On the relationship between parameters of melt spreading over the surface of substrates of variable composition and state diagrams

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Abstract. On of metered-dose drops of various concentrations on a substrate of variable composition. The basis for the substrates and droplets is the contact melting (CM) method related to state diagrams which are used to study the concentration dependence of surface characteristics (spot shape and size, wetting and spreading, surface tension, etc.) under the same conditions which improves accuracy of the characteristics. It was found that the microstructure of the transition zone of the substrate-drop depends on the location of the drop on the substrate, i.e. on the concentration of the substrate.

1. Introduction

The aim of the study is to analyze approaches to the formation and application of metered droplets (bubbles) on solid substrates of variable composition; to develop a less time-consuming approach to obtain drops of metal liquids (alloys) of the same size, under the same conditions, in the right amount from pure metals and alloys of various concentrations; to show the relationship between the state diagram and surface characteristics, the configuration and the diameter of the spreading spot.

This article continues the studies described in [1] which showed that the configuration and the size of the spreading spot depend on the concentration of the substrate of a variable composition. The first solution to the problem was suggested by M. Simon. In 1831, he developed an accurate method of applying drops of the same size. The method was substantiated in the works by M. Cantor and E. Schrödinger [2, 3]. For the practical implementation of the maximum pressure method, various instruments and devices have been developed (M. Simon, S. Sanden, F. M. Jaeger, P. A. Rebinder, Pugachevich, etc.) [4–7].

Further development of the method for studying surface characteristics was continued in [8–10 et al.]. The methods can be used to study surface characteristics at high temperatures.

Using the ideas suggested in [11], we developed a method for producing metered drops from pure metals and alloys as well as substrates of variable composition. To apply this method on interlayers produced by contact melting, a special holder was used.
The main node of the holder is a set of plates of equal thicknesses and with equal holes, which ensure the separation of the liquid diffusion zone into separate parts (plates, tablets). Each plate has a hole equal to the diameter of the sample, which allows you to adjust the size of future drops. The hole is filled with metal or a composition of various concentrations along the cylindrical sample obtained by contact melting, from which it is necessary to obtain droplets. The cell is placed in an appropriate medium with a temperature sufficient to melt metal (alloy) in the hole. After that, a “layer” of the liquid metal is produced, leading to the formation of disks (tablets) (Figure 1).

Figure 1. a) the layout of the plates after the "cut"; b) gallium droplets of a metered size obtained by the "cut" method

The liquid disks crystallize (sometimes in liquid nitrogen). In order to the same dosage of drops, each sample was weighed on an analytical balance.

The concentration of each individual sample was determined by contacting with one of the pure components (A or B) (Figure 2) and placed in a thermostat.

Figure 2. Determination of C (x) by taking liquid samples (determining the concentration of samples): a) solid-phase contacting; b) thermodynamic equilibrium – solid-liquid, at T = const

The thermostat should have a temperature below the melting temperature of the pure component, but above the liquidus temperature of the alloy A + B. At the initial moment, the pure component is in the solid state, and the analyzed sample is in the liquid state.

Since the temperature of the thermostat exceeds the liquidus temperature of the sample, the pure component will dissolve in the liquid sample and the liquid-solid interface begins to move. The movement of the boundary continues until the concentration of the liquid reaches a value corresponding to the liquidus in the melting diagram at the temperature of the thermostat. Upon reaching a thermodynamic equilibrium, the displacement of the liquid – solid boundary ceases.

To reduce the time of equilibrium, a less dense was taken as a substrate (convection develops).
Knowing the mass m of the analyzed sample, the liquid concentration corresponding to the liquidus at a given temperature of the thermostat, and the height h of the molten part of the pure component, we can determine the desired concentration:

\[
C_A = \frac{C_i \left( \rho h \frac{\pi d^2}{4} + m \right)}{m},
\]

where \(C_A\) is the desired concentration in weight fractions, \(C_i\) is the weight fraction A corresponding to the liquidus in the melting diagram at the test temperature, \(\rho\), d, h are density, diameter and height of the melted part of the pure sample, respectively.

