BEHAVIOUR OF DOUBLE LAYER OF CYCLIC STRAINED 13% Cr STEEL IN AQUEOUS SOLUTION

David Varner [a)] and Miroslav Varner [b)]

[a)] David Varner, Kotvrdovice, Czech Republic
[b)] Miroslav Varner, Litostroj Engineering a.s. Technická 3029, 61600 Brno, Czech Republic

Abstract

The paper deals with results of electrochemical measurement performed at harmonic cyclic stressed of the supermartensitic stainless steel in the 0,01Mol NaCl water solution environment. Application of dynamic load modified double layer polarization characteristics: the anodic current in the passive range increased and the breakdown and pitting range were extended to more negative values. The waveform of both current noise and potential noise was harmonic and the phase of current response was –9° approximately. Both current and potential noise are linear functions of stress amplitude. An electric model of the loaded double layer is submitted. The amplitude of the modelled current is proportional to the load frequency. The course of the model current and its amplitude dependence on the stress cycle amplitude are in good agreement with the experiment.

1. INTRODUCTION

The properties of double layer of stainless steel formed in aqueous solutions are studied using electrochemical measurements (EM) [1], [2] and [3]. The instrumentation of corrosion fatigue tests of stainless steels often includes electrochemical measurement equipment [4], [5], [6], [7], [8] and [9]. EM provide means to control the environmental parameters and obtain information about the nature and course of the damage.

EM results are known in the area of corrosion fatigue crack initiation during low-cycle and high-cycle fatigue. In the area of low-cycle fatigue, periodic fluctuations of the corrosion current were detected that correlate with the course of plastic deformation [4]. The fluctuations of the corrosion current are explained by repeated mechanical breakthrough of the passive layer. The breakthrough events are caused by extrusions and intrusions and feature initial depassivation and subsequent repassivation of the metal surface. The initiation of corrosion fatigue cracks during high-cycle fatigue is associated to aperiodic oscillations of the corrosion current, indicating an uneven accumulation of damage with breakthroughs of the passivation layer and subsequent repassivation of the metal surface [7]. In the incubation stage preceding the initiation stage of corrosion fatigue cracks, the current course is harmonic and correlated with mechanical loading [5] and [8]. In the area of passivity, or transpassivity, the phase shift of the current with respect to mechanical loading was practically zero, or with a value of $\pi/2$ [5]. Martin and Talbot [5] attributes the observed current flow to the development of persistent slip bands. However, the observed phase shifts indicate a direct connection with the electrical properties of the passivation layer [8].

In this paper, we present a model of a mechanically cyclic loaded double layer with static parameters obtained experimentally in the incubation stage of the corrosion fatigue life of supermartensitic steel. The dynamic parameters of the model were determined by simulating the actual current course.

2. MATERIALS AND EXPERIMENT METHODS

The cylinder-shaped test rods and auxiliary electrodes of the electrochemical noise were made of wrought weldable supermartensitic steel X80-12 Cr 4.5 Ni 1.5 Mo (SM) melted in an electric arc furnace and processed by the VOD (Vacuum Oxygen Decarburization) process [10]. The chemical composition and mechanical properties of the steel are given in Table 1.

Table 1: Chemical composition and mechanical properties of the steel used.

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]		ferrite [%]	
681		893		35		150, 142, 140		0.5	

The experiments were focused on the area of high-cycle corrosion fatigue with the number of cycles to fracture N > 10^6. The test rods were loaded with a resonant pulsator in push - pull with a mean value of S_m = 322 MPa and a frequency of f = 104 Hz in an aqueous solution of 0.01Mol NaCl with free access to air and at a temperature of 18 – 22°C. The surface of the smooth working part on the test rod (diameter of 0.8 cm and a length of 3 cm) and on the auxiliary electrodes made of the same steel (area 7.5cm^2) were ground underwater using a 400-grit sandpaper. The corrosion vessel was made of plexiglass and sealed with AK 22 sealant (made by HBM) that was electrochemically inert, waterproof and non-conductive. The non-working parts of the test rod and auxiliary electrodes were covered with the same sealant.

