V. M. AGOSHKOV

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Abstract

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V. M. AGOSHKOV

USE OF ZONE MELTING FOR ESTABLISHING THE CRYSTALLIZATION FIELDS AND THE COMPOSITION OF EUTECTICS IN MULTICOMPONENT SYSTEMS OF MOLTEN SALTS

(Presented by Academician A. P. Vinogradov, 29 IV 1963)

Determining the exact composition of the eutectic point in a multicomponent system is a very difficult problem. Often the compositions of these points obtained by different authors differ noticeably. While studying the process of zone melting of molten salt systems as a function of the type of phase diagram and the position of the figurative point, we noted a number of regular features that make it possible to use zone melting to determine the exact composition of eutectic points in systems with any number of components.

Table 1

System and type of system	Crystallization field	Initial composition of mixture	Composition of mixture after remelting: beginning of sample	Composition of mixture after remelting: end of sample (eutectic)	Composition of eutectic according to data of (3)
$NaNO_3$—NaCl eutectic	$NaNO_3$ NaCl	1.0 wt.%NaCl 10.0 wt.%NaCl	0.02 wt.%NaCl 23.5 wt.%NaCl	4.83 wt.%NaCl 4.86 wt.%NaCl	4.80 wt.%NaCl
KNO_3—Ba×$(NO_3)_2$ eutectic	KNO_3 $Ba(NO_3)_2$	9.8 equiv.%$Ba(NO_3)_2$ 32.0 equiv.%$Ba(NO_3)_2$	0.98 equiv.%$Ba(NO_3)_2$ 39.7 equiv.%$Ba(NO_3)_2$	23.84 equiv.%$Ba(NO_3)_2$ 22.8 equiv.%$Ba(NO_3)_2$	22.5 equiv.%$Ba(NO_3)_2$
KNO_3—$NaNO_3$ solid solutions with a minimum	KNO_3 $NaNO_3$	42.0 mol.%$NaNO_3$ 59.0 mol.%$NaNO_3$	38 mol.%$NaNO_3$ 62 mol.%$NaNO_3$	47.7 mol.%$NaNO_3$ 49.8 mol.%$NaNO_3$	48— mol.%$NaNO_3$

System and type of system	Crystallization field	Initial composition of mixture	Composition of mixture after remelting: beginning of sample	Composition of mixture after remelting: end of sample (eutectic)	Composition of eutectic according to data of (3)
KCl–$K_2Cr_2O_7$limitedsolid solution-swith a minimum	KCl$K_2Cr_2O_7$	16.5 wt.%KCl3.9 wt.%KCl	21.4 wt.%KCl2.6 wt.%KCl	8.45 wt.%KCl8.39 wt.%KCl	8.77 wt.%KCl

At present the method of zone melting is widely used for the deep purification of semiconductor materials, metals, organic and inorganic compounds ([1], [2], [4], [6]). This method is one type of fractional crystallization, characterized by the slow displacement of a narrow molten zone along a comparatively long sample ([1]), as a result of which redistribution of the components of the sample occurs.

Experimentally, zone melting of salts was carried out by the slow displacement (3; 12 mm/hr) of a small tubular resistance furnace along

tube ($d \sim 1$ cm, length 20-25 cm) filled with a mixture of salts of definite composition, corresponding to some point of the phase diagram. The width of the molten zone in the furnace was 1.8-2.5 cm, and the cooling rate at the crystallization front was 0.5-2.0 deg/min. After several (3-6) zone passages in one direction along the whole tube, samples 0.5-1.0 cm long were taken for determination of the composition. It was found that in binary systems with a eutectic (Table 1), after zone melting, at the beginning of the specimen, whence the motion of the molten zone begins, the component accumulates in whose crystallization field the initial homogeneous composition lies. At the end of the specimen, where the zone arrives after a complete passage, a mixture of components crystallizes that is very close to the eutectic (Table 1), and the composition of the eutectic obtained practically does not depend on the field in which the given composition point lies. The distribution of the components from the beginning to the end of the tube has a periodic character, which has also been noted in a number of works on growing single crystals by the pulling method ([6,8]). The periodicity of the distribution of components along the specimen is due to the accumulation of the eutectic composition ahead of the crystallization front in the liquid phase and is determined by the composition of the mixture, the type of phase diagram, the ratio of the length of the molten zone to the length of the specimen, the cooling rate, etc. ([5,6]).

