

The Physicochemical Features of Binary Immiscible Metal Systems in a New Method of Synthesis and Crystallization

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Abstract—Features of the structure of phase diagrams of immiscible binary metal systems for synthesis and crystallization of various compounds by a new method are considered: temperature and concentration limits of immiscibility, ratio of densities of system components, use of mixed solvents, and processes of hardening of pure immiscible systems. An example of obtaining crystals of refractory compounds is given.

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INTRODUCTION

Earlier, information was reported about development of a new method of technology and research of interaction of elements in immiscible binary metal systems (immiscibility gap method) [1–3]. Unlike the usual solution-melt method [4], where one dissolvent L is used (flux method), in the new method, synthesis and crystallization of the compound occur at the immiscibility boundary of two solvents ($L_1 + L_2$) [1–3]. In the short form, the key conditions of the new method consist in the following.

1. $\rho_{L1} < \rho_A < \rho_{L2}$; $\rho_{L2} > \rho_B > \rho_{L1}$, where ρ are the densities of initial reacting components A and B and two solvents. This relation of densities means that initial component A must be dissolved and go down in the layer L_1 , but must be lighter than the lower layer L_2 , and other initial component B must be dissolved and come to the surface in the layer L_2 , but must be heavier than the upper layer L_1 accordingly.

2. The availability of wide temperature (several hundred degrees) and concentration (in almost the entire concentration range) immiscibility limits ΔT and ΔC in the system for synthesis of compounds and their crystal growth is necessary.

3. The existence of solubility of at least one of the initial reacting components A (or B) in their layers or of their reaction products AL_1 (BL_2) with the element of the layer is necessary.

4. $\Delta F_{AB} < \Delta F_{AL1}$ (AL_2 , BL_2 , BL_1 , L_1L_2 , etc.). ΔF is the free energy of formation, and it should be the smallest for the synthesized compound.

Diagrams of processes that take place in immiscible systems are shown in Fig. 1. In this paper, the authors pay attention to some characteristic properties and differences of phase diagrams of such systems [5–7]. Production of both pure ingots and ingots with reacting components of immiscible systems, preparation

and examination of metallographic sections, and extraction of synthesis products from a solvent metal matrix are carried out in the same way as in [2, 3]. Systems Ga/Pb and Al + Ga/Pb are exceptions. In these systems, various refrigeration methods of an ingot are used during grinding and polishing in connection with the low melting temperature of Ga (29.77°C).

Only three systems (Al/Pb, Al/Cd, and Pb/Zn) have wide temperature and concentration immiscibility ranges (Table 1) [6, 7] of five metal systems that are the most suitable for experiments in standard conditions. Systems Cd/Ga and Ga/Pb are practically useless for technology because of small values ΔT and ΔC or low separation temperatures.

Generic aspects of the new method concern the boundary temperature and concentration immiscibility conditions of melts of elements, the presence of an immiscibility region bounded by a binodal, and the relation of densities of initial reacting components,

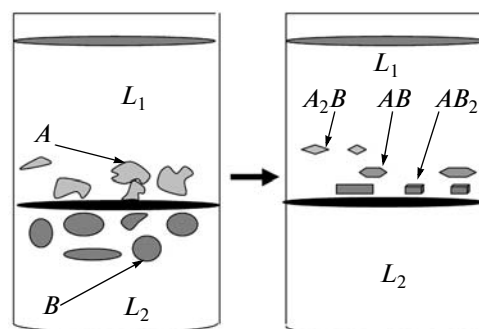


Fig. 1. Diagram of synthesis and crystallization in immiscible systems by the new method. The accumulation of initial reacting components on either side near immiscibility boundary and location of synthesis products in upper layer of immiscible systems (according to condition (1), see text) is displayed.

