The influence of small impurity additions and direct electric current on the kinetics of contact melting in metals

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Abstract. Using the experimental data on contact melting of polycrystalline indium, tin and lead – based solid solutions with low–melting alloys we show that besides the diffusive, adhesive and low – dimensional mechanisms of contact melting it is necessary to take into account the segregational mechanism as well. The surfaces of a contact between the polycrystalline solid solutions and low – melting metals enrich in lower melting components due to the grain-boundary and surface segregation. One can influence on the kinetics of contact melting using alkali metals as impurity additives and applying the direct electric current. For example, the sodium addition to indium results in 3 times expansion of contact layer in the (In + 0.1 at. % Na) – Bi system, but in 2 times shrinking of that layer in the (In + 0.1 at. % Na) – Cd system in comparison to experiments without impurities.

1. Introduction
In spite of the huge massive of studies on influence of impurities on the parameters of contact melting (CM) [1–6] and on the electrical charge transfer there is a gap in knowledge of CM in metals with solid solutions including alkalis and of the charge transfer in contact layers. Known theoretical studies on the kinetics of CM taking into account the charge transfer deal with binary systems only [7,8]. The presence of alkali metal ions in melts, however, may remarkably change the effective charges $Z_i^*$ of components and even reverse their signs.

Therefore, study of CM in metals with additions of alkali and alkali – earth metals is necessary for the development of a CM theory. On the other hand, one can control the kinetics of CM by addition of the impurities and/or by the applying a voltage, and this opportunity is of practical importance.

In this paper we study the influence of small alkali and alkali – earth additions on the kinetics of contact melting of Cd–, In– and Pb– based solid solutions with metals taking into account a possible charge transfer.

2. Experimental
The hosting Pb of very high purity 99.9995% (Super High Quality – 000), was purified by zone melting. Maximum impurity content afterwards was less than $3 \times 10^{-4}$ wt. %. The purity of other metals
used was: tin of 99.9995 wt.% (Tin – 000); indium and bismuth both of 99.999 wt.%; sodium of 99.99 wt.% and lithium of 99.6 wt.% (Lithium Experimental – 1). The ultra fine cadmium of a purity of 99.9999 wt. % was used as well. The cadmium was purified by vacuum distillation method proposed by B.N.Akeksandrov and co–workers [3]. All solid solutions were prepared at B.I.Verkine Physical – Technical Institute for Low Temperatures of Ukrainian Academy of Sciences (Kharkov).

The alloying was carried out in glass ampoules in the helium atmosphere. The prepared solid solutions were: Pb–Li, In–Na, Cd–Li, Cd–Na, Cd–Ba. Solubility of the alkali metals in solutions Pb–Li, In–Na, Cd–Li, Cd–Na is low but the concentration of the solid solutions was chosen below the solubility limit and was controlled by the residual resistance.

The ingots of solid solutions and solid solution samples were held in vacuum oil (Vacuum Oil–1) before the experiments.

The samples of a diameter of 2.2 mm and a thickness of 15 mm were cut from ingots and put into the contact with samples of pure metals in special tubules of the same diameter as initial ingots but of a height of 10–12 mm and then placed into the holder, which was immersed into the thermostat with the silicon oil (PFMS–2). The holder allowed passing of the direct electric current through the samples.

In order to study the structure of alloy layers and to determine the rate of CM we prepared longitudinal sections. The microstructure of layers was studied by metallographic method after etching the samples. The error in size definition was 10 μm. The average speed of CM $<\nu_{CM}>$ was estimated as $<\nu_{CM}> = <\delta>$ per 1 hour, $<\delta>$ being the average thickness of the contact layer.

3. Results

3.1 The influence of impurity atoms on the kinetics of contact melting, without current

Results of our measurements of the speed of contact melting in solid solutions with metals are given in Figures 1 to 3.

![Figure 1](image.png)

Figure 1. The dependence of the average speed of CM, $<\nu_{CM}>$, versus reverse value of solubility limit, $C_{lim}^{-1}$, for the systems:

a) (Sn+Me:Bi, In, Zn, Pb, Cd)–In;

b) (In+Me:Pb, Bi, Sn, Na, Zn)–Sn;

c) (Pb+Me:Bi, Ag, In, Sn, Li)–Bi.

