Preferred Orientation in Microstructures of Eutectics Between Compounds

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The microstructures of eutectics between compounds were studied for systems MnO-MnS, NaCl-NaF, NaBr-NaF, LiF-NaF, and FeO-FeS. With the exception of FeS, all the compounds had the NaCl-type structure. In the systems having only NaCl-type structures, the lamellas of the two eutectic phases had matching crystal orientations. There was less consistency among the eutectic systems, however, than between the phase pairs. The crystal growth directions in all five systems were different, and no more than two of the systems had the same set of interfacial planes. One must conclude that the two phases within a eutectic of compounds do not solidify independently of one another. It is suggested that the two phases of an NaCl-type eutectic pair crystallize as a "single" ionic crystal with imperfections present to accommodate the dimensional mismatch.
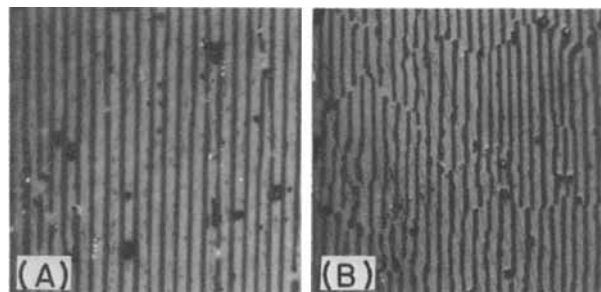
Fig. 1. Photomicrographs of transverse (A) and longitudinal (B) cross sections of a typical MnO-MnS unidirectionally solidified lamellar eutectic. (Light, MnS; dark, MnO. ×500.)

I. Introduction

PFANN'S[1] analysis of single phase solidification during zone-melting, extended by Chalmers and his associates,[2,3] has been applied by several investigators[4-10] to the study of solidification in simple two-phase eutectic systems. Studies have been confined primarily to low melting point metallic systems except for work on alkali halide eutectics by Hellawell et al.[11-14]

Microstructures in unidirectionally solidified, high-purity, two-phase metallic eutectics generally consist of (1) rods of one of the phases distributed uniformly in a matrix of the second, or (2) alternating plates of the two eutectic phases in a lamellar structure. In both cases, the discontinuous rods or plates appear in a regularly spaced array with their longer dimensions oriented in the direction of solidification and normal to the solidification front.

Specific crystallographic relations exist between the two phases in many unidirectionally solidified eutectic pairs. Investigators, however, have not always reported identical preferred growth directions and interfacial planes for the same eutectic systems. The factors which cause orientations to be preferred are not yet well understood.

This paper describes the results of the investigation of the relative crystallographic orientation of the lamellar or rod-like phases in the unidirectionally solidified eutectics of five systems involving compounds MnO-MnS, NaCl-NaF, NaBr-NaF, LiF-NaF, and FeO-FeS. With the exception of FeS, all the compounds have the same NaCl-type structure. The lamellar microstructure obtained by the authors for the MnO-MnS eutectic is illustrated in Fig. 1.

II. Experimental Procedure

The MnO was prepared by reducing 99.9% pure MnO_2 in hydrogen at 950°C. The MnS was prepared by deoxidizing 98.8% pure $MnSO_4 \cdot H_2O$ by sulfur after the method of Chao et al.[15] The FeS was prepared by reacting stoichiometric quantities of 99.98% iron wire and sulfur in an evacuated and sealed Vycor glass tube at 880°C. The other raw materials were reagent grade alkali halides and Fe_2O_3.

The above materials were mixed as powders to provide the proper eutectic compositions and melted in Ferrovac iron crucibles (for the MnO-MnS and FeO-FeS eutectics) or in spectrographic grade graphite crucibles (for the alkali halide eutectics). The ingots were unidirectionally solidified under an argon atmosphere by drawing them vertically from the bottom of a silicon carbide resistance furnace, using an Instron crosshead drive at rates from 9 to 50×10^{-5} cm/sec.

The resulting ingots were sectioned, polished transversely and longitudinally, and carefully photographed in the areas selected for X-ray study. Laue back-reflection X-ray photographs were used to determine the relations among the crystal orientations, lamellar interfaces, and growth directions. Chips were then cleaved from the same regions and mounted on the goniometer head of a Buerger precession X-ray camera. These cleavage chips were oriented with respect to the microstructure by optical reflections from previously polished and cleaved orthogonal faces. Zero-level precession X-ray patterns from two or three orthogonal directions of these chips provided the precise relative relations of the two eutectic phases (Fig. 2). Several samples were taken from each eutectic microstructure.

