Journal of Applied Mechanics and Technical Physics, Vol. 40, No. 3, 1999

CONDITIONS OF BUBBLE FORMATION IN THE INTERGRANULAR LAYER OF A GLASS PHASE IN CERAMICS SINTERING

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UDC 536.421.5:539.4

Calculation results for the evolution of the gas-concentration distribution in the intergranular layer of a glass phase cooling from the sintering temperature to room temperature are presented. The calculations are performed for two stages of cooling of the glass phase. The calculation results suggest that gas dissolution in the intergranular layer of the glass phase leads to substantial softening of the conditions of bubble formation in it, and the second (low-temperature) stage of cooling makes a major contribution to the saturation of the glass phase with the gas.

1. The microstructure of ceramic specimens is an ensemble of randomly oriented crystal grains, pores, and a thin film of a glass phase between them, which is subjected to cracking in places [1, 2]. This ceramic microstructure is formed during preparation of specimens at high temperatures, and it is almost unchanged at room temperature because ceramic specimens practically do not undergo plastic deformation while in service. Thus, the problem of optimizing the microstructure of ceramics at the stage of manufacture (sintering) becomes especially pressing. This problem can be solved by numerical simulation, which allows one to study the influence of numerous factors on the strength properties of ceramics [3–6] in detail. In the present paper, of the variety of phenomena related to sintering of ceramics, we consider only the problem of formation of discontinuities (bubbles) in the liquid phase filling the space between ceramic-powder grains at high temperature.

In the sintering of ceramics, a liquid phase can appear at the melting point of the low-melting component or as a result of contact melting [7]. It can also be formed by addition of glass-forming components into the mixture prior to sintering [8]. Lange [9] was the first to study the role of the liquid phase as an adhesive film at the boundary between ceramic grains. Under the action of negative pressure p (i.e., tension), the liquid is metastable. Gas bubbles form in it and grow until failure of the liquid [10–12]. Lange [9] estimated the condition of athermic origin of bubbles and obtained a value of $p_c = 60$ MPa for the minimum tensile stress. Marion et al. [13] and Rodin [14] studied the factors responsible for the origin of tensile stresses in the intergranular layer. Slavyanskii [15, 16] examined the influence of the gas dissolved in glass on the conditions of gas-bubble formation in it.

We study the origin of bubbles in a gas-saturated viscous liquid. Under these conditions, the critical tension of the liquid p in which a gas bubble of radius r_c forms and the maximum free energy $F_{\max}$ of the liquid with the gas bubble are defined by

$$p = 2\gamma_l/r_c - p', \qquad F_{\max} = 16\pi\gamma_l^3/3(p + p')^2, \tag{1.1}$$

where γ_l is the specific surface energy of the glass phase, $p' = k_{\rm B}TN\ln[c/c_{0s}]$ [17], N is the number of possible positions of gas atoms in a unit volume of the glass phase, T is the temperature, $k_{\rm B}$ is the Boltzmann constant, c_{0s} is the equilibrium concentration of the dissolved gas, defined by Henry's law [18], and $c_{0s} = \Gamma p_0$ (Γ is Henry's constant and p_0 is the gas pressure in the ambient medium). At $T = 1470$ K, $N = 10^{29}$ m^{-3}, and

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Translated from Prikladnaya Mekhanika i Tekhnicheskaya Fizika, Vol. 40, No. 3, pp. 175–181, May–June, 1999. Original article submitted February 7, 1997; revision submitted July 3, 1997.

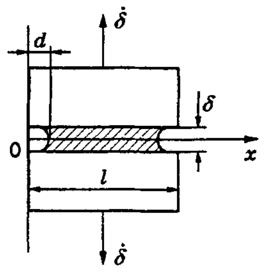

Fig. 1

$c/c_{0s} = 1.01$, p' is estimated as $p' = 20$ MPa. Then, from (1.1) it follows that the external tensile stress p decreases considerably when a critical bubble originates. For the indicated estimates, of importance is the mechanism whereby the glass-phase layer is saturated with the gas during sintering to a magnitude at which the value of p' has a marked influence on the conditions of bubble formation. In this connection, it is reasonable to study the influence of gas dissolution in the glass phase on bubble formation.

2. We study the evolution of the concentration distribution of the gas dissolved c in the glass-phase layer that separates a pair of ceramic grains under tensile loading across the intergranular boundary (Fig. 1). The calculations are based on the following model:

1) The pair of grains cools from high temperature to room temperature as a result of heat removal from the lateral faces of the grains and the glass-phase layer;

2) The divergence $\delta(t)$ of the pair of grains proceeds perpendicular to the layer;

3) The layer thickness δ varies as a result of leak-in of the viscous liquid at high temperature ($T >$ 1000 K);

4) The evolution of the concentration of the gas dissolved in the glass phase c is caused by sorption processes on the surface of menisci of the glass phase and diffusion of the dissolved gas into the layer;

5) At $T < 1000$ K (up to room temperature), the glass phase is regarded as a viscoelastic layer between immovable grains and the gas diffusion in it is due to internal stresses developing because of the difference in the thermal-expansion coefficients between the solidified and liquid phases.

