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# SURFACES AND INTERFACES OF CERAMIC MATERIALS

NATO ADVANCED STUDY INSTITUTE, CAES-CNRS Oléron (France), September 4-16, 1988

## Organizing Committee:

Drs Louis-C. Dufour, Dir., CNRS, Dijon, France  
 Claude Monty, CNRS, Bellevue, France  
 Georgette Petot-Ervas, CNRS, Orsay, France

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## PROGRAMME

TL = Tutorial lecture  
 L = Invited lecture (Seminar)  
 P = Contributed paper

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### SUNDAY, SEPTEMBER 4

14.00 - 22.00 Reception and registration of participants

### MONDAY, SEPTEMBER 5

8.45 - 9.00 Welcoming address

9.00 - 10.30 **TL1** / Introductory lecture. *Materials science of ceramic interfaces*, R.J. BROOK, Univ. Leeds, UK and MPI, Stuttgart, FRG

10.30 - 11.00 Coffee break

11.00 - 12.30 **TL2** / *Atomic structure of ceramic surfaces*, G. KALONJI, MIT, Cambridge, USA

12.30 - 17.00 Lunch and free time

17.00 - 17.55 **TL3** / *Structure and microstructure of grain boundaries in ceramic materials (1)*, C.B. CARTER, Cornell Univ, Ithaca, USA

18.05 - 19.30 Cocktail party

19.30 - 20.30 Dinner

### TUESDAY, SEPTEMBER 6

9.00 - 10.30 **TL3** / *Structure and microstructure of grain boundaries in ceramic materials (2)*, C.B. CARTER, Cornell Univ, Ithaca, USA

10.30 - 11.00 Coffee break

11.00 - 12.30 **TL4** / *Ceramic-metal interfaces*, M.G. NICHOLAS, UKAEA, Harwell, UK

12.30 - 17.00 Lunch and free time

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DISTRIBUTION STATEMENT A

- 17.00 - 17.55 **L1** / *Microstructure of grain boundaries in carbide ceramics*, G. NOUET, CNRS, Caen, France
- 18.05 - 19.00 **L2** / *Interfaces in directionally solidified oxide-oxide eutectics*, A. REVCOLESCHI and G. DHALENNE, Univ. Orsay, France
- 19.30 - 20.30 Dinner
- 20.30 - 21.30 **L3** / *The role of surfaces in ceramic processes*, H. SCHUBERT, MPI, Stuttgart, FRG

WEDNESDAY, SEPTEMBER 7

- 9.00 - 10.30 **L4** / *Segregation at ceramic surfaces and effects on mass transport*, J. M. BLAKELY, Cornell Univ, Ithaca, USA
- 10.30 - 11.00 Coffee break
- 11.00 - 12.30 **TL6** / *Segregation in oxide ceramics*, J. NOWOTNY, MPI, Stuttgart, FRG
- 12.30 - 17.00 Lunch and free time
- 17.00 - 19.30 **ROUND TABLE 1** : Segregation and microchemistry at ceramic surfaces and interfaces (Discussion leader: J.M. BLAKELY, Cornell Univ, Ithaca, USA)
- P1** / *Study of non stoichiometric, pure and Zr-doped yttria surfaces by X-ray photoemission and scanning electron microscopy*, M. GAUTIER, J.P. DURAUD, F. JOLLET, N. THROMAT, Ph. MAIRE and C. LE GRESSUS, CEN Saclay, France
- P2** / *Segregation aspects in the  $ZrO_2$  -  $Y_2O_3$  ceramic system*, G.S.A.M. THEUNISSEN, A.J.A. WINNUBST and A.J. BURGGRAAF, Univ. Twente, Enschede, The Netherlands
- P3** / *Demixing tendency under chemical potential gradient in oxide solid solutions*, G. PETOT-ERVAS, Univ. Paris-Sud, Orsay, France
- P4** / *Dynamic segregation and microstructural changes near an interface formed by reduction of  $Fe_{1-x-y}Co_yO$* , J. KUCINSKI, S. JASIENSKA, School of Mining and Metallurgy, Krakow, Poland, C. MONTY and A. RIVIERE, CNRS, Bellevue, France
- P5** / *Use of SIMS to study surface segregation and insulating materials*, G. BORCHARDT, Technische Universität Clausthal, FRG and M. PERDEREAU, CNRS, Univ. Bourgogne, Dijon, France
- 19.30 - 20.30 Dinner

**THURSDAY, SEPTEMBER 8**

- 9.00 - 10.30 **TL7** / *Grain boundary diffusion*; A. ATKINSON, UKAEA, Harwell, UK and C. MONTY, CNRS, Bellevue, France
- 10.30 - 11.00 Coffee break
- 11.00 - 12.30 **TL8** / *Surface diffusion and surface energies of ceramics (with application to the behaviour of volatile fission products in ceramic nuclear fuels)*,  
Hj. MATZKE, CEC, Karlsruhe, FRG
- 12.30 - 17.00 Lunch and free time
- 17.00 - 18.30 **TL11** / *Thermodynamics and chemistry of ceramic-metal interfaces*; J.T. KLOMP, TNO Inst. of Applied Physics, Eindhoven, The Netherlands
- 18.30 - 19.30 **ROUND TABLE 2 (Part 1)**: Ceramic-metal interfaces (Discussion leader : M.G. NICHOLAS, UKAEA, Harwell, UK)
- P6** / *Silicon nitride/carbon steel joining by HIP technique*, M. COURBIERE, M. KINOSHITA and I. KONDOH, Government Industrial Research Inst, Osaka, Japan
- P7** / *Copper-cordierite cosintering*, V. OLIVER, J. GUILLE, J.C. BERNIER, S. HAN, J. WERCKMANN, J. FAERBER, P. HUMBERT, B. CARRIERE
- P16** / *W-TiN-SiC material for high temperature application*, L.R. WOLFE, Univ. Eindhoven, The Netherlands
- 19.30 - 20.30 Dinner
- 21.00 - 22.30 **ROUND TABLE 2 (Part 2)**: Ceramic-metal interfaces (Discussion leader : M.G. NICHOLAS, UKAEA, Harwell, UK)
- L7** / *Modeling of metal-oxide interface behaviour during oxide scale growth controlled by cation diffusion*, B. PIERAGGI, Univ. Toulouse, France, and R.A. RAPP, Ohio State Univ., Columbus, USA
- L8** / *Small particles and thin films of metals on oxides*, L.C. DUFOUR and M. PERDEREAU, CNRS, Univ. Bourgogne, Dijon, France

**FRIDAY, SEPTEMBER 9**

- 9.00 - 10.30 **TL9** / *Fractal surfaces (1)*, B. SAPOVAL, Ecole Polytechnique, Paris, France
- 10.30 - 11.00 Coffee break
- 11.00 - 12.30 **TL10** / *Intergranular phases in polycrystalline ceramics*, D.R. CLARKE, IBM, New York, USA
- 12.30 - 17.00 Lunch and free time

