Features of gallium spreading over surfaces of Ag–Au–Ga thin films

V.M.Andronov, I.P.Grebennik, S.V.Dukarov*

Kharkiv State University, 4 Svobody Sq., 310077 Kharkiv, Ukraine
*Scientific Center of Physical Technologies,
1 Novgorodskaya St., 310145 Kharkiv, Ukraine

Linear spread of gallium over thin films of Ag–Au–Ga ternary alloys with continously varying concentrations along quasi-binary sections of the ternary diagram has been studied. The observed concentration dependence of the spread zone size is attributed to structural changes occurring in alloys and resulting in an unmonotonous dependence of the spread motive force on the alloy composition.

Исследовано линейное растекание галлия по поверхности тонких пленок тройных сплавов серебро-золото-галлий с непрерывно изменяющейся концентрацией вдоль квазибинарных сечений тройной диаграммы. Обнаруженная немотонная зависимость размера зоны растекания от концентрации объясняется влиянием происходящих в сплавах структурных изменений, приводящих к немотонной зависимости движущей силы растекания от состава сплава.

Wettability is one of important physico-chemical characteristics of various materials. The spreading of a liquid (unrestricted wetting) is known to be defined by a combination of interphase surface energy values, σ_{ik}, on interfaces between a solid (1), a liquid (2) and a medium (3) expressed as

$$\Delta\sigma = \sigma_{13} - \sigma_{12} - \sigma_{23} \qquad (1)$$

where $\Delta\sigma$ is the motive force for the spreading process [1]. It is of interest to study the spreading of melt droplets over surfaces of thin films of alloys. Gallium spreading over thin films of silver-gold and silver-gallium alloys within a wide concentration range was investigated in [2, 3]. The concentration dependence of the spread zone X was shown to have a very unmonotonous character (the linear spreading was studied characterized by the spread region size in the direction perpendicular to the boundary of a strip-shaped melt film). This points to a unmonotonous character of concentration dependences of σ_{ik}; values of those define, in turn, the dimension X [1].

This work presents the investigation results of gallium spreading features over thin films of ternary silver-gold-gallium alloys. In [4], ternary alloys were obtained by evaporation and subsequent deposition of mentioned metals onto a system of substrates placed at different heights with respect to three evaporators positioned in vertices of an equilateral triangle; by that means, the same film thickness was attained on all substrates thus eliminating the possibility of size effect manifestation in the wetting and spreading [5, 6] due to σ_{ik} dependence on the layer thickness [7]. In contrast, the ternary alloys were obtained in this work by condensation onto a flat extended substrate, while components were evaporated from two sources. Therewith, a set of ternary alloys with a continuous concentration variation can be obtained on the substrate by varying the number of components on each evaporator and their masses,
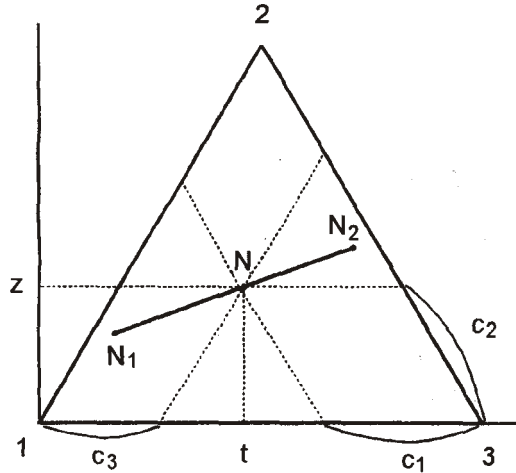
Fig.1. Concentration triangle position in $z-t$ plane. Points N_1 and N_2 designate boundaries of sections corresponding to concentrations of alloys on an infinite substrate.

similarly to the known S.A.Vekshinsky method. An advantage of that technique consists in that the composition of ternary alloys obtained does not correspond to arbitrary points within the concentration triangle, as in [4], but it represents a portion of a straight line, namely, of a quasi-binary section of the ternary system diagram. This allows to construct the property-composition relationships for ternary alloys on a plane as in the case of binary ones. Since it is reasonable to prearrange the composition of films to be obtained, it is necessary to relate compositions of alloys being evaporated from two evaporators to the required position of the above-mentioned straight line inside the concentration triangle.

Let granules of metals $i = 1$, 2, 3 of masses m_{ik} be placed on each evaporator $k = 1, 2$. In this case, ternary alloys formed on a substrate after the components interaction will have concentrations lying between points N_1, N_2 (see Fig.1) related to concentrations corresponding to those of alloys placed on evaporators, no matter what is the law of condensates distribution in depth for various points of the substrate. If the evaporation occurs from both evaporatots, then alloys of initial compositions are not formed on a restricted substrate.

