The Growth of Oriented Ceramic Eutectics

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Received 5 May 1969

Controlled microstructures of the two eutectics in the alumina-titania system have been grown using a special electron beam heating technique. In the aluminium titanate-titania system, the eutectic interlamellar spacing λ varies with the freezing rate R as $\lambda = AR^{-n}$ where $n = 0.5$ and the value of the constant A is 8.5×10^{-6} $cm^{3/2}sec^{-1/2}$. Primary plate-like dendrites of aluminium titanate in a matrix of discontinuous aluminium titanate-titania eutectic are formed on solidifying a composition TiO_2-20 wt % Al_2O_3. These dendrites appear to deflect cracks in this ceramic. In the alumina-aluminium titanate system, primary rod-like dendrites of alumina were grown in a ribbon-like eutectic of alumina and aluminium titanate on solidifying a composition Al_2O_3-38.5% TiO_2.

1. Introduction

Ceramic materials are generally highly susceptible to brittle failure and show little toughness. The strengths of polycrystalline ceramics are controlled by flaws and pores which act as crack sources. It has been suggested that the toughness of ceramics would be improved if cracks could be blunted plastically by dislocation motion [1], however, in most ceramics, dislocations are very difficult to move at low temperatures, apparently because diffusion rates are low [2, 3]. An alternative method to crack blunting for improving the toughness of ceramics might be to produce microstructures which would allow the deflection of cracks, thereby making fracture more difficult. Precipitation increases the strengths of ceramics considerably, but there is no evidence of improved crack resistance [4].

The production of controlled microstructures by the unidirectional solidification of metal alloys is well known [5, 6]. The techniques of zone melting [7, 8] and floating zone melting [9] which were introduced for the purpose of purifying single phase materials have been found to be equally applicable to the growth of highly oriented binary eutectics [5, 6]. Most investigations have been made on metal systems, but controlled microstructures have been produced in eutectics of ionic crystals with the rock salt structure [10, 11] by unidirectional solidification. Recently, eutectic solidification has been examined in the Al_2O_3-$Y_3Al_5O_{12}$ system [12]. Colony growth and both rod- and plate-like structures were seen under different growth conditions. The production of continuous eutectics in this system, where the constituents have high entropies of melting, appears to be another exception to the rule of Hunt and Jackson for classifying eutectics [13].

Few crucible materials are available for melting oxide ceramics, thus floating zone (crucible free) melting offers a convenient way in which to deal with reactive materials. Recently, equipment for heating insulators by electron bombardment has been developed [14, 15]. Previously, the technique had been limited to heating electrical conductors simply because of the ease of removal of the impinging electrons. With insulators, where electrons cannot leave the sample surface, a negative electrostatic charge builds up which prevents the arrival of further electrons from the filament. The incorporation of a positively biased grid between the sample and the filament allows electrons to be drawn from the sample surface by a phenomenon similar to secondary emission [15].

A eutectic of β aluminium titanate and titania melting at 1705° C is reported to occur at a composition of approximately TiO_2-20 wt % Al_2O_3 [16]. A second eutectic occurs at 1840° C

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at approximately Al_2O_3-38.5 wt % TiO_2, the components being alumina and β aluminium titanate [16]. Lamellar structures are expected to form in those binary eutectics where the volume fraction of the minor phase is > 0.28 [17, 18]. For lower volume fractions, a rod-like morphology is expected. From the phase diagram of the alumina-titania system, the eutectic at 1840° C contains a volume fraction of approximately 0.13 of alumina and should be fibrous while that at 1705° C contains a volume fraction of approximately 0.45 of aluminium titanate which should therefore assume a lamellar habit.

In the work reported here, floating zone melting, using a special electron bombardment technique was used to produce controlled microstructures of the two eutectic compositions found in the alumina-titania system. The main purposes of the work were firstly to investigate solidification in eutectic ceramics and secondly to determine whether the microstructures of directionally solidified ceramic alloys offered any resistance to crack propagation.

