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METALLIC SURFACES AND FILMS

Study of Phase Diagrams Using Two-Layered Films

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Characteristic temperatures of binary phase diagrams have been determined using two-layered films obtained by sequential vacuum condensation. For Pb-Sn and In-Bi films with variable compositions deposited onto substrates with temperature gradient, we show that one sample is sufficient to illustrate the main contours of the phase diagram.

Thermal analysis is the most simple and elaborate method of studying phase diagrams. However, despite the simplicity of measurements, the method requires a large number of specimens. The recent development of microsystem technology, such as production of vacuum-condensed films, has raised interest to retrieving data on the main contours of phase diagrams and their variation with typical structural size (grain size or film thickness), i.e., differences between bulk and film specimens. Method [1] uses films of various compositions obtained by condensation of elements evaporated from separate sources and has been applied to study of structure and properties of binary and ternary alloys with continuously changing composition under isothermal conditions. Studies [2-4] developed a method allowing the entire phase diagram pattern to be retrieved from one specimen and the variation of this diagram due to change in film thickness to be traced. However, this method requires strictly constant condensation rate of elements in order to ensure homogeneous film composition over the surface. Moreover, rapid quenching involved by condensation may produce metastable intermediate phases which may undergo transformations during further condensation or achievement of a steady-state temperature gradient and, hence, hinder the treatise of phase distribution.

Isothermal contact melting [5, 6] has been used for determination of eutectic temperatures. However, mechanical contact of specimens is often ineffective because contact melting requires a physical contact on an atomic scale.

This work suggests a method of studying phase diagrams using two-layered films obtained by sequential condensation of elements evaporated from separate sources.

The principle of the method is as follows (Fig. 1). A film of one element is deposited onto a rectangular plate so the film thickness change continuously across the plate, the equal thickness lines being parallel to its long side. Immediately upon that, without breaking the vacuum, a film of the second component is deposited symmetrically to the former film so the total thickness of the two films remain constant. The ratio of elements in this system will change continuously, the equal concentration lines being parallel to the long plate side. If we produce a longitudinal temperature gradient by heating one of the plate ends and cooling the opposite end, then, because the thickness of the two-layered film is far smaller than its other two dimensions, the composition discontinuity in the thickness will be smoothed, while retaining the initial concentration gradient in width. As a result, each point of the film will have phase composition corresponding to its specific temperature and composition in accordance with the phase diagram. Thus, a single film will contain .the entire set of alloys in the desired range whose composition and temperature will vary continuously in width and length, respectively.

We chose the Pb-Sn and In-Bi systems as test materials. The former phase diagram has well been studied and has limited solubility in the solid state. Its eutectic is at 61.9% Sn and melts at 456 K [7]. The In-Bi system has been shown to form two compounds, InBi and In_2Bi as observed in bulk samples [8]. InBi melts congruently at 383 K, and

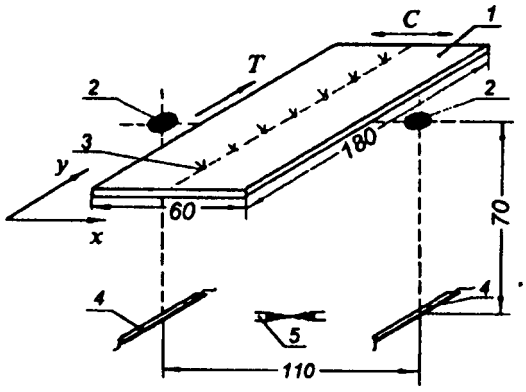

Figure 1. Schematic of test film preparation: (1) substrate, (2) thickness gage, (3) thermocouples, (4) metal evaporators, and (5) carbon evaporator.

In_2Bi forms by a peritectic reaction at 362 K. Condensed films of these alloys with thickness less than 700 Å contain In_3Bi_2 compounds, which decomposes incongruently into melt and abovementioned InBi [9]. According to [10], the InBi system forms three compounds, out from which In_2Bi and InBi melt congruently at 362 and 382 K, respectively, while the melting point of In_3Bi_2 was not given in the cited work. Also, this work showed that In_3Bi_2 forms by a peritectic reaction at 362 K, which result is at variance with the phase diagram presented therein. Thus, stability limits of the compounds are not yet ascertained.

