DEVISING MANUFACTURING TECHNIQUES TO CONTROL THE PROCESS OF ZONAL SEGREGATION IN LARGE STEEL INGOTS

A method of physical modeling was applied to study the effect of external actions on the processes of crystallization and the formation of the structure of ingots. A brief review of existing hypotheses about the evolution of physical, structural, and chemical heterogeneities in large steel ingots is given. The parameters of the structure and the two-phase zone have been determined, as well as the nature of the distribution of segregated materials along the cross-section of ingots, depending on the conditions of their curing. The decisive importance of convective and capillary mass transfer in the interdendritic channels of hardening ingots on the formation of a zonal heterogeneity at their cross-section has been proven.

Experimentally, when crystallizing a model environment (camphene), it has been visually confirmed that the flow of segregated materials in interdendritic channels occurs when a certain amount of impurities accumulates in them. A clear dependence of the speed of this flow on the rate of melt crystallization has been established. With an increase of the hardened part of the melt, the rate of segregated material movement (V_l) increases while the rate of crystallization (R) decreases due to worsening heat release conditions. At a certain distance from the ingot's surface, these rates become equal, and impurities are carried to the curing border, which is the main cause of the formation of zonal segregation.

The results reported here show that the evolution of zonal segregation in ingots can be controlled using various techniques involving external influence on the hardening melt. This study has demonstrated that the adjustable intensity of heat removal from an ingot, as well as the addition of external excess pressure on the hardening melt, could be used as such tools. In the study, to obtain ingots with a minimum level of chemical heterogeneity, it would suffice to provide the following conditions for the curing of the alloy: a value of the alloy crystallization speeds at the level of $R_{cr} \geq 9 \cdot 10^{-2}$ mm/s, or external pressure on the free surface of ingots $P_{ext.} \geq 135$ kPa.

The industrial implementation of the reported results could make it possible to improve the technology of obtaining large blacksmith ingots, provide savings in materials and energy resources, increase the yield of a suitable metal, and improve its quality

Keywords: physical modeling, large ingot, zonal segregation, convective and capillary mass transfer

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1. Introduction

The quality of large steel ingots is mainly determined by the evolution degree of the physical, structural, and chemical heterogeneities. The process that forms physical heterogeneity in ingots is due to the phenomena of shrinkage of steel at hardening [1–3]. Structural heterogeneity depends on the processes of crystallization of steel – directed, volumetric, or volumetric-directed and is determined by the value of the temperature gradient at the ingot's cross-section at its hardening [4–6]. Chemical heterogeneity is formed due to the uneven distribution of impurities in ingots as a result of the decrease in their solubility during the transition of metal from a liquid state to a solid [1, 4, 7].

One of the main defects in large steel ingots is the zonal segregation of impurities. At present, there are many hypotheses that indicate that this process depends on many factors [1, 4, 7]. The contradiction among existing hypotheses is due to a different explanation of the mechanism of the distribution of impurities in ingots during crystallization.

Therefore, it is a relevant task to advance the theory of the emergence of zonal segregation in large steel ingots based on the fundamental studies into the processes that form the

structure and mass transfer of impurities under the conditions of external influences on hardening metal.

2. Literature review and problem statement

As metal alloys harden under equilibrium conditions, the solubility of impurities in them decreases. As a result, before the front of the crystallization of steel, a layer is formed, with a higher concentration of impurities ($C_{max}=C_o/K_o$) compared to the average in the alloy. An increase in the concentration of impurities in steel ingots from C_o to C_{max} proceeds more intensively in the boundary diffusion layer $\delta_d=D/K_o$. Works [4, 7, 8] explain this by the fact that there is a diffusion distribution of impurities during the transition of metal from a liquid state to a solid state. However, the diffusion mass transfer of impurities in alloys is a relatively long process. And in large ingots, the bands of chemical heterogeneity appear in the first minutes of hardening, which is impossible with the diffusion mechanism of this phenomenon. At low values of the coefficient of molecular diffusion of segregation impurities in metals (according to [2], this coefficient is $D=(2\div18)\cdot10^{-8}$ m^2/s), this should have happened within a few dozen hours. That suggests the conclusion that this process, in addition to diffusion, includes other types of the mass transfer of impurities.

