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The structure of solid salt eutectics — Why lamellar or conglomerate?

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ABSTRACT

Using $KCl/ZnSO_4$ eutectic it has been shown that cooling the melt into a room temperature enclosure forms a lamellar structure, whereas cooling into a heated enclosure (225 °C) forms a conglomerate structure, while an enclosure temperature of 125 °C gave a partially conglomerate structure with some lamellae in process of forming conglomerates.

Consideration of the thermal gradients imposed on solidification and consequently the relative time available during which the ions are sufficiently mobile to rearrange their positions, can explain the observation that lamellar structures are formed by higher melting point eutectics, whereas eutectics of lower melting point form conglomerate structures.

1. Introduction

The current interest in small, self-assembling structures, of from nanometre to micron size, makes it desirable to establish the main factors causing the structures of solidified salt eutectics to change from the laminar to the conglomerate form. Regrettably, while molten and solid single salt structures have been the subject of much investigation over many years, the structure of salt eutectics has been largely neglected. In the classical binary phase diagram, see Fig. 1, the field below the eutectic temperature has been described as composed of $\alpha+\beta$ (the two limiting solid solutions). However, the arrangement and constitution of this area has often been largely ignored.

The few papers published on this subject have frequently reported lamellar eutectic structures ([1–8]), i.e. parallel sheets of alternating composition. Metallurgists, who have found many similar structures in metallic systems, have thought that lamellae are formed because of the limited distance that ions can normally diffuse before solidification is complete [9]. Thus the formation of a nucleus of the α phase causes accumulation of component B around it and when saturation is reached the nucleation of phase β starts. Growth of these nuclei along the thermal gradient results in the formation of rods or laminae if the cooling rate is not too high [2,3]. Similarly, growth of the β phase causes rejection of component A and similar nucleation and growth of laminae of the α phase (Fig. 2).

This nucleation effect occurs if the solidifying components are not constrained to form solid–melt interfaces along the crystallographic faces. Jackson [10] has shown that the latter occurs if the entropy of fusion, ΔS_s, is more than 16.8 J/K/mol, implying that the interface is “smooth” and the crystal plane is close to fully occupied. However, when $\Delta S_s < 16.8$ J/K/mol, the interface is described as “rough”, and is typically about 50% occupied, and able to take up orientations other than the crystallographic ones. In Table 1 ΔS_s for a number of salts, metals and organic compounds are listed. It indicates that inorganic salts would be expected to form “rough” interfaces not following crystallographic planes and hence form both the structures found (i.e. either alternating lamellar layers of α and β or roughly spherical particles of α and β randomly arranged (conglomerate structure)).

Initially the salt eutectics examined were found to have laminar structures, but more recently several nitrate/nitrite eutectics have been shown to have conglomerate structures of roughly rounded alternating particles of α and β [8]. The reasons for this dichotomy and the relationship between these structures have been clarified by the present work and a single mechanism of formation can now be postulated.

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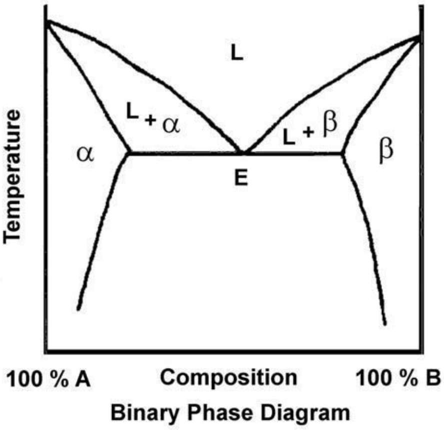

Fig. 1. Binary A–B phase diagram with limited mutual solid solution. L = liquid and E = eutectic. The field under the eutectic point is often labelled α + β, where α is the solid solution of B in A and β that of A in B.

2. Experimental

2.1. Materials

Potassium chloride and zinc sulphate heptahydrate (Reidel-De Haën, für Analyse, >99.5%) were dried in an oven for 24 h at 180 °C and for 27 h at 200 °C, respectively.

The eutectic mixture, (KCl–$ZnSO_4$, 66.6:33.4 mol%, melting point 295 °C [11]) was made up by weighing. The sodium nitrite–sodium nitrate eutectic was prepared as previously described [8].

2.2. Apparatus

Sample mixtures of about 2 g were placed in quartz tubes (8 mm internal diameter and 10 cm long) with an external lug, and were pushed via a stainless steel wire to a translation stage, the “pusher”. The translation apparatus tilted to 30° from the horizontal plane allowed for pushing the samples out of a tube furnace (obtained from W. C. Heraeus, Hanau, Type ROK/A, 3 cm internal diameter, 30 cm long, 9 A, 1 phase). A quartz tube (3 cm i.d. and 65 cm long) was placed in the furnace for the sample tubes to slide down. This furnace made heating samples to 1100 °C possible, controlled by a Ni/Cr thermocouple and a Heraeus on/off regulator. All openings were plugged so that the thermal gradients were not disturbed by draughts (“stovepipe” effects).

