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A MECHANISM OF OCCURRENCE OF PERIODIC MACROSTRUCTURES IN MOVING FREEZING MELTS

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The present paper deals with an interesting physical phenomenon that has been discovered in studies of a metallic coating applied to a silica fiber light pipe by the freezing technique.

In recent years, light pipes coated with metals are being used more and more in practice, and the process of applying a protective metallic coating is one of the most important stages of their manufacture. This process is carried out by a freezing technique that consists in pulling a silica fiber through a liquid metal layer of finite thickness. Obviously, when the thickness of this layer is such that the duration of contact with the melt is less than the time required to heat the pipe to the metal melting point T_{melt}, some amount of the metal must be frozen as a continuous layer onto the fiber surface [1].

Investigations have shown, however, that coatings applied by the freezing technique have the property that they have inhomogeneities in the form of cavities that are not filled with metal on the inside (adjacent to the glass). These inhomogeneities would probably not attract considerable attention if it were not for the surprising regularity in the location of the cavities along the fiber. This is illustrated in Fig. 1, which shows a section of a typical metal-coated light pipe photographed by means of a microscope from the side from which the metal has been removed. The inner surface of the remaining opposite part of the coating is clearly seen through the glass of the light pipe, where the cavities have the form of bands separated by wider sections of the metal adjacent to the glass. In fact, the cavities are, as a rule, spaces that are closed around the fiber. The projections of these spaces onto the surface of the fiber are ellipses of fairly regular shape. The centers of gravity of the cavities are located equidistant along the axis of the fiber.

What is the mechanism of formation of these cavities in the frozen metal layer? Why do they occur regularly?

Since the glass surface is a surface that bounds each of the cavities, the answer to the first question should be looked for in the molten-flow instability caused by the fiber moving in the melt.

As an illustration, Fig. 2 shows a schematic diagram of the freezing technique. A constructional feature of the setup for manufacturing glass fibers is that the fiber is pulled through the metal spray gun from top to bottom. Molten metals are liquids with high surface tension σ [2], and most of them wet silica poorly [3]. Therefore, a meniscus forms when the fiber enters a melt. The meniscus curvature near the glass surface is the larger, the higher the fiber pulling rate. Unfortunately, it is impossible to investigate experimentally what happens to the liquid metal inside the metal spray gun when it comes in contact with the fiber having a temperature below T_{melt}. Therefore, we use the results of the numerical calculations performed by the two-dimensional hydrodynamic model developed for the freezing technique and based on the Navier–Stokes equations [4]. The fact that the boundaries of the domain of integration include both free surfaces (menisci F_1 and F_2 in Fig. 2) and the phase-transition surface R which separates the melt and the frozen metal is taken into account.

The results of such calculations are qualitatively predictable from a physical point of view. It is clear that crystallization of the melt begins instantaneously (practically at the point of contact of the melt with the cold fiber). When moving through the melt, the fiber is gradually heated, and the crystallization rate of the metal decreases to zero at point z_0. At this point, the thickness of the frozen-metal layer reaches a

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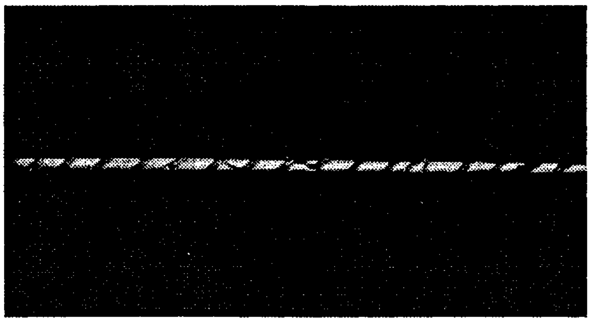

Fig. 1

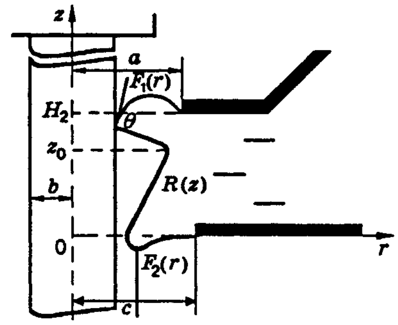

Fig. 2

maximum. Later on, when the fiber temperature approaches $T_{\rm melt}$, the reverse process of melting of the frozen layer begins. From these considerations, according to the calculations performed, we conclude that, in the steady-state process, the metal frozen on the fiber must be an immovable body of revolution. An exemplary cross-section of such a body is shown in Fig. 2 by the curve of $R(z)$.

