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ELECTROMECHANICAL THERMAL DIFFUSION PROCESSES IN CONTACTING BODIES WITH POINT DEFECTS*

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A closed system of differential equations that describe interconnected electromechanical thermal diffusion, electromagnetic and chemical processes in electrically-conducting bodies with point defects, where these bodies are separated by a transition layer, which is modelled by a physical surface without resistance to flexure is obtained. Using generalized conditions for the conjugation of contacting phases, for solid deformed bodies a formula is derived that is analogous to Antonov's emiprical relationship.

The stress-deformed state of elements of constructions of combined metal parts (for instance, bimetal) under the influence of an agressive external medium, heating, and the radiation of particle currents depends effectively on processes of impurity redistribution, chemical reactions, and electrical transport, and also the generation and recombination of point defects in the volume of the bodies and in the surface layers /1, 2/. In many important practical cases the state of bodies and the processes in thin surface regions when the above-mentioned actions occur have a decisive effect on the behaviour of the body as a whole /1/ and appropriate models must be developed for the mechanics of a continuous medium.

1. A model of a system of bodies. We consider the motion of a system of two contacting bodies which are located in force, temperature and electromagnetic fields. We neglect fiction and slippage between the bodies. Each body is a one-phase mixture of chemical components, which include point defects (vacancies and atoms introduced into interstitial sites). We confine ourselves to considering impurity diffusion, chemical reactions, and the generation and recombination of point defects in a system of elastic-deformation, thermal and electromagnetic processes /2-4/.

We model the contacting bodies by continuous phases, ascribing "plus" and "minus" superscripts to the corresponding values of the parameters, and we replace the thin region between them by continuous two-dimensional physical surface without resistance to flexure (index s) with the properties of a transition layer imparted to it. We use the local equilibrium hypothesis /4/ at each small volume element $\Delta V^+, \Delta V^-$ and the physical phase boundary in their classical formulations.

For a macroscopic description of the state of the system, taking account of the processes occurring in it, we use methods of the mechanics of continuous media and the thermodynamics of irreversible processes, /4, 6/, using the generalized function formalism /6/. A model of contacting multicomponent electrically-conducting defectless continuous media with the collection of processes listed above (apart from the redistribution, generation and recombination of point defects) was set out in /4/, where the balance relations were obtained using integral theorems.

At a given time $\tau = \tau_0$, let contacting thermoelastic bodies occupy the regions V^+, V^- bounded by the surfaces $S^+ + S^s$ and $S^- + S^s$ (S^s is the interface).

In accordance with the processes, we introduce the following thermodynamic state parameters: the second-order deformation tensor e and mechanical stress tensor σ, the tempeature T, the specific entropy S, the mass concentration C_k of impurity of component k ($k = 3, \ldots n-2$), the chemical potentials M_k, the electric charge density ω, the moments of electric charge distribution and of thermodynamic electric potential Q^s and Ψ^s /4/, the thermodynamic electric potential $\Phi = (M_{n-1} - M_n)/(z_{n-1} - z_n)$, where z_n and z_{n-1} is the electric charge of unit mass of each component, the subscripts n and $n-1$ correspond to ions of the main substance that forms the framework of the elastic body, and to conduction electrons, and n is the overall number of chemical components, including conduction electrons, ions, and point defects.

For vacancies ($k = 1$), interstices ($k = 2$) and atoms of the main material ($k = n$) we introduce N_α, the number of particles per unit mass of the mixture, and also the chemical potentials computed on one particle M_α' ($\alpha = 1, 2, n$; $M_2' = M_2 m^{(2)}$; $M_n' = M_n m^{(n)}$; $m^{(2)}, m^{(n)}$ are the masses of an interstice and an atom of the basic substance).