Papers [1, 4, 9] explain the appearance of zonal segregation by the development of natural convection, which is caused by a gradient of temperatures in the liquid phase. As a result of convection, the melt of metal, enriched with impurities, moves from the mouth of the dendrites to their peaks, that is, to the surface of the crystallization front. The presence of a temperature gradient at the cross-section of the solid-liquid zone is not necessarily a guarantee of convective flows in the interdendritic space. For example, between crystals growing from the vertical faces of castings in a horizontal plane, that generally seems unrealistic in terms of physics and the geometric dimensions of this space.

The authors of works [3, 10, 11] associate the occurrence of chemical heterogeneity in ingots with the movement of free crystals, which, having a higher density than the surrounding liquid metal, descend and create a gravitational flow. The main role of the gravitational flow in the transfer of segregated materials by them is explained by the fact that during the curing of ingots, the temperature gradient in the liquid phase of metals significantly decreases and, as a result, the intensity of convective flows decreases. The correctness of this hypothesis raises doubts, first, due to the fact that large blacksmith ingots harden for a very long time (sometimes over several tens of hours) and, as a result, the gradient temperature over time falls insignificantly (that is, the convection of metal exists for a long time in them). Second, the number of free crystals before the front of crystallization in the initial moments of curing such ingots is so small compared to liquid metal that it inevitably involves their melting with an overheated melt. And, as noted above, the bands of chemical heterogeneity in large ingots appear in the first minutes of their hardening.

The authors of works [3, 4, 12] believe that the occurrence of zonal segregation may be associated with the movement of metal within the two-phase zone under the influence of capillary forces when the impurity-enriched melt moves from the periphery of the ingot to its center. Given the distance between the axes of the first, second, etc.

order in the dendrite, one can admit that the liquid metal saturated with impurities in the spaces between them can move in line with the law of the moistened capillary. That is, one can say that taking segregated materials to the surface of growing dendrites is a micro process. However, the chemical heterogeneity in large ingots in the form of segregation cords is a macro-phenomenon, so one can assume that the capillary movement of impurities, although it plays an important role, is not the main type of mass transfer in this process.

The issue of zonal segregation in large steel ingots is addressed in many works where the multifaceted nature of this phenomenon in terms of influence exerted on it by various parameters of metal hardening becomes obvious. Paper [13] reports results that indicate that the process of formation of segregation defects in steel is significantly influenced by the rate of ingot crystallization, which, in turn, is determined by the amount of metal overcooling. That is, the higher the rate of crystallization, the lower the degree of zonal segregation. The cited paper suggests a criterion for determining concentration overcooling in steel at hardening (in other words, the release of impurities to the surface of the crystallization front):

$$G/R < \frac{mC_0(1-K_o)}{DK_o}, \tag{1}$$

where D is the molecular diffusion coefficient, m^2/s; G, R is the gradient of temperatures and the rate of steel crystallization, °C/m, m/s; $m=dT/dC$ is the inclination of the liquidus temperature line; K_o is the ratio of the concentrations of impurities dissolved in the solid and liquid phases.

It is obvious from this formula that with a decrease in the rate of crystallization (R), the concentration of segregation impurities (C_o) increases. However, work [13] gives no explanation why that happens.

In large ingots where there are no conditions for equilibrium heat and mass exchange, the melt movement occurs in the interdendritic cavities and along the front of steel hardening. The structure of the ingot is significantly influenced by the nature of melt movement near the front of steel crystallization where the diffusion δ_d and hydrodynamic δ_h border layers are simultaneously formed. Work [1] proved that those layers radically change the concentration distribution of impurities in the ingot when it hardens.

The thickness of the diffusion layer δ_d in the direction of movement of the melt flow for the height of the ingot increases and, under a turbulent mode of its movement, equals [1]:

$$\delta_d = 4.64\frac{1}{Re^{1/2}}(D/\nu)^{1/3}x, \tag{2}$$

where Re is the Reynolds' criterion; ν is the kinematic viscosity of the melt, Pa·s; x is the distance from the front of steel hardening, m.

The thickness of a hydrodynamic boundary layer δ_h for the same mode of melt movement can be determined from the following formula [1]:

$$\delta_h = 0.37(1/Re^{1.5})\cdot x. \tag{3}$$

Formulas (2), (3) demonstrate that the thickness of the layers depends on the value of Reynolds' criterion, that is, on the rate of convective movement of the melt in the ingot. Then the critical speed of the melt is W_{cs}, above which impurities would be washed off the front of steel hardening,

can be determined from the equal thickness of the diffusion and border layers. For the turbulent movement of melt in the ingot, this equality is:

$$4.64 \frac{1}{Re^{1/2}} \left(\frac{D}{\nu} \right)^{1/3} = 0.37 \frac{1}{Re^{1.5}}. \tag{4}$$

It can be assumed that the speed of delivery of impurities to the zone where they are influenced by the hydrodynamic and convective flows of melt is more expedient to determine not by the coefficient of molecular diffusion D but by its effective value D_{ef}. The effective coefficient takes into consideration the effect exerted on the process of mass transfer by segregated materials, as well as their thermocapillary movement in interdendritic channels.

