Abstract. The growth of the liquid interlayer in the system lead-tin at 463 K is studied experimentally in the nonstationary diffusion process of contact melting. The contact melting was carried out between pure tin and solid solution of tin in lead (0.59, 11.5, 17.8, 24.8 mol. % Sn). The results indicate that the concentration range of the liquid interlayer corresponds to the interval of homogeneity of the liquid phase in the phase diagram at the experiments temperature. It is shown that the solid solution corresponding to the solidus near the liquid/crystal interface can not be generated by the diffusion of atoms from the liquid into the crystal. An explanation is offered that the solid solution of solidus composition at the liquid/crystal interface occurs as a result of the precipitate from the metastable (supersaturated by lead) melt.

1 Introduction

Contact melting is melting of the crystal as a result of exposure to the surface of another adjacent phase – an extrinsic crystal, liquid or vapor [1]. In this paper is considered the emergence and the growth of the liquid phase in the contact of the crystals at the temperature $T$, which is above the melting point of eutectic $T_e$, but below the melting temperature of some of the original crystals (figure 1).

In this paper we carried out contact melting in the nonstationary diffusion process. This process occurs if samples A and B are fixed and arranged vertically and a denser material is located at the bottom [2]. In this case in the contact zone the isoconcentration planes move in accordance with the parabolic law [2, 3]:

$$z(n_k,t) = \lambda(n_k)\sqrt{t},$$

where $n_k$ is the concentration of one of the components of the system A-B, $z(n_k,t)$ is the coordinate of the isoconcentration plane with the concentration $n_k$ in an instant $t$, $\lambda(n_k)$ is the kinetic factor, corresponding the concentration of $n_k$. The concentration $n_k$ and the relative concentration $c_k$ are linked by the expression $c_k = n_k/(n_A + n_B)$, $k \in (A,B)$. In the expression (1) it is taken into account that the diffusion process between the two samples, each of which is homogeneous, begins at time $t=0$ in the plane $z=0$.

A number of papers (e.g., [4]) propose a sequence of processes leading to the contact melting: the diffusion of atoms from the adjacent phases into the crystal, the formation of supersaturated solid solution in the near-contact area of the crystal, the appearance of liquid in the decay of supersaturated solid solution. The main disadvantage of this scheme is the impossibility of formation of saturated and supersaturated solution in an initial crystal for a finite time with known mechanisms of diffusion.
From the experiments [2, 3] it follows that by the diffusion growth of the intermediate phases the interfaces move in accordance with the parabolic law (1). This means that during the experiment the compositions of phases in the planes adjacent to the interfaces are constant. In the present paper a possible mechanism for the establishment of quasi-equilibrium state at the crystal-liquid interface is proposed in contact melting in a simple two-component eutectic system.

Fig. 2. Distribution of component B in the contact zone

A system of lead-tin served as the object of study. According to [5] the melting temperature of eutectic of this system is equal to 456 K. The solubility of tin atoms in a solid lead at this temperature reaches 28.1% tin, and the solubility of lead atoms in a solid tin – 1.3% lead. The diffusion annealing was performed at the thermostat temperature of 463 K.

2 Diffusion of atoms from liquid to solid phases in contact melting

We shall investigate the possibility of establishing a quasi-equilibrium state at the crystal-liquid interfaces by diffusion of atoms from liquid to solid phase under the condition of diffusion growth of the liquid phase. Figure 2 schematically shows the distribution of component B in the diffusion zone, consisting of the initial crystals and the intermediate liquid phase. Figure 3 shows the curves of the Gibbs energy for the liquid L and for crystals α and β. In thermodynamic equilibrium the liquid with a relative concentration \( c_B(L/L_\alpha) \) is conjugated with a solid solution, the relative concentration of which \( c_B(\alpha/L_\alpha) \).

