DETERMINATION OF THE DISSIPATIVE EFFECTS DURING SINTER TREATMENT OF CERAMICS

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The feasibility is established here of analyzing and describing the sinter treatment of ceramics by solving the differential equations of heat and mass transfer on the basis of nonequilibrium thermodynamics.

According to the results obtained in earlier experimental studies of sinter processes in the ceramic industry, the interdependent processes of heat and mass transfer during phase transformations and chemical conversions can be described by the equations of nonequilibrium thermodynamics.

The thermodynamic concept of heat dQ supplied to the sensible phase in a given system during an infinitesimally small change of state is an appropriate one to use for describing the energy balance as follows:

$$dQ = du + PdV - dW_{\text{diss}} - \sum_k H_k d_a n_k. \tag{1}$$

Quite evidently, according to Eq. (1), the external heat supplied to the sensible phase during an infinitesimally small change of state is subsequently expended on a change in the internal energy (du), on mechanical work (PdV), on dissipative effects of molecular friction (dW_{diss}), and on chemical reactions (also on heating as a result of mass transfer: $\sum\limits_k H_k d_a n_k$, with H_k denoting the partial molar enthalpy of the given substance (k) and n_k denoting the number of moles of substance (k) produced by mass transfer to the ambient medium).

The mass balance in this case is described by the following equation:

$$dn_k = d_a n_k + \sum_r V_{k,r} d\xi_r, \tag{2}$$

with dn_k denoting the total change in moles of substance (k), $d_a n_k$ denoting the change in moles of substance (k) due to mass transfer to the ambient medium, $\sum\limits_r V_{k,r} d\xi_r$ denoting the change in moles due to chemical reactions, $V_{k,r}$ denoting the stoichiometric factor for substance (k) in the chemical reaction (r), and ξ denoting the degree of completion of the chemical reaction (r).

The classical Gibbs equation, which describes the total differential change in entropy within one region of a variable-mass and variable-composition body

$$TdS = du + PdV - \sum_k \mu_k dn_k, \tag{3}$$

is known to apply equally well to systems isolated from the amibent medium and systems in contact with it, inasmuch as a change in moles of a substance is affected by a chemical reaction within such a region as well as by mass transfer to the ambient medium.

Combining Eqs. (1)-(3) and introducing the chemical potential for the case of isobaric-isothermal coupling

$$\mu_k = H_k - T \cdot S_k,$$

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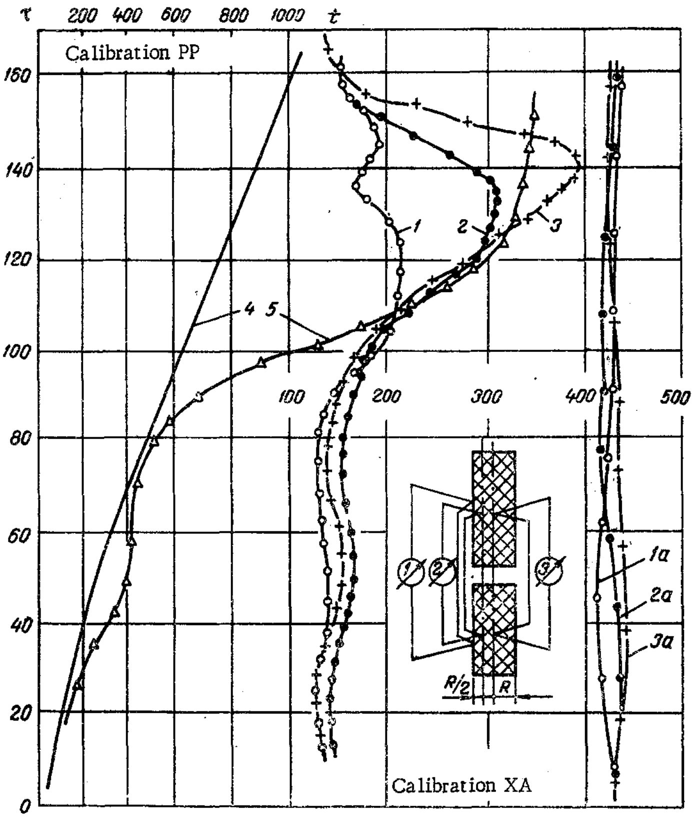

Fig. 1. Thermogram of the heating process, for two test specimens of kaolin: one presintered (curves 1a, 2a, 3a) and one unsintered (curves 1, 2, 3), plotted from the readings of three differential thermocouples; 4) oven heating-rate curve, 5) specimen loss-of-weight curve; temperature t (°C), time τ (min).

we obtain the following equation to describe the process

$$TdS = dQ + T\sum_k S_k d_a n_k + dW_{\text{diss}} + \sum_r A_r d\xi_r, \tag{4}$$

with $A_r = -\sum_r V_{k,r}\mu_r$ denoting the affinity of reaction (r).

