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FINAL REPORT

Ceramic Films and Interfaces:
Chemical and Mechanical Properties

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CERAMIC FILMS AND INTERFACES: CHEMICAL AND MECHANICAL PROPERTIES

1. Summary of Results

This report summarizes the important results obtained in this work under the sponsorship of the Department of Energy. These results lie in two areas: (a) the understanding of the mechanism of superplasticity in those that show unusual resistance to intergranular cavitation, and (ii) new understanding of the growth of heteroepitaxial films of oxides by the CVD process.

A new mechanism has been proposed to explain the unusual superplastic ductility of yttria stabilized zirconia (reported by Wakai), magnesium aluminate spinel (reported by us), and nearly all functional ceramics. A common feature of these oxides is that they are non-stoichiometric. In addition to the ductility, the oxides exhibit non-linear in the stress/strain-rate behavior, which may be interpreted as an apparent threshold stress. In contrast, "non-superplastic" ceramics generally show a linear relationship between the stress and the strain rate.

The proposed mechanism explains the above threshold stress in terms of a space charge layers that are known to exist next to the interfaces in non-stoichiometric ceramics. The diffusional transport from one grain boundary to another, that leads to superplasticity, is equivalent to an electrolytic cell where the electrodes are the grain boundaries and where the potential gradient between the electrodes is created by the applied stress. This approach allows us to draw an equivalence between the threshold stress and the potential difference across the space charge layer. In magnesium aluminate spinel this approach leads to an estimate of boundary space charge potential of a few tens of mV, which is in broad agreement of studies of enhanced ionic conductivity in the space charge layers associated with interface.

In the area of CVD processing of oxides, we have obtained two significant new results. The first relates to the nucleation of NiO crystals on (100)MgO in a CVD process using nickel-bromide as the precursor. We have shown that nucleation is preferred on the {110} planes. Therefore, on cleaved surfaces of (100)MgO the nuclei form at the cleavage steps where the {110} planes are exposed. However, by carefully polishing the surface and reducing supersaturation, nucleation on the (100) surface can be prevented. Subsequently the {110} planes were exposed at periodic locations by lithography and chemical etching, leading to a

highly regular nucleation of NiO crystals. The spacing of these nuclei could be controlled from 10-100 μ m. Controlled nucleation led to detailed study of the kinetics of the growth process. These experiments also led to the general result that nucleation at steps depends not only the interfacial energy but also on the step height, that is, there is a critical step height below which the steps cannot serve as preferred nucleation sites.

The second CVD result pertains to the understanding of monolayer by monolayer growth of titanium dioxide films from high purity metalorganic precursor (titanium isopropoxide) in a UHV-CVD system. These experiments have shown that stoichiometric TiO₂, without measurable carbon contamination, can be obtained at temperatures as low as 300°C. We have also shown that in cycling experiments where the surface is first saturated with the precursor and then heated to high temperature, the growth rate is five times slower pregrown TiO₂ surface than on fresh (1000)sapphire surface. We have also shown that the growth per cycle on the sapphire is the equivalent of a densely packed monolayer of isopropoxide, that is, the maximum possible growth rate is stereologically limited.

Recommendations for Further Work

The fundamental research on superplasticity of ceramic materials has led to new insights into the classification of ceramic materials into three categories based upon the structure and defect chemistry of interfaces. These are: (A) interfaces in ceramics which are essentially stoichiometric, (B) ceramics where interfaces contain very thin films of a glass phase, and (C) interfaces in non-stoichiometric ceramics. In most instances Type A and Type C ceramics are oxides, while Type B ceramics are usually non-oxides having a higher degree of covalent bonding.

The superplastic properties of the above ceramics suggest that the non-stoichiometric, Type C ceramics exhibit a much greater resistance to intergranular cavitation than the stoichiometric, Type B ceramics. Also, the Type C materials invariably exhibit a threshold stress for superplastic flow while Type A ceramics show the classical linear stress/strain-rate behavior. These differences are so significant that they require a new approach to the fundamental study of mechanical properties of interfaces, that is, an approach that explains why stoichiometry has such a remarkable effect on interfacial cohesion. This understanding could lead to the chemical design of interfaces for high creep-fracture resistance in ceramics.

The work carried out under the DOE grant has led to the hypothesis that the space charge layers that are known to be associated with interfaces in non-stoichiometric ceramics have a dominant influence on the mechanical behavior. The threshold stress measured in superplastic experiments leads to an estimate of the potential difference across the space charge layers of few tens of mV, in agreement with the numbers obtained from the measurements of ionic conductivity in non-stoichiometric ceramics. Transmission electron microscopy studies, of which there are very few, confirm the presence of the space charge layer (magnesium aluminate spinel) and at least in one instance (nickel-oxide) suggest that the interfaces may contain a very high density of point defects. It is conceivable that the low interfacial energy of interfaces in this class of ceramics is related to the influence of high defect density on the electron structure.