Let the initial α-sample consists of A-sort atoms only. We shall suppose that the constant composition \( c_B(\alpha/L_\alpha) \) is realized in some way at the interface with the liquid from the α-crystal. Then the distribution of the component B in the α-crystal, formed by diffusion, has the form

\[
n_B(\lambda) = n_B^{(\alpha/L)} \frac{1 + \text{erf}\left(\frac{\lambda}{2\sqrt{D_S}}\right)}{1 + \text{erf}\left(\frac{\lambda^{(L/\alpha)}}{2\sqrt{D_S}}\right)}, \quad \lambda \leq \lambda^{(L/\alpha)} \leq 0
\]

(2)

Fig. 3. The curves of molar Gibbs energy describing the phase equilibrium at temperature \( T > T_c \) in a simple eutectic system

According to our measurements, details of which are listed below, the interface movement of liquid-lead is estimated by the kinetic factor \( \lambda^{(L/\alpha)} \approx 10^{-5} \text{ m/s}^{1/2} \) for contact pair Pb-Sn at 463 K. To estimate the diffusion coefficient in the solid phase \( D_S \), required for the formula evaluation (2), we shall use the available data on the diffusion of tin atoms in a solid lead [6]. These data extrapolation to a temperature of 463 K leads to the result \( D_S = 2.05 \times 10^{-16} \text{ m}^2/\text{s} \). If we shall substitute these values in argument of function \( \text{erf}(\psi) \) in the formula (2), then \( \text{erf}(\psi) \approx -1 \) and the direct formula evaluation (2) is difficult. Therefore, we shall expand the function \( \text{erf}(\psi) \) in an asymptotic series [7] and confine to the first two expansion terms:

\[
\text{erf}(\psi^2) = 1 - \frac{\exp(-\psi^2)}{\psi \sqrt{\pi}} + \ldots, \quad \psi < 0.
\]

(3)

then from (2) we obtain

\[
\frac{n_B(\lambda)}{n_B^{(\alpha/L)}} = \frac{\lambda^{(L/\alpha)}}{\lambda} \exp\left(\frac{(\lambda^{(L/\alpha)})^2 - \lambda^2}{4D_S}\right), \quad \lambda \leq \lambda^{(L/\alpha)}.
\]

(4)

After the transformation of (4) we shall obtain subject to (1) an estimate of the penetration depth of the tin atoms diffusion from liquid into solid lead:

\[
z^{(L/\alpha)} - z(n_B) = \frac{2D_S}{\lambda^{(L/\alpha)}} \ln\left(\frac{n_B}{n_B^{(\alpha/L)}}\right) \cdot \sqrt{t}, \quad z \leq z^{(L/\alpha)}
\]

(5)

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For example, it results from (5) that the filling 

\[ n_B/n_B^{(aL)} = 0.75 \]

achieved after 3600 s from the beginning of the experiment at a depth equal to two atomic diameters of lead \( d_{\text{B}} = 3.62 \times 10^{-10} \text{ m} \).

Thus, in terms of diffusion forming of a contact zone, which includes a liquid interlayer, the depth of penetration of extrinsic atoms from liquid to solid sample is so small that it does not provide conditions similar to a stable equilibrium at the interface. The degree of validity of the conclusion of unattainability by diffusion the states close to equilibrium \( c_B \) of the liquid concentration at the interface from \( \varphi \) more if we shall abandon the artificial fixation of penetration of extrinsic atoms from liquid to solid sample which includes a liquid interlayer, the depth of

\[ \varphi = \text{constant} \], \( \varphi = \text{constant} \)

Based on (10), we shall formulate the interface conditions:

\[ \frac{z^{(L/i)}}{V^{(i)}} \Omega^{(S)} = \left( \frac{z^{(L/i)}}{V^{(i-L)}} \right) \Omega^{(L)} \], \( i \in (\alpha, \beta) \),

where \( \psi^{(i)} \) is the molar volume of the substance in the \( i \)-phase, \( \psi^{(i-L)} \) – the molar volume, which would take the substance of the \( i \)-phase at the congruent melting. From the system of equations (7) \( \Delta \alpha \) and find the velocity \( w = \frac{d(z_0)}{dt} \). Subject to (1) we obtain

\[ w = \frac{\left( \psi^{(\alpha)} - \psi^{(\beta)} \right)}{\Delta \alpha} \Omega^{(L)} \], \( \frac{1}{2} \sqrt{t} \equiv \frac{\lambda_0}{2 \sqrt{t}} \).

We shall substitute (6) using (8) in the equation of continuity \( \frac{\partial n_k}{\partial t} + \frac{\partial j_k^0}{\partial z} = 0 \). In this case we use the result of [10] where it was concluded that there was no in shear in explicit dependence of the diffusion coefficient on composition. We obtain

\[ \frac{\partial n_k}{\partial t} - D^{(L)} \frac{\partial^2 n_k}{\partial z^2} + \frac{\lambda_0}{2 \sqrt{t}} \frac{\partial n_k}{\partial z} = 0 \], \( k \in (A, B) \).

