off and the potential decay recorded with respect to the time elapsed. This experiment was performed with a fresh sample for each different system.

Results and Discussion

The anodic polarization curves of 316 SS in 14 M phosphoric acid in the presence of varying amounts of HCl at 298 K are shown in Fig. 1. The polarization curves exhibit similar features at all the concentrations of HCl, i.e. a small active zone followed by a rather large passive region leading finally to the transpassive region. The basic anodic parameters: primary passivation potential (E), passivation potential (E), critical current density (i,) and passivity current density (ip) have been determined from the polarization curves and recorded in Table 1.

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It can be seen from the polarization curves that the critical current density \( (i_c) \) and passivity current density \( (i_p) \) attain higher values, while the primary passivation potential \( (E_{pp}) \), passivation potential \( (E_p) \) and breakdown potential \( (E_b) \) attain more active values with increasing concentrations of HCl (Table 1). This observed behaviour has been explained earlier.7

To analyze the effect of temperature on the corrosion behaviour of 316 SS, the anodic polarization curves at two selective concentrations of 0.055 M and 0.411 M HCl are shown in Figs 2 and 3 respectively. At both these concentrations, with rise in temperature both \( E_{pp} \) and \( E_p \) show a marked shift towards active values in the 298-308 K range, while the shift observed in the 308-318 K range is smaller. The influence of temperature on the breakdown potential \( E_b \) is evident from an approximate 300mV shift in its value in the lower temperature range for both the selected concentrations. In the higher temperature range this shift is quite negligible. This trend is in keeping with the observations of Forchhammer and Engell6.

A monotonic rise in the current densities \( i_c \) and \( i_p \) with HCl content is witnessed at all three temperatures, the increase again being larger in the 298 to 308 K range as compared to that in the 308 to 318 K range. The increase in \( i_c \) may be due to the strong depolarizing action of the chloride ions, which brings about more rapid dissolution of the alloy to

![Anodic polarization curves of 316 SS in 14 M H₃PO₄ containing different concentrations of HCl at 298 K: 1 – Blank solution; 2 – 0.027 M; 3 – 0.055 M; 4 – 0.082 M; 5 – 0.110 M; 6 – 0.137 M; 7 – 0.219 M; 8 – 0.274 M; 9 – 0.411 M; 10 – 0.550 M.](image1)

![Anodic polarization curves of 316 SS in 14 M H₃PO₄ containing 0.055 M HCl at different temperatures: 1 – 298 K; 2 – 308 K; 3 – 318 K.](image2)