III. Results

The interfacial planes between the lamellar platelets had a low index and high density in each of the eutectic systems studied (Table I). Low index orientations also defined the growth directions and directions within the lamellas perpendicular to the growth direction (Table I and Figs. 3 and 4). The crystallographic orientations were the same for both phases of the eutectic pair in the systems having only NaCl structures (MnO-MnS, NaCl-NaF, NaBr-NaF, and LiF-
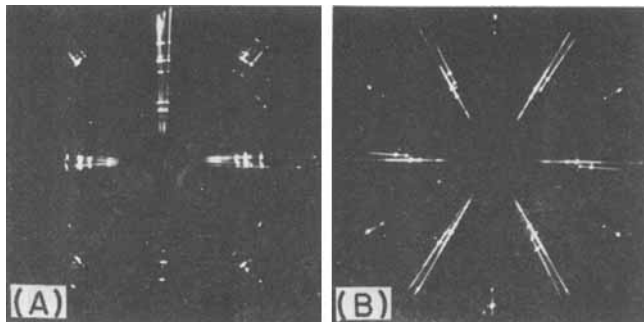
Fig. 2. Buerger precession zero-level X-ray transmission photographs of a lamellar MnO-MnS eutectic (*A*) parallel to [112] growth direction, and (*B*) parallel to [111] interface normal. (Spots on larger radius represent MnO phase with a smaller unit cell size. Twist, 6°; tilt, 3°.)

Table I.   Summary of Crystallographic Relations

Eutectic	Structure types	Interface planes	Growth directions
MnO–MnS	NaCl–NaCl	(111)–(111)	[11$\bar{2}$]–[11$\bar{2}$]
NaCl–NaF	NaCl–NaCl	(110)–(110)	[001]–[001]
NaBr–NaF	NaCl–NaCl	(110)–(110)	[1$\bar{1}$1]–[1$\bar{1}$1]
LiF–NaF	NaCl–NaCl	(1$\bar{1}$1)–(1$\bar{1}$1)	[110]–[110]
FeO–FeS	NaCl–NiAs	(100)–(0001)	[011]–[10$\bar{1}$0]

NaF). However, two sets of planes served as the mutual interface [(111) for MnO-MnS and LiF-NaF, and (110) for NaCl-NaF and NaBr-NaF]. None of these four systems had the same growth direction. In the FeO-FeS system, where the phases have NaCl and NiAs structures, respectively, the interfacial planes were heteropolar (100) for FeO and homopolar (0001) for FeS.

Misorientations in twist and tilt of 6° or less were observed between the phases in all the eutectic structures except the NaBr-NaF system. The relative misorientations are shown schematically in Figs. 3 and 4.

IV.   Discussion

The noteworthy results are: (1) The identical crystal orientation of the two NaCl-type phases within a eutectic pair; and (2) the variation in growth directions for specific phases from one eutectic pair to another. Thus it is necessary to conclude that the crystal orientations were determined jointly by the phase pairs.

Previous studies on orientation of eutectics indicate a simultaneous edgewise growth of the lamellar phases in the directions of heat flow, as was verified experimentally by Straumanis and Brakss.[16] Tiller[7] proposed that eutectic interface configurations consist of parallel crystallographic planes to minimize the solid-solid interfacial energy, thus reducing the depth of the interlamellar groove at the solid-liquid solidification front. This would form a more nearly plane solidification front and facilitate lateral diffusion in the liquid ahead of the front. Thus, from the beginning, it seemed natural to assume that nucleation and growth would result in certain preferred crystallographic orientations and bounding planes for the lamellar eutectic phases. Many X-ray diffraction studies have indicated that low index planes and directions of both phases of binary lamellar eutectics are orthogonally related to lamella interfaces and growth directions.[4,12,13,17,18] There has been disagreement, however, as to precisely what were the orientations for a particular system.[4,17] This is not completely unexpected, since studies of heterogeneous nucleation have shown many inconsistencies, due to impurity effects and also to the fact that more than one crystallographic orientation can be nucleated in a single system.

Penfold and Hellawell[13] reported (111) lamellar interface planes and [110] growth directions for both NaCl-NaF and LiF-NaF unidirectionally solidified eutectics. The LiF-NaF results of this study agree with their observations but the NaF-NaCl results do not (Table I and Fig. 3).

Truelove and Hellawell[14] also reported that NaCl precipitates as octahedra bounded by (111) planes in an NaF matrix with the same crystallographic orientation as the matrix. They indicate, however, that there is not an exclusive preference for the homopolar habit planes among the
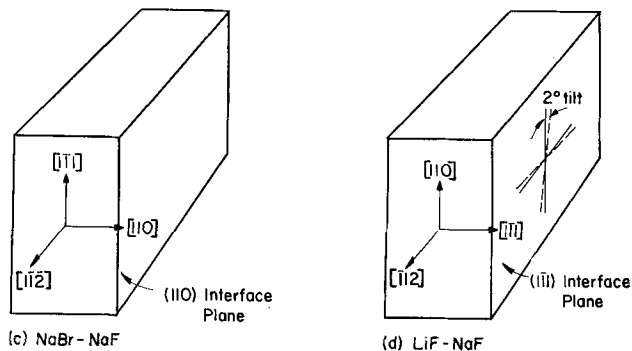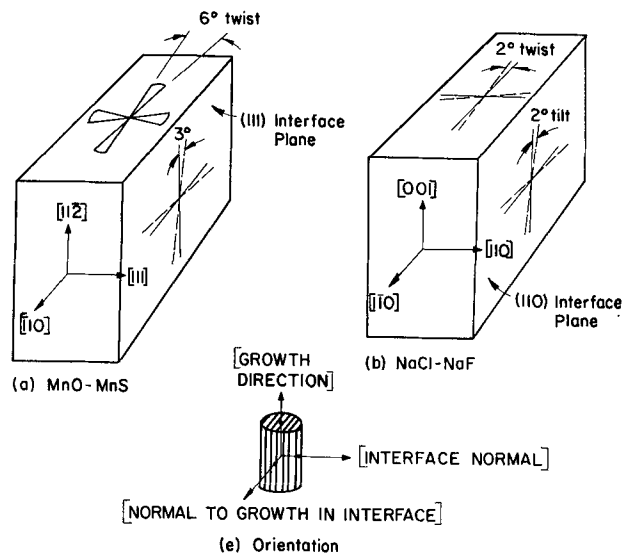

