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Directional solidification, oxide eutectics, microstructure, crystallography, mechanical properties.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Preparation, microstructure, crystallography and mechanical properties of high melting oxide eutectics are described. It is shown that the microstructure can be predicted from the volume fraction of the minor phase. Two basic criteria control the interface and crystallographic orientation: (i) minimization of the misfit between oxygen sublattices (ii) neutralization of ionic charge across the interfacial plane.

Mechanical properties of $MgO-MgAl_2O_4$ eutectic were investigated. (cont'd)

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20. Abstract (cont'd)

The fracture strength is related to the colony size and decreases only slightly from room temperature to 1600°C. The fracture surface energy does not exhibit any dependence on fiber spacing. Knoop microhardness is greater than that of either the magnesia or spinel sep rately.

The creep resistance of the grain microstructure is greater than that of the colony microstructure and $MgAl_2O_4$ single crystal. A void nucleation and growth mechanism may best describe the deformation process with eutectic ingots containing colonies or grains.

"CONTROLLED CERAMIC-CERAMIC EUTECTIC MICROSTRUCTURES"

FOREWORD

Preparation, microstructure, crystallography and mechanical properties of high melting oxide eutectics were studied for several years. The results of these studies are described extensively in two Ph.D. theses.

1. F. L. Kennard III, "Directional Solidification of High Temperature Eutectics" Ph.D. thesis, The Pennsylvania State University, 1973.

2. W. J. Minford "Microstructure, Crystallography, and Creep of Directionally Solidified Oxide Eutectics", 1976.

The results obtained by F. L. Kennard are described in the Part I of this report and the results obtained by W. J. Minford in the Part II.

PART I

The three binary oxide eutectics, mullite-alumina, zirconia-magnesia, and magnesia-spinel, were directionally solidified and studied as to microstructure, crystallographic orientations and the parameters affecting the solidification process. The mechanical properties, including elastic modulus, hardness, fracture strength, fracture surface energy, and creep resistance were also investigated, but only for the magnesia-spinel eutectic.

With regard to the solidification process for these three eutectics, it was concluded that:

(1) The microstructures obtained in the mullite alumina-system are highly dependent on the melting and solidification procedures and do not resemble a characteristic oriented eutectic microstructure.

(2) Both the zirconia-magnesia and the magnesia-spinel eutectics form standard composite eutectic microstructures that appear to be correctly described by Hunt and Jackson's classification of eutectics.

At solidification rates above about 2 cm/hr, cellular growth occurred in both systems. At solidification rates less than 2 cm/hr plane front growth occurred and both phases in both eutectics possessed [111] growth directions. The interlamellar or interfiber spacing in both eutectics was found to be proportional to the inverse square root of the solidification rate, the generally accepted relationship. The colony size, however, did not appear to vary over the solidification rates studied.

(3) Ingots in both the zirconia-magnesia and the magnesia-spinel systems were badly microcracked at both the fastest and slowest solidification rates studied. The cracking at the fast solidification rates has been attributed to thermal shock, while at the slower rates

it has been attributed to the longer fibers formed under these conditions.

The mechanical properties of the magnesia-spinel eutectic were extensively investigated over a range of solidification rates, all within the cellular growth region. It was concluded that:

(4) The room temperature elastic modulus was relatively constant over the range of solidification rates studied. It agrees closely with a random mixture of the [100], [110], and [111] growth directions observed in colony microstructures.

(5) The Knoop microhardness was greater than that of either the magnesia or spinel separately and appears to be described by a Hall-Petch type of mechanism based on interfiber spacing. The possibility of some precipitation hardening also exists.

(6) The fracture strength appears to be related to the colony size as no dependence on the interfiber spacing was observed. Samples cut from ingots parallel to the solidification direction were consistently stronger than those cut perpendicularly. At 1400°C and 1600°C, the fracture strengths decreased only slightly from the room temperature values and, even at these temperatures, the fracture was elastic with little evidence of plastic flow prior to failure.

(7) The fracture surface energy also did not exhibit any dependence on fiber spacing; however, beyond 1200°C the work of fracture increased rapidly to approximately double the room temperature value at 1600°C.

(8) The creep resistance of the eutectic composite was very high, exceeding the projected values for pure magnesia or spinel by about five orders of magnitude. Again little indication of plastic flow was in evidence, in spite of the known plastic tendencies of

magnesia or spinel at these temperatures.

Generally, it is apparent that the oriented fibrous eutectic microstructure in the magnesia-spinel system appears to inhibit the tendency for plastic flow or dislocation motion.