We use the representations

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$$R = R^+\theta^+ + R^-\theta^- + R^s\delta^s \tag{1.1}$$

$$(R = e, \sigma, T, S, C_k, M_k, \omega, \Phi, N_\alpha, M_\alpha')$$

$$\theta^+ = \theta^- = 0, \quad f = 0; \quad \theta^+ = 1 - \theta^- = \begin{cases} 0, & f < 0 \\ 1, & f > 0 \end{cases}$$

$\delta^s = \delta(f)\,|\operatorname{grad} f|$, $\delta(f)$ is a Dirac delta-function, $f(x, y, z, \tau) = 0$ is the equation of the interface, $f > 0$ corresponds to the "plus" body, and $f < 0$ corresponds to the "minus" body, and x, y, z are Cartesian coordinates.

Using the state parameters N_1, N_2, M_1', M_2' we have introduced, we can more fully and accurately calculate the stress-deformation state of elements of the constructions, estimating the influence of an aggressive medium and intense currents of electrons, protons, ions and photons on the mechanical behaviour of the bodies and of their surface layers, here taking account of the change in the internal structure, in particular the number of point defects produced by the radiation, the time-relaxing residual stresses being connected with these defects.

2. Basic relationships. Substituting these parameters into the balance relationships

$$\rho da/d\tau + \nabla \cdot \mathbf{J} = \zeta$$

and taking account of the independence of the generalized functions $\theta^+, \theta^-, \delta^s$, we arrive at differential equations in the "plus" and "minus" phases, and also at generalized conditions of physico-mechanical field conjugation on the partition surface

$$\rho^\pm da^\pm/d\tau + \nabla \cdot \mathbf{J}^\pm = \zeta^\pm \tag{2.1}$$

$$\rho^s da^s/d\tau + \nabla_s \cdot \mathbf{J}^s + J_N{}^+ - J_N{}^- = \zeta^s \tag{2.2}$$

Here ρ is the mass density of the material, a is the conventional notation for the concentration of chemical components and point defects, the electric charge density, the mechanical impulse, the entropy, the internal energy U, and the electric charge distribution moment; $\mathbf{J}, \zeta$ are the conventional symbols for currents and sources; $J_N{}^+, J_N{}^-$ are the projections of the currents onto the normal to the phase boundary on approaching the phase boundary; S^s; ∇ is the Hamiltonian operator, and ∇_s is the Hamiltonian operator for the surface S^s /4-6/. We use representation (1.1) for $\rho, a, U, \mathbf{J}, \zeta$. It is necessary to note that the sources of electric charge ω' and energy U are equal to zero.

If there are $r = (r^+, r^-, r^s)$ chemical reactions at each internal point of the "plus" and "minus" phases and of the physical surface S^s, then according to the stoichiometric equations

$$\sum_{k=1}^{k_j^s} \nu_{kj}^s = 0, \quad \sum_{k=1}^{k_j^\pm} \nu_{kj}^\pm = 0, \quad j = 1, 2, \ldots, r \tag{2.3}$$

where $k_j^s, k_j^\pm$ is the number of components taking part in the j-th chemical reaction, and $\nu_{kj} = (\nu_{kj}{}^+, \nu_{kj}{}^-, \nu_{kj}{}^s)$ are the stoichiometric coefficients of the reagents and reaction products.

The equation for the recombination (generation) of point defects takes the form

$$N_{1*}^\pm + N_{2*}^\pm = N_{n*}^\pm, \quad N_{1*}^s + N_{2*}^s = N_{n*}^s \tag{2.4}$$

Here N_{1*}, N_{2*}, N_{n*} are the numbers of particles of each sort that correspond to one kilomole.