Two-layered Pb-Sn and In-Bi specimens were synthesized in $5 \cdot 10^{-7}$ - $5 \cdot 10^{-8}$ mm Hg vacuum produced by an oilless pump. 99.99% Sn, Pb, In, and Bi were evaporated from elongated tantalum sources arranged parallel to the long plate side. The polished stainless steel plates were 16 cm in length, 6 cm in width, and 3 mm in thickness. To avoid interaction of films with the plate, the latter was capped with a 50 nm thick carbon film at room temperature before condensation. The evaporators and the plate were separated with mobile shields which allowed two-layered films to be obtained by sequential condensation. For two-layered Pb-Sn films, the thickness ratio in each point corresponded to the eutectic composition, and some films had hypoeutectic compositions, i.e., >62% Sn. For In-Bi films, the experimental geometry and the amounts of evaporated metals were chosen in such a way to ensure change in the composition from 40 to 70 % Bi, i.e., in the range where In_2Bi, InBi, and In_3Bi_2 occur. To avoid the size effect, the films were made thicker than 10^2 nm.

Upon the condensation, without breaking the vacuum, one end of the plate with film was heated to 500-550 °C, the opposite end being held at room temperature. After holding in steady-state temperature mode, heating was ceased and the plate was cooled to room temperature. Eutectic Pb-Sn films exhibited a clear, naked eye visible boundary perpendicular to the plate length, above which the film melted (Fig. 2, a). The melted region contained single spherical particles, and below the boundary the film was single crystal. The temperature of this boundary is the eutectic temperature of Pb-Sn. One may also see that, during heating, this boundary shifted along with drops of the melt. The liquid phase moistened the crystalline phase and, because of the unmoistened carbon film on the plate, the drops moved with the crystalline phase along the plate with an increase in temperature. This phenomenon also originates from capillary effects because of the temperature gradient on the plate. Since two-layered films start to melt in their contact region, relatively rapid heating of Pb-Sn films caused some melt drops moving with the melting boundary to stop in points corresponding to the Sn melting point (Fig. 2, a).

To ensure that the melting boundary of the two-layered films corresponds to the eutectic Pb-Sn temperature, we performed the following tests. Pb-Sn film with the eutectic ratio

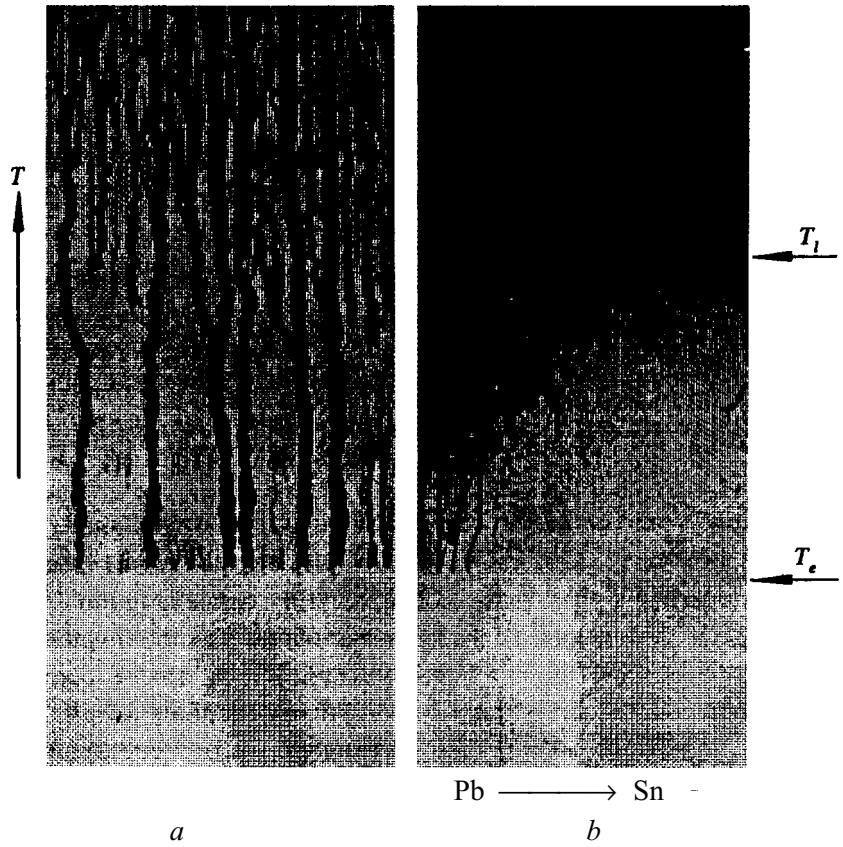

Figure 2. Photographs of Pb-Sn films of (a) constant (eutectic) and (b) variable (hypereutectic) compositions on substrates with temperature gradients.