PART II

The directional solidification of eutectic melts, which has been extensively investigated in metal systems for the production of aligned composites, is investigated in a number of high temperature oxide systems. The microstructure and crystallographic orientation of the phases have been examined to determine what parameters control the resultant structures. The creep deformation of the directionally solidified MgO-$MgAl_2O_4$ eutectic has been investigated to study further the mechanical properties of this in-situ composite.

The crystallography of directionally solidified oxide eutectics in the following systems was investigated: $CaZrO_3$-ZrO_2, $SrZrO_3$-ZrO_2, MgO-$MgAl_2O_4$, MgO-ZrO, MgO-CaO, Al_2O_3-ZrO_2, and $MgTi_2O_5$-TiO_2. Some generalizations concerning the type of microstructure as well as the interlamellar or interfiber spacing was achieved for all reported oxide eutectics. The crystallographic relationship determined from the directionally solidified oxide eutectics suggests that:

(1) For eutectic systems containing only cubic phases (the MgO-$MgAl_2O_4$, MgO-ZrO_2, and MgO-CaO systems) all the planes and directions of the eutectic phases are parallel and the [111] direction is parallel to the solidification direction.

(2) For the eutectic systems containing at least one noncubic phase (the $CaZrO_3$-ZrO_2, $SrZrO_3$-ZrO_2, Al_2O_3-ZrO_2 and $MgTi_2O_5$-TiO_2 systems), the interfacial planes and growth directions have low Miller indices.

From the misfit and charge density measurements of the inter-

facial planes in these systems, it can be concluded that:

(3) In oxide systems, two basic criteria control the interface and orientation of the directionally solidified eutectics: (i) minimization of the misfit between the phases which may be calculated from the oxygen sublattice and (ii) neutralization of ionic charge across the interfacial plane.

The microstructures of directionally solidified oxide eutectics has been compiled and the effects of the volume fraction of the phases and solidification rates has led to the following conclusions:

(4) The eutectic microstructures obtained from directionally solidified oxide melts can be predicted from the volume fraction of the minor phase as proposed by Cooksey et.al. (1964) from minimization of the surface energy.

(5) The interlamellar or interfiber spacing is proportional to inverse square root of the solidification rate for the majority of oxide systems investigated as predicted by Tiller (1957) for lamellar eutectics.

(6) Two factors are particularly important in Tiller's equation for determining the microstructure and its variation with solidification rate, the interfacial surface energy and the volume ratio of the phases. An interfacial energy of 850 ergs/cm^2 was calculated for the MgO-$MgAl_2O_4$ eutectic from Tiller's equation.

The creep properties of the MgO-$MgAl_2O_4$ directionally solidified eutectic with colony and grain structures and a nearly stoichiometric $MgAl_2O_4$ single crystal were investigated in four-point bend. It was concluded that:

(7) Due to the crystallographic orientation of the eutectic phases, dislocations were impeded by the fibrous phase preventing

any extensive plastic deformation of the in-situ composite.

(8) The deformation process of the directionally solidified $MgO-MgAl_2O_4$ eutectic with a colony structure has a stress exponent of approximately one and an activation energy of 27 $\pm$ 5 kcal/mol over a temperature range of 1550 to 1650°C and 10 to 18 ksi.

(9) The creep resistance at 1600°C of the grain structure was greater than that of the colony structure and $MgAl_2O_4$ single crystal which is the matrix material.

The occurrence of voids along the grain and colony boundaries in regions of creep specimens which were subjected to tensile stress suggests that:

(10) A void nucleation and growth mechanism may best describe the deformation process in the eutectic.

A void growth model was developed for the case of a square array of voids on a grain boundary normal to the tensile stress direction. The flux of vacancies was solved for one void under stress in which the stress concentrations about the void led to a vacancy gradient. It was concluded that:

(11) Two creep regimes are described: (i) for the initial stage when the radius of the void is much smaller than the spacing between voids:

$$\dot{\varepsilon}_i = \frac{0.56\ D_s \Omega r_o \sigma}{GkT}$$

and (ii) for the final stages of the deformation when the void radius approaches one-half the void-spacing:

$$\dot{\varepsilon}_f = \frac{0.14\ D_s \Omega \sigma}{GkTr_o}$$

From available data a strain rate of 2×10^{-7} min^{-1} was calculated for the MgO-$MgAl_2O_4$ eutectic compared to the 1×10^{-7} min^{-1} measured.

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