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Foundations of mechanics of corroding materials

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IN THIS PAPER the basic principles of mechanics concernning the balance laws of the corrosion process models are presented. The corrosion process has been described by a linear law of creation of the oxide layer using a single corrosive rate constant. The mass defect is neglected in the balance law of mass. In the balance of momentum, the corrosion processes are treated as a source of the additional compressive stresses. The kinematic magnitudes are treated independently of the corrosion processes. This approach is based on the infinitesimal strains and linear constitutive equations. Two linear versions of the theory, which are from the formal point of view certain variants of the Coupled Fields Theory, have been proposed. The first of them includes the corrosive term in the displacement equation of motion and has no mechanical term in the equation of corrosion. The second of them contains the coupling terms, both in the equation of motion and in the equation of corrosion.

1. Introduction

PROCESS OF CORROSION plays a negative role in technology and it is a source of economical losses. The costs which people have to pay for protection against corrosion are high and they are not justifiable from the economical viewpoint. The economical aspect of the mentioned problem is not only limited to the loss of the materials, but it is mainly connected with the necessity of permanent replacement of the corroded elements of the constructions. The corrosion processes lead to degradation of the materials and reduce their capability of transferring the loads.

Fast development of the modern technology creates the increasing requirements concerning the metallic constructions which are assumed to work in various oxidation environments. In the modern chemical industry, where the elements of construction are exposed to the action of the gases and vapours, the gaseous corrosion of the metals has particularly drastic forms. The car, aircraft and space industry as well as nuclear technologies require the use of materials of the appropriate mechanical properties.

Speaking in short words, we can say that the corrosion processes increase forces and tensions which are transferred through the parts of machines and the elements of structures. When we take into consideration the basic chemical

reactions, it is possible to model the influence of the corrosion process on the loss of the mass of the materials which transfer the loads.

In this paper, the basic principles of mechanics in the concept of the balance laws [1, 2] are presented taking into consideration the model of the corrosion process. The corrosion process has been described by a linear law of the oxidised layer creation using a single corrosive rate constant [3, 4, 5]. The mass loss is neglected in the balance law of mass. In the balance of momentum, the corrosion processes are treated as a source of the additional compressive stresses. From the formal point of view, the compression stresses are introduced as the additional, external field forces. In the presented model of the corrosion processes, the classical symmetry of the stress tensor follows from the balance of moment of momentum. It is worth to remember that the theoretical and experimental results confirm the influence of the mechanical stresses on the corrosive rate constants. It means that the corrosion and mechanical processes can be treated as coupled fields in the formal description.

2. Basic equations

From the point of view of mechanics of materials it seems convenient to create the theory using the laws of the balance of mass, of momentum and of moment of momentum.

Let us consider the body B which occupies space $\tau(B)$. The surface $S(B)$ is the fringe of the space τ. We will take advantage of the general equation of the balance formulated by KOSIŃSKI [2]:

$$\frac{d}{dt}\Psi = -W(\Psi) + P(\Psi) + R(\Psi). \tag{2.1}$$

In Eq. (2.1) the symbols have the following meaning: $W(\Psi)$ – is the outflow of the quantity Ψ through the fringe of the space τ, $P(\Psi)$ – is the creation of the quantity Ψ inside the space τ, $R(\Psi)$ – is the inflow of the quantity Ψ to the space τ from the surroundings.

The quantity R is very often assumed to be equal to zero, thus in this paper we will make the same assumption.

The law of the balance has to be fulfilled for the body B and for each subsystem. The physical quantities in Eq. (2.1) are generally described by means of the proper constitutive equation.

The balance of mass is assumed to be expressed by the equation of the conservation law [1]:

$$\frac{d}{dt}\int_{\tau} \rho d\tau = 0, \tag{2.2}$$

where ρ is mass density.

The balance of momentum can be expressed as follows:

$$\frac{d}{dt}\int_{\tau}\rho v_k d\tau = \oint_{S} t_{kl} dS_1 + \int_{\tau}\rho f_k d\tau, \tag{2.3}$$

where v_k is the velocity, t_{kl} is the stress and f_k is the body force.
The balance of the moment of momentum leads to the conclusion that the stress tensor is the symmetric tensor [1]:

$$t_{kl} = t_{lk}. \tag{2.4}$$

We will neglect the balance of energy since we do not consider the thermodynamic aspects of the investigated processes.

