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INVESTIGATION OF THERMAL CONDITIONS OF THE MOLDING PROCESS OF SLURRY BERYLLIUM OXIDE

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Results of experiments and calculations of the mathematical model of the motion and heat exchange of the slurry mass in the annular cavity are presented. Temperature distribution, estimated during the experiments, in the form-building cavity of bushing depending on the molding velocity and heat extraction conditions on the walls of form-building of annular cavity lets us determine the transition from liquid (viscous-plastic) state to solid-plastic one. The experiment results were analyzed and generalized using mathematical model of the thermoplastic slurry molding process. The results of calculation are in agreement with the experimental data, and they show physical validity of the proposed mathematical model of the molding process of the beryllium thermoplastic slurry.

Keywords: beryllium ceramics, thermoplastic slurry, suspension, molding process, heat transfer, phase transition, solidification of casting.

Introduction

Technology of slurry molding (extrusion) is very actually nowadays in connection with intensive development of metal injection molding (MIM) technology, where there are the same physical processes. This technology played the important role in the production of functional ceramic for the need of the nuclear, defense and electronic industry.

The development of new areas of science and directions of technology advances increased requirements to the level of properties and to the quality of ceramic fabrications, are increasingly becoming more popular products of complex configuration from new non-metallic materials (high thermal conductivity, oxygen-free, superconducting, etc.). Technology of hot casting under pressure [1, 2] remains the basis for the obtaining long-length, multi-channel, complex shaped ceramic fabrications from non-plastic powders, in spite of the using of isostatic pressing.

However, in spite of the fact that last years a lot of attention has been paid to improving of the technology and creation of the new equipment. Up to now unsolved problem of obtaining without defects products by this method has remained. As a result, in practice it does not often achieve the desired quality of moldings and obtaining of acceptable products, that makes this process low profitability. Obtaining of ceramic fabrications by hot molding from dispersion materials with anomalous physical properties, such as BeO is particularly complicated. In this case, the difficulties of obtaining of quality products were caused firstly by thermal properties of beryllium oxide, in particular, its unique thermal conductivity [2, 4]. Clearly, it is impossible to eliminate taking place technological limitations and problems without the development which they are based on all experience and knowledge of theoretical representations about regularities and mechanisms of regulation of the thermal regime of the casting on the forming process of molding. The results of experimental researches and the generalization by calculations of mathematical model of process molding of the thermoplastic slurry beryllium oxide are presented in this paper.

1. Experimental data of rheological properties of the thermoplastic slurry

The thermoplastic slurry (highly-viscous suspension) represents a two-phase disperse system, where the solid minerals phase - beryllium oxide powder, liquid phase - organic binder [3]. The organic coupler consists of three components: paraffin, beeswax and the oleic acid in the proportion 82%: 15%: 3%. The Shvedov-Bingham rheological model was used to describe the rheological property, the relation between the shear stress τ and shear rate $\frac{\partial u}{\partial r}$ of the thermoplastic slurry:

$$\tau = \tau_0 + \mu\frac{\partial u}{\partial r}, \tag{1}$$

where τ is the shear stress, τ_0 is the yield strength, μ is the plastic viscosity coefficient.

The ultrasonic effect (USE) influences the rheological properties of the slurry. The plastic viscosity coefficient $\mu(Pa \cdot s)$ and the yield strength$\tau_0(Pa)$ of the slurry depend on temperature$T$, and the experimental data at the relative mass fraction of the binder $\omega = 0.1$ prior the USE are described by the empirical dependencies

$$\mu = 5.5 + 6.2exp(-(T-334)/6),$$

$$\tau_0 = 19 + 11.41exp(-(T-340)/5.47) \tag{2}$$

after the USE:

$$\mu = 2.5 \cdot 10^{14} exp(-0.09068\,T),$$

$$\tau_0 = 5.93 \cdot 10^8 exp(-0.04968T) \tag{3}$$

The slurry density is determined by the concentration of the beryllium powder and the binder:

$$\rho = \frac{\rho_{BeO} \cdot \rho_{bin}}{((1-\omega)\rho_{bin} + \omega \cdot \rho_{BeO})} \times 10^3 \tag{4}$$

where ρ_{BeO} is the beryllium density, ρ_{bin} is the coupler density, ω is the relative mass fraction of the coupler in the fractions of unity.