### Table 1 – Anodic parameters of AISI 316 SS in 14 M phosphoric acid containing different concentrations of HCl

<table>
<thead>
<tr>
<th>Conc of HCl (M)</th>
<th>Blank Sol.</th>
<th>0.027</th>
<th>0.055</th>
<th>0.082</th>
<th>0.110</th>
<th>0.137</th>
<th>0.219</th>
<th>0.274</th>
<th>0.411</th>
<th>0.550</th>
</tr>
</thead>
<tbody>
<tr>
<td>( i_c ) (mA cm(^{-2}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298 K</td>
<td>0.002</td>
<td>0.008</td>
<td>0.340</td>
<td>0.380</td>
<td>0.400</td>
<td>1.600</td>
<td>2.200</td>
<td>3.500</td>
<td>5.000</td>
<td>6.200</td>
</tr>
<tr>
<td>( i_p ) (mA cm(^{-2}))</td>
<td>0.001</td>
<td>0.002</td>
<td>0.004</td>
<td>0.006</td>
<td>0.006</td>
<td>0.008</td>
<td>0.014</td>
<td>0.020</td>
<td>0.024</td>
<td>0.030</td>
</tr>
<tr>
<td>( E_{pp} ) (mV)</td>
<td>-100</td>
<td>-100</td>
<td>-100</td>
<td>-110</td>
<td>-110</td>
<td>-120</td>
<td>-130</td>
<td>-140</td>
<td>-140</td>
<td>-140</td>
</tr>
<tr>
<td>( E_p ) (mV)</td>
<td>-70</td>
<td>-70</td>
<td>-20</td>
<td>+30</td>
<td>+30</td>
<td>+30</td>
<td>+40</td>
<td>+40</td>
<td>+80</td>
<td>+90</td>
</tr>
<tr>
<td>308 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( i_c ) (mA cm(^{-2}))</td>
<td>0.150</td>
<td>1.500</td>
<td>2.000</td>
<td>2.400</td>
<td>2.500</td>
<td>3.000</td>
<td>3.000</td>
<td>6.000</td>
<td>6.900</td>
<td>13.500</td>
</tr>
<tr>
<td>( i_p ) (mA cm(^{-2}))</td>
<td>0.010</td>
<td>0.030</td>
<td>0.040</td>
<td>0.070</td>
<td>0.100</td>
<td>0.200</td>
<td>0.200</td>
<td>0.500</td>
<td>0.630</td>
<td>0.730</td>
</tr>
<tr>
<td>( E_{pp} ) (mV)</td>
<td>-250</td>
<td>-250</td>
<td>-260</td>
<td>-280</td>
<td>-290</td>
<td>-250</td>
<td>-270</td>
<td>-260</td>
<td>-250</td>
<td>-250</td>
</tr>
<tr>
<td>( E_p ) (mV)</td>
<td>-200</td>
<td>-210</td>
<td>-200</td>
<td>-200</td>
<td>-200</td>
<td>-100</td>
<td>0</td>
<td>+50</td>
<td>+100</td>
<td>+100</td>
</tr>
<tr>
<td>318 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( i_c ) (mA cm(^{-2}))</td>
<td>0.500</td>
<td>1.800</td>
<td>2.400</td>
<td>3.000</td>
<td>3.600</td>
<td>6.000</td>
<td>6.000</td>
<td>7.600</td>
<td>8.200</td>
<td>15.600</td>
</tr>
<tr>
<td>( i_p ) (mA cm(^{-2}))</td>
<td>0.020</td>
<td>0.025</td>
<td>0.050</td>
<td>0.090</td>
<td>0.150</td>
<td>0.300</td>
<td>0.300</td>
<td>0.620</td>
<td>1.200</td>
<td>1.800</td>
</tr>
<tr>
<td>( E_{pp} ) (mV)</td>
<td>-250</td>
<td>-260</td>
<td>-260</td>
<td>-270</td>
<td>-270</td>
<td>-270</td>
<td>-280</td>
<td>-280</td>
<td>-280</td>
<td>-280</td>
</tr>
<tr>
<td>( E_p ) (mV)</td>
<td>-180</td>
<td>-180</td>
<td>-180</td>
<td>-160</td>
<td>-160</td>
<td>-40</td>
<td>10</td>
<td>50</td>
<td>120</td>
<td>120</td>
</tr>
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</table>
form chlorides and chlorocomplexes. The change in $i_p$ may be attributed to changes in the nature of the passive film formed on the alloy surface at different temperatures.

In order to estimate the relative stability of passive films formed on 316 SS at different temperatures, potential decay experiments were performed on the steel samples. The variation of potential of 316 SS with time, recorded in phosphoric acid containing 0.405 M (critical concentration of HCl) after polarization of the samples in the passive region at 200 mV for 30 min at the above temperatures are presented in Fig. 4. The curves are characterized by a gradual decrease in potential towards more active values. It is clear from the figure that at any instant the potential of the system is more active at a higher temperature. It may be due to the fact that a more porous film is formed on the alloy surface at a higher temperature. It may also be observed from the figure that after some time the potential ultimately attains the steady state value of the system. The time taken to attain the same is of course, temperature dependent. In the case reported here these were 100, 80 and 70 s at 298, 308 and 318 K respectively. It seems that at higher temperatures a more rapid dissolution of the passive film occurs.

It is common knowledge that upon increasing anodic polarization in the presence of passivity-destroying anions the metal undergoes pitting above the pit initiation potential $E_{pitt}$. However, once pitting has occurred, it is stable even below $E_{pitt}$ and growing pits cannot be repassivated unless the electrode potential is less noble than another potential—the repassivation or protection potential $E_{prr}$ (ref. 7).

