Model of corrosion fatigue of 13%Cr steel in passive state

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Abstract

The paper deals with a model of corrosion fatigue of stainless steel in the passive electrochemical conditions for more than one million load cycles characterized by two stages with different damage mechanisms. In the first stage - crack incubation - the growth of the micro-crack is controlled by a periodic anodic current at the crack tip, which is still in a passive state. The microcrack incubation phase is terminated after the first breakdown of the passive layer at the crack tip due to plastic deformation. In the second stage - crack initiation - the growth of the micro-crack is controlled by the kinetics of dissolution - repassivation event during repeated passive layer breakdowns at the crack tip, as well as the critical crack depth derived by fracture mechanics. The results of previously performed corrosion fatigue tests were used for successful verification of the model. The main contribution of this work is the development of a model of the damage mechanism in the incubation stage of corrosion fatigue life and its verification.

Abstrakt

Článek se zabývá modelem korozní únavy korozivzdorné oceli v pasivních elektrochemických podmínkách pro více než jeden milion zatěžovacích kmitů charakterizovaným dvěma etapami s různými mechanismy poškození. V první etapě, inkubaci trhliny, je růst mikrotrhliny řízen periodickým anodickým proudem na špici trhliny, která je stále v pasivním stavu. Etapa inkubace mikrotrhliny je ukončena po prvním průrazu pasivní vrstvy na špici trhliny v důsledku plastické deformace. Ve druhé fázi, iniciaci trhliny, je růst mikrotrhliny řízen kinetikou rozpouštění a repasivace během opakovaného prorážení pasivní vrstvy na špici trhliny a také kritickou hloubkou trhliny odvozenou lomovou mechanikou. K úspěšnému ověření modelu byly použity výsledky dříve provedených únavových zkoušek tyčí ve vodě. Hlavním přínosem této práce je vývoj modelu mechanismu poškození v inkubační fázi korozní únavy a jeho ověření.

Introduction

Stainless steels containing more than 13% Cr are usually used in corrosive environments with the steel surface in a passive electrochemical condition. The characteristic of a passive corrosion behaviour is the existence of a very thin oxide layer on the metal surface, which decreases the corrosion rate by five up to seven orders of magnitude compared to active dissolution. It is traditionally considered that an effective corrosion reaction is possible only if this passive layer is at least partially destroyed. In the case of corrosion fatigue, cyclic stress leads to repeated damages of the protective passive film [1], [2].

Müller assumed the corrosion fatigue crack initiation behaviour under passive corrosion is controlled by repassivation kinetics as well as by critical crack depth, derived using fracture mechanics [2]. Daeubler et al. [3] developed a model of corrosion fatigue crack initiation under passive electrochemical conditions. The model is based upon the existence of a stable passive layer on the metal surface which causes the metal not to be subjected to active dissolution except at slip step, when the metal is attacked by surrounding corrosion medium. Dissolution - repassivation process (event) is repetitively initiated and eventually penetrates along a slip step and into the metal matrix. For each dissolution - repassivation event, the penetration depth along a slip step equivalent to the amount of dissolved metal can be calculated, which is proportional to the area under the corrosion current decay curve. The damage in the incubation stage (before the 1st event) is not particularly elaborated, but it is being considered. The good agreement of the experiment with model's data is attained for cycle asymmetry $R = 0$, for number of cycles less than 10^6, approximately. El May at al. [4] proposed a model distinguishing the incubation and initiation phases of fatigue life in corrosive environments. The number of cycles of the termination of the incubation phase is determined by the breakthrough of the passive film when the slip band height threshold is reached. In the initial phase, the value of the current density at the crack tip is 3 orders of magnitude smaller than in the Müller model and the Murakami approach is used to terminate the crack.

The model assumptions based on the main role of plastic deformation of the metal (measured at the sample surface) in the rupture of the passive layer may be incorrect due to the extrapolation of the plastic behaviour in the crack tip namely in incubation stage.