- 17.00 - 17.55 **L6** / *Investigation of the fractal structure of the pore-grain interface in alumina ceramics*, E. BROUERS, Univ. Strasbourg, France and A. RAMSAMUGH, Univ. West Indies, Mona, Jamaica
- 18.05 - 19.00 **TL12** / *Microstructure of composite interfaces and its relation to interfacial strength*, P. PIROUZ, CWRU, Cleveland, USA)
- 19.30 - 20.30 Dinner
- 20.30 - 22.30 **TL9** / *Fractal surfaces (2)*, B. SAPOVAL, Ecole Polytechnique, Paris, France with projections of films

SATURDAY, SEPTEMBER 10

Social programme

MONDAY, SEPTEMBER 12

- 9.00 - 10.30 **L5** / *Growth and mass transport in ceramic type protective scales on metals*, W.W. SMELTZER, McMaster University, Hamilton, Canada
- 10.30 - 11.00 Coffee break
- 11.00 - 12.30 **L9** / *The role of grain boundaries and interfaces on superconductivity*, D. DIMOS and D.R. CLARKE, IBM, New York, USA
- 12.30 - 17.00 Lunch and free time
- 17.00 - 17.55 **TL13** / *Ceramic membranes and nanoscale composite layers*, A.J. BURGGRAAF, Univ. of Twente, Enschede, The Netherlands
- 18.05 - 19.25 **TL5** / *The theory of dopant and impurity segregation in ceramic oxides*, R.G. EGDELL, Imperial Coll, London, UK (Presented by A. ATKINSON from transparencies and indications sent by Dr EGDELL)
- 19.30 - 20.30 Dinner
- 20.30 - 21.30 **L11** / *Structure and properties of the grain boundaries in MgO bicrystals*, E. YASUDA, Tokyo Inst. of Technology, Japan
- 21.30 - 22.30 **L10** / *Influence of microstructure on mechanical properties of ZrO<sub>2</sub>*, A. DOMINGUEZ-RODRIGUEZ, Univ. Sevilla, Spain

TUESDAY, SEPTEMBER 13

- 9.00 - 10.30 **TL14** / *Electron spectroscopic determination of the geometric and electronic structure of oxide surfaces*, V.E. HENRICH, Yale Univ., New Haven, USA

- 10.30 - 11.00 Coffee break
- 11.00 - 12.30 **TL15** / *The role of defects in the electronic structure of and chemisorption on oxide surfaces*, V.E. HENRICH, Yale Univ, New Haven, USA
- 12.30 - 17.00 Lunch and free time
- 17.00 - 17.55 **TL16** / *Solid-gas and solid-solid interactions of ceramic materials at high temperatures*, H.J. GRABKE, MPI, Dusseldorf, FRG
- 18.05 - 19.00 **TL17** / *Mechanisms involved in chemical vapor deposition and evaporation of ceramics at high temperature*, F. TEYSSANDIER, CNRS, Perpignan, France
- 19.30 - 22.30 Banquet

### WEDNESDAY, SEPTEMBER 14

- 9.00 - 10.30 **TL18** / *Structure of ceramic oxide - water interfaces. Reactions of ceramic oxides with aqueous solutions (including dissolution)*, M.A. BLESÁ, CNEA, Buenos-Aires, Argentina
- 10.30 - 11.00 Coffee break
- 11.00 - 12.30 **TL19** / *Ionic conductivity and the role of surfaces and interfaces in ceramic electrolytes*, W. WEPPNER, MPI, Stuttgart, FRG
- 12.30 - 17.00 Lunch and free time
- 17.00 - 17.55 **L12** / *Dissolution mechanisms of oxides and titanate ceramics: electron microscopy and surface analytical studies*, P.S. TURNER with C.F. JONES, F.B. NEALL, D.K. PHAM and R. STC SMART, Griffith University, Nathan, Australia
- 18.05 - 19.00 Oral presentation of posters (10-12 minutes long without discussion)
- P11** / *A vibrational study of tetracyanoethylene adsorbed on magnesia*, J.L. HOAGLAND and K.W. HIPPS, Washington State Univ, USA
- P18** / *Interfaces between pigeonite, amphibole and augite*, W. SKROTZKI Univ. Göttingen, FRG, and W.F. MÜLLER, Technische Hochschule Darmstadt, FRG
- P22** / *The role of grain boundary modifications to the thermal decomposition of Mn-ferrites*, J.H. BOY and G.P. WIRTZ, Univ. Illinois, Urbana, USA
- P23** / *Electrical properties of BaTiO<sub>3</sub> PTCR materials*, D.C. SINCLAIR and A.R. WEST, Univ. Aberdeen, UK
- P15** / *Colloidal filtration of chemically modified alumina*, A.P. PHILIPSE and H.J. VERINGA, Netherlands Energy Research Foundation, ECN, Petten, The Netherlands



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Poster session (first part)

**P2 /** *Segregation aspects in the  $ZrO_2$  -  $Y_2O_3$  ceramic system*, G.S.A.M.

THEUNISSEN, A.J.A. WINNUBST and A.J. BURGGRAAF, Univ. Twente, Enschede, The Netherlands

**P4 /** *Dynamic segregation and microstructural changes near an interface formed by reduction of  $Fe_{1-x-y}Co_yO$* , J. KUCINSKI, S. JASIENSKA, School of Mining and Metallurgy, Krakow, Poland, and C. MONTY, CNRS, Bellevue, France

**P7 /** *Copper-cordierite cosintering*, V. OLIVER, J. GUILLE, J.C. BERNIER, S. HAN, J. WERCKMANN, J. FAERBER, P. HUMBERT, B. CARRIERE

**P8 /** *Sintering of  $Nd_2O_3$  and ceramic stability to hydration*, J.M. HEINTZ, CNRS, Bordeaux, France, P. POIX and J.C. BERNIER, IPCMS, Strasbourg, France

**P9 /** *FT-IR analysis of the surface of a cordierite aerogel*, M.I. BARATON, T. MERLE-MEJEAN and P. QUINTARD, Univ. Limoges, France

**P10 /** *Characterization, before sintering, of high surface area silicon nitride and carbide, using FT-IR*, M.I. BARATON, T. MERLE-MEJEAN, P. QUINTARD, Univ. Limoges, France, G. RAMIS, G. BUSCA, V. LORENZELLI, Univ. Genova, Italy, M. CAUCHETIER, CEN Saclay, France

**P11 /** *A vibrational study of tetracyanoethylene adsorbed on magnesia*, J.L. HOAGLAND and K.W. HIPPS, Washington State Univ., USA

**P12 /** *Nickel deposition on  $TiO_2(100)$ : characterization by AES and SIMS*, S. BOURGEOIS, D. DIAKITE, F. JOMARD, M. PERDEREAU and R. POIRAULT, CNRS, Univ. Bourgogne, Dijon, France

**P13 /** *Interfacial tension and contact angle in immiscible systems by capillarity pressure measurements*, L. LIGGIERI, E. RICCI and A. PASSERONE, CNR, Genova, Italy

**P14 /** *Role of carbon - silicate interface area in the elaboration of SIMON powders*, E. KOOL, F. BERGAYA and H. VAN DAMME, CNRS, Orléans, France

**P15 /** *Colloidal filtration of chemically modified alumina*, A.P. PHILIPSE and H.J. VERINGA, Netherlands Energy Research Foundation, ECN, Petten, The Netherlands