2. Experimental

The electron beam heating unit was based on that described by Neuman and Huggins [15], with the introduction of a graphite grid, which was designed to act also as a muffle to reduce temperature gradients and cracking. The electron optical system is shown schematically in fig. 1.

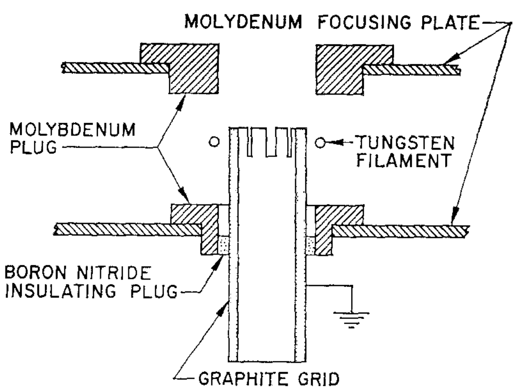

Figure 1 Schematic diagram of the electron beam heating system for zone melting insulators.

The grid consisted of a graphite tube with slots cut in the end adjacent to the filament. The sample (not shown) would lie concentrically in the centre of the graphite tube. The filament was maintained at a high negative potential so that electrons were accelerated towards the sample. Most of the electrons passed through the slots in the grid and impinged on the sample from which they were re-emitted onto the grid, which was at earth potential. The grid became heated by those electrons which struck it directly from the filament and by radiation from the sample. The geometry of the system was rather critical and the relative positions of filament, grid, and focusing plates had to be determined experimentally for optimum heating. The heating system was attached to a carriage on a screwdrive mechanism to provide smooth vertical travel. The system operated under a bell-jar at air pressure of approximately 10^{-5} torr.

The starting materials for the work were 99.98% pure alumina* and 99.95% pure titania*. Rectangular bars 10.2 × 1.3 × 0.3 cm were cold-pressed from well mixed powders of titania with 18, 19 and 20 wt % alumina, and alumina with 38.5 wt % titania, using a binder of Methocell†. The bars were sintered in air at 1400° C for 4 h. Rods 0.3 cm square were cut from the bars which were up to 90% of the theoretical density. The rods were zone melted at rates between approximately 1 and 30 cm/h, keeping the samples stationary and moving the electron source upwards. The resulting material was examined metallographically and phases were identified using an electron microprobe analyser.

3. Results and Discussion

3.1. Aluminium Titanate-Titania Eutectic

All the zoned rods were black in colour, probably because of a loss of oxygen during heating under vacuum. Some gross lateral cracks occurred in most samples even at the lowest zoning rates and in spite of the use of the heated graphite grid muffle. Fig. 2 shows a longitudinal section of a rod of TiO_2-18 wt % Al_2O_3, zone melted at 30.5 cm/h. The structure consists of very fine lamellae of aluminium titanate (dark phase) in a matrix of titania. The lamellae were generally well aligned along the rod axis, but since the growth direction follows the temperature gradient, considerable off-axis growth was seen at the periphery of the rod. Most ceramics have lower thermal conductivities than metals so lateral temperature gradients are expected to be much

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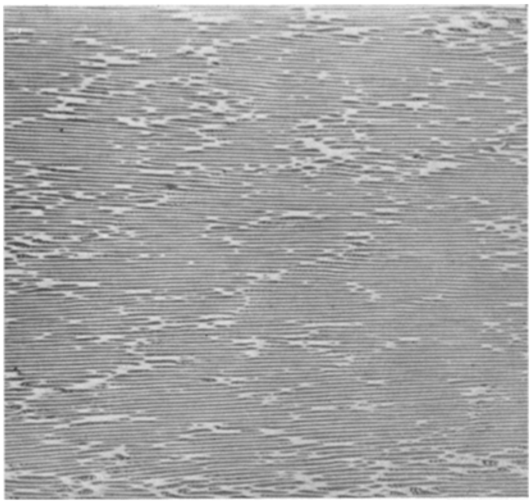

Figure 2 Longitudinal section of zone melted TiO_2-18 wt % Al_2O_3 showing lamellar eutectic structure (× 500).