The pitting potential $E_{pitt}$ was calculated from chronocamperographs recorded at various concentrations of HCl at each investigated temperature. To determine the protection potential at different temperatures, the potential was reversed at a certain point in the transpassive region. The polarization curve exhibited a loop and the point of intersection with the passive range curve yielded the value of protection potential $E_{prr}$ (ref. 7). Representative curves of forward and reverse polarizations at 318 K at various concentrations of HCl above critical concentration are given in Fig. 5. The values of breakdown potential $E_{b}$, pitting potential $E_{pitt}$ and protection potential $E_{prr}$ at different temperatures and concentrations of HCl are recorded in Table 2. It follows from the data that at each temperature both the pitting and protection potentials tend to become more active with increase in HCl.

![Fig. 3](image_url)

Fig. 3—Anodic polarization curves of 316 SS in 14 M H$_3$PO$_4$ containing 0.411 M HCl at different temperatures: 1 – 298 K; 2 – 308 K; 3 – 318 K.

![Fig. 4](image_url)

Fig. 4—Potential decay curves of 316 SS in 14 M H$_3$PO$_4$ containing 0.405 M HCl at different temperatures: 1 – 298 K; 2 – 308 K; 3 – 318 K.

![Fig. 5](image_url)

Fig. 5—Cyclic anodic polarization curves of 316 SS in 14 M H$_3$PO$_4$ containing different concentrations of HCl at 318 K: 1 – 0.219 M; 2 – 0.274 M; 3 – 0.411 M; 4 – 0.550 M.
concentration. A more active $E_{\text{pit}}$ may be due to an increase in the porosity of the film with rise in temperature (as observed earlier from potential decay experiments), which is supposed to favour the starting of irreversible pitting event at more active potentials. Moreover, with rise in temperature the physical structure of the passive film is affected resulting in variation of density of vacancy or voids in the film as suggested by Smialowska et al.\textsuperscript{16}. As a result, a decrease in the resistance to breakdown of the film is witnessed as the temperature is raised.

The test samples were subjected to Scanning Electron Microscopy, which showed the presence of a large number of pits with hemispherical geometry on the alloy surface. The severity of pitting was found to increase at higher temperatures but there was no change in their morphology with change in temperature. It was also observed that the number of pits increases with rise in temperature, but the size of the pits becomes smaller. From the surface analysis of steel samples of 316 SS the critical concentration of HCl at which pitting starts was ascertained to be 0.405, 0.134 and 0.123 M at 298, 308 and 318 K respectively.

**Table 2**—Influence of HCl content in 14 M HPO$_4$ on breakdown potential, pitting potential and repassivation potential of 316 SS

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>$E_{\text{b}}$ (mV)</th>
<th>$E_{\text{pit}}$ (mV)</th>
<th>$E_{\text{pr}}$ (mV)</th>
<th>$E_{\text{b}}$ (mV)</th>
<th>$E_{\text{pit}}$ (mV)</th>
<th>$E_{\text{pr}}$ (mV)</th>
<th>$E_{\text{b}}$ (mV)</th>
<th>$E_{\text{pit}}$ (mV)</th>
<th>$E_{\text{pr}}$ (mV)</th>
</tr>
</thead>
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<tr>
<td>0.137</td>
<td>720</td>
<td>732</td>
<td>712</td>
<td>600</td>
<td>628</td>
<td>580</td>
<td>600</td>
<td>624</td>
<td>580</td>
</tr>
<tr>
<td>0.274</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>580</td>
<td>612</td>
<td>550</td>
<td>570</td>
<td>600</td>
<td>550</td>
</tr>
<tr>
<td>0.411</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>560</td>
<td>604</td>
<td>530</td>
<td>530</td>
<td>580</td>
<td>510</td>
</tr>
<tr>
<td>0.550</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>550</td>
<td>600</td>
<td>520</td>
<td>520</td>
<td>572</td>
<td>500</td>
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**References**