The coupler density is temperature-dependent and is determined by the empirical formula

$$\rho_{bin} = 0.8485 + 0.0755 \cdot \cos(0.0571 \cdot T - 16.736)$$

The beryllium density is $\rho_{BeO} = 3.02\ g/cm^3$. The coupler density in temperature range from 348 to 318℃ varies within the limits $\rho_{bin} = 0.784 - 0.8845\ g/cm^3$, and at the solidification, the thermoplastic slurry density increases from 2.3498 to 2.4327 g/cm^3 for $\omega = 0.1$.

As the experimental data of [5] show, the USE does practically not affect the slurry thermal conductivity and heat capacity, they depend on temperature in the form

$$\lambda = 7.1exp(-0.01T + 2.73),\ \frac{W}{m \cdot K} \tag{5}$$

$$c_p = 1000exp(0.00345T - 0.94),\ \frac{J}{kg \cdot K} \tag{6}$$

Thus, the rheological properties of the slurry of the beryllium are the functions of temperature, and an aggregative change of the liquid suspension to its solid-plastic state occurs in the molding process.

2. Determination of thermo-physical properties of ceramic products molding process

According to experimental data, the temperature of thermoplastic slurry solidification $T_s = 55℃$, and the releasing heat of the aggregative change does not affect significantly and scatters rapidly. Determination of the coefficients of heat exchange and heat transfer on the walls of the cavity presents considerable difficulties and it requires a solution of the dual problem. In this

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aspect, the solution of the inverse problem with using of experimental data for evaluation of the coefficient of the heat transfer is the simplest.

For simplicity motion of the slurry in the cavity can accept one-dimensional and parameters of the cross section are constant. Heat transfer through the side surface of the filler leads to reduces the temperature of the slurry, and its variation is describing by the equation

$$Gc_p\frac{dt}{dz} = -\pi d_2 k(t - t_w),$$

where G - mass flow rate of the slurry, k - the coefficient of heat transfer through the wall of the cavity, t_w-the temperature of the cooling medium.

Heat capacity of the slurry changes in the transition zone. Increase of the enthalpy during the phase transition can be determined by the apparent heat capacity method [4, 5]. In this method, the latent heat is taken into account by increasing the heat capacity in the phase transition zone. Changing of heat capacity can be represented as [2, 4]:

$$c_p = \begin{cases} c_s, \ \ t < t_s & solid\ phase \\ c_{in}, \ t_s \le t \le t_l & transition\ zone \\ c_l, \ \ \ t > t_l & liquid\ phase \end{cases} \tag{7}$$

where $c_{in} = \frac{\int_{t_2}^{t_1} c(t)dt + H_{1\to 2}}{t_l - t_s}$, $H_{1\to 2}$ - the phase transition specific enthalpy of beryllium slurry is determined by experimental data and is equal to $H_{1\to 2} = 7800$ J/kg.

In phase transition function $\alpha(\bar{t})$ is introduced to the transition zone to consider the latent heat, and changing of the slurry heat capacity is expressed by:

$$c_p = c_s \cdot \left(1 - \alpha(\bar{t}) + \ c_l \cdot \alpha(\bar{t}) + H_{1\to 2}\frac{d\alpha}{dt}\right) \tag{8}$$

where c_s– specific heat of the slurry in the solid state, c_l– specific heat of the slurry in the liquid state, $\alpha(\bar{t}) = 0$ for the pure solid slurry and $\alpha(\bar{t}) = 1$ for the pure liquid slurry, $\bar{t}$ – dimensionless temperature of slurry ($\bar{t} = \frac{t}{t_0}$, t_0-initial temperature of the slurry at the inlet of the cavity). According to the experimental data of beryllium oxide slurry with binder mass fraction of $\omega = 0{,}117$ function $\alpha(\bar{t})$ takes a form:

$$\alpha(t) = 5.712 \cdot t - 2.85 \tag{9}$$

The equations (7)-(8) of the method of apparent heat capacity include the latent heat of the phase transition, and are convenient for calculations. For convenience position of the transition zone is not known in advance and is determined as a result of the calculations.