**P16 /** *W-TiN-SiC material for high temperature application*, L.R. WOLFE, Univ. Eindhoven, The Netherlands

**P18** / *Interfaces between pigeonite, amphibole and augite*, W. SKROTZKI Univ.

Göttingen, FRG, and W.F. MÜLLER, Technische Hochschule Darmstadt, FRG

**P19** / *Residual stresses in porous plasma-sprayed alumina coatings on titanium*

*alloy for medical applications*; H. CARREROT, J. RIEU, ENSM, Saint-Etienne,

France and A. RAMBERT, SERF, Décines, France

**P20** / *Microstructure dependent toughening mechanisms in Mg-PSZ*, C.A.

LEACH, Imperial College, London, UK

**P21** / *Tentative modeling of surface reactivity with oxidizing-reducing mixtures*

*on rutile TiO<sub>2</sub>*, F. MORIN, IREQ, Varennes, Canada and L.C. DUFOUR, CNRS,

Univ. Bourgogne, Dijon, France

**P22** / *The role of grain boundary modifications to the thermal decomposition of*

*Mn-ferrites*, J.H. BOY and G.P. WIRTZ, Univ. Illinois, Urbana, USA

**P23** / *Electrical properties of BaTiO<sub>3</sub> PTCR materials*, D.C. SINCLAIR and A.R.

WEST, Univ. Aberdeen, UK

19.30 - 20.30 Dinner

20.30 - 22.00 Poster session (second part)

#### THURSDAY, SEPTEMBER 15

9.00 - 10.30 **TL20** / *Surface determined properties in vitreous silicate solids*, A.A. KRUGER,

Battelle Pacific Northwest Labs, Richland, USA

10.30 - 11.00 Coffee break

11.00 - 12.30 **TL21** / *Physical and chemical properties of silicate materials*, G. BORCHARDT,

Technische Universität Clausthal, FRG

12.30 - 17.00 Lunch and free time

17.00 - 17.55 **TL22** / *Characterization, properties and processing of ceramic powders (1)*, T.A.

RING, Ecole Polytechnique Fédérale, Lausanne, Switzerland

18.00 - 18.45 **TL22** / *Characterization, properties and processing of ceramic powders (2)*, T.A.

RING, Ecole Polytechnique Fédérale, Lausanne, Switzerland

18.55 - 19.30 **L13** / *Some aspects of the influence of granulometry on properties and behaviour*

*of a dielectric material: example of barium titanate*, J.C. NIEPCE, Thomson-LCC,

France

19.45 - Barbecue and garden party

FRIDAY, SEPTEMBER 16

- 8.30 - 9.30 **TL23** / *Some current issues on grain growth in sintered ceramics*, A. MOCELLIN, Ecole Polytechnique Fédérale, Lausanne, Switzerland
- 9.30 - 10.30 **ROUND TABLE 3**: Sintering processes, (Discussion leader: A. MOCELLIN, Ecole Polytechnique Fédérale, Lausanne, Switzerland)
- P25** / *Grain boundary phenomena in the early stages of sintering MO oxides*, A.M.R. SENOS, M.R. SANTOS, A.P. MOREIRA and J.M. VIEIRA, Univ. Aveiro, Portugal
- P26** / *Preparation of an  $Al_2O_3$ - $ZrO_2$  sol for producing microspheres*, L. MONTANARO, Politecnico, Torino, Italy
- 10.30 - 11.00 Coffeebreak
- 11.00 - 12.15 **ROUND TABLE 3**: Sintering processes (second part) (Discussion leader: A. MOCELLIN, Ecole Polytechnique Fédérale, Lausanne, Switzerland)
- P27** / *Electrical evidences in Me-MeO sintering*, D. GOZZI, Univ. La Sapienza, Roma, Italy
- P8** / *Sintering of  $Nd_2O_3$  and ceramic stability to hydration*, J.M. HEINTZ, CNRS, Bordeaux, France, P. POIX and J.C. BERNIER, IPCMS, Strasbourg, France
- 12.15 - 12.30 Concluding remarks
- 12.30 - Lunch and end of the meeting

## STRUCTURE & MICROSTRUCTURE OF GRAIN BOUNDARIES IN CERAMIC MATERIALS

C. Barry Carter

Department of Materials Science & Engineering, Bard Hall, Cornell University,  
Ithaca, NY 14853, USA

### *Abstract*

The purpose of this two-part tutorial is to open the discussion of some of the fundamental concepts of grain boundaries in ceramic materials with extensive use of recent experimental illustrations. Although most of the analysis will concentrate on homophase boundaries (i.e., interfaces between grains of the same structure and composition), examples will also be discussed of heterophase boundaries (i.e., where the structure or chemistry is different for the adjoining grains).

The primary experimental tool used for the analysis of the structure of these interfaces is the transmission electron microscope, both in the conventional diffraction contrast mode and at high ( $<2\text{\AA}$  point-to-point) resolution. In practice, a wide range of imaging techniques are employed and these will be briefly specified during the presentation. The importance of selected-area diffraction for determining local misorientations will also be emphasized.

The materials discussed in this talk will include those with the structures of, or related to, alumina, magnesia and spine! This choice allows the effects of changing crystal structures and chemistry, both separately and together, to be examined and yet covers a wide range of technologically important ceramics; it also allows direct comparison with the much greater and more detailed body of knowledge concerning grain boundaries in metallic systems.

The particular interfaces to be included in the discussion are low-angle grain boundaries, where the structure of the interface can be related to the allowed lattice dislocations with both perfect and partial Burgers vectors, twin boundaries, where either the whole of the crystal is affected by the presence of the interface or where, to a first approximation, only one sublattice is affected, and high-angle grain boundaries. In the latter case, the importance of the grain boundary plane will be emphasized. This factor can be related to both the structure of surfaces in these materials and the structure of other grain boundaries which may be wet by an amorphous phase; these two topics will be dealt with more extensively elsewhere in the program. Finally the relationship between this faceting parallel to certain favored planes and the structures of steps on these interfaces will be considered. In particular, factors affecting the height of such steps will be discussed.

## CERAMIC-METAL INTERFACES

M.G. NICHOLAS, Harwell Laboratory, Oxon, U.K.

Ceramic-metal interfaces are common in nature and are becoming increasingly important in technology. Natural interfaces such as those between carbide precipitates and their metal matrices or oxide films and their metal substrates often display a high degree of structural perfection and mechanical adhesion. However the achievement of adequate structures and properties with synthesised technical interfaces can be difficult because the nature of chemical bonding in ceramics and metals differs. Hence ceramic-metal interfaces can be regions of severe electronic discontinuity that are difficult to create and are poorly bonded. In selecting ceramic-metal systems and processing them to create interfaces it is important to minimise these discontinuities, often by permitting chemical reaction to occur and new microstructures to develop.

High resolution electron microscopy and other advanced techniques are revealing the detailed atomic structures of interfaces but useful guidance about some interface characteristics can be gained also by considering macroscopic characteristics. Thus the non-wetting of many ceramics by common braze metals and alloys can be related to their ionicities and dielectric constants. In practice, if high integrity wetted interfaces are to be synthesised it is usually necessary to change the chemistry and often also the microstructures of the ceramic surfaces, just as in glass-metal joining it is a common practice to promote wetting and bonding by preoxidising the metal surfaces.