Dividing all terms in (4) by T will yield the entropy equation for this process

$$dS = \frac{dQ}{T} + \Sigma S_k d_a n_k + \frac{1}{T}\, dW_{\text{diss}} + \frac{1}{T}\sum_r A_r d\xi_r. \tag{5}$$

Considering Eq. (5) and taking into account the additivity property of entropy, we arrive at important results which allow us to determine the entropy of dissipation:

$$dS_{\text{diss}} = \frac{1}{T}\, dW_{\text{diss}} \tag{6}$$

as well as the entropy of chemical reactions within the system

$$dS_r = \frac{1}{T}\, \Sigma A_r d\xi_r. \tag{7}$$

In order to demonstrate the gist of the problem more precisely, we will determine the entropy of a process in two specific cases.

In the first case the entropy is determined from test values of the specific heat of a sintered ceramic specimen, in the second case the entropy is determined from the effective thermal characteristics of the sinter treatment of a molded (clay) specimen.

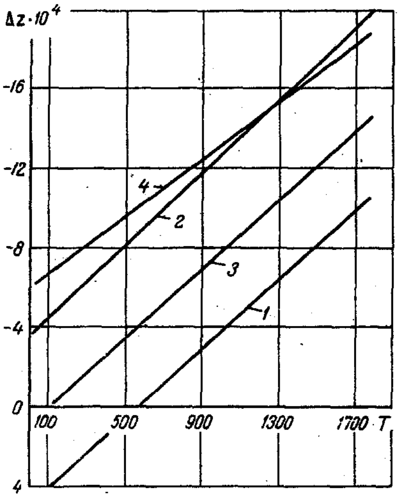

Fig. 2

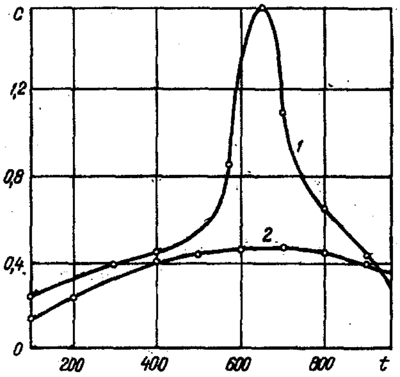

Fig. 3

Fig. 2. Isobaric-isothermal potential of decomposition reactions during heating of kaolinite, as a function of the temperature: 1) $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O = Al_2O_3 \cdot 2SiO_2 + 2H_2O$, 2) $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O = Al_2O_3 \cdot SiO_2 + SiO_2 + 2H_2O$, 3) $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O = Al_2O_3 + 2SiO_2 + 2H_2O$, 4) $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O = 1/3(3Al_2O_3 \cdot 2SiO_2) + 4/3SiO_2 + 2H_2O$; temperature T(°K); potential Δz (cal/mole).

Fig. 3. Specific heat of kaolin C (kcal/kg·°C) as a function of the temperature t(°C), based on test values: 1) effective specific heat during the sinter treatment, 2) specific heat of a sintered specimen.

In the first case there occurs no chemical reaction during the heating of a sintered specimen and, consequently, all except the first term on the right-hand side of Eq. (5) are equal to zero.

In the second case, where raw clay is sintered, all terms will appear in Eq. (5).

The entropy due to mass transfer to the ambient medium, within the temperature of dehydration, is equal to the product of the phase-transformation entropy and the quantity of crystallization water (gram moles) removed from the specimen during the sinter process. Therefore, Eq. (5) yields

$$\sum S_k d_a n_k = S_T \Delta n. \tag{8}$$

The entropy due to chemical reactions is, analogously,

$$\frac{1}{T} \sum_r A_r d\xi_r = \frac{\rho \Delta n}{T}. \tag{9}$$

The entropy of dissipation is equal to the difference between the total entropy of the process and all its other components combined, namely

$$S_{\text{diss}} = \frac{\Delta W_{\text{diss}}}{T} = S_T - S_T \cdot \Delta n - \frac{\rho \Delta n}{T}, \tag{10}$$

$$\Delta W_{\text{diss}} = S_{\text{diss}} \cdot T. \tag{11}$$

The thermogram in Fig. 1 illustrates comprehensively the thermal process during dehydration of kaolin, including the dissipative effects. In this experiment the hot junctions of three differential thermocouples had been installed in each of two specimens of modeling kaolin: a sintered one and an unsintered one, as shown schematically in Fig. 1.

