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ON AN APPROACH TO THE DERIVATION OF CONSTITUTIVE EQUATIONS OF PHOTOCHROMIC MATERIALS

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The paper presents constitutive equations of deformed solids, the state parameters of which, apart from the displacement vector, include concentrations of photochromic compounds. Equilibrium equations are completed with chemical kinetic equations, which are a system of, in a general case, nonlinear ordinary differential equations or parabolic-type equations accounting for the diffusion of products of photochromic reactions. Coefficients of such equations (for example, quantum reaction yield, reaction rate) can be assumed to depend on the stressed state. Several versions of the dependence of coefficients of chemical kinetic equations on the stressed-strained state are introduced. Also, in the assumption of electrostatics, possible effects of electric fields are taken into account. In analogy with mechanics of semiconductors and conductors, related equations of state are proposed.

The introduced model of a coupled photo-electro-mechanical effect is a strongly nonlinear boundary-value problem, the equations of which contain a large number of material constants that must be determined experimentally. For conducting potential mechanical experiments, a simplified one-dimensional model is proposed, which is analogous to problems of tension-compression and bending in mechanics of bars and beams. In the framework thereof, solutions of related one-dimensional problems are constructed, which make it principally possible to define dimensionless complexes containing unknown material constants.

Keywords: constitutive relations, photochromic materials, concentrations, chemical kinetic equations, diffusion, stressed-strained state, electric fields, coupled photo-electro-mechanical effect, one-dimensional model.

Introduction

Nowadays, photochromic, as well as electrochromic and piezochromic materials are of considerable interest to manufacturers of various data storing and processing devices, electronics and nano-photonics, in particular, required for creating novel computer devices (molecular computers). Latest achievements in chemistry have made it possible to synthesize a wide range of photochromic compounds. The class of photochromic materials, as well as similar to them electrochromic and piezochromic compounds, are a fairly large group of substances, both organic (such as spirans, anthraquinones) and nonorganic (for example, some oxides). Some nanostructures, such as carbon nanotubes also manifest photochromic properties.

Kinetics of photochromic reactions in dilute solutions is fairly well understood, whereas kinetic processes in a condensed state are less well known.

At the same time, construction of practical devices using photochromic compounds necessitates solving a number of problems of mechanics and material science. In particular, it is necessary to study the interrelation between characteristics of photochromic compounds and stressed-strained state, both determined by external loading and induced by the change of states of the molecules of a photochromic compound, to investigate the effect of stressed-strained state on aging characteristics of photochromic compounds, including the effect of the number of cycles of the direct-reverse photochromic reaction.

An important task in solving the above problems is developing a theory of defining relations of photochromic materials, accounting for the coupling of stress and strain fields with chemical reactions. The paper presents constitutive equations of deformed solids, the state parameters of which, apart from the displacement vector, include concentrations of photochromic compounds. Equilibrium equations are completed with chemical kinetic equations, which are a system of, in a general case, nonlinear ordinary differential equations or parabolic-type equations accounting for the diffusion of products of photochromic reactions. Coefficients of such equations (for example, quantum reaction yield, reaction rate) can be assumed to depend on the stressed state. Several versions of the dependence of coefficients of chemical kinetic equations on the stressed-strained state are introduced. Also, in the assumption of electrostatics, possible effects of electric fields are taken into account. In analogy with mechanics of semiconductors and conductors, related equations of state are proposed.

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By now, a huge number of studies on photochromic, as well as piezochromic and electrochromic compounds have been published. Books [1–5] should be noted. Progress in chemistry of photochromic compounds is naturally connected with the advances of chemical science as a whole, as well as of photochemistry, photoconductance, etc. [6–9]. Most of those works are on chemical aspects, such as synthesis, properties, description of structures, characteristics of chemical reactions etc. (see, for example, [10–18]). Articles [10, 13, 19–21] are dedicated to application of photochromic compounds. Thus, [10] considers use of photochromic materials in optical lenses. Dissertation [19], in particular, tackles the issues of using electrochromic materials in electronic devices (diodes etc.). Chemical kinetics of photochromic compounds was studied in [22–24]. It is to be noted that the works on chemical kinetics are of special interest in constructing a model of a photo-electro-mechanical effect, as these equations are a component part of such a model. In [25, 26], photo-degradation was studied. Despite the fact that chemical processes play a decisive role in describing photochromic compounds, the piezo-effect (the effect of pressure, strain) can also considerably affect the behavior of such compounds (see [21, 27–30] where experimental investigations of macroscopic specimens of photochromic

compounds are also described). Magnetic properties of photochromes were the subject of study in [16], and electric ones in [17, 31].

