Phase Formation in Contact of Dissimilar Metals

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Abstract. Formation and growth of intermediate phases in contact of the crystalline samples forming a two-component eutectic system is considered. It is shown that during the competition to a growing liquid phase the intermediate solid phases cannot grow by diffusion. The alternative is formation of metastable areas of a liquid phase.

Measurements of liquid layers extent in Pb-Bi and In-Bi systems have allowed to define the composition of liquid on interface where formation of metastable liquid is possible. The results show that the concentration interval of a liquid layer corresponds to a stable constitution diagram.

In order to explain the experimental results the hypothesis according to which the intermediate solid phases are formed as a result of precipitation from metastable melt is considered.

The experimental confirmation of formation and crystallization of a metastable liquid is the fact that intergrowth of the samples forming system with an intermetallic phase at temperatures below the temperature of fusion of the most low-melting eutectic is observed.

The possibility of the processes concerned with the occurrence of metastable areas of a liquid is showed by means of computer imitation.

1. Introduction

Let us consider the growing one-dimensional diffusion zone of a two-component system. If the diffusion zone is formed for a sufficiently long time at a constant temperature, it contains all intermediate phases encountering along the corresponding isotherm in the phase diagram. It is known that some phases are not present in the diffusion zone during the period of the diffusion annealing. The reason for the absence of the phase can be the small value of the diffusion coefficient which characterizes the growth of the absent phase in comparison with the diffusion coefficients of competing phases [1]. If some phase is not present in the diffusion zone, then the phases adjoining to it in the phase diagram would contain metastable ranges.

Figure 1 shows molar Gibbs energy of three phases in the quasi-equilibrium diffusion zone depending on the molar fraction of one of the components. Tangents to the lines of Gibbs energy allow to determine the fractions of the component at the interphase boundaries. If they-phase is absent in the diffusion zone then existence of metastable ranges (c1, c5) in α-phase and (c6, c4) in β-phase is required to retain the continuity of the chemical potentials of the components. Thus, the absence of the phase provided for by the phase diagram leads to an extension of the concentration range of the competing phases.

2. About the possibility of growth of an intermediate solid phase

Let us ascertain the possibility of diffusion growth of an intermediate solid phase during the competition with a liquid phase. Figure 2 shows a hypothetical diffusion zone formed as a result of contact melting.
It is known that in a one-dimensional diffusion zone the motion of isoconcentration planes, including interphase interfaces, is described by a parabolic law [1]

$$z = \lambda \sqrt{t},$$ \hspace{1cm} (1)

where $\lambda = \lambda(c)$ is the kinetic factor that depends on the concentration, $t$ is the time of diffusion annealing under a constant temperature.

Let $\lambda_{L/\gamma}$ be a kinetic factor that characterizes the motion of the boundary between the liquid (L) and solid $\gamma$ intermediate phases in a diffusion zone. "0" is the plane of initial contact of $\alpha$- and $\beta$-phase

In (2) the coefficient "2" is taken to estimate the size of the liquid layer because it is natural that the size of a liquid layer is approximately twice as wide as that of one of its parts.

The projection on the $Z$-axis of the flux density of particles A which move from the interphase boundary (L/$\gamma$) into the $\gamma$-phase is

$$j_A = n_A^{(\gamma/L)} u_A^{(\gamma/L)},$$ \hspace{1cm} (3)

where $n_A^{(\gamma/L)}$ and $u_A^{(\gamma/L)}$ are the molar concentration of the A-component and the projection of the mean velocity of particles A at the interphase boundary (L/$\gamma$) in the $\gamma$-phase. This velocity cannot be less than the velocity of the motion of the interface (L/$\gamma$). Otherwise the $\gamma$-phase would not be formed as a result of the deficiency in A-particles. Since the velocity of motion of the interface (L/$\gamma$) is $\lambda_{L/\gamma} / (2\sqrt{t})$ according to the parabolic law (1) we obtain
To estimate, we assume that the component distribution in the \( \gamma \)-phase that occupies the concentration range \((n_A^{(\gamma/L)} - n_A^{(\gamma/L)})\) (Figure 2) is linear. Then, according to Fick's first law,

\[
j_A = D^{(\gamma)} \frac{n_A^{(\gamma/L)} - n_A^{(\gamma/L)}}{\Delta \xi^{(\gamma)}}.
\]

where \( D^{(\gamma)} \) is the diffusion coefficient which characterizes the growth of the \( \gamma \)-phase and \( \Delta \xi^{(\gamma)} \) is the size of the \( \gamma \)-phase. Then, from equations (3)–(5), we obtain

\[
\Delta \xi^{(\gamma)} \leq \frac{2D^{(\gamma)} \frac{n_A^{(\gamma/L)} - n_A^{(\gamma/L)}}{\Delta \xi^{(\gamma)}}}{\lambda_L^{(\gamma)}} \frac{n_A^{(\gamma/L)} - n_A^{(\gamma/L)}}{\Delta \xi^{(\gamma)}} \sqrt{t}.
\]

