Effect of applied stress on passivation kinetics and passivation modelling of 304L stainless steel in acidic medium

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1 Passivation Role in Stress Corrosion Cracking (SCC):

- **Film rupture-dissolution model (FRM):** describes intergranular SCC, shown in Fig.1, as repetitive cycles of local surface activation, dissolution, and passivation near the crack tip [1]. Fig. 2 illustrates one of these cycles as described next:

Mechanical: Slip-induced passivity breakdown causing fresh surface exposure to corrosive environment. (process1-2 in Fig.2 and 3)

Electrochemical: Excessive material dissolution takes place until the surface repassivates again. (process 3-4 in fig. 2 and 3)

Objectives

- To develop a model quantifying the passivation kinetics and parameters of passive films constructed in acidic medium.
- To use this model to check the influence of stress on stainless steel passivation and passive film quality.

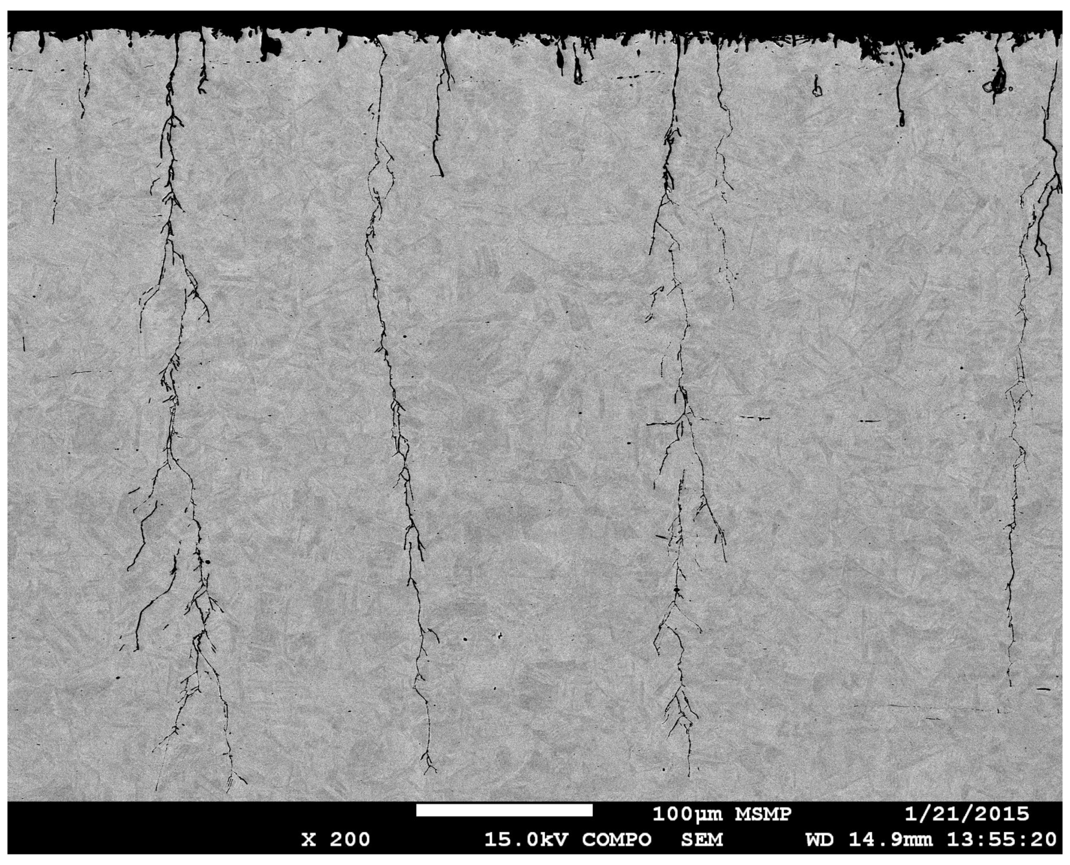

Fig.1: SCC of 304L stainless steel after 88 h immersion in 2 M H2SO4 + 0.5 M NaCl.

