AMBIGUOUS EFFECT OF CATHODIC POLARIZATION ON SPEED OF CRACK GROWTH DURING STRESS CORROSION CRACKING OF HIGH-STRENGTH STEELS IN INHIBITED SODIUM CHLORIDE SOLUTIONS

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It was established in [1] that cathodic polarization (all other conditions such as the composition of the material and the solution, temperature, and so on being equal) during stress corrosion cracking of high-strength steels may retard crack growth, accelerate crack growth, or leave it unaffected, depending on the initial speed of crack growth at the corrosion potential. The object of the present work is to study the effect of cathodic polarization on speed of crack growth during stress corrosion cracking of high-strength martensitic steels in naturally aerated 0.5 N sodium chloride solutions containing from 0 to 30 g/liter potassium chromate.

The experiments were carried out on 210 × 25 × 1.6-mm test pieces with one lateral fatigue crack 5 mm long under uniaxial tension and at room temperature. The methods of test-piece preparation and of continuous measurement of crack-growth speed (by reference to the electrical resistance of the central sector of test pieces with cracks) are set out in [1]. The chemical composition of the steels, their mechanical characteristics, and certain of their electrochemical characteristics are given in Table 1.

The minimum crack-growth speed (of the order of 10⁻³ mm/h) was selected by increasing the load, after the test piece with the cell fixed to it had been mounted in the tensile-test machine clamps and given the 20-h exposure sufficient to determine the corrosion potential. The test pieces were then subjected to potentiostatic cathodic polarization at 200 or 500 mV and the change in crack-growth speed caused by the cathodic polarization was assessed from the diagram showing changes in electrical resistance. When the time necessary to establish the corrosion potential had elapsed, a somewhat higher initial speed of crack growth was obtained by increasing the load and the test piece was again subjected to cathodic polarization. These cycles were repeated with a gradual increase in the initial speed of crack growth up to maximum values of the order of 10 mm/h.

Curves showing the relationship of the effect of cathodic polarization on crack-growth speed in corrosion cracking of steel 4Kh3 in 0.5 N sodium chloride solution with additions of 0-30 g/liter potassium chromate.

TABLE 1

<table>
<thead>
<tr>
<th>Steel (Rockwell C hardness 45)</th>
<th>Alloying element content, wt. %</th>
<th>(E_0)</th>
<th>(E_{0.2})</th>
<th>Corrosion potential (mV, normal hydrogen electrode with (KCrO_4) g/liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>Si</td>
<td>Mn</td>
<td>Cr</td>
</tr>
<tr>
<td>4X1</td>
<td>0.40</td>
<td>1.00</td>
<td>0.50</td>
<td>0.99</td>
</tr>
<tr>
<td>4X3</td>
<td>0.39</td>
<td>1.09</td>
<td>0.45</td>
<td>0.95</td>
</tr>
<tr>
<td>4X6</td>
<td>0.38</td>
<td>0.95</td>
<td>0.50</td>
<td>0.95</td>
</tr>
</tbody>
</table>


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The extent to which cathodic polarization affects crack-growth speed is assessed as the ratio of crack-growth speed after polarization ($V_p$) to the initial speed of crack growth at the corrosion potential ($V_i$). If cathodic polarization retards crack growth, then $(V_p/V_i) < 1$; if it accelerates crack growth, then $(V_p/V_i) = 0$, and when polarization has no effect on initial speed of crack growth, then $(V_p/V_i) = 1$. When this assessment is used, each curve in Fig. 1 can be defined in terms of three parameters: 1) the critical speed of crack growth $V_{cr}$ at which retarded growth during cathodic polarization is replaced by accelerated growth; 2) the maximum polarization effect ($V_p/V_i$)$_{max}$; 3) the crack-growth speed at which cathodic polarization ceases to affect the initial crack-growth speed ($V_D$).

It is apparent from Fig. 1 that an increase in the inhibitor concentration results in a sharp increase in the critical speed of crack growth, reduces the maximum effect of cathodic polarization on crack-growth speed, and has little effect on the speed of crack growth at which polarization ceases to affect the initial crack-growth speed.

The relationship of the main parameters $V_{cr}$ and ($V_p/V_i$)$_{max}$ (cathodic polarization at 500 mV) to the inhibitor concentration for steels with various chromium contents is shown in Fig. 2. It is apparent that inhibition of the solution leads to a continuous increase in $V_{cr}$ and a drop in ($V_p/V_i$)$_{max}$. The $V_{cr}$ and ($V_p/V_i$)$_{max}$ values for steel 4Kh3 remain practically unchanged as the inhibitor concentration rises, whereas for steel 4Kh6 ($V_p/V_i$)$_{max}$ decreases by 10 times at a chromate concentration of 30 g/liter and $V_{cr}$ increases by almost 50 times. It follows from this that the effectiveness of inhibitor action on the basic parameters of the curves increases as the chromium content of the steel rises.

It should be noted that even the maximum (30 g/liter) concentration of potassium chromate in the 0.5 N sodium chloride solution is not a protective concentration for the steels studied and does not lead to any substantial improvement in the corrosion potential (see Table 1) or to an increase in corrosion resistance. However, as was shown above, critical crack-growth speed and the maximum effect of cathodic polarization on the initial crack-growth speed alter drastically at the same inhibitor concentrations and even at concentrations one order of magnitude lower. This indicates a difference in the kinetics of inhibitor-metal reaction on the surface of the test piece and at the tip of the growing crack, and possibly a difference in the mechanism of this reaction.

The experimental results in this work can be interpreted on the basis of concepts of the stress corrosion-cracking mechanism [1, 2], according to which the dominant factor, all other conditions being equal (the same material, test solution, temperature, and so on), may be local anodic solution of the material at the tip of the growing crack, hydrogen embrittlement, or an adsorptive reduction in strength, depending on the initial crack-growth speed and the potential. We will assume hydrogen embrittlement and its associated jump in crack growth to be possible provided that a concentration of hydrogen $C_H$ in excess of the critical concentration $C_{cr}$ forms in the metal at the distance of the "jump" in front of the crack tip in the time necessary to prepare for the jump. The jump in crack growth in stress corrosion cracking in high-strength steels has been studied in detail in [3], where the distances by which the crack elongates as a result of the jump and the jump preparation time are indicated.

Let us examine the relationship between the protective properties of the film (T, see Fig. 3a) on the metal at the tip of the growing crack and $V_i$. When the crack is not mobile, a film with definite protective properties develops. When the crack-growth speed is infinitely high, the film will be completely absent. If we assume as a first approximation that the protective properties of the film alter continuously between these two situations we may conclude that the protective properties of the film must decrease as the speed of crack growth increases, because the time for its formation is reduced.

Let us assume that deterioration in film protective properties with the increase in crack-growth speed in an uninhibited solution corresponds to curve 1 in Fig. 3a. The protective properties in an inhibited solution at identical crack-growth speeds will then be higher, i.e., curve 2, which represents the fall...