Compare the size of the \( \gamma \)-phase and that of the liquid phase. With allowance for equations (2) and (6) we obtain that

\[
\frac{\Delta \xi^{(\gamma)}}{\Delta \xi^{(L)}} \leq \frac{D^{(\gamma)} \frac{n_A^{(\gamma/L)} - n_A^{(\gamma/L)}}{\Delta \xi^{(\gamma)}}}{\left(\lambda_L^{(\gamma)}\right)^2} \frac{n_A^{(\gamma/L)} - n_A^{(\gamma/L)}}{\Delta \xi^{(\gamma)}}.
\]

For numerical estimate we use values that are characteristic of the In–Bi system: \( D^{(S)} \sim 10^{-15} \text{ m}^2/\text{c} \) [2], \( \lambda_L^{\text{InBi}} \sim 10^{-5} \text{ m} \cdot \text{V}^{-1/2} \) (from our experiment), \( \Delta n_{\text{InBi}} / n_{\text{InBi}} = 0.01 \) [3], where \( \Delta n_{\text{InBi}} \) is the homogeneity range of the Bi-In phase. As a result, the ratio of the \( \gamma \)-phase size to that of the liquid phase is less than \( 10^{-7} \). Let a liquid interlayer 3 mm thick be formed during the period of diffusion annealing. According to the obtained result (7), the formal thickness of the intermetallic should make 3·10^{-10} \text{ m}, that is equal to an atomic layer in the order of magnitude. Such object cannot be a thermodynamic phase, that is it does not possess physical characteristics which are inherent to a phase consisting of the same atoms under the same ambient conditions. We arrive at the conclusion that under the condition of competitive growth with a liquid phase, the intermediate solid phase cannot be formed for a period of the real experiment.

3. Basic equations

The absence in the diffusion zone of intermediate solid phases serves as a guide for a search for deviations of the boundary concentrations on the liquid-phase side from the stable liquidus line. For this purpose we should take advantage of the results of growth kinetics measurements of the intermediate liquid phase between fixed initial samples. The details of the experiment realization can be found in [4].

The solution of Fick’s second law for a liquid phase growing by diffusion allows to find the distribution of the components in the liquid layer in the form of

\[
n_i(\psi) = P_i + Q_i \cdot \text{erf}(\frac{\psi}{\lambda_0}),
\]

where \( i \in \{A, B\} \) is the identifier of a component, \( n_i \) is the concentration of the \( i \)-th component, \( P_i \) and \( Q_i \) are constants,

\[
\psi = \frac{\lambda - \lambda_0}{2\sqrt{D}},
\]

\( \lambda_0 \) is the kinetic factor characterizing total displacement of the liquid interlayer as a result of bulk effect of the melting of the initial solid samples. The solution (8)–(9) is based on the independence of the diffusion coefficient and partial molar volumes of the components from the composition of a liquid. Diffusion which is characterized by the coefficient \( D \) in a liquid phase, is considered with respect to the reference system in which the balance of fluxes of the component volumes (Fick’s reference system [5]) is observed.

The distribution (8)–(9) allows to obtain a system of equations on the basis of which the assigned problem is solved:
where \( \psi' \) and \( \psi'' \) are identifiers of the interphase boundaries of the liquid with \( \alpha \)- and \( \beta \)-phase respectively.

Equation (10) follows from Fick’s first law written down for the interphase boundary \( L/\beta \). Thus, it is supposed that the \( \beta \)-phase contains only the B-component. Equations (11) and (12) are edge conditions written down on the basis of (8). Equation (13) is based on the statement that all the quantity of the A-component which was present in the melted part of the \( \alpha \)-phase is in the liquid layer after fusion. Thus, it is supposed that the \( \alpha \)-phase may contain both of the components. The magnitude \( v(\psi'\rightarrow\psi'')c_A^{(\alpha)} \) represents the molar volume of substance of \( \alpha \)-phase after congruent fusion. Besides, we take it into account in (10)–(13) that the quantity of the A-component which diffused from the liquid phase into \( \beta \)-phase is negligible in comparison with the quantity of the A-component being in liquid layer [6].

4. The Phase composition of diffusion zone upon contact melting

As the objects of our investigation [7, 8], we selected the Pb–Bi (figure 3) and Bi-In (figure 4) systems forming intermediate solid phases.