We first consider the gas dissolution in the glass-phase layer of the specimen at high temperatures $T > 1000$ K, at which the glass phase can be considered a viscous liquid. The equilibrium pressure distribution $p(x)$ in the glass phase along the boundary between the pair of grains is defined by [13]

$$p(x) = 6\eta(T)\dot{\delta}/\delta^3[d^2 - x^2 + l(x - d)] + \gamma_l/\delta, \tag{2.1}$$

where d is the distance from the coordinate origin to the meniscus surface. The viscosity $\eta(T)$ of the glass phase is calculated (in pascal-seconds) by the Tamman–Fulcher formula [19, 20]

$$\log(\eta(T)) = A + \frac{B}{T - T_g}. \tag{2.2}$$

In (2.1), (2.2), $A = -2.78$, $B = 5574$ K, $T_g = 500$ K, $\delta(t)$ is the thickness of the glass-phase layer, $\dot{\delta}$ is the rate of change of δ, and l is the grain size.

We calculate the gas diffusion in this layer taking into account the pressure distribution in it $p(x)$. The equation for the thermomechanical diffusion of the gas (the Konobeevskii–Gorskii effect) [21] along the layer has the form

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\Big(\frac{Dc}{k_{\rm B}T}\,\frac{\partial \mu}{\partial x}\Big), \tag{2.3}$$

where the chemical potential of a weak solution of the gas $\mu = k_{\rm B}T(x,t)\ln(c/c_{0s}) - \Omega p(x,t)$ $(\Omega = N^{-1})$, $D(T) = D_0 T \exp\left[-E_D/(RT)\right]$ is the diffusivity of the gas in the viscous liquid (D_0 is a constant), E_D is the activation energy of diffusion, and R is the gas constant. The form of $D(T)$ is chosen according to [22] for the

B_2O_3 glass melt. The initial condition for (2.3) is $c(x,0) = c_{0s}$, and the boundary conditions have the form [18]

$$-D\frac{\partial c}{\partial x} = h(c^2 - c_{0s}) \quad \text{for} \quad x = d,\ x = l - d, \tag{2.4}$$

where h is the constant of mass exchange for the gas on the surfaces of menisci. The temperature distribution $T(x,t)$ along the glass-phase layer is determined from the heat-conduction equation

$$\frac{\partial T}{\partial t} = a\frac{\partial^2 T}{\partial x^2}, \tag{2.5}$$

where a is the thermal diffusivity of the glass. The initial condition for (2.5) is $T(x,t) = T_{\max}$, and the boundary conditions at $x = d$ and $x = l - d$ are given by

$$-\lambda\frac{\partial T}{\partial x} = \alpha(T - T_0), \tag{2.6}$$

where λ is the thermal conductivity of the glass phase, α is the constant of heat exchange of the layer with the ambient medium, and T_0 is the ambient temperature. Reducing (2.3)–(2.6) to dimensionless form, we obtain the system

$$\Delta_0\frac{\partial c'}{\partial t'} = \frac{\partial^2 c'}{\partial x'^2} - \frac{\Delta_1}{k_{\rm B}T}\Big[(1 - 2x')\frac{\partial c'}{\partial x'} - 2c'\Big], \qquad \Delta_2\frac{\partial T}{\partial t'} = \Delta_3\frac{\partial^2 T}{\partial x'^2}, \tag{2.7}$$

with the boundary and initial conditions

$$\frac{\partial c'}{\partial x'} = \Delta_4(c' - 1), \qquad \frac{\partial T}{\partial x'} = \Delta_5(T - T_0)$$

at $x' = 0.1$, $c'(x',0) = 1$, and $, T(x',0) = T_{\max}$.