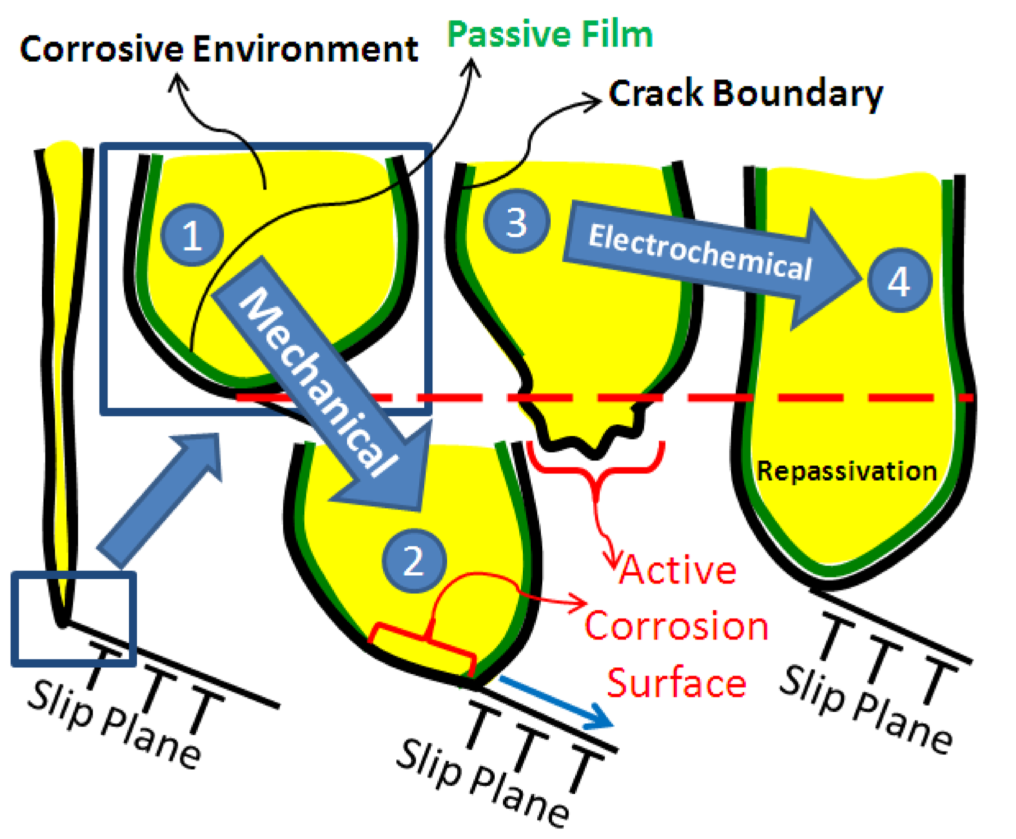

Fig.2: Representation of crack propagation by the film rupture-dissolution model.