The assigned problem of determination of the boundary concentrations in the liquid phase was solved in two stages. At the first stage the solution \( \psi' \) and \( \psi'' \) of system (10) - (13) was found for contact pairs \( \varepsilon-\text{Bi} \) at 150°C (the system Pb-Bi) and Bi-In at \( t>110^\circ \text{C} \) between the components of which there were no intermediate solid phases in the phase diagrams, and also for pairs BiIn-In at \( t \in (89-110^\circ \text{C}) \) and BiIn2-In at \( t \in (72-89^\circ \text{C}) \). The data of the phase diagrams and partial molar volumes of the components in a liquid state were used at the same time. The calculated values \( \psi' \) and \( \psi'' \) and the kinetic factors of liquid phase growth obtained from the experiment \( \Delta\lambda'=\lambda''-\lambda' \) allow to find the diffusion coefficient on the basis of (9):

\[
D = \left( \frac{\Delta\lambda}{2(\psi''-\psi')} \right)^2.
\]

At the second stage contact pairs between which intermediate solid phases are present in the phase diagrams were used, namely, Pb–Bi at 150°C, BiIn–In at \( t \in (72–88^\circ \text{C}) \), Bi–In at \( t \in (72–88^\circ \text{C}) \), Bi–In at \( t \in (89–109.5^\circ \text{C}) \). The required concentration \( n' \) and the corresponding molar fraction \( e' \) were found.
from set of equations (10)–(14) on the basis of the diffusion coefficients obtained at the first stage and experimentally found kinetic factors.

It was found that at 150°C the molar fraction of lead in the liquid phase at the border from the side of lead is $c_{\text{Pb}}^{(L/Pb)} = 0.516 \pm 0.006$ at confidence probability of 95%. Within the limits of the error the obtained value coincides with the liquidus value of the stable phase diagram which is equal to 52 molar % Pb. We will obtain 62 molar % Pb at 150°C if we extrapolate from the high-temperature branch of the liquidus line to the low-temperature area (the extrapolation of the liquidus line is shown by a hatched line in Figure 3).

Let us pass over to the results obtained from investigation of Bi–In system, the phase diagram of which is shown in figure 4.

**Figure 4.** Phase diagram of the Bi–In system (scheme, after [3])

Diffusion coefficients for the pairs listed above which do not form intermediate solid phases were preliminary found. The temperature dependences of the obtained diffusion coefficients were extrapolated to the area of lower temperatures. Thus, the diffusion coefficients were estimated for the layers containing metastable ranges of a liquid.

Generalization of the obtained results for the Bi–In system is reduced to the following (figures 5–7). For the contact pairs which form intermetallic compounds at temperatures of diffusion annealing according to the phase diagram (figure 4) it is revealed that at the boundary with a sample containing bismuth (Bi, BiIn), the composition of the liquid is close to stable liquidus values. The exception is the In-Bi pair at $t \in (89-109.5)^\circ\mathrm{C}$. In this case displacement of boundary composition from the stable liquidus line toward bismuth-side is observed which exceeds the measurement error.

Thus, on the one hand it is shown that intermediate solid phases cannot be formed together with a liquid phase in the diffusion zone. On the other hand, it follows from the results of the experiment that concentration intervals of liquid layers correspond to stable phase diagrams. This contradiction can be explained as follows.

Between initial samples at the initial moment of time, and later on between a liquid and an initial sample contact melting occurs according to the metastable phase diagram without the formation of intermediate compounds. As a result, the part of the liquid adjoining to the initial sample is in a metastable state. The time of metastable liquid existence depends on random processes leading to the formation of nuclei of intermetallic compounds. Then the metastable part of the liquid layer disintegrates into stable intermediate compounds and a stable liquid. Further on, contact melting of intermediate compounds occurs according to a stable phase diagram. After complete melting of the
Figure 5. Molar fractions of Bi in a liquid interlayer at the interface with the crystal upon the contact melting of the Bi-In pair (72-88°C): (1) equilibrium liquidus; (2) and (3) lines obtained by the extrapolation of the liquidus formed by the BiIn compound and Bi, respectively; and (✓, ✗, ○) calculations based on the effective diffusion coefficients obtained from the results on the contact melting of BiIn$_2$-In, BiIn-In, and Bi-In pairs, respectively. The shaded band stand for a 95% confidence region of results designated by ○.

