Mechanistic model for stress corrosion cracking-anodic dissolution mechanism

L. Lazzari

This paper illustrates a model for the quantitative evaluation of the crack growth rate of stress corrosion cracking (SCC) according to the slip anodic dissolution mechanism. The proposed algorithm is based on the revision and a combination of two previous models, namely the Andresen-Ford model that allows to calculate the dissolution rate of the crack tip, by introducing the macrocell model, and the Galvele’s mobility theory of dislocations to take into account the mechanical effect. Based on the principle of independence of the two effects, electrochemical and mechanical, the resulting crack growth rate is the sum of the two contributions. The comparison with the field and laboratory available data allows us to conclude that the model is robust and able to justify the experimental data for the most case studies of SCC. Remarkable examples are: carbon steels (in carbonate/bicarbonate solutions, high temperature alkalis); copper in ammonia containing environment; stainless steels (chloride-containing environment, pure water at high temperature, boiling magnesium chloride) Ni-alloys (pure water at high temperature).

INTRODUCTION

The first mention of Stress Corrosion Cracking, anodic dissolution mechanism (SCC-AD) dates 1940s [1, 2], then reviewed and investigated since the 1960s by Hoars, Parkins and others [3, 4]. Staehle coined the name slip-anodic dissolution in late 1960s [5]. It was agreed that crack grows after the fracture of the pre-formed passive film, generally as an oxide, by anodic dissolution, then followed by the repassivation: accordingly, cracking is a discontinuous process in nature. Starting from Staehle’s definition as slip dissolution mechanism, a perception was clear by which, in addition of the anodic dissolution as purely corrosion mechanism, a mechanical crack propagation would occur. Evidences of this appeared to be the cracking of Ni-based alloys and austenitic stainless steels in PWR plants as well as copper alloys in ammonia containing solutions, where expected localized corrosion rate is much lower than the experienced crack growth rate. Andresen and Ford [6] proposed a model based on the slip-dissolution mechanism through the following paths:

- The passive film at the crack tip breaks after the time $t_f$ as consequence of the tensile stress acting at the tip, then exposing bare active metal
- The crack tip starts corroding while contemporarily tends to repassivate. Dissolution rate decreases by following a quasi-parabolic law
- The crack tip repassivates and breaks again due to the mechanical stress after the time $t_f$.

KEYWORDS: STRESS CORROSION CRACKING; SLIP ANODIC DISSOLUTION MECHANISM, CRACK GROWTH RATE.
The relationship obtained is the following:

\[ CGR \approx i_a \cdot \frac{t_0^{n}}{1 + \left( \frac{t}{t_0} \right)^{m}} \]  \[\text{[1]}\]

where \( CGR \) is average crack growth rate; \( i_a \) is anodic current density at the crack tip; \( t_0 \) is a time scaling parameter to be determined experimentally, having the meaning of repassivation time and is a constant once fixed the operating conditions; \( \varepsilon_c \) and \( \dot{\varepsilon} \) are critical strain and strain rate of the oxide film, respectively.

On the other hand, Galvele \[7, 8\] investigated the role of dislocation movement at the crack tip, called surface mobility mechanism, assuming that the growth of the crack is mainly mechanical through the movement of dislocations at crack tip. It follows that the crack growth rate can be given by the following relationship:

\[ CPR = \frac{D_s}{L} \left[ \frac{\sigma e^k}{kT} - 1 \right] \]  \[\text{[2]}\]

where \( D_s \) and \( L \) are related to the diffusion of vacancies in the metal, \( a \) is metal lattice size, \( k \) is Boltzmann constant, \( T \) is temperature and \( \sigma \) is applied stress. Therefore, Galvele’s model is important because allowing the estimation of the influence of the pure mechanical aspects.

A NEW MODEL

Based on Staehle’s suggestion for which crack growth is the result of a twofold action, electrochemical and mechanical, and according to Parkins, for whom the two effects are independent, growth rate can be considered as the sum of two terms:

\[ CGR_{SCC-AD} \approx CGR_{CORR} + CGR_{MECH} \]  \[\text{[3]}\]

where \( CGR_{CORR} \) is a term for electrochemical dissolution and \( CGR_{MECH} \) for the mechanical process. Fig. 1 depicts schematically the two contributions.