Measurement, recording and signal processing were carried out using the XEDO apparatus (made by DAKEL) and a computer. The signal sampling frequency was 1000 Hz. Measurement of polarization curves was carried out using a RADELKIS potentiostat with an EKOF compensator, a reference calomel electrode (SCE) and an auxiliary Pt electrode (area 0.5cm^2) with a scanning speed of 0.010 V/s.

The current noise generated on the surface of the test rod was measured on a 100 MΩ resistance instrumented between the test rod and the auxiliary SM electrode and at the same time, SCE potential was measured [8]. Measurement of potential noise with a converter with an input resistance of 100 MΩ was carried out with two noise sensor arrangements. 1SM variant – one SM electrode was placed in the corrosion vessel [8]. 2SM variant – two SM electrodes were placed in the corrosion chamber: the first one was short-circuited to the test rod and the second one was a potential noise sensor [8]. The force signal was adjusted in the control unit of the resonance machine by filtering which caused its phase shift. The test bars had been exposed in the corrosive environment for approximately 24 hours before the actual fatigue test started. Free corrosion conditions were controlled by measuring the test rod potential SCE.

3. RESULTS OF THE MEASUREMENTS

The polarization curves determined successively with the value of the stress amplitude S_a = 0 MPa and S_a = 55 MPa, and again S_a = 0 MPa are shown in Figure 1. Near the free corrosion potential, the polarization curves do not differ much. In the case of a non-zero value of the stress amplitude, an increase in the anodic current and a shift of the boundary of the pitting corrosion area to more negative potential values is noticeable in the passive region. The corrosion current density of the unloaded rod is J_{cor} = 0.105 µA/cm^2 (polarization resistance R_p=0.409 MΩcm^2) and when loaded with stress amplitude of 55 MPa, it reaches the value of 0.125 µA/cm^2.