3. Discussion of optimization calculations data

Systematic calculations of the process of forming beryllium ceramics allow to analyze the phenomenon of phase transition at various casting speeds. Numerical calculations take into account the influence of latent heat of crystallization on heat transfer and solidification of the slurry. The process of solidification proceeds as a result of heat release during the phase transition from a liquid to a solid state. The heat of the slurry mass is transferred to the coolant.

The interval of crystallization temperature is an important factor determining the characteristic parameters of the forming process of slurry. The effect of range of the crystallization temperature is to a large extent balanced by the action of thermophysical factors. Depending on the magnitude of this interval and the properties of the slurry, different conditions are created for the formation of the slurry and the flow of the solidification process.

The parameters have changed in the optimization calculations: casting speed, cooling conditions (2 or 3 contour molds) and the design of the cooling circuit. At the inlet of the cylindrical part of the annular cavity the temperature of the slurry is constant and equal 80°C, which corresponded to the industrial casting conditions.

The release of heat of crystallization during the phase transition of the slurry from the viscous-plastic state to the solid-plastic takes into accounting numerical calculations. The coaxial cavity consists of two concentric cylinders with radii of 6 and 10 mm, respectively, which makes it possible to obtain a ceramic product in the form as a tube. The cooling contour of the cavity is divided into 3 parts (Fig.1). Temperature of the cooling water in the first part is $t_1 = 80℃$, in the second part is $t_2 = 59℃$, in the third part is $t_3 = 20℃$.

The results of calculations of the process of forming beryllium oxide slurry for a three-circuit coaxial annular cavity are considered, which are shown in Figs. 2-4. At the first stage, the process of cooling the hot slip through the walls of the cavity is realized by means of the boundary condition of the first kind.

The total cavity length amounts to $l = 28\,mm$, the lengths of the first, second, and third sections are $l_1 = 9.4,\ l_2 = 9.2,\ l_3 = 9{,}4$ (fig.2a); $l_1 = 7,\ l_2 = 7,\ l_3 = 14$ (fig.2b); $l_1 = 7,\ l_2 = 14,\ l_3 = 7$ (fig.2c); At the same time changing the casting speed (U_0 =10 mm/min, 20 mm/min и 50 mm/min) we observe, how to change of the rate of crystallization and the character of the motion of the slurry in the annular cavity.

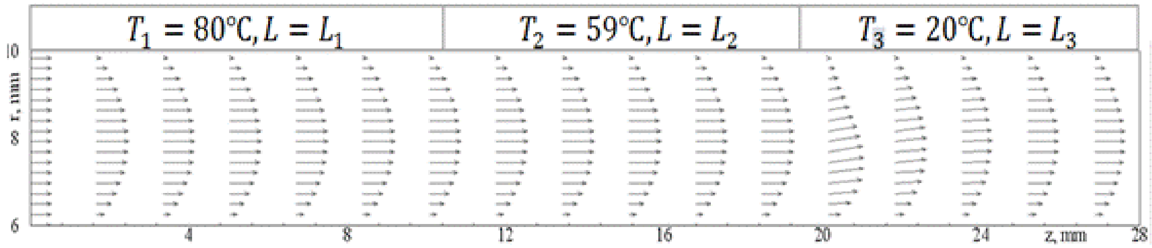

Fig.1. Scheme of flow of thermoplastic slurry in the annular cavity in case of three-circuit cooling.