We take a state of thermodynamic equilibrium as the initial state, and in it the values of the initial parameters are as follows:

$$T_0^\pm,\ S_0^\pm,\ \sigma_{ij0}^\pm = e_{ij0}^\pm = 0,\ C_{k0}^\pm,\ M_{k0}^\pm,\ \omega_0{}^\pm = 0,\ N_{\alpha0}^\pm,\ \Phi_0^\pm,\ M_{\alpha0}^\pm;\ T_0^s,\ S_0^s \tag{2.5}$$

$$\sigma_{\alpha\beta}^{0s},\ e_{\alpha\beta}^{0s},\ C_{k0}^s,\ M_{k0}^s,\ \omega_0^s,\ \Phi_0^s,\ Q_0^s,\ \Psi_0^s,\ N_{\alpha0}^s,\ M_{\alpha0}^{\prime s}$$

$$(i, j = 1, 2, 3;\ \alpha, \beta = 1, 2;\ k = 3, 4, \ldots, n - 2)$$

From the first fundamental equation of thermodynamics (postulated as the Gibbs equation) there follow the equations of state

$$T^\pm = \frac{\partial U^\pm}{\partial S^\pm}, \quad M_k{}^\pm = \frac{\partial U^\pm}{\partial C_k{}^\pm}, \quad \sigma_{ij}{}^\pm = \rho^\pm \frac{\partial U^\pm}{\partial e_{ij}{}^\pm}, \quad \Phi^\pm = \frac{\partial U^\pm}{\partial \omega^\pm}, \tag{2.6}$$

$$M_\alpha'^\pm = \frac{\partial U^\pm}{\partial N_\alpha{}^\pm}, \quad T^s = \frac{\partial U^s}{\partial S^s}, \quad M_k{}^s = \frac{\partial U^s}{\partial C_k{}^s}, \quad \sigma_{\alpha\beta}^s = \rho^s \frac{\partial U^s}{\partial e_{\alpha\beta}^s},$$

$$\Phi^s = \frac{\partial U^s}{\partial \omega^s}, \quad \Psi^s = \frac{\partial U^s}{\partial Q^s}, \quad M_\alpha{}'^s = \frac{\partial U^s}{\partial N_\alpha{}^s}$$

If the state function U is determined experimentally or by the methods of statistical physics, using (2.6) we can express some of the parameters in terms of the others. We substitute expressions (2.6) into the balance Eqs.(2.1), (2.2). As a result, the number of unknown parameters in the defining relations decreases.

Using the balance relations (2.1), (2.2) and the Gibbs equations, we find an explicit form of the expression for the production of entropy $\sigma_s^{\pm}, \sigma_s^{s}$, with the aid of which (as in /4/) we construct the second fundamental thermodynamic equation for the "plus" and "minus" phases, and also for the physical surface

$$d\Pi^{\pm} = \mathbf{Y}_m^{\pm} \cdot d\mathbf{X}_m^{\pm} + \zeta_p^{\pm} dA_p^{\pm} \qquad d\Pi^{s} = \mathbf{Y}_q^{s} \cdot d\mathbf{X}_q^{s} + \zeta_l^{s} dA_l^{s} \tag{2.7}$$

where $(\mathbf{X}_m^{\pm}, \mathbf{X}_q^{s}, A_p^{\pm}, A_l^{s})$ are vectors and scalar thermodynamic forces, $(\mathbf{Y}_m^{\pm}, \mathbf{Y}_q^{s}, \zeta_p^{\pm}, \zeta_l^{s})$ are vector and scalar thermodynamic currents, and $\Pi^{\pm}, \Pi^{s}$ are the kinetic potentials, which are the characteristic functions of the thermodynamic forces.

From (2.7) there follow the equations of the processes

$$\mathbf{Y}_m^{\pm} = \frac{\partial \Pi^{\pm}}{\partial \mathbf{X}_m^{\pm}}, \quad \zeta_p^{\pm} = \frac{\partial \Pi^{\pm}}{\partial A_p^{\pm}}, \quad \mathbf{Y}_q^{s} = \frac{\partial \Pi^{s}}{\partial \mathbf{X}_q^{s}}, \quad \zeta_l^{s} = \frac{\partial \Pi^{s}}{\partial A_l^{s}}$$

We present the currents so obtained in (2.1), (2.2).