was sequentially deposited onto one half of the plate using shields, and Pb and Sn were deposited simultaneously in the same ratio onto the other half. After the temperature distribution along the plate stabilized, the melting boundaries of these films coincided and corresponded to $T_e = 456$ K [7].

Apart from the eutectic boundary, two-layered eutectic Pb-Sn films (Fig. 2, *b)* had one more smeared boundary separating the liquid phase from the binary region (liquid phase and Sn grains). Microscopical study showed that this boundary corresponds to the liquidus line T_l of hypoeutectic Sn-rich alloys. The drops of the eutectic melt stopped at T_e, and those of the hypoeutectic melts stopped at T_l. This behavior is attributed to the presence of Sn grains in the liquid phase below the liquidus temperature, which stop the drops.

This data shows that two-layered films obtained by sequential condensation of metals allows one to visualize the desired region of the phase diagram. This may also be quite

useful for alloys with several eutectic and peritectic temperatures, i.e., for more complex diagrams.

To illustrate this latter possibility, we studied two-layered In-Bi films. After temperature stabilization, the films (Fig. 3, *a)* exhibited four boundaries perpendicular to the long plate side: *AB* (344), *CD* (362), *EF* (366). and *HK* (382 K); between them, there were three boundaries (*CB, ED,* and *GHF*) parallel to the equal concentration lines. After temperature stabilization (Fig. 3, a), the two-layered films exhibited four boundaries, i.e., *AB* (344), *CD* (362), *EF* (366), and *HK* (382 K); between them, there were three boundaries *(CB, ED,* and *GHF),* which were parallel to the equal concentration lines. Calculations and experiment showed that *CB* corresponds to In_2Bi, *ED* coresponds to In_3Bi_2, and *GHK,* to InBi. The deviation of the equal concentration lines from the line strictly parallel to the long plate side (Fig. 3, *a)* is caused by the finite size of the evaporators.

Microscopical study showed that the films are single crystals below the *ABCDEFHK* line. In the ranges *ABC, CDE,* and *EFHG,* the films have two-phase composition and contain spherical liquid phase particles and corresponding crystals, the latter having specific shapes in these ranges. To the left and above the line *ACEG,* the films contain

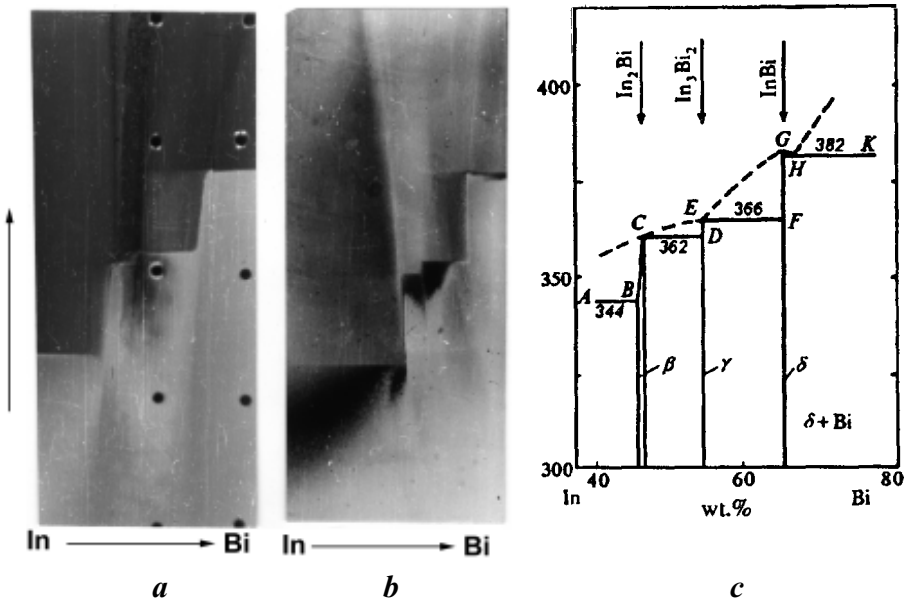

Figure 3. Photographs of variable composition films- obtained by (a) sequential and (b) simultaneous condensation and (c) corresponding part of the In-Bi phase diagram.