Figure 6. Molar fractions of Bi in a liquid interlayer at the interface with the crystal upon the contact melting of the BiIn-In pair (72-88°C): (1) equilibrium liquidus and (2) extrapolation of the liquidus formed by Bi; (✓, ✗) calculations based on the effective diffusion coefficients obtained from the results on the contact melting of BiIn$_2$-In and BiIn-In pairs, respectively. The hatched band stands for a 95% confidence region of the results given by circles (○).
Figure 7. Molar fractions of Bi in a liquid interlayer at the interface with the crystal upon the contact melting of the Bi-In pair (89-109.5°C): (1) equilibrium liquidus and (2) extrapolation of the liquidus formed by Bi; (○, ) calculations based on the effective diffusion coefficients obtained from the results on the contact melting of the BiIn-In and Bi-In pairs, respectively. The hatched band stands for a 95% confidence region of the results designated by ○.

intermetallic compounds the liquid interacts with the initial sample again, after what the sequence of the processes recurs. The longer the duration of existence of metastable conditions of a liquid is, the higher is the deviation of average in time of concentration of a liquid at the boundary with the initial sample from a stable liquidus line.

5. Investigation of the ΔT-effect of contact melting
The direct confirmation of occurrence of metastable liquid in contact of dissimilar metals is the ΔT-effect of contact melting. This effect is observed in systems containing intermediate solid phases. If two samples which form such a system are brought into contact at a temperature below the least eutectic temperature of the stable phase diagram, a strong bonding of the samples occurs within several seconds. It is supposed that bonding takes place as a result of the occurrence and crystallization of a liquid.

One of the possible explanations of the effect is based on the so-called “thermal hypothesis” [9]. According to the hypothesis, diffusion between samples brought into contact leads to the formation of an intermediate solid phase. It is believed that the quantity of heat released during this process is sufficient for reaching the eutectic temperature, which results in contact melting according to the equilibrium phase diagram. The solution of a corresponding heat problem has the form [10]

\[ \Delta T = \frac{\alpha \chi}{4} \left( \frac{nD}{\kappa c \rho} \right) \]

(15)

where \( \Delta T \) is the temperature difference between the contact plane (where the exothermic reaction takes place) and the thermostat, \( \alpha \) is a constant lying in the range 2-4, \( D \) is the diffusion coefficient of an intermediate solid phase, \( \chi \) is the heat (per unit volume) of formation of the intermediate phase, \( \kappa \) is the thermal conductivity of the material, \( c \) is its heat capacity, \( \rho \) is its density. Substituting values typical of the Bi–Tl system in equation (15), we find that the reaction zone is heated by 0.3 mK. The insignificant heating of the contact zone during solid-state reactions argues against the thermal hypothesis. If an intermediate phase is the liquid then, according to the formula, the decrease in temperature should make one kelvin.
The measurement of temperature of the contact can give helpful information upon usual contact melting that is above the eutectic temperature, corresponded to estimation (15).

Systems Bi-Me (Tl, In, Pb) have been investigated. We measured the temperature in contact of the samples at the temperature of the thermostat 5-48 K below the least eutectic temperature. A rise in the contact temperature of 0.15-0.24 K was observed.

The possibility of occurrence of a metastable liquid upon $\Delta T$-effect is illustrated by Figure 8. According to Ostwald's rule of stages [11], a liquid phase must appear first. Next, the liquid must crystallize into an intermetallic phase. This sequence must be accompanied by a change in the sign of the thermal effect, in contrast to what was observed in our experiments: sintering was always accompanied by heat release. Therefore our results on the contact temperature during sintering are inconsistent with the rule of steps.

Note that the measured contact temperature is at least two orders of magnitude higher than predicted by calculations. This discrepancy suggests that the formation of intermetallics via solid-state reactions plays an insignificant part in rapid sintering.

It is, therefore, reasonable to assume that the sintering process is assisted by a nonequilibrium liquid. Bringing two different samples into contact drives the system out of equilibrium. The jump in chemical potential across the interface is then reduced owing to the simultaneous nucleation of equilibrium intermetallic phases and a nonequilibrium liquid phase. The heat needed for the formation and growth of nonequilibrium liquid-phase nuclei comes directly from neighboring nuclei of the equilibrium intermetallic phases. The amount of the liquid phase increases at the expense of the parent material, but concurrently the liquid phase crystallizes into equilibrium intermetallics. The quantity of heat released in this process notably exceeds that expected for solid-state reactions and was detected in our experiments. At the end of the rapid sintering stage, there is no jump in chemical potential, and most of the liquid is crystallized.