In (2.7), we have $c'(x',t') = c(x',t')/c_{0s}$, $x' = (x-d)/(l-2d)$, $t' = D_0T_0t/(l-2d_0)^2$, $\Delta_2 = (\delta_0/\delta)^2$, $\Delta_0 = (\delta_0/\delta)^2(T_0/T)\exp[E_D/(RT)]$, $\Delta_1 = 6\Omega\eta(T)(\dot{\delta}/\delta^3)D_0T_0(\delta_0/\delta)^2$, $\Delta_3 = a/(D_0T)$, $\Delta_4 = -h(l - 2d_0)\delta_0/(D_0\delta)$, and $\Delta_5 = -\alpha(l-2d_0)\delta_0/(\lambda\delta)$. In the derivation of (2.7), it was assumed that the glass phase is incompressible. Then, the quantities $d(t)$ and $\delta(t)$ are related by $\delta(l-2d) = \delta_0(l-2d_0)$, where δ_0 and d_0 are the initial values of these quantities. System (2.7) was solved numerically, and the nonlinear boundary conditions (2.4), which correspond to dissolution of diatomic gases, were linearized according to [18].

The calculations for B_2O_3 glass melt were performed for the following values of the constants: $a = 3 \cdot 10^{-7}$ m^2/sec, $\lambda = 0.84$ W/(m $\cdot$ K) [22]; $\alpha = 600$ W/(m^2 $\cdot$ K), $R = 8.3$ J/(mole $\cdot$ K), $T_0 = 300$ K, $T_{\max} = 1500$ K, $\Omega = 10^{-29}$ m^3, $D_0 = 9.3\cdot 10^{-11}$ m^2/(sec $\cdot$ K), $E_D = 20$ kJ/mole [22], $l = 10^{-6}$ m, $\delta_0 = 10^{-8}$ m, and $d_0 = 0$. The divergence of the pair of grains is given by $\delta(t) = \dot{\delta}t + \delta_0$, where $\dot{\delta}/\delta = 10^{-5}$ sec^{-1} or, in dimensionless form, $\delta = [(l - 2d_0)^2/(D_0T_0)]\dot{\delta}t' + \delta_0$.

3. We now study the gas dissolution in the glass phase at $T < 1000$ K, at which the glass phase has the properties of a viscoelastic body. In this case, problem (2.3)–(2.6) is solved with allowance for the dilatation stress field $p(x,t)$, which arises when a layer of the glass-forming melt of thickness δ cools from the initial temperature $T(x,0) = 1000$ K to room temperature. According to [19], we regard the thermomechanical state of the cooling glass melt as a simple thermorheological material; its behavior is described using the notions of thermoviscoelasticity theory — the reduced time $\zeta(x,t)$ and fictitious temperature $T_f(x,t)$. These quantities are given by the formulas [19]

$$T_f(x,t) = T(x,t) - \int_0^t \exp[\zeta(x,t) - \zeta(x,t')]^{0,68}\, dT(x,t'), \quad \zeta(x,t) = \int_0^t \Big[\frac{\eta_{ref}}{\eta(x,t')}\Big]\, dt', \tag{3.1}$$

were η and η_{ref} are the real viscosity of the glass-phase layer and reference viscosity [19, 20, 23]. The initial time is the moment the layer reaches the temperature $T = 1000$ K. The thermal strain of the layer at time t is given by

$$\varepsilon_t(x,t) = \beta_g[T(x,t) - 1000] + \beta_s[T_f(x,t) - 1000],$$

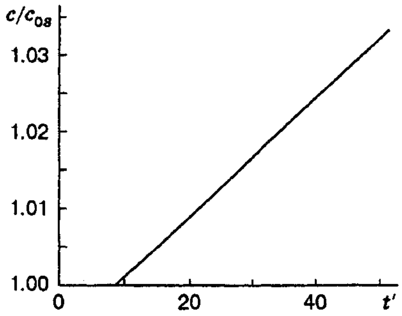

Fig. 2

where β_g and β_s are the thermal-expansion coefficients in the glass and liquid states. Similarly to [23], the relaxation function has the form

$$R(x,t,t') = \exp\left[(\zeta(x,t) - \zeta(x,t'))/\tau_\sigma\right]^{0.68} \tag{3.2}$$

($\tau_\sigma = 1$ at $T \geqslant T_g$ and $\tau_\sigma = \infty$ at $T < T_g$). The temperature stresses in the cooling viscoelastic layer with free boundaries satisfy the conditions

$$\sigma_x = 0, \qquad \sigma_z = \sigma_y = p(x,t), \qquad \int\limits_d^{l-d} p(x,t)\,dx = 0, \tag{3.3}$$

where

$$p(x,t) = \int\limits_0^t R[\zeta(t) - \zeta(t')] \frac{\partial \sigma_*(x,t')}{\partial t'}\,dt', \qquad \sigma_*(x,t) = E/(1-\nu)[\varepsilon(t) - \varepsilon_t(x,t)],$$

[$\varepsilon(t)$ is the instantaneous strain of the layer].