In large ingots, the bands of chemical heterogeneity appear at a depth of 150–200 mm from the side surface after 10–12 minutes of steel hardening. At the values of the coefficient of molecular diffusion of segregation elements $D=(2÷18)\cdot10^{-8}$ m²/s [2], this distance, as shown by the calculations using formula (2), can be traveled by segregated materials in a few days. Therefore, works [12–14] hypothesized that the indicated movement of the interdendritic liquid phase can occur both due to diffusion and due to the evolution of capillary and convective mass transfer processes. It is clear that under the action of such types of mass transfer, the rate of movement of impurities in liquid metal should be orders of magnitude larger compared to their molecular diffusion (according to [12], 10^3–10^6 times more). However, no experimental data that prove this assumption were given in the cited works.

Paper [15] suggested the following dependences in order to determine the volumetric filtration flow and the rate of movement of the melt through the cross-section of the capillary (dendrite):

$$J_\alpha = \alpha \frac{S}{L} \Delta P; \tag{5}$$

$$\omega_\alpha = \frac{\alpha}{L} \Delta P, \tag{6}$$

where α is the filtration coefficient, m/s; S is the capillary cross-section (dendrite), m²; L is the length of filtration zone, m; ΔP is the pressure difference at the ends of capillaries, Pa.

The pressure difference (ΔP) at the ends of capillaries (dendrites) moistened with melt can be determined from the known Laplace dependence [1]:

$$\Delta P = 2\sigma_{s-l}/r, \tag{7}$$

where σ_{s-l} is the surface tension at the crystal-fluid interface, N/m; r is the capillary radius, m.

When molding large steel ingots, the pressure difference at the ends of capillaries is [1]:

$$\Delta P = \frac{2\sigma_{s-l}}{r} - \nu h - P_{ext}, \tag{8}$$

where ρ is the specific weight of liquid steel, kg/m³; h is the height of the metal column above the capillary, m; P_{ext} is the external pressure, which, under the normal ingot hardening conditions is equal to atmospheric, Pa.

The average filtration rate of melt in large steel ingots under the influence of external pressure can be determined from the following equation [1]:

$$\omega_\alpha = \frac{r^2}{8\eta L} \left(2 \frac{\sigma_{s-l}}{r} - \nu h - P_{ext} \right), \tag{9}$$

where η is the coefficient of dynamic viscosity of a liquid, Pa·s.

Paper [4] notes that the amount of melt filtered may also depend on the temperature gradient along the width of the two-phase zone in the ingot. Under the action of such a gradient, hot metal moves to the closed ingot layer, and cold metal to the tops of growing dendrites. The volumetric flow of the melt and its speed in this type of movement can be determined as follows [4]:

$$J_t = B \frac{S}{L} G; \tag{10}$$

$$\omega_t = \frac{B}{L} G, \tag{11}$$

where B is the coefficient of thermal filtration, which is determined experimentally; G is the temperature gradient along the width of the two-phase zone in the ingot, °C/m.

If one assumes the presence of both types of melt movement in the interdendritic space, then the total volumetric flow of segregated materials and the speed of their movement between dendrites can be determined as the sum of their corresponding values from formulas (5), (6), (10), and (11).

When segregated materials move between the dendrites, capillary pressure P_c occurs, due to the interphase tension, which, when reaching the surface of the crystallization front, equals [2]:

$$P_c = 2 \frac{\sigma_{s-l} \cdot \cos\theta}{r}, \tag{12}$$

where θ is the angle of contact of the liquid phase with the surface of the channel, degrees; σ_{s-l} is the interphase tension, N/m.

Formula (12) clearly shows that when $\theta>90$ °C, the segregated materials do not move in the interdendritic space.

The movement of segregated materials between dendrites is also hindered by friction forces, which are due to a change in their viscosity. From the theory of hydrodynamic resistance of the medium, a value of friction forces (P_η) can be determined from the following equation [2]:

$$P_\eta = \frac{32}{\nu} \eta \frac{L}{d^2} W, \tag{13}$$

where ρ and η is the specific weight and coefficient of dynamic viscosity of liquid phase, kg/m³, and Pa·s; L is the length of the interdendritic channel, m; W is the fluid movement speed, m/s; d is the capillary diameter, m.