Sometimes the chemistries of ceramic surfaces are changed not before but during the joining process; thus reactive species are added to conventional braze alloys to promote the wetting of ceramics. The most favoured additive is titanium, and while the actual interactions of this and other reactive elements with ceramics are complex, some understanding of their behaviour with both oxide and non-oxide ceramics can be gained from simple thermodynamic calculations. These associate the creation of wetting, low energy, interfaces with the formation of hypostoichiometric low valent compounds. To cause wetting, high activities of the reactive species are required and hence the effects of solvent composition on activity coefficients are of importance.

The nucleation and growth of reaction product compounds affects not only the creation of interfaces but also their properties such as strength and toughness. The mechanical properties of interfaces are difficult to treat because of the paucity of reliable data but it is clear that while microstructural changes can be beneficial initially, the growth of thick reaction product layers is usually detrimental. Some theoretical treatments have related to maximum strengths achieved to the chemical reactivity of the additives and certain experimental evidence provides support.

For interfaces created between solid metals and solid ceramics, reaction induced wetting is not required and hence chemically inert combinations can be fabricated by diffusion bonding techniques. Some of these display

lattice perfections akin to those of natural interfaces and have notably good mechanical properties. In many cases, however, reactions do occur during the formation of solid-solid interfaces and once again chemical concepts can be of value in understanding both fabrication behaviour and joint properties.

#### BIBLIOGRAPHY

ELSSNER G., SUGA T., TURWITT M., Structure of ceramic-to-metal interfaces, J. Phys. C4, 46 (1985), 597-612.

NAIDICH Yu, The wettability of solids by liquid metals, Prog. Surf. Membr. Sci., 14 (1981), 354-483.

PASK J.A., From technology to the science of glass/metal and ceramic/metal sealing, Ceram. Bull., 66 (1987), 1587-1592.

PAULING L., The nature of the chemical bond, Cornell University Press, Ithaca N.Y., 1939,

STONEHAM A.M. and TASKER P.W., Oxide interfaces, theory of oxide-oxide and oxide-metal interfaces: in Pask J.A. and Evans A.G., Ceramic microstructures '86 - role of interfaces, Plenum Press, New York 1987, 155-165.

## THE THEORY OF DOPANT AND IMPURITY SEGREGATION IN CERAMIC OXIDES.

R.G. EGDELL AND W.C. MACKRODT

The factors which may lead to dopant or impurity segregation in oxides will be briefly reviewed. Theoretical approaches to segregation will then be introduced (1). Parameterization of the interionic potentials will be considered, including different approaches to treatment of the short range repulsive interactions. Here attention will focus on short range potentials derived from ab-initio calculations on the ions. The role of ion polarisability and its treatment in terms of the shell model will also be discussed (2).

Models for calculating segregation behaviour will then be considered, starting from the heat of segregation at zero surface coverage of the segregant. The possible role of the entropy of segregation will be discussed. A thermodynamic approach to calculation of surface coverage where the heat of segregation is strongly coverage dependent will then be presented and the dangers of assuming Langmuir-type behaviour in experimental work will be emphasised.

The second lecture will involve detailed consideration of a range of selected systems, together with comparison with relevant experimental studies.

Isovalent dopants in MgO will first be discussed. The role of ion size in determining segregation behaviour will be emphasised and effects of relaxation and reconstruction will be introduced (3). Experimental studies of the enthalpy of segregation of Ca in MgO (4) and of the surface structure of Ba segregated MgO (5) will then be treated in detail in relation to the simulation studies. In particular problems of obtaining absolute values for surface segregant coverage and segregant depth profile will be considered.

A briefer discussion of isovalent dopants in  $Al_2O_3$  will follow. Next problems involved in dealing with aliovalent dopants will be introduced and topics such as the formation of new surface phases will be considered in relation to Ti in MgO (6) and Mg in  $Al_2O_3$ .

Finally we will consider the possible role of ionic model simulation work in relation to metallic oxides, including the new families of high temperature oxide superconductors.

## REFERENCES

1. Catlow C.R.A., Computational techniques and simulation of crystal structure in: Solid State Chemistry Techniques eds. Cheetham A.K. and Day P., Clarendon Press, Oxford, 1987 p. 231-278.
2. Catlow C.R.A., Dixon M., and Mackrodt W.C., Interionic potentials in ionic solids in: Computer Simulation of Solids eds. Catlow C.R.A. and Mackrodt W.C., Springer-Verlag, Berlin, 1982 p. 130-161.

- (3) Tasker P.W., Colbourn E.A. and Mackrodt W.C., Segregation of isovalent impurity cations at the surfaces of MgO and CaO. J. Amer. Ceram. Soc. 68 (1985) p. 74-80.
- (4) McCune R.C. and Wynblatt P.W., Calcium segregation to a MgO(001) surface. J. Amer. Ceram. Soc. 66 (1983) p. 111-117.
- (5) Cotter M.D., Campbell S., Egdell R.G. and Mackrodt W.C., Growth of ordered BaO overlayers on MgO(001). Surface Science 197 (1988) p. 208-234.
- (6) Mackrodt W.C., Tasker P.W. and Colbourn E.A., The segregation of titania in magnesium oxide. Surface Science, 152/153 (1985) p. 940-946.

## SEGREGATION IN OXIDE CERAMICS

J. NOWOTNY, Max-Planck Institut für Festkörperforschung, 7000  
Stuttgart 80, FRG

Segregation to interfaces has a severe impact on many phenomena and materials properties such as sintering of ceramics, catalytical processes, transport of matter and electrical phenomena. There has been an accumulation of experimental data indicating that the effect of segregation also has a substantial effect on superconductivity of ceramic materials.

For a long time the studies on segregation have been mainly oriented towards the surface of metals and alloys. In contrast little empirical materials has so far been accumulated for ionic solids, despite of their significant practical importance. Accordingly our knowledge on segregation is still very limited.

In the present paper the bulk vs near-surface defect chemistry of binary metal oxides will be considered in terms of equilibrium segregation of both intrinsic and extrinsic lattice defects. As a direct consequence of segregation, the defect equilibria in the near-surface layer should be considered as a position function with respect to the distance from the surface. Predominant driving forces of segregation in ionic solids will be analyzed and experimental approaches to evaluate the equilibrium segregation will be reviewed for oxide materials of non-stoichiometric composition. Difficulties associated with the determination of reliable surface composition will be considered and a survey of available experimental results will be presented. In this kind of studies it is important to obtain information on equilibrium segregation. In this case, "in situ" studies at elevated temperatures are required when the oxide surface is in equilibrium with the gas phase and the crystalline bulk. In these studies the main effort should not be oriented towards imposition of UHV conditions but on controlling the oxygen activity in the gas phase which is the main parameter determining well defined equilibrium conditions. The surface analysis data obtained for quenched samples should be regarded with caution as quenching may lead to significant changes in the nature of the materials.

Segregation leads to formation of concentration gradients of lattice

elements and resulting electric fields within the near-surface layer. The effect of the near-surface gradients on oxide reactivity will be analyzed. Finally examples will be given on the effect of segregation on the rate of gas-solid equilibration processes in the metal oxide/oxygen system.

