

**MATHEMATICAL MODELING  
OF FILM CHEMICAL REACTIONS  
OF CONDENSED-PHASE METAL OXIDES  
WITH THERMAL PROTECTIVE MATERIALS**

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A physicomathematical theory of the thermophysical processes of interaction of high-temperature two-phase flows with disintegrating (ablating) thermal protective materials (TPM) under the thermal, chemical, and mechanical action of particles of condensed-phase (c-phase) metal oxides has been developed in [1–5]. However, not all features of the action of the c-phase particles on ablating TPM have been adequately studied. This first of all concerns the mechanisms of zone and film chemical reactions, which does not allow the well-founded prediction of a number of possible anomalous operating conditions of power plants.

The aim of the present work is to mathematically model the film chemical reaction of particles of c-phase oxide metals that have been inertially precipitated from a high-temperature two-phase flow with carbon-graphite TPM.

The interaction of high-temperature two-phase flows with carbon-graphite TPM of multilayer walls in the vicinity of the frontal point of spreading of flat or blunt bodies at low collision velocities and substantial mass flows of inertially precipitated polydispersed liquid particles of the c-phase is examined. Under conditions of intense combined heating, a liquid c-phase film appears on the surface of carbon-graphite TPM. It is chemically active and enters into the reduction reaction with carbon, accompanied by the formation of condensed gaseous products. During the direct chemical reaction, the condensed components ensure wettability of the surface, while the gaseous products cool the melt layer by transpiration through it. The liquid c-phase film is an additional thermal resistance to the incident total heat flow, thus ensuring relatively low and moderate contact temperatures, and also has a damping effect through the impact of liquid particles. The liquid film thickness is determined by the competition of mass-transport processes: inertial precipitation of the c-phase particles, spreading and spraying of the melt, its dispersion (mechanical destruction during the transpiration of gaseous products), and suction due to the chemical reduction reaction.

A physical diagram of the direct chemical reaction of the melted c-phase metal oxides with carbon-graphite TPM of multilayer walls is shown in Fig. 1.

We introduce the following main assumptions concerning the mathematical modeling of the interaction of high-temperature two-phase flows with carbon-graphite TPM of multilayer walls by the mechanism of a direct film chemical reaction under conditions of inertial precipitation of polydispersed particles of the c-phase metal oxides in the vicinity of the frontal point of spreading.

1. The hydrodynamics and heat and mass transport in a relatively thin reacting film of the c-phase are described by a model of a laminar incompressible boundary layer of a two-phase, one-temperature, two-component "frozen" gas-liquid medium. The inertia and convective terms in the momentum equation are neglected. The dynamic viscosity coefficient of the liquid phase is assumed to be constant.

2. The ablation of the carbon-graphite TPM proceeds by an overall heterogeneous reduction reaction at the contact between the carbon and melted metal oxides, which is described by efficient kinetics and the

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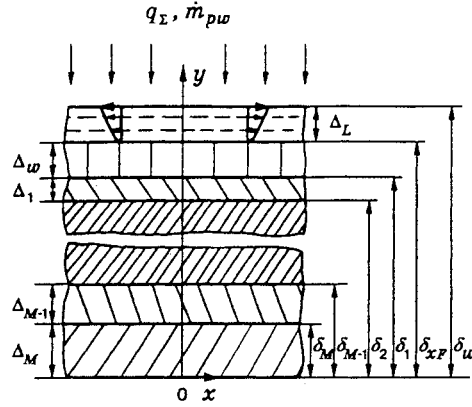
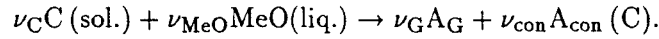


Fig. 1

stoichiometric equation



Here  $\nu_C$ ,  $\nu_{\text{MeO}}$ ,  $\nu_G$ ,  $\nu_{\text{con}}$  are the stoichiometric coefficients; MeO,  $A_G$ ,  $A_{\text{con}}$  are conventional chemical symbols for the metal oxides and the gaseous and condensed reaction products.

3. The gaseous product of the heterogeneous reduction reaction is free to pass through the liquid film of the c-phase predominantly in the normal direction. The volume gas content is considered a model parameter.

4. The problem of nonstationary heat conduction is solved in a one-dimensional approximation for a plane multilayer wall.

5. Conditions of perfect thermal contact between layers of different materials and the liquid melt of the c-phase are satisfied.

6. The size distribution of the c-phase particles is approximated by a distribution of particles in a finite number of groups, each containing particles of the same size.

