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Forecast of Geometric Characteristics of Low-Temperature Ceramics with Multilevel Hierarchical Pore Structure

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Abstract. On the base of micromechanics of heterogeneous media the approach of computer simulation of the process of low-temperature ceramic sintering being synthesized by additive technologies of layer-by-layer build-up of the original polydisperse mixture and subsequent sintering is offered. The possibility of refractory component skeleton formation at different structural levels, being determined by particle fraction size is taken into account. Formation of the skeleton of refractory components of interacting particles causes the formation of the pore structure, and non-uniform distribution of pores in the layer thickness determines the initial anisotropy of shrinkage of sintered ceramics.

INTRODUCTION

The development of additive technology of structure element production formed by layer-by-layer material formation and subsequent sintering requires the development of dispersive media models and structure prediction methods at all stages of the process. Material consolidation in low-temperature ceramics is provided by the presence in the mixture of low-melting components forming the matrix at a temperature of no more than the melting or degradation (dissociation) temperature of any initial critical refractory components. Initial low-temperature ceramic compacts under additive technologies are formed from layers of material in which the inhomogeneity of the particle size and packing density are certain process parameters of layer formation after removal of the binder (slurry). The inhomogeneity of different interface layers and the formation of interlayer interfaces should be added to this inhomogeneity. An adequate model structure of the compact should reflect the overall inhomogeneity of concentrations and sizes of powdered components and pores in the initial layers and interlayer interfaces. From the standpoint of micromechanics of media with the structure, the heterogeneous materials can be associated with an effective medium with periodic macrostructure under natural limitations of statistical averaging. The sintering process is accompanied and limited by the possibility of the free boundaries of initial component particles and relative pore volume [1]. The possibility to form a dense packing of coarse fractions of refractory components, in which each particle has a number of contacts with neighboring refractory particles, is one of the determining factors in the formation of material pore structure. At different structural levels defined by the fraction size the dense packings form a sintered body frame that provides the strength and stability of the structure but limits further consolidation of particles from the moment of its final formation.

The modeling methods of packaging of spherical and other smooth particles of different size into a specified volume and the evaluation of polydisperse particle fractional composition that achieve maximum density are investigated in [2–7]. The theoretical results show that the densest packing is observed for three fractions [7].

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Further increase in the number of factions does not lead to an increase in the degree of mixture filling. The dispersion characterized by a ±5% scatter of particle diameters can be considered as monodisperse material or separate fractions of size d_i. In this case, the formation of the ”crystal“ macrostructure of particle packing in the flow occurs only after many hours of exposure [8]. The Hodakov model [9] is based on the possibility of taking into account the proportion of the low-melting component occluded in the refractory aggregates and the components attached to the surface of large refractory particles. In the case of multimodal particle size distribution of refractory particles depending on their size, particles with finer fraction ”displace“ the occluded fusible component fraction and thereby reduce the effective viscosity of dispersion. The actual volume content of solids in the slurry with the attached volume of a part of dispersion medium is determined by the expression

$$\varphi_0 = \frac{\dfrac{\varphi_\mathrm{m}}{\rho_\mathrm{m}} + (\Gamma_\mathrm{m} + S_\mathrm{m}\delta)\dfrac{\varphi_\mathrm{m}}{\rho_\mathrm{c}}}{\dfrac{\varphi_\mathrm{m}}{\rho_\mathrm{m}} + \dfrac{1-\varphi_\mathrm{m}}{\rho_\mathrm{c}} - (\Gamma_\mathrm{m} + S_\mathrm{m}\delta)\dfrac{\varphi_\mathrm{m}}{\rho_\mathrm{c}}},$$

where Γ_m is the absorption (binding) of dispersion medium, S_m is the specific surface area of dry powder (cm^2/g), δ is the thickness of dispersion medium sorbed by particles surface (cm), φ_m and ρ_m are the weight content and powder density, and ρ_c is the density of dispersion medium.

We assume that coarse particles of refractory components have a ball shape, and the results of [4–7] are applicable to them. The dense packing of a mixture of polydisperse particles takes place if the size ratio of individual fractions of powder particles satisfies the relation

$$d_{i-1} < 0.25 d_i, \tag{1}$$

In this case, the particles of fine fraction of sintered ceramics are located between large particles without creating cramped packing conditions.

A polydisperse composition of refractory components composed of three particle factions d_max, d_midi and d_mini with volume fractions D_max, D_midi and D_mini, respectively, is considered.

For three fractions $d_\mathrm{max} > d_\mathrm{midi} > d_\mathrm{mini}$ of refractory particles the condition of close packing achievement can be formulated as follows: a reduction of the initial porosity of the body during sintering is possible until the volume concentration of large refractory component particles achieves the limit value equal to Tl.

For given volume distributions of initial component concentrations through the layer thickness we can estimate the local values of the initial porosity sufficient to achieve a dense packing of particles of considered factions. The difference between the value of the initial porosity and the porosity required to achieve a dense packing determines the minimum value of the ultimate porosity in local microvolumes of sintered compact.

For each ith particle of refractory component fraction the value $Tl = Tl_i$ can be estimated through the average value of bulk density of used powder fractions, determined mainly by their form.