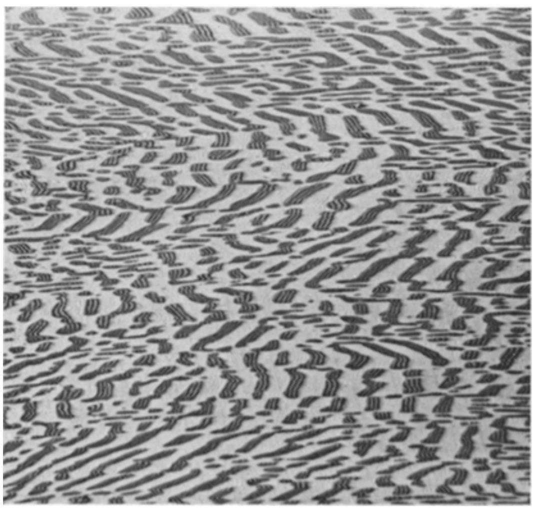

Figure 3 Another area of the same sample as in fig. 2 showing a subgrain of different orientation (× 520).

steeper and hence off-axis growth will be more apparent. The structure of fig. 3 was seen in some areas of the same longitudinal section as fig. 2. The rod contained subgrains which have a common growth direction along the rod axis, but which are rotated about this axis with respect to each other. In fig. 3 the fringes visible in the aluminium titanate are due to optical interference. Similar effects were seen in the matrix where cracks intersected the surface obliquely.

Using a starting composition TiO_2-19 wt % Al_2O_3, a small volume fraction of primary plate-like aluminium titanate occurred in a matrix of continuous lamellar eutectic. For the same freezing rates, the interlamellar spacings in the eutectic, away from any primary phase, were the same in the 18 and 19 % Al_2O_3 materials. Table I lists solidification rates and the corresponding interlamellar spacings of the eutectic. At similar solidification rates these values of interlamellar spacing are very nearly the same as those found previously in other directionally solidified non-metallic eutectics [10, 11] and are several times those found in most metal systems. A logarithmic plot of the data of table I is linear, as indicated in fig. 4, which means that the growth kinetics can be expressed in the form $\lambda = AR^{-n}$ where λ is the interlamellar spacing, R is the solidification rate and A and n are constants. The slope of the line gives a value for n of 0.5, which agrees with data from other directionally solidified eutectic systems and is predicted by several theoretical treatments of eutectic solidification [5, 6]. A plot of λ and $R^{-1/2}$ is a straight line passing through the origin. The slope of the line, A, is 8.5×10^{-6} $cm^{3/2}sec^{-1/2}$. The value of A depends upon several factors including the liquid diffusion coefficient and the interphase boundary energy. Due to the paucity of data in the alumina-titania system, little can be said about the value of A except that it is very nearly the same as in the Al-Ag_2Al system [18]. The entropies of melting of alumina and titania are approximately 11 and 7 cal/gm mole/°K respectively [19]. Similar data for aluminium titanate were not found, but its entropy of melting is expected to be not less than that of either alumina or titania. The observation of lamellar eutectics in the aluminium titanate-titania system agrees with the suggestion that the criteria devised for classifying organic eutectic microstructures [12] might not apply to oxides [13].

Material of composition TiO_2-20 wt % Al_2O_3 was also directionally solidified. In this case, large primary plate-like dendrites of aluminium titanate were grown in a matrix of lamellar eutectic. It can be seen in fig. 5 that the eutectic is now quite discontinuous and the primary aluminium titanate is of irregular width. In addition, the structure contains numerous fine transverse cracks which were not as frequent in the samples of lower alumina content. Transverse cracking probably arises from the stresses set up by the differential contraction between the two phases during cooling since the coefficients of thermal expansion of the phases differ consider-

TABLE I Solidification data for the eutectic of aluminium titanate and titania

Solidification rate $R \times 10^4$ cm/sec	Interlamellar spacing $\lambda \times 10^4$ cm
2.82	5.2
4.52	4.2
7.20	2.6
11.3	2.3
21.2	1.8
22.9	1.8
48.6	1.3
84.8	1.0