With the substitution

\[ \psi = \frac{\lambda - \lambda_0}{2 \sqrt{D^{(L)}}} = \frac{z - z_0}{2 \sqrt{D^{(L)}} t} \],

we shall transform the equation (9) to the form

\[ 2 \psi \frac{dn_k}{d\psi} + \frac{d^2 n_k}{d\psi^2} = 0 \], \( k \in (A, B) \).

The solution (11) has the form

\[ n_k(\psi) = P_k + Q_k \cdot \text{erf}(\psi) \], \( k \in (A, B) \),

where \( P_k \) and \( Q_k \) are constants. Based on (12), we shall formulate the interface conditions:

\[ \frac{c^{(L/\alpha)}}{c^{(L/\alpha)}} = \frac{P_A + Q_A \cdot \text{erf}(\psi^{(L/\alpha)})}{\psi^{(L/\alpha)}} \]

\[ \frac{c^{(L/\beta)}}{c^{(L/\beta)}} = \frac{P_A + Q_A \cdot \text{erf}(\psi^{(L/\beta)})}{\psi^{(L/\beta)}} \],

where, in accordance with (10),

\[ \psi^{(L/\alpha)} = \frac{\lambda^{(L/\alpha)} - \lambda_0}{2 \sqrt{D^{(L)}}}, \quad \psi^{(L/\beta)} = \frac{\lambda^{(L/\beta)} - \lambda_0}{2 \sqrt{D^{(L)}}}, \]

and \( \psi^{(L/\alpha)} \) and \( \psi^{(L/\beta)} \) are the partial molar volumes of components in the liquid.

From (14) we have

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\[
D^{(L)} = \left[ \frac{\lambda^{(L/\beta)} - \lambda^{(L/\alpha)}}{2(\mu^{(L/\beta)} - \mu^{(L/\alpha)})} \right]^2 
\]

where \( \lambda = \frac{z^{(L/\beta)} - z^{(L/\alpha)}}{\sqrt{t}} \) is the kinetic factor characterizing the increase in the extent of the liquid layer and being the experimentally measured value.

In the sequel we shall agree that the \( \beta \)-phase is a pure substance, for the system under study – tin, and \( \alpha \)-phase may represent as a pure substance – lead, as well as a solid solution of tin in lead.

We obtain the next system equation based on (6) and (12), applying these expressions to the liquid at the interface with the \( \beta \)-phase. From the previous section it follows that the amount of matter which diffuses from the liquid to the solid phase in the growth process of the liquid interlayer can be neglected. Therefore, the velocity of the interface \( \nu^{(L/\alpha)} = \frac{d z^{(L/\alpha)}}{d t} = \lambda^{(L/\alpha)} / (2\sqrt{t}) \). Subject to (1), (8) and (10) we obtain

\[
- \frac{Q}{\sqrt{\pi}} \exp[-(\psi^{(L/\beta)})^2] = \frac{c^{(L/\beta)}_A}{c^{(L/\beta)}_A + c^{(L/\beta)}_B} \psi^{(L/\beta)}
\]

Another equation is an obvious statement that all amount of the component \( A \), located in the melt part of the \( \alpha \)-phase, transferred to the liquid interlayer:

\[
n_A^{(a/\alpha)} z^{(L/\alpha)} \delta z = n_A^{(a/\alpha)} z^{(L/\alpha)} - z_0 \Omega^{(L)} = \int n_A^{(z)}(\psi) d\psi
\]

After changing the variable \( z \) to the variable \( \psi \) and expression \( n_A^{(a/\alpha)} \) – the congruent melting of the \( \alpha \)-phase – through a molar fraction of \( c_A^{(a)} \) of component \( A \) in the \( \alpha \)-phase, the expression (17) becomes

\[
\frac{c_A^{(a)} \psi^{(L/\alpha)}}{c_A^{(a)} v_A^{(L/\alpha)} + c_B^{(a)} v_B^{(L/\alpha)}} = \int [P_A + Q_A \cdot \text{erf}(\psi)] d\psi
\]

The equations (13), (15), (16) and (18) constitute a system, which connects the values determining the growth of the liquid interlayer in contact with the initial solid samples.