The effect of the gas phase composition (oxygen activity) on the extent of segregation will be analyzed. Oxygen activity leads to imposition of intrinsic defects concentration. Segregation of these defects and possible approaches to evaluate the resulting near-surface enrichment will be discussed. The picture of the intrinsic segregation has a direct impact on the equilibria of extrinsic defects. The effect of the gas phase composition on segregation will be illustrated for oxide solid solutions.

Finally the effect of segregation on formation of low dimensional surface structures will be discussed. These structures are formed when the near-surface enrichment of segregated species surmounts a certain critical value. The superficial structures may have a significant, sometimes controlling effect on many materials properties of technological importance such as catalytical properties and superconductivity. Both negative and positive effect of grain boundaries on high  $T_c$  superconductivity have been reported. It will be also shown that segregation has a strong effect on the heterogeneous transport kinetics and diffusion data determined in this way.

Although the main attention will be focused on surface segregation, the grain boundary phenomena will also be shortly discussed.

Basic references in the review articles:

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## GRAIN BOUNDARY DIFFUSION

A. ATKINSON AND C. MONTY

Diffusion at a grain boundary occurs at a different rate from that in the bulk crystalline lattice. In some cases, when bulk diffusion is particularly rapid, transport at a grain boundary may be slower than in the bulk. This situation arises in many solid electrolytes for example. The slow diffusion across the boundary acts as a barrier to mass transport in series with bulk lattice transport and can only be studied by indirect means such as electrical conductivity. More commonly, however, bulk lattice diffusion is relatively slow and boundary diffusion is much more rapid. In this case, which is the subject of this article, diffusion along the boundary acts as an easy (or short circuit) path for transport in parallel with bulk diffusion. It is important in the stability of thin films, the performance of protective coatings, corrosion, sintering and the creep of polycrystalline materials, and can be studied either indirectly (through these phenomena), or directly using tracer atoms.

The experimental approaches to direct measurement of tracer diffusion along grain boundaries are well-established and, in principle, can give the grain boundary diffusion coefficient and the grain boundary width (or, in the case of an impurity atom, the product of boundary width and the segregation coefficient). In polycrystalline materials some average over all the grain boundaries is measured and in single crystals one may observe diffusion along low angle boundaries (dislocation array). To study the influence of boundary structure (misorientation) on diffusion, bicrystal specimens must be used.

Published data cover a range of materials in doped and undoped forms (halides, oxides and carbides), and specimen types (single crystals, bicrystals, sintered powders and thin films), with host atoms or impurities as the diffusing species. In addition, atomistic simulations have been carried out using static lattice methods to help interpret the experimental observations. There is much disagreement in the detailed results in this field, but certain general conclusions are emerging:

- (i) the region of fast diffusivity is only about 1 nm wide.
- (ii) diffusivity increases with increasing misorientation for relatively low angle boundaries.
- (iii) fast lattice diffusers are fast boundary diffusers.
- (iv) boundary diffusion occurs by point defects which are similar to the corresponding lattice point defects.
- (v) boundary diffusion is very sensitive to impurities, many of which can effectively block the boundary as a fast diffusivity pathway.

## SURFACE DIFFUSION AND SURFACE ENERGIES OF CERAMICS with application to the behavior of volatile fission products in ceramic nuclear fuels

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### ABSTRACT

Surface diffusion and matter transport driven by surface tension or surface free energy of solids are phenomena which are well known to material researchers. For example, the change in surface energy provides the driving force for material transport during sintering which, in some stages, can be rate-controlled by surface diffusion. Surface diffusion of matrix atoms can also provide bulk mobilities of gas-filled bubbles. Also, the formation of equilibrium surface states at high temperatures can be influenced by surface diffusion, though evaporation - condensation processes and volume diffusion in surface-near layers are always competing and often dominating mechanisms. Finally, most materials researchers will recall the visual impression of actual jumps of atoms by surface diffusion from field emission microscopy on metal tips.

In contrast to the importance of surface diffusion, relatively few reliable data sets for surface diffusion exist, in particular for ceramics. Most work has been devoted to metals but even this work is only a very small fraction of that devoted to lattice diffusion. However, a number of experimental techniques has been developed in this work on metals. Examples are tracer methods with a point source, an edge source or a half source, and techniques not using tracers but rather involving surface smoothening of different types, e.g. of scratches or of sinusoidal surface profiles, and grain boundary grooving. Additional data can e.g. be derived from well defined sintering experiments, e.g. sintering of sphere-to-sphere, sphere-to-plane, wire-to-wire or wire-to-plane. Often, a surface diffusivity product  $\alpha D_s \delta$  is obtained, where  $D_s$  is the desired surface diffusion coefficient,  $\alpha$  is a segregation factor and  $\delta$  is the thickness of the high diffusivity surface layer.

The available data for ceramics (mainly oxides  $\text{MgO}$ ,  $\text{NiO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{UO}_2$ , and recently  $\text{Fe}_3\text{O}_4$ , but also carbides like UC) are discussed. Often, effects of evaporation - condensation interfere with surface diffusion on ceramics which therefore often can only reliably be measured at comparatively low temperatures. For surface diffusion on oxides, mechanisms very similar to those of bulk diffusion are indicated.

Surface energies  $\gamma$  can a priori also be deduced from experiments similar to those for surface diffusion. Grooving and surface relaxation measurements yield usually the product  $\gamma D_s$ . Other techniques, such as wetting or the multi-phase equilibration technique yield independent values of  $\gamma_s$ , and indentation methods (Hertz or Vickers) yield supporting results on (fracture) surface energies. Computational methods are also available and were applied to some ceramics. Again, as for  $D_s$ , available data on  $\gamma_s$  are critically discussed.

The available knowledge is applied to a description of the operational performance of ceramic nuclear fuels, and in particular to the behavior of gaseous fission products. Mobility of rare-gas bubbles rate-controlled by surface diffusion is indicated for specific conditions in all types of ceramic nuclear fuels, oxides, carbides and nitrides. Phenomena interfering with the resultant fast mobility of rather large bubbles exist during most irradiation and operation conditions and are discussed in detail as well.

## FRactal SURFACES IN DIFFUSION AND CORROSION

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Fractal geometry (MANDELBROT B.M.) may be used to describe many statistical objects or phenomena like random walks. We will show how fractal geometry permits to describe diffusion fronts in 2 or 3 dimensions (SAPOVAL B. et al. 1985, SAPOVAL B. et al. 1986, ROSSO M. et al. 1986, GOUYET J.-F et al. 1988).

This geometry can appear in mixed objects made with a juxtaposition of different homogeneous components or crystallites as minerals or ceramics. Ceramics are produced by high temperature sintering. In all these systems, diffusion is present and fast at the temperature where interfaces are formed. Chemical species travel over semi-macroscopic distances. In this situation the question of the very geometry of the interfaces which are formed may be of interest. Often, when the temperature is lowered, the thermally activated diffusion is slowed down so efficiently that, most probably, a memory of a diffusion state geometry is kept in many systems. In that sense a "diffusion geometry" may be quenched.

We shall study the geometry of the interface between two media through an approach which is opposite to the usual "low temperature" picture. We shall consider a "high temperature" situation in which the interface geometry is the consequence of random diffusive motions of the constituents. This is the subject of the study of "diffusion fronts".

