

Influence of Electric Transfer on Mutual Diffusion and Macroscopic Flow in Binary Melts Growing During Contact Melting

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Abstract – The theoretical foundations of the process of electric transfer (ET) in melts growing during contact melting (CM) of binary systems are considered. It is shown when the modes of this process will be carried out - speed-up and speed-down. It has been established that electro transfer makes an additional contribution to the magnitude of the rate of macroscopic flow (determined by the displacement of inert tags), due to the inequality of the partial diffusion coefficients of the melt components. The electric current passing through the liquid layer, formed by the CM, can have a very significant impact on the rate of its growth. Depending on the direction of the current, both increase and decrease in the speed of the CM can be observed. The paper also discusses the main regularities of the ET process at a CM, studies the effect on its parameters of the degree of difference in some physicochemical characteristics of the melt.

Keywords – contact melting; electro transfer; X-ray phase analysis; intermetallic; Kirkendall effect; hydrodynamic flow; metals; alloys; diffusion.

I. INTRODUCTION

Contact melting is the appearance and growth of the liquid phase in contact with two solids at a temperature lower than the melting point of the fusible component. If the CM is carried out in the unsteady-diffusion mode in the absence of convective mixing, the growth process of the liquid phase obeys the pattern $\delta \sim \sqrt{\tau}$, where δ is the thickness of the liquid interlayer, τ is the exposure time. We have studied the process of CM in the presence of a constant electric current in the interlayer. In this case, the growth rate of the interlayer is limited by diffusion and electro power (ET) [1]

In the classical Kirkendall experiment [1-3], thin side molybdenum wires were placed on the side faces of a brass sample (70% Cu, 30% Zn). The bar was electrolytically covered with a thick layer of copper, after which the sample was subjected to continuous annealing. As a result, there was a convergence of molybdenum wires located on opposite sides of the bar.

The explanation of the Kirkendall effect is that the diffusion mobilities of copper and zinc atoms are unequal: the exchange of places between vacancies and zinc atoms occurs more intensively than the exchange of places between vacancies and copper atoms [4]. Residual pores are detectable metallographically.

The following features inherent in the Kirkendall effect were noted in [4]. Diffusion occurs by the vacancy mechanism. Atoms at each time point belong either to diffusing or to the components of the crystal lattice with which molybdenum wires are connected. In this way, the classical Kirkendall effect is possible only in crystals.

In our opinion, the Kirkendall effect occurs in binary systems with unequal partial diffusion coefficients of the components [4, 5]. Experimental studies on this issue relate mainly to solid phases. However, studies on contact melting suggest that the Kirkendall effect may also occur in liquid metallic systems. Thus, in [5], it was found that inert labels placed in the plane of the initial contact, when the CM are shifted towards a lower diffusion flow. This is explained by the inequality of diffusion fluxes of the components in the liquid contact layer. In this paper, the Bi-Cd system is studied, since ET is more pronounced in it.

We have considered the theoretical foundations of the process of electric transfer (ET) in melts growing during contact melting (CM) of binary systems. It is shown when the modes of this process will be carried out - speed-up and speed-down. It has been established that electro transfer makes an additional contribution to the magnitude of the rate of macroscopic flow (determined by the displacement of inert tags), due to the inequality of the partial diffusion coefficients of the melt components. This new term also depends on the ratio of the partial volumes of the components.

The electric current passing through the liquid layer, formed at the expense of CM [1, 6], can have a very significant impact on the rate of its growth [7, 8]. Depending on the direction of the current, both increase and decrease in the speed of the CM can be observed [1, 6–10]. In the second case, with some limiting exposure, the growth of the liquid layer practically stops. This phenomenon serves as a convenient and illustrative method for studying ET in melts; it allows one to determine the effective charges of the components [11, 12].

This paper discusses the main laws of the process of ET with a non-stationary CM [1], studies the effect on its parameters of the degree of difference of some physicochemical characteristics of the components of the melt [11-14].

II. METHODS AND MATERIALS

For a binary solution (melt) through which current I passes, the substance fluxes of the components are written as [1, 13]:

$$j_1 = l_1 \frac{I}{\chi} - D_1 \nabla C_1, \quad (1)$$

$$j_2 = l_2 \frac{I}{\chi} - D_2 \nabla C_2, \quad (2)$$

where χ is the electrical conductivity of the system, D_i is the intrinsic diffusion coefficient of the components, C_i is the concentration (the number of moles of component i per unit volume), $l_i = b_i C_i$; b_i – ion mobility in an electric field,

$$\nabla C_i = \frac{\partial C_i}{\partial x}, \quad (i = 1, 2).$$

The effective ion charges (e_i^*) are entered according to the relation [12, 13]:

$$b_i = \frac{D_i^0}{kT} e_i^* \quad (3)$$

where D_i^0 is the coefficient of self-diffusion.

