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# Formation of Green Compact Structure of Low-Temperature Ceramics with Taking into Account the Thermal Degradation of the Binder

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**Abstract.** The solution of the tasks in the field of creating and processing materials for additive technologies requires the development of a single theory of materials for various applications and processes. A separate class of materials that are promising for use in additive technologies includes materials whose consolidation is ensured by the presence of low-melting components in the initial mixture which form a matrix at a temperature not exceeding the melting point, recrystallization or destruction of any of the responsible refractory components of the initial dispersion. The study of the contribution of the binder thermal destruction to the structure and phase composition of the initial compact of the future composite is essential for the development of modern technologies for the synthesis of low-temperature ceramics. This paper investigates the effect of the thermal destruction of a binder on the formation of a green compact of low-temperature ceramics and the structural-mechanical characteristics of sintered ceramics. The approach proposed in Ref. [1] for evaluating the structure and physical characteristics of sintered low-temperature ceramics is improved to clarify the structure of green compacts obtained after thermal destruction of the polymer binder, with taking into account the pores formed and the infusible residue. The obtained results enable a more accurate prediction of thermal stresses in the matrix of sintered ceramics and serve as a basis for optimization.

## THERMAL DESTRUCTION OF A BINDER

Low-temperature ceramics is a promising class of composite materials obtained by additive technologies. A distinctive feature of the sintering of such ceramics is that the consolidation of the material is provided by forming a matrix with a low-melting component. Computer simulation of related thermophysical processes that determine the kinetics of processes and structure formation in low-temperature ceramics was used to identify the determining technological factors and synthesis regimes [1, 2]. It is shown that the effective characteristics of sintered ceramics are determined by the macroscopic structure of the initial (green) compact, the distribution of components and pores in it, as well as by the heterogeneity of the concentrations, phase and fractional composition of the initial components. In industrial technologies, the initial compact is formed by slip casting with subsequent drying and thermal destruction of the binder to form a gas phase of decomposition products and a crystalline residue [3]. This leads to the formation of additional porosity of the initial dispersion and an increase in the number of solid components in the green compact. In the DuPont ceramic sintering profile shown in Fig. 1, the binder removal zone is marked with a rectangle. Taking into account the contribution of the binder thermal destruction to the structure and phase composition of the original compact is essential for the development of modern technologies for the synthesis of low-temperature ceramics.

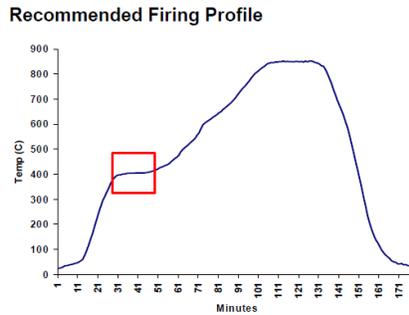


FIGURE 1. Temperature profile of DuPont ceramics sintering [4]

An approach and an adapted scheme of computer simulation of mechanochemical processes in reacting powder systems [2] are used which combine physical mesomechanics approaches, the ideology and instruments of solid state physics and micromechanics of media with structure. A heterogeneous body is represented in the form of a periodic structure of representative volumes, namely, cells of periodicity characterizing the concentration and fractional heterogeneity of the original components and porosity. It is believed that the kinetics of the destruction process is determined by the intensity of the heat input.

A problem of heat transfer with heat sinks, characterizing the binder thermal destruction, is solved numerically for a layer of initial dispersed components consolidated by a binder. For each microlayer of the medium formed during the discretization of the calculation area, all effective physical characteristics are determined with taking into account the values of the local concentrations of the components and pores, which are iteratively refined at each time step. The values of the threshold temperature and the specific work of thermal destruction are set.

The approach to modeling structure formation in the initial compact during the thermal destruction of the binder is developed by considering a model layer of a two-component powder mixture:  $\alpha\text{Al}_2\text{O}_3$  and borosilicate glass consolidated with polyorganosiloxane as a binder. During the polyorganosiloxane decomposition, a solid residue is formed which is crystalline silicon oxide [3]. We assume that the dispersed residue of the thermal destruction of the binder represents the third component of the initial powder mixture. The newly formed component of the mixture together with  $\alpha\text{Al}_2\text{O}_3$  forms an ensemble of refractory particles in a low-melting matrix during sintering.