We show that the problem of the diffusion front geometry is very closely related to the problem of "percolation in a gradient" ( SAPOVAL B. et al. 1985, ROSSO M. et al. 1985)

We shall also observe that diffusion interfaces are unstable in a surprising manner : they do fluctuate at frequencies much higher than the average probability per unit time for atomic jump. Fluctuations of diffused interfaces may then be a source of noise in heterogeneous systems which could be otherwise considered as quenched.

There exists a close relation between the diffusion front and a conceptually different but similar object : an invasion front. Invasion is a basic mechanism for the semi-macroscopic propagation in a random macroscopic medium (WILKINSON D. and WILLEMSSEN J.F). For example when pouring water on sand, water invades the space between the grains. Many chemical treatments of raw material involve such a process which may also play a role in the way hot corrosion finally breaks through an anti-corrosion layer ( TAM S.W. and KYLES K.M.).

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## INTERGRANULAR PHASES IN POLYCRYSTALLINE CERAMICS

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One of the most revealing findings produced during the examination of ceramics using the techniques of high resolution transmission electron microscopy has been the fact that many of these materials contain a thin intergranular (generally siliceous) glass phase. Such phases have been observed in almost all structural ceramics including the silicon nitride based materials, the majority of transformation toughened zirconia alloys, nuclear waste ceramics, and the majority of alumina ceramics. It has been observed that the intergranular phase is both continuous throughout the microstructure and, significantly, is located at the majority of grain boundaries (two grain junctions). Furthermore, the thickness of the intergranular glass phase can be quite small, being 0.8 nm to 2 nm, in some silicon nitride and zirconia ceramics. These intergranular phases are believed to be the remnants of a liquid phase present during the liquid phase densification of the ceramics.

As presently understood, the presence of a remnant intergranular glass phase can be produced by a number of different processes. In many ceramics, the phase results from the liquid phase sintering process used to densify them. Examples of these include the silicon nitride alloys, the zinc oxide varistor materials, and alumina substrate materials. (In these materials, particularly the covalent ceramics, additives are deliberately added to the powders before sintering so as to promote or facilitate densification during firing). In others, such intergranular films are present because the materials are prepared by the controlled but incomplete crystallization of a glass (glass-ceramics). A third, but practically important category, is that in which the phase forms from the impurities present in the starting materials. For instance, a number of the ceramics developed for nuclear waste encapsulation and certain of the polycrystalline, tetragonal zirconia ceramics contain such intergranular films. In all these instances, the existence of the intergranular phase is the result of the inability of the crystalline phases to accommodate into solid solution the constituents of the intergranular phase and the inability of the constituents to crystallize out as distinct phases. The former appears to be particularly marked, again, in the case of the strongly covalent materials. (In many respects the microstructures in many ceramics may be likened to the liquid layer grain boundary model for metals introduced by Rosenhain and current during the early decades of this century).

The presence of such a glass phase can have a profound effect on the properties of such polyphase ceramics. For instance, the unique electrical properties of a number of electrical ceramics, such as the barrier layer capacitors, results from the presence of an intergranular phase. It is also well established now that many of the high temperature

properties (creep deformation, creep fracture, oxidation and corrosion resistance) of the silicon nitride based ceramics are determined by the properties of the intergranular glass phase at these temperatures. This growing recognition of the roles of the intergranular phase has spurred interest in how the wetting behavior of such films can be altered and, perhaps, controlled. In the liquid phase sintering process it is envisaged that the crystalline grains precipitate and grow from out of the liquid phase. As they grow their surfaces approach one another with a consequent decrease in thickness of the intergranular phase until an equilibrium value is attained. In discussing the intergranular phase it has generally been assumed that it behaves as a liquid at high temperatures, and that the pertinent microstructural features of the phase are frozen in when the materials are cooled for subsequent examination at room temperature by, for instance, transmission electron microscopy.

This tutorial reviews the current concepts concerning the stability of intergranular phases in polycrystalline ceramics, and in particular addresses the questions as to why grain boundaries are wet, what determines the observed thicknesses, the structure of the glass phase, and how a boundary might be dewet. In addition, the role of the intergranular phase in providing a short circuit diffusion path through the microstructure and its consequences for the macroscopic properties of ceramics will be described. Finally, a number of ways in which the presence of an intergranular phase might be exploited in altering the properties of a polycrystalline ceramic will be outlined.

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THERMODYNAMICS, CHEMISTRY AND MICROSTRUCTURE OF METAL-CERAMIC INTERFACES.

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Abstract

The fundamentals of metal-ceramic bonding include the wetting of a solid ceramic by a liquid metal or vice versa, the effect of the gas atmosphere on the interaction of the materials and the kinetics of chemical reactions at the interface between the materials.

The type of interaction can be of physical and of chemical nature, depending on the properties of the selected materials, and this determines the interface morphology. This aspect is of great technological importance since it determines to a large extent the properties of the metal-ceramic bond whether it is related to electrical or to structural ceramics.

In this lecture the bonding of metals to ceramics will be considered from the equilibrium thermodynamics point of view which includes the topics mentioned above. This will be illustrated by the description of reactions in metal-oxide ceramic and metal-nonoxide ceramics ( $\text{Si}_3\text{N}_4$  and  $\text{SiC}$ ).

From this approach the conditions for a metal-ceramic reaction to proceed can be predicted and it also gives indications to the chemical stability of the metal-ceramic bond.

Attention will be given to the presence of impurities in the materials and the effects of their segregation to the metal-ceramic interface.

Finally the effects of the interface morphology on the strength of metal-ceramic bonds will be briefly discussed.

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## MICROSTRUCTURE OF COMPOSITE INTERFACES AND ITS RELATION TO INTERFACIAL STRENGTH

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An important method in the manufacture of composites with high toughness is the reinforcement of a brittle material by high-strength fibers. The strength and toughness of the composite then depends on the interfacial shear strength,  $\tau$ , between the fibers and the matrix. The fibers themselves are also usually made of brittle materials such as SiC or TiC. Since both the matrix and the fibers are brittle, a strong interfacial strength results in easy propagation of the cracks from the matrix into the fibers and the subsequent catastrophic failure of the composite. On the other hand, weak interfacial strength between the fibers and the matrix leaves the fibers intact during crack propagation in the matrix resulting in a bridging of the matrix crack by the unfailed fibers. Because of this bridging effect, the opening of the crack surfaces is restrained and the composite has a higher toughness. It then fails in a non-catastrophic manner through the pullout of fibers from the matrix.

In general, the interfacial shear strength depends on the debonding of chemical bonds at the interface between the fiber and the matrix, and the frictional sliding between the fibers and the matrix. In many cases, the chemical bonding is negligible, of the order of Van der Waals forces, and the interfacial shear strength is then approximately equal to frictional sliding stress. On the other hand, in some other systems, the bonding makes a significant contribution to the interfacial shear strength. This is specially true at higher temperatures where chemical reactions may take place at the interface resulting in stronger chemical bonds.