Considering (3) and Ohm's law ($I = \chi E$), we write equations (1) – (2) in the form:

$$j_1 = \frac{C_1 D_1^0}{kT} e_1^* E - D_1 \nabla C_1 \quad (4)$$

$$j_2 = \frac{C_2 D_2^0}{kT} e_2^* E - D_2 \nabla C_2 \quad (5)$$

The effective charges of the components are related by the relation [13]:

$$C_1 e_1^* + C_2 e_2^* = 0 \quad (6)$$

Due to the difference in the partial atomic volumes of the components (Ω_i) and the partial diffusion coefficients ($D_1 \neq D_2$) in the solution, in order to avoid the appearance of a pressure gradient, a macroscopic flow should occur [1, 15, 16], whose speed is denoted by w . We now write the equations for substance flows for a fixed (laboratory) coordinate system:

$$J_1 = j_1 + C_1 w, \quad (7)$$

$$J_2 = j_2 + C_2 w, \quad (8)$$

The flows of the components can be considered as related by the relation [13]:

$$\Omega_1 J_1 + \Omega_2 J_2 = 0 \quad (9)$$

Substituting (4) - (5) into (7) - (8), using (9), and entering the volume fractions of the components ($n_i = \Omega_i C_i$), we get:

$$w = (D_2 - D_1) \nabla n_2 - \frac{n_2}{kT} E e_2^* \left(D_2^0 - \frac{\Omega_1}{\Omega_2} D_1^0 \right), \quad (10)$$

$$J_1 = \frac{C_1 F}{\Omega_1 kT} e_1^* E - \tilde{D} \nabla C_1, \quad (11)$$

$$J_2 = \frac{C_2 F}{\Omega_2 kT} e_2^* E - \tilde{D} \nabla C_2, \quad (12)$$

where $F = n_1 \Omega_2 D_2^0 + n_2 \Omega_1 D_1^0$, \tilde{D} - the value of the value of the coefficient of mutual diffusion:

$$\tilde{D} = n_1 D_2 + n_2 D_1 \quad (13)$$

In the absence of EP (11) - (12), they will take the form of the Fick equations, and (10) will resemble the well-known Darken relation (for the Kirkendall effect) [1, 12, 16]:

$$w_0 = (D_2 - D_1) \nabla n_2 \quad (14)$$

Comparison of (10) and (14) shows that the EP changes the rate of macroscopic flow in the melt (determined in practice by the displacement of inert tags [1,12,16]) by the value:

$$\Delta w = - \frac{n_2}{kT} E e_2^* \left(D_2^0 - \frac{\Omega_1}{\Omega_2} D_1^0 \right) \quad (15)$$

Thus, the speed of a macroscopic flow in the presence of ET will be determined not only by the inequality of the coefficients D_1 and D_2 , but also depends on the magnitude and direction of $\Delta \vec{w}$.

Since e_1^* and e_2^* have opposite signs [1, 10, 11, 13], the sign of the vector $\Delta\vec{w}$ is determined not only by the direction of the current, but also by the ratio of the values $n_1 D_1^0 e_1^*$ and $n_2 D_2^0 e_2^*$.

For definiteness, we will assume in what follows that $\nabla C_2 > 0$, a $\nabla C_1 < 0$.

Considering (15), equations (11) - (12) can be represented as:

$$J_1 = C_1 \Delta w - \tilde{D} \nabla C_1, \quad (16)$$

$$J_2 = C_2 \Delta w - \tilde{D} \nabla C_2, \quad (17)$$

Depending on the sign of the magnitude Δw , two variants of the process development are possible. If $\Delta w > 0$, then the first term on the right-hand side of (16), due to the presence of ET, will add up to a positive value of $(-\tilde{D} \nabla C_1)$, so that there will be an increase (compared to the currentless variant of CM) of the flux of component 1 by the value of $C_1 \Delta w$. However, the flux of component 2, as can be seen from (17), will also be reduced.

If $\Delta w < 0$, then the change (caused by ET) of the component flux values will be opposite.

Since the values and signs of the effective charges should not depend on the direction of the current, when switching it should occur, as can be seen from (15), the sign change Δw . In this case, the mode of the process (accelerating or slowing down compared to the current-free version) will change to the opposite.

A noteworthy detail is that we consider the CM process in a non-objective state, that is, it is considered that a practical experiment will be carried out so that there are no convective flows in the melt. For that end, prototypes of the selected system of components 1-2 are fixed in a vertical position, with a sample with a lower density located on top.

Thus, the ET process at the CM changes the speed of macroscopic flow in the melt by an amount Δw , which is directly proportional to the strength of the passing current, inversely proportional to the electrical conductivity of the system (given that $E = I/\chi$) and also depends on temperature, average concentration of the melt, self-diffusion coefficients and effective charges of components.