In accordance with the above assumptions, the nonstationary equations of heat and mass transport in the direct film chemical reaction of the melted c-phase metal oxides with carbon-graphite TPM of multilayer walls in the vicinity of the frontal point of spreading have the form (see Fig. 1)

$$(1 - \Phi) \rho_L c_L \left( \frac{\partial T}{\partial t} + v_L \frac{\partial T}{\partial y} \right) = \frac{\partial}{\partial y} \left( \lambda_\Sigma \frac{\partial T}{\partial y} \right) - \dot{m}_G c_{pG} \frac{\partial T}{\partial y}, \quad \delta_{xF}(t) < y < \delta_{xF}(t) + \Delta_L, \quad t > 0; \quad (1)$$

$$(\rho c)_{\text{cgm}} \frac{\partial T}{\partial t} = \frac{\partial}{\partial y} \left( \lambda_{\text{cgm}} \frac{\partial T}{\partial y} \right), \quad \delta_1 < y < \delta_{xF}(t), \quad t > 0; \quad (2)$$

$$(\rho c)_m \frac{\partial T}{\partial t} = \frac{\partial}{\partial y} \left( \lambda_m \frac{\partial T}{\partial y} \right), \quad \delta_{m+1} < y < \delta_m, \quad t > 0, \quad m = \overline{1, M}, \quad (3)$$

where  $v_L$  is the normal component of the liquid film velocity;  $\rho_L$  is the density of the liquid phase;  $T$  is temperature;  $\Phi$  is the volume part of the gaseous phase;  $\dot{m}_G$  is the mass velocity of transpiration of the gaseous phase;  $\mu$  is the dynamic viscosity coefficient;  $\rho$  is the density;  $c$  is the specific heat;  $\lambda$  is the thermal conductivity;  $t$  is time;  $M$  is the number of different materials of the multilayer wall; subscripts  $L$ ,  $G$ ,  $\Sigma$ ,  $\text{cgm}$ ,  $m$  refer to the liquid and gaseous phases and the effective characteristics of the gas-liquid mixture, carbon-graphite TPM, and different materials of the multilayer wall, respectively.

Nonlinear system of Eqs. (1)–(3) is solved in an inertial (stationary) system of coordinates subject to the following boundary conditions on the free surface of the liquid film of the c-phase  $y = \delta_w(t)$ , at the front of film thermochemical destruction  $y = \delta_{xF}(t)$  at the contacts, and on the outer surface of the multilayer wall:

$$\begin{aligned}
\lambda_{\Sigma} \frac{\partial T}{\partial y} \Big|_{\delta_w-0} + \dot{m}_G h_w &= q_{\Sigma} + \dot{m}_G h_G, & \lambda_{\Sigma} \frac{\partial T}{\partial y} \Big|_{\delta_{xF}+0} &= \lambda_{cgm} \frac{\partial T}{\partial y} \Big|_{\delta_{xF}-0} + \dot{m}_{xF} \Delta H_{xF}, \\
T|_{\delta_{xF}+0} &= T|_{\delta_{xF}-0} = T_{\text{con}}(t), & \lambda_{cgm} \frac{\partial T}{\partial y} \Big|_{\delta_1+0} &= \lambda_1 \frac{\partial T}{\partial y} \Big|_{\delta_1-0}, \\
T|_{\delta_1+0} &= T|_{\delta_1-0} = T_{\text{con},1}(t), & \lambda_m \frac{\partial T}{\partial y} \Big|_{\delta_{m+1}+0} &= \lambda_{m+1} \frac{\partial T}{\partial y} \Big|_{\delta_{m+1}-0}, \\
T|_{\delta_{m+1}+0} &= T|_{\delta_{m+1}-0} = T_{\text{con},m+1}(t), & \lambda_M \frac{\partial T}{\partial y} \Big|_{+0} &= q_M, \quad m = \overline{1, M-1}, \quad M > 1.
\end{aligned} \tag{4}$$

Here  $q_{\Sigma}$  is the total heat flux;  $h$  is the enthalpy;  $\dot{m}_{xF}$ ,  $\Delta H_{xF}$  is the mass velocity and specific heat release of the direct film chemical reaction;  $q_M$  is the total heat flux on the outer surface of the multilayer wall; subscripts  $w$  and  $c$  refer to the interface and conditions at the contacts, including the front of the film thermochemical destruction.

The following initial conditions at  $t = 0$  are set:

$$T = T_{L,0}, \quad \delta_0 \leq y \leq \delta_{w,0}, \quad T = T_{\text{in}}, \quad 0 \leq y < \delta_0, \tag{5}$$

where  $T_{L,0}$  is the initial temperature of the liquid c-phase layer;  $T_{\text{in}}$  is the initial temperature of the carbon-graphite TPM and of the multilayer wall;  $\delta_{w,0}$  is the initial position of the liquid c-phase layer.