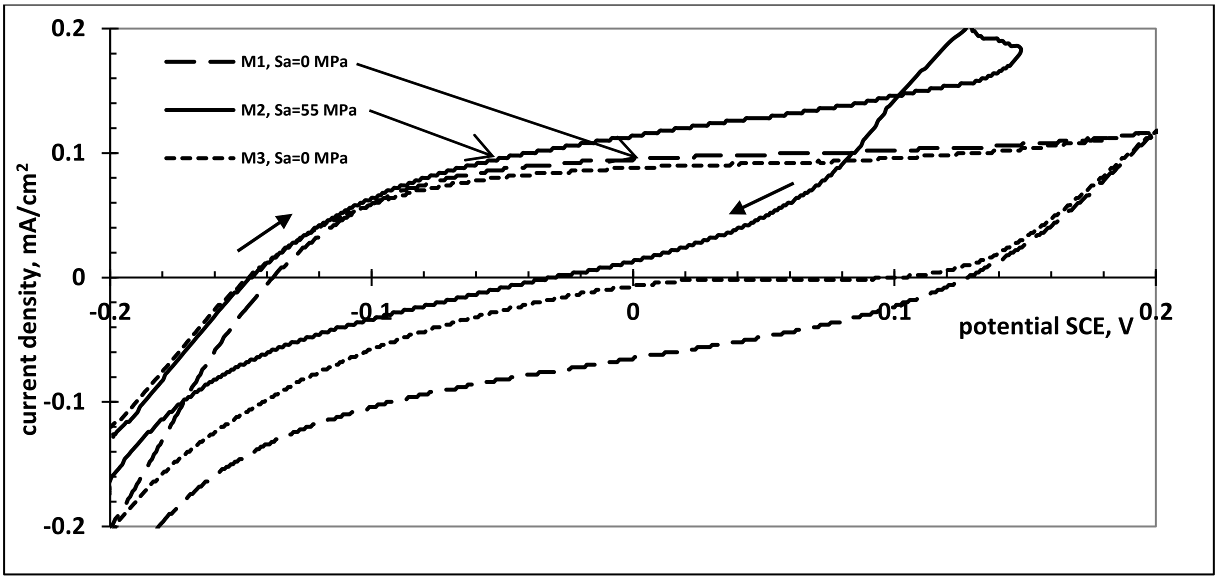

Figure 1. Polarization curves of the loaded rod

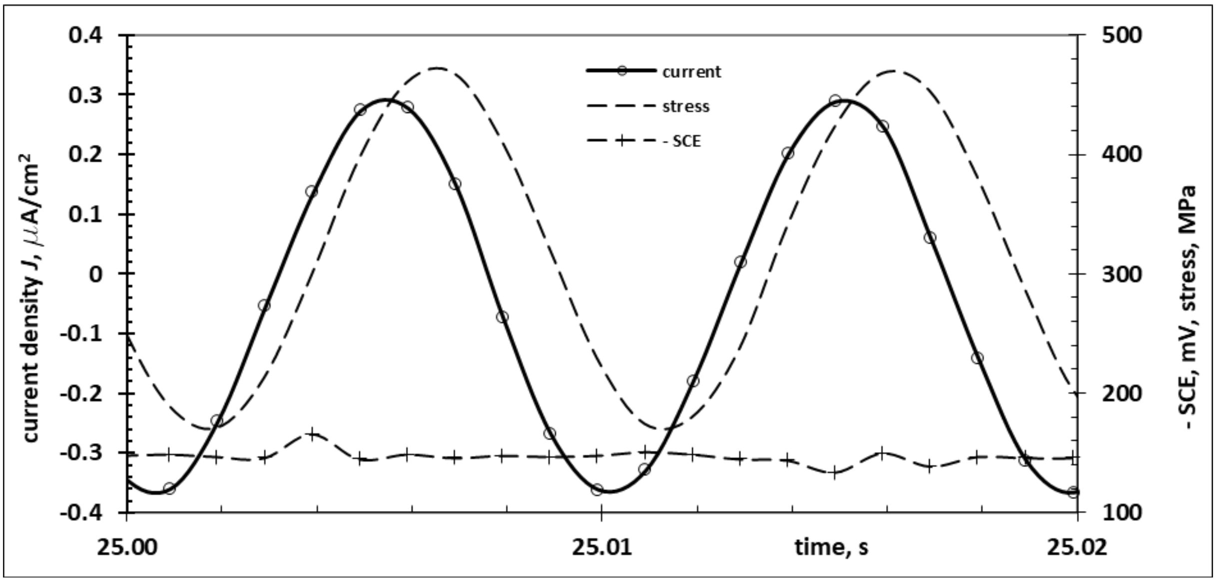

Figure 2. Time course of the current density

The time course of the current density noise, the *SCE* potential and the stress with the amplitude S_a = 150 MPa is shown in Figure 2. The current density and the stress are periodic functions of time and are closely correlated with each other. The course of the *SCE* potential has a random character with a symmetric non-Gaussian distribution. The standard deviation of the *SCE* potential of the unloaded rod is 1.34 mV and when loaded with a stress amplitude S_a = 150 MPa it equals 4.37 mV, i.e. it is 3.26 times greater. The amplitude of the current density is a linear function of the stress amplitude S_a as shown in Figure 3.