The values of $p(x,t)$ are calculated by the procedure of [23] using formulas (3.1)–(3.3) for $\beta_g = 1.44 \cdot 10^{-5}$ K^{-1}, $\beta_s = 21 \cdot 10^{-5}$ K^{-1}, $E = 7 \cdot 10^4$ MPa, $\nu = 0.3$ for B_2O_3 glass melt. Substituting the internal stresses $p(x,t)$ into (2.3), we obtain the evolution of the concentration distribution of the gas dissolved in the viscoelastic layer of the glass phase. In the calculation, we take into account the stress and concentration of the dissolved gas that have been previously accumulated in the intergranular layer (at $T > 1000$ K).

The results of the calculations of the formation of internal thermal stresses in the cooling viscoelastic glass phase show that in the initial stage of cooling, the stresses distributed on a parabola grow, but further cooling leads to "overturning" of the parabola (the sign of stresses in the outer and middle regions of the layers is reversed). In the viscoelastic layer, in contrast to the thermoelastic layer, complete cooling gives rise to residual stresses: the outer regions of the layer are compressed and the inner regions are extended. Therefore, one should expect penetration of the dissolved gas into the depth of the cooling viscoelastic layer. In this case, the action of mechanical stresses can be imagined as a "pump" that distributes the gas over the entire depth of the glass-phase layer.

4. We now discuss the results of the calculations performed. Over the period of cooling of the intergranular layer, the gas is redistributed along the intergranular layer of the glass phase. In the first stage of cooling from 1500 to 1000 K, the dissolved-gas concentration is accumulated nonuniformly along the layer. For the chosen values of the parameters, the maximum value of $c'_{\max}$ reaches 1.007. Further cooling of the glass-phase layer gives rise to internal thermal stress gradients that compensate the decrease in the diffusivity $D(T)$ and are responsible for an increase in $c'_{\max}$ to 1.035 (Fig. 2). The calculation results obtained can be used to determine the concentration of critical nuclei of gas bubbles in the glass phase as a function of time t:

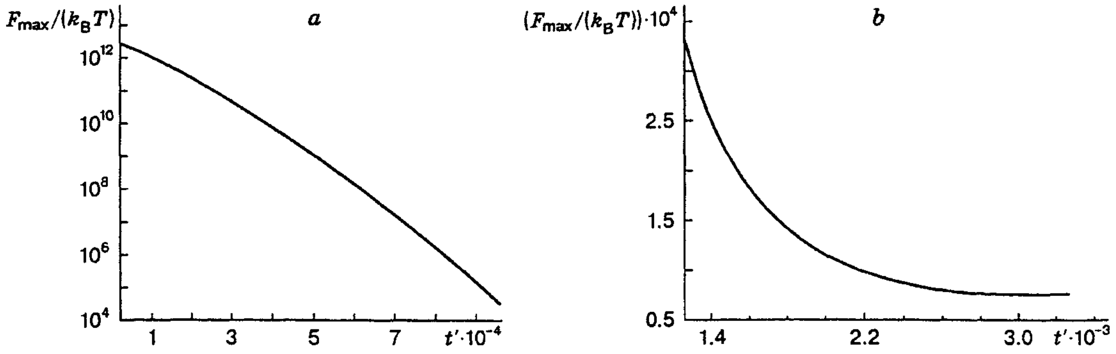

Fig. 3

$$c^*(x,t) = N\exp\left[-F_{\max}/(k_BT)\right]$$

[$F_{\max}$ is given in (1.1)]. The evolution of c^* in the intervals $10^{-4} \leqslant t' \leqslant 10^{-3}$ and $10^{-3} \leqslant t' \leqslant 10^{-2}$ is shown in Fig. 3a and Fig. 3b, respectively. These calculation results indicate that the height of the energy activation barrier for bubble formation $F_{\max}$ decreases extremely rapidly with time as the dissolved-gas concentration increases. In the calculation, the normal atmospheric ambient gas pressure $p_0 = 0.1$ MPa was assumed. Strictly speaking, in the calculations the dependence of Henry's constant (Γ) and the diffusivity (D) on the stress state of the intergranular layer of the glass phase was ignored. However, insufficient experimental data for the chosen glass melt over a wide temperature range [22] does not permit this dependence to be taken into account. The data available in [22] on the effect of mechanical stresses on the gas saturation of glass melts indicate that D increases markedly in a tensile stress field and decreases under compressing stresses. In the calculations performed, we ignored the dependences of γ_l on the temperature and concentration of the dissolved gas.

The main conclusions of this work are as follows:

1. Gas dissolution in the intergranular layer of the glass phase facilitates bubble formation in it.
2. The second (low-temperature) stage makes a major contribution to the saturation of the glass phase with the gas.

This work was supported by a grant from the Competitive Center on Fundamental Natural Sciences of St. Petersburg University.

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