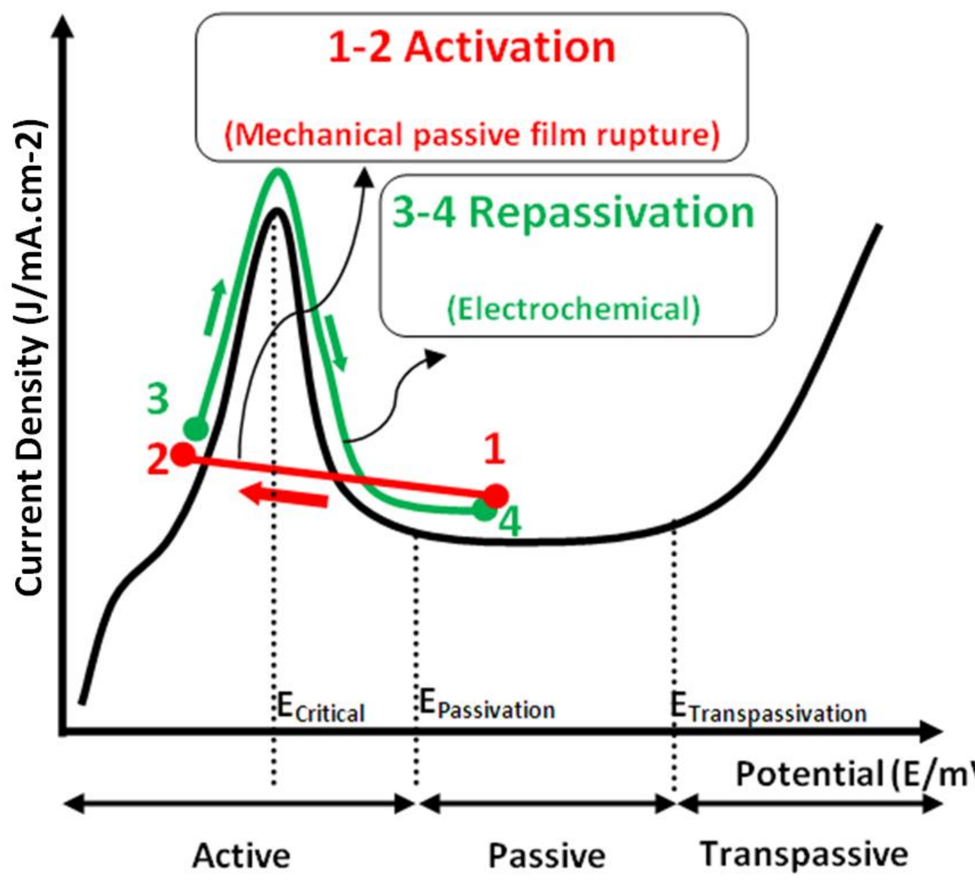

Fig.3: Polarization curve showing an activation/passivation cycle.

2 Quantification of Passive Film Thickness and Quality in Acidic Medium:

Atomic Emission Spectroscopy and Conventional Electrochemical Experiments

- Stressed and non-stressed samples of 304L stainless steel are subjected to potentiodynamic cycling tests as shown in Fig. 2. ➔These serve as an electrochemical simulation of SCC activation/passivation cycle as described by FRM.
- Experiments were performed in 2 M H2SO4 solution at room temperature.
- In-situ atomic emission spectroelectrochemistry **(AESEC)** [3] was coupled with conventional electrochemistry during the tests. ➔ By this, the passivation current due to metallic dissolution can be quantified, as shown by Fig. 4.