The phenomena described depend quantitatively on numerous process parameters, such as the fiber pulling rate V, the radius of the fiber cross section b, the actual temperature of the melt, the geometrical dimensions a, c, and H_2, and the physical properties of the metal used. It is also clear that each point of the body bounded by the curve R is moving at a speed that coincides with the speed of the fiber. The immovability of the boundary R is caused by the fact that the melt enters the domain bounded by R through the upper part of the curve up to the point z_0, and is then subjected to phase transition, and is removed from the remaining part of the boundary R during the reverse process of melting.

It should be borne in mind that, since metals are wetted well by their own melts, a part of the liquid metal must be carried over by viscous forces from the metal spray gun above the frozen layer. This contributes to the resulting thickness of the coating upon freezing. The qualitative agreement between the calculated resulting thickness of the frozen coating and experimental data indicates the validity of our concepts of the basic phenomena in the metal spray gun unit [4].

The liquid flow in the metal spray gun is initiated and sustained by the interaction of the melt with the metal that has already frozen on the fiber rather than by the viscous interaction of the melt with the fiber. Actually, it follows from the law of conservation of mass flow that, for example, the longitudinal velocity component of the melt must be equal to V over the entire boundary R and not only near the surface of the fiber, as it would be with no phase transition. In other words, if the metal were not frozen on the fiber, the motion of the melt in the metal spray gun would be less intense. In accordance with the conservation law, the melt follows the just-frozen metal under the entrance meniscus and can sink to a considerable depth without coming into contact with the fiber. In this case, the excess of surface tension over the internal pressure in the liquid is the force that delays contact of the meniscus with the fiber. The calculations of [4] have also shown that, because of the high values of σ, the depth of the meniscus can be great ($\sim$300 μm for a fiber diameter $2b = 125$ μm and for the typical value of $V \sim 0.2$ m/sec).

So far we have used the results of the calculations performed by a model of viscous incompressible flow. In the general case, such flow is described by nonlinear equations which, being subjected to steady boundary conditions, always have a steady solution. But the motion described by this steady solution is not always realized in reality, because it can be unstable against small perturbations.

Let a steady solution of hydrodynamic equations that describe some flow be known, i.e., the distributions of the pressure $p_0(\mathbf{r})$ and of the velocity components $\mathbf{V}_0(\mathbf{r})$ are known. In principle, this solution can be investigated for stability. We assume, for example, that small unsteady perturbations of $p_1(\mathbf{r}, t)$ and $\mathbf{V}_1(\mathbf{r}, t)$ are superimposed on the solution. These small perturbations satisfy with high accuracy the following system of equations [5]:

$$\frac{\partial \mathbf{V}_1}{\partial t} + (\mathbf{V}_0\nabla)\mathbf{V}_1 + (\mathbf{V}_1\nabla)\mathbf{V}_0 = -\frac{\nabla p_1}{\rho} + \nu\Delta\mathbf{V}_1 + \mathbf{g}, \quad \operatorname{div}\mathbf{V}_1 = 0. \tag{1}$$

This system is obtained if we substitute the perturbed pressure and velocity into the equations of hydrodynamics and assume that p_0 and $\mathbf{V}_0$ satisfy these equations. Here ρ is the liquid density, $\mathbf{g}$ is the acceleration of gravity, and ν is the dynamic viscosity.

Since the coefficients in the system obtained are functions only of the space coordinates, the general solutions of Eqs. (1) are series whose terms depend on time as $\exp(-i\omega t)$, where ω is generally a complex perturbation frequency to be also determined by solving (1). If the desired solution of (1) attenuates with time, the steady solution $(p_0, \mathbf{V}_0)$ investigated and the flow described by this solution are stable. This is the case if the imaginary parts of all possible perturbation frequencies ω are negative.

It is, as a rule, impossible to perform the stability analysis described, because one should specify initial and boundary conditions to find a solution of (1). In practice, however, we can only state with assurance that the relative velocity must vanish at solid surfaces.

