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NONEQUILIBRIUM PHASE DIAGRAMS IN THE $PbCl_2$–AgCl EUTECTIC SYSTEM

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Abstract

It is well-known that eutectics do not necessarily grow at the eutectic temperature, or with the eutectic composition. Thus, the eutectic point can be shifted due to nonequilibrium conditions in the system. This fact was observed in many experiments. We try to explain this behaviour on base of the study of phase transformation kinetics. We construct the kinetic phase diagrams of $PbCl_2$–AgCl within the framework as of the nucleation theory as of the theory of growth on the phase interface. Our models are based on the molecular model of the difference of chemical potential of components for the liquid and solid phases. The proposed model describes the position of the eutectic point very well and is practically applied for the study of nonequilibrium directional growth in the $PbCl_2$–AgCl system.

Keywords: eutectics, kinetics, $PbCl_2$–AgCl system, phase diagram

Introduction

In the $PbCl_2$–AgCl system there exist no compounds, only a eutectic composition of about 40 mol% $PbCl_2$ and about 60 mol% AgCl. There is a very narrow region of solid solution on the AgCl side of the phase diagram containing maximal 2 mol% $PbCl_2$ in AgCl at the eutectic temperature (Fig. 1) laying between 564 and 591 K. Equilibrium study was carried out [1, 2] showing nonideal behaviour of the melt well fitted by the interaction parameter $\Omega = -13.6$ ($kJ\cdot mol^{-1}$) of the regular model applied [2] wit the experimental and theoretically derived excess enthalpy equal 19.05 and 20.67 $kJ\cdot mol^{-1}$ respectively.

We tried to explain the change of phase diagram of $PbCl_2$–AgCl system under microgravity conditions. The results of experiments performed at microgravity were published in [3] and can be summarized as follows:

Very interesting features can be observed at the interface between the part of the ingot (of the eutectic composition) solidified in terrestial conditions and the other which was remelted and solidified at microgravity conditions. This inter-

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face contains markedly larger $PbCl_2$ crystals beside the eutectics. The eutectic composition in interfacial layer differs markedly from the equilibrium composition (about 5 mol%) – see Fig. 1. We can see change of $PbCl_2$ concentration in AgCl which reaches about 8 mol% (in equilibrium max. 2 mol%). As is shown in [3], the estimated undercooling is about 50 K in comparison with maximum undercooling of several K which we can obtain on Earth in the same experimental conditions.

We believe that this phenomenon is caused by the lack of convection. In that case diffusion is the only process which can provide mass and heat transport in the melt [4]. It is well known that the shift of eutectic point needs to be connected with the nonequilibrium conditions in the melt-solid phase system. These nonequilibrium conditions can be realized in two levels of the phase transformation: in the nucleation process (in the undercooled homogeneous melt) and in the growth process (so at the phase interface eutectic – melt).