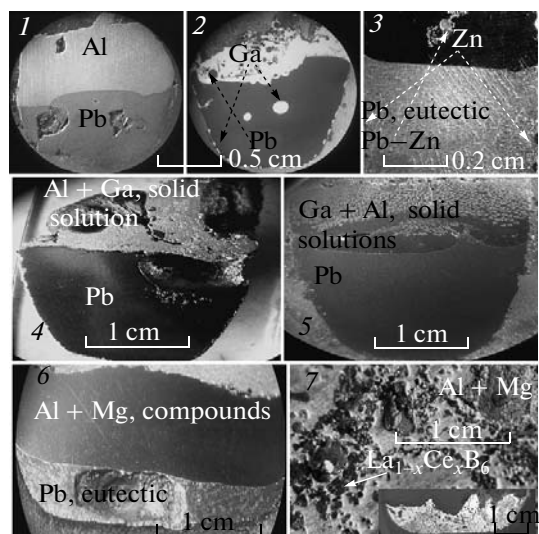


Fig. 3. Overall view of polished sections of binary and triple systems with an immiscibility: (1) Al/Pb system with contraction cavities in Al and Pb; (2) Ga/Pb system; arrows indicate inclusions of one layer in the other both inside and on ingot perimeter; (3) Zn/Pb system; eutectic is visible in layer of Pb; (4) “ideal” system Al + Ga/Pb with Al excess (Al : Ga = 80 : 20, at %); inclusions of one layer in the other are visible; layer of Al maintains granules of solid solutions of Al + Ga; (5) the same system as in 4, but with Ga excess (Ga : Al = 80 : 20, at %); extraction of solid solutions of Ga + Al are visible in layer of Ga; (6) Al + Mg/Pb system with compounds between Al and Mg in (Al + Mg) layer and eutectic in Pb layer in which a larger contraction cavity is located; (7) the same system as in 6 with isomeric crystals of solid solution of hexaborides of La and Ce: $\text{La}_{1-x}\text{Ce}_x\text{B}_6$ (where $x \approx 0.05$) obtained in it.

state depends on various reasons: the taken ratio of components, cooling rate, difference of melting temperatures of upper and lower metal, viscosities of layers, sizes of contraction cavity, etc. One can see the significant contraction cavities in the layer of Pb (system Al/Pb) and ones smaller in size in systems Pb/Zn and Ga/Pb (2, 3) from Fig.3 (1, 4). The existence of mutual inclusions, as a rule, oval in the bulk, on the boundary surfaces is significant and on surface of ingots of both layers is significant.

This is due to the reasons mentioned above, including the flow of more low-melting metal of the upper layer between the solidified lower layer and a bowl (Fig. 3 (2), system Ga/Pb). A distinguished boundary surface between the two metals above which, according to condition (1) of the new method, synthesis and crystallization products should be located are visible in all systems (because component *B* floating up in the lower layer to the immiscibility boundary must be heavier than the upper layer according to the condition, but after interacting on this boundary with component *A* from the upper layer produces compound A_xB_y , which will be lighter than pure component *B* and should transfer to the upper layer in connection with the reduction of density).

A so-called ideal triple system Al + Ga/Pb in which Al and Ga are mutually soluble in almost the entire interval of concentrations and both delaminate with Pb, forming wide ΔT and ΔC , is rather interesting. Experiments with excess Al (Al : Ga = 80 : 20, at %) and Ga (Ga : Al = 80 : 20, at %) upon heating (3 h) to 1000°C, soaking for 60 min, and cooling at a rate of 1.9 K/min were performed. Correct boundary surfaces are formed in both cases, as follows from Fig. 3 (4, 5), and in the upper layer, granules of solid solutions $x\text{Al} \cdot y\text{Ga}$ and $x\text{Ga} \cdot y\text{Al}$ are visible. Good mutual solubility of Al and Ga allows one to change the density of the upper layer, increasing it in Al excess and decreasing in Ga excess. Utilization of mixed solvents in one of the layers for synthesis of compounds by the new method is applied by the authors for the first time [3].

Utilization of Mixed Solvents

In synthesis of high-melting compounds, in particular, metals borides (and also carbides and silicides) by the new method, the main complication consists in selection of the solvent for a light nonmetal, for example, boron ($\rho = 2.34 \text{ g/m}^3$; hereinafter, ρ is omitted). Low-melting metals are the most reasonable for synthesis: Al (2.70), Zn (7.14), Cd (8.64) are heavier than boron. In AlB is slightly soluble (and produces compounds), and in Zn and Cd melts, it is practically insoluble. Synthesis is attained by means of prolonged heating and soaking of the system in the usual solution-melt method. During the prolonged heating and soaking, boron is dissolved, distributed by volume of Al solvent through thermal diffusion and convection flows, and interacts in the bulk with another reaction component, for example, with a transition metal which is also distributed by volume of solvent. It is necessary that boron be dissolved and go down in its layer and another initial compound, for example, a rare-earth metal (REM), be dissolved and come to the surface in its layer to achieve interdiffusion and convection in the new method. Synthesis of compounds in this case proceeds on the immiscibility boundary, to which boron and REM move from either side. The solvent for boron can be extracted by mixing a light metal, for example, Mg (1.74), with a heavier metal, for example, Al (2.70), in the system Al/Pb, by choosing such a ratio of them which in density will be less than the density of boron (2.34) and will still maintain the immiscibility process. The obtained mixed solvent (Al + Mg) with a density of, for example, 2.2 like Al forms an immiscible system with Pb because of Al excess. There are intermetallic semiconductors between Al and Mg and between Mg and Pb in this system. But they are much less stable (their melting temperature $T_{\text{melt}} = 550^\circ\text{C}$) than, for example, synthesized hexaborides of REM ($T_{\text{melt}} = \sim 2300\text{--}2500^\circ\text{C}$).

