

# 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).

**KEYWORDS:** STRESS CORROSION CRACKING; SLIP ANODIC DISSOLUTION MECHANISM, CRACK GROWTH RATE.

## 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  $t_f$ .

**Luciano Lazzari**

Cescor srl

# Corrosion

The relationship obtained is the following:

$$\overline{CGR} \cong i_a \cdot \frac{t_0^m}{1-m} \cdot \left(\frac{\dot{\epsilon}}{\epsilon_f}\right)^m \quad [1]$$

where  $\overline{CGR}$  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;  $\epsilon_f$  and  $\dot{\epsilon}$  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:

$$CPR = \frac{D_s}{L} \left[ e^{\frac{\sigma a^3}{kT}} - 1 \right] \quad [2]$$

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:

$$\overline{CGR}_{SCC-AD} \cong \overline{CGR}_{CORR} + \overline{CGR}_{MECH} \quad [3]$$

where  $\overline{CGR}_{CORR}$  is a term for electrochemical dissolution and  $\overline{CGR}_{MECH}$  for the mechanical process. Fig. 1 depicts schemati-

cally the two contributions.

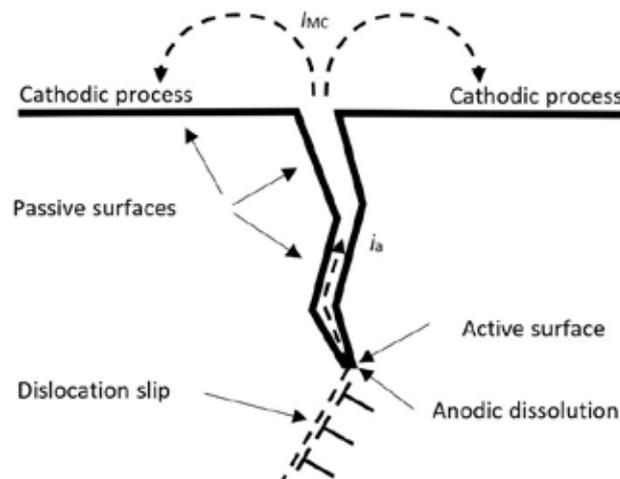


Fig. 1 - Schematic representation of the slip-anodic dissolution mechanism for SCC

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:

$$\overline{CGR}_{CORR} \cong 0.5 \cdot i_a \sqrt{t_0} \sqrt{\frac{\sigma - \sigma_{TH}}{\sigma_y}} \quad [4]$$

where the ratio  $\frac{\epsilon}{\epsilon_f}$  for the film is assumed equivalent to  $\frac{\sigma - \sigma_{TH}}{\sigma_y}$ , where  $\sigma_y$  is yield strength of the metal and  $\sigma_{TH}$  is a tensile stress threshold for the rupture of the passive film, which can be approximated to the SCC threshold strength of the metal (often taken as zero);  $\sigma$  is applied stress. Andresen-

Ford model does not explicit the anodic current density,  $i_a$ , as claimed complex. In this new model, the anodic current density,  $i_a$ , is assumed to be calculated by the so-called macrocell model described elsewhere [9, 10]. Accordingly, equation (4) becomes:

$$\overline{CGR}_{CORR} \cong \frac{z_0}{k_{CORR}} \cdot \sqrt{\frac{i_c \Delta V}{\rho}} \cdot \sqrt{\frac{\sigma - \sigma_{TH}}{\sigma_y}} \quad [5]$$

where  $k_{CORR}$  is an experimental constant depending on the metal;  $\Delta V$  (V) is driving voltage of the established macrocell;  $\rho$  ( $\Omega m$ ) is resistivity of the electrolyte (external the crack);  $i_c$  ( $A/m^2$ ) is cathodic current density on external surface taken as uniform and constant. It should be noted that all these

parameters are easily available. The second term of equation (3) based on Galvele's theory, can be rewritten by introducing the dependence of dislocation mobility from stress and temperature, based on work of Gilbert [11] and Dorn-Rajnak [12]:

$$\overline{CGR}_{MECH} \cong \sqrt{\frac{\sigma - \sigma_{TH}}{T + 273}} \cdot e^{1 - \frac{k_M \sigma_y}{T + 273}} \quad [6]$$

$k_M$  ( $K \cdot MPa^{-1}$ ) depends on metal, specifically on ease of dislocation slip. On this concern, dislocation slip is much easier in face centred cubic (FCC) metals than body centred cubic (BCC) and hexagonal close packing (HCP), hence the fol-

lowing values were derived from comparison with experimental data: FCC:  $k_M = 1$  for Al, Cu;  $k_M = 3$  for Ni and austenitic stainless steel; BCC/HCP:  $k_M = 5$  for Cr, Fe, Mg and Zn. The final equation is:

$$\overline{CGR}_{SCC-AD} \cong \left[ \frac{z_0}{k_{CORR}} \cdot \sqrt{\frac{i_c \Delta V}{\rho}} \cdot \sqrt{\frac{\sigma - \sigma_{TH}}{\sigma_y}} \right] + \left[ \sqrt{\frac{\sigma - \sigma_{TH}}{T + 273}} \cdot e^{1 - \frac{k_M \sigma_y}{T + 273}} \right] \quad [7]$$