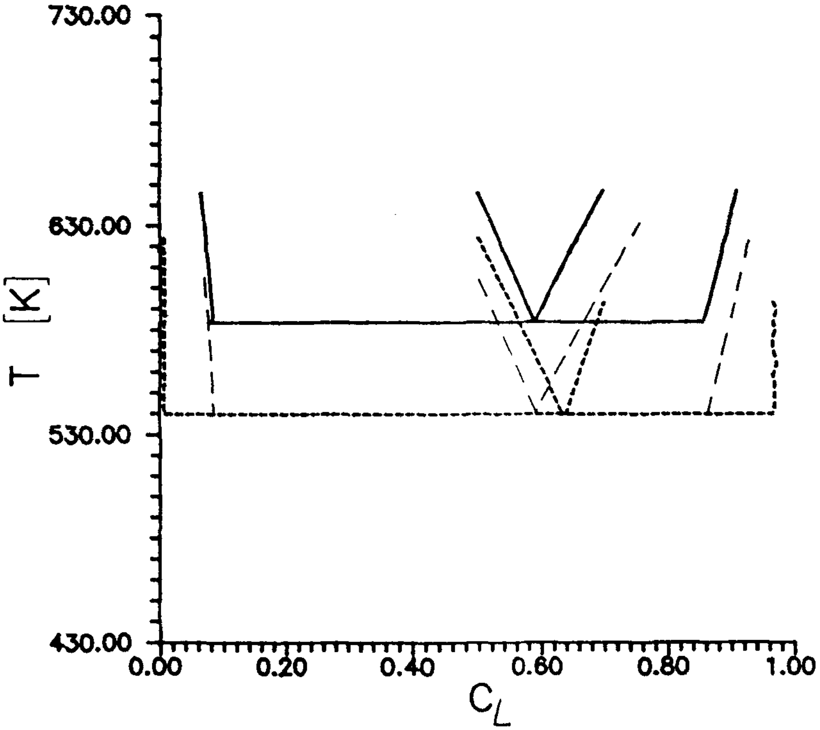

Fig. 1 $PbCl_2$–AgCl system: equilibrium investigated (full line) and theoretically calculated (dotted) equilibrium phase diagram in comparison with experimental results of kinetic phase diagrams (dashed)

The kinetics of nucleation

Since we aim at comparing the kinetic phase diagrams calculated as for nucleation as for growth on phase interface processes, we summarize results published in [5, 6] in the case of nucleation processes.

In Ref. [5], the relation for the probability density of the rise of the first critical nucleus of the solid phase with the concentration C_s (the mol% of AgCl in the system) in the melt with concentration C_L was derived. Further we supposed that the temperature of the system decreases linearly with time deriving the criterion which reflect the definition of the kinetic phase diagrams:

$$p(T_M,C_L,C_S) \geq -\dot{T}\left(\frac{\mathrm{d}\ln(p)}{\mathrm{d}T}\right)_{T=T_M} \tag{1}$$

where $p(T, C_L, C_S)$ is the probability of the formation of one critical nucleus (of concentration C_S) per unit time at temperature T in the melt (of concentration C_L). It means that during the decrease of the temperature (with the rate $\mathrm{d}T/\mathrm{d}t = \dot{T}$) we shall control the criterion (7) for all values C_S. The values C_S and $T_M(C_S)$, for which the relation (7) is fulfilled for the first time, are the points of our kinetic phase diagram. The results of our calculations of kinetic phase diagrams are presented on Fig. 2.

The kinetics of growth

Phase transformation occurring at the phase interface is completely opposite to nucleation. In the case of homogeneous nucleation, the new phase in the medium of the liquid phase is formed mainly in consequence of fluctuations. In growth at the phase interface, on the other hand, the new phase already exists in system. This is why the phase transformation occurs via a different mechanism with a lower energy barrier. In practice this means that rather less undercooling is usually necessary for the growth of the new phase. However, this undercooling depends on the cooling rate and may be influenced.

For description of the growth on phase interface we have chosen the microscopic model (determined in [6]). In the case of stationary processes (it means at constant undercooling) the following equation was derived for the mean value C_S, which describes the kinetic phase diagrams during growth of the solid phase on the solid-liquid interface in binary systems:

$$C_S\left[(1-C_L)\left(1-\exp\left(-\frac{\Delta\mu_B}{k_BT}\right)\right)+C_L\left(1-\exp\left(-\frac{\Delta\mu_A}{k_BT}\right)\right)\right]-$$

$$- C_L\left(1 - \exp\left(-\frac{\Delta\mu_A}{k_BT}\right)\right) = 0 \qquad (2)$$

The main role in the statistical theories plays the difference of chemical potential of components $\Delta\mu_i$:

$$\Delta\mu_i = \mu_i^L - \mu_i^S \qquad (3)$$

where $\mu_i^{L(S)}$ is the chemical potential of i-th component in liquid (solid) phase. We have chosen the molecular model for eutectic system proposed in [4]:

$$\Delta\mu_A = l_{AA}F_{AA} + l_{AB}F_{AB} - \left(Q_A - \ln\frac{C_L}{C_S}\right)k_BT \qquad (4)$$

$$\Delta\mu_B = l_{BA}F_{BA} + l_{BB}F_{BB} - \left(Q_B - \ln\frac{1 - C_L}{1 - C_S}\right)k_BT \qquad (5)$$