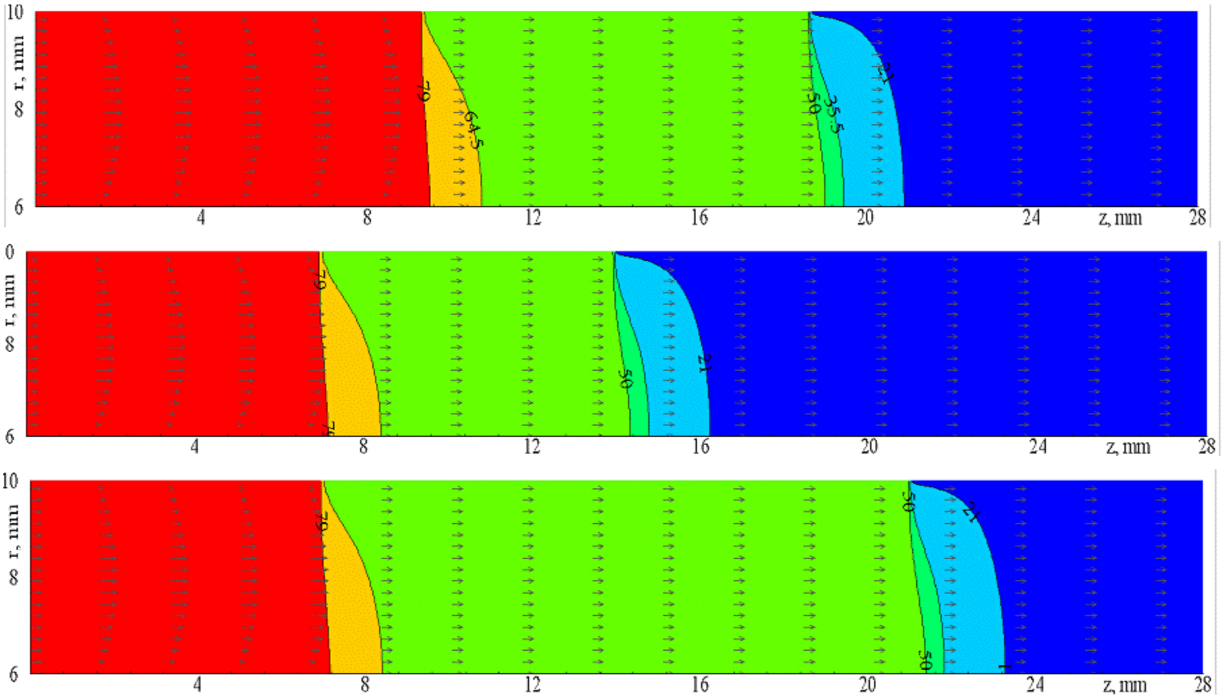

Fig.2. Distributions of the temperature over the annular cavity length at different ratio of the length of the cooling circuits at $U_0 = 10\ mm/min$: a) $L_1=L_3=9{,}4$ mm, $L_2=9{,}2$ mm; b) $L_1=L_2=7$ mm, $L_3=14$ mm; c) $L_1=L_3=7$ mm, $L_2=14$ mm.

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The temperature of the slurry at the inlet of the channel is constant across the cross-section. The profile of the longitudinal component of the velocity attains the shape of shear flow of the fluid near the inlet section due to high viscosity of the thermoplastic slurry (Fig. 2). Wall temperature in the first cooling contour is $t_1 = 80℃$ and temperature field changes from $t = 80℃$ to $t = 64.5℃$ in this zone (Fig. 2). Temperature isolines (isotherms) show the regions of the constant temperature and internal structure of the slurry mass which is in liquid state.