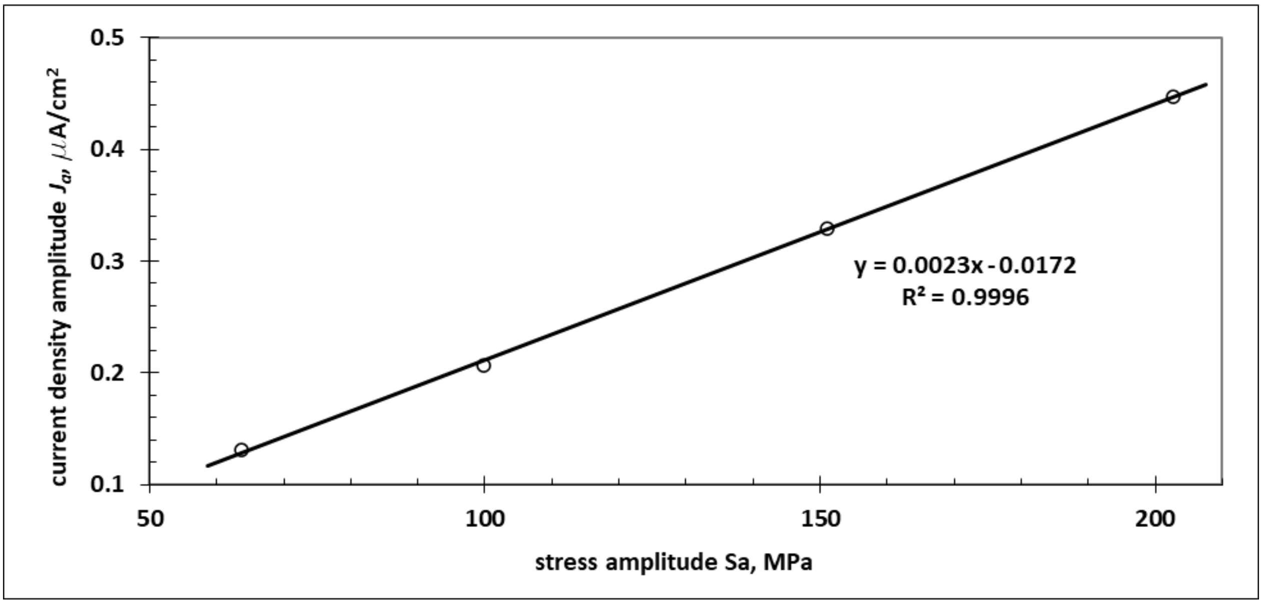

Figure 3. Dependence of current density amplitude on stress amplitude

The time course of potential noise (alternative to 2SM measurement) and stress with amplitude S_a = 207 MPa is shown in Figure 4. Potential noise is a periodic function of time and is closely correlated with mechanical stress.

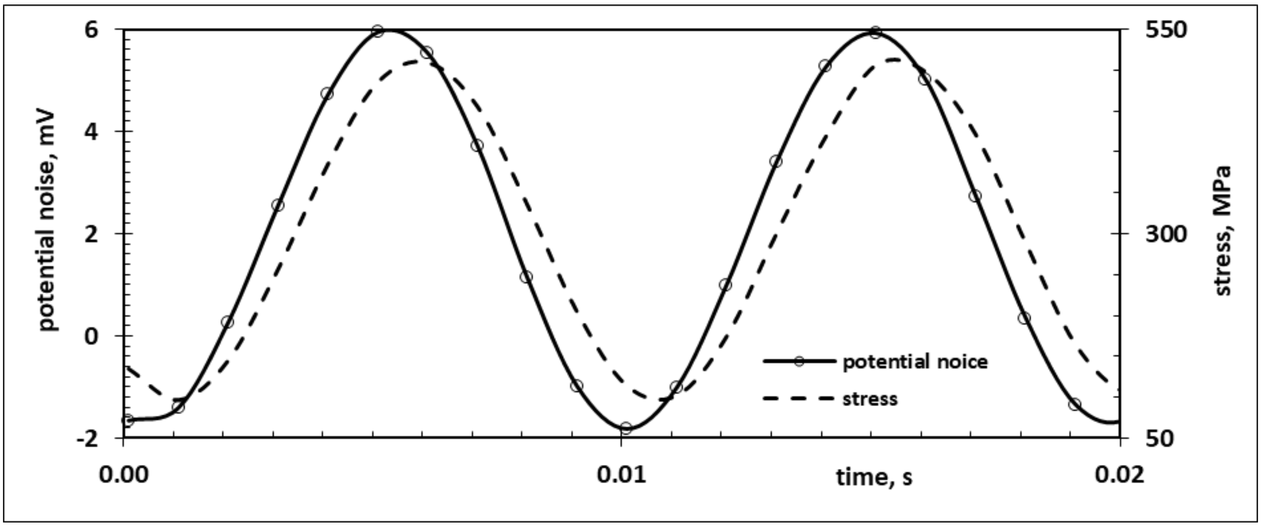

Figure 4. Time course of the potential noise

The amplitudes of potential noises for both electrode arrangement alternatives are a linear function of the stress amplitudes S_a as shown in Figure 5.