The release of segregated materials from the interdendritic space to the front of steel crystallization is also hindered by external pressure P_{ext}, the value of which depends on the hydrostatic pressure of liquid metal over the capillary P_{hr} and the medium P_{aver} in which the ingot hardens [16]. Taking into consideration the external pressure, the total pressure in the capillary (P_σ) at its release to the front of steel crystallization is [2]:

$$P_\sigma = \frac{4\sigma_{s-l} \cdot \cos\theta}{d} - \frac{32}{\nu} \cdot \frac{L}{d^2} \eta \cdot W - P_{ext}. \tag{14}$$

Force F, under the action of which the segregated materials are ejected from the interdendritic space, depends on the total pressure [2]:

$$F = P_{ext} \cdot S = (P_\sigma - P_{int}) \cdot S, \tag{15}$$

where S is the cross-sectional area of the liquid phase flow, m^2.

Capillary pressure P_c value is constant for the specified stage of ingot hardening. The pressure of external forces P_{ext}, which depends on many factors, significantly affects the process of formation of chemical heterogeneity in ingots. Therefore, the upper half of steel ingots, where the hydrostatic pressure of the metal is less, always has a more developed zonal chemical heterogeneity compared to the lower layers.

This issue has been addressed by many works whose authors applied numerical research methods to develop mathematical algorithms that make it possible, within the permissible limits, to determine the parameters of zonal segregation in steel ingots [17–20]. Papers [17, 18] employed a method of mathematical modeling based on Darcy's law to investigate the capillary mass transfer of segregated materials through the porous area of columnar dendrite structures at different volumetric shares of the liquid phase of the metal. The authors performed a comparative analysis of the obtained results with known experimental data; the correlation coefficient is in the range from 0.5 to 0.95, depending on the dimensions of the ingot. The authors of works [19, 20] report a mathematical model for predicting the macrosegregation of impurities by convection when hardening steel ingots of different masses (3.3 and 231 tons). The proposed model takes into consideration the effect of the gravitational movement of equiaxed dendrites before the front of crystallization on the convection of liquid metal and, as a result, the resulting pattern of the macrosegregation of impurities at the ingot's cross-section. However, in those works, the authors conducted studies into the specific dimensions of ingots made from different grades of steel. Therefore, there is no universal mathematical model that would make it possible to predict with sufficient accuracy the evolution of processes that form chemical heterogeneity for a wide range of steel ingots.

Given the existing hypotheses regarding this phenomenon (the zonal segregation of impurities), it can be stated that at present there is no common opinion about the processes that form chemical heterogeneity in large steel ingots. Therefore, there is reason to consider it expedient to conduct research in this area.

3. The aim and objectives of the study

The aim of this work is to study the processes of the occurrence of zonal segregation in large steel ingots under equilibrium hardening conditions. This would make it possible to manage the process of zonal segregation and produce ingots with a higher chemical uniformity.

To accomplish the aim, the following tasks have been set:
– to establish a mechanism of mass transfer of segregation impurities during the crystallization of alloys under the equilibrium hardening conditions;
– to devise scientifically based recommendations on the choice of optimal parameters for the external influences on hardening metal in order to control the process of mass transfer of segregation impurities in steel ingots.

4. The study materials and methods

Metals in both solid and liquid states are opaque, in addition, their hardening processes occur at very high temperatures. Therefore, direct studies of the processes occurring during their hardening are extremely difficult; therefore, it is most appropriate and fruitful to use transparent model substances. In our study, the organic substance camphene ($C_{10}H_{16}$) was used as such an environment. Camphene is a transparent environment characterized by a low melting point, prone to supercooling, a small rate of crystallization, the reproducibility of results, and low toxicity (safety in work). In addition to the above properties, camphene, like metals, crystallizes with the formation of a dendrite structure and has a crystallization interval. When camphene crystallizes, the segregation impurities in the ingots are tricyclene and air.

Our research employed a method of local physical modeling under which the conditions of similarity are met in a separate region of the object. The chosen region was an axial ingot zone. In local modeling, complex processes and their interactions that occur in the ingot during crystallization [21, 22] can be excluded from consideration.

The study was carried out using a transparent model, which was cooled with water. Such a setup made it possible to adjust the intensity of heat release from the hardening ingot through the bottom, side, and upper parts simultaneously or separately (Fig. 1).