Electrochemical measurements carried out during corrosion fatigue tests of stainless steels specimens in passive condition by Martin and Talbot [5] and Varner [6] show approximately harmonic current transients (altering current AC) that correlate with harmonic mechanical load. Martin and Talbot, traditionally, attributed the origin of the harmonic current to rupturing of passivation film by acting of persistent slip bands (PSB). Varner [7] has developed a cyclically strained double layer electric model showing compliance with the parameters of the measured harmonic current during corrosion fatigue test. The detected harmonic current is, thus, the response of the passivation layer to the cyclic strain.

Hagen [8] and Bergin [9] experimentally confirm the significant influence of alternating current on the corrosion weight loss of stainless steel. A fraction of the AC amplitude detected during corrosion fatigue tests has therefore Faraday nature.

Corrosion fatigue life is usually divided into three stages with different damage mechanisms:

- an incubation stage with a yet unpublished mechanism in the region of the number of cycles N > 106, which is terminated by penetration of the passivation layer by streak in the PSB,
- an initiation phase characterized by repeated dissolution - repassivation event at the tip of the corrosion-fatigue micro-crack, which are terminated by reaching a threshold value of the stress intensity factor amplitude
- and the stage of corrosion-fatigue crack growth controlled by stress intensity factor amplitude.

In this paper, we are particularly concerned with damage mechanism in the incubation stage of corrosion fatigue life. Damage during the initiation stage is considered using a modified Müller model.

Corrosion fatigue damage model

The model describes damage by deepening of the notch/micro-crack in the incubation and initiation stages of life. The deepening of the notch/micro-crack is caused by repeated loading of the stainless steel in neutral aqueous solution with the surface in an electrochemical passive state. Notch/micro-crack is defined by depth d, tip radius r and width $w = 2 \cdot r$. An aqueous solution with a maximum content of 585 mg/l NaCl is considered, where, according to AFM observations [10], corrosive pits form from micro-cracks. Pitting corrosion is not taken into account in the early stage of corrosion fatigue damage.

The model will be obtained for a number of loading cycles higher than $N > 10^6$ and for a set of loading cycle asymmetry values given by inequality $-1 \leq R$.

A. Incubation stage

Harmonic mechanical loading of a metal with a passive surface condition generates harmonic current density noise j_{AC} [5], [6] with amplitude current density j_a proportional to the amplitude of the mechanical stress S_a with coefficient k [7]:

$$j_a = k \cdot S_a. \tag{1}$$

It is assumed that small fraction of the generated alternating current has a Faraday nature and causes an increase in mass loss [8] and [9]. This fraction of current is given by the coefficient K_{FAC} <<1.

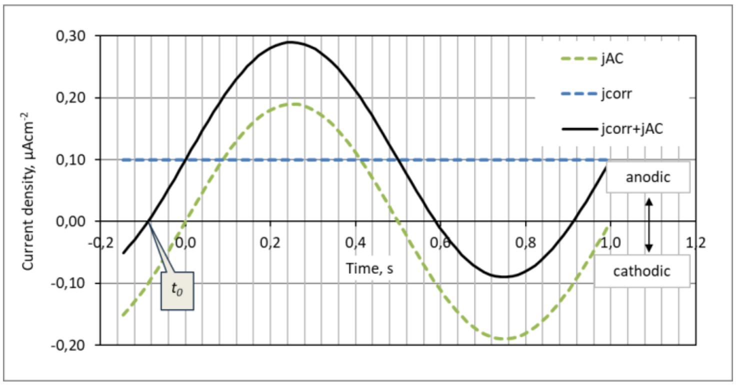

Fig. 1 Trace of j_{corr}, j_{AC}, j_{corr}+ j_{AC} and t_0

In the incubation phase, damage is assumed to be possible if the effective amplitude of the alternating current density in the initial notch is greater than the corrosion current density j_{corr}, see Fig. 1.