POSSIBILITY OF FORMING THE REFRACTORY COMPONENT SKELETON AT THE MACROSCOPIC LEVEL

During sintering local volume concentrations of mixture components rise due to a decrease in porosity. Refractory particles of the coarse fraction come into contact when the current value of the concentration of particles with the maximum size during sintering reaches the limit Tl_max of volume concentration. At each local section of the sintered body we can assess the minimum value of the relative pore volume, providing growth to the limit of coarse particle concentration:

$$C_{P1} = 1 - \frac{D_\mathrm{max} C_\mathrm{refractory}}{Tl_\mathrm{max}}. \tag{2}$$

With the decrease in porosity to the C_{P1} value, coarse particles form a macroskeleton that prevents further reduction of porosity. If this value is less than the local pore concentration C_pore of the original body, it is possible to estimate the value of local minimum porosity

$$P_{\min 1} = C_\mathrm{pore} - C_{P1}, \tag{3}$$

If the initial porosity at the local section is less than C_{P1}, the skeleton formation of large particles does not occur and hence it is necessary to assess the prospects of skeleton formation of medium-sized ceramic particles, i.e., mesoskeleton.

POSSIBILITY OF FORMING THE REFRACTORY COMPONENT SKELETON AT THE MESOSCOPIC LEVEL

If for d_{midi} fraction of refractory particles the condition of possibility of mechanical contact is satisfied, it can be considered as the condition of mesoskeleton formation that limits the volume reduction process only in parts of the local volume located inside the skeleton of d_{midi} particle fraction. This part of the local volume is determined by subtracting the coarse fraction and the attached share of the dispersion medium from the initial amount (Hodakov model).

For d_{midi} fraction of refractory components the initial porosity value C_{pore} sufficient to achieve a dense packing of particles is represented as:

$$C_{P2} = 1 - D_{\text{midi}} \frac{C_{\text{refractory}}}{Tl_{\text{midi}}} - \varphi_0 D_{\max} C_{\text{refractory}}. \quad (4)$$

The mesoskeleton formation in a sintered body limits the compaction of the above-specified mixture mesovolumes, which allows us to estimate the value of the local minimum porosity if the value C_{P2} is less than the local volumetric pore concentration of the original body:

$$P_{\min 2} = (C_{\text{pore}} - C_{P2})(1 - \varphi_0 D_{\max} C_{\text{refractory}}). \quad (5)$$

The particle fraction $d_{\min}$ may form the mesoskeleton for the corresponding structural level if the initial porosity in local volumes of the powder mixture is greater than C_{P3}:

$$C_{P3} = 1 - D_{\text{mini}} \frac{\mathrm{C}_{\text{refractory}}}{Tl_{\text{mini}}} - \varphi_0 (D_{\max} + D_{\text{midi}}) C_{\text{refractory}}. \quad (6)$$

The local minimum porosity in this case is

$$P_{\min 3} = (C_{\text{pore}} - C_{P3})(1 - \varphi_0 (D_{\max} + D_{\text{midi}}) C_{\text{refractory}}). \quad (7)$$

The latter result is easily generalized to any number of fractions of a mixture of refractory components above 3.

ANISOTROPY OF SINTERED CERAMICS SHRINKAGE

The structure of a sintered body is estimated based on shrinkage. The anisotropy of shrinkage under external influence is explained by the anisotropy of the substructure of particles and pore geometry. Volumetric shrinkage in various sintering conditions is not affected by external mechanical influences: an artificial obstacle to shrinkage in any direction reduces shrinkage in this direction with mainly constant value of volumetric shrinkage and, therefore, leads to a corresponding increase in shrinkage in other areas [10].

The heterogeneity of microvolumes of a sintered porous body with respect to the particle size and their packing density can be considered as the determining factor in the behavior of disperse systems during sintering [11]. At the same time, microvolumes of a sintered body in which the local level of Laplace capillary pressure is sufficiently different from the average value always exist. This means that the study of the sintering process, regardless of the flow mechanism of substances should be carried out with taking into account the structural and geometric factor with appreciating the principles of translational symmetry [12]. From the viewpoint of the mechanics of microinhomogeneous media the macrostructure periodicity elements of an effective medium must preserve common boundaries. This defines the principle of translational symmetry which provides conditions for the continuity of the effective medium. In this formulation, the result of translational symmetry is the anisotropy of sintered ceramics shrinkage: shrinkage in the plane of the layer ceases as soon as the porosity stops to decrease in the zone of the periodicity element, and therefore shrinkage over the layer thickness increases.

CONCLUSION

The investigation of the technological conditions of low temperature ceramics synthesis during sintering of layers formed from mixtures of different material powders requires the development of computer-aided approaches to material design based on rheological processes in powder bodies and modifications of hierarchically organized structures. For polydisperse compositions the possibility of skeleton formation of refractory components is the determining factor in the pore structure formation of low temperature sintered ceramics, and the characteristics of the minimum porosity distribution are the parameters of initial dispersion. The proposed approach provides a forecast of shrinkage anisotropy as a result of the continuity conditions of the effective medium.

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