Usually, the Reynolds number Re is a criterion for stability: the higher this number, the less stable the flow. Viscous friction in the flow suppresses the development of instability. The viscosity of liquid metals is known to be small [2], and the flow dimensions and velocities that are typical for the freezing technique are also small. In the process of applying a metal coating to a fiber, the melt flow Reynolds number is $\mathrm{Re} = Vb/\nu = 30$–$300$. At the same time, numerous experiments have shown that the critical Reynolds numbers Re_{cr} for the onset of instability are on the order of several tens for various flows (see, for example, [5]). This means that the conditions for the most reliable metallic coating of fibers correspond to $\mathrm{Re} \geqslant \mathrm{Re}_{cr}$. Thus, in reality, the melt flow is unstable in the overwhelming majority of cases.

As Re increases, the following takes place. When $\mathrm{Re} < \mathrm{Re}_{cr}$, the imaginary parts of all perturbation frequencies are negative, and the flow is stable. As soon as $\mathrm{Re} = \mathrm{Re}_{cr}$, the imaginary part of at least one frequency becomes zero, and the perturbation at this frequency gives only a small oscillating additive to the basic stationary solution. When Re is only slightly larger than Re_{cr}, the imaginary part of this frequency becomes positive, and this makes the motion unstable with time. A further increase in Re leads to a gradual increase in various perturbation frequencies with positive imaginary parts. Interaction between many periodic perturbations with commensurable (multiple) frequencies causes the steady laminar flow to become unsteady. Under these conditions, each particle moves randomly, and the motion as a whole in a specific direction is realized only on the average.

Thus, we can conclude that, as Re increases, the spectral distribution of perturbation intensity becomes wide and unsteady.

In our case, however, although the relation $\mathrm{Re} \geqslant \mathrm{Re}_{cr}$ is satisfied, the instability of the melt moving under the meniscus does not develop considerably and breaks down from time to time. Actually, in the development of the instability, a portion of the energy of the ordered translational motion transforms to random fluctuation components. Thus the flow generally slows down, whereas the fiber with the metal frozen on it continues to move at a constant speed.

The intensity of the random momentum components increases with time. The melt lags behind the frozen metal somewhere near the phase-transition boundary, and, as a result, the flow discontinues, i.e., the meniscus breaks down to produce new elements on the surface of the melt. The downstream part of the discontinuity moves behind the metal frozen on the fiber and freezes, making a contribution to the already available metal coating. The capillary forces tend to make the area of the new surface as small as possible by rounding it off and thereby moving it somewhat off from the fiber. The forces of internal pressure press the lagging part of the meniscus to the fiber.

As a result of the interaction of these two processes, the point of contact of the melt with the moving fiber is somewhat higher than the sunken part of the phase-transition boundary, in which the meniscus has broken down. Touching the fiber surface, the melt freezes, as if fixing the point of contact. Thus, a cavity forms. However, it is seldom that the meniscus ruptures simultaneously at all points of a cross section perpendicular to the axis of the fiber. In this case, the resulting cavity would be a body of revolution (in Fig. 1, such cavities would correspond to the bands perpendicular to the axis of the fiber).

As a rule, the development of instability is nonsymmetric, and the rupture of the meniscus is initiated locally because of the small deviations of the system from axial symmetry. As a result, the formation of a cavity develops back in time owing to the motion of the fiber, and the cavity itself is no longer a body of revolution, but rather an ellipse. After the cavity has been formed owing to the contact between the melt and the fiber, a part of the melt, due to inertia, continues to be pressed to the fiber and to be frozen on it above the point of contact, thereby increasing the surface area of the frozen metal layer. In this case, the flow instability is suppressed, and the reverse process for the wetted perimeter ends when the inertial force becomes equal to the capillary forces.

From this point on, the entire cycle described above is repeated. This does not mean, however, that it is repeated exactly, because the transverse momentum component caused by the suppression of instability and the resulting inertial force depend not only on the components of the basic ordered motion but also on the liquid. Therefore, the location of the point at which the melt touches the fiber again and the location to which the wetted perimeter rises along the fiber starting from this point should be different in the general case. In other words, the phenomena considered are not periodic. Why then do the experimentally observed cavities occur with such a surprising periodicity?

The fact is that, for media of unlimited extent, it is impossible to introduce a characteristic geometrical dimension of the system, and elastic perturbations with arbitrary wavelengths can propagate. In contrast to this, the upper meniscus in each particular situation has specific dimensions and, hence, an infinite but discrete set of natural oscillations. The meniscus dimensions are determined, for example, by its curvature at an arbitrary point. Natural oscillations can be excited by fluctuations of the light-pipe diameter, of the speed of its motion, and of its location relative to the entrance edges. However, the viscous-friction force generating when the fiber is pulled through the melt is the key source of oscillations of the meniscus. This force acts permanently, in contrast to the sources listed. Clearly, because of the nonperiodic character of exciting perturbations with a continuous spectrum of intensity, only those meniscus oscillations are actually excited that correspond to its natural frequencies. The oscillations of the remaining frequencies that are not resonant for the meniscus must be damped. In other words, the observed regularity of the locations of cavities in the coating must correspond to one of these natural frequencies of the meniscus.