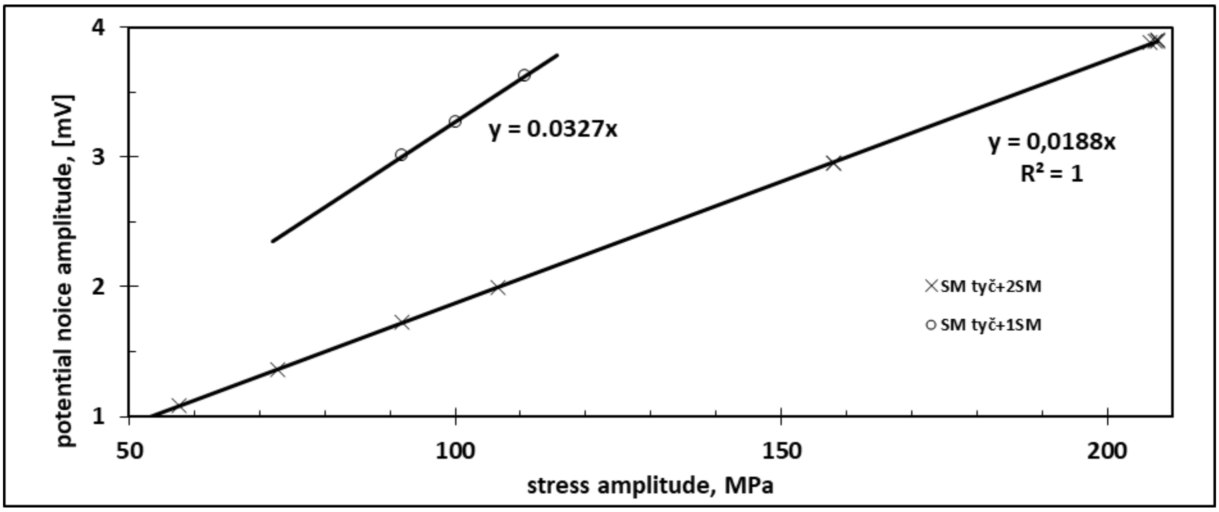

Figure 5. Dependence of potential noise amplitudes on stress amplitude

By comparing Figure 2 and Figure 4, the phase shift of the current and potential noise can be estimated to be minus 9º. This measured phase shift of the electrochemical noises at the mechanical loading frequency $f = 104$ Hz, measured polarization resistance $R_p = 0.409$ MΩcm^2 and the electrical impedance spectroscopy (EIS) relations valid for the Randels equivalent circuit allowed to calculate double layer capacitance $C_{dl} = 2.41$ μF/cm^2.

4. MODEL

The basis of the model of the passivation film covering a harmonically loaded sample is a current generator represented by an equivalent circuit with a parallel-connected variable capacitance and variable resistance, as shown in Figure 6. The sample a is loaded by a harmonic stress with amplitude S_a and frequency f, i.e. the stress waveform in time t is $S(t) = S_a\sin(2\pi ft)$.

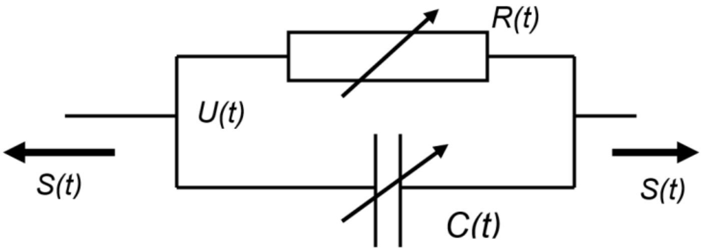

Figure 6. Model of strained double layer

The passivation layer is coupled to the surface of the loaded sample and is therefore subjected to deformation loading. The deformation loading of the passivation layer causes time changes in its resistance R, capacitance C and voltage U in the shape of harmonic functions. The changes in resistance, capacitance and voltage are then given by the following relations:

$$R(t) = R_p - R_a\sin(2\pi ft),$$

$$C(t) = C_{dl} + C_a\sin(2\pi ft),$$

$$U(t) = U_p + U_a\sin(2\pi ft),$$

where R_a is resistance amplitude, C_a is capacitance amplitude, U_m je mean value of voltage and U_a is voltage amplitude.