### 4 Methods of measurements

In this paper we used the method of contact melting, as proposed in [2]. We used metals containing 99.999% Pb and 99.999% Sn. Initial samples were made by retraction of the melt in a glass tube with a diameter of about 3 mm. The ends of the samples designed for the contact were polished. The samples were inserted on both sides of a short segment of a glass tube, which prevents the leakage of the liquid from the contact zone in the process of diffusion annealing, and gives a liquid interlayer the form close to cylindrical. In this case the ends of the samples do not contact. The result assembly is fixed in a special holder and placed in an upright position into a liquid thermostat. To prevent a convective mixing of the liquid formed in the samples contact the sample from the more dense matter, lead, placed underneath.

The thermoregulation liquid was glycerol. To equalize the temperature in the thermostat the thermostatic liquid was continuously mixed with a vane-type agitator. Temperature variations do not exceed ±0.2 K. The absence of temperature gradient near the sample was fixed with the help of a differential thermocouple. After the temperature stabilization in the thermostat the solid samples were juxtaposed before touching with polished ends, after which the liquid interlayer starts to grow. In the process of diffusion annealing the solid samples are fixed. After the diffusion annealing the samples were quenched in cold water, a longitudinal thin section was produced and the extent of the crystallized liquid interlayer, formed during the diffusion annealing, was measured.

The diffusion annealing was carried out at a thermostat temperature of 463 K. The duration of diffusion annealing was typically three hours. During this time the extent of the liquid interlayer reaches ~ 2.5 mm. In all experiments the sample of \( \beta \)-phase was a pure tin. The composition of \( \alpha \)-phase in different experiments varied from pure lead to solid solution with 24.8% tin.

In order to clarify the influence of the homogeneity degree of solid solutions on the results of the contact melting, some samples of the solid solution with 24.8% tin were annealed before putting in contact with pure tin at 463 K for 8 hours. The dependence of the results on the preliminary heat treatment of samples was not detected.

### 5 Results and discussion

The measurements data of the kinetic factor \( \Delta \kappa_{\exp} \), characterizing the growth of the liquid interlayer, are shown in figure 4. The shaded band in figure 4 shows the 95% confidence field relative to obtained approximation, which is designed according to recommendations [11].

Since the solubility of lead in solid tin is relatively small, the deviation of the liquid composition at the interface with tin can differ markedly from liquidus values of the equilibrium phase diagram at this temperature. Therefore, the calculations assumed that the molar fraction of lead in the liquid at the interface with tin equals to liquidus value at 463 K, i.e. \( c_{Pb}^{(L/\beta)} = 0.219 \)
The partial molar volumes of components in the liquid interlayer are calculated by [8] and for the study temperature are assumed to be equal $v_{Pb}^{(L)}=1.913\times10^{-5}$ and $v_{Sn}^{(L)}=1.695\times10^{-5}$ m$^3$/mol.

At the first stage of calculations we obtained diffusion coefficient for tin-lead melts at 463 K. We used for this the contact melting results between the $\alpha$ solid solution with 24.8% tin and with pure tin. Because of this solid solution is close to the composition of a solid solution maximum possible at the experiment temperature, i.e. to solidus composition of the lead-side, it is natural to assume that in this case the liquidus concentration at the interface with the $\alpha$-phase is ensured by force. Therefore we accepted that the molar fraction of lead in the liquid at the interface of the $\alpha$-phase is equal to the corresponding liquidus value at 463 K, i.e. $c_{Pb}^{(L)}=0.280$ [5].

![Fig. 4. The kinetic factor characterizing the growth of the liquid layer in contact melting in lead-tin system at the temperature of 463 K, depending on the composition of $\alpha$-phase.](image)

The solution of equations (13), (15), (16) and (18) relative to the diffusion coefficient leads to the result $D=0.84+0.01\times10^{-9}$ m$^2$/s. The error indicated here is the 95% confidence limit, and considers only the error in measuring the kinetic factor $\Delta \lambda$. The received diffusion coefficient is comparable with the results of [10], where the results of measuring the diffusion coefficient in melts lead-tin are represented at temperatures from 500 to 1000 K for several compositions from 17.6 to 33.9% of lead. It is found out the absence of the significant concentration dependence of the diffusion coefficient. The extrapolation of the results [10] to a temperature of 463 K leads to the value $D=0.92\pm0.12\times10^{-9}$ m$^2$/s, which is coincides within the error with our result.