Natural frequencies are easily found only for bodies of simple configuration. In our case, however, the meniscus shape is itself determined by a system of nonlinear hydrodynamic equations, and is a solution of a nonlinear differential second-order equation [1] even for a static meniscus (a fixed fiber). Therefore, determination of natural frequencies is a complicated mathematical problem. It is not necessary, however, to find the entire spectrum of natural frequencies to prove the hypothesis that the period of cavity locations in the frozen coating is the period of a natural oscillation of the meniscus. It would suffice to show the same dependence of these periods on the physical parameters of the system, which can be done without complicated calculations.

Indeed, we are dealing with relatively thin fibers ($b \leqslant 1$ mm), for which the characteristic size ξ of the meniscus is much smaller than the capillary constant ($æ = \sqrt{2\sigma/\rho g}$). In this case, the natural oscillations of the meniscus are capillary waves. For low-viscosity liquids such as liquid metals, the frequencies ω of capillary waves are given (see, for example, [5]) by the expression

$$\omega = A[\sigma/(\rho\xi^3)]^{1/2} \tag{2}$$

with accuracy up to the constant A that depends on the indices of the oscillating modes in each specific case. In particular, for the natural frequencies of a spherical liquid drop of radius ξ, we have $A = \sqrt{l(l-1)(l+2)}$, where l is the index of the spatial spherical harmonic [5]. In this case, $l = 2$ for the lowest frequency ω^*, so that $A = 2\sqrt{2} \approx 2.8$. The remaining higher frequencies are proportional to ω^*.

In our case, where the problem of finding the natural oscillations of the meniscus should be solved in cylindrical coordinates, the modes should be classified in accordance with the indices of the corresponding cylindrical functions. Since the domain of solution does not contain a zero radial coordinate, the solution

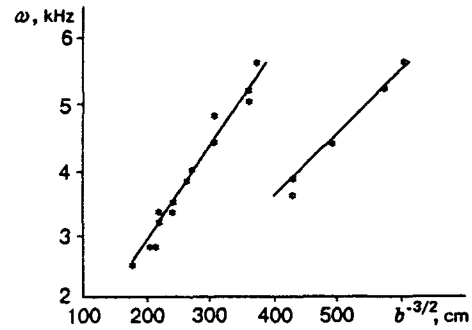

Fig. 3

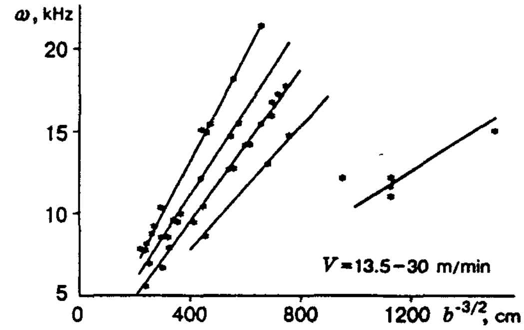

Fig. 4

should be a linear combination of cylindrical functions of both the first and the second kind.

Generally speaking, a combination of the fiber radius b and the entrance size a of the metal spray gun having the dimension of length should be used as the characteristic dimension ξ in (2) (Fig. 2). The contribution of b to this combination must decrease with an increase in a. The reciprocal of the meniscus curvature, for example, near the wetted perimeter can be such a combination that satisfies the above requirements. To find it, it is necessary to know the meniscus shape, which, as was already noted, can be found only on the average because of the oscillatory motions of the meniscus. When $b \ll a$, the curvature, which is generally determined as $(1/R_1 + 1/R_2)$, can be found approximately with acceptable accuracy (R_1 and R_2 are the main curvature radii). In this case, one of the radii, for example, R_2, greatly exceeds the other, so that $\xi \approx R_1 \approx b/\cos\alpha$, where $\alpha = (\pi - \theta]$ and θ is the angle of contact [4].