As far as  $k_{CORR}$  is concerned, it is related to the intrinsic resistance to the metal dissolution. Good fit was obtained by inputting the following values:  $k_{CORR} = 1$  for Fe, Al, Cu;  $k_{CORR} = 10^{0.1(Y-18)}$  for chromium containing alloys, as stainless steels and nickel alloys.  $Y = \%Cr$  for nickel alloys;  $Y = PREN$  (Pitting Resistance Equivalent Number,  $PREN = \%Cr + 3.3\%Mo$ ) for

stainless steels. Equation (7) applies for electrolyte resistivity,  $\rho$ , in the range 1 - 1000  $\Omega m$ ; Tab. 1 reports cathodic current density,  $i_c$  taking place on external surface and the driving voltage of the macrocell,  $\Delta V$ . Other symbols are known.

**Tab. 1** - Electrochemical parameters used for the model input

	Hydrogen evolution	Oxygen reduction	Chlorine reduction	Nitrate/nitrite reduction
$i_c$ ( $mA/m^2$ )	$i_{c,H} \cong i_{0,H} \cdot 10^{\frac{\Psi_{c,H} T + 273}{0.12 \cdot 273}}$	$i_{c,O_2} \cong i_t \cong 10 \cdot 2^{\frac{T-25}{25}} \cdot [O_2] \cdot (1 + \sqrt{v})$		$\geq 1 A/m^2$
$\Psi_{c,H}$ (V)	0.05 - 0.15 V (mild steel and copper) 0.7 - 1.0 V (aluminium)			
$\Delta V \cong E_C - E_{eq,M}$ (V)	$\leq 0.1$ $\approx 0.5$ in $CO_3^{2-}/HCO_3^-$	0.1 - 0.5	$\approx 1$	$\approx 1.5$

## 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 interested 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  $MgCl_2$  solutions and solutions with temperature exceeding the threshold of  $50^\circ C$ , 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.

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

BCC ( $k_M=5$ )	Metal related data			Cathodic process data					Macrocell related data		
	T	$\sigma_y$	$\Delta\sigma$	$\Psi_{C,H}$	$i_{0,H}$	$i_{C,H}(i_{NO3})$	[O <sub>2</sub> ]	$i_{C,O_2}$	$\rho$	$\Delta V$	$i_{MC}$
	°C	MPa	MPa	V	A/m <sup>2</sup>	A/m <sup>2</sup>	ppm	A/m <sup>2</sup>	$\Omega m$	V	A/m <sup>2</sup>
CS+CO <sub>3</sub> <sup>2-</sup> /HCO <sub>3</sub> <sup>-</sup> (Lab)	77	450	500	0.1	0.001	0.137			1	0.5	1.5
CS+OH <sup>-</sup>	180	450	450	0.1	0.001	0.024			1	0.15	1.2
BCC ( $k_M=5$ )	SCC Crack Growth Rate (mm/y)				Experimental data	≈ % corr.	Ref.				
	$CGR_{CORR}$	$CGR_{MECH}$	$CGR_{SCC}$								
CS+CO <sub>3</sub> <sup>2-</sup> /HCO <sub>3</sub> <sup>-</sup> (Lab)	1.6	0.01	1.6	3-4	100	[14]					
CS+OH <sup>-</sup>	1.2	0.02	1.2	1-3	99	[10, 13]					

CS = carbon steel

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

FCC ( $k_M=1$ )	Metal related data			Cathodic process data					Macrocell related data		
	T	$\sigma_y$	$\Delta\sigma$	$\Delta E$	$i_{0,H}$	$i_{C,H}$	[O <sub>2</sub> ]	$i_{C,O_2}$	$\rho$	$\Delta V$	$i_{MC}$
	°C	MPa	MPa	V	A/m <sup>2</sup>	A/m <sup>2</sup>	ppm	A/m <sup>2</sup>	$\Omega m$	V	A/m <sup>2</sup>
Cu+NH <sub>3</sub> (no O <sub>2</sub> )	20	150	150	0.1	0.0001	0.0008			50	0.1	0.03
Al+NaCl (pH=9)	25	190	150	0.6	0.00001	2.9	5	0.05	1	1	34
FCC ( $k_M=1$ )	SCC Crack Growth Rate (mm/y)				Experimental data	≈ % corr.	Ref.				
	$CGR_{CORR}$	$CGR_{MECH}$	$CGR_{SCC}$								
Cu+NH <sub>3</sub> (no O <sub>2</sub> )	0.03	1	1	≈ 1	3	[10]					
Al+NaCl (pH=9)	30	0.8	31	> 2000	97	[15]					

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

FCC ( $k_M=3$ )	Metal related data			Cathodic process data					Macrocell related data		
	T	$\sigma_y$	$\Delta\sigma$	$\Delta E$	$i_{0,H}$	$i_{C,H}$	[O <sub>2</sub> ]	$i_{C,O_2}$	$\rho$	$\Delta V$	$i_{MC}$
	°C	MPa	MPa	V	A/m <sup>2</sup>	A/m <sup>2</sup>	ppm	A/m <sup>2</sup>	$\Omega m$	V	A/m <sup>2</sup>
SS+MgCl <sub>2</sub>	150	250	200	0.1	0.001	0.02			1	0.1	0.9
SS+Chlorides	60	250	200				1	0.03	1	0.5	2.3
Ni/H <sub>2</sub> O (PWR) (10 ppb)	320	350	120	0.1	0.001	0.1	0.01	0.36	1000	0.5	0.3
Ni/H <sub>2</sub> O (PWR) (10 ppm)	320	350	120	0.1	0.001	0.1	10	357	1000	0.5	8.4
FCC ( $k_M=3$ )	SCC Crack Growth Rate (mm/y)				Experimental data	≈ % corr.	Ref.				
	$CGR_{CORR}$	$CGR_{MECH}$	$CGR_{SCC}$								
SS+MgCl <sub>2</sub>	0.8	0.8	1.6	0.3-6	49	[4, 13]					
SS+Chlorides	2	0.8	2.8	2-5	72	[13]					
Ni+H <sub>2</sub> O PWR (10 ppb)	0.17	0.24	0.4	< 0.1	41	[6, 16]					
Ni+H <sub>2</sub> O PWR (10 ppm)	5	0.24	5	9	95	[16]					

SS = stainless steel

## 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.

## REFERENCES

- [1] E.H. Dix, "Acceleration of rate of corrosion by high constant stresses", *Trans. Am. Inst. Min. Metall. Eng.*, 137, 1940, p.11-40.
- [2] R.B.Mears, R.H.Brown, E.H. Dix Jr., "A generalized theory of stress corrosion cracking", Symposium on Stress-Corrosion Cracking of Metals, Am. Soc. Testing and Materials, Inst. Mining Engineers, 1944, pp. 329–323.
- [3] T.P. Hoar, J.M. West, "Mechano-chemical anodic dissolution of austenitic stainless steel in hot chloride solution", Proceedings of the Royal Society of London A268, 1962, p. 304–315.
- [4] R.N. Parkins, "Mechanism of stress corrosion cracking", in *Corrosion*, ed L.L. Shreir, 2nd ed., London, Newnes-Butterworths, 1976
- [5] R.W. Staehle, "Current understanding of film rupture model of stress corrosion cracking", *Corrosion* 28, (1972): p 470-471.
- [6] P. L. Andresen, F. P. Ford, "Life prediction by mechanistic modeling and system monitoring of environmental cracking of iron and nickel alloys in aqueous systems", *Materials Science and Engineering*, A103, (1988): p. 167–184.
- [7] J R. Galvele, "A stress corrosion cracking mechanism based on surface mobility", *Corrosion Science*, 27, (1987): p. 1–33
- [8] J. R. Galvele, "Surface mobility mechanism of stress-corrosion cracking", *Corrosion Science*, 35, (1993): p. 419–434.
- [9] L. Lazzari, *Engineering Tools for Corrosion. Design and Diagnosis*, EFC Series n.68, WoodHead Publishing, 2017
- [10] P. Pedferri, *Corrosion science and engineering*, Springer, Engineering Materials, 2018 (ISBN 978-3-319-97624-2), p.730.
- [11] M. R. Gilbert, S. Queyreau, J. Marian, "Stress and temperature dependence of screw dislocation mobility in  $\alpha$ -Fe by molecular dynamics", *Physical Review*, B 84, 174103 (2011)
- [12] J. E. Dorn, S. Rajnak, "Nucleation of kink pairs and the Peierls mech. of plastic deform.", *Trans. AIME* 230, (1964), p. 1052 – 1064.
- [13] D. Sinigaglia, G. Re, P. Pedferri, *Cedimento per fatica ambientale dei materiali metallici*, Ed CLUP, Milan, Italy, 1979 (in Italian)
- [14] C. Brossia, C. Scott, J. Beavers, G. Edgemon, G. Frankel, H. Berman, and K. Boomer, "Stress Corrosion Cracking Carbon Steel in Nitrate and Carbonate Wastes at Hanford", Corrosion Nace Conference 2008, Paper N. 08599 (Houston, TX: NACE, 2008), p. 14.
- [15] J. Gao, D. J. Quesnel, "Stress corrosion cracking of sensitized AA5083 in NaCl Solution", Corrosion Nace Conference 2011, Paper N. 11284 (Houston, TX: NACE, 2011), p. 14.
- [16] FP Ford, MJ Povich, "The effect of oxygen/temperature combinations on the stress-corrosion susceptibility of sensitized 304 stainless steel in high purity water", Corrosion Nace Conference 1979, Paper N. 94 (Houston, TX: NACE, 1979), p. 14.