The concentration of tablets can be achieved in another way. The concentration of this component lies between the liquidus of the state diagram. The concentration of tablets (disk, drops) can be determined using the state diagram of the system. We place the tablet in a crucible with a deoxidizing liquid (glycerin), raise the temperature and fix the melting point of the tablet (disk), which allows us to determine the concentration (C) based on the fusibility diagram.

The correspondence of the concentration of disks (droplets) is controlled by the x-ray phase and X-ray diffraction methods.

The tablets are contacted with the substrate at various points. The temperature of the system is increased until the tablets melt, turning it into a drop. They are monitored for their wetting and spreading, which makes it possible to determine temporary and concentration dependences of the shape and the diameter of the spreading spot.

Depending on the experimental conditions, two options are possible. The crystallized drop on the inert surface is transferred to the test substrate or the disk (tablet) contacts with the substrate whose temperature is sufficient to transfer the disk into a drop and examine the wetting and spreading of this drop.

2. Results

The methods make it possible to construct concentration distributions – \(C(x)\) in contact interlayers [11–13]. If \(C(x)\) is known for any system, this dependence can be used to study the dependence of wetting and spreading on concentration.

Figure 3 reflects the dependence of the state diagram and the concentration of spreading on the concentration along transition zones (contact interlayers of variable composition).

![Figure 3](image_url)

**Figure 3.** Relationship of the concentration distribution along the contact layer and the state diagram, (a) – state diagram of a two-component system; (b) the concentration distribution in the contact layer; (c) – contact layer in a two-component system

The concentration of liquid melt in contact with solids coincides with the liquidus concentrations on the state diagram of the two-component systems [14–16]. In the plane of the initial contact, the
concentration of contact melt always coincides with the eutectic concentration on the state diagram. Contact interlayers obtained in the nonstationary diffusion mode (NDM) have new phases, for example, intermetallic compounds whose concentration is indicated on the state diagram.

When metal melts come into contact with solid surfaces, a spreading phenomenon accompanied by dissolution of the body, diffusion of the melt components into the solid, and chemical reactions leading to the formation of new phases is observed [10].

Figure 4 shows photos of the interaction of gallium at three points on the surface of a zone of variable composition (contact layer) of the Bi-Pb system.

![Figure 4](image)

**Figure 4.** The microstructure of the diffusion layer during the spreading of gallium droplets over the surface of the contact layer in the bismuth-lead system: a) the bismuth-substrate interface; b) the zone of eutectic concentration; c) the lead-substrate boundary

An analysis of the microstructure patterns of the interaction zone of gallium droplets shows that the depth of dissolution of the substrates depends on the location of droplets on the substrate surface, i.e. on the concentration of the substrate at a given point of contact. An increase in the concentration of bismuth leads to the rearrangement of a dendritic growth due to changes in the nature of diffusion at the interphase boundary – the structure is crushed.

Thus, knowledge of the concentration distribution in contact interlayers (substrates of variable composition), the approaches to the formation and application of metered droplets on the surface of substrates allow us to study the temperature and concentration dependences of the surface characteristics of melts during wetting and spreading. The state diagram specifies the concentration of components at four points of the contact layer: at two liquid-solid boundaries (two liquidus concentrations of this component); the concentration at the point of the initial contact.

3. **Conclusion**
1. A method for producing metered drops from pure metals and alloys by the “shear” method under the same conditions has been developed.
2. The basis for the preparation of substrates of variable composition and droplets of various concentrations is a contact melting phenomenon related to state diagrams, which allows the study of the concentration dependence of the surface characteristics of interacting metals. The relationship between the state diagram and surface characteristics (the configuration and the size of the diameter of the spreading spot) was identified.
3. The nature of the substrate-drop diffusion varies depending on the location of the droplet (substrate concentration) – as the bismuth concentration increases, the structure is crushed.

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