Fig. 3. NaCl-NaCl structure type eutectic pairs showing crystallographic orientations of each pair in relation to lamellar interfaces and growth directions of crystals. Small twist and tilt misorientations between phases are also noted.
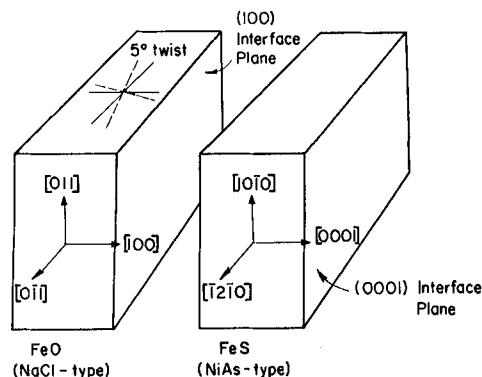

Fig. 4. NaCl-NiAs structure type eutectic pair of FeO-FeS showing crystallographic orientations of each phase in relation to their lamellar interface and growth direction. A 5° tilt misorientation between the phases is also shown. (See Fig. 3 for orientation notation.)

alkali halide systems. Again the differences noted may be due to impurity effects caused by variations in starting materials or crucibles. Crucibles in this work were spectrographic grade graphite; Hellawell and co-workers used recrystallized alumina crucibles.

Evidence indicates further that more than one crystallographic relation between phases can be nucleated in a single system. Sundquist and Mondolfo[19] studied solidification undercooling and relative crystallographic phase orientations in self-nucleated eutectic alloys of lead and concluded that many orientation relations can occur, but that they usually involve low index planes with low linear lattice misfits when the crystal structures are simple. Since the lowest possible misfit was not always the most frequent orientation relation, these workers concluded that other factors were involved. Good symmetry relations between mating planes seemed to be a second important factor, corresponding to the findings in previous experiments on epitaxial overgrowth.[20] The amount of observed undercooling did not seem to alter the orientation relations or lattice disregistries.

Although the results of the current study agree with the above requirements for low index direction interfaces and planes, the lattice mismatch between phases is significant (approximately 25 linear percent in the NaF-NaBr eutectic pair), and we cannot conclude that the boundary energy is low. The matching orientations, however, permit octahedral coordinations of positive and negative charges across the boundary and a minimum of coulombic repulsion such as would be found with any misorientation of the two phases. Thus, in spite of the lattice mismatch and necessary dislocations and strain energy, the common orientation may still represent the lowest possible boundary energy. In effect, the two phases of the eutectic pair crystallize as a "single" ionic crystal with internal imperfections to accommodate the dimensional mismatch. Even so, slight twists and tilts result, as shown in Figs. 3 and 4.

It would be natural to predict that the matching planes in the FeO-FeS eutectic would be (111)-(0001) and homopolar rather than the observed (100)-(0001). There is, however, a difference in symmetry in the two phases of this system so that it is never really possible to have a "single" crystal as we did when the two phases of the eutectic pair had the same NaCl-type crystal structure. Furthermore, the FeS must be more covalent to form the NiAs structure. The long range ionic coordination is thus no longer the governing factor and the dimensions become relatively more important. In the observed relation, the Fe-Fe spacing along the $10\overline{1}0$ growth direction of FeS is 5.96 A, or approximately twice the Fe-Fe

spacing of 3.04 A in the 011 growth direction of FeO. Other dimensions require 11.6 A^2/Fe on the (0001) plane of FeS and 9.2 A^2/Fe on the (100) plane of FeO so that the average linear mismatch between the two structures is 12%. These factors apparently permit the observed FeO-FeS relation.

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Phase Diagrams for the Systems Si-O and Cr-O

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Equilibrium studies in the systems Si-O and Cr-O at high temperatures indicate that no stable intermediate compounds exist between the metals and the oxides, SiO_2 or Cr_2O_3, up to solidus temperatures. In both systems, there is a large concentration range of coexistence of two liquid phases above liquidus temperatures.

I. Introduction

THE determination of high-temperature equilibria in systems containing metal and oxide phases coexisting in