The investigation shows that the speed depends weakly on the sort of impurity in a given system $(A+Me)–B$, Me denoting the impurity. For instance, the replacement of one impurity by the other of the same concentration does not influence almost on $\nu_{CM}$, except the alkali additions (see Figures 2 (a) and (b)). It is seen in these figures that replacement of sodium by the same content of lithium in cadmium results in a considerable increase in the speed of CM.

The increasing content of impurity atoms, however, results in increase in $\nu_{CM}$ and in structure transformations within the contact layer in all cases. For example, let us consider the contact layer in
3.2. The influence of impurity atoms on the kinetics of contact melting, with current

3.2.1. The (Pb+0.5 at.% Li)–Me (Bi, Sn) system

Figure 4 represents dependence of squared thickness of the contact layer, $\delta^2$, for the (Pb+0.5 at.% Li)–Sn and (Pb+0.5 at.% Li)–Bi systems versus duration of CM experiment and direction of electrical current [12]. One can see that the contact layer in case of the current existence is thicker in comparison to current–free variant of experiment independently on the direction of the current. The curve $\delta^2(\tau)$, $\tau$ being the duration of experiment, is higher than in current – free regime at positive polarity on the upper sample (Bi). One should notice that the dependencies $\delta^2(\tau)$ at the reverse (braking) direction of the current are always located between the $\delta^{\text{accelerated}}$ and $\delta^{\text{current-free}}$ in all binary systems without alkali metals studied previously.
The contact melting in the solid solution (Pb+0.5 at.% Li)–Sn is peculiar, see Figure 4(a). If the polarity on the tin is negative then the thickness $\delta(t)$ of the contact layer increases with duration of the experiment, then, at $\tau$ about 7 hours, it approaches the values for current – free variant of measurements, $\delta^0$, and later may become less than $\delta^0$. Similar dependence of $\delta(t)$ is, apparently, associated with the inversion of the effective charge of the ions of one compound, which may result in the alternation of the charge transfer flux of this compound.

![Figure 4. The squared thickness of the contact layer $\delta^2(\tau)$ in the systems:](image)

(a) (Pb+0.5 at.% Li)–Sn, b) (Pb+0.5 at.% Li)–Bi.  
1 – current – free variant of experiment;  
2 – polarity on tin is «minus»; 3 – polarity on tin is «plus»,  
b) 1 – current – free variant of experiment;  
2 – polarity on bismuth is «minus»; 3 – polarity on bismuth is «plus».

The metallographic analysis of the contact layers in the (Pb+0.5 at.% Li)–Sn system shows that dendrites grow in both directions of the current in contrary to the “current – free” layer containing almost no dendrites. The interesting fact is the predetermined orientation of dendrites, namely along the current. The boundaries of liquid and solid phases are almost smooth.

As the experiments show, the lithium addition to the Pb–Bi system results in an increase in thickness of the contact layer and in a bending of the interface (in case of Bi$^+$ and Bi$^-$) in comparison to current – free variant. The redistribution of density of the current passing through the boundaries dividing the areas of different conductivities may be one of the reasons of that bending. Mentioned redistribution may initiate microconvection of a liquid on the liquid – solid boundary leading to the bending of the interface. The other reason for the observed boundary bending may be the axial pressure produced by the electric current passing through the liquid conductor (this pressure is maximal on the axis of the conductor).

The dendrites were observed in all cases after the time of 6 hours of current passing in the (Pb+0.5 at.% Li)–Bi system.

3.2.2. The (In+0.1 at.% Na) – Me (Bi, Cd) system
The results of $\delta^2(t)$ measurements in the (In + 0.1 at.% Na) – Bi system are shown in Figure 5 (a) [13]. One can see that $\delta^2$ is proportional to $\tau$ in the current – free regime. This fact points out the diffusive mechanism of the contact melting. The sodium impurity negligibly influences on the shape of the curve $\delta^2(t)$ even if the current exists. The speed of contact melting $u_{CM}$, however, increases approximately 3 times in case of impurity in comparison to “impurity – free” variant of experiments. The picture changes if the voltage is applied: $\delta$ depends on the direction of the current in both cases. The order in the In–Bi system becomes $\delta^+ > \delta^0 > \delta^-$, that is the thickness of contact layer in current – free regime, $\delta^0$, lies between the “current” samples. But if sodium is added, then the order becomes $\delta^+ > \delta^-$.
>d^0 (see Figure 5 (a)), that is the presence of the current (of any direction) results in a layer thickness in increase in comparison to current – free regime. The maximal value of the speed of CM is obtained when indium is switched to the positive pole of the battery. Established dependencies could be confirmed by photos of microsections.

