HIGH RESOLUTION MICROSTRUCTURAL AND MICROCHEMICAL ANALYSIS
OF ZIRCONIA EUTECTIC INTERFACES

Progress Report

for Period July 1, 1990 - *June '92*
~~January 28, 1992~~

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January 28, 1992

Prepared for

THE U. S. DEPARTMENT OF ENERGY
AGREEMENT NO. DE-FG02-84ER45150**DISCLAIMER**

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Progress Report (1 July 1991 - June 1992)

The goal of the research performed here is to study and understand the nature of fine scale microchemical variation, on the order of the lattice periodicity, in ceramic oxides. To that end, during the past year, emphasis was placed on the selection of appropriate materials systems and their fabrication into samples suitable for study using advanced high resolution analytical electron microscopy (work to be performed in the coming year). The work concentrated on two materials systems:

1. ZrO₂-MnO

During the previous year (July 1990-June 1991) we had investigated the structure and microchemistry of the lamellar ZrO₂-MnO eutectic using specimens grown by Professor A. Revcolevschi in the solar furnace at the University of Paris. It was observed that the cubic ZrO₂ phase was stabilized by MnO in solid solution, and the valence of the transition metal ion was Mn⁺². The only previous report of cubic stabilization of ZrO₂ by Mn was that of Shultz and Muan (1971) and is therefore of extreme interest, as this is believed to be a simple eutectic system, similar to ZrO₂-MgO, although ZrO₂-MgO is a rod-type eutectic. Our prior work with lamellar stabilized ZrO₂ eutectics was limited to the ZrO₂-CaZrO₃ and ZrO₂(CaO)-NiO systems; this latter system is a ternary system, requiring the addition of CaO to stabilize the ZrO₂ phase in the presence of NiO.

During the current year, we performed a broad range of experimentation with bulk ZrO₂-MnO solid solution samples in order to elucidate the phase-equilibria in this system. A composition of 15 wt% MnO-ZrO₂ was chosen as this was believed to be near, but below, the maximum solubility, based on initial electron microprobe analysis performed on the eutectic sample. Specimens of this composition were fabricated from high purity ZrO₂ and MnO powders by hot pressing for 2 hours at 20 MPa and 1500°C, to near-theoretical density. X-ray powder diffraction patterns indicated the material to be nearly single-phase cubic ZrO₂ with only a small amount of the monoclinic or tetragonal phase present. Optical and scanning electron microscopy indicated the material to have an equiaxed ~50µm grain size, and also showed the presence of a small amount of second phase present at grain-boundaries. Energy dispersive x-ray spectroscopy indicated this phase to be rich in Si and Mn; Si is a common residual even in high purity ZrO₂, and appears to combine preferentially with the manganese. More detailed analysis of this phase is currently underway.

Thin foils of the hot pressed ZrO₂-MnO were prepared by ion-thinning and the specimens were examined using transmission electron microscopy (Philips EM400T at 120kV), after carbon coating to stop charging. The matrix phase is indexed from the selected area diffraction pattern to be the cubic fluorite structure, and considerable diffuse scattered intensity is observed just off the [100] zone axis. This is attributed to short range ordered vacancy microdomains ~ 5-10 nm in size; it is also consistent with Mn⁺² or Mn⁺³ (as noted previously in the eutectic samples) rather than Mn⁺⁴ as this higher valence would not produce oxygen vacancies in the ZrO₂ structure. A mottled contrast is also observed in the cubic phase under strong 2-beam conditions, and is also attributed to the presence of the small ordered microdomains. Similar effects have been noted in the literature for Mg-PSZ materials.

A very small volume fraction of second phase particles was also observed. Energy dispersive x-ray analysis gives peaks only for Mn, and this could indicate low temperature precipitation of MnO as the composition falls below the solvus temperature on the ZrO_2 -rich solid solution side of the ZrO_2 -MnO phase diagram. A small Cu peak was also noted, but attributed to scattering and fluorescence from the specimen holder/microscope column.

2. Sintering and Crystallization of α -cordierite glass-ceramic

During the past year IBM announced the replacement of alumina in their TCM (thermally cooled module) multilayer ceramic packages by a direct crystallization cordierite. This material has a composition in the range (50-55) SiO_2 -(18-23) Al_2O_3 -(18-25) MgO -3 B_2O_3 -3 P_2O_5 . The B_2O_3 delays crystallization to higher temperature, allowing the glass to first sinter to full density, and the P_2O_5 encourages a direct crystallization from the glass to α -cordierite (enstatite), rather than the more usual indirect route via μ -cordierite which produces an incomplete transformation product having a multiphase microstructure. However, the presence of B_2O_3 and P_2O_5 could lead to interfacial microchemical segregation at the glass/ α -cordierite boundaries. We desired to study this microchemical behavior, and to that end set out to prepare suitable specimens from cordierite powder obtained from IBM. Specimens were cold pressed and sintered in air, with the following results:

<u>T, °C</u>	<u>t, hr</u>	<u>Density %</u>	<u>X-ray Diffraction</u>
900	2	>99	α -cordierite
850	5	>99	"
850	1	>99	most amorphous, small α -cord
825	5	>99	"
825	1	little densification	-----
800	2	"	-----

Higher temperatures produced fully crystallized specimens; lower temperatures produced incomplete densification. A narrow window between 825-850°C produced the best results. Further work is now in progress to fabricate specimens at 850°C for times between 1 and 5 hours, and at 825°C for times longer than 5 hours, to determine the best route to produce a range of partially crystallized specimens fabricated at the same temperature. These specimens will then be thinned for study using transmission electron microscopy and x-ray microchemical analysis.

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