The computational experiment is conducted on a model powder mixture characterized by the mass fractions of glass  $M_{\text{glass}}$ ,  $\alpha\text{Al}_2\text{O}_3$   $M_{\text{ceram}}$  and binder  $M_{\text{binder}}$ , the initial relative pore volume  $P$ , and the inhomogeneity parameter of the mixture component concentrations, which is a standard deviation of the volume concentrations of the components  $\sigma$ .

Figure 2 shows the distributions of the volumetric concentrations of the initial components and pores before and after the binder removal for the following characteristics of the initial mixture:  $M_{\text{glass}} = 0.55$ ,  $M_{\text{ceram}} = 0.3$ ,  $M_{\text{binder}} = 0.15$ ,  $\sigma = 0.15$ ,  $P = 0.1$ .

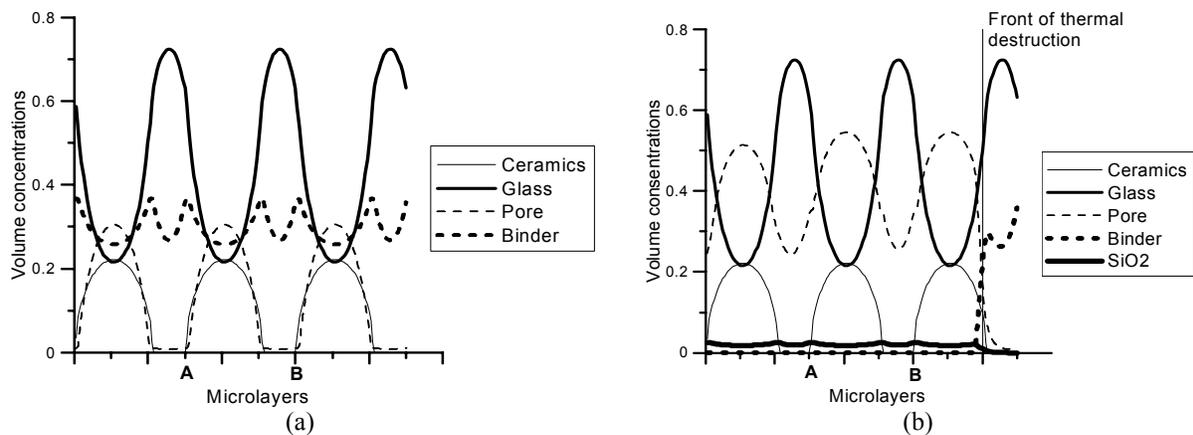
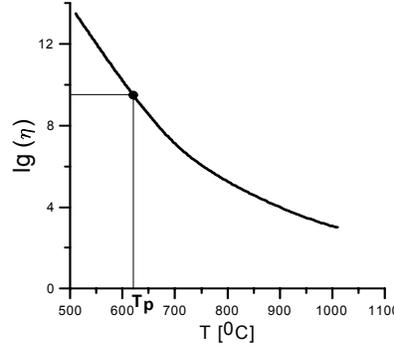


FIGURE 2. Distribution of the volumetric concentrations of the initial components and porosity across the model layer thickness: (a) initial, (b) after the thermal destruction of the binder



**FIGURE 3.** Temperature dependence of the viscosity of borosilicate glass

The interval between microlayers *A-B* corresponds to a separate representative volume. The binder removal completes the formation of the green compact.

### THERMAL RESIDUAL STRESSES

Thermal residual stresses caused by the difference in the thermal expansion coefficients of the dispersed components and the matrix may arise in the sintered composite material. Polyorganosiloxane thermal degradation leads to the formation of a refractory crystalline  $\text{SiO}_2$ , which must be taken into account when estimating the residual thermal stresses in the matrix of the sintered ceramics along with the dispersed  $\alpha\text{Al}_2\text{O}_3$ .