Figure 5. The squared thickness of the contact layer \( d^2 \) in the systems:

- a) (In + 0.1 at. % Na) – Bi;
- b) (In + 0.1 at. % Na) – Cd:
1 – current is directed from the solid solution In–Na to Bi;
2 – current – free variant of the experiment;
3 – current is directed from Bi to solid solution In–Na.

Figure 5 (b) gives the dependence \( \delta^2 \) versus the duration \( \tau \) of contact melting in the (In + 0.1 at.% Na)–Cd system. It indicates that sodium addition to indium results in the change of the order of contact layer thicknesses, namely \( \delta^+ > \delta^0 > \delta^- \) similarly to the (In + 0.1 at.% Na) – Bi system. In other words, the contact layer at current – free regime is thinner than in any “current” regime. One should notice that accelerating CM direction of the current in the (In + 0.1 at. % Na) – Cd system is realized when indium is switched to the negative and cadmium to the positive poles, in contrary to the (In + 0.1 at. % Na) – Bi system. This also could be confirmed by photos of microsections in those systems.

It can be seen from Figure 5, that the characteristic features of the \( \delta^2(\tau) \) dependence in the (In+ 0.1 at. % Na)–Cd system are: 1) the speed \( u_{CM} \) with impurity is about 2 times less that in impurity – free regime and 2) the contact melting follows diffusive mechanism similar to the current – free regime despite of a short durations of the experiment. Deviations from the parabolic law at the beginning of CM were observed for the majority of systems studied earlier. Apparently, such behavior of \( \delta^2(\tau) \) in the (In+0.1 at. % Na) – Cd system is associated to the influence of Na atoms on the migration of the major components of melt resulting in a more ordered movement of ions under the applied electric field.

So, the analysis of contact melting in our systems reveals that sodium added to indium diversely influences on CM: the CM speed \( u_{CM} \) increases 3 times in the (In + 0.1 at. % Na)–Bi system and the contact layer shrinks 2 times in the (In+ 0.1 at. % Na)–Cd system in comparison to impurity – free regime of experiments. The passing current do not influence on the “diffusivity” of CM.

3.2.3. The (Cd+0.1 at.%Na)–Me (Sn, Bi) and (Cd+0.1 at.%Li)–Me (Sn, Bi) systems

Figure 6 (a) gives the dependence \( \delta^2 \) versus duration of CM in the Sn–(Cd – 0.1 at.% Na) system [14]. It reveals that \( \delta^+ - \delta^- \) in current – free regime that points diffusivity of the process. The order \( \delta^+ > \delta^0 > \delta^- \) for the Sn–Cd system with current is known. The speed of CM \( u'_{CM} \) in the (Cd–0.1 at.% Na)–Sn system at both directions of the current and any duration of the measurements is anyway greater than that of current – free regime, \( u''_{CM} \) (see curves 1 and 3 in Figure 6 (a)). However the order of
thicknesses of the contact layer changes during the experiments: the order $\delta^+ > \delta > \delta^0$ on the initial stage of CM lasting during the first 6 hours is replaced by the $\delta^- > \delta > \delta^0$ one after 6 hours. The latter is probably associated with the sign inversion of the effective charge dependent on the concentration of the compounds.

The sign inversions and linked peculiarities of CM kinetics also were observed in ternary systems studied earlier, but features of Figure 6 (a) are reported for the first time.

Photos of microsections obtained at contact melting in the (Cd+0.1 at.%Na)–Sn system after 8 hours confirm the validity of the orders just described.

Figure 6 (b) shows the dependence $\delta^2(\tau)$ in the Bi–(Cd–0.1 at.%Na) system. One can see that curves $\delta^2(\tau)$ in this case considerably differ from those of Figure 6 (a): for instance, the dependence $\delta^2(\tau)$ in the (Cd + Na)–Bi system is almost linear at studied durations of CM.