Let us use a Cartesian co-ordinate system $z-t$ positioned so that its origin coincides with one vertex of the concentration triangle (for example, with 1, Fig.1) while abscissa axis, lies along one side of the latter (1-3). Then, the equation for the

straight line passing through points N_1 and N_2 can be written as

$$z = At + B. \qquad (2)$$

Cartesian co-ordinates of any point lying inside the concentration triangle are related to concentrations of a ternary alloy corresponding to that point:

$$z = c_2\sin 60°, \quad t = 1 - c_1 - c_2\cos 60°. \qquad (3)$$

Using (3) for points N_1 and N_2, we obtain parameters for straight line (2)

$$A = \frac{\sqrt{3}(c_{22} - c_{21})}{[2(c_{11} - c_{12}) + c_{21} - c_{22}]},$$
$$B = \frac{\sqrt{3}[c_{21}(1 - c_{12}) - c_{22}(1 - c_{11})]}{[2(c_{11} - c_{12}) + c_{21} - c_{22}]}. \qquad (4)$$

Concentrations of ternary alloys formed at various points (x, y) of the substrate are defined by evaporated metal masses, m_{ik}, and the condensate distribution laws depending on the evaporator type; they are described by expressions

$$c_i = \frac{(m_{i1} + \beta m_{i2})}{\sum m_{i1} + \beta \sum m_{i2}}, \qquad (5)$$

where $\beta(x,y)$ is a function, its specific form depending on the condensate thickness distribution law over the substrate. At the same time, parameters of the straight line (2) after substitution of expressions (5) into (4) are independent of $\beta(x,y)$ and governed only by evaporated metal masses:

$$A = \frac{\sqrt{3}[m_{22}\sum m_{i1} - m_{21}\sum m_{i2}]}{[(2m_{11} + m_{21})\sum m_{i2} - (2m_{12} + m_{22})\sum m_{i1}]} \qquad (6)$$

$$B = \frac{\sqrt{3}[m_{21}m_{32} - m_{22}m_{31}]}{[(2m_{11} + m_{21})\sum m_{i2} - (2m_{12} + m_{22})\sum m_{i1}]}$$

So, straight lines passing through one of the triangle vertices, for example, through 1 (corresponding to the case when one of metals is positioned on one of evaporators, i.e. $k = 1$), are characterized by parameters $A = \sqrt{3}m_{22}/(m_{22} + 2m_{32})$, $B = 0$, $0 < \varphi < 60°$ ($\varphi = \text{arctg } A$). Sections parallel to the side 1 - 2 correspond to the same concentration of component 3 on both evaporators, i.e.

$$\frac{m_{31}}{(m_{31} + m_{21} + m_{11})} = \frac{m_{32}}{(m_{32} + m_{22} + m_{12})} = c_3.$$
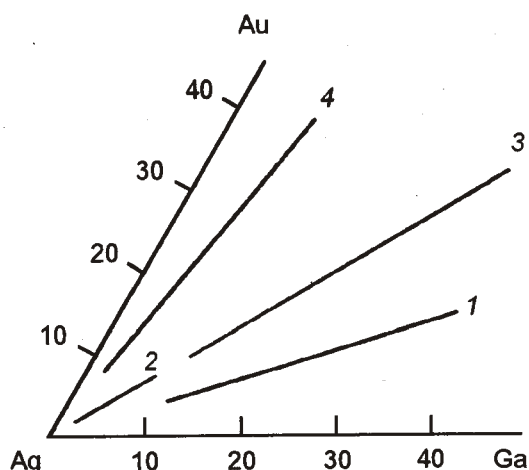
Fig.2. Portions of quasi-binary sections of Ag–Au–Ga system diagram corresponding to studied alloys.

At $m_{12} = m_{21} = 0$, end points of the straight line portion lie on the triangle sides, in that case, $A = \sqrt{3}$, $B = -\sqrt{3}\,c_3$, $\varphi = 60°$.