Table 2

Parts of the specimen	$CdCl_2$, mol. %	NaCl, mol. %	KCl, mol. %	Crystallization temp., °C
Field $CdCl_2$				
Entire specimen before melting	70.0	10.0	20.0	
Beginning after melting	96.1	2.6	1.3	
End after melting (eutectic)	59.6	18.2	22.2	356$±1\|\|FieldKCl· CdCl_{2}$
Entire specimen before melting	50.0	20.0	30.0	
Beginning after melting	50.2	8.7	41.1	
End after melting (eutectic)	59.5	18.5	22.0	355$±1\|\|Field2NaCl· CdCl_{2}$
Entire specimen before melting	43.9	46.1	10.0	
Beginning after melting	31.8	61.6	6.6	
End after melting (eutectic)	59.6	18.2	22.2	355$±$1
Eutectic (3), cooling-curve method	58.66	19.66	21.66	354
Eutectic (7), visual-polythermal method	56.2	25.8	18.0	362

In binary systems with limited and unlimited solid solutions, as in eutectic systems, after zone melting the component in whose crystallization field the original mixture lies is concentrated at the beginning of the specimen, while at the end of the specimen there is a composition corresponding to the eutectoid point or to the mixture with the minimum melting temperature (Table 1). It should be noted that in systems of this type, sufficiently complete separation of the components and accumulation of the low-melting mixture at the end of the specimen are possible after repeated passage (6–10 times) of the zone along the specimen. The relatively low efficiency of component separation here is associated with the fact that, in these systems, the coexisting solid and liquid phases differ little in composition.

In the ternary system NaCl—KCl—$CdCl_2$, at the end of the specimen after zone melting, the composition of the mixture obtained from different crystallization fields converging at one point of the ternary eutectic proved to be the same and coincided with the data (3) obtained by the method of cooling curves with visual recording (Table 2). At the beginning of the specimen, in comparison with the initial composition, the component crystallized preferentially in whose crystallization field the selected composition point lay. For this ternary system the compositions of the remaining eutectics were also obtained,

which agreed satisfactorily with the data of (3, 7). The crystallization path in the composition triangle, according to analyses of the entire specimen from beginning to end, is a straight line connecting the vertex of the pure component with the point of mixture composition and continuing to the line of separation of two components. Subsequently, the change in specimen composition proceeds along the boundary curve to the corresponding eutectic point. In the case of the formation of solid solutions, the crystallization path in the field of one of the components becomes curved, but nevertheless reaches the eutectic.

Table 3

<table>
<tr><th>Parts of the specimen</th><th>$PbCl_2$</th><th>$CaCl_2$</th><th>NaCl</th><th>KCl</th><th>Crystallization temp., °C</th></tr>
<tr><td>Volume KCl · $CaCl_2$
Entire specimen before melting</td><td>44.1</td><td>24.4</td><td>22.8</td><td>8.7</td><td>391$±1||Beginningaftermelting|43.7|26.2
*VolumePbCl_{2}**
|||||||Entirespecimenbeforemelting|54.8|1
for the eutectic, cooling-curve method</td></tr>
</table>

In the ternary reciprocal system Cd, Na Cl, SO_4, the composition of one of the eutectics obtained by the visual-polythermal method (³) practically did not differ from the composition obtained at the end of the specimen after zone melting. In the quaternary system NaCl—KCl—$CaCl_2$—$PbCl_2$, corresponding mixtures of components were taken from two adjacent crystallization volumes; after zone melting, at the end of the specimen they gave compositions very close to one of the quaternary eutectics (Table 3) indicated in (³). Finally, in the unstudied system $CdCl_2$—KCl—LiCl—NaCl, certain crystallization volumes were isolated and the compositions of several quaternary eutectics were obtained.

In the quinary system NaCl—KCl—LiCl—$CdCl_2$—$BaCl_2$, a quinary eutectic was obtained from two crystallization hypervolumes (Table 4).

Table 4

<table>
<tr><th>Parts of the specimen</th><th>$BaCl_2$</th><th>$CdCl_2$</th><th>KCl</th><th>LiCl</th><th>NaCl</th><th>Crystallization temp., °C</th></tr>
<tr><td>**Hypervolume $CdCl_2$**</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Entire specimen before melting</td><td>10.5</td><td>59.0</td><td>15.2</td><td>8.8</td><td>6.5</td><td>390$±2||Beginningaftermelting|8.9|72.
HypervolumeCdCl_{2}·KCl
*|||||||Entirespecimenbeforemelting|6.</td></tr>
</table>

All eutectic compositions obtained by zone melting in 2-, 3-, 4-, and 5-component systems showed on cooling and heating curves the presence of only one temperature arrest, due to melting or crystallization of the eutectic. It should be noted that in multicomponent systems the distribution of components after remelting along the entire specimen also has a periodic character.

Thus, the use of the zone-melting method in the study of phase diagrams of systems makes it possible, for a given figurative point of compo-

to determine: a) from the component accumulating at the beginning of the specimen, the crystallization field or volume in which this composition point is located; b) from the composition of the intermediate sections of the specimen, the crystallization path; c) from the composition of the final section of the specimen, the composition of the eutectic to which this point arrives after crystallization.

A drawback of this method is the impossibility of fixing transition points.

Moscow State University
named after M. V. Lomonosov

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