Strain concentration factor in steel is calculated by the formula

$$\alpha = 1 + 2 \cdot \sqrt{\frac{d}{r}}. \tag{2}$$

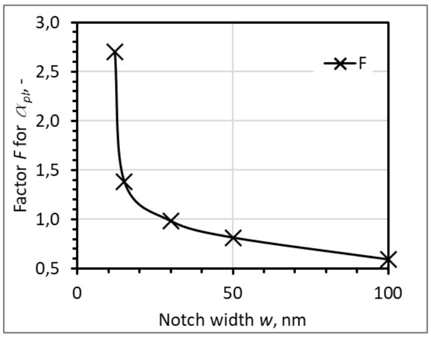

Fig. 2 Factor F, equation (3)

It is assumed that the amplitude of the current density is directly proportional to the average amplitude of the strain in the passive layer at the tip of the notch. Average strain passive layer in notch is determined by finite element method for plane strain condition using measured mechanical properties of the passive layer [11]. Finite element analysis of strain in the notch showed the suitability of calculating the coefficient of increase of the average strain in the passive layer at the tip of the notch according to the relation

$$\alpha_{pl} = 1 + F \cdot \sqrt{\frac{d}{r}}, \tag{3}$$

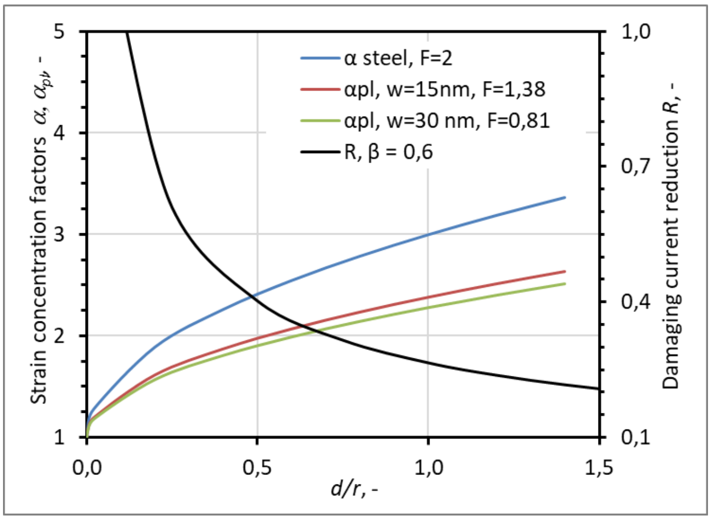

Fig. 3 Stress amplifying and reducing factor (3) and (4)

where F is coefficient dependent on the width w of the notch see Fig. 2. The dependence of strain concentration factor α and average strain concentration factor α_{pl} on the ratio of the notch depth and notch tip radius are plotted in Fig. 2.In the incubation phase of corrosion fatigue, the notch deepens by local dissolution of the metal at notch tip caused by alternating current generated by cyclic strain of the passive layer with current density amplitude $\alpha_{pl} \cdot j_a(S_a)$, see (1).

As the notch depth increases, the damaging current at the tip of the notch is reduced due to ohmic drop, concentration overvoltage in electrolyte between the notch mouth and the notch tip and potential drop across salt film [12] and [13]. Considered reduction of the damaging current is described by a power function

$$R = \frac{1}{A} \cdot \left(\frac{d}{r}\right)^{-\beta}, \tag{4}$$

where A is depended on initiated notch depth and $\beta > 0$ is exponent.
The function for $\beta = 0.6$ and $A = 3.75$ is shown in Fig. 3.

The increment of notch depth Δd_i during the i^{th} cycle is calculated by integral

$$\Delta d_i = \frac{M}{z \cdot F \cdot \rho} \cdot \int_{t_i}^{\frac{1}{2f} - t_i} [k \cdot K_{FAC} \cdot R_i \cdot \alpha_{pli} \cdot S_a \cdot \sin(2\pi \cdot f \cdot t) + j_{corr}]\, dt - d_0, \tag{5}$$