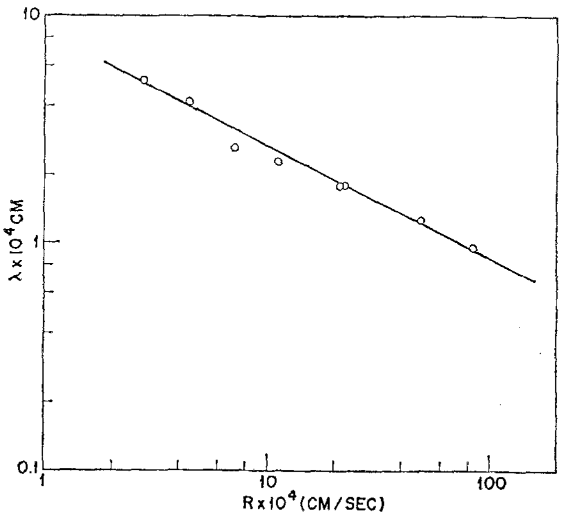

Figure 4 A logarithmic plot of the interlamellar spacing λ and corresponding solidification rate R for the eutectic between aluminium titanate and titania.

ably [16, 20]. The cracks pass through the titania and the fine aluminium titanate of the eutectic matrix, but they appear to be stopped at the interfaces with the primary aluminium titanate plates. The primary dendrites have a rectangular cross-section, and the lamellar nature of the eutectic can be seen clearly in fig. 6. It is also notable that the matrix immediately adjacent to each primary dendrite is denuded of aluminium titanate.

The eutectic between aluminium titanate and titania is reported to occur at an approximate composition of TiO_2-20 wt % Al_2O_3 [16]. Figs. 5 and 6 indicate that sintered rods of this composition produce an alloy containing primary aluminium titanate on melting, whereas a zone melted rod of initial composition TiO_2-18 wt % Al_2O_3 consisted almost entirely of eutectic. Some loss of oxygen probably occurred during melting, as was evidenced by the blue-black

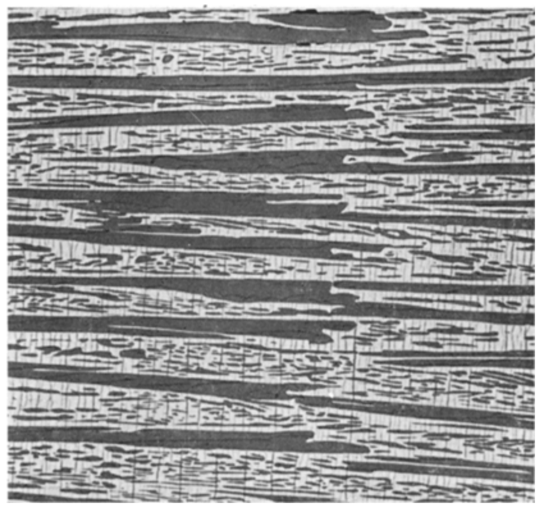

Figure 5 Longitudinal section of TiO_2-20 wt % Al_2O_3 zone melted at 5 cm/h showing primary aluminium titanate in a matrix of discontinuous aluminium titanate-titania eutectic (× 275).

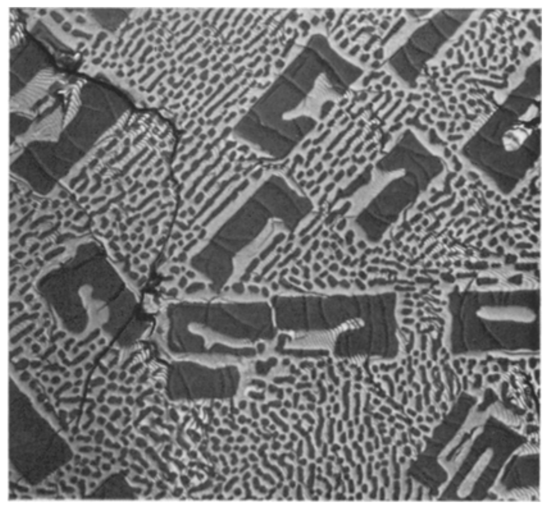

Figure 6 Transverse section of the sample shown in fig. 5, illustrating the lamellar nature of both the primary phase and the eutectic. Optical interference fringes occur where cracks intersect the surface (× 550).

colour of the samples; even so it is thought that the eutectic composition lies close to TiO_2-18 wt % Al_2O_3.