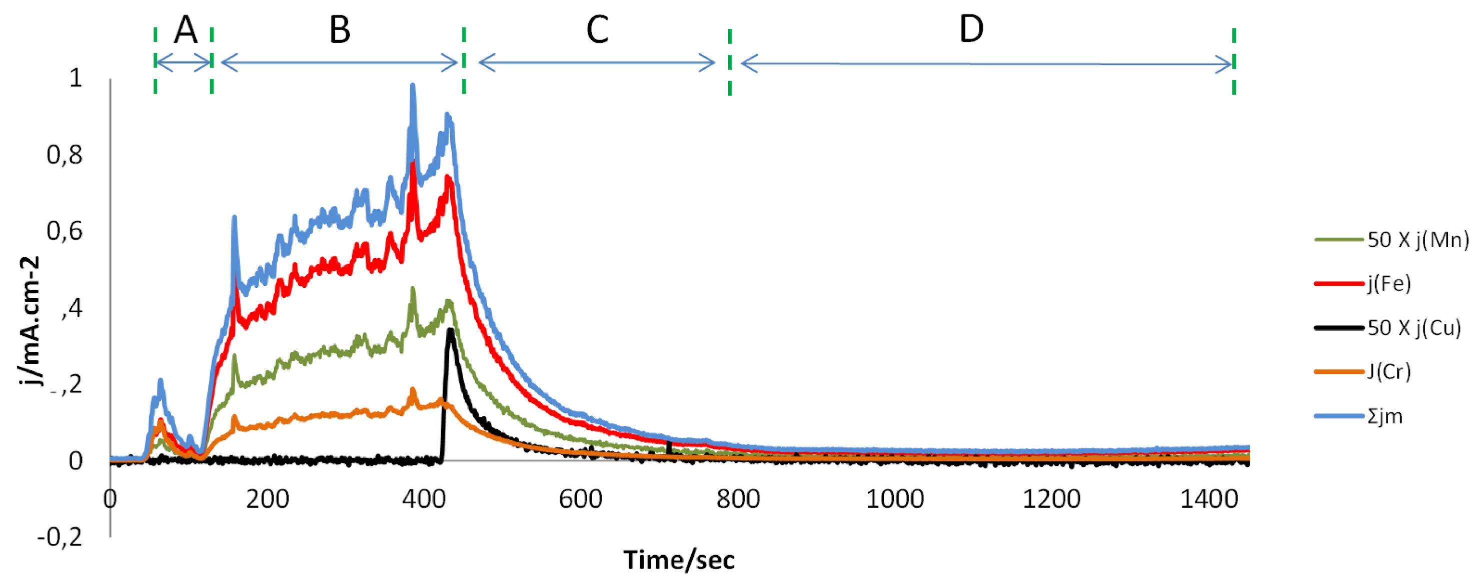

Fig.4: AESEC experiment showing the metallic dissolution current densities during a potentiodynamic activation/passivation cycle.
A: activation pulse. B: Open circuit potential **(OCP)**. C: Passivation pulse. D: OCP.

High Field Ion Conduction Model and Passive Film Thickness (HFIC)

- HFIC was adapted to describe the current evolution during passivation [2], as given by eq.1.
- Passive film thickness can be calculated using Faraday's law as indicated by eq.2.
- The term q_{film} represents the charge exchange responsible for passive film formation.
- The external current during passivation is due to three components as explained by eq.3.
- In acidic solutions, the major part of anodic current measured during passivation is due to metallic dissolution [2,3], where $i_{cathodic}$ is negligible [3].
- The portion of charge due to film formation can be calculated by quantifying the dissolution component as given by equation 5 and 6.
- A particular approximation is taken as $i_{external} = i_{dissolution}$ to calculate the current fraction due to iron dissolution f_{Fe} . By this, f_{Fe} can be calculated as given by eq.7.
- The calculation of f_{Fe} is based only on the metallic mass fractions in the alloy and their oxidation numbers in such acidic medium as derived from Faraday's second law ➔ eq.8.
- Using AESEC quantified data for metallic dissolution during passivation (region C in Fig.4), i_m/i_{Fe} can be calculated. This ratio can be used in eq.9 to calculate f_m for the concerned metals. ➔ By eq.2, passive film thickness is calculated as shown in Fig.5.

$$i(t) = A\exp\left(\frac{BV}{h(t)}\right) \quad (1)$$

$$h(t) = \frac{Mq(t)_{film}}{zF\rho} \quad (2)$$

$$i_{external} = i_{dissolution} + i_{film} + i_{cathodic} \quad (3)$$

$$q(t)_{total} = \int_{t=0}^{t} i_{external}(u)\,du \quad (4)$$

$$q(t)_{film} = q(t)_{total} * (1 - f_{dissolution}) \quad (5)$$

$$f_{dissolution} = (f_{Fe} + f_{Cr} + f_{Mn} + f_{Cu})_{dissolved} \quad (6)$$

$$f_{Fe} = \frac{i_{Fe}}{i_{Fe} + i_{Cr} + i_{Mn} + i_{Cu}} \quad (7)$$

$$i_m = \frac{m.F.z}{t.M} \quad (8)$$

$$f_m = \frac{i_m}{i_{Fe}} \times f_{Fe} \quad (9)$$

$$\log i(t) = \log A + \frac{BzF\rho V}{2.3\,M\,q(t)_{film}} \quad (10)$$

3 Influence of Stress on Passive Film Thickness and Quality:

- For stressed samples ➔ slightly higher charge exchange ➔ thicker passive film. (1.64 vs 1.58 nm ±0.03).
- Slopes of curves in Fig. 6 = cBV. ➔ a direct measure of the passivation rate and the film ionic conductivity.
  ➔ cBV is inversely proportional to the film quality [4]. Fig. 7 shows this factor for stressed and unstressed cases.