Preparatory to analyzing the results of investigations of coatings applied to fibers in various regimes of the freezing process, let us turn once again to expression (2), which determines the natural frequencies of the meniscus. From this expression follows the linear function $\omega = \omega(\xi^{-3/2})$, whose slope is equal to $A\sqrt{\sigma/\rho}$ and changes discretely for different A. Also, it is clear from physical considerations that all straight lines for different A pass through the coordinate origin. Actually, to the situation with $\xi \to \infty$ corresponds a medium of infinite extent in which discrete natural oscillations are absent ($\omega = 0$), but perturbations of arbitrary wavelengths can propagate.

The repetition frequency of elliptical cavities is determined as $\omega = 2\pi V/\Delta l$ by using the pulling rate of the fiber and the measured distance Δl between the centers of gravity of the cavities. When the speed of the fiber is varied (the other parameters being constant), the frequency turned out to be constant within the measurement accuracy over a not too wide range of Re for each metal, in agreement with (2). Variation of b in the same range of Re and with the other parameters being constant leads to a variation of the frequency according to relation (2).

As an example, Fig. 3 shows the results of investigations for coatings applied at a pulling rate of 9.4 m/min, when only the fiber thickness was varied. The condition $b \ll a$ is satisfied, and, hence, $\xi \approx b/\cos\alpha$. First, in agreement with (2), the linear function $\omega = \omega(b^{-3/2})$ is evident. Second, the discrete character of the natural frequencies manifests itself in the fact that for the same specific value of b, these frequencies can only be present in curves with different slopes [different A in (2)].

Furthermore, as is shown in [4], the range of fiber pulling rate in the process of applying a metallic coating by the freezing technique is specific for each metal. In particular, this range is limited by the time of fiber heating to the temperature T_{melt}. Therefore, the fiber speeds for metals with relatively high T_{melt} must be as high as possible.

We now compare two different metals with considerably differing melting points, for example, copper and aluminum. Then, the pulling rate in the real process of coating with copper exceeds the corresponding rate for aluminum by a factor of approximately two. The copper viscosity, however, is lower than the aluminum viscosity by a factor of ~2.5. Therefore, the value of Re for copper exceeds the value of Re for aluminum by a factor of ~5, for the same thickness of the fiber. Thus, the spectrum of flow perturbations for liquid copper must be much wider than that for aluminum. In this case, natural oscillations of the meniscus with different frequencies can be excited for the same value of b. For copper, this has been observed in practice.

For example, two (sometimes three) frequencies in straight lines with different A correspond to a value of b in the function $\omega = \omega(b^{-3/2})$ in Fig. 4. In other words, sequences of cavities located in accordance with one or another natural frequency of oscillations of the meniscus are found in each 1–3-cm-long section of a fiber only. This indicates again that the spectrum of the perturbations is unsteady, so that at different times one or another natural oscillations of the meniscus are resonant with the perturbations.

Likewise, for other speeds and other ranges of Re, the natural frequencies of the meniscus as functions of $b^{-3/2}$ for aluminum (Fig. 3) will be straight lines with different slopes.

Thus, the wetted perimeter accomplishes complex periodic motion over the fiber surface with a frequency that is equal at each instant of time to a natural frequency of the entrance meniscus. An experimentally observed cavity forms in the lowest position of the meniscus internal edge near the surface of the fiber.

The occurrence of regular cavities in a melt that moves and freezes on a fiber exemplifies the self-organization of initially disordered systems. Such phenomena have been much studied for ordered structures at the microlevel. These include, for example, crystallization processes in the liquid–solid phase transitions, generation of coherent light in lasers, etc. The nonequilibrium character of the phenomenon is common for them. This is typical of open systems [6], for which a situation can arise that causes a decrease in entropy. At the same time, self-organization phenomena at the macrolevel also occur in nature. The well-known Benard convection cells are the simplest example of self-organization in physical systems (see, for example, [7]).

The occurrence of periodic cavities described above can be regarded as an example of self-organization at the macrolevel. It is not to be assumed, however, that this example is unique and typical only of the process of metal coating. An extension to other process related to the freezing of moving melts on cold supports in which Re exceeds Re_{cr}, suggests itself. One additional example of such a phenomenon can be cited. The case in point is the process called spinning or casting in the literature. This process is used to produce thin ribbons of an amorphous metal for high-quality transformers.