The components of the velocity of the gas-liquid c-phase film in the vicinity of the frontal point of spreading can be represented as

$$\begin{aligned}
u_L &= \frac{\tau_{\Sigma} \Delta_L \eta_L}{(1-\Phi) \mu_{\Sigma}} - \frac{\Delta_L^2}{\mu_{\Sigma}} \frac{dP_e}{dx} \left( \eta_L - \frac{\eta_L^2}{2} \right), \quad 0 < \eta_L < 1, \\
v_L &= v_{L,\text{con}} - \Delta_L \left[ \frac{\Delta_L^2}{\mu_{\Sigma}} \left( \eta_L^2 - \frac{\eta_L^3}{3} \right) C_1 + \frac{\Delta_L \eta_L^2 C_2}{(1-\Phi) \mu_{\Sigma}} \right], \\
C_1 &= \rho_{\infty} \left( \frac{du_e}{dx} \right)_s^2, \quad C_2 = \rho_{\infty} V_{\infty} \text{St} \left( \frac{du_e}{dx} \right)_s \text{Pr}^{2/3}, \quad \eta_L = \frac{y - \delta_{xF}(t)}{\Delta_L}.
\end{aligned} \tag{6}$$

Here  $u_L$  is the longitudinal component of the velocity of the liquid film;  $(dP_e/dx)_s$  and  $(du_e/dx)_s$  are the pressure and velocity gradients of nonviscous flow in the vicinity of the frontal point of spreading;  $\rho_{\infty}$  and  $V_{\infty}$  are the density and velocity of the incoming flow;  $\text{St}$  is the Stanton number;  $\text{Pr}$  is the Prandtl number.

The mass velocity of transpiration of the gaseous phase through the liquid c-phase film is determined by the relationship

$$\dot{m}_G = \left( \frac{\nu_G m_{AG}}{\nu_C m_C} \right) \dot{m}_{xF} \tag{7}$$

where  $m$  is the molecular mass.

Closing relationships determining the current position of the front of the film thermochemical destruction and the thickness of the reacting gas-liquid c-phase film are necessary for practical use of the above mathematical model (1)-(7).

The linear velocity and current position of the front of the film thermochemical destruction of carbon-graphite TPM are found from the relationships

$$\frac{d\delta_{xF}}{dt} = -\frac{\dot{m}_{xF}}{\rho_{cgm}}, \quad \delta_{xF}(t) = \delta_0 - \int_0^t \frac{\dot{m}_{xF}}{\rho_{cgm}} dt. \tag{8}$$

The current thickness of gas-liquid the c-phase film in the case of an axisymmetrical flow in the vicinity

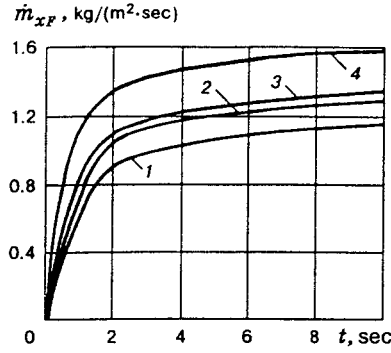


Fig. 2

of the frontal point of spreading is found from the solution of the macroscopic mass balance equation

$$\frac{d\Delta_L}{dt} + \left( \frac{2\Delta_L^3}{3\mu_\Sigma} \right) C_1 + \frac{\Delta_L^2 C_2}{(1-\Phi)\mu_\Sigma} = \frac{1}{(1-\Phi)\rho_L} \left[ \sum_j \dot{m}_{pw,j} (1 - G_{sh}) - \left( \frac{\nu_{MeO} m_{MeO}}{\nu_C m_C} \right) \dot{m}_{xF} - \dot{m}_d \right], \quad \Delta_L(0) = \Delta_{L,0}, \quad (9)$$

where  $\Delta_L$ ,  $\Delta_{L,0}$  are the current and the initial thickness of the film;  $\dot{m}_{pw,j}$  is the mass flow of the inertially precipitating liquid c-phase particles of the  $j$ th fraction ( $j = \overline{1, N_{pw}}$ );  $N_{pw}$  is the number of fractions of the polydispersed c-phase particles.