where $M = 56$ g·mol^{-1} is the molar mass of the metal, $z = 2$ eq·mol^{-1} is the amount of transferred charge, $F = 96\,500$ A·s·eq^{-1} is the Faraday constant, $\rho = 8$ g·cm^{-3} is the density of the metal, and $i = 1, 2, 3, \ldots, N_{incub}$ is indicated cycle in the incubation stage, f is the loading frequency and d_0 is the metal loss on smooth surface per cycle ie. for $R_i = \alpha_{pli} = 1$:

$$d_0 = \frac{M}{z \cdot F \cdot \rho} \cdot \int_{t_{0i}}^{\frac{1}{2f} - t_{0i}} [k \cdot K_{FAC} \cdot S_a \cdot \sin(2\pi \cdot f \cdot t) + j_{corr}]\, dt. \tag{6}$$

. The lower integration limits t_{0i}, t_i is determined from the conditions

$$K_{FAC} \cdot j_a \cdot \sin(2\pi \cdot f \cdot t_{0i}) + j_{corr} = 0, \tag{7}$$

$$K_{FAC} \cdot R_i \cdot \alpha_{pli} \cdot j_a \cdot \sin(2\pi \cdot f \cdot t_i) + j_{corr} = 0 \tag{7a}$$

by relations, see Fig. 1:

$$t_{0i} = -\frac{1}{2\pi \cdot f} \cdot \arcsin\left(\frac{j_{corr}}{K_{FAC} \cdot j_a}\right), \tag{8}$$

$$t_i = -\frac{1}{2\pi \cdot f} \cdot \arcsin\left(\frac{j_{corr}}{K_{FAC} \cdot R_i \cdot \alpha_{pli} \cdot j_a}\right). \tag{8a}$$

We consider the coefficients R_i and α_{pli} to be constant during the i^{th} cycle and then equation (5) can be rewritten in the form:

$$\boldsymbol{\Delta d_i = \frac{M}{z \cdot F \cdot \rho} \cdot \frac{\cdot k \cdot K_{FAC} \cdot R_i \cdot \alpha_{pli} \cdot S_a}{2 \cdot \pi \cdot f} \cdot \left[\cos(2\pi \cdot f \cdot t_i) - \cos(\pi - 2 \cdot \pi \cdot f \cdot t_i) + \left(\frac{1}{2 \cdot f} - 2t_i\right) \cdot j_{corr}\right] - d_0}. \tag{9}$$

The incubation phase is terminated by the first breakthrough of the passive layer at the bottom of the notch with a depth of d_c. This is conditioned by the formation of intrusion/extrusion streaks in the PSB with a height of 4 to 5 nm, which are comparable to the thickness of the passive film t_{pl}. Such high streaks are observed at a plastic strain of 0.004 [14]. The stress S_c corresponding to this value of plastic deformation is estimated from the cyclic strain curve determined at a stress cycle asymmetry $R = -1$ [15]. When loading with a different asymmetry of the stress cycle – mean of stress cycle $S_m > 0$ and S_m = const. – the incubation stage is terminated when the Bergmann parameter [16]

$$\boldsymbol{PSWTB = \sqrt{S_a \cdot (S_a + b \cdot S_m)}} \tag{10}$$

in the notch reaches the stress value S_c. The constants b, which depend on the asymmetry of the stress cycles R and the number of cycles N, are determined from experimental data [17].

Number of cycles N_{incub} in incubation stage of corrosion fatigue corresponding to the notch depth d_c is calculated by numerical integration of the notch depth increments Δd_i of equation (9). The integration is terminated when the *PSWTB* parameter in the notch reaches the stress value S_c.

B. Initiation stage

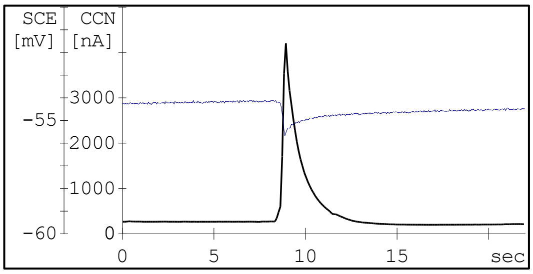

Fig. 4 Dissolution-repassivation event

In initiation stage corrosion fatigue the growth of the micro-crack is controlled by the kinetics of dissolution - repassivation during repeated passive layer breakdown at the micro-crack tip. The corrosion current noise (CNN – black line) during dissolution - repassivation event is shown in Fig. 3 [18]. The repassivated current density trace j_{RP} in time is described by an exponential law [2]:

$$j_{RP}(t) = j_{max} \cdot \exp\left(-\gamma \cdot t\right), \tag{11}$$

where j_{max} is maximum current density and γ is parametr of regression model.

The calculation of the number of N_{init} cycles in the initiation stage is performed in the first approximation according to the modified Müller model derived for passive corrosion conditions [2]:

$$N_{init} = (d_{th} - d_c) \cdot \frac{z \cdot F \cdot \rho}{M} \cdot \frac{\gamma}{0{,}5 \cdot j_{max}} \cdot \left[1 - exp\left(-\frac{\gamma}{f}\right)\right]^{-1}, \tag{12}$$

where d_{th} is the critical micro-crack depth derived from the threshold amplitude of the stress intensity factor $K_{ath}(d_{th})$ valid for small cracks [19]. According to the analysis of the results of corrosion current measurements in the initial phase [18], it is advisable to reduce the maximum current density considered in Muller's model by half, see the product $0.5 \cdot j_{max}$ in the denominator of equation (12).

The total lifetime N for a critical micro-crack depth d_{th} is given by the sum of the number of cycles in the incubation stage and the number of cycles in the initiation stage:

$$N = N_{incub} + N_{init}\,. \tag{13}$$

Model verification

The validation of the corrosion fatigue model is based on the comparison of the calculated corrosion fatigue curve (S_a versus N) for the threshold crack depth d_{th} and the corrosion fatigue curve of the supermartensitic steel X80-12 Cr 4.5 Ni 1.5 Mo determined by tests. Chemical composition and mechanical properties of the steel are in Tab 1 [20].

Tab. 1 Chemical composition and mechanical properties of the steel X80-12 Cr 4,5 Ni 1,5 Mo

C, %	Mn, %	Si, %	P, %	S, %	Cu, %	Ni, %	Cr, %	Mo, %	Al, %
0.014	1.030	0.380	0.024	0.003	0.250	4.730	11.650	1.420	0.001
$R_p0.2$, MPa		R_m, MPa]		A_{50}, %		*KV*-40°C, J		ferit, %	
681		893		35		150, 142, 140		0.5	

The push-pull corrosion fatigue test of smooth specimens with mean stress about 322 MPa was carried out at a loading frequency of 104 Hz in an aqueous solution of 0.01 mol NaCl with free air access at a temperature range of 18° to 22°C [6].

The parameters used in the modelling of corrosion-fatigue of the supermartensitic steel X80-12 Cr 4.5 Ni 1.5 Mo are given in Tab. 1

and Tab. 2.

Tab. 2 Parameters of the model in incubation stage

w	j_{corr}	k	K_{FAC}	F	β	S_c	b^*
[mm]	[A/cm^2]	[A/(MPa·cm^2)]	[-]	[-]		[MPa]	[-]
1.5E-05	1.05E-07	2.2E-07	0.005	1.38	0.71	740	1.35 to 1.43

b^* is sensitive to the number of cycles N and the asymmetry of the stress cycles.

Tab. 3 Parameters of the model in initiation stage

j_{max}	γ	K_{ath}**	d_{th}
[A/cm^2]	[-]	[MPa·m$^{0.5}$]	[mm]
8.0E-03	0.78	3.1	0.016 to 0.035

**K_{ath} is valid for long crack.

The ratio of 0.91 of the crack tip radius r and the initial crack depth d is considered for modelling the incubation stage of corrosion fatigue. The calculated and experimental results of the corrosion fatigue strength S_a in relation to the number of cycles N are shown in Fig. 4. The calculated curves of the respective incubation and initiation stages of corrosion fatigue are also plotted in the Fig. 4.

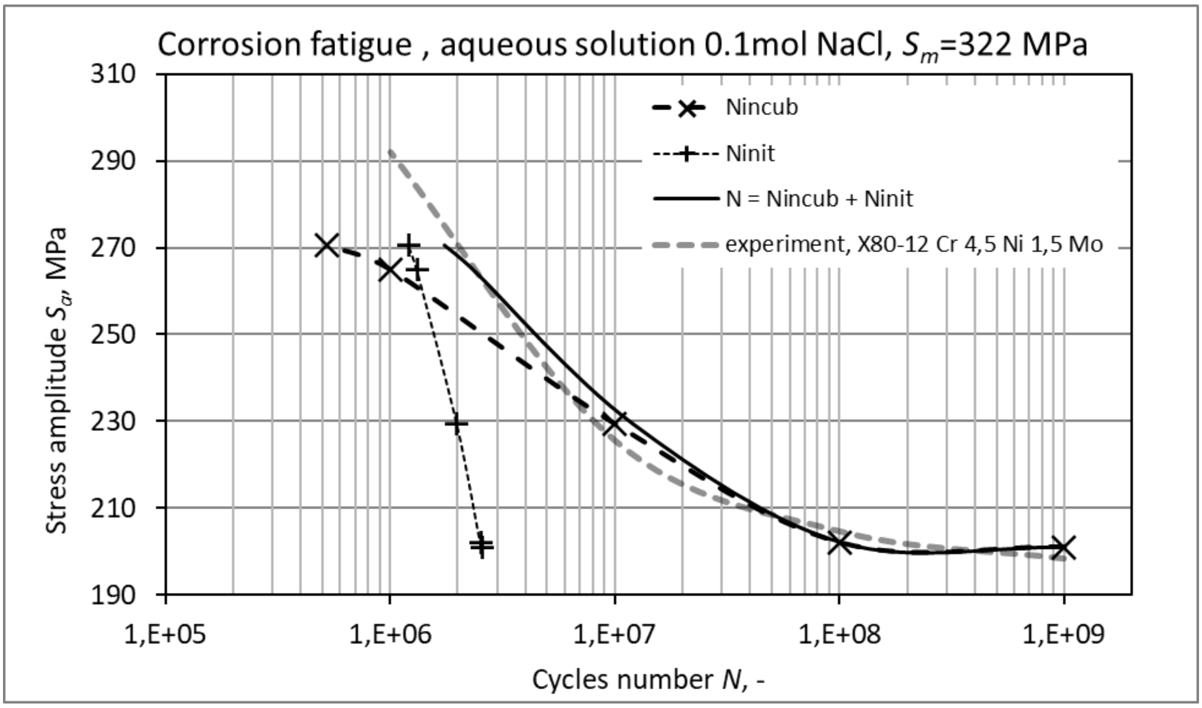

Fig. 5 Calculated and experimental corrosion fatigue curves of the steel X80-12 Cr 4.5 Ni 1.5 Mo

The incubation stage represents the majority of the corrosion fatigue life for number of load cycles greater than 1.4 million. The cycles number N_{int} of initiate stage is between 1.2 million and 2.5 million.

The maximum stress deviation between the modelled corrosion fatigue curve and the experimental curve is 3% and the standard deviation is about 4.1 MPa.

The calculated corrosion fatigue curve complies with the corrosion fatigue curve evaluated from experimental data.

Conclusion

A model of the damage mechanism in the incubation stage of corrosion fatigue of stainless steel under passive electrochemical conditions for more than one million load cycles is formulated and the relationships controlling the damage kinetics by notch deepening are derived. Faraday's law and the derived relations are used to calculate the increments of the notch depth per load cycle and to calculate the number of load cycles in the incubation stage.

The number of cycles of the initiation stage is calculated by the modified Müller's model.

Predicated corrosion fatigue curve is in good agreement with the corrosion fatigue curve evaluated from experimental data.

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