The process is as follows. A molten metal jet is supplied from a pool onto the smooth lateral surface of a rapidly rotating cylindrical wheel which is cooled from the inside. Hitting the wheel, the jet forms a puddle of finite dimensions, which is extended by viscous forces along the rapidly moving surface, and is left on it until freezing. The finished ribbon is then separated from the wheel by centrifugal forces. The jet flow stage of the liquid melt can be eliminated altogether by decreasing the spacing between the pool and the wheel to the point of contact between the wheel and the puddle (see, for example, [8]). If we make a hole in the form of a narrow slit in the pool, we obtain ribbons of up to 40 mm wide and 20–60 μm thick.

Various cavities between the freezing ribbon and the wheel surface are also observed in this process. The smoother this surface, the more systematic the location of the cavities, which eventually form a structure of equally spaced bands. These bands are parallel to each other and are oriented along the axis of rotation of the wheel. In contrast, the cavities corresponding to these bands are oriented along the direction of movement of the wheel. They are not always linear and parallel to each other and, as a rule, are different in length. In the literature, such a structure is called a "fish's scale," and the typical repetition frequency of the bands in this structure is ~5 kHz [8].

Clearly, in this case, the occurrence of cavities is also associated with the melt-flow instability, because the typical value of Re is larger by a factor of 10^2 than that in the case of the fiber considered above. Actually, the typical linear speed of the wheel surface is $\sim 1.5 \cdot 10^3$ cm/sec, which is ~100 times as high as the typical fiber pulling rate in the freezing technique.

The curvature radius of the puddle at the point of contact with the wheel surface should probably be used as the typical value for Re. This radius can differ only slightly from the curvature radius of the meniscus at the point of its contact with the fiber. At the same time, the viscosities of the metals are on the same order of magnitude. Thus, the puddle flow is unstable, and the phase transition "fixes" the consequences of this instability as a band of cavities, which is an analogue of ellipses in a system with cylindrical symmetry.

The closeness of the typical dimensions in (2) that are responsible for the occurrence of cavities leads to comparable natural frequencies of menisci in both cases considered. The fact that, in the latter case, the cavities do not merge into one continuous band, but are separated by the intervening space, is not crucial. This only indicates that resonance of the transverse oscillations of the entrance meniscus in the puddle at some frequencies of exciting perturbations takes place in addition to the resonance of the longitudinal oscillations. The mechanism of these perturbations is practically the same as the mechanism described above for the freezing technique.

The mechanisms whereby regular inhomogeneities occur in metallic layers for both examples considered are not only of theoretical interest, but they are also important in the search for ways of preventing the phenomena generating these inhomogeneities. The presence of cavities leads to undesirable variation in the thickness of the frozen layers. In the case of metal-coated light pipes, this can be a source of both additional optical losses and degradation of the fiber strength with time. In addition, the cavities formed at the entrance of a metal spray gun put a lower bound of 10–15 μm on the coating thickness that can be reached by the freezing technique.

REFERENCES

1. A. S. Biriukov, V. A. Bogatyrjov, E. M. Dianov, A. G. Khitun, "Calculation of the thickness of a metal coating for a fibre produced by the freezing technique," *Sov. Lightwave Commun.*, **3**, No. 4, 235 (1993).
2. I. K. Kikoin (ed.), *Tables of Physical Quantities: Handbook* [in Russian], Atomizdat, Moscow (1976).
3. R. Sangiorgi, M. L. Muolo, D. Chatain, N. Eustathopoulos, "Wettability and work of adhesion of nonreactive liquid metals on silica," *J. Amer. Ceram. Soc. Bull.*, **71**, 742 (1988).
4. A. S. Biryukov, V. A. Bogatyrev, and A. G. Khitun, "On the nature of regular macroinhomogeneities of the metallic coatings of fibers obtained by the freezing of a melt," Preprint No. 3, Inst. Org. Chem., Russ. Acad. of Sci., Moscow (1995).
5. L. D. Landau and E. M. Lifshits, *Hydrodynamics* [in Russian], Nauka, Moscow (1988).
6. G. Nicolis and I. Prigogine, *Self-Organization in Nonequilibrium Systems* [in Russian], Mir, Moscow (1979).
7. H. Haken, *Advanced Synergetics. Instability Hierarchies of Self-Organizing Systems and Devices*, Springer, Berlin–Heidelberg (1984).
8. Huang Shyh-Chin, H. C. Fiedler, "Effects of wheel surface conditions on the casting of amorphous metal ribbons," *Met. Trans.*, **12A**, 1107 (1981).