Wall temperature is$t_2 = 59℃$ in the second cooling contour. Sharp reduction of the wall temperature generates intensity growth of the slurry cooling, it also leads to the change of the rheological and thermo-physical properties of the slurry. Dynamic viscosity $\mu(t)$, density $\rho(t)$ and yield point $\tau_0(t)$ increase with temperature decrease, and viscous-plastic property of the slurry obviously begins to be evident. The slurry slides along the cavity wall, and sliding velocity ascends down the length of the second contour. It resulted in that profile of the longitudinal component of the velocity down the flow will level with constant center in the near-axial region (Fig. 2).

Heat pick-up growth results in reduction of the temperature field in the second cooling contour (Fig. 2). There is a transition zone in the beginning of the second contour, where temperature field is variable and expresses the transition of the slurry from the liquid state into the viscous-plastic state. The slurry temperature changes from $t = 80℃$ to $t = 59℃$ and defines upper boundary of the zone with constant temperature $t_2 = 59℃$. The slurry mass is viscous-plastic near the wall due to the heat pick-up, while the slurry is liquid in the central part of the cavity. Presence of different structural conditions across the cross-section results in the change of the rheological and thermo-physical properties of the slurry. Isotherms become flat with the motion of the slurry mass. Thermo-physical properties become homogeneous, and all the mass of the slurry turns into viscous-plastic state. Wall temperature in the third cooling contour is $t_3 = 20℃$, which leads to the further cooling of the slurry mass and temperature reduction from$t = 59℃$ to $t = 45℃$ in the transition zone. According to the experimental data, change in aggregate state takes place at temperature$t_f = 55℃$. In energy equation heat release during aggregate state change occurs due to solidification of the viscous-plastic slurry. Solidification results in density change of the slurry.

Increase of molding velocity $u_0 = 20\ mm/min$ by twice, while the other parameters stay the same, has an impact on the structural change of the slurry (Fig. 3). Unlike in the previous formation mode, molding velocity leads to the extension of the transition zone of structural changes from one state into another, i.e. from the liquid state into viscous-plastic state and from viscous-plastic state into solid-plastic state (Fig. 3). It is also observed from isotherms distribution, and is explained by the increase of convection component of thermal flow.

Transition zone stretches in the second contour area, and temperature field shows minute rearrangement of the liquid state of the slurry into the viscous-plastic. And the slurry is viscous-plastic near the wall due to the heat pick-up, while in the central part – in a liquid state, i.e. convectional thermal flow exceeds at the expense of molding velocity.

In this area, the slurry temperature changes from 79 to 59 ° C and defines upper boundary of the zone with constant temperature$t_2 = 59℃$. Structural change of the slurry from viscous-plastic state into solid-plastic state occurs in the region of the third cooling contour. Broad transition zone is also observed here, where temperature field is defined by convection, heat conductivity and the slurry aggregate state change heat.

At the molding velocity$u_0 = 50\ mm/min$, the slurry does not solidify in the central part over the entire cavity length, and the main flowing mass is in liquid state (Fig.4). This can lead to shrinkage of the slurry and the formation of shells and voids and a decrease in the strength of the casting.

The molding of the thermoplastic slurry in the annular cavity with three cooling circuits at low molding velocity (10-20 mm / min) shows the hardening of the casting within the mold cavity.