3. Model of the mass defect

In the studies of the corrosion of materials [4, 5], the laws of the growth of the layer thickness of the corrosive product are formulated and they can be interpreted as the constitutive law for the quantity $P(\Psi)$ in the Eq. (2.1) with Ψ as mass. Generally speaking, in such a study the polynomial laws can be expressed in the form

$$P(m) = \sum_{i=1}^{u} k_i (m)^i, \tag{3.1}$$

m being the mass. For simplicity we will assume the linear law as follows:

$$P(m) = -\nu I m = -\alpha m, \tag{3.2}$$

where symbols denote: ν – the stechiometric coefficient, I – reaction rate constant, $\alpha = \nu I$, and they correspond to the linear chemical reaction [3].
In such a case the balance of mass is expressed by the integral formula:

$$\frac{d}{dt}\int_{\tau}\rho d\tau = -\alpha \int_{\tau}\rho d\tau, \tag{3.3}$$

and the corresponding differential formula has the following form:

$$d_t \rho + \rho \partial_k v_k = -\alpha\rho, \tag{3.4}$$

where d_t is the material derivative and ∂_k is the space derivative. The application of the balance of mass (3.3) and (3.4) to the balance of momentum (2.3) enables us to obtain the local balance of momentum in the form:

$$\rho d_t v_k = \partial_l t_{kl} + \alpha\rho v_k + \rho f_k. \tag{3.5}$$

Moreover, it is found that the balance of the moment of momentum has not changed and has the form of Eq. (2.4). The balance of momentum (Eq. (3.5)) is the classical differential equation of motion, however the term on the right-hand side with the coefficient α is due to the mass defect (Eqs. (2.3) and (2.4)).

Let us assume now that we consider the isotropic, elastic material which is described by the Hooke's law:

$$t_{kl} = 2\mu\varepsilon_{kl} + \lambda\delta_{kl}\varepsilon_{rr}, \tag{3.6}$$

where: λ, μ, are the Lamé elastic constants, δ_{kl} is the Kronecker delta, $2\varepsilon_{kl} = \partial_k ku_l + \partial_l u_k$ is the infinitesimal strain tensor and u_k is the displacement vector.

By substitution of Eq. (3.6) to Eq. (3.5) we will obtain the Lamé displacement equations:

$$c_T^2\partial_s\partial_s u_r + (c_L^2 - c_T^2)\partial_r\partial_s u_S + \alpha_t\partial_t u_r = \partial_t\partial_t u_r, \tag{3.7}$$

where $c_T^2 = \mu/\rho$, $c_L^2 = (\lambda + 2\mu)/\rho$ and it is assumed that $f_k = 0$.

Symbols c_T and c_L denote the transverse and longitudinal wave phase velocity, respectively. Let us assume that perturbation depends only on the one space co-ordinate and time:

$$u_r = u_r(x_1, t), \qquad r = 1, 2, 3...$$

Then Eq. (3.7) has a form:

$$\begin{aligned} c_L^2\partial_1^2 u_1 + \alpha\partial_t u_1 &= \partial_t^2 u_1, \\ c_T^2\partial_1^2 u_2 + \alpha\partial_t u_2 &= \partial_t^2 u_2, \\ c_T^2\partial_1^2 u_3 + \alpha\partial_1 u_3 &= \partial_1^2 u_3. \end{aligned} \tag{3.8}$$

On the basis of Eq. (3.8) we can draw the conclusion that both the longitudinal and transverse perturbations undergo the modification which is connected with the mass defect. In the asymptotic case when α approaches zero, one obtains the classical equation of perturbation. Taking into account the general character of this paper, we will not explore this problem any further.

4. Model of additional stresses

Now we will present another model of the chemical reaction which describes the corrosion processes. Let us suppose that the mass defect is sufficiently small and can be neglected in the balance equation of mass, and that the corrosion processes create the particular centres on the surface of the body which contribute to the balance of momentum. The corrosion process can be described as the

chemical reaction by the progress variable. Time derivative describes the reaction rate. We assume that the progress variable and the reaction rate are the time-space fields. The progress variable can be expressed as

$$z = z(x_i, t),$$

and the rate of reaction as

$$I(x_i, t) = \partial_t z(x_i, t).$$

The contribution of the corrosive processes in the balance of momentum is described by the scalar function of the progress variable which can be expressed as a surface source in the form:

$$\frac{d}{dt}\int_\tau \rho v_k d\tau = \oint_S P(z)\delta_{kl} dS_l + \oint t_{kl} dS_l + \int_\tau \rho f_k d\tau. \tag{4.1}$$