It should be noted that the model of ingot had a small thickness (5 mm) and made it possible to clearly observe the origin and topography of the propagation of the hardening front, the appearance of segregated materials in the solid-liquid zone, as well as to measure the rate of crystallization and the propagation of segregated materials in the interdendritic space.

The hardening processes of the camphene alloy were modeled under the following thermophysical conditions: at different temperatures of heat-releasing faces of the model of 4; 22.5; and 42 °C, which ensured the hardening of the ingot under the conditions of intense, moderate, and weak heat release; that approximately corresponds to the conditions of hardening a natural workpiece in a copper water-cooling mold, cast-iron casting, and thermal insulation form.

The experiments were carried out in the following sequence: the melt of camphene was poured into the model at the same overheating temperature of 47 °C, which corresponds to the temperature of steel casting (in accordance with the selected temperature scale); then, at intervals of 2 minutes, we registered readings from the thermocouples and measured the parameters of crystallization.

The following parameters were determined during the experiments:
– a quantitative assessment of the nature and speed of the propagation of a hardening front;
– a value of the temperature gradient in different zones of the ingot during the hardening of an alloy;
– the assessment of the nature and rate of the mass transfer of impurities in the solid-liquid ingot zone, depending on the hardening conditions;
– the duration of the total hardening time of ingots;
– the resulting structures of the hardened ingots were photographed.

The procedure used in this work makes it possible to manage the process of zonal segregation in ingots by controlling the thermophysical conditions of hardening and external force influences.
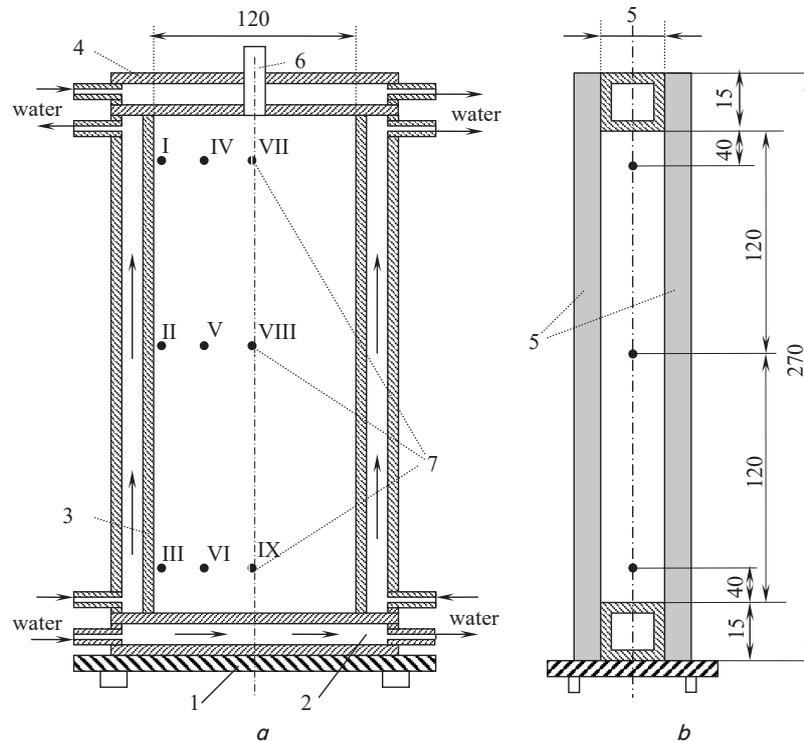
Fig. 1. Physical model for studying the processes of structure formation and the occurrence of zonal segregation in ingots:
1 — base; 2 — cooled bottom; 3 — side faces; 4 — cover; 5 — transparent walls; 6 — nozzle to create a vacuum or pressure in the ingot; 7 — thermocouples; I—IX — thermocouple numbers; *a* — frontal view; *b* — cross-cut view along the ingot axis

5. Results of studying the processes of the mass transfer of segregated materials during the hardening of ingots

5. 1. The mechanism of the mass transfer of segregation impurities during the crystallization of alloys under the equilibrium hardening conditions

The results of our studies have established that the movement of segregated materials is observed only after the accumulation of a certain amount of them in the interdendritic space at which capillary pressure is created. The speed of segregated material movement V_l in the interdendritic spaces of the flow at the beginning of hardening an ingot is small (Fig. 2). With subsequent crystallization of the ingot, the concentration of impurities in the melt of camphene in the interdendritic channels increases, and, with an increase in the number of impurities, the speed of their movement increases (Fig. 2, red curve). At the same time, the intensity of displacement of the crystallization front of the ingot due to the growth of the thermal barrier (that is, the thickness of the hardened crust) decreases (Fig. 2, blue curve). At a certain distance from the surface of the ingot, their speeds become the same, which contributes to the accumulation of segregated materials near the front of the alloy hardening.