Curves 1, 2, 3 in Fig. 1 clearly indicate the endothermal effect in a sintered cylinder and they describe the process kinetics. On the right-hand side of the same diagram is also depicted the second heat treatment of the two cylinders, both having been sintered now, taking place under the same test conditions. Curves 1a, 2a, 3a indicate equal heating rates of both cylinders.

Curve 4 indicates a constant ambient heating rate inside the oven, where two specimens were sintered while their temperature fields were recorded and where a third specimen was sintered while its loss of weight was recorded (curve 5) as a function of temperature and time (mass-transfer kinetics).

As a typical numerical example, we will consider the decomposition reactions of the argillaceous mineral kaolinite during heating (Fig. 2) and the isobaric-isothermal potentials of these reactions.

According to the curves in Fig. 2, the reaction most likely to occur within the 600-800°C temperature range is the formation of metacaolinite $Al_2O_3 \cdot 2SiO_2$ with the release of water vapor.

The sinter treatment of ceramic articles is effected under constant pressure in a constant volume (the volume change due to shrinkage is negligible as compared to the total volume of a sample). It is thus permissible to calculate the entropy of the system accurately enough, for practical purposes, from the test values of the specific heat for kaolin (Fig. 3). The change in entropy of a sintered kaolinite at oven temperatures from 600 to 800°C, i.e., from the beginning of dehydration to the maximum endothermal effect, has been plotted on the differential temperature curve. The entropy of dehydration has been calculated here in two stages.

The first stage represents the temperature range from the beginning of the endothermal process to its peaking, as indicated on the differential curve, when the dehydration proceeds at an increasing rate (when the entropy decrease is less than the entropy increase), and as confirmed by the differential loss-of-weight kinetics (curve 5 in Fig. 1) with its peak at 650°C.

The second stage represents the range of decreasing dehydration rate, when the entropy decrease is more than the entropy increase.

As has been mentioned earlier, a ceramic article is sintered under normal atmospheric pressure and in an almost constant volume, making it much simpler to calculate the change in entropy within the system between temperatures T_1 and T_2, i.e., under the assumption that the test values of the specific heat at these temperatures satisfy the relation

$$S_{T_2} - S_{T_1} = \Delta S'_1 = c_{T_2} \ln T_2 - c_{T_1} \ln T_1. \tag{12}$$

According to Fig. 1, the dehydration of clay occurs first at the surface and then proceeds toward the center so that a dehydration region appears within the specimen. A model of this process can be constructed as follows. Let the dehydration process be completed within the surface layer (first layer) at a fixed instant of time, whereupon the process shifts into the second layer under the surface, then into the third layer, etc. until it reaches the center.

Thus, in each layer at a fixed instant of time there may arise conditions close to thermodynamic equilibrium, which is necessary for rendering the Gibbs equation valid.

According to this model of the sinter process, a mass of water is transferred from the specimen to the ambient medium, passing through the upper layers and performing dissipative work (producing dissipative entropy).

Thus, with the dissipative entropy (work) of mass transfer taken into account, the equation of the isobaric-isothermal potential becomes

$$\Delta z = H - T(S + S_{\text{diss}}). \tag{13}$$

The rate of increase of dissipative entropy per volume is, according to nonequilibrium thermodynamics, described by the well known equation

$$\frac{dS_{\text{diss}}}{dV \cdot d\tau} T = \frac{dS_{\text{diss}}}{Fdxd\tau} T = q\chi, \tag{14}$$

where $Fd\tau = dV$ is a volume element, τ denotes time, q denotes the thermal flux, and χ denotes the potential (thermodynamic force).