![Fig. 1 - Schematic representation of the slip-anodic dissolution mechanism for SCC](image)

The first term is given by the Andresen–Ford model and the second by the Galvele model. Andresen – Ford equation can be rewritten as follows:

\[ CGR_{CORR} \approx 0.5 \cdot i_a \sqrt{\frac{T - \sigma_{cm}}{\sigma}} \]  \[\text{[4]}\]
RESULTS FOR MODEL VALIDATION

Tabs. 2, 3 and 4 report the comparison between results from literature data and those given by this proposed new model. To follow the application of the model, all input parameters, grouped as properties for stress level, cathodic process and macrocell current, are reported. It was considered interesting to investigate the behaviour of copper in ammonia-containing solutions, where hydrogen evolution is possible because ammonia complexes form. Results confirm that dissolution rate of copper, although possible, is very low compared to the mechanical effect. For austenitic stainless steel in chloride-containing solutions, two case studies are reported: in classical boiling MgCl₂ solutions and solutions with temperature exceeding the threshold of 50°C, at a stress level close to the yield strength. The behaviour of Ni-alloys in pressurized water reactor (PWR) conditions, typically for nuclear plant, was also considered.
Corrosion

### DISCUSSION AND CONCLUSIONS

As examples reported show, the model seems to predict the SCC behaviour of all main combinations of metal and environment that follow the slip-anodic dissolution mechanism. Therefore, main conclusions are the following:

- This new model is based on the independence of the two effects, electrochemical and mechanical, by revisiting two previous models developed by Andresen-Ford for the anodic dissolution and Galvele for the mechanical effects.
- The quantification of the dissolution rate, which was not developed previously, is here carried out by the adoption of the macrocell model which allows to estimate the maximum dissolution rate regardless the geometry of the crack and any diffusion process within the crack.
- This new model shows that the contribution of corrosion to the crack growth is about less than 50% for FCC metals and almost 100% for BCC metals.
- The comparison between model results and experimental data shows a good agreement for all examined SCC occurrences.

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**Tab. 2 - Input data and results for SCC of metals with BCC structure**

<table>
<thead>
<tr>
<th>BCC (k_m=5)</th>
<th>Metal related data</th>
<th>Cathodic process data</th>
<th>Macrocell related data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T</td>
<td>σ_f</td>
<td>ΔE</td>
</tr>
<tr>
<td></td>
<td>°C</td>
<td>MPa</td>
<td>MPa</td>
</tr>
<tr>
<td>CS + CO₂^3 / HCO⁻ (Lab)</td>
<td>77</td>
<td>450</td>
<td>500</td>
</tr>
<tr>
<td>CS + OH⁻</td>
<td>1.6</td>
<td>0.01</td>
<td>1.6</td>
</tr>
</tbody>
</table>
| CS = carbon steel

**Tab. 3 - Input data and results for SCC of metals with FCC structure (k_m=1)**

<table>
<thead>
<tr>
<th>FCC (k_m=1)</th>
<th>Metal related data</th>
<th>Cathodic process data</th>
<th>Macrocell related data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T</td>
<td>σ_f</td>
<td>ΔE</td>
</tr>
<tr>
<td></td>
<td>°C</td>
<td>MPa</td>
<td>MPa</td>
</tr>
<tr>
<td>Ca + NH₃ (no O₂)</td>
<td>20</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Al + NaCl (pH=9)</td>
<td>25</td>
<td>190</td>
<td>150</td>
</tr>
</tbody>
</table>
| Ca = stainless steel

**Tab. 4 - Input data and results for SCC of metals with FCC structure (k_m=3)**

<table>
<thead>
<tr>
<th>FCC (k_m=3)</th>
<th>Metal related data</th>
<th>Cathodic process data</th>
<th>Macrocell related data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T</td>
<td>σ_f</td>
<td>ΔE</td>
</tr>
<tr>
<td></td>
<td>°C</td>
<td>MPa</td>
<td>MPa</td>
</tr>
<tr>
<td>SS + MgCl₂</td>
<td>150</td>
<td>250</td>
<td>200</td>
</tr>
<tr>
<td>SS + Chlorides</td>
<td>60</td>
<td>250</td>
<td>200</td>
</tr>
<tr>
<td>Ni + H₂O (PWR) (16 ppm)</td>
<td>320</td>
<td>350</td>
<td>120</td>
</tr>
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<td>Ni + H₂O (PWR) (16 ppm)</td>
<td>320</td>
<td>350</td>
<td>120</td>
</tr>
</tbody>
</table>
| SS = stainless steel

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REFERENCES