The fundamental conclusion from the above figure is that one can control the movement of segregated materials in hardening ingots by adjusting the rate of crystallization. For a given case, to prevent the release of the segregated materials to the surface of the hardening front, it is necessary to ensure the level of crystallization speeds above R_{cr} (Fig. 2, horizontal dashed line).

At the bottom of the ingot, the number of segregation channels is greater compared to the upper one (Fig. 3).

This is due to the fact that at low growth rates of crystals at the top of the ingot, the amount of segregated materials that are formed is not enough to fill the interdendritic spaces. Therefore, the number of segregation channels at the top of the ingot is smaller, where the melt temperature is higher. At elevated temperatures, the number of impurities released when hardening steel is not enough to form such channels.
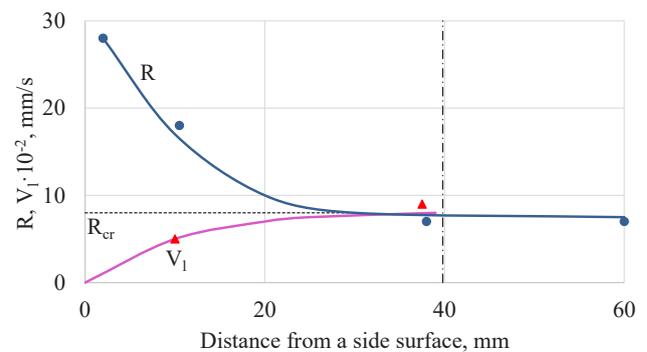

Fig. 2. The movement rate of crystallization front *R* and segregated materials V_l at the middle level of an ingot made from camphene

The length of the segregation channels in the horizontal direction depends on the value of the temperature gradient in the cross-section of the ingot. When tempering individual volumes of liquid metal along the front of steel hardening, their temperature decreases. At the same time, the rate of steel crystallization, the intensity of the process of release of impurities, and the length of the segregation channels increase.

Fig. 3. Segregation channels in an ingot made from camphene

With an increase in the thickness of branches in a growing crystal, the concentration of segregated materials in the liquid phase increases, and the size of the channels for their movement decreases. The amount of the surface tension of liquid impurities along the growing branches of dendrites varies. In this case, the segregated materials move from areas with increased surface tension to areas with its lower value. The process of moving liquid segregated materials is facilitated by the difference in their temperature at the beginning of the channel and at its outlet to the front of steel hardening. The speed of movement of liquid impurities between crystals also depends on a value of the ratio of the perimeter to the cross-sectional area of the channel. At high values of this ratio, the melt hardens in the intracrystalline spaces with little or no movement of segregated materials.

We studied the processes of the crystallization of ingots made from camphene at the different intensities of heat removal from them. It was established that with intensive cooling of the ingot (Fig. 4, *a*) the speed of movement of the segregation impurities in the vertical (curve 1) and horizontal (curve 2) directions are almost the same. With moderate heat release (Fig. 4, *b*), these speeds remain equal at a distance of 20 mm from the water-cooled faces. Then the flow rate of the segregated materials from the bottom of the ingot significantly exceeds the intensity of their lateral movement. This is due to the fact that with slow (volumetric) crystallization in steel, no zones are formed with an increased concentration of segregated materials and impurities are evenly distributed into the ingot.
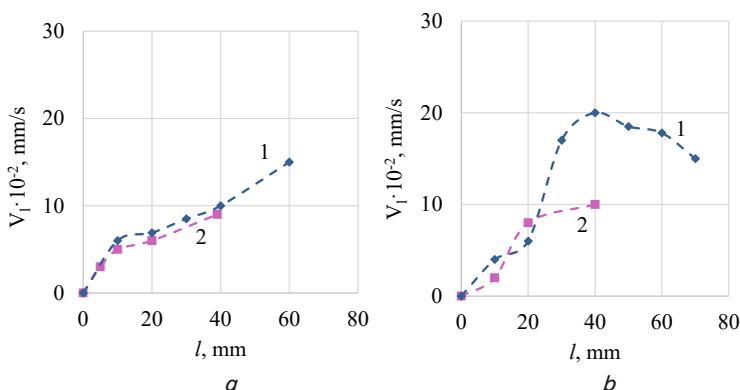
5. 2. Defining the techniques to manage the process of the mass transfer of segregation impurities in steel ingots