We consider the amplitudes of resistance R_a, capacitance C_a and voltage U_a as linear functions of the stress amplitude S_a:

$$R_a = k_R R_P S_a,\ C_a = k_C C_{dl} S_a,\ U_a = k_U U_p S_a,$$

where k_R, k_C, k_U are the coupling coefficients between the products of the amplitude of the stress amplitude S_a and the parameters of the unloaded passivation layer and the amplitudes of the parameters of the passivation layer loaded by stress amplitude with amplitude S_a.

The currents $I_R(t)$ or $I_C(t)$ flowing through the resistance $R(t)$ or capacitance $C(t)$ are given by the following relations:

$$I_R(t) = U(t)/R(t) \text{ or}$$

$$I_C(t) = (\mathrm{d}C(t)/\mathrm{d}t)\, U(t) + C(t)\, \mathrm{d}U(t)/\mathrm{d}t.$$

The total current generated by the equivalent circuit, given by the sum of the currents $I_R(t)$ and $I_C(t)$, can be expressed in the following form:

$$I(t) = U_p \cdot \{[2\pi f \cdot \cos(2\pi f t) \cdot C_{dl} \cdot S_a \cdot (k_C + k_U) + 0{,}5 \cdot 2\pi f \cdot \sin(4\pi f t) \cdot k_C \cdot k_U \cdot C_{dl} \cdot S_a{}^2] + [1 + \sin(2\pi f t) \cdot k_U \cdot S_a]/[R_p \cdot (1 - \sin(2\pi f t) \cdot k_R \cdot S_a)]\}.$$

The generated current course is a function of the polarization resistance R_p, the double layer capacitance C_{dl}, the voltage U_m, the mechanical load frequency f, the stress amplitude S_a and the coupling coefficients k_R, k_C *and* k_U.

The time course of the current density generated by the passivation film of a sample with a uniformly loaded area of 7.5 cm^2 of stress cycles with an amplitude S_a = 200MPa at a frequency of f = 104Hz and with measured parameters of the passivation layer of unloaded sample R_p = 0.409 MΩcm^2 and the double layer capacitance C_p = 2.41 μF/cm^2, the voltage U_m = 0.04 V determined by the 0.5 of product of the polarization resistance and the corrosion current, and the chosen constants $-k_R = k_C = k_U$ = 0.003MPa^{-1} is shown in Figure 7.

The course of the modeled current density is nearly harmonic with the mean value corresponding to the corrosion current.