The “pusher” translator was mounted co-axially with the furnace at its higher end. Its controller was a programmable system with a clock, a step motor with a geared system of toothed wheels and a toothed bar sliding in a groove. The electronics were based on a design made by the former Ib Baagoe/MicroSupport ApS company.

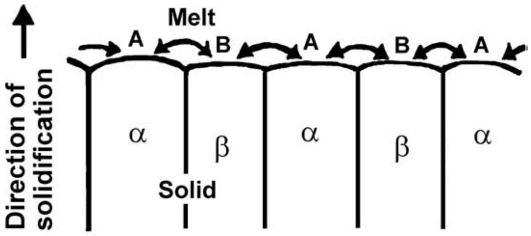

Fig. 2. Binary eutectic mixtures A–B when crystallizing at the melting point often form lamellar structures because removal of α increases the concentration of B above saturation which then nucleates β. Vice versa for α.

Table 1
Fusion entropies ΔS_s for a number of salts, metals and organic compounds.

	$J\,K^{-1}\,mol^{-1}$		$J\,K^{-1}\,mol^{-1}$
Ag	9.6	Anthracene	59.2
Cu	9.6	Catecol	60.5
Ga	20.4	Cetyl alcohol	107.4
$NaNO_3$	9.3	Phenol	38.4
KNO_3	12.7	Salol	60.0
$NaNO_2$	13.3	Trinitrotoluene	48.1

2.3. Procedure

The sample tubes were attached by the stainless steel wire through the furnace to the sliding bar of the “pusher” which lowered the tubes at a constant predetermined rate, in this case at a constant rate close to 3 cm/h. The loaded sample tubes were placed in the centre of the furnace, melted at 400 °C and held there until all bubbles were dispersed. The sample at the furnace temperature was then pushed downwards out into a colder zone which could be at ambient laboratory temperature or alternatively downwards into an environment made by a small extra furnace (W.C. Heraeus Hanau, Type M/K, which could be heated to 900 °C by a Variac). The temperature of this, lower, zone was measured by a further thermocouple. Temperatures of 125 and 225 °C were in fact used. A further alternative to increase the gradient was to cool the zone at the end of the tube by placing it in a well insulated enclosure cooled at the bottom with a liquid nitrogen bath, through which a stream of gaseous nitrogen was passed so as to increase the evaporation rate. The solidified specimens were stored in sealed tubes kept in a desiccator.

2.4. Scanning electron microphotographs

SEM images were taken of fresh fracture surfaces obtained by breaking the solid ingots just before placing in the SEM sample chamber. The SEM was operated under conventional high vacuum conditions, using an accelerating voltage of 6 kV. Images were obtained in both secondary electron and back scattered electron imaging modes. Local chemical analysis was performed using energy dispersive X-ray spectrometry.

3. Results and discussion

The salt eutectic solid structures reported so far in the literature fall into two distinct groups, lamellar or conglomerate. Arranging these studied eutectics in order of their melting points (Table 2) shows clearly that those with the higher melting points are of lamellar structure while those of lower melting point are of conglomerate type. We do not claim that the magnitude of the melting point itself is the deciding factor, but it is an indication of the thermal gradient

Table 2
Studied eutectic salts arranged in order of their eutectic melting points and with indication of whether the structure is lamellar or conglomerate type.

Eutectic system	Mole ratio	Eutectic point (°C)	Structure	References
LiF/CaF_2	78/22	760	Lamellar	[1]
LiF/LaF_3	83.5/16.5	756	Lamellar	[5–7]
$LiF/MgF_2/CaF_2$	59/28/13	672	Lamellar	[4]
LiF/NaF	61/39	652	Lamellar	[2,3]
KCl/Na_2SO_4	60/40	520	Lamellar	[8]
$KCl/K_2Cr_2O_7$	25/75	368	Conglomerate	[8]
KNO_2/KNO_3	24/76	316	Conglomerate	[8]
$NaNO_2/NaNO_3$	59/41	227	Conglomerate	[8]
$NaNO_3/KNO_3$	50/50	220	Conglomerate	[8]
$KNO_3/Ca(NO_3)_2$	65.8/35.2	145	Conglomerate	[8]
$NaNO_2/NaNO_3/KNO_3$	48.9/6.9/44.2	142	Conglomerate	[8]