To perform the spreading experiments, ternary Ag–Au–Ga alloys (in what follows, Ag is designated as 1, Au as 2, Ga as 3) of variable composition with concentrations varying smoothly along corresponding section were obtained by evaporation and condensation on glass plates under 10^{-4} Pa pressure. Alloys corresponding to the portions of sections through the triangle vertex 1 (portions 1, 2, 3, 4 in Fig.2) at angles $\varphi = 17°$ (1), $30°$ (2, 3), $50°$ (4) to the axis 1–3 were used in this work. The alloy concentrations were calculated using the relationship (5). If the substrate is so positioned that the line connecting both evaporators and coincident with the y axis direction goes along the substrate length, the expression for β takes the form

$$\beta = \left[\frac{R^2 + (x^2 + y^2)}{R^2 + (L - \sqrt{x^2 + y^2})^2} \right] 2, \qquad (7)$$

where R is the distance from evaporators to the substrate, L is that between evaporators projected into $(0,0)$ and $(0,L)$ points of the substrate, corresponding to concentration in N_1 and N_2 points (see Fig.1). The expression (7) corresponds to the used law of condensate distribution on a flat substrate under metal evaporation from small-area flat directional evaporators.

Mass ratios of metals being evaporated were $m_{11} : m_{22} : m_{32} = $ 3.3 : 1 : 2.3 (1), 17.2 : 1 : 1 (2), 2.35 : 1 : 1 (3), 19.3 : 4.4 : 1

(4), i.e. silver was evaporated from one source and gold and gallium in various ratios from another one. The total condensate thickness at various substrate points $(0, y)$ deviated from the averaged one (30 nm) within 5 to 20% for all ternary alloys films. Therewith, dependences $c_i = f_i(0,y)$ turn out to be nearly linear.

Linear spread of gallium from a 0.4 mm wide strip of 70 nm thickness positioned along the y axis was studied. The strip was obtained by gallium evaporation and condensation onto the glass substrate with a ternary alloy film deposited using a slit diaphragm pressed to the film surface. Prior to the gallium source application, the ternary alloy film was subdivided into transverse 2 or 3 mm wide bands for convenience of subsequent X measurements. This allowed to obtain data on the spread zone size, X, over surfaces of 20 to 30 various alloys in each section in the course of the same experiment and thus to construct dependences $X = f(c_1, c_2, c_3)$. Those relations $X = f(y) = f(c_1, c_2, c_3)$ allow, in turn, to judge the concentration dependences of the spread motive force, $\Delta\sigma$ [1]. Values of X were measured to within $\pm 1.43 \cdot 10^{-2}$ mm. The measurements were performed at a room temperature. Judging from microinterference photos made using MII-4 microscope, the spread region had a constant thickness and a step at the spreading zone boundary.

Fig.3 presents $X = f(y)$ dependences for (4) and (3) portions of ternary alloy sections shown in Fig.2. The dependences for (2) and (1) portions are of a similar shape. It is seen from the curves of Fig.3 that dependences $X = f(y)$ are very unmonotonous with both strong and weak maxima. (The latter having an appearance of inflexion points; moreover, their presence causes an asymmetric run of $X = f(y)$ dependences near strong maxima).

Concentration data for Ag–Au–Ga ternary alloys corresponding to maxima on $X = f(y)$ curves in all studied sets are presented in the Table. It is to note that, as in the case of gallium spread over binary alloy surfaces (Ag–Ga, Ag–Au [2, 3]), weak maxima correspond to atomic compositions $n/(Z + 1)$, where $Z = 12$, $n = 1, 2, 3..., n/(Z + 1) \approx C_{Au} + C_{Ga}$; that is, they point probably to the formation of a cluster structure in substrate alloys based on the FCC lattice in three-component solid solutions. If, in a binary solid solutions A–B clusters, based on A lattice with the coor-
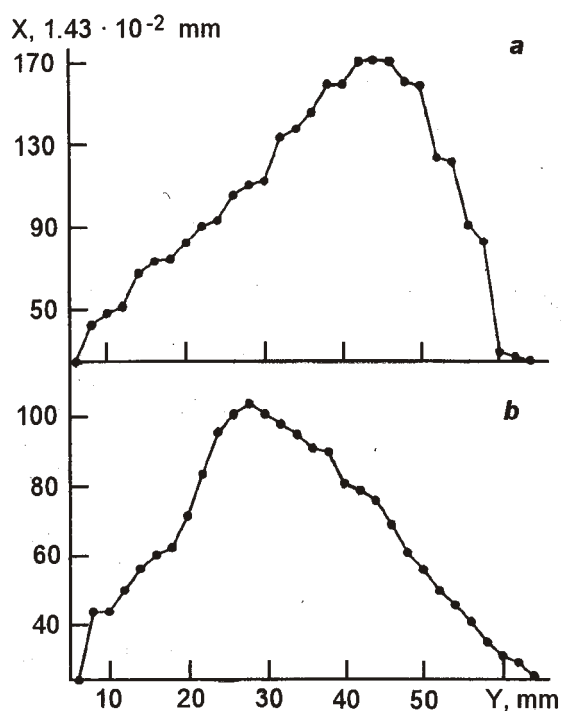
Fig.3. Linear spread zone size relations for gallium drops over thin films of Ag–Au–Ga alloys corresponding to portions c (a) and d (b) (see Fig.2).