where l_{ij} is the number of the nearest to i-th particle neighbours of j sort; F_{ij} is the difference of the interaction energies of the nearest neigbour pair particles of i,j sort in solid and liquid phase; Q_i is the entropy factor; $C_{L(s)}$ is concentration of A component in liquid (solid) phase, k_B is the Boltzmann constant; T – temperature. The solution gives us the kinetic phase diagram in dependence on the temperature T (undercooling) at phase interface. The result for the undercooling 50 K is presented on Fig. 2. We can see the shift of the phase diagram, but for the constant parameters of our model the eutectic point has the same position. If we suppose the temperature dependence of entropy of the system, we can also obtain the shift of eutectic point within the framework of this model. In comparing we can see for nucleation the shift of the eutectic point C_E at the constant values of entropy. This shift is influenced by the mutual drift of molecules which influences the probability of critical nucleus creation. In the nucleation processes the surface energy plays the important role and influences on the constitution of clusters. In our model surface energy depends on the constitution of critical nuclea. In the case of the growth on the phase interface the drift of molecules and the surface energy are not considered. The shift of C_E can be influenced, for example, by the change of the concentration near the phase interface owing to the transport of mass in the system. Also the temperature dependence of the energy of intermolecular bindings ($F_{i,j}$) and hence the temperature dependence of coefficients Q_A, Q_B can change the kinetic phase diagram [8–10].

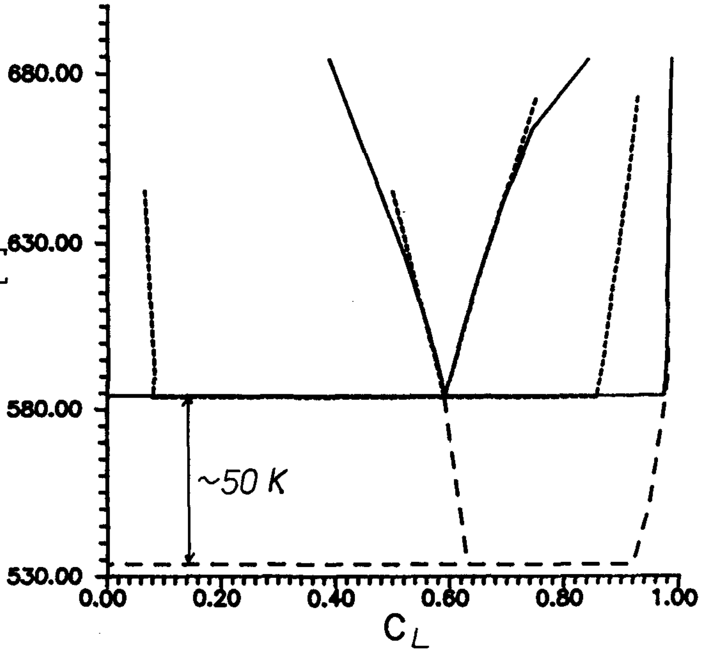

Fig. 2 Kinetic phase diagrams of the $PbCl_2$–AgCl system: (full line) – the equilibrium phase diagram, (dashed) – kinetic phase diagram in the case of the growth on phase interface, and (dotted) – kinetic phase diagram in the case of nucleation as the rate-controlling process

Practical aspects of directional solidification

Directionally solidified dielectric eutectics have interesting application prospects in technical practice, providing that their presentation in a geometrically highly ordered form is successfully solved. This objective has not yet been attained so far. It is also not yet satisfactorily clear where the practical limits lie. Therefore it is necessary to amplify fundamental theoretical and technological knowledge in this field. Experiments under gravityless conditions represent a promising alternative in this respect.

Results of our previous experiments [11–13] performed in microgravity (on boards of the Saljut-6 and MIR orbital station in CSK-1 crystallizer) strongly indicated that solidification of multi-component systems occur at higher supercooling than that one done in terrestrial environment. We have studied solidification of the $PbCl_2$–AgCl eutectic system prepared under various conditions in both terrestrial and microgravity environment. Methods of chemical and image analysis have been employed in order to evaluate quantitatively differences in

Fig. 3 The beginning of the interfacial layer remelted in conditions of microgravity; direction of solidification: from the left to the right; the part of ingot $PbCl_2$–AgCl solidified under terrestrial conditions is on the left side; $PbCl_2$ phase is white, AgCl phase is black (backscattered electron image, magn. 300×, white abscissa on the right =100 μm)