An important technique for the direct measurement of the interfacial shear strength is the method due to Marshall<sup>1</sup>. It is based on loading an indenter at the center of a fiber, normal to the fiber axis, and measuring the relative displacement of the fiber and matrix at a given load. Depending on the thickness of the specimen, the fiber surface may either be depressed below the matrix surface without the fiber being pushed out of the matrix (here termed as the "push-in" technique), or, it may be actually pushed out of the specimen (here termed as the "push-through" technique). In the latter case, the interfacial shear strength,  $\tau$ , is independent of the relative displacement of the fiber and matrix and can be calculated from the applied force and the dimensions of the fiber. Because, in general, the fibers in a composite are not uniform in alignment, or in diameter, and because of non-uniformity of the fiber/matrix interface due to inhomogeneities in processing, the determination of interfacial shear strength by the Marshall technique is basically statistical. Also, although the technique is compressive in nature, the measured interfacial strengths do not seem to be significantly different from those obtained by fiber pullout in tensile cracking<sup>2</sup>.

In the present work the push-through technique has been applied to a composite consisting of SCS-6 AVCO SiC fibers set in a reaction-bonded Si<sub>3</sub>N<sub>4</sub> matrix. The interfacial shear strength has been measured in vacuum as a function of temperature by using a hot hardness machine up to 1350°C. In general, there is an increase in the interfacial shear strength from values as low as 5 MPa at room temperature to ~31 MPa at 1350°C. This seems to be mainly due to thermal mismatch, i.e.

different coefficients of thermal expansion between the fiber and the matrix; however, changes in the interfacial bonding with temperature cannot be ruled out.

When the tested specimen, with the pushed out fibers, is subsequently turned around and the fibers are pushed back in, it is found that the interfacial shear strength,  $\tau_2$ , is generally lower than  $\tau_1$ . An estimate of the bonding contribution to the interfacial shear strength may then be obtained by subtracting  $\tau_2$  from  $\tau_1$ . This is based on the assumption that in the first step, i.e. the push-through stage, the chemical bonds are broken and therefore do not make any contribution to the interfacial shear strength in the second step, i.e. the push-back stage. Preliminary experiments at room temperature, using this technique has shown that the bonding strength in the present system is at least 3-5 MPa.

The SCS-6 fibers in the composite have been investigated in cross-section by transmission electron microscopy (TEM)<sup>1</sup>. The fiber is a complicated composite in itself consisting of a non-graphitic carbon core at the center (~32  $\mu\text{m}$ ). Moving out from this central carbon core, there is a ~1.5  $\mu\text{m}$  layer of turbostratic carbon, an inner SiC coating (~21  $\mu\text{m}$  thick), an outer SiC coating (~29  $\mu\text{m}$  thick) and an outermost coating of turbostratic carbon. This latter coating itself consists of an inner and an outer carbon layer (each ~2  $\mu\text{m}$  thick) with SiC particulates, and an intermediate ~0.2  $\mu\text{m}$  layer which is completely free of SiC. The pushed-out fibers have been investigated by Tolanski interference microscopy and scanning electron microscopy (SEM). In the majority of cases, the fiber failure occurs at the intermediate thin carbon layer, which is free from SiC particulates, within the outermost coatings of pyrolytic carbon. However, in some cases, the failure takes place at the interface between the second SiC coating and the inner layer of turbostratic carbon. The results of this microstructural investigation are related to the determination of the interfacial shear strength and the variation of the latter with temperature are discussed.

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## CERAMIC MEMBRANES AND NANOSCALE COMPOSITE LAYERS AND MATERIALS

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Synthesis methods to obtain nanoscale materials will be briefly discussed with a focus on sol-gel methods.

Two types of nanoscale composites (membranes and ion implanted layers) will be discussed and exemplified with recent original research results.

Crack and defect free ceramic membranes with a thickness of 1-10  $\mu\text{m}$  consist of a packing of elementary particles with a size of 3-7 nm. The smallest obtainable mean pore size is about 2.5-3 nm and the pore size distribution is sharp. The preparation routes are based on sol and sol-gel technologies. The pores can be modified by liquid as well as by gas deposition techniques. This leads to modification of the chemical character and the effective pore size and give rise to microstructure elements well below the size of the pores (3 nm).

In this way membranes of  $\gamma\text{-Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{CeO}_2$ ,  $\text{RuO}_2$ , C and/or combinations of them has been produced, starting with sol particles of 2-7 nm. The structure is modified with metals (Ag), hydroxides and oxides of Mg, Al, V or Fe, and with aluminosilicates. By these modifications the pore size is further decreased and/or the chemical character of the surface is changed. This influences the transport properties and introduces catalytic properties. The membranes are suitable for liquid or gas (vapour) separation and in membrane reactors they can be used for influencing the conversion and selectivity of chemical reactions. Some illustrative results will be given [1-4].

The modification of ceramic surface layers with a thickness of 0.05-0.5  $\mu\text{m}$  by ion implantation and annealing procedures yields amorphous or strongly supersaturated metastable solid solutions of e.g.  $\text{Fe}_2\text{O}_3$  (or  $\text{TiO}_2$ ) in Zirconia-Yttria solid solutions or of very finely dispersed metal particles in the ceramic surface layers. Particle sizes are of the order of 2-4 nm. Both types of structures have interesting transport and catalytic properties and mechanical properties [5,6].

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## ELECTRON SPECTROSCOPIC DETERMINATION OF THE GEOMETRIC AND ELECTRONIC STRUCTURE OF OXIDE SURFACES.

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The surfaces of metal oxides display a rich array of complex electronic and geometric structures. This is due in part to the diversity of their bulk electronic properties, which range from highly localized to itinerant; some of the most fascinating oxides exhibit electronic properties that have both localized and band-like components. Although the technological uses of oxides generally involve powders or polycrystalline thin films, detailed information on basic surface properties can only be obtained on more nearly ideal surfaces. This lecture will consider the ways in which surface-sensitive electron spectroscopies have been used during the past few years to study the properties of single-crystal surfaces prepared in an ultrahigh vacuum environment. Nearly perfect surfaces are generally prepared by cleaving in vacuum. Relatively low energy electron spectroscopies are then used that sample only the first few atomic layers of the surface.

Detailed determination of the positions of atoms on oxide surfaces has been performed primarily by using low-energy-electron diffraction (LEED). Only a few different oxides have been studied to date. Rocksalt monoxides have surface structures very similar to that of the bulk, with only a few percent relaxation or rumpling of the outermost atomic layer. Some other oxides having more open surfaces exhibit somewhat more rumpling. Only preliminary studies of surface geometry have been conducted to date using the scanning tunneling microscope. (The atomic force microscope does not yet have sufficient resolution to differentiate individual surface atoms on oxides.) The chemical composition of oxide surfaces can be determined by using Auger electron spectroscopy or x-ray photoelectron spectroscopy (XPS).

The most fruitful technique for studying the electronic structure of valence and conduction bands on oxide surfaces is ultraviolet photoelectron spectroscopy (UPS). The binding energies of the core levels of surface atoms can be determined by XPS; the shape of core level photoemission peaks also gives valuable information about surface structure. Using the tunable radiation obtainable from synchrotrons and storage rings, the spectrum of empty electronic states can also be studied. Inverse photoelectron spectroscopy and electron energy loss spectroscopy also give information on empty electronic states.