Table.

φ°	C, at.%				n/(Z+1), %	X× ×1.43·10⁻², mm
	C_{Ag}	C_{Au}	C_{Ga}	$C_{Au} + C_{Ga}$		
17	46.3	7.1	46.6	53.7	53.85	58
17	39.3	8.0	52.7	60.7	61.52	44
30	93.0	1.9	5.1	7.0	7.60	70
30	88.3	3.0	8.7	11.7	–	140
30	84.3	4.0	11.7	15.7	15.38	69
30	68.3	8.3	23.4	31.7	30.76	67
30	63.2	9.6	27.2	36.8	38.46	93
30	52.7	12.3	35.0	47.3	46.10	159
30	48.7	13.3	38.1	51.3	–	171
30	43.9	14.7	41.4	56.1	53.85	158
30	40.7	15.5	43.8	52.3	61.52	121
50	84.6	9.3	6.1	15.4	15.38	75
50	83.5	9.9	6.6	16.5	15.38	78
50	82.4	10.7	6.9	17.6	–	89
50	77.7	13.6	8.7	22.3	23.0	103
50	70.1	18.2	11.7	22.9	30.76	56

dination number Z are formed at electron concentrations $n/(Z + 1) = C_B$, then for a ternary solid solution at $n = n_B + n_C$, $n/(Z + 1) = C_B + C_A$. Therewith, the same $n/(Z + 1)$ value, for example, 15.38 % ($n = 2$), corresponds to ternary Ag–Au–Ga alloys lying on various sections, $\varphi = 30°$ and $\varphi = 50°$, where totals of impurity concentrations, C_{Au} and C_{Ga}, are in different ratios (see Table). The same is valid also for other $n/(Z + 1)$ values.

As it follows from the Table, some maxima (including strongest ones) on $X = f(y)$ curves do not fit compositions $n/(Z + 1)$ at $Z = 12$. This is like to be associated with formation of phases in corresponding ternary alloys having a higher surface energy σ_{ik}, that results in an increase of the spread motive force $\Delta\sigma$ and, consequently, of the spread zone size. A similar effect was observed under gallium spreading over surfaces of binary alloys where the maximum spread was found to occur within the zone of inter-metallic phases existence having lattices of gamma-phase type (silver-gallium system) and on the cubic phase of $AuGa_2$ type.

Thus, the use of quasi-bidimensional sections when studying the wettability of ternary alloys by liquid melts allows to reveal alloy compositions exhibiting a "good" and "poor" wettability. So, Ag–Au–Ga alloys having compositions corresponding to the section $\varphi = 17°$ are wetted by gallium considerably worse than those corresponding to certain portions of sections with $\varphi = 30°$ and $50°$. Moreover, the dependence $X = f(y)$ is found to have an unmonotonous run.

To explain an unmonotonous (oscillating) character of concentration dependences of various physical properties of binary solid solutions, a macroscopic clusterization based on atomic crystal groups of discrete composition was supposed to occur [8]. Since, in our case, the spread zone size is defined by the spread motive force, $\Delta\sigma$, it is just the interphase surface energy σ_{13} that can be supposed to have such an oscillating character with respect to the composition within the region of continuous solid solutions for Ag–Au–Ga ternary system. The cluster structure within limits of the first coordination sphere may result in such oscillations at atomic concentrations equal to

$n/(Z+1)$, where $n/(Z+1) \approx C_{\mathsf{Au}} + C_{\mathsf{Ga}}$ for Ag–Au–Ga ternary system.

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Особливості розтікання галію по поверхні тонких плівок сплавів системи срібло-золото-галій

В.М.Андронов, І.П.Гребенник, С.В.Дукаров

Досліджено лінійне розтікання галію по поверхні тонких плівок потрійних сплавів срібло-золото-галій з концентрацією, яка неперервно змінюється вздовж квазібінарних перетинів потрійної діаграми. Виявлена немонотонна залежність розміру зони розтікання від концентрації, яка пояснюється впливом структурних змін, що відбуваються в сплавах та призводять до немонотонної залежності рушійної сили розтікання від складу сплаву.