The change is dissipative entropy associated with heat transfer within the system (Fig. 4) is

$$dS_{\text{diss}} = \frac{dQ}{T + dT} - \frac{dQ}{T} = \frac{dQ \cdot dT}{T^2}. \tag{15}$$

The thermal flux and the thermodynamic force are related according to the Onsager equation

$$q = L_1 x_1 + \dots \tag{16}$$

Combining Eqs. (14), (15), and (16), we obtain the classical Fourier differential equation of heat conduction

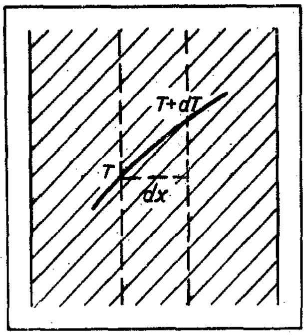

Fig. 4

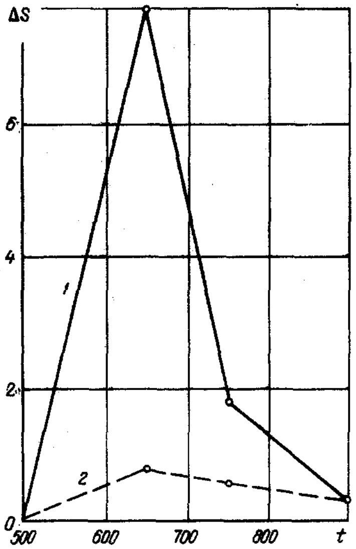

Fig. 5

Fig. 4. On determining the entropy in an elementary layer of the thermodynamic system here.

Fig. 5. Diagram of dissipation effects during the heating and the sintering of kaolin specimens: 1) entropy change during the sinter treatment of a specimen, 2) entropy change during the heating of a presintered specimen; entropy change ΔS(kcal/kg · °C), temperature t(°C).

$$\frac{\partial t}{\partial \tau} = \frac{\lambda}{c\gamma_0} \frac{\partial^2 t}{\partial x^2}. \tag{17}$$

A simultaneous occurrence of heat conduction and chemical conversions in the material will be reflected in the equation of heat transfer with chemical conversion

$$\frac{\partial^2 t}{\partial \tau} = \frac{\lambda \partial^2 t}{c\gamma_0 \partial x^2} - \frac{\rho}{c} \frac{\partial u}{\partial \tau}, \tag{18}$$

where ρ denotes the heat of reaction and $\partial u/\partial \tau$ denotes the rate of change of mass in the chemical process, this rate of change being also a function of the temperature gradient:

$$\frac{\partial u}{\partial \tau} = \frac{\partial u}{\partial t} \frac{\partial t}{\partial \tau}. \tag{19}$$

Inserting expression (19) into Eq. (18), we obtain the effective thermal diffusivity a_{eff} and the effective specific heat

$$a_{\text{eff}} = \frac{\lambda}{c\gamma_0 + \frac{\rho}{c} \frac{\Delta u}{\Delta \tau}}, \tag{20}$$

$$c_{\text{eff}} = c\gamma_0 + \frac{\rho}{c} \frac{\Delta u}{\Delta \tau}. \tag{21}$$

According to (20) and (21), an increase in the rate of chemical conversions $\Delta u/\Delta \tau$ in the material results in a higher specific heat and a lower thermal diffusivity, as has also been confirmed experimentally.

Following the method shown here, we have calculated and plotted (Fig. 5) the entropy change in a sintered kaolin specimen (1) during heating.

These graphs indicate that during the first stage of dehydration, from the beginning of the process to the time when the temperature difference between the center and the surface of a specimen becomes maximum, when the dehydration process zone shifts from the surface to the center of the specimen, the decrease in entropy as well as the increase in entropy become larger and, consequently, the dissipative entropy also increases, while during the second stage of the process the decrease in entropy becomes smaller and, therefore, the dissipative component of entropy also decreases.

The work of dissipation was calculated as equal to the area bounded between curve 1 of entropy change during the sinter process and curve 2 of entropy change in the already sintered specimen during heating.

The intensity of dissipative effects during sinter treatment of ceramics or during glass heating and blowing is of practical concern, becuase they are associated with the breakdown of the crystal lattice in argillaceous minerals and they affect appreciably the mechanical strength of tiles — especially during an accelerated sinter treatment, when the dissipative work at large temperature differences can easily exceed the resilience of a tile. This, in turn, causes breakage of ceramic articles as well as glass articles during blowing.

NOTATION

t	is the temperature of the ambient medium and of the specimens;
Δz	is the isobaric-isothermal potential;
c	is the specific heat of the material;
ΔS	is the change in entropy;
dx	is the change in specimen dimensions;
dT	is the change in temperature;
$\Delta u/\Delta\tau$	is the change in the rate of chemical conversions in the material;
a_{eff}	is the effective thermal diffusivity;
c_{eff}	is the effective specific heat.

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