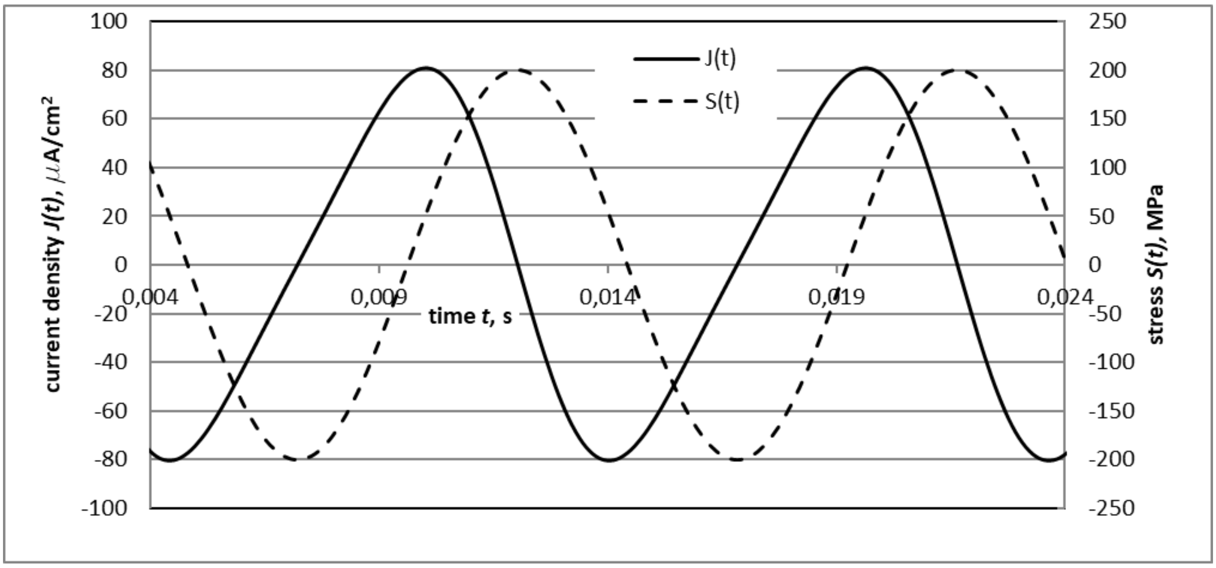

Figure 7. Modeled current density waveform for an oscillation stress amplitude of 200 MPa

The dependence of the amplitudes of the modeled current density cycles J_a = (max J(t) – min J(t))/2 and the mean value $J_m = J_{cor}$ on the amplitude of the stress amplitude S_a with frequencies of 104Hz and 26Hz are shown in Figure 8.

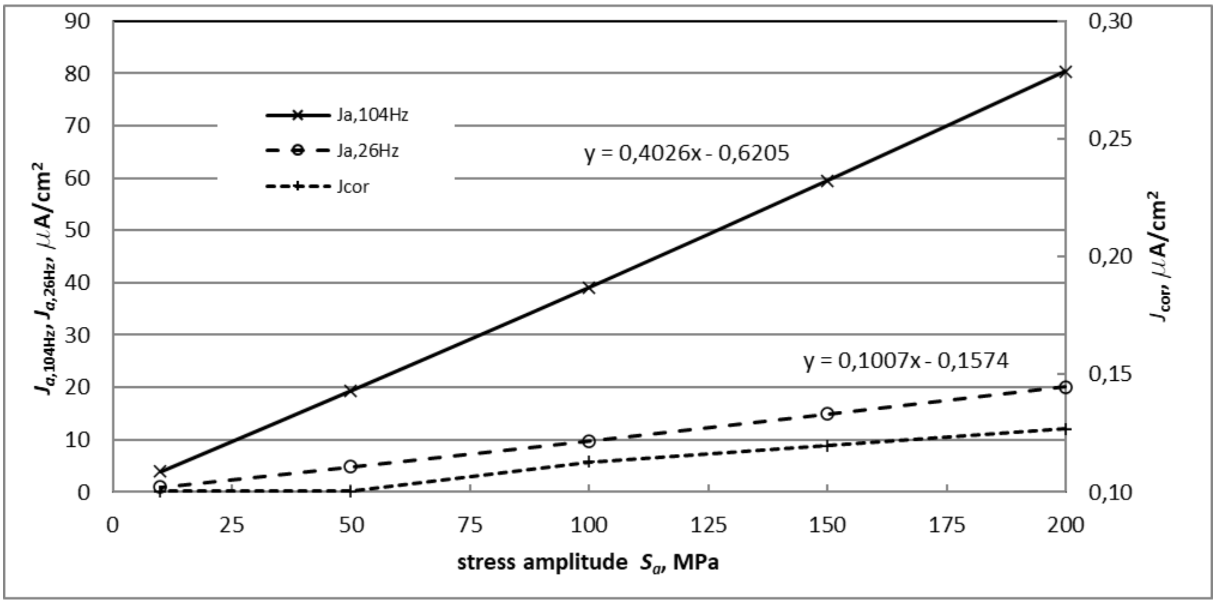

Figure 8. The current density amplitude versus the amplitude and frequency of the load

The amplitude of the current density is a linear function of the stress amplitude and is proportional to the frequency of the stress. The corrosion current density increases slightly with the stress amplitude.

4. DISCUSSION

Passivation film of stainless steels subjected to stress oscillations below the fatigue limit in neutral chloride-containing waters changes its electrochemical behavior. The *SCE* potential changes [2] and [6] and current and potential noise correlated with the stress waveform is observed [5] and [8].