6. Computer Simulation
The possibility of the processes concerned with the occurrence of metastable ranges of a liquid can be investigated by means of computer imitation. Let's observe a computational experiment on the contact melting in a two-component system containing an intermediate solid phase [12]. The model under examination is a linear sequence of cubic cells. All the cells are assumed to contain the same total...
amount of substance. Each cell has its order number \( i \) and is characterized by a fraction \( c_i \) of the component A and a fraction \( f_i \) of the liquid phase in it. At the initial time instant, one half of the cells corresponds to the sample A and the other half, to sample B, and all the cells are supposed to be solid.

A change in the characteristics of the cell occurs due to the exchange of substance between the cells, which is realized by the rule

\[
\delta c = -\sigma \left( c_{i+1}^{(b)} - c_i^{(b)} \right) \tag{16}
\]

where \( \delta c \) is the amount of the component A transferred from the \( i \)th cell to the \((i+1)\)th cell and is expressed in fractions of the total amount of substance per cell; \( c_i^{(b)} \) is the concentration of the component A in the region of the \( i \)th cell that is adjacent to the face through which an exchange \((c_i^{(b)}, f_i)\) takes place at \( 0 < f_i < 1 \); and \( \sigma \) is the transfer coefficient. When the cells that exchange substance are not separated by an interphase interface, then \( \sigma = \sigma_S \) if on either side of the face separating the cells the substance is in a solid state, and \( \sigma = \sigma_L \) if the substance is in a liquid state. If the cells are separated by an interphase interface then \( \sigma = \sigma_I \) corresponds to the experimental results. Formula (16) is a discrete analog of the first Fick’s law:

\[
\sigma = D \frac{\Delta t}{(\Delta z)^2} \tag{17}
\]

where \( D \) is the diffusion coefficient and \( \Delta z \) is the distance at which the diffusion process propagates during time \( \Delta t \). Besides it is accepted that \( \sigma_S = 0.1 \) and \( \sigma_L = 10^{-7} \).

The fraction \( f_i \) of liquid in the cell is determined in terms of the phase diagram of the system under study. Figure 9 displays the phase diagram of the model system under consideration whose prototype is the Bi–In system at a temperature of 85°C. Unlike the real system, the model system forms a single intermediate solid phase \( AB_2 \) whose prototype is an intermetallic compound BiIn\(_8\). In a cell with a mixed phase composition, the concentrations of the solid and liquid phases correspond to the solidus and liquidus, and the solid part of the cell is adjacent to the solid part of the sample and the liquid part of the cell adjoins the liquid interlayer.

If metastable states can occur in the cell, a random number \( r \) is selected in the line segment \([0, 1]\) to ascertain the phase composition \( f_i \) with the help of a random number generator and a quantity

\[
\mu(\theta) = \left[ (c - c_{L1}) / (c_{S1} - c_{L1}) \right]^{\theta}
\]

is compared with this number. Within fields II, III, and IV, the quantity in square brackets, representing the degree of stability, takes values in the line segment \([0, 1]\). The stability of the metastable (supersturated) state of the melt can be controlled using the metastability index \( \theta \). As \( \mu(\theta) < r \), the phase composition of the cell is determined from the metastable phase diagram; otherwise, i.e., at \( \mu(\theta) > r \), from the stable phase diagram. With increasing \( \theta \) at \( \theta > 1 \), the probability of the formation and retention of the metastable state grows, because \( \mu(\theta > 1) < \mu(1) \).

Thus, it was established on the basis of a computer simulation of contact melting in a system with an intermediate solid phase that the concept of the formation of intermetallic compounds due to the crystallization of the metastable part of the liquid interlayer does not contradict the offered above model. In the computational experiment at small (\( \theta \sim 1 \)) and large (\( \theta \sim 100 \)) stability of the metastable states, a parabolic law of growth of the liquid interlayer is obeyed. In intermediate cases (for example, at \( \theta = 20 \)), a piecewise linear dependence of the liquid-interlayer extension on the square root of time is observed. At small stability of the metastable states, the boundary values of the liquid-phase concentration correspond to the liquidus of the stable phase diagram (Figure 10). If the metastable states are sufficiently stable, the boundary concentrations in the liquid interlayer are shifted toward the metastable liquidus.
Figure 9. The phase conditions of the model system

Figure 4. The time-base sweep of the molar fraction of the A-component in the liquid on the boundary with A-sample at $\theta=18$. $c_{L1}$ and $c_{L1m}$ are values on the stable and the metastable liquidus curves.

4. Conclusion
It is found that the concentration region of a liquid phase corresponds to a stable phase diagram. The obtained results are explained by the formation at the interphase boundary with crystals of metastable ranges of a liquid. Stable intermediate compounds precipitate from the metastable liquid. Continuity of the chemical potentials of components is provided during the listed processes in the diffusion zone.

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