At the second and final stage the kinetic factor $\Delta \lambda$ was calculated with the help of equations (13), (15), (16) and (18) for different compositions of $\alpha$ solid solution. The calculation is made on the assumption that the interface concentration of the liquid corresponds to the liquidus values of the phase diagram. In the calculation of $\Delta \lambda$ we used the diffusion coefficient obtained in the first stage of calculations. In the process of obtaining results we used the insensitivity of the diffusion coefficient in melts lead-tin to the composition of the liquid, which was revealed in work [10].

The results of calculations are shown in figure 4. The calculated values $\Delta \lambda_{\text{comp}}$ lie within 95% confidence area of approximation of experimental values $\Delta \lambda_{\text{exp}}$, which indicates the adequacy of the initial assumption relative to the correspondence of the concentration range of the liquid layer to the interval of homogeneity of the liquid phase at the experiment temperature on the phase diagram. In order to demonstrate the sensitivity of the result of calculation $\Delta \lambda_{\text{comp}}$ to the liquid composition at the interface with the $\alpha$-phase the kinetic factors were calculated for the case when the liquid from the $\alpha$-phase side is limited by metastable liquidus $c_{Sn}^{(L/\alpha,m)}$. The definition scheme $c_{Sn}^{(L/\alpha,m)}$ for the case when the sample of the $\alpha$-phase is a pure substance $A$, is shown in figure 3. The values $c_{Sn}^{(L/\alpha,m)}$ for solid solutions are determined similarly. The values estimate $c_{Sn}^{(L/\alpha,m)}$ was made on the basis of thermodynamic data on the system lead-tin [5] with the correction on the phase diagram. The results of calculations $\Delta \lambda_{\text{comp}}$ using $c_{Sn}^{(L/\alpha,m)}$ for solid solutions of different compositions are shown in figure 4 with line 2. It is seen that with the decrease of tin in a solid solution the calculated kinetic factor $\Delta \lambda_{\text{comp}}$ for metastable interface ($L/\alpha$) deviates more significantly from the experimental values $\Delta \lambda_{\text{exp}}$.

Thus, the composition of the liquid at the interface with a solid sample coincides with the liquidus value at the temperature of diffusion annealing: $c_{Sn}^{(L/\alpha,m)}=c_{Sn}^{(L/\alpha,s)}$. It was shown above that the quasi-equilibrium at interfaces can not be achieved by the liquid diffusion into the crystal diffusion. Therefore, we propose the following model to achieve the quasi-equilibrium state at interfaces.

Initial samples are melted under the influence of an extrinsic phase with the formation of metastable, i.e. supersaturated by the substance of the original sample, liquid. The role of a extrinsic phase in the initial moment is adjacent solid sample, and further the liquid formed under the contact of solid samples. As a result the part of the liquid interlayer which is adjacent to the initial sample is in a metastable, i.e. in the supersaturated by the substance of the original sample, condition. The lifetime of the metastable liquid depends on the random processes leading to the formation of nuclei of a stable solid solution. The probability of nucleation of a stable solid solution on the surface of a solid sample is significantly higher than in the liquid volume. As a result of the decay of the metastable liquid region adjacent to the solid sample is the growth of stable solid solution of solidus composition on the surface of the original solid sample. Further there is a contact melting of stable solid solutions in the stable phase diagram. After complete melting of the solid solution the liquid reacts with the initial sample again, after which the sequence of states is repeated.

The observed interface composition of the liquid is a superposition of stable and metastable liquidus values with factors, proportional to the time of existence of solid solution and of metastable liquid. The melting of the solid solution is limited by diffusion transport of atoms through the liquid interlayer and occupies most of the period of an iterative process, a smaller part of which is the
crystallization of metastable liquid. This explains the slight, not docked by the experiment shift the interface composition of the liquid with respect to the equilibrium liquidus to metastable one. It should be borne in mind that different regions of the interface surface at the same time are in various stages of the process.

6 Conclusion

The kinetics of growth of the liquid interlayer is studied in contact melting in system lead-tin. It was stated that the liquid interlayer corresponds to the interval of homogeneity of the liquid phase in the phase diagram. The result is explained by the formation and decay of sections of the metastable liquid at the boundaries of the initial solid samples. The solid solutions of solidus composition providing a concentration range of liquid, bounded with liquidus concentrations are formed in the process of the decay of metastable liquid on the surface of the initial samples.

References

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