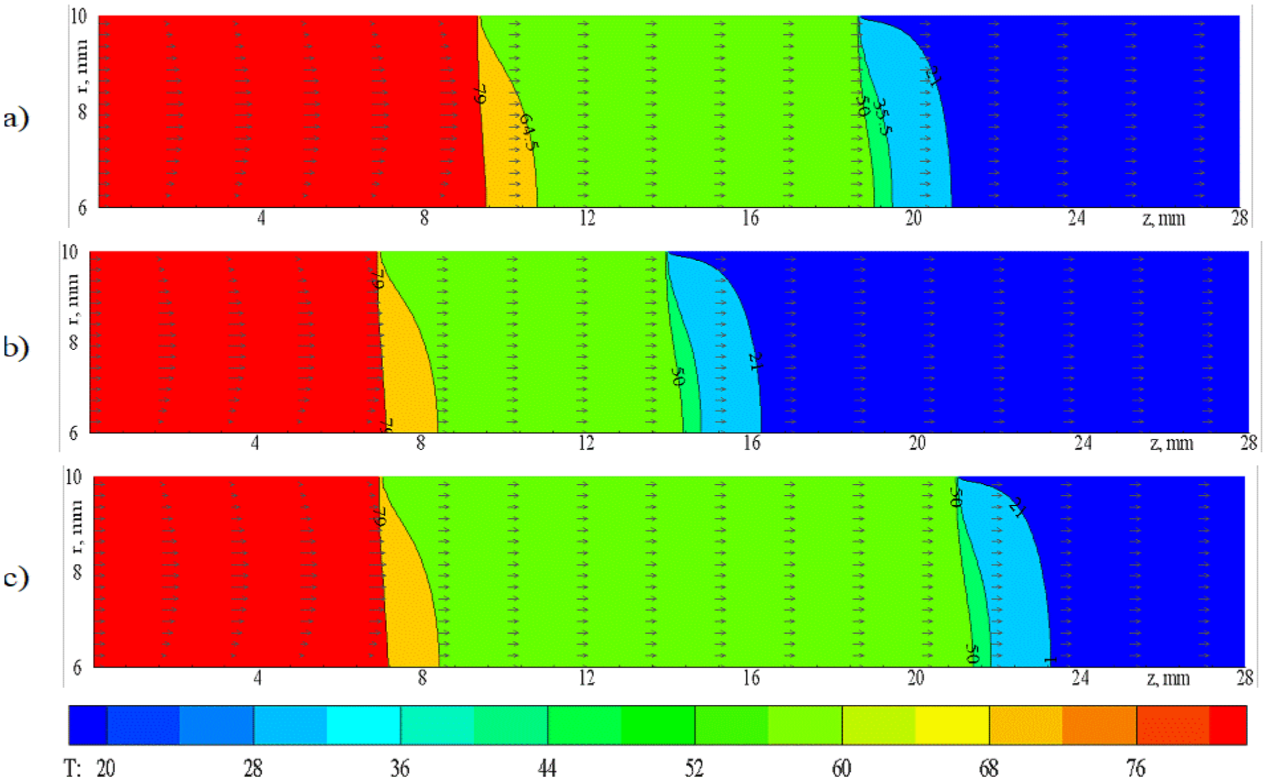

Fig.3. Distributions of the temperature over the annular cavity length at different ratio of the length of the cooling circuits at $u_0 = 20\ mm/min$: a) L_1=L_3=9,4 mm, L_2=9,2 mm; b) L_1=L_2=7 mm, L_3=14 mm; c) L_1=L_3=7 mm, L_2=14