only liquid phase particles. X-ray examination on a DRON-3 diffractometer and electron diffractometry showed that In_2Bi, In_3Bi_2, and InBi compounds are present in appropriate ranges after melting and cooling to room temperature.

X-ray and electron diffraction data on In_2Bi and InBi agree completely with data [8, 11]. In_3Bi_2 was first observed in study [9]; the cited electron diffraction data suggested that this compound has a hexagonal lattice (a = 11.72 Å and c = 8.54 Å) with three molecules per unit cell. However, study [9] reported ambiguous electron diffraction data on the interplane spacing of In_3Bi_2. The present study showed that a = 11.68 Å and c = 8.58 Å.

Figure 3, *b* shows micrograph of In-Bi film with variable composition obtained using method [2-4] by simultaneous condensation of In and Bi on the substrate with subsequent application of temperature gradient. These specimens also show clear *AB, CD, EF,* and *HK* boundaries perpendicular to the long plate side.

Detailed microscopical and diffraction data showed that the phase compositions of the films obtained by simultaneous and sequential deposition are identical.

Thus, condensed In-Bi films with thicknesses of more than 50 nm agree with the InBi phase diagram [10] and show the limits of In_2Bi, In_3Bi_2, and InBi compounds. In_2Bi [8] and In_3Bi_2 [9] form by peritectic reactions, which can be seen from the lines *CD* and *EF* (Fig. 3). The line *HG* shows that InBi melts congruently, which is in accordance with data [8, 10].

The present data shows that appropriate ranges of the In-Bi phase diagram can be shown using condensed films (Fig. 3, c). Here we show the liquidus lines by dashes because they cannot be clearly seen by naked eye and, unlike peritectic and eutectic boundaries, their positions remain somewhat ambiguous even after electron microscopical examination.

Concerning the possibility of using contact-melted two-layered films for study of phase diagrams, we would like to make the following notes. Heating of films and their holding at a stable temperature involve diffusion processes which will cause homogenization in the direction parallel to the short plate side, in the surface plane. These processes can be described using the relation $x^2 = 2Dr$, where x is the characteristic distance (the size of the homogenized region), D is the interdiffusion coefficient of the elements in hand, and τ is the time of holding. For example, for $\tau = 3 \cdot 10^2$ s in the In-Bi system [6] with $D = 2 \cdot 10^{-5}$ cm^2/s at 350 K, the size of the homogenized region should be $x = 1.1 \cdot 10^{-1}$ cm, the concentration gradient along the plate being dc/dx = 0.5 %/mm. However, the melt does not moisten the preliminary deposited carbon film and, therefore, it forms single drops whose size is about three times the film thickness. In this case, the homogenization is determined by the slower process, i.e, diffusion of In and Bi atoms on the carbon film

surface. Taking the surface diffusion coefficient $D_s \cong 10^{-10}$ cm^2/s, the characteristic size will be $x \cong 2.5 \cdot 10^{-4}$ cm at the same time. Thus, the positions of the boundaries will undergo only slight changes. Diffusion also occurs below the melting temperature. For example, slightly below the In_2Bi eutectic temperature, at the same time and $D = 3 \cdot 10^{-12}$ cm^2/s, the characteristic size will be $5 \cdot 10^{-5}$ cm, which is negligible. These estimates are additional evidence that, over a reasonably chosen time of holding at a steady-state temperature, two-layered films with thicknesses of 10^{-13}-10^{-5} cm will not undergo significant changes and, hence, they will give practically adequate images of the phase diagram limits.

Thus, two-layered films with variable composition obtained by sequential condensation of pure components with subsequent application of temperature gradient along the substrate show good promise for study of phase diagrams since they visualize the general contours of the diagrams and are sensitive to slight temperature variation.

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