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NUMERICAL INVESTIGATION OF NITRIDING OF REFRACTORY METALS (WITH ACCOUNT OF THE PHASE CONSTITUTION DIAGRAMS FOR METAL-GAS SYSTEMS)

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A mathematical model of dissolution of gas in a metal is suggested with account of phase formation in accordance with the phase constitution diagram (PCD). The stage-by-stage saturation process to the final product formation is shown for an individual particle, through which a reaction wave passes, depending on the diffusion permeability of the metal and solubility conditions that obey Sieverts's law. The effect of the filtration supply of the oxidant to the reaction zone and the process exothermicity on the course of the process is shown.

Metal-oxidant interaction problems attract the attention of researchers involved in the development of SHS theory [1-4].

A porous specimen manufactured by compacting metal particles of a specified size is used as the object of study. Its porosity is assumed to be constant during the process. The specimen is placed in a gaseous atmosphere with the pressure kept constant. The reaction is initiated by the ignition temperature, kept constant at an end face of the specimen, which is substantially higher than the initial temperature of the metal and gas. As the gas was absorbed by the metal, the specimen formed low-pressure zones, to which gas was supplied by filtration through pores, following Darcy's law. In combustion theory heat release is usually modeled by a relation of the Arrhenius type, neglecting the gas dissolution mechanism in the metal. In this study emphasis is placed on processes occurring inside the particles compacted to form the specimen. It is assumed here that the specimen has a reinforced side surface, the metal particles are small, the compositional distribution of the phases is instantaneous, the gas redistribution inside the phases follows a diffusion law, the gas solubility on the particle surface is described by Sieverts's law, and gas outflow from the particle is impossible.

With the above assumptions in view, the process can be modeled by the following system of equations:

$$\frac{\partial}{\partial t}[(C_g\rho_g + C_k\rho_k)T] + \frac{\partial}{\partial x}(C_g\rho_g vT) = \frac{\partial}{\partial x}\left(\lambda\frac{\partial T}{\partial x}\right) -$$

$$-\sum_{\text{ph}} \frac{q_{\text{ph}}\rho_k^0}{R^{\nu+1}}(1-\eta)\frac{\partial r_{\text{ph}}^{\nu+1}}{\partial t} + \frac{\nu+1}{R}\, q_d\rho_k^0 D_R \left.\frac{\partial c}{\partial r}\right|_R - \alpha_T(T - T_N);$$

$$\frac{\partial\eta}{\partial t} = \frac{\nu+1}{R^{\nu+1}}\,\frac{1}{C_{\max} - C_N}\,\frac{\partial}{\partial t}\int_0^R c(r)\, r^\nu dr; \quad \rho_k = \rho_k^0 + \eta\rho_k^0\frac{\mu_g}{\mu_k};$$

$$\frac{\partial\rho_g}{\partial t} + \frac{\partial}{\partial x}(\rho_g v) = -\rho_k^0\frac{\mu_g}{\mu_k}\,\frac{\partial\eta}{\partial t}; \quad P = \frac{R_y\rho_g T}{\mu m_n};$$

$$v = -K_{\text{ph}}(\eta, T)\frac{\partial P}{\partial x}; \quad \frac{\partial c}{\partial t} = \frac{1}{r^\nu}\,\frac{\partial}{\partial r}\left(r^\nu D_{\text{ph}}\frac{\partial c}{\partial r}\right),$$