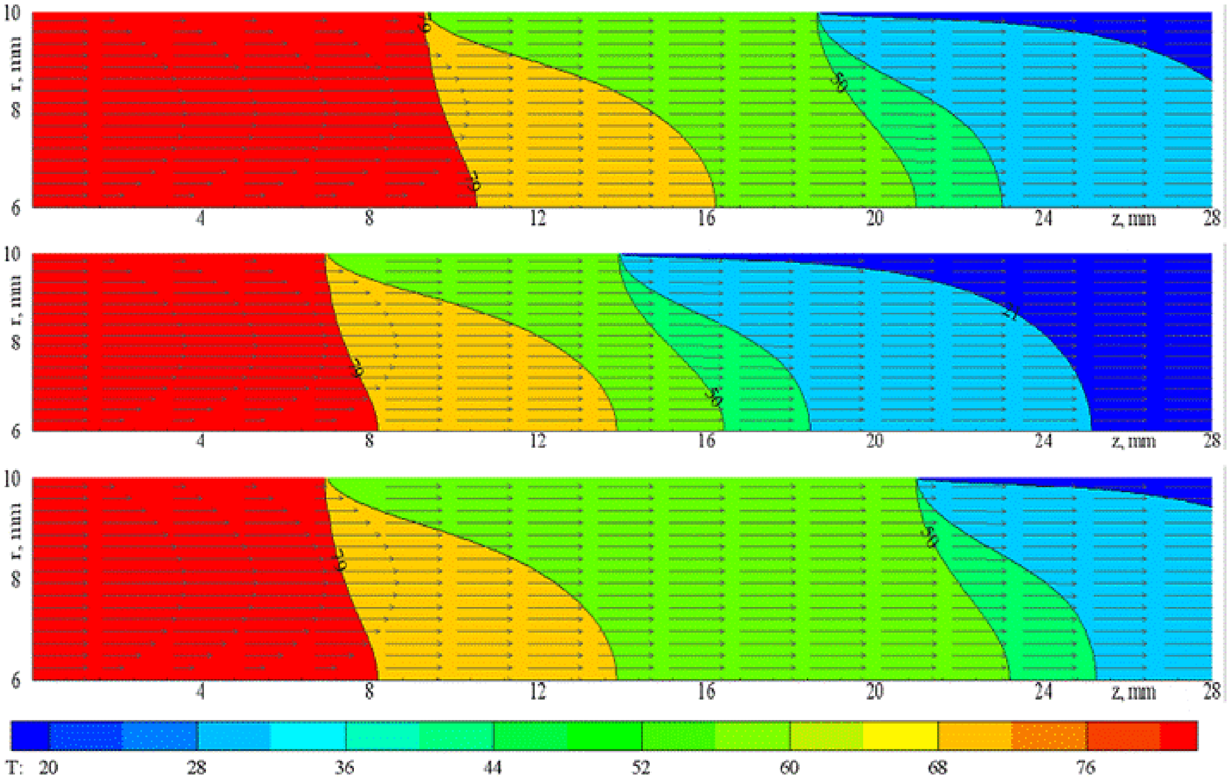

Fig.4. Distributions of the temperature over the annular cavity length at different ratio of the length of the cooling circuits at $u_0 = 50\ mm/min$: a) L_1=L_3=9,4 mm, L_2=9,2 mm; b) L_1=L_2=7 mm, L_3=14 mm; c) L_1=L_3=7 mm, L_2=14 mm

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During the experiments, stated distribution of the temperature in the form-building cavity of filler depending on the molding velocity and conditions of heat extraction on the walls of form-building of annular cavity lets us determine the transition from liquid state to viscous-plastic and from viscous-plastic to solid-plastic state. The results of experiment were analyzed and generalized with using of mathematical model of the process of molding of the thermoplastic slurry. The system of equations of the laws of conservation of mass, momentum and energy of non-Newtonian fluid is considered in common with the rheological Shvedov-Bingham’s model.

Rheological and thermo-physical properties of the slurry were found on the basis of experimental data, and they express dependence on the temperature. The coefficients of heat exchange and heat transfer on the walls of the annular cavity were evaluated by solving the inverse problem, and they were refined in the optimization calculations carried out according to the conditions of the experiments.

Obtained coefficients of heat exchange and heat transfer in the calculation let us determine the conditions of heat exchange between the slurry and cooling water, find operational parameters for controlling of heat exchange of molding of the beryllium oxide in the mold cavity.

Conclusion

Investigation of thermo physical properties of the thermoplastic slurry depending on the temperature, the heat at the phase transition is the main problem, in that they largely determine the technological and operational characteristics of beryllium ceramics.

Velocity and temperature fields allowed detecting the peculiarities of motion and heat transfer determining the internal structure of molding process, transformation of the viscous-plastic liquid slurry into solid-plastic state, and establishing the influence of the parameters (velocity, coolant temperature, rheological properties) on solidification process of ceramic slurry mass. One can find in computations the optimal conditions of the ceramics molding process, which allow obtaining the output hardened product with a uniform structure of beryllium.

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