The actual value of the generated current can be inferred from the electrochemical noise measurements. When measuring the potential noise in the 1SM arrangement [12], we find a cyclic overvoltage with an amplitude of U_a, which corresponds to product of the actual current amplitude I_{atrue} and the impedance Z of the passivation film with taking into account the resistance of the environment. In this arrangement, the generated current returns through the passivation layer to the loaded rod. If the current loop closes at the location of the generated current, the resistance of the environment is close to zero and then the impedance of the passivation layer is Z = 76 Ohm for a frequency f = 104 Hz. The actual current amplitude generated during loading with a stress amplitude of S_a = 200 MPa, frequency f = 104 Hz and test rod area of 7.5 cm^2 is then $I_{atrue} = Ua/Z$ = 0.00654/76 = 86.04 μA. The measured amplitude of the current noise under the same conditions is I_{amer} = 7.5 (0.0023·200-0.0171) = 3.32 μA. The actual amplitude of the generated current is therefore 26.91 times the measured amplitude of the current noise.

When creating a model of a mechanically loaded passivation film, it is assumed that the polarization resistance R_p and the capacitance C_{dl} are not dependent on the amplitude of the stress oscillation. In fact, we expect that the parameters of the double layer under cyclic loading are weakly dependent on both the amplitude S_a (see Figure 1) and the mean value of the stress S_m. In accordance with the idea of the correlation of the value of the potential jump of the double layer with its capacitance [11], the value of the amplitude of the electric voltage U_a value is considered much like the value of the amplitude of the capacitance C_{dl}.

In the passivity or transpassivity region, the phase shift of the current relative to mechanical loading was measured to be practically zero or π/2 [5] in corrosion fatigue tests of AISI 316 steel [5]. The phase shifts cannot be related to the development of plastic deformation during cyclic loading, because plastic deformation is mainly controlled by mechanical loading. The determined phase shift shows a direct connection with the electrical properties of the passivation film. The ratio of the values of the constants k and k_R corresponds to the current course and the phase shift in the passivity region when loaded with stress amplitude and frequency of 25 Hz [5]. The values of the coupling k between the stress amplitude and the parameters of the passivation layer are determined from the condition of equality of the calculated current oscillation amplitude I_a and 26.91 times the measured current amplitude, i.e. the estimated actual current oscillation amplitude.

At the contractual limit of corrosion fatigue of SM steel for 10^8 oscillations (S_a=200 MPa), the amplitude of the current density is therefore J_{atrue} = 26.91·(0.0023·200-0.0171) = 44.28 µA/cm^2, which is more than two orders greater than the corrosion current density J_{cor} = 0.105 µA/cm^2.

If at least a fraction of the amplitude of the generated current has a Faraday nature and if this fraction of the current amplitude is greater than the corrosion current, an increase in the anodic current can be inferred. The Faraday nature of at least part of the alternating current, i.e. an increase in material loss under the action of an alternating current, has been experimentally verified [13] and [14]. This increase in the anodic current directly proportional to the stress amplitude is significant from the point of view of notch-sensitive corrosion fatigue damage in the incubation stage. From the point of view of the intensity of corrosion fatigue damage, which is determined in the first approximation mainly by the current amplitude, the ratio of the amplitude of the current density and the loading frequency is significant. The determined ratio allows us to infer a strong dependence of the number of oscillations of stainless steel bodies on the loading frequency in the considered environments in the incubation stage of the body's life.

5. CONCLUSION

The potential and current noise measured in the incubation stage of the corrosion fatigue life of stainless steels loaded with harmonic waveform stress and frequency of 104 Hz show an almost harmonic waveform. The amplitudes of the current and potential noise are linear functions of the stress amplitude.

The basic electrical parameters of the double layer determined from the experiment were used in a derived simplified model of a mechanically cyclic loaded double layer. The model is based on the concept of response of the electrical parameters of the double layer due to cyclic strain. For realistically determined model parameters, the generated current waveforms are almost harmonic and the current amplitude is directly proportional to the stress amplitude and the loading frequency.

The detected harmonic current noise generated by a double layer during mechanical cyclic loading of a stainless steel body may be the cause of corrosion fatigue damage in the incubation stage of its service life.

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