In summary, the understanding of the bonding and space charge effects in non-stoichiometric ceramics, and their relationship to high temperature mechanical behavior, and the understanding of how to influence the local non-stoichiometry by doping with trace elements, could usher in a new era of high temperature structural ceramics.

I now return briefly to the case of Type B ceramics, those that contain very thin layers of a glass phase at interfaces. The influence of the glass on creep and cavitation at high temperatures has received considerable attention in the last decade. It is recommended that future work in this field concentrate not on the techniques for eliminating the glass phase, but instead designing it so that the crystallization of the glass can be used to create two phase structures where the second phase consists of a crystallized glass that forms the matrix for the crystal grains of the major phase. Recent theoretical and experimental work suggests that about 10% (volume) of the second "nanophase" may lead to unusual thermal shock resistance and very high values of the Weibull modulus. The material of interest here is silicon nitride consisting of an acicular grain structure embedded in a second phase that is derived from the glass precursor. Thermodynamic and kinetic studies that provide insights into the processing of such microstructures are recommended.

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3. Publications under the DOE Grant DE-FG02-87ER45303

The following publications have resulted and are acknowledged to the work supported by DOE¹. They are available upon request:

1. "Estimate of the Activation Energies for Boundary Diffusion from Rate Controlled Sintering of Pure Alumina, and Alumina Doped with Zirconia and Titania", J. Wang and R. Raj, Journal of the American Ceramic Society, 73, [5], 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], 2032-2037, (1990).
3. "Premelting at Triple Grain Junctions", R. Raj, Acta Metallurgica et Materiala, 38, 1413-1416 (1990).
4. "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).
- 5.* "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-L17 (1991).
- 6.* "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).
7. "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).
8. "Interface Effects in Superplastic Deformation of Alumina Containing Zirconia, Titania, or Hafnia as a Second Phase", J. Wang and R. Raj, Acta Metallurgica et Materiala, 39, [11], 2909-2919 (1991).
- 9.* "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, 205, 236-240 (1991).

¹The publications marked by * received partial support from DOE.

- 10.* "Ultra-High Vacuum Metalorganic Vapor Deposition of Rhodium Thin Films on Clean and TiO_2 -covered Si(111)", J.-P. Lu, P. Chu, and R. Raj, Thin Solid Films, 208, 172-176 (1992).
11. "Superplastic Flow in a Non-Stoichiometric Ceramic: Magnesium Aluminate Spinel", R. Lappalainen, A. Pannikkat and R. Raj, Acta Metallurgica et Materiala, 41, [4], 1229-1237 (1993).
12. "A Phenomenological Model for Serrated Flow During Superplastic Flow and Its Application to Nanograin Ceramic Thin Films", R. Lappalainen and R. Raj, Acta Metallurgica et Materiala, under revision (1993).
13. "MgO Epitaxial Thin Films on (100) GaAs as a Substrate for the Growth of Oriented PbTiO_3 ", W.-Y. Hsu and R. Raj, Applied Physics Letters, 60, [25], 22 June 1992.
14. "Fundamental Research in Structural Ceramics for Service Near 2000°C ", R. Raj, Journal of the American Ceramic Society, accepted with minor revisions (1993).
15. "A Model for Interface Reaction Control in Superplastic Deformation of Non-Stoichiometric Ceramics", R. Raj, Materials Science and Engineering, in press (1993).
16. "Controlled Epitaxial Nucleation of Nickel Oxide Onto Micro-Fabricated Magnesium Oxide Substrates in a CVD Process", B. Hoghooghi and R. Raj, Journal of the American Ceramic Society, [], submitted February 1993.
17. "Heteroepitaxial Growth Kinetics in a CVD Process Using Nickel Oxide on MgO as a Model System", B. Hoghooghi and R. Raj, Journal of the American Ceramic Society, [], submitted February 1993.
18. "The Design of the Interface Phase for Obtaining Thermal Shock Resistance in Silicon Nitride", R. Raj, Proceedings of a Workshop on Thermal Shock and Thermal Fatigue Behavior of Advanced Ceramics, Kluwer Press, Netherlands, in press (1993).
19. "Reply to 'Comment on 'Analysis of the Sintering Pressure''", R. Raj, Journal of the American Ceramic Society, 76, [7], (1993).

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