However, the value Δw , as can be seen from (15), does not depend on time, whereas the "kirkendall" term of the macroscopic flow (w_0) will decrease with time, because, as can be seen from (14), it is proportional to the concentration gradient in the melt.

Only under the condition that $\Omega_1 = \Omega_2$ and $D_1^0 = D_2^0$, the value Δw , as can be seen from (15), will be equal to zero. Note that $\Delta w \sim E$, the direction of the vector $\Delta\vec{w}$ depends on the sign $E e_2^*$, as well as the signs of the differences ($D_2^0 = D_1^0$) and $(1 - \frac{\Omega_1}{\Omega_2})$.

For definiteness, we assume in the following that $\nabla C_2 > 0$, and $\nabla C_1 < 0$.

III. RESULTS

A simple analysis of equations (11)-(12) shows that, depending on the direction of the current and the signs of the effective charges, two variants of the process development are possible:

Option 1. $E e_1^* > 0$, ($E e_2^* < 0$). In this case, the first term on the right-hand side of (11) will be positive, and a positive value will be added to it $(-D \nabla C_1)$. Thus, there will be an increase (compared to the currentless version of the CM) of the diffusion flux of component 1 by the magnitude of the first term. And in equation (12), the first term will be negative, from which the positive value of the $D \nabla C_2$ is subtracted. At the same time, an increase (in absolute value) of the diffusion flux of component 2 also occurs. Thus, the electric field will increase the absolute values of the diffusion fluxes that occur in the melt at the time of the beginning of the CM process. Since the rate of KP is directly proportional to the values of $|J_1|$ and $|J_2|$ [1, 2], this means that in this variant there will be an increase in the speed of the process (compared to the currentless version of the CM).

Option 2. $E e_1^* < 0$, ($E e_2^* > 0$). The first term on the right-hand side of (11) will be negative, while the second term $D \nabla C_1$ will be positive. Thus, there will be a decrease (in absolute terms) of the diffusion flux of component 1 by the magnitude of the first term. And in equation (12), the first term will be positive, while the second term will be negative. When this occurs, a decrease (in absolute value) of the diffusion flux of component 2 occurs by the magnitude of the first term. Thus, in this embodiment, the electric field will reduce the absolute values of the diffusion fluxes of both components, that is, the process speed will decrease (compared to the currentless version of the CM).

It should be noted that we consider the CM process in a non-convective mode, that is, it is believed that a practical experiment will be carried out so that there are no convective flows in the melt. To do this, prototypes of the selected system of components 1-2 are fixed in a vertical position, with a sample with a lower density located on top.

Assume that $e_1^* > 0$, and $e_2^* < 0$. Then the accelerating variant of the process will be carried out at $E > 0$ (the electric current is downward, that is, towards the heavier component), and with the reverse direction, the current will be slowed down.

If $e_1^* < 0$, and $e_2^* > 0$, then the accelerating mode will be executed at $E < 0$ (the electric current is directed upwards), and at the reverse direction of the current there will be a retarding process variant. The above analysis is confirmed by the results of [9].

Note that if a change in sign E would result in a change (inverse) of the signs of the effective charges of the components, then in practice there would not be a transition from an accelerating to a slowing down (or vice versa) when changing the direction of the current.

If the process proceeds in a slowing variant, then at a certain exposure a moment comes when the difference in the fluxes of the components in the melt becomes zero (this is due to the fact that the second terms of the right sides of equations (11) - (12), being inversely proportional to the thickness of the interlayer, decrease with time due to its growth, whereas the first implicit ones do not change with time). When such a moment is reached, a "steady state" occurs when the liquid layer remains unchanged in magnitude (if the magnitude and direction of the current does not change). This limit value (L^*) can be found by equating equalities (11) - (12) to zero, as well as accepting for limit concentration gradients: $\nabla C_i \approx \frac{\Delta C_i}{L^*}$, where ∇C_i , is the interval (range) of concentrations of component i in the melt at the temperature of the experiment:

$$L^* = \frac{\Omega_1 D k T \Delta C_1}{C_1 F e_1^*} = \frac{\Omega_2 D k T \Delta C_2}{C_2 F e_2^*} \quad (18)$$

where C_i is the average concentration of component i in the melt.

At $E \rightarrow \infty$ we will have from (16): $L^* \rightarrow 0$. If $E \rightarrow 0$, then $L^* \rightarrow \infty$ (which corresponds to the currentless version of the CM).

IV. CONCLUSION

It is not too difficult to see that in order to get out of the "stationary state" under consideration in order to further increase the contact layer, it is enough to only slightly reduce the amount of direct current passing through the system.

If there is an increase in E , then we will have a reverse exit from the "stationary state": a decrease in the thickness of the contact layer (L). that is, the crystallization of some part of it.

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