Nearly perfect (i.e., cleaved) surfaces of metal oxides generally exhibit an electronic structure that is very similar to that of the bulk. Although the ligand coordination of surface cations is reduced from that in the bulk, the surface cations generally retain their bulk electronic configuration, with little or no change in valence state. For some transition-metal oxides, however, differences between bulk and surface structure are observed. Theoretical electronic structure calculations have been performed for perfect surfaces of a few oxides, and there is general agreement between theory and experiment. The case of surface defects will be treated in the next lecture.

The adsorption of a variety of molecules on nearly perfect oxide surfaces has been studied by several techniques. UPS has been particularly valuable in determining the molecular orbital structure of adsorbed species. High resolution electron-energy-loss spectroscopy (HREELS) has been used to measure vibrational frequencies of adsorbed molecules, although the very strong surface phonon modes that exist in ionic materials complicate the interpretation of the spectra. Nearly perfect surfaces of maximal valency oxides are generally virtually inert. Suboxide surfaces are considerably more reactive, although there are large differences in their interaction with various molecules. The largest reactivity occurs for surfaces containing defects; that is the subject of the following lecture.

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## THE ROLE OF DEFECTS IN THE ELECTRONIC STRUCTURE OF AND CHEMISORPTION ON OXIDE SURFACES

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As discussed in the previous lecture, nearly perfect surfaces of metal oxides generally exhibit an electronic structure essentially the same as that of the bulk, even though both cations and anions have a reduced ligand coordination at the surface. Even oxide surfaces possessing a high density of steps, where the ligand coordination is still further reduced, do not exhibit distinguishably different electronic properties. Thus ligand coordination *per se* does not seem to be the dominant factor in determining surface electronic properties. Large changes in surface electronic structure occur, however, when point defects are present on oxide surfaces. The most prevalent type of defect on oxides is a surface oxygen vacancy, which can be produced in a controlled way in the laboratory by ion or electron bombardment or by heating to high temperatures and quenching. Since the oxygen ions in oxides are essentially  $O^{2-}$ , removal of a surface  $O^{2-}$  ion requires that roughly two electrons be trapped at the resulting vacancy in order to maintain local charge neutrality. Cluster calculations have been performed for a few specific point defects on oxides, and the trapped charge is found to be localized in the region of the missing  $O^{2-}$  ion and on the cations adjacent to the defect. Thus, to first order, one can talk about the electronic structure at point defect in terms of an increase in charge on surface cations.

For insulating or semiconducting oxides, surface defects generally increase surface conductivity. The one notable exception is  $CoO$  (100), where creation of a small number of point defects decreases the conductivity. This is presumably due to the conversion of  $Co^{2+}(3d^7)$  ions to  $Co^{3+}(3d^6)$  on the surface; increasing the charge to  $3d^6$  fills the  $a_{1g}$  orbital, thus stabilizing the cation electron configuration.

Surface point defects are generally the active sites for chemisorption on oxides (although a few cases have been found in which defects are less active than perfect terraces). The surfaces of maximal valence oxides such as  $TiO_2$  are nearly inert to  $H_2O$  into  $OH^\cdot$  radicals in the presence of defects. The (11 $\bar{2}$ 0) cleavage surface of the suboxide  $Ti_2O_3$  adsorbs  $H_2O$  molecularly, but when point defects are present  $H_2O$  dissociates, hydroxylating the surface.

Recent studies of the interaction of sulfur-containing molecules with oxide surfaces have yielded surprising results.  $SO_2$  is found to oxidize the surfaces of titanium oxides much more rapidly than does  $O_2$ . The  $SO_2$  dissociates, with the S atoms catalyzing the oxidation of the surface. On the contrary, exposure to  $H_2S$  stabilizes the reduced electronic structure at defects and inhibits or halts oxidation of the surface by  $O_2$ .

Both UPS and HREELS have also been used to study the interaction of other molecules with oxide surfaces.  $O_2$  normally dissociates at defect sites, while for large  $O_2$  exposures there is evidence for adsorbed  $O_2^-$ . On  $NiO(100)$   $H_2O$  will not stick on either perfect or defect surfaces unless the surface has been pre-exposed to  $O_2$ .  $MnO$  is unique in that both cleaved and defect surfaces interact strongly with several molecules.

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SOLID-GAS AND SOLID-SOLID INTERACTIONS OF CERAMIC MATERIALS  
AT HIGH TEMPERATURES

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In the interaction of gases and ceramics the solubility of nonmetal atoms such as H, C, N, S and Cl in oxides is a first point of interest. C. Wagner /1,2/ has discussed the solubility of  $H_2O$  and H in solid oxides and proved the solubility of  $H_2O$  in  $ZrO_2 \cdot Y_2O_3$ . Permeation, diffusion and solubility of hydrogen were demonstrated for  $TiO_2$  and  $Al_2O_3$  /3/. Several authors /4-7/ had claimed a solubility of C in oxides such as  $MgO$ ,  $FeO$ ,  $MnO$ ,  $Cr_2O_3$ ,  $Al_2O_3$ ...and tried to explain some peculiar kinetic phenomena with effects of dissolved C, however, careful investigations with radiotracer methods have shown that there is virtually no solubility ( $<0.01$  ppm) /8/, the same applies for sulfur and chlorine. Even hydrogen seems not to permeate  $Cr_2O_3$  if the material is really dense /9/.

Oxides can be oxidized to oxides with higher cation valencies or can be reduced to lower oxides or to the metal, - the oxidation and reduction also can take place within the range of nonstoichiometry of the oxide. Such reactions in  $CO_2$ -CO or  $H_2O$ - $H_2$  had been studied in detail for an oxide with high reactivity, i.e. wustite  $FeO$  /10-12/. The rate laws of the surface reactions in the oxygen transfer to and from the solid are discussed for  $FeO$ , in principle they also can be applied on very stable oxides. However, for example in the reduction of  $Cr_2O_3$  by  $H_2$  the diffusional transport of the  $H_2O$  generated from the surface into the gas flow is rate limiting, except for very high flow rates /13/. Since  $Cr_2O_3$  is of great importance as the protective oxide layer forming on Fe-Ni-Cr and Ni-Cr-base high temperature alloys, also its conversion to chromium carbides by carburizing gas mixtures has been studied /14,15/, its evaporation as  $CrCl_2$  in  $H_2$ - $H_2O$ -HCl mixtures /16/ and the evaporation of  $CrO_3$  in high  $pO_2$  environments at high temperature.  $Al_2O_3$  is much less reactive than  $Cr_2O_3$ .

Si containing ceramics,  $SiC$ ,  $Si_3N_4$  but also silicates are endangered at high temperatures in reducing atmospheres by  $SiO$ -evaporation. There is an active/passive transition for the oxidation of Si,  $SiC$  and  $Si_3N_4$  in dependence on  $pO_2$  /17,18/. The compounds  $SiC$  and  $Si_3N_4$  must form a dense vitreous  $SiO_2$ -layer to be protected against oxidation at high temperatures. Silicates are also reacting with volatile anorganic compounds  $Na_2O$ ,  $PbO$ ...to form glasses.

Solid-solid interactions rarely play a great role in reaction kinetics since the physical contact of the solