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PROGRESS REPORT

"Ceramic Films and Interfaces: Chemical and Mechanical Properties"

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CERAMIC FILMS AND INTERFACES: CHEMICAL AND MECHANICAL PROPERTIES

In 1991 we have made good progress in unraveling one of the basic questions in the study of interfaces in ceramic materials: is it possible to enhance the cohesive strength of interfaces by the deliberate addition of impurities, and if so, what is the underlying atomistic mechanism?

The above idea, which was proposed to the Department of Energy under this program, is in contrast with the conventional wisdom deriving from our experience with metals: that impurities generally weaken grain boundaries, the classic example being the intergranular embrittlement of nickel by the segregation of sulphur. However, in the case of nickel-aluminide intermetallic the resistance to intergranular fracture is increased by the addition of boron, although the mechanism by which this occurs is not yet understood.

In this progress report we begin by highlighting our work on the enhancement of interfacial cohesion in alumina by small additions of transition metals. A possible mechanism by which grain boundaries in ceramic can be strengthened is proposed towards the end of this report and is further elaborated in the continuation proposal.

The results given in the following three figures support the view that the addition of zirconia lowers the interfacial energy in alumina. The lower interface energy has the effect of (i) increasing interfacial cohesion, (ii) increasing the activation energy for diffusional transport required for superplastic deformation and sintering, and (iii) delaying nucleation in the crystallization of an amorphous alloy of alumina and zirconia.

The influence of transition metal dopants on the superplastic flow properties of fine grained alumina is shown in Fig. 1. These results show that hafnium and zirconium enhance the strain to failure. The addition of 5%ZrO₂ increases the magnitude of the fracture strain to more than 0.5 from 0.2¹. The remarkable feature of these results is that the ductility increases despite the increase in the flow stress in the presence of the dopants. Usually a higher flow stress reduces the ductility. Taken together these two results strongly suggest that the bonding at interfaces in alumina is enhanced by the addition of zirconium or hafnium. Note that both these elements have a similar electronic structure and ionic radius.

¹Although these experiments were done in compression they still fail by intergranular fracture because of the tensile stress that develops normal to the compressive axis.

Figure 1: Stress strain curves for superplastic flow in fine grain alumina with and without the addition of zirconium and hafnium. Note that doping increases ductility despite the higher value of the flow stress.

A second result described in Fig. 2 shows how the addition of zirconia changes the activation energy for sintering of alumina. The activation energy for sintering the alloy is greater than the value for either pure alumina or zirconia. While a wide range of composition was studied the result at the alumina rich end is the most striking where it is seen that even a 1% addition of zirconia increases the activation energy by a factor of about 1.5; this increase must therefore be a result of atomistic segregation of zirconium to the grain interfaces in alumina, and not due to the formation of small particles of zirconia at the triple junctions. Since these activation energies represent boundary diffusion, its increase reflects a corresponding lowering of the interface energy. This inference is consistent with the finding of greater interfacial cohesion in the presence of zirconium.

Figure 2: The activation energy of sintering, which is boundary diffusion controlled, increases with the addition of zirconia to alumina. The result at the alumina rich end where even a 1% addition of zirconia is seen to increase the activation energy by a factor of 1.5 is particularly noteworthy as discussed above.

In a third result we show that amorphous alloys of alumina and zirconia, prepared from inorganic salts, are much more resistant to crystallization than either alumina or zirconia. Figure 3 below shows the DTA/TGA measurements for amorphous precursors derived from (a) aluminum nitrate, (b) zirconium oxynitrate, and (c) a mixture of aluminum nitrate and zirconium oxynitrate. While both (amorphous) alumina and (amorphous) zirconia begin to crystallize below 400°C, the alloy must be heated to 800°C before crystallization can begin. This delay in the nucleation is attributed to stronger A-B bonds as compared to the A-A and B-B bonds, following the concepts of regular solution theory.

Figure 3: Influence of composition on the onset of crystallization in amorphous precursors of alumina and zirconia obtained from inorganic salts. The arrows, which point to crystallization peaks, show that the crystallization in the alumina/zirconia alloy occurs at a higher temperature than either alumina or zirconia by itself.

The mechanism by which the addition of zirconium enhances bonding at interfaces in alumina remains entirely unspecific at the present time. To a certain extent this lack of direction reflects our inadequate understanding of the fundamental basis for adhesion at interfaces in ceramic materials. The present thinking of the structure and bonding at ceramic interfaces is dominated by the ideas carried over from hard-sphere models of grain boundary structure in metals. We are increasingly convinced that bonding at ceramic interfaces should be approached from the point of view of its electronic structure. A clue to the strengthening mechanism, as described above, then emerges by contrasting this behavior to the embrittling effect of sulphur in nickel. In the latter case, it is understood that sulphur localizes the electrons from nickel to itself, thereby reducing the sharing of electrons between nickel atoms on either side of the interface; this has the effect of reducing the bond between nickel atoms across the interface. We believe that in ceramics the situation may be the opposite. In pure and highly stoichiometric oxides the electrons may be so localized that the sharing of electrons across the interface is weak; in these instances the segregation of impurities can increase the cross talk between electrons across the interface provided that the impurity atoms have multiple and flexible ionization states, as is the case with the transition metals that contain unfilled d bands. Theoretical and experimental approaches for investigating these ideas are briefly described in the next section.

Over the last three years we have been building facilities for fundamental studies of the mechanisms for heteroepitaxial growth of ceramic films from the vapor phase. One important facility in this effort is a UHV-CVD system for studying the layer by layer growth of an oxide from metalorganic precursors. Current experiments are focussed on the growth of films of titanium oxide on sapphire from titanium-isopropoxide. The system is now fully operational. It is equipped with XPS, LEED, Auger Spectroscopy and QMS. Initial experiments have shown that highly stoichiometric titanium oxide, without residual carbon, can be grown in the UHV-CVD chamber.

A number of doctoral theses were completed in the year 1991. These are listed below. Papers based upon them will be prepared and submitted for publication during 1992.

Publications under the DOE Grant DE-FG02-87ER45303

In Year 1990

1. "Estimate of the Activation Energies for Boundary Diffusion from Rate Controlled Sintering of Alumina Doped with Zirconia or Titania" J. Wang and R. Raj, Journal of the American Ceramic Society, 73[5], pp 1172-1175, 1990.
2. "Better Sintering Through Green State Deformation Processing", C. P. Cameron and R. Raj, Journal of the American Ceramic Society, 73[7], pp 2032-2037, 1990.
3. "Premelting at Triple Grain Junctions", R. Raj, Acta Metallurgica et Materialia, 38, pp 1413-1416, 1990.

In Year 1991

1. "Control of the Microstructure of Alumina-Zirconia Composites starting from Inorganic Salts", J. Wang and R. Raj, Journal of the American Ceramic Society, 74, [7], 1707-1709 (1991).
2. "Solution Precursor-Low Pressure Chemical Vapor Deposition of Titanium Oxide Thin Films", J.-P. Lu, J. Wang and R. Raj, Thin Solid Films, 204, L13 (1991).
3. "Ultra High Vacuum Chemical Vapor Deposition and in-situ Characterization of Titanium Oxide Thin Films", J.-P. Lu and R. Raj, Journal of Materials Research, 6, [9], 1913-1918, (1991).
4. "Interface Effects in Superplastic Deformation of Alumina Containing Zirconia, Titania, or Hafnia as a Second Phase", J. Wang and R. Raj, Acta Metallurgica et Materialia, 39, [11], 2909-2919 (1991).
5. "Activation Energy for the Sintering of Two-Phase Alumina/Zirconia Ceramics", Jenqdaw Wang and R. Raj, Journal of the American Ceramic Society, 74, [8], 1959-1963, (1991).

1992*

1. "Ultra-High Vacuum Metalorganic Vapor Deposition of Rhodium Thin Film on Si(111)", J.-P. Lu, P. Chu, R. Raj and H. Gysling, Thin Solid Films, under review (1992).
2. "Ultra-High Vacuum Metalorganic Vapor Deposition of Gallium Arsenide on Si(100) Using a Single Source Precursor", J.-P. Lu, R. Raj and A. Wernberg, Thin Solid Films, in press (1992).

Doctoral Theses Completed in 1991

Bahar Hoghooghi: "Nulceation and Growth by Chemical Vapor Deposition of Nickel-Oxide onto Engineered Surfaces of {100} Magnesium-Oxide".

James R. Conner: "Studies of Structure and Bonding at Interfaces in Multilayer Heteroepitaxy of Barium Silicide, Barium Oxide, and Barium Titanate on {100} Silicon".

Hasung Lee: "Enhancement of Mechanical Strength and Reliability of Silicon Nitride by Shear Deformation in the Green State".

Jengdaw Wang: "Effects of Transition Metal Oxide Addition on Sintering, Creep and Fracture Properties in Alumina".

*Papers based upon the work of Hoghooghi, Conner and Lee will be submitted for publication in 1992. The topics covered by these papers are listed in the Continuation Proposal.

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