The possibility of boundary surface production in ingots in the system Al + Mg (Mg : Al = 7 : 10 wt %)/Pb

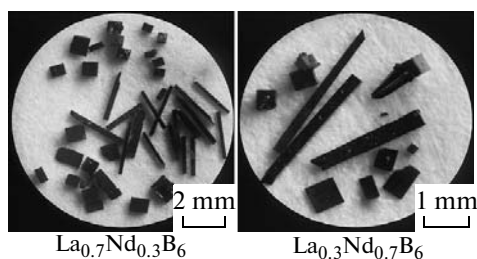


Fig. 4. Needle, lamellar, and isomeric crystals of solid solutions of high-melting hexaborides of La and Nd obtained in system with mixed solvent (Al + Mg, + B)/Pb (+La, + Nd) (analogous to the system presented in Fig. 3 (7)).

was investigated. The system was heated up to 850°C (2 h), soaked for 60 min, and chilled at a cooling rate of 1.5 K/min. Production of solid solutions of hexaborides of La and Ce experiments in the system Al (+ Mg, + B)/Pb (+ La, + Ce) was made at higher temperatures: heating (4 h) to 1300°C, soaking for 4 h, and chilling at a cooling rate of 39 K/h. These systems in a solidified state without initial components (6) and with synthesis products, $\text{La}_{1-x}\text{Ce}_x\text{B}_6$, $x \approx 0.05$ (7), are presented in Fig. 3 (6, 7). One can clearly distinguish the boundary surface between Al and Pb layers, which contain a significant amount of taken Mg in picture (6). The presence of Mg in the upper layer of Al led to formation of unfaceted granules. Judging by the nonuniform, spotty surface of the Al layer (according to the phase diagram [7]), it is most likely that an interphase eutectic between β (Al_3Mg_2) and γ ($\text{Al}_{12}\text{Mg}_{17}$) is formed. The formation of compounds Mg_2Pb and eutectics between Mg_2Pb and Pb (~83 at % according to [7]) is possible in the lower layer of Pb.

The polished section (Fig. 3 (7)) was prepared only from the upper part of the ingot (Al + Mg + hexaboride) in the experiment with reacting components from the obtained ingot because the whole ingot had large voids (cavities) separating the upper part from the lower part (containing Pb) and the lower part was pulled off when cut (Fig. 3 (7), interpolation). On the polished section, one can clearly see extraction of crystals of a solid solution of hexaborides of La and Ce, $\text{La}_{1-x}\text{Ce}_x\text{B}_6$, $x \approx 0.05$ (having a characteristic crimson color, like pure LaB_6), located mainly at the bottom of the upper part, which corresponds to this method's synthesis requirements. Apparently, the existence of the possibility of formation of Al and Mg borides in the system does not prevent formation of more high-melting solid solutions of hexaborides of REM since the latter are more stable (see above, condition 4).

Synthesis (heating to 1360°C, soaking for 6 h, and chilling at a cooling rate of 175 K/h) of solid solutions of hexaborides of La (6.7) and Ce (6.78) and La and Nd (7.00) was performed earlier [3] in the system Al (+ Mg, + B)/Pb (+La, + Nd). Meanwhile, the boron "sank" in compound Al + Mg and went down to the boundary surface, and La and Nd "rose" to this

boundary surface in the layer of Pb (11.4). From the upper layer (Al + Mg + hexaboride) with dissolution in HCl (1 : 2 to 1 : 4), crystals of solid solutions of hexaborides ($\text{La}_{0.75}\text{Nd}_{0.25}\text{B}_6$ and $\text{La}_{0.25}\text{Nd}_{0.75}\text{B}_6$) were extracted in the form of isomeric formations, needles, and plates (Fig. 4), while the lower part was pulled off. Crystals of high-melting TiB_2 with various shapes [3] were obtained earlier in the system Ca (+ B)/Ce (+ Ti) by the same method.

CONCLUSIONS

The experiments that were carried out indicate the possibility of obtaining various compounds and crystal forms by this method, as well as the existence of various processes in immiscible systems whose analysis presents great interest [1–3]. The new method uses the ratio of densities of components in immiscible systems to perform processes of interdiffusion and convection for realization of chemical reactions on the immiscibility boundary and subsequent crystallization of the generated compounds. The method has a number of advantages in comparison with usual solution-melt method.

The interdiffusion and convection promote a fuller contact of reacting components on the immiscibility boundary of melts. This leads to a more complete yield of synthesis. It is possible to save the upper layer metal if one can carve this region (and further extract synthesis products from it) and use the remaining metal for synthesis a second time, under well-proven synthesis conditions of certain compounds which settle in certain regions of the upper layer over the immiscibility boundary.

The new method allows one to obtain various shapes of crystals (isomeric, lamellar, needle), while the solution-melt method obtains crystals of one shape (for example, plates of TiB_2). It is possible to produce nanoparticles (or particles of size close to them) (for example, needles of TiB_2 in system Ca/Ce) under appropriate conditions and initial sizes and shape of reacting particles in certain systems.

The interdiffusion and convection can facilitate production of various solid solutions and also can contribute to production of new compounds from initial reacting components with sharply distinguished densities, since in the usual solution-melt method such components settle above and below the melt and cannot react.

It is necessary to emphasize that synthesis and crystallization of compounds in immiscible systems is a rather new method, which is necessary to research and develop further.

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