3.2.4. The (Cd+0.3 at. % Ba)–Me (Me: Sn, Bi) system

Figures 7 (a) and (b) give the dependencies of squared thicknesses of contact layer versus the duration of contact melting for the (Cd +0.1 at.%Li)–Sn and (Cd+0.1 at.%Li)–Bi systems, respectively. The samples follow the same order of the layer thicknesses as before. One can see that lithium addition to cadmium considerably influences on the kinetics of CM. If polarity on tin in Cd–Sn based solid solutions is positive then the dependence $\delta^2(\tau)$ is totally non – linear and even crosses the dependence $\delta^2(\tau)$ near 6 hours of observations.

In both the systems shown in Figure 7 we observe the same order in the sequence of the contact layer thicknesses, namely $\delta^+ > \delta^0 > \delta^-$. Photos of microsections confirm this rule.

The order $\delta_{accel} > \delta^0 > \delta_{break}$ for the binary metal – metal systems is no longer valid when passing electric current through the solid solution – metal system. At the presence of impurities this order depends on the nature of impurity and pure metals in contact (see, for example, above mentioned comments on the Sn – (Cd + Na) and Sn – (Cd + Li), Sn – (Cd + Na) and Bi – (Cd + Na) systems). The described behavior of the $\delta(\tau)$ dependence is obviously associated with the inversion of effective charge of one compound.

3.2.5. The (Cd+0.3 at. % Ba)–Me (Me: Sn, Bi) system

Figures 8 (a) and (b) give the dependencies of squared thicknesses of the contact layer versus the duration of contact melting for the (Cd+0.3 at.% Ba)–Me (Me: Bi, Sn) systems, respectively. The experimental conditions are the same as in the previous sections.
One can see from Figure 8 that alkali–earth additions act by the same way as alkalis do. The so called breaking regime of charge transfer [2, 15] is of special interest (see plots (a) in figures 4, 6, 7 and 8) that is when the direction of the transfer breaks the kinetics of contact melting. Last phenomenon can be used in technologies of solidification in electric field [16].

4. Conclusions

Let us draw some conclusion in order to summarize the experimental results presented in this paper.

It is shown that the speed of contact melting in solid solutions with metals in non–stationary diffusion regime depends on the type of impurity weakly except alkali additions. Nevertheless, concentration of any impurity influences on the speed of contact melting and the structure of contact layers. The speed of contact melting in solid solutions with metals correlates to the reciprocal value of limiting solubility.
The structure and the thickness of the contact layer considerably depend on the direction of the current at melting of the (Pb+0.5 at.% Li) alloy in contact with Sn and Bi, (In + 0.1 at. % Na) alloy with Bi and Cd, (Cd + 0.1 at.% Na), (Cd + 0.1 at.% Li) alloys with Sn and Bi and (Cd+0.3 at. % Ba–Bi alloy. The squared thickness of the contact layer is irrelevant to the type of impurity and obeys the rule $d^2 \sim t$ in current – free variant of the experiment. The typical order $\delta_{\text{accel}} > \delta_0 > \delta_{\text{break}}$ for binary metallic systems (where $\delta_{\text{accel}}$ and $\delta_{\text{break}}$ denote the thickness of contact layer at accelerating and braking directions of the current, respectively, and $\delta_0$ corresponds to the thickness without current) is no longer valid and depends on the nature of impurity and pure metals in contact.

The kinetics of contact melting in the (Pb+0.5 at.% Li)–Sn, (Cd+0.1 at.% Li)–Sn and (Cd+0.1at.%Na)–Sn systems is peculiar. If tin is switched to the negative pole of the battery then the contact layer becomes thicker with the duration of the contact melting but after 4 to 7 hours (for various systems) stops its expansion and its thickness trends to the value fixed in the current – free experiments. This could be explained by the inversion of the effective charge sign of lithium and sodium ions.

The sodium added to indium expands 3 times and shrinks 2 times the contact layer in the (In + 0.1 at. % Na) – Bi and (In + 0.1 at. % Na) – Cd systems, respectively, in comparison to the current – free observations.

The kinetics of contact melting in the (Cd+0.3 at.% Ba)–Me (Me: Bi, Sn) systems is reported for the first time. The regularities of current influence on the kinetics of contact melting are shown to be similar to those of contact melting in cadmium – based solid solutions with alkalis added.

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