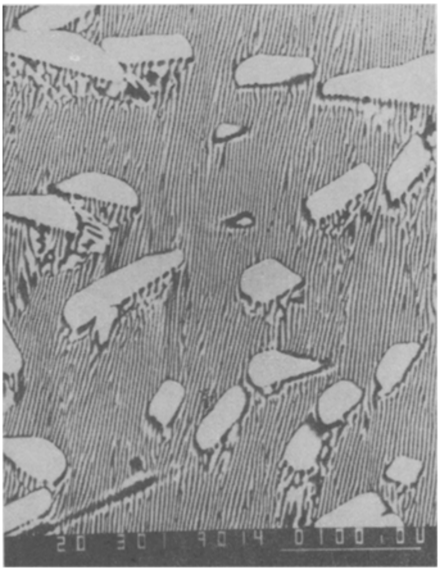

Fig. 4 The part of the interfacial layer at a distance of 2.4 mm from the beginning of remelted zone (magn. 300×, white abscissa on the right =100 μm)

chemical composition and microstructure between the terrestrial and space samples.

Very interesting features can be observed e.g. at the interface between that part of ingot solidified under terrestrial conditions and the comparable one which was remelted and solidified at G→0. A characteristic pictures of different sections of the directionally solidified sample prepared in a temperature gradient ΔT=50 K/cm with the growth velocity 10 mm/h can be seen in Figs 3–5. The interface can be characterized by more than a 3 mm thick interfacial layer (zone) that contains markedly larger $PbCl_2$ crystals beside the eutectics. As it is seen in comparison of Fig. 3 and Fig. 4 these $PbCl_2$ crystals are most frequent and smaller close to the interface, however, some of crystals become larger and are preferably oriented perpendicularly to the growth direction. The details of quantitative image analysis of the growth process are described in Refs [3, 14]. Similar phenomena can be observed in samples prepared at G→0 in a temperature gradient ΔT=50 K/cm at a growth velocity of 4 mm/h. The only difference can be seen in thickness of the interfacial layer which is about 0.7 mm thick in this case ([14], p.589).

Chemical analysis [3] of these samples along the solidification direction is very informative, too. We can observe two interesting dependencies. The first one describes the content of $PbCl_2$ lamellas in the eutectics in various distances

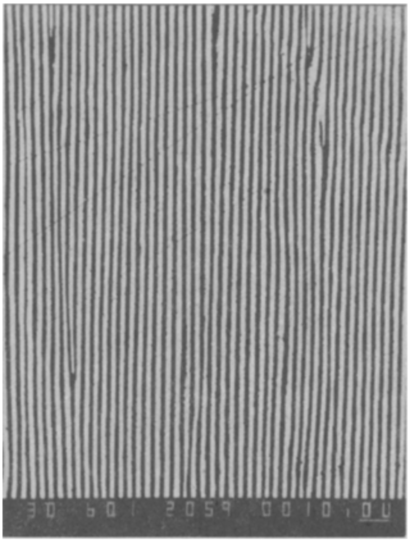

Fig. 5 The part of remelted zone behind the interfacial layer at a distance of 3.8 mm from the beginning of remelted zone; ordered lamellar structure of the directionally solidified eutectics $PbCl_2$–AgCl (magn. 600×, white abscissa on the right =10 μm)

from the beginning of the interfacial zone. The other important dependence shows the content of $PbCl_2$ crystals in $PbCl_2$ (both crystals and lamellas). As can be seem from Figs 3–5 that in the part of the sample prepared at $G \rightarrow 0$ volume $PbCl_2$ crystals decreases to zero. At the same time concentration of $PbCl_2$ in eutectic lamellas of AgCl reaches the equilibrium eutectic composition. Eutectic composition in the interfacial layer differs markedly from the equilibrium composition. The greatest difference from equilibrium composition occurs at the interfacial section where the eutectic contains a less amount of $PbCl_2$ compared with equilibrium (decrease about 5%). At the same time volume of $PbCl_2$ crystals reaches its maximum.

None of these phenomena were observed in samples prepared under terrestrial conditions. In case $G=1$ interface was sharp in all cases. It has to be pointed out that the composition of the starting ingot was strictly eutectic and identical for all experiments.