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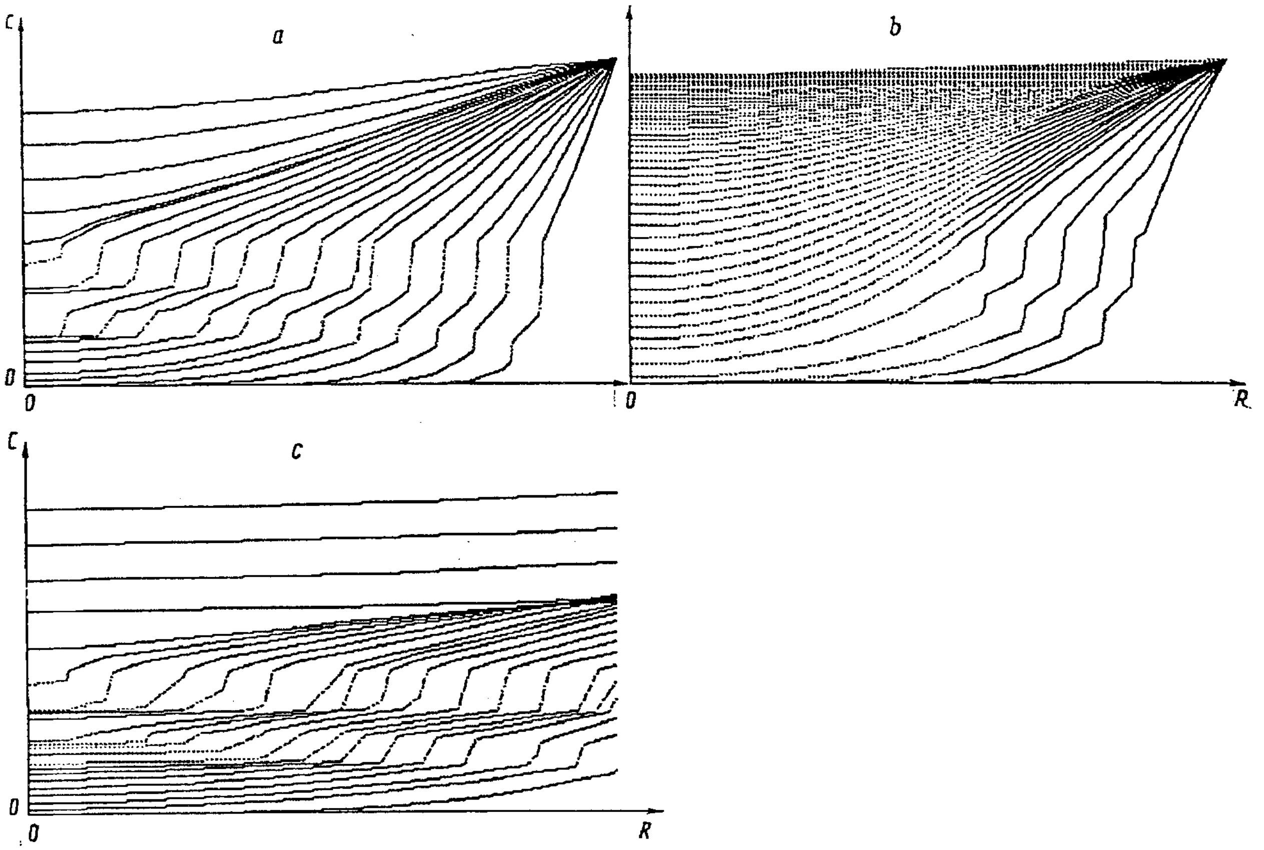

Fig. 1. Distribution of the oxidant concentration in a particle of radius R at successive moments of time (a variable time step): a) evolution of the phase composition of the particle; change of the sizes of the regions, in which the substance is present in the β-, $(\alpha + \beta)$-, α-, $(\alpha + \delta)$-, and δ-phases, respectively; b) the gas-metal interaction with formation of a liquid phase in the particle; the concentration graphs for the melt are shown by dotted lines; c) dissolution of the oxidant in the metal with a gas deficiency.