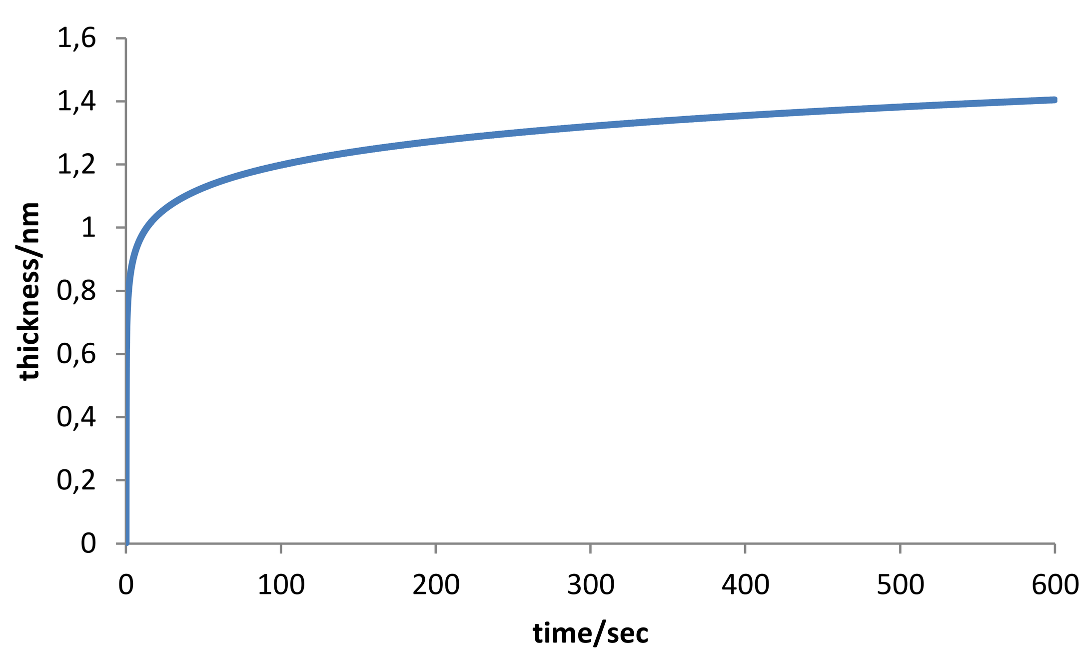

Fig.5: Passive film thickness formed during the passive as calculated by eq.2.