1. Kinetics of photochromic transformations

Equations of chemical kinetics describing photochromic reactions are a system of nonlinear differential equations of the following form [8, 22, 23, 32]:

$$\frac{dc_k}{dt} = F_k(c_1, c_2, \dots, c_m; p, \theta, \lambda, I_0), \quad k = 1, \dots, m, \quad (1)$$

where c_k is concentration of substance, the right-hand sides of equation (1) depend, generally speaking, on temperature θ , pressure p , wavelength of absorbed light λ , light flux intensity I_0 , t is time. The dependence of F_k on concentration can be fairly complex and nonlinear. The material constants (quantum yield of the reaction, reaction rate etc.), included in (1), in a number of cases are well enough determined from experimental data [33], using the spectrophotometric method [9].

Equation set (1) adequately describes kinetics of chemical transformations under the conditions of ideal mixing, i.e., when concentration is the same at any point of the space. If this assumption does not hold, system (1) is transformed with the account of the diffusion and convective transfer processes [34–36]

$$\frac{dc_k}{dt} = F_k(c_1, c_2, \dots, c_m; p, \theta, \lambda, I_0) + D_k \Delta c_k, \quad k = 1, \dots, m, \quad (2)$$

where D_k are diffusion coefficients, $d/dt = \partial/\partial t + \mathbf{v} \cdot \nabla$ is material derivative, \mathbf{v} is rate vector.

In what follows, we shall confine ourselves with binary reactions of the form



representing the direct and reverse photoreactions for components A and B , the concentrations of which will be designated by c_A and c_B , respectively.

This will be exemplified by an equation of chemical kinetics for a photochromic reaction of the following form [22, 33]:

$$\frac{dc_A}{dt} = I_0 F (\Phi_{BA} \varepsilon_B c_B - \Phi_{AB} \varepsilon_A c_A) + k_{AB} c_A, \quad F = \frac{1 - 10^{-Abs}}{Abs}, \quad (4)$$

$$Abs(\lambda) = \varepsilon_A(\lambda) c_A + \varepsilon_B(\lambda) c_B.$$

Reaction rate is found using the Arrhenius formula $k_{AB} = k_o \exp(-E_a/(R\theta))$, where k_o is pre-exponential multiplier, R is universal gas constant, E_a is activation energy. In (4), F is photo-kinetic coefficient, Φ_{AB} and Φ_{BA} are quantum yields of the direct and reverse reactions, respectively, ε_A and ε_B are molar extinction coefficients depending on wavelength.

Considering equation (4) with the account of the specimen thickness, the change of the light flux due to absorption must be accounted for. To this end, value I_0 in (4) must be substituted for by light flux I related with I_0 through Bouger's law

$$I = I_0 10^{-\varepsilon c h},$$

where c is concentration of the light-absorbing substance, h is thickness, ε is molar extinction coefficient. In the case of two absorbents, Firordt's law can be used

$$I = I_0 10^{-\varepsilon_A c_A h - \varepsilon_B c_B h}$$

To account for the stressed-strained state effect on kinetics of phase transformations, it will be natural to assume that the coefficients of the chemical kinetic equations depend on stresses. Moreover, in the case of diffusion of a photochromic compound, not only diffusion transfer, proportional to the concentration gradient, must be accounted for, but also the transfer due to the pressure and electric field gradients:

$$\frac{dc_k}{dt} = F_k(c_1, c_2, \dots, c_m; p, \theta, \lambda, I_0; \sigma_{ij}) + D_k \Delta c_k + D_k^\sigma \Delta \sigma + D_k^E \Delta E, \quad \sigma = \sigma_{ij}, \quad k = 1, \dots, m.$$