The balance relationships (2.1), (2.2), the boundary conditions on the surfaces S^+, S^-, following from the generalized conjugation conditions (2.2), the equations of electrodynamics /4-6/, the Cauchy relations between the deformations and displacements /5/, the initial conditions for the volumes V^+, V^-, the stoichiometric equations for of the chemical reactions (2.3), and the generation (recombination) Eq.(2.4) for point defects constitute a closed (complete) system of equations that describe the interaction of the thermomechanical diffusion, electromagnetic, and chemical processes, and also the redistribution and generation (recombination) of point defects in contacting electrically-conducting bodies with physical partition surfaces. Neglecting the parameters corresponding to point defects, we obtain well-known relationships /4/.

3. Computing the interfacial tension. As an example, we use the equations for the model for determining the connection between the interfacial tension and the surface tensions of the contacting phases.

We consider two equilibrium states of solid elastically-deformable bodies with homogeneous plane surfaces (a semispace) irradiated by protons: a) the bodies are in contact with a vacuum and b) the bodies are in contact with each other. We confine ourselves to describing the changes in the mechanical parameters of the interface S^s in consequence of the increase or decrease in the electric charge distribution moment and the number of point defects when the system is irradiated. In future, for brevity we will omit the index s everywhere.

We are given the surface stresses in the a state when there are no point defects induced by radiation, and also the change in the thermodynamic electric potential moment $\Psi_{\pm}$ in the transition from the a-state to the b-state, calculated on the basis of known solutions of the model with ideal physico-mechanical field matching conditions on the geometrical boundaries of the interface /7/.

We find the interfacial tension σ_1 from the linear equations of state written for the physical interface:

$$\begin{aligned}
&\sigma_{1\pm} = \sigma_{10\pm} + K_{\pm} e_{1\pm} + \gamma_{e\pm} K_{\pm} q_{\pm} - \beta_{\pm} K_{\pm} \varphi_{\pm} + \beta_{e\pm} K_{\pm} N_{\pm} \\
&\psi_{\pm} = \gamma_{q\pm} q_{\pm} + \gamma_{e\pm} K_{\pm} e_{1\pm}/\rho_{\pm} + \gamma_{\varphi\pm} \varphi_{\pm} + \beta_{\psi\pm} N_{\pm} \\
&\omega_{\pm} = C_{q\pm} \varphi_{\pm} + \beta_{\pm} K_{\pm} e_{1\pm}/\rho_{\pm} + \gamma_{q\pm} q_{\pm} + \beta_{\omega\pm} N_{\pm} \\
&\varphi = \Phi - \Phi_0, \quad q = Q - Q_0, \quad \psi = \Psi - \Psi_0, \quad N_1 = N_2 = N
\end{aligned} \tag{3.1}$$

Here $K_{\pm}, C_{q\pm}, \beta_{\pm}, \beta_{\psi\pm}, \beta_{\omega\pm}, \beta_{e\pm}, \gamma_{q\pm}, \gamma_{q\pm}, \gamma_{e\pm}, \sigma_{10\pm}$ are physical constants of the material surfaces; $\sigma_1 = \sigma_{11} + \sigma_{22}$, $e_1 = e_{11} + e_{22}$ are the first invariants of the surface stress and deformation tensors; parameters with plus (minus) indices correspond to a physical surface in state a for a body to which the index plus (minus) corresponds in state b; $N_{\pm}$ is the number of Frenkel pairs in unit mass of the physical surface.

In the problem under consideration, we neglect changes in the volume phases, and we also assume that the surface characteristics are constant in the transition from a to b.

We assume that in the equations of state there are averaged material characteristics $(\gamma_{i\pm})$, which correspond to an imaginary continuous transition between states a and b, that is

$$\gamma_{i\pm} = (\gamma_{i\pm}^{0} + \gamma_{i\pm}^{\mp})/2, \quad i = 1, 2, \ldots, n$$

Here n is the number of characteristics of the material; $\gamma_{i\pm}^{0}, \gamma_{i+}^{-} = \gamma_{i-}^{+}$ are the values of the physical characteristics in states a and b respectively.