Samples of zone melted TiO_2-20 wt % Al_2O_3 were broken in three point bending. Although the strength was only about 5000 psi, because of the presence of many cracks, a continuous load had to be applied after the initiation of the fracture crack in order to break the rods in two, as can be seen from the load-deflection curve of fig. 7. This type of load-deflection curve is

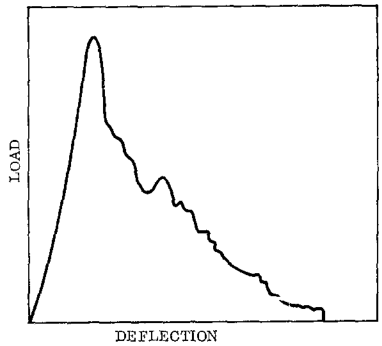

Figure 7 Load-deflection curve for TiO_2-20 wt % Al_2O_3 zone melted at 5 cm/h, tested in three point bending.

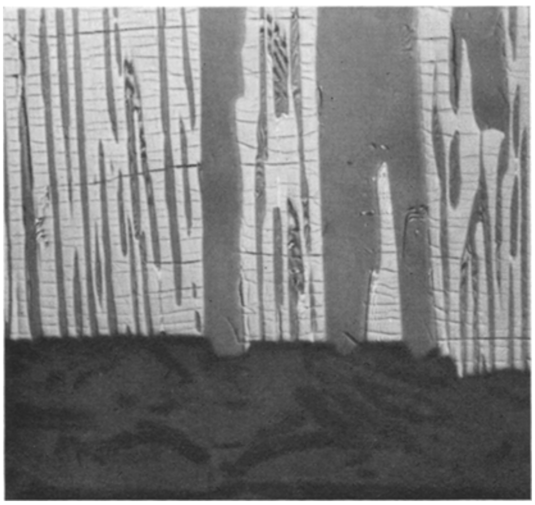

Figure 8 Fracture surface of TiO_2-20 wt % Al_2O_3 zone melted at 5 cm/h and broken in three point bending (× 550).

characteristic of notch insensitive materials. Fig. 8 shows part of a fracture surface. The eutectic lamellae seem to have little effect in diverting the path of the fracture crack. However, the protruding aluminium titanate plates suggest that some crack deflection occurred at the interfaces with the primary phase. The ability to deflect cracks probably depends upon the shape and the area of the second phase encountered by the crack. Thus slow solidification rates, producing coarse eutectic lamellae, or compositions which give primary lamellae in a eutectic matrix, are expected to yield material most resistant to cracking. Unfortunately, ceramics of the aluminium titanate-titania system contain many grown-in cracks, but in systems where the components have more similar coefficients of thermal expansion, crack-free tough ceramics might be obtained.

3.2. Alumina-Aluminium Titanate Eutectic

The eutectic between alumina and aluminium titanate is reported to melt at 1840° C and to have a composition Al_2O_3-38.5% TiO_2 [16]. Zone melted rods of this composition were again blue-black in colour and contained large surface cracks. Longitudinal and transverse sections of a sample solidified at 25.4 cm/h are shown in figs. 9 and 10 respectively. The structure

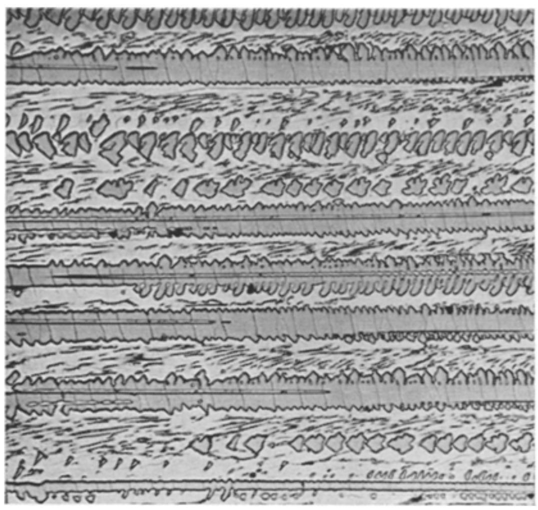

Figure 9 Longitudinal section of zone melted Al_2O_3 38.5 wt % TiO_2 (× 275).