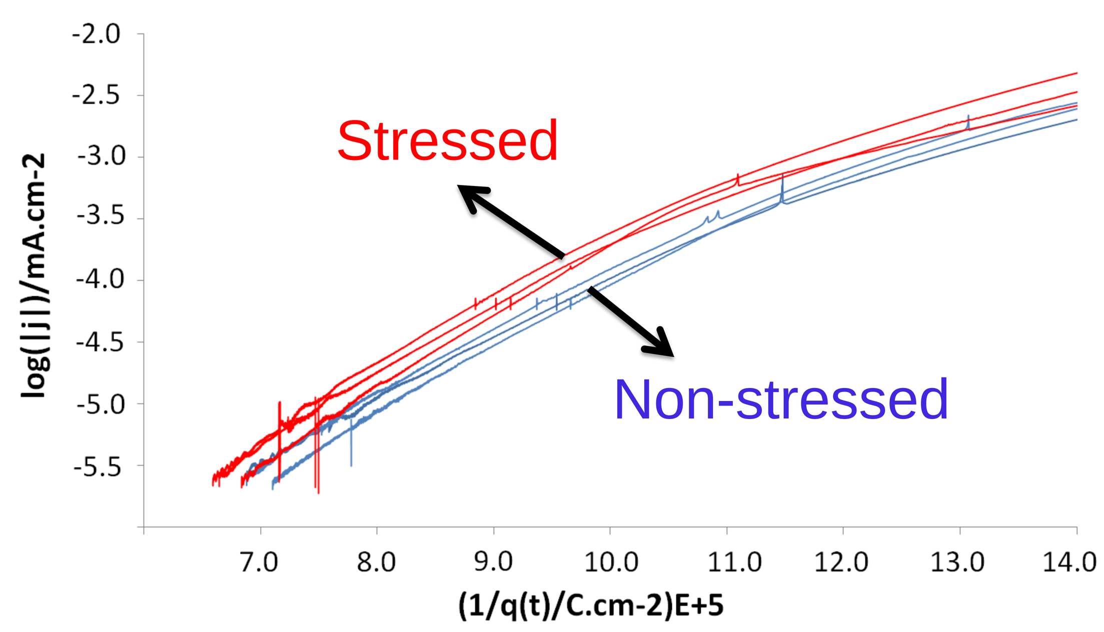

Fig.6: Experimental passivation transients based on eq.10 during the anodic pulse.

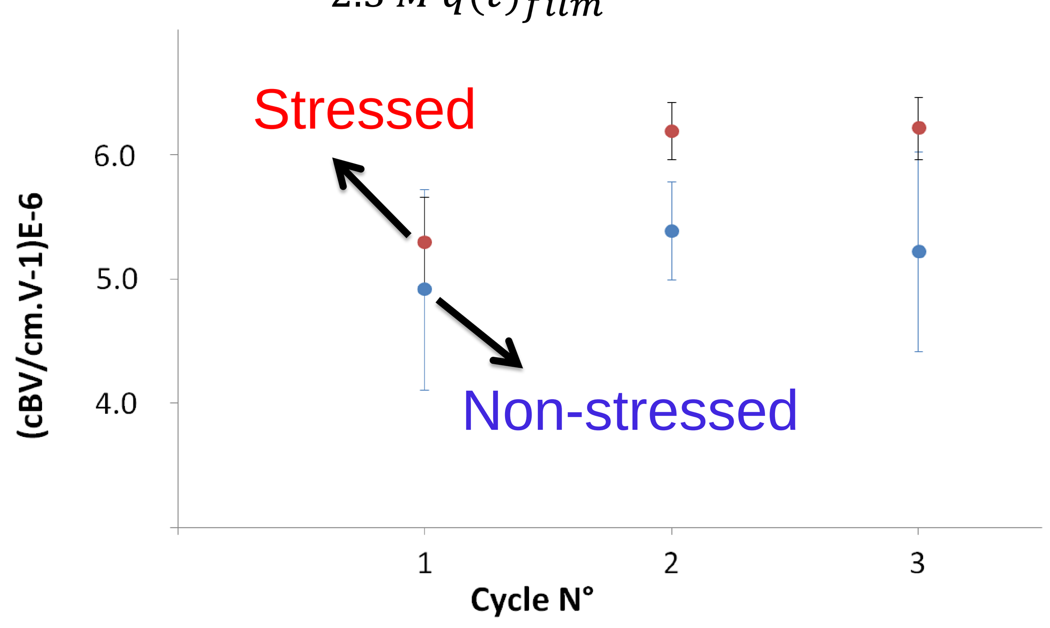

Fig.7: cBV values indicate less protective passive film built over stressed samples than that for non-stressed ones.

References:
[1] J.C. Scully, Corrosion Science, 15 (1975): p 207.
[2] P.I. Marshall, G.T. Burstein, Corrosion Science, 24 (1984): p. 463.
[3] K. Ogle, M. Mokaddem, P. Volovitch. Electrochimica Acta, 55 (2010): p. 916.
[4] N. Cabrera, N.F. Mott, Rep. Prog. Phys. 12 (1948): p. 163

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