The mass velocity of the film thermochemical destruction of the carbon-graphite TPM under continuous contact with the melted metal oxides is determined by a zeroth-order kinetic equation of the chemical reaction in the form of the Arrhenius law

$$\dot{m}_{xF} = k_{xF} P_{con}^{\omega_1} T_{con}^{-\omega_2} \exp\left(-\frac{E_{xF}}{RT_{con}}\right). \quad (10)$$

Here  $k_{xF}$ ,  $E_{xF}$  are the effective thermokinetic constants of the direct film chemical reaction, which are to be found from agreement of (10) with experimental data;  $\omega_1$  and  $\omega_2$  are constants.

The mass velocity of mechanical removal of the liquid c-phase film due to splashing by incident particles (the process of collisional removal of sprays [6]) has the form

$$\dot{m}_{sh} = G_{sh} \sum_j \dot{m}_{pw,j}, \quad (11)$$

where  $G_{sh}$  is the coefficient of spraying intensity [7].

The mass velocity of mechanical removal of the liquid c-phase film due to dispersion during transpiration of the gaseous products of the heterogeneous reduction reaction (bubble removal of sprays [6]) is determined from the formula

$$\dot{m}_d = G_d \dot{m}_G \quad (12)$$

where  $G_d$  is the coefficient of dispersion intensity.

Thus, the new mathematical model (1)–(12) makes it possible to find the most important hydrodynamic and thermophysical parameters of the interaction of high-temperature two-phase flows with carbon-graphite TPM of multilayer walls by the mechanism of a direct film chemical reaction under conditions of inertial precipitation of polydispersed c-phase oxide metal particles in the vicinity of the frontal point of spreading.

Using the computer program ACMAG developed on the basis of [8], which implements model (1)–(12), we carried out a numerical study of the direct film chemical reaction of the gas-liquid c-phase film of aluminum oxide with graphite. The following input parameters were used:  $P_\infty = 4.0$  MPa,  $T_\infty = 3,260$  K,  $V_\infty = 200$  m/sec,  $(du_e/dx)_s = 2.35 \cdot 10^4$  1/sec,  $\rho_\infty V_\infty St_0 = 2.27$  kg/(m<sup>2</sup> · sec),  $Pr = 0.72$ ,  $\rho_L = 2,400$  kg/m<sup>3</sup>,  $\mu_L = 0.02$  Pa · sec,  $\Phi = 0.3$ ,  $G_{sh} = 0.32$ ,  $\Delta_0 = 4 \cdot 10^{-2}$  m,  $T_{in} = 300$  K,  $q_M = 0$ ,  $t_d = 10$  sec.

The mass velocity of the film chemical reaction versus different model parameters is plotted in Fig. 2,

where curve 1 is a reference calculation, curve 2 is for a dynamic viscosity coefficient of 0.01 Pa · sec, curve 3 is without considering the gaseous phase, and curve 4 is without splashing. The most important parameter is the coefficient of spraying intensity, whose value is known with great uncertainty. Neglect of the splashing, which cools the gas-liquid c-phase film, increases the mass velocity of the film chemical reaction by 37% due to more intense heat supply to the front of thermochemical destruction despite a small increase in  $\Delta_L$  and  $\dot{m}_G$ .

The resulting strong relationship  $\dot{m}_{xF} = \dot{m}_{xF}(G_{sh})$  obtained from the numerical calculations reflects indirectly the effect of the velocity of the incoming two-phase flow on the mechanism of the film chemical reaction, whereas in the drop chemical reaction this relationship is explicit [2, 3]. Neglect of the effect of the gaseous phase on changes in the physical parameters and also of its convection in the liquid layer produces an approximately 16% increase in the temperature  $T_{con}$  and the mass velocity of the film chemical reaction with a decrease in the value of  $\Delta_L$ . A two-fold decrease in the dynamic viscosity coefficient of liquid aluminum leads to a marked (by 30%) thinning of the gas-liquid c-phase film and a 11% increase in  $\dot{m}_{xF}$ . A change in the gas content from  $\Phi = 0.3$  to  $\Phi = 0.15$  produces a slight increase in  $\dot{m}_{xF}$  (by 4.4%) due to a decrease in the film thickness. An increase in the dispersion coefficient of the gas-liquid c-phase film from  $G_d = 0$  to  $G_d = 1.0$  during transpiration of gaseous products has an effect on the mass velocity  $\dot{m}_{xF}$  only up to 3%, which is accounted for by the minor role of this mechanism of ablation.

Thus, the above numerical study revealed the main parameters that have an effect on the film chemical reaction of the c-phase metal oxide particles that have been inertially precipitated from a high-temperature two-phase flow with carbon-graphite TPM.

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