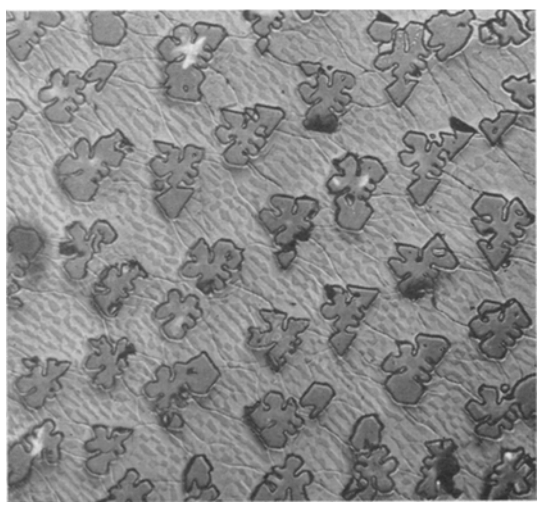

Figure 10 Transverse section of the sample shown in fig. 9 (× 275).

consists of primary dendritic rods of alumina in a matrix of discontinuous eutectic of aluminium titanate and alumina. Electron microprobe analysis showed the presence of some titanium in the alumina. Evidently, these samples were not of the eutectic composition, which probably contains more titania than 38.5%. Discontinuous eutectics were noted in the aluminium titanate-titania system when primary aluminium titanate was present, and in both systems the areas immediately adjacent to the primary phases were free from eutectic. The dendritic appearance of the alumina in fig. 9 suggests that considerable lateral growth must have occurred during solidification. Under non-equilibrium conditions, the growing dendrites cause lateral temperature gradients to arise. Also, the dendrites deplete the liquid of alumina, thus setting up lateral concentration gradients which vary locally. Such effects are expected to influence the mode of solidification of the eutectic and could lead to a discontinuous structure. The eutectic regions shown in fig. 10 are composed of fine ribbons which might be considered to be a modification of the expected fibrous structure. In a sample of the same composition zoned at about 1 cm/h, primary alumina, of a similar morphology to that shown in fig. 9, occurred in a well-defined rod eutectic. At this low solidification rate lateral growth was enhanced so that the alumina dendrites linked up, and the eutectic lay in small islands between the dendrite arms.

4. Conclusions

(i) Controlled microstructures of compositions close to the two eutectics of the alumina-titania system have been grown by floating zone melting.
(ii) The interlamellar spacing of the eutectic of aluminium titanate and titania varies inversely with the square root of the freezing rate.
(iii) Some crack deflection occurs at the interface between the matrix and primary plates of aluminium titanate in an alloy of composition TiO_2-20 wt % Al_2O_3.
(iv) The composition of the eutectic in the aluminium titanate-titania systems is close to TiO_2-18 wt % Al_2O_3 and the eutectic between alumina and aluminium titanate is probably richer in titania than Al_2O_3-38.5 wt % TiO_2.
(v) Zone melted rods of Al_2O_3-38.5 wt % TiO_2 consist of primary rod-like dendrites of alumina in a matrix of aluminium titanate-titania discontinuous eutectic.

Acknowledgement

The authors wish to thank J. W. Wilson of Centre for Materials Research, Stanford, California, for the use of electron beam heating equipment at the beginning of this study. The metallography was performed by W. C. Coons of the Lockheed Palo Alto Research Laboratory and the work was supported by the Independent Research Funds of the Lockheed Missiles and Space Company.

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