Discussion

The findings mentioned above support our earlier conclusion on the increased tendency of the melts to the non-equilibrium solidification under microgravity conditions. Our experiments show that solidification starts with higher supercooling compared with that one observed under terrestrial conditions (which is for the eutectic composition about 1–2 K in this experimental arrangement and less that 10 K at spontaneous cooling of the melt). We believe that this phenomenon is caused by the lack of convection. In that case diffusion is the only process which can provide mass and heat transfer in the melt. Because it is a very slow process (compared to convection) we can see a relatively thick interfacial layer between those parts of the sample solidified under microgravity and on Earth. In the case described above the thickness of the interfacial layer was about 3 mm. Because the length can be related to time ($v=10$ mm/h) we can see that it takes almost 20 minutes to overcome original supercooling and to reach equilibrium solidification. The fact that we have to deal with strong non-equilibrium phenomena causes great difficulties with interpretation and explanation of our results, because concept of phase diagrams can be used only for systems near ideal equilibrium state. But when we take into account kinetics of the described phenomena, we can see, that our metastable state becomes time dependent as can be seen from relaxation of chemical composition of the eutectics to equilibrium state mentioned above. It shows that we have to deal with a metastable state which looks like we would have started with off eutectic composition (on the $PbCl_2$ rich side). In that case we can see single crystals of $PbCl_2$ crystallized from the melt interconnected through the eutectic of the $PbCl_2$–AgCl system of nonequilibrium composition. At the same time (owing to the release of crystallization heat during solidification) the originally high undercooling decreases and finally our system reaches the equilibrium state where we can see only a perfect eutectic composition with the geometrically ordered lamellar structure (Fig. 5). During the course of crystallization a number of $PbCl_2$ crystal decrease but their individual volume increases and they also have certain orientation to the growth direction (Figs 3, 4). This phenomenon is usually observed in such systems and we believe that it is connected with Ostwald ripening or coarsening. Because we have to take into account the kinetic nature of the described phenomena we have to consider in detail all interactions existing on the microscopic scale and to match them with their external (cumulative) effects. This concept was introduced by M. E. Glicksman and his coworkers [15] for the systems where solidification occurs in isothermal diffusion regime. This, however, is different in comparison with our case where we have directional solidification in temperature gradient. The only similarity is that our transport regime is diffusive. Our situation is also complicated by the fact that the total volume of the growing phase is not constant, but it is decreasing with time.

Conclusion

In agreement with observations and research we can conclude that under microgravity conditions the melts exhibit an increased tendency towards non-equilibrium solidification. Owing to a lack of convection the undercooling decreases very slowly because diffusion is unable to balance the concentration gradients. This means that we have to take this phenomenon into account when starting solidification. Particularly in melts with low thermal conductivity we have to consider non-equilibrium phenomena on relative long time scale. On the other hand we can use benefits of higher undercooling in such cases, where metastable states are not accessible under terrestrial conditions. Particularly glassy systems [8] with low thermal conductivity and multicomponent systems with possible 'fine-structure' in metastable state of the phase diagrams can be of great interest. Our results show that if we reach equilibrium solidification, structural ordering and structural perfection can be achieved.

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Zusammenfassung — Es ist allgemein bekannt, daß Eutektika nicht unbedingt bei der eutektischen Temperatur oder mit der eutektischen Zusammensetzung wachsen. Somit kann der eutektische Punkt aufgrund von Nichtgleichgewichtsbedingungen im System verschoben werden. Diese Tatsache wurde in zahlreichen Versuchen beobachtet. Vorliegend wurde auf der Grundlage einer Untersuchung der Phasenumwandlungskinetik ein Versuch zur Erklärung dieses Verhaltens unternommen. Dabei wurden die kinetischen Phasendiagramms von $PbCl_2$–AgCl sowohl innerhalb der Keimbildungstheorie als auch der Theorie des Wachstums an der Phasengrenze konstruiert. Unsere Modelle basierten auf einem molekularen Modell der Differenzen zwischen den chemischen Potentialen der Komponenten für die flüssigen und die festen Phasen. Das vorgeschlagene Modell beschreibt die Lage des eutektischen Punktes sehr gut und wurde praktisch bei einer Untersuchung des Nichtgleichgewichts-Richtungswachstumes im $PbCl_2$–AgCl System angewendet.