According to dependence (15), with the same values of the capillary P_σ and external $P_{ext.}$ pressures, the force under which the segregated materials move through the interdendritic spaces to the front of steel hardening, is zero. Therefore, the amount of external pressure at which the segregated materials do not move in an ingot should exceed the capillary:

$$P_{ext.} \geq P_\sigma. \tag{16}$$

The capillary pressure (P_σ) for camphene, calculated from equation (14), excluding the forces of viscous resistance, is ~135 kPa. It was determined that at the values of external pressure ≥135 kPa, the interdendritic movement of segregated materials in the hardening camphene is absent (Fig. 5).
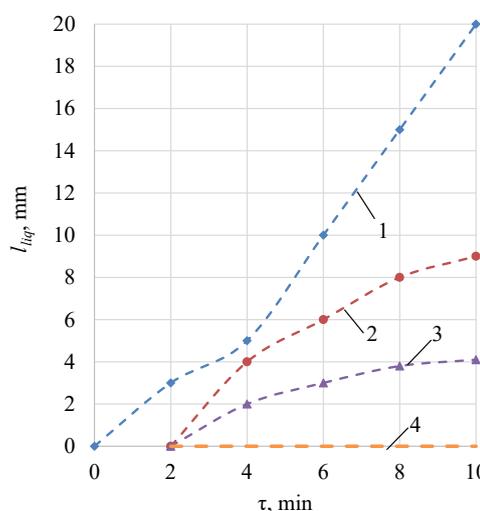

Fig. 5. Length of the segregation channels l_{liq} at the middle level of camphene ingots that harden at different external pressures: 1 — $P_{ext.} = 0$ kPa; 2 — $P_{ext.} = 50$ kPa; 3 — $P_{ext.} = 100$ kPa; 4 — $P_{ext.} = 150$ kPa

With increasing external pressure, the length of the segregation channels in an ingot decreases. At an external pressure of 150 kPa, the thermocapillary mass transfer of segregated materials in camphene is absent at all (line 4 coincides with the horizontal, Fig. 5). This is due to the slowing down of the process of the release of segregated materials in camphene and counteracting capillary pressure. Such a mechanism of mass transfer is confirmed by the fact that after relieving the pressure on the ingot, the active process of the release and movement of segregated materials between dendrites begins.

During the crystallization of camphene under atmospheric conditions, the segregation channels extend to a low depth from the ingot surface (Fig. 6, *a*). In the case of increasing the external pressure on an ingot to 150 kPa, the release of the segregated materials in camphene does not occur at all (Fig. 6, *b*).

Reducing the pressure on camphene (creating a vacuum) intensifies the thermocapillary mass transfer of segregated materials between dendrites. With an increase in rarefication over the modeling

Fig. 4. Movement of the capillary flow of segregated materials in an ingot made from camphene when hardening: *l* — distance from the walls of the model; 1 — vertical direction; 2 — horizontal direction; *a* — with intensive heat release from the ingot (4 °C); *b* — with moderate heat release from the ingot (22.5 °C)

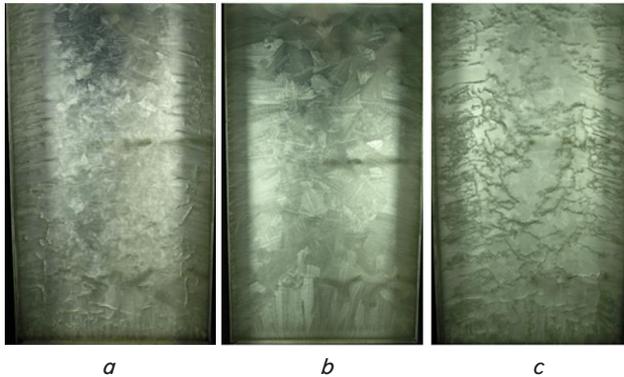medium above 90 kPa, the segregated materials are distributed throughout the entire ingot (Fig. 6, c).

Fig. 6. Segregated materials in the interdendritic spaces of camphene ingots, which harden at different pressures: a — under atmospheric conditions; b — under the pressure of ~150 kPa; c — in a vacuum — 95 kPa

When external pressure is applied to an ingot during the crystallization of steel, the process of the capillary mass transfer of segregated materials in the interdendritic spaces slows down. In case of a decrease in this pressure (creating a vacuum), the intensity of the mass transfer of segregation impurities to the front of steel hardening, on the contrary, increases.