where x and r are the coordinates along the specimen and along the particle radius, respectively; t is the time; T is the temperature; v is the filtration rate; c is the concentration; P is the pressure; η is the transformation depth; ρ_g, ρ_k, and ρ_k^0 are the gas density, the k-phase density, and the initial k-phase density; λ is the effective thermal conductivity; D_{ph} and D_R are the diffusion coefficients in the phases and on the particle surface; ν is a geometrical factor; C_g and C_k are the heat capacities of the gas and the k-phase; R is the particle radius; R_y is the gas constant; c_N and c_{max} are the initial and admissible concentrations; m_n is the porosity; K_{ph} is the filtration coefficient; μ is the molecular weight of the gas; μ_g and μ_k are stoichiometric coefficients; α_T is a coefficient determining the heat loss level; q_{ph} and q_d are the heat effects of phase formation and dissolution per gram of condensed material. The initial pressure P_N, temperature T_N, transformation depth η_N, and ignition temperature T_{ig} are prescribed. Adiabaticity at the end faces of the specimen and the mass balance equation at the phase interfaces are used as boundary conditions.

The problem was solved in dimensional form. A mobile nonuniform computational net adapting to the solution was used along the x-axis. Along the radius of every particle a nonuniform scale was constructed, taking into consideration the phase structure of the material in this particle. Apart from the temperature distribution, pressure transformation depth, and phase radii along the specimen, information on the concentration and phase constitution of an individual particle at successive moments of time were input to a graph plotter. The diffusion coefficients of the intermediate phases $\alpha + \beta$ and $\alpha + \delta$ in the present calculations were assumed to be an order of magnitude smaller than those of the main phases β, α, and δ. In this case the concentration plot has a stepwise form, as shown in Fig. 1a. As the gas dissolves in the metal and the temperature increases, due to the process exothermicity near the particle surface the phases presented in the PCD appear successively, their interfaces being displaced toward the particle center with time in the course of dissolution of the gas in the metal. Microsections obtained after appropriate experiments show a similar pattern of dissolution of the gas in the metal [5]. Having passed the reaction front, the particle has a homogeneous phase composition since its whole volume is occupied by the δ-phase (Fig. 1a).

When the diffusion coefficient increases, dissolution of the gas in the metal follows the same law but occurs at a higher rate.

It is interesting to consider saturation of the metal with the gas, which is accompanied by a somewhat larger heat release than in the case shown in Fig. 1a. In this case, as the particle temperature rises, a meting zone appears at the particle center, since the metal with a lower concentration of gas dissolved in it melts at lower temperatures in accordance with the PCD. The melting zone in the particle enlarges with increase in temperature, but as the gas concentration increases, more refractory phases are developed, resulting in reduction of the melting zone (Fig. 1b). If the combustion temperature is lower than the melting point of the phase occupying the particle volume after passing the front, the whole particle will be crystallized, even though there are no heat losses.

When the process takes place at low gas pressures and with hindered filtration, the substance in the kinetic combustion zone may not be transformed completely. In Fig. 1c the concentration graphs for the moments of time, at which a particle remains in the kinetic combustion region have a stepwise shape. It should be emphasized that the increase in concentration on the particle surface is retarded (in accordance with Sieverts's law). Subsequently, as the gas is supplied by concurrent filtration (if the end face, on which the reaction is initiated, is open), transformation of the material takes place to full completion. Since the filtration rate in this case is less than the diffusion rate, the concentration is leveled throughout the particle volume (the particle is of single-phase composition).

The results of the present numerical analysis are in good agreement with experimental data.

REFERENCES

1. S. G. Vadchenko and Yu. M. Grigor'ev, Fiz. Met. Metalloved., **40**, No. 6, 1204-1209 (1975).
2. A. P. Aldushin, B. S. Seplyarskii, and K. G. Shkadinskii, Fiz. Goreniya Vzryva, **13**, No. 1, 36-45 (1980).
3. E. V. Okolovich, A. G. Merzhanov, B. I. Khaikin, and K. G. Shkadinskii, Fiz. Goreniya Vzryva, **13**, No. 3, 326-335 (1977).
4. V. K. Smolyakov, E. A. Nekrasov, and Yu. M. Maksimov, Fiz. Goreniya Vzryva, **20**, No. 2, 63-73 (1984).
5. Yu. V. Levinskii, P-T-x Constitution Diagrams of Two-Component Systems [in Russian], p. 112, Moscow (1982).