It will be assumed, in particular, that reaction rates are defined by a modified formula $k_{AB} = k_o \exp((-E_a - \alpha \sigma_{ij} \sigma_{ij}) / (R\theta))$, where α is dimensionless coefficient, and the other coefficients, in the assumption of the linear dependence on stresses or strains, can be represented by a sum of two summands of the following form:

$$I = I^o + \sigma I^\sigma,$$

where I^o is value of a quantity for the zero stress level, and σI^σ is correction. For a light flux, such a representation is obtained directly, taking into consideration the fact that the thickness of the layer on which the flux is defined changes linearly during the deformation of the body. If diffusion transfer processes are neglected, then, taking into account the high rate of transformations as compared with the deformation processes, it can be assumed that concentrations of a photochromic compound in various forms (A and B) can be found from the conditions of chemical equilibrium, i.e., as stationary solutions of equations

$$F_k(c_1, c_2, \dots, c_m; p, \theta, \lambda, I_0; \sigma_{ij}) = 0, \quad k = 1, \dots, m.$$

In this case, naturally, equilibrium concentrations are affected by the stressed-strained state, and incident light flux I_0 is a controlling parameter altering the properties of the medium.

It is to be noted that, for multiple cycles of photochromic transformations, the photo-degradation phenomenon [25, 26] is observed, which is manifested in the fact that, alongside with direct and reverse reactions (3), other reactions take place, which bring the reacting substances out of the photochromic transformation process. The concentration of such substances will be designated by c_c . If the coefficient of photo-degradation during one cycle of 'the direct-reverse reaction' is designated by f_d , then, after N cycles, the total concentration of the photochromic compounds can be found using the following formula [25]:

$$(c_A + c_B)|_N = (c_A + c_B)|_0 (1 - f_d)^N.$$

Thus, the concentration of sub-products c_c can be determined as a function of number of cycles N .

As a result of the assumptions made, it is postulated that concentrations of a photochromic compound can be determined using the following phenomenological relations:

$$c_A = \tilde{c}_A(I_0, \sigma)(1 - f_d)^N, \quad \tilde{c}_A(I_0, \sigma) = c_A(I_0) + B_A \sigma,$$

$$c_B = \tilde{c}_B(I_0, \sigma)(1 - f_d)^N, \quad \tilde{c}_B(I_0, \sigma) = c_B(I_0) + B_B \sigma,$$

where B_A and B_B are piezocoefficients ($\tilde{c}_A + \tilde{c}_B = 1$), and for \tilde{c}_A the following relation is used.

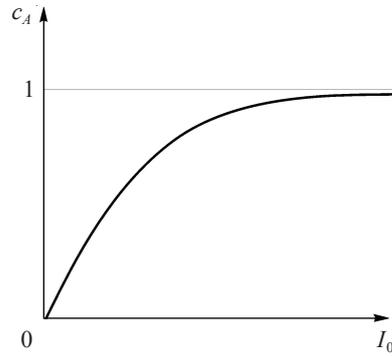


Fig. 1

It should be noted that kinetics of photochemical reactions may differ for diluted solutions (both liquid and solid) of photochromic compounds and for photochromic compounds in a condensed state. For instance, absorption of a quantum of light by a molecule in a condensed state may fail to result in its transformation because of the interaction between the molecules of the photochromic compound. For solid solutions, the orientation of the molecules of the photochromic compound and the resulting anisotropy of the optical properties can be essential. A photoreaction can also be affected by photoluminescence of the substance surrounding the photochromic material of the substance.

2. The one-dimensional model

Consider a spatially one-dimensional continuum model consisting of a photochromic material. As rates of chemical reactions are much higher than characteristic times of deformation processes, it is assumed that concentration of the substances taking part in photoreactions do not depend on time and at each point of the body are determined from the chemical equilibrium conditions for the given temperature, pressure and other parameters.

Without going into the details of chemical kinetics, concentrations c_A and c_B , as well as number of cycles N of ‘the direct-reverse photoreaction’ will be introduced as variables “in charge” of photochromic reactions in the continuum.

Equations of state will be written in the following form:

$$\sigma = cu' - eE, \quad D = eu' + \varepsilon E, \quad j = q(n_0 + fn)\mu E + qfdn'. \quad (5)$$

In (5), σ is stress, u is displacement, a stroke designates a derivative along space coordinate x , E is intensity of electric field, D is induction, j is current, c , e , ε are elasticity modulus, piezo-modulus and dielectric permeability of the medium, respectively, q is electronic charge, $n_0 + n$ is concentration of electrons (free charge carriers), n is concentration of electrons in the absence of mechanical strains, μ is mobility, f is trapping factor, d is diffusion coefficient of the carriers. Equations of state (5) are a special case of the equations of state of elastic semiconductors [32, 33, 37, 38]. Equation (5) does not account for the photo-effect, i.e., the appearance of free carriers under the effect of radiation [7].