When hardening steel under pressure, the critical size of the embryos r_c and the amount of work for their formation A_c decrease. At the same time, the time of steel crystallization is reduced [23]. As a result, the mass of the segregated materials that are carried by diffusion decreases. A value of the molecular diffusion coefficient depends on the temperature, viscosity of the melt, and pressure [24]:

$$D = Rt/\delta \cdot \eta \cdot e^{PV/Rt}, \tag{17}$$

where R is the gas constant, J/(mol·K); t is the melt temperature, °C; δ is the length of the free run of an atom, m; η is the coefficient of dynamic viscosity of the melt, Pa·s; P is the pressure over liquid metal, Pa; V is the primary volume of the liquid phase, m^3.

Formula (17) clearly demonstrates that with an increase in the pressure and viscosity of the melt, while reducing its temperature, the diffusion coefficient decreases, as well as the diffusion rate of impurities in steel. At the same time, the rate of the release of segregated materials in the hardening melt decreases, which slows down the intensity of their movement in the interdendritic spaces.

Thus, it can be assumed that the results reported here could form the basis for improving the technology of producing large blacksmith ingots with high chemical homogeneity.

6. Discussion of results of studying the processes of the mass transfer of segregated materials during the hardening of ingots

When casting steel in the casting in hardened ingots, along with many defects, there is also a characteristic chemical heterogeneity in the form of zonal segregation. With an increase in the mass of ingots (especially characteristic of blacksmith ingots), this heterogeneity increases, which leads to their refusal in the manufacture of forgings. As it follows from the results of our research, during the crystallization of alloys there are a number of processes such as the origin and growth of crystals, the diffusion of impurities, convective and capillary mass transfer, contact and non-contact heat exchange, etc. These processes under the normal conditions of ingot hardening occur with different intensities, which is the main reason for the evolution of chemical inhomogeneity in them.

Standard methods for determining chemical heterogeneity in steel ingots include metal science research into their macro-microstructures, which is associated with high time, material, and technical costs. The advantage of our study is that the transparency of the model environment has made it possible to visually observe the process of the occurrence and mass transfer of segregated materials in the solid-liquid zone of crystallized ingots in real time (Fig. 3, 6). This aspect makes it possible to draw unambiguous conclusions on the nature of the phenomenon under study (the zonal segregation in ingots).

The procedure used in this work has made it possible to establish that the degree of the evolution of chemical heterogeneity depends on the overheating temperature of the melt, the intensity of heat release from hardening metal, and the external pressure on it (Fig. 4, 5). That allowed us to devise technological principles for managing the process of zonal segregation in ingots by controlling the thermophysical conditions of hardening and the external force influences (in this case, external pressure).

Despite all the clarity in presenting the results in this work, the development of proper practical recommendations for managing the process of the occurrence of zonal segregation in actual ingots necessitates the consideration of a large-scale factor. To this end, the current study might be advanced in two main areas.

First, it is necessary to more thoroughly calculate the time, temperature, and force scales of modeling at all levels of the technological process – from the melting unit to the casting – in relation to actual production conditions.

Second, it is necessary to adapt the developed principles to the most popular sizes of steel ingots. Today, such is the production of large blacksmith ingots, in which one of the most common defects is zonal segregation.

7. Conclusions

1. We have analytically and experimentally confirmed the hypothesis that the movement of segregated materials in the interdendritic space occurs not only as a result of molecular diffusion. Mainly, this is the result of the evolution of capillary and convective mass transfer, associated with the emergence of interphase forces at the border of segregation substances and crystals, as well as a gradient of temperatures for their height.

2. The result of the clarification of the mechanism of mass transfer of segregation impurities in the interdendritic space of hardening ingots is the established prerequisites for devising the means to reduce the chemical and zonal heterogeneity of ingots. The effective means, suggested here, which could inhibit the interdendritic movement of segregated materials, include techniques such as the high speed of metal crystallization or the application of external pressure on the open

surface of the metal in the casting. In the study reported here, ingots with a minimum level of chemical heterogeneity were obtained under the following conditions of their hardening: the values of the melt crystallization speeds are at the level of $R_{cr} \geq 9 \cdot 10^{-2}$ mm/s; the external pressure on the free surface of ingots is $P_{ext} \geq 135$ kPa.

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