NONEQUILIBRIUM PHASE DIAGRAMS IN THE PbCl₂–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 PbCl₂–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 PbCl₂–AgCl system.

Keywords: eutectics, kinetics, PbCl₂–AgCl system, phase diagram

Introduction

In the PbCl₂–AgCl system there exist no compounds, only a eutectic composition of about 40 mol% PbCl₂ 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% PbCl₂ 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·mol\(^{-1}\)) of the regular model applied [2] with the experimental and theoretically derived excess enthalpy equal 19.05 and 20.67 kJ·mol\(^{-1}\) respectively.

We tried to explain the change of phase diagram of PbCl₂–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 terrestrial conditions and the other which was remelted and solidified at microgravity conditions. This inter-
face contains markedly larger PbCl\textsubscript{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\textsubscript{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\textsubscript{2}–AgCl system: equilibrium investigated (full line) and theoretically calculated (dotted) equilibrium phase diagram in comparison with experimental results of kinetic phase diagrams (dashed)](image)

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