Using the standard approach, the local balance of momentum can be expressed in the following differential form:

$$\rho d_t v_k = \partial(t_{kl} + P(z)\delta_{kl}) + \rho f_k. \tag{4.2}$$

From Eq. (4.2) it is easily seen that the extended stress tensor:

$$T_{kl} = t_{kl} + P(z)\delta_{kl}, \tag{4.3}$$

can be used in our theoretical approach. On the basis of the balance of moment of momentum we can show that the extended stress tensor is a symmetric tensor:

$$T_{pk} = T_{kp}. \tag{4.4}$$

We will postulate the evolution equation of the corrosive rate in the simple form [1]:

$$\partial_t z = \frac{1}{\tau_r} z + r(I_1, I_2, I_3), \tag{4.5}$$

where τ_r is the relaxation time of the corrosion process and r is the function of invariants of strain, I_1, I_2, I_3. Introduction of the r function means that one takes into account the influence of the strain on the corrosion processes.

In order to formulate this problem as a linear problem, we will make the following assumptions:

1. The corrosion process is stable; it means that the relaxation time approaches infinity.

2. The corrosive rate is the linear function of the first invariant of strain, i.e. it is the linear function of the relative volume change.

3. The corrosion source of momentum is linearly dependent on the progress variable.

The above assumptions can be formulated as: relaxation time $\tau_r \to \infty$, the evolution equation of the corrosive rate

$$\partial_t z = AI_l = |A\frac{\Delta\tau}{\tau} = A\varepsilon_{kk} = A\partial_k u_k, \tag{4.6}$$

where A is constant.

The corrosion source of momentum can be expressed by

$$P(z) = \gamma z, \tag{4.7}$$

where γ is constant.

On the basis of the above equation and Eq. (4.3), we obtain the extended stress tensor in the form

$$\tau_{kl} = 2\mu\varepsilon_{kl} + (\lambda\varepsilon_{rr} + \gamma z)\delta_{kl}. \tag{4.8}$$

It leads to the displacement equations:

$$c_T^2\partial_s\partial_s u_r + (c_L^2 - c_T^2)\partial_r\partial_s u_s + g\partial_r z = \partial_t\partial_t u_r, \tag{4.9}$$

where $g = \gamma/\rho$.

The evolution equation of the corrosive rate (4.6) and displacement Eqs. (4.9) form the set of equations which describe the coupled fields of displacement and progress variable.

In the one-dimensional particular case:

$$u_r = u_r(x_1, t), \qquad z = z(x_1, t), \tag{4.10}$$

we obtain

$$c_L^2\partial_1\partial_1 u_1 + g\partial_1 z = \partial_t\partial_t u_1, \tag{4.11}$$

$$\partial_t z = A\partial_1 u_1, \tag{4.12}$$

$$c_T^2\partial_1\partial_1 u_2 = \partial_t\partial_t u_2, \tag{4.13}$$

$$c_T^2\partial_1\partial_1 u_3 = \partial_t\partial_t u_3. \tag{4.14}$$

It is easily noticed that the coupled problem concerns only the voluminal strains (Eqs. (4.11) and (4.12)). In other words, in the assumed model, perturbation of the displacement u_1 is coupled with the corrosion effects. The transverse perturbations u_2 and u_3 are independent of these effects. It is the result of the previous Assumption 2 that the corrosive rate depends on the relative change

of the volume only. On the basis of the assumptions made it is not possible to obtain addditional coupled effects.

5. Concluding remarks

The presented models of the corrosion, the model of the mass defect and the model of the additional stresses, are qualitatively different. They differ from each other in the character of coupling between the field of displacement and the corrosion effects. To stress the character of the two models, one-dimensional problems are formulated. In Eqs. (3.8) of the model of the mass defect, the α parameter which describes the corrosion process is present in all equations, both in the longitudinal perturbation and in the transverse perturbation.

In the model of the additional stresses, the coupling between the voluminal strain and the progress variable is shown (Eqs. (4.11) and (4.12)). Eqs. (4.13) and (4.14) do not show such a coupling. The obtained results open the field for the further investigations.

It seems that the model of the additional stresses creates more possibilities by introducing fewer simple assumptions. It is obvious that it is possible to complete the evolution Eqs. (4.6) by further invariants of the strain tensor and with the relaxation time.

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