Equations of motion and Maxwell's equations, in the case of electrostatics in a one-dimensional case, take the following form

$$\rho \ddot{u} = \sigma', \quad D' = -q(n_0 + n), \quad j' = q\dot{n}, \quad (6)$$

where ρ is density of the photochromic compound.

It is to be noted that the material constants (c , e , ε and others) entering the equation, generally speaking, depend on the chemical composition of the medium, i.e., concentrations c_A and c_B , which, in their turn, are assumed to depend on stress field σ according to the latter formulas of the previous section.

Consider a stationary solution of problem (5), (6) under the conditions of a constant homogeneous electric field. It is then evident that

$$\sigma = \sigma_0 = \text{const}, \quad j = j_0 = \text{const}, \quad n_0 + n = 0.$$

Thus, based on a static experiment, it is, in principle, possible to measure some of the constants, for example, the elasticity modulus, depending on the presence of a light flux and its intensity, as well as the number of cycles of photochromic transformations, or determining displacements as a function of the light flux. In particular, as the absorption of light is inhomogeneous through the thickness, bending of the photochromic compound plate under the conditions of radiation is possible.

Nevertheless, studying oscillations or wave propagation in such a one-dimensional medium, for instance, in analogy with studying sound wave propagation in semiconductors [39], appears to be more promising, though more difficult.

Conclusion

The paper presents equations of chemical kinetics for photochromic compounds and proposes resolving equations of photo-electro-mechanical effect in a spatially one-dimensional case.

In a three-dimensional case, the formulation can be confined to the case of a diluted solid solution of a photochromic compound in a solid matrix. To this end, it appears sufficient, in the first approximation, to use equations of thermal diffusion [40], completed with equations of chemical kinetics in form of (1) or (2). At the same time, it is well known that dynamic processes in solids are accompanied by the interaction of sound and light waves (acoustic-optics) [39] and the dependence of the refraction coefficient on stresses in the body (the piezo-optic effect) [41, 42]. In optoelectronics, other nonlinear interactions also appear to be essential [42]. Besides, unavoidable presence of various kinds of defects (dislocations, impurities) and anisotropy of the properties of the body containing a photochromic compound can also substantially complicate the processes.

For a photochromic compound distributed over the surface of a body, all kinds of surface phenomena can play an important part [43, 44].

The above effects also appear, to this or that degree, in a one-dimensional case. Naturally, determining the most important factors affecting coupled processes of photo-chemistry and stressed state must be based on related experiments.

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ОБ ОДНОМ ПОДХОДЕ К ПОСТРОЕНИЮ УРАВНЕНИЙ СОСТОЯНИЯ ФОТОХРОМНЫХ МАТЕРИАЛОВ

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Предложены уравнения состояний деформируемой твердой среды, параметрами состояния которой наряду с вектором перемещений являются концентрации фотохромных соединений. Уравнения равновесия дополняются уравнениями химической кинетики, которые представляют собой систему в общем случае нелинейных обыкновенных дифференциальных уравнений или уравнений параболического типа при учете диффузии продуктов фотохромных реакций. Коэффициенты этих уравнений (например, квантовый выход реакции, скорости реакции) могут предполагаться зависящими от напряженного состояния. Предложены различные варианты зависимости коэффициентов уравнений химической кинетики от напряженно-деформированного состояния. Также в приближении электростатики учтено возможное воздействие электрического поля. По аналогии с механикой упругих полупроводников и проводников предложены соответствующие уравнения состояния.

Предложенная модель связанного фото-электро-механического эффекта представляет собой сильно нелинейную краевую задачу, уравнения которой содержат большое количество материальных постоянных, подлежащих определению экспериментально. Для постановки возможных механических экспериментов предложена упрощенная одномерная модель, аналогичная задачам растяжения-сжатия и изгиба в механике стержней и балок. В ее рамках построены решения соответствующих одномерных задач, которые дают принципиальную возможность определения безразмерных комплексов, содержащих неизвестные материальные постоянные.

Ключевые слова: уравнения состояния, фотохромные материалы, концентрация, уравнения химической кинетики, диффузия, напряженно-деформированное состояние, электрическое поле, связанный фото-электро-механический эффект, одномерная модель.