The calculation of residual thermal stresses should take into account the stage of viscoplastic stress relaxation when the sintered ceramics is cooled to laboratory temperature. There is no clear boundary in the transition of the sintered material matrix from the viscoplastic to elastic state. In Ref. [5], it is proposed to introduce the temperature point of material transition to the elastic state  $T_p$  in order to estimate the residual thermal stresses. An assumption is made of an abrupt transition to the elastic state, with allowance for which it can be assumed that thermal stresses relax to a negligible level in the temperature range from the sintering temperature to the temperature point of transition. It is assumed that the transition to the elastic state stops the residual stress relaxation, and the evaluation of thermal stresses is possible from the position of thermoelasticity [6].

When glass is cooled to a certain temperature, its viscosity  $\eta$  increases by 8 orders of magnitude or more in comparison with the viscosity at the moment of sintering, causing a corresponding decrease in the rate of relaxation processes [7]. For borosilicate glass we can use the temperature value  $T_p = 900$  K, indicated in Fig. 3 as the point of transition to the elastic state.

The following temperature range is considered for the estimation of thermal residual stresses:

$$\Delta T = T_p - T_0, \quad (1)$$

where  $T_p$  is the temperature of the transition point, and  $T_0$  is the initial temperature. It is assumed that for the temperature values  $T \geq T_p$  the temperature stress values  $\sigma_T \approx 0$ .

From the position of thermoelasticity, the following expression can be used to estimate the residual thermal stresses in the matrix of sintered ceramics:

$$\sigma_T = \int_{T_0}^{T_p} K_{\text{glass}}(T) \left[ \frac{\beta_{\text{glass}}(T)C_{\text{glass}} - \beta_{\text{ceram}}(T)C_{\text{ceram}}}{C_{\text{glass}} + C_{\text{ceram}}} + \frac{\beta_{\text{glass}}(T)C_{\text{glass}} - \beta_{\text{SiO}_2}(T)C_{\text{SiO}_2}}{C_{\text{glass}} + C_{\text{SiO}_2}} \right] dT, \quad (2)$$

where  $K_{\text{glass}}(T)$  is the temperature dependence of the elastic volume modulus of glass,  $\beta_{\text{glass}}(T)$ ,  $\beta_{\text{ceram}}(T)$ ,  $\beta_{\text{SiO}_2}(T)$  are the temperature dependences of the thermal expansion coefficients of the matrix and refractory components, and  $C_{\text{glass}}$ ,  $C_{\text{ceram}}$ ,  $C_{\text{SiO}_2}$  are the volumetric concentrations of the matrix and refractory components.

The results of the computational experiments on the evaluation of thermal residual stresses in the matrix of low-temperature ceramics are summarized in Table 1. To obtain numerical estimates, the characteristics and properties of the materials used for the production of low-temperature ceramics are taken from Refs. [7–10].

As we can see from Table 1, the tensile and compressive residual stresses may arise in the matrix of sintered ceramics for various compositions of the initial components.

**TABLE 1.** Averaged residual stresses in the matrix of sintered ceramics with different contents of the initial components

Example No.	$M_{\text{ceram}}$ , mass %	$M_{\text{glass}}$ , mass %	$M_{\text{binder}}$ , mass %	$\sigma_T$ , MPa
1	40	30	30	152.8
2	40	40	20	49.1
3	40	45	15	11.8
4	30	40	30	17.5
5	30	50	20	-2.3
6	30	55	15	-20.7

The sign of residual stresses in temperature range (1) is determined by the signs of the numerators in integrand (2). The values of  $\beta_{\text{glass}}(T)$  can be varied by varying the chemical composition of glass [11].

## CONCLUSION

The approach to evaluating the structure and properties of low-temperature ceramics proposed in Refs. [1, 12] was developed with taking into account the thermal destruction of the binder during the formation of the green compact structure of low-temperature ceramics. The approach makes it possible to clarify the structure and distribution of the component concentrations across the thickness of the initial compact after removal of gaseous products of the binder thermal destruction, with taking into account residual refractory crystalline  $\text{SiO}_2$ , and to estimate the degree of thermal stresses in the matrix of the sintered ceramics.

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