KINETICS OF SPREADING OF MOLTEN TIN OVER DISCONTINUOUS MODEL COATINGS APPLIED TO GLASS CERAMIC

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Currently there is a considerable amount of work devoted to theoretical and experimental aspects of the spreading of molten metals over the surface of solids. As far as nonuniform surfaces are concerned then such studies have not been carried out. In view of the extensive use of composite reinforced materials interest in this problem has increased considerably.

The surface of actual solids with a nonuniform structure normally consists of randomly placed heterogeneous areas with different surface energy which makes it practically impossible to study features of wetting and spreading. It would be desirable to prepare model surfaces consisting of ordered heterogeneous areas since they would make it possible to follow movement of the wetting perimeter over surface elements.

The aim of the present work is to study features of molten metal spreading over model inhomogeneous surfaces, and the effect of the proportion and relative position of areas with different wettability on the kinetics of spreading and wetting.

Nonuniform solid surfaces consist of areas which are wetted differently by molten metal. There is poor wetting for components such as glass ceramic grade ST-51 which has a polycrystalline structure and it consists in particular of SiO₂, TiO₂, CaO, and components which are satisfactorily wetted, i.e., a molybdenum film deposited on glass ceramic. Tin was used as the molten metal. Wetting contact angles for glass ceramic and molybdenum with tin are 120 and 18°, respectively.

Specimens for study were prepared by the procedure used in radio electronics in manufacturing transistors and microcircuits. At first a series of photographic templates with the required surface patterns were prepared. Then on glass ceramic plates a layer of molybdenum 0.1 μm was deposited which was covered with photosensitive emulsion, i.e., photoresist grade FP-051K. The plates were exposed through the photographic templates as a result of which the illuminated areas of the photoresist were broken down. The plates were developed, washed, and in order to duplicate the remaining photoresist they were placed for 10 min in a drying cabinet in which a temperature of 100°C was maintained. Etching of molybdenum was carried out in exposed areas in a mixture of phosphoric, nitric, and acetic acids. Thus, nonuniform surfaces were obtained with prescribed dimensions and shape of the areas.

Melt spreading kinetics were studied on the example of surfaces consisting of: alternating strips of molybdenum and glass ceramic with a width of 100 μm (type 1); ordered square areas of glass ceramic with a size of 60 x 60 μm on a field of molybdenum (Fig. 1) with distances between the areas of 120 μm (type 2); a solid film of molybdenum applied to glass ceramic (type 3). As a result of this the dimensions of the uniform areas of the heterogeneous surfaces used were quite small compared with the linear dimensions of a droplet and the spots of solid surfaces wetted by the melt.

Melt spreading kinetics were studied by means of high-speed photorecording in a high-temperature automatic unit [1] by the procedure of flow of a droplet onto a plate brought into contact from above. Tests were performed in a vacuum of (1-2) x 10⁻³ Pa at T = 850°C. The required droplet volume due to the structural features of the cine camera was 0.25 mm³. A weighed portion of tin (0.175 g) was placed on nonwetting substrate made of graphite grade MPG-6. Before contact of the solid surface with a molten droplet thermovacuum treatment was carried out for specimens for 30 min. Then the test plate was lowered, and at the instant of contact the cine camera was automatically switched on and the droplet wetting process was recorded on cone film. The varying values of contact angles and the diameter of the wetting spots were determined in cine pictures by means of a UIM-21 measuring microscope.

It should be noted that in these systems there are no processes of dissolution and chemical reaction at an interphase boundary which may affect the kinetics of liquid spreading. For wetting of inhomogeneous surfaces proceeding from the Young equation and assuming additiveness for surface tensions at the solid–gas and solid–liquid boundaries, an equation has been obtained [2]

\[ \cos \theta_0 = \varphi_1 \cos \theta_1 + \varphi_2 \cos \theta_2, \]

where \( \theta_1 \) and \( \theta_2 \) are equilibrium wetting contact angles for uniform surfaces of type 1 and 2; \( \varphi_1 \) and \( \varphi_2 \) are the proportions of total area occupied by areas 1 and 2 (\( \varphi_1 + \varphi_2 = 1 \)); \( \theta_2 \) is equilibrium wetting contact angle for an inhomogeneous solid surface.

However, in the majority of cases it is not possible to describe clearly the wetting of inhomogeneous surfaces by this equation. Depending on the conditions for performing experiments (infiltration or flow back of the melt) this process is characterized by a different value of contact angle. The difference between the greatest and least value of \( \theta \) is the value of wetting hysteresis. The greatest resistance to melt front movement under conditions of infiltration applies to areas of the wetting perimeter with the maximum content of poorly wetting component. By considering interphase tension as a linear force related to a unit length of wetting perimeter Horsthemke and Schröder [3] suggested the following equation for determining the spreading angle \( \theta_{spr} \):

\[ \cos \theta_{spr} = z_{\text{max}} \cos \theta_2 - (1 - z_{\text{max}}) \cos \theta_1, \]

where \( z_{\text{max}} \) is the greatest proportion of poorly wetting component at the perimeter depending not only on the ratio of inhomogeneous areas at the surface, but also on their relative position. Previously we have studied wetting of model inhomogeneous surfaces under melt infiltration and flowback conditions [4]; here experimental results were compared with those calculated by a model [3].

With spreading the resultant force of tension for the three interfaces related to a unit length of perimeter is determined by the equality

\[ \Delta \gamma = \gamma_{\text{SG}} - \gamma_{\text{SL}} - \gamma_{\text{LG}} \cos \theta, \]

where \( \gamma_{\text{SG}} \), \( \gamma_{\text{SL}} \), and \( \gamma_{\text{LG}} \) are forces of tension for the solid–gas, solid–liquid, and liquid–gas interfaces. Taking account of Young's equation

\[ \Delta \gamma = \gamma_{\text{SG}}(\cos \theta_0 - \cos \theta), \]

where \( \theta_0 \) and \( \theta \) are equilibrium and dynamic contact angles, respectively.

In the case of spreading over an inhomogeneous surface in the approximation of additiveness for interphase tensions at interfaces this equation may be written as follows:

\[ \Delta \gamma = z_1 \gamma_{\text{SG}} + z_2 \gamma_{\text{SG}}' - z_1 \gamma_{\text{SL}} + z_2 \gamma_{\text{SL}}' - \gamma_{\text{LG}} \cos \theta = \gamma_{\text{LG}}(z_1 \cos \theta_1 + z_2 \cos \theta_2 - \cos \theta), \]

where \( \gamma_{\text{SG}} \) and \( \gamma_{\text{SL}} \) are surface tensions at the boundary with gas and liquid for a type 1 surface, and \( \gamma_{\text{SG}}' \) and \( \gamma_{\text{SL}}' \) are the same for a type 2 surface; \( z_1 \) and \( z_2 \) are proportions of components 1 and 2 at the wetting perimeter.

Spreading of tin over a surface consisting of alternating strips of equal width was studied in two directions. For this the plate was positioned so that strips were either perpendicular or parallel to the optical axis of the cine camera. With movement of the melt across the strips \( z_{\text{max}} = 1 \), and with movement along a strip \( z_{\text{max}} = 0.5 \). Spreading angles also have different values, and droplets acquire an extended shape along a strip. Calculated and experimental values for spreading angles, initial spreading rate (average value for the first \( 5 \cdot 10^{-4} \text{ sec} \)) and duration of the process (spreading time) are presented in Table 1. Kinetic