Taking into account the fact that in state b $e_{1+} = e_{1-} = e_1$, we obtain

$$\begin{aligned}
&\sigma_1 = \{(\sigma_{10+} + \sigma_{0+}^{*}) K_{-}^{*} - (\sigma_{10-} + \sigma_{0-}^{*}) K_{+}^{*}\}/(K_{-}^{*} - K_{+}^{*}) \\
&K_{\pm}^{*} = K_{\pm} \{1 + K_{\pm} (C_{q\pm} (\gamma_{e\pm})^2 - (\beta_{\pm})^2 \gamma_{q\pm})/(\rho_{\pm} ((\gamma_{\varphi\pm})^2 - \gamma_{q\pm} C_{q\pm}))\}
\end{aligned} \tag{3.2}$$

$$\sigma_{0\pm}^{*} = -\Phi_{\pm}^{*}K_{\pm}(\beta_{\pm}\gamma_{q\pm} + \gamma_{e\pm}C_{q\pm})/((\gamma_{q\pm})^2 - \gamma_{q\pm}C_{q\pm}) +$$
$$K_{\pm}\{\beta_{\pm} + (\beta_{\psi\pm}(\gamma_{\varphi\pm}\beta_{\pm} + \gamma_{e\pm}C_{\varphi}^{\pm}) - \beta_{\omega\pm}(\gamma_{e\pm}\gamma_{\varphi\pm} + \beta_{\pm}\gamma_{q\pm}))/((\gamma_{\varphi\pm})^2 -$$
$$\gamma_{q\pm}C_{q\pm})\}N_{\pm}$$
$$\Phi_{+}^{*} = |\Phi_0^{-}|/2, \quad \Phi_{-}^{*} = |2\Phi_0^{-} - \Phi_0^{+}|/2$$

Taking

$$\sigma_{10+} = 1.6\ \text{N/m}, \sigma_{10-} = 1.45\ \text{N/m}, \beta_{+} = \beta_{-} = 0.1\ \text{V}^{-1}$$
$$\gamma_{q+} = \gamma_{q-} = 2\times10^{-5}\ \text{V.kg/C}, \gamma_{\varphi+} = \gamma_{\varphi-} = 10, \gamma_{e+} = \gamma_{e-} = 10^{-9}\ \text{kg/C},$$
$$C_{\varphi+} = C_{\varphi-} = 3\times10^{5}\ \text{C/V.kg}, \rho_{+} = \rho_{-} = 10^{-5}\ \text{kg/m}^2, \Phi_0^{+} = -5\ \text{V},$$
$$\Phi_0^{-} = -4.5\ \text{V}, K_{+} = 5\ \text{N/m}, K_{-} = 4.5\ \text{N/m}, \beta_{\psi+}N_{+} = \beta_{\psi-}N_{-} = 0.1\ \text{V}^{-1}$$
$$\beta_{\omega+}N_{+} = \beta_{\omega-}N_{-} = 6\times10^{3}\ \text{C/kg}, \beta_{e+}N_{+} = 0.01, \quad \beta_{e-}N_{-} = 0.012$$

we find the following, without taking account of the influence of radiative illumination (the values for irradiated materials are given in brackets):

$$\sigma_1 = 0.218\ (0.308)\ \text{N/m}, \ e_1 = -0.253\ (-0.246), \ \varphi_{+} = 0.237\ (0.227)\ \text{V},$$
$$\varphi_{-} = 0.21\ (0.201)\ \text{V}, \ q_{+} = -5.837\ (-6.194)\ \text{kC/kg}, \ q_{-} = -5.174\ (-5.527)\ \text{kC/kg}$$

The values of $\sigma_{10\pm}, \beta_{\pm}, \gamma_{q\pm}, \gamma_{\varphi\pm}, \gamma_{e\pm}, C_{\varphi\pm}, \rho_{\pm}, \Phi_0^{\pm}, K_{\pm}$ are determined on the basis of known experimental data*,(*Yuzevich V.N., On the estimation of cited characteristics of phase boundaries in electrically-conducting bodies. Proceedings of the 9th Conference of Young Scientists. In-ta Prikl. Probl. Mekhaniki i Matematiki Akad. Nauk Ukr.SSR (Lvov, 10-14 May, 1982). Part 1 Dep. v VINITI 10.01.84; 323-84.) and $\beta_{\omega\pm}N_{\pm}, \beta_{e\pm}N_{\pm}, \beta_{\psi\pm}N_{\pm}$ are estimated using the results of experiments /8/.

The values calculated for interfacial tension and deformations agree to an order of magnitude with data for metals /9/.

As a special case, an empirical confirmation for immiscible liquids of the well-known Antonov rule /10/ follows from (3.2):

$$\sigma_1 = |\sigma_{10+} - \sigma_{10-}|$$

if the following conditions are satisfied:

$$|\{(\sigma_{10-} + \sigma_{0+}^{*})K_{-}^{*} - (\sigma_{10+} - 2\sigma_{10-} - \sigma_{0-}^{*})K_{+}^{*}\}/(K_{+}^{*} - K_{-}^{*})| \ll |\sigma_{10+} - \sigma_{10-}|$$

In the specific example we give, the deviation from Antonov's rule is

$$p = 1 - \sigma_1/|\sigma_{10+} - \sigma_{10-}|$$

which is characteristic for solid bodies; $p = 46\%$ for non-irradiated metals and 106% for irradiated metals.

Using the expression for σ_1, we find a relationship for the adhesion work of the contacting materials /10/

$$w_{(+)(-)} = \sigma_{10+} + \sigma_{10-} - \sigma_1 = \{(\sigma_{10+} - \sigma_{0-}^{*})K_{+}^{*} - (\sigma_{10-} - \sigma_{0+}^{*}) \times K_{-}^{*}\}/(K_{+}^{*} - K_{-}^{*}) \qquad (3.3)$$

Substituting the numerical data into (3.3), we obtain $w_{(+)(-)} = 2.83$ N/m for non-irradiated metals and $w_{(+)(-)} = 2.74$ N/m for irradiated metals.

REFERENCES

1. On the development of fundamental and applied investigations in the field of the physico-chemical and mechanical properties of surfaces (in the Praesidium of the USSR Academy of Sciences). Vestn. Akad. Nauk USSR, 9, 1979.
2. BORZYKH A.A. and CHEREPANOV G.P., On the destruction of solids by intense pulsed electron beams. Prikl. Mat. Mekh., 44, 6, 1980.
3. CHEREPANOV G.P., The motion of point defects in solids. Prikl. Mat. Mekh. 50, 3, 1986.
4. YUZEVICH V.I., Contact conditions in electrically-conducting systems with a phtsical interface. Dokl. Akad. Nauk Ukr.SSR, Ser. A, 8, 1984.
5. IL'YUSHIN A.A., Mechanics of a Continuous Medium, Izd. MGU, Moscow, 1978.
6. WOLFF P.A. and ALBANO A.M., Non-equilibrium thermodynamics of interfaces including electromagnetic effects. Physica Ser. A, 98, 3, 1979.
7. YUZEVICH V.N., Analytical investigation of the kinetics of the change of surface tension on adsorption and diffusional saturation in a solid electrically-conducting ball. Fiz.-Khim Mekhanika Materialov, 6, 1986.
8. KAN R. (Ed.), Physical metallurgy, Mir, Moscow, 3, 1968.
9. MISSOL V., Surface Energy of the Phase Interface in Metals, Metallurgiya, Moscow, 1978.
10. ADAMSON A., Physical Chemistry of Surfaces, Mir, Moscow, 1979.

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