

PROPOSITION OF THEORETICAL IMPROVEMENT ON MODELS OF PRIMARY WATER STRESS CORROSION CRACKING¹

Omar Fernandes Aly²
Miguel Mattar Neto³

Abstract

One proposes a theoretical improvement of two existing models for initiation on primary water stress corrosion cracking of Nickel Alloys in nuclear pressure water reactors. These models are the semi-empiric-probabilistic and the slip dissolution/ film rupture. The first includes an equation rated with stress and with thermal-activation. Some authors were showed that the initiation depends mainly on strain or strain rate rather than stress: one departs from Ramberg - Osgood equation and from relationships between stress and strain for Nickel Alloy 600 obtained from slow strain rate tests and constant load tests by Boursier et al., to propose an improvement suggestion which shall be validated. The second one was first formulated by Ford and Andresen and developed by GE laboratories for austenitic stainless steel. One departs from the oxidation film rupture activated by sliding bands and dislocations and which is enhanced through electrochemical Faraday law. It's a well accepted model, but was received critical appointments of authors like Gutman and Hall Jr.: one departs from the own's Gutman theory of mechanochemical interactions to propose a new mathematical equation for this model.

Key words: Nickel Alloys; Stress Corrosion Cracking Models; Slow Strain Rate Testing; Stress Corrosion.

¹Technical Contribution to the 65th International Congress of the ABM, July 26-30th 2010, Rio de Janeiro – RJ – Brazil.

²Doctor in Nuclear Technology-Materials , Post- Doctoring, CEN-IPEN, São Paulo University, Brazil (ofaly@ipen.br)

³Professor, Doctor in Structural Engineering , CEN-IPEN, São Paulo University, Brazil (mmattar@ipen.br)

PROPOSTA DE APERFEIÇOAMENTO TEÓRICO EM MODELOS DE CORROSÃO SOB TENSÃO EM ÁGUA PRIMÁRIA

Resumo

É proposto um aperfeiçoamento de dois modelos existentes para iniciação de trincas de corrosão sob tensão em água primária, de ligas de níquel para reatores nucleares de água pressurizada. Esses são o semi-empírico-probabilístico e o de deslizamento, dissolução e ruptura do filme passivo. O primeiro inclui uma equação em função da tensão e da ativação térmica. Alguns autores mostraram que a iniciação depende principalmente da deformação/ taxa de deformação ao invés da tensão: partiu-se da formulação de Ramberg - Osgood e das relações entre tensão e deformação para a liga 600 obtidas dos ensaios de taxa de deformação lenta e de carga constante de Boursier et al., para uma sugestão de aperfeiçoamento que deve ser validada. O segundo foi inicialmente formulado por Ford e Andresen e desenvolvido nos laboratórios da GE, para aço inoxidável austenítico. Nele se parte da ruptura do filme de óxido ativada por bandas de deslizamento e discordâncias, acelerada eletroquimicamente pela lei de Faraday. É um modelo bem aceito, mas foi criticado por autores como Gutman e Hall Jr.: parte-se da própria teoria de Gutman das interações mecanoquímicas para se propor uma nova equação matemática para esse modelo.

Palavras-chave: Corrosão Sob Tensão; Ensaios de Taxa de Deformação Lenta; Ligas de Níquel; Modelos de Corrosão Sob Tensão.

1 INTRODUCTION

Stress corrosion cracking initiation and propagation are very complex phenomena, one modality of environment assisting cracking besides corrosion fatigue and hydrogen embrittlement, depending on several parameters that can be classified in microstructural, mechanical and environmental. The microstructural ones are: (1) grain boundary microchemistry and segregation M; (2) thermal treatment TT which can causes intragranular and intergranular metallic carbide distribution; (3) grain size gs and cold work CW or plastic deformation: these two last ones fix another variable the yield stress σ_{ys} . Mechanical ones are: (4) residual stress σ_r ; (5) applied stress σ_a – the tensions referred and geometry can be summarized as stress intensity K_I ; (6) strain ϵ and strain rate $\dot{\epsilon}$. Environmental factors include: (7) temperature T; (8) activity of $[H]^+$ or pH; (9) solution or water chemistry, including inhibitors or pollutants in solution SC; (10) electrochemical potential V; (11) partial pressure of hydrogen p_{H_2} . This environmental cracking susceptibility can be expressed as equation (1)^[1].

$$SCC=f(M,TT,gs,CW,K_I,\epsilon, \dot{\epsilon},T,pH,SC,V,p_{H_2}) \quad (1)$$

So there are various models to mathematically express these phenomena: the semi-empiric-probabilistic developed by Staehle, Gorman et al.^[2], the slip dissolution / film rupture of Ford and Andresen^{[3],[4]}, the coupled environment fracture model of Macdonald and Urquidi-Macdonald, the internal oxidation mechanism of Scott and Le Calvar, the numerical model of Rebak and Smialowska, the enhanced surface mobility model of Galvele, and others^[1].

Two models, a semi-empiric–probabilistic one and the slip dissolution / film rupture of Ford and Andresen, are considered in this paper.

1.1. Semi- Empiric- Probabilistic Model

The semi-empiric-probabilistic model^[2] is derived from the deterministic dependencies of time-to-failure shown in equation (2) treated statistically by a Weibull distribution, as showed in equation (3).

$$t_f = A t_{ref} (\sigma / \sigma_{ref})^n \exp [(Q/R)(1/T-1/T_{ref})] \quad (2)$$

with: t_f = time to failure; σ = stress; n = exponent of stress; Q = thermal activation energy; T =absolute temperature; R =universal gas constant; A = non-dimensional material constant which reflects the effect of material properties on time to 1% PWSCC ($t_{1\%}$); t_{ref} = time to selected fraction of PWSCC for a reference case; σ_{ref} = reference value of stress; T_{ref} = reference value of temperature.

$$F = 1 - \exp [-0.0101(t/t_{1\%})^b] \tag{3}$$

with: F= fraction of population of components under consideration all susceptible to the same failure mode that experience PWSCC; t= time normally given in effective full power years (EFPY); b=Weibull slope, a fitted parameter determined by analysis of failure data; t_{1%}=Weibull characteristic time that corresponds to the time when 63.2% of the components have experienced PWSCC.

There are several applications of this model, which is a basic engineering model for immediate application, mainly in nuclear and petrochemical industries since at least the 1970's in USA. One of the main applications in nuclear power plants is the modeling of stress corrosion cracking in nuclear steam generators, like as showed in reference [3].

1.2. Slip Dissolution / Film Rupture Model

The slip dissolution / film rupture of Ford and Andresen model (FA)^[4] is according with Hall Jr., the result of more than 64 years of research, studied by Mears, Brown, and Dix Jr. since 1944^[5]. By this model, crack occurs due metallic corrosion preferentially along an active path as a grain boundary or crystal sleep plane, in an interactive process with the weakening of the metallic oxide film. The crack growth rate is postulated to be sustained by periodic strain-induced rupture of the film, and the required rupture strain provided by transient creep as depicted in Figure 1.

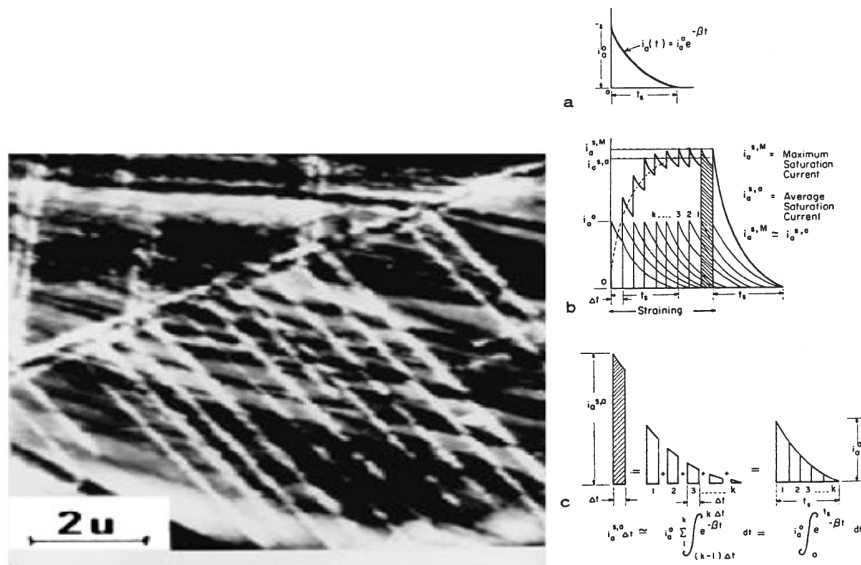


Figure 1. View of dissolution occurring preferentially at slip on metal surface as shown in a thin foil of a Fe-Cr-Ni alloy stressed while exposed to an environment and then viewed in a transmission electron microscope; at rights, the schematic view of sequential dissolution events as they contribute to an average current for advance of SCC^[3].

The FA model^[6] is mainly deterministic and based on electrochemical dissolution through the anodic current density in crack tip (by Faraday's law), during the film rupture period, according equations (4), (5), and (6).

$$\text{CPR} = \text{MQ}_f / \rho z F t_f = \text{M} I_{\text{av}} / \rho z F \quad (4)$$

$$Q_f = \int_0^{t_f} I_t dt = I_{\text{av}} t_f \quad (5)$$

$$t_f = \epsilon_f / \dot{\epsilon} \quad (6)$$

with: CPR= crack propagation rate; M=atomic weight; ρ =density; z=valency; F=Faraday constant; t_f =film rupture period; Q_f = oxidation charge density; I_t =anodic current density on the crack tip bare surface at moment t; I_{av} = average anodic current density on the crack tip bare surface during period t, which produces Q_f ; ϵ_f = required deformation for film rupture (about 10^{-3}), and $\dot{\epsilon}$ =crack tip strain rate, so that the crack advance can be maintained only if the film rupture is repetitive with the frequency $\nu=1/t_f$.

This model is also an engineering model developed by Ford and Andresen in the Corporate Research and Development Center of General Electric Company, mainly for nuclear steam supply of structural components fabricated from types 304 and 316L stainless steel, nickel alloys 600 and 182, low alloy steels A533B and A508, in the late 1980's in USA. This model also has used for a critical review of components life evaluation according ASME XI Code^[4]. Some application examples can be found in reference [4].

2 PROPOSITIONS AND RESULTS OF THEORETICAL IMPROVEMENT

2.1. Semi- Empiric- Probabilistic Model

The proposition includes only the deterministic part of this model. It's based on the assumption done by some authors^{[7],[8]}, which were showed that the stress corrosion cracking initiation depends mainly on strain or strain rate rather than stress. Shoji^[8] had established the relationship between stress and strain as showed in equation (7).

$$\begin{aligned} \epsilon &= \sigma/E \quad \text{for } \sigma \leq \sigma_y \\ \epsilon &= (\sigma/E) + c(\sigma - \sigma_y)^n \quad \text{for } \sigma > \sigma_y \end{aligned} \quad (7)$$

The equation (7) is named as Gao et al. relationship, a variation of Ramberg-Osgood's, and Shoji has transformed it in an expression to crack tip strain as equation (8).

$$\epsilon_{ct} = \beta(\sigma_y / E) \{ \ln[(\lambda/r)(K/\sigma_y)^2] \}^{n/(n-1)} \quad (8)$$

with: r =crack tip depth; λ, β = adimensional constants.

One departs from equation (9), a variation of equation (2), considering (7), and failure time equal initiation time.

$$\begin{aligned} t_i &= A' \epsilon(\sigma)^m \exp(Q/RT) \\ \epsilon(\sigma) &= \sigma/E + c(\sigma - \sigma_y)^n \end{aligned} \quad (9)$$

For $\epsilon(\sigma)$ can be used also the Ramberg-Osgood relationship^[9] as equation (10).

$$\epsilon = \sigma/E + (\alpha\sigma/E)(\sigma/\sigma_0)^n \quad (10)$$

with: $\sigma_0 = \sigma_y$, α = material's constant determined from the strain deviation of 0,2% = $\alpha\sigma_y/E$.

Shall be also considered the following relationships (11) to (13) from Boursier et al.^[7] obtained from slow strain rate tests (SSRT or CERT, constant extension rate test) and constant load (CL) tests, applied to Alloy 600.

(a) Between creep strain rate on SSRT/CL for the stress level 600-650 MPa and $T=360^\circ\text{C}$, according equation (11).

$$\dot{\epsilon}_{\text{creep}} = K\sigma^{2.76} t^{-0.5} \quad (11)$$

(b) Primary water stress corrosion cracking (PWSCC) crack tip creep at apparent strain rate in CL tests and SSRT respectively, according equations (12) and (13).

$$\dot{\epsilon}_{ct} = A \dot{\epsilon}_{\text{creep}} + B\dot{a}/x^* \quad (12)$$

$$\dot{\epsilon}_{ct} = C \dot{\epsilon}_{\text{app}} + D\dot{a}/x^* \quad (13)$$

with: $\dot{\epsilon}_{ct}$ = crack tip strain rate; $\dot{\epsilon}_{\text{creep}}$ = creep rate; $\dot{\epsilon}_{\text{app}}$ = macroscopic strain rate; \dot{a} = crack velocity; x^* = calibration length.

One supposes for initiation $\dot{a} \approx 0$, and it follows that the relationship between apparent and crack tip creep is mediated only by a constant, according the authors and validated through experiments: this constant is about 3^[7].

So, the relationship (11) considering (13) takes the form (14), with constants rating $K_1 \approx A/3 K$, and $\dot{\epsilon}_{\text{CERT/SSRT}} = \dot{\epsilon}_{\text{app}}$.

$$\dot{\epsilon}_{\text{CERT/SSRT}} = K_1 \sigma^{2.76} t^{-0.5} \quad (14)$$

From (14), it can be separate $\sigma = \sigma(\dot{\epsilon}_{\text{CERT/SSRT}})$, according equations (15a) to (15c).

$$\sigma^{2.76} = 1/K_1 \dot{\epsilon}_{\text{CERT/SSRT}} t^{0.5} \quad (15a)$$

$$\sigma = (K_1)^{-1/2.76} \dot{\epsilon}_{\text{CERT/SSRT}}^{1/2.76} t^{0.5/2.76} \quad (15b)$$

$$\sigma = K_2 \dot{\epsilon}_{\text{CERT/SSRT}}^{0.362} t^{0.181} \quad (15c)$$

Entering in equation (16), a variation of equation (2) combined with equation (9), with $\sigma = \sigma(\dot{\epsilon}_{\text{CERT/SSRT}})$, results the equation (17).

$$t_i = A' \sigma^n \exp(Q/RT) \quad (16)$$

$$t_i = A' K_2^n \dot{\epsilon}_{\text{CERT/SSRT}}^{0.362n} t^{0.181n} \exp(Q/RT) \quad (17)$$

When one uses a n-proper value for alloy 600 MA, like from Shah et al.^[10] considering CRDM nozzles exposed to PWSCC: $n = -4$, results equation (18), with a constant $A'' = A' \cdot K_2^n$.

$$t_i = A'' \dot{\epsilon}_{\text{CERT/SSRT}}^{-1.45} t^{-0.72} \exp(Q/RT) \quad (18)$$

When $t = t_i$ results the equation (18a).

$$t_i^{1.72} = A'' \dot{\epsilon}_{\text{CERT/SSRT}}^{-1.45} \exp(Q/RT) \quad (18a)$$

or, with $A''' = (A'')^{1/1.72}$ and being $-1.45/1.72 = -0.84$, results equation (18b).

$$t_i = A''' \dot{\epsilon}_{\text{CERT/SSRT}}^{-0.84} \exp(Q/1.72 RT) \quad (18b)$$

For a strain rate $\dot{\epsilon}_{\text{CERT/SSRT}} = \text{constant}$, equation (18b) assumes the form (19), according the new-proposed model, $A^{iv} = \text{constant}$.

$t_i = A^{iv} \exp(Q/1.72 RT) \quad (19)$

The interpretation of this model is that with SSRT/CL tests, the initiation time is constant for a parameter assembling (applied strain rate, material, thermo-mechanical treatment), being only environment-dependent (temperature and thermal activation energy), according Arrhenius law affected with constant 1/1.72.

2.2. Slip Dissolution / Film Rupture Model

This model had received critical analysis of some researchers, including Gutman ^[6], and Hall Jr. ^[5]. The main are: (a) the model mechanism is not perfectly distinguished in all stages; (b) the slip bands action is not included in the model; (c) a doubt if the part of anodic current (another part is to form soluble corrosion products) is enough to enhance the crack growth; (d) how the oxidation charge density (Q_f in equations (4) and (5)) is related to actual processes in the crack tip; (e) what the actual extension of the time interval between film rupture events (t_f in equation (4) to (6)); (f) crack tip current density as time function does not includes any dependence on the crack tip strain rate; (g) it has been experimentally proved that the current transients do not decay logarithmically with equation normally used as crack tip current density as time function, on model; (h) the use of an integral rather than differential rate equation to describe the crack tip current density as time function.

The critic point (b) concerning the slip bands action can be viewed as a mechanic contribution to the crack growth rate further the electrochemical process: the contribution of this paper is the suggestion that this mechanical contribution can be described also by equations in Gutman and Ke ^[11] presentation accessible on line, according following issues.

The key issue is contained in this presentation, when are distinguished two kinds of different activities: the electrochemical activity of metal ion in electrolyte and mechanochemical activity of atoms in solid metal which are respectively expressed by equations (20) and (21).

$$\tilde{a}_c = a_{ox} \exp (-\beta z F \phi / RT) \quad (20)$$

$$\tilde{a}_a = a_{red} \exp (n \Delta \tau / \alpha^* R' T + z F \phi / RT) \quad (21)$$

with: a_{red} and a_{ox} are ordinary activities of the species in reduced and oxidized forms, respectively; ϕ is the electrode potential; z is a valency; F is Faraday number; R is the gas constant; T is the temperature; R' is a special constant ($R' = k N_{max}$, where k is the Boltzmann constant and N_{max} is the maximum possible dislocation density); α^* is the coefficient of proportionality in the linear dependence of dislocation density on plastic strain; $\Delta \tau$ is the mechanical stress increase due to strain hardening; n is the number of dislocations in the pile-up.

So, equation (4) can be improved as to include a mechanic contribution to the crack growth which had enhanced by electrochemistry: it can be seen at the first member of

the sum in brackets in equation (21), corresponding to a formulation of an enhanced slip dissolution/film rupture model.

The equation (21) can be written as equations (22) or (23).

$$\ln (\tilde{a}_a / a_{red}) = (n\Delta\tau/\alpha^*R'T + zF\phi/RT) \quad (22)$$

$$zF\phi/RT = \ln (\tilde{a}_a / a_{red}) - (n\Delta\tau/\alpha^*R'T) \quad (23)$$

So, equation (4) can be written as equation (24).

$$CPR = [(\phi M/RT)/(\rho zF\phi/RT)] I_{av} \quad (24)$$

Replacing equation (23) in (24), results a final expression for an enhanced model according equation (25).

$$CPR = \{ (\phi M/RT)/\rho [\ln (\tilde{a}_a / a_{red}) - (n\Delta\tau/\alpha^*R'T)] \} I_{av} \quad (25)$$

3 DISCUSSION

The semi-empiric probabilistic model improvement (equation (19)) has been proposed considering SSRT/CERT developed at CDTN-Nuclear Technology Development Center located in Belo Horizonte-MG, Brazil, which is not a kind of test specifically for initiation time of PWSCC, but can furnish experiments which can be used with some bias approaches with the use of statistical distributions. Boursier et al.^[7] have developed a consistent methodology for SSRT and CL tests for Alloy 600: this improvement is based on this reference, and in the fact that the PWSCC is mainly directed by strain rather than stress.

It was been done a preliminary testing with the modified model, using SSRT data for alloy 600 at 303°C, modeling these to 360°C with equation (19), and comparing with literature data at 360°C: the modeling data was about plus 50% of the actual initiation time; but using original model (equation (16)), the difference between the modeling and the actual data, considering the temperature variation, was of plus 90%^[12] (this original model seems very conservative); so, it had an improvement, but there are many issues which yet shall be checked, such as PWSCC of Nickel Alloys scattering, differences on compared tests methodologies and materials. Also it has been done until now few tests to compare, and to do proper statistical approaches.

4 CONCLUSIONS

One has proposed a theoretical improvement of two important models for initiation on primary water stress corrosion cracking of Nickel Alloys in nuclear pressure water reactors: the purpose is to improve prediction capability of these models. Concerning the semi-empirical-probabilistic model this proposal follows that the initiation depends mainly on strain or strain rate rather than stress: a preliminary model test showed better adjustment to real data, but yet shall be improved. Concerning the slip dissolution/rupture film model, this is pure theoretical improvement proposal which could be proper transformed in algorithm, and/or together with another remarks included in references [5] and [6].

REFERENCES

- 1 ALY, O.F., ANDRADE, A., MATTAR NETO, M., SZAJNBOK, M., TOTH, H.J. Modelling of Primary Water Stress Corrosion Cracking (PWSCC) at Control Rod Drive Mechanism (CRDM) Nozzles of Pressurized Water Reactors (PWR), In.: Shipilov, S.A.; Jones, R.H.;Olive, J.-M.; Rebak, R.B. (Eds.) "EICM-2 - Second International Conference on Environment-Induced Cracking of Metals, The Banff Centre, Banff, Alberta, Canada, September 19-23, 2004, Proceedings Elsevier: London, 1st Ed., 2008, V.2, p.143-151.
- 2 GORMAN, J.A., STAVROPOULOS, K. D., ZEMITIS, W.S., DUDLEY, M. E., PWSCC Prediction Guidelines, EPRI Final Report TR-104030 Project 2812-15, Palo Alto, July 1994.
- 3 STAEHLE, R.W. Major Technical Advances from the Work of Staehle and Collaborators, Roger W. Staehle Consulting: North Oaks, Minnesota, 2000, access: <http://www.staehleconsulting.com/pdf/staehletechadv.pdf>
- 4 ANDRESEN, P.L.; FORD, F.P. Life Prediction by Mechanistic Modeling and System Monitoring of Environmental Cracking of Iron and Nickel alloys in aqueous Systems. **Materials Sci. and Eng.**, A 103, p. 167-184, 1988.
- 5 HALL JR., M. M. Film rupture model for aqueous stress corrosion cracking under constant and variable stress intensity factor **Corrosion Sci.** 2009, vol.51, p. 225-233.
- 6 GUTMAN, E. M. An inconsistency in "film rupture model" of stress corrosion cracking **Corrosion Sci.** 2007, vol.49, n°5, p. 2289-2302 [doi:10.1016/j.corsci.2006.10.023](https://doi.org/10.1016/j.corsci.2006.10.023)
- 7 BOURSIER, J-M., DESJARDINS, D., VAILLANT, F. The influence of strain-rate on the stress corrosion cracking of Alloy 600 in high temperature primary water. **Corrosion Sci.** v.37, n°3, p. 493-508, 1995.
- 8 SHOJI, T., LU, Z., XUE, H., YOSHIMOTO, K., ITOW, M., KUNIYA, J., WATANABE, K. Quantification of the effects of crack tip plasticity on environmentally-assisted crack growth rates in LWR environments, In.: In.: Shipilov, S.A.; Jones, R.H.;Olive, J.-M.;

Rebak, R.B. (Eds.) "EICM-2 - Second International Conference on Environment-Induced Cracking of Metals, The Banff Centre, Banff, Alberta, Canada, September 19-23, 2004, Proceedings Elsevier: London, 1st Ed., 2008, V.2, p. 107-122.

9 WIKIPEDIA, "Ramberg–Osgood relationship", access in October 2009, http://en.wikipedia.org/wiki/Ramberg%E2%80%93Osgood_relationship

10 SHAH, V.N., WARE, A. G., PORTER, A. M. ***Assessment of pressurized water reactor control rod drive mechanism nozzle cracking.*** Idaho Falls: Idaho National Engineering Laboratory, Oct.1994. (NUREG/CR-6245).

11 GUTMAN, E. M., KE, W., "Mechanochemical Interactions", presentation access in March 2009, <http://www.ustb.edu.cn/skl/upfile/document/mechanochemical.ppt>

12 ALY, O.F. Proposta Teórica de Aperfeiçoamento de Modelo Semi-Empírico-Probabilístico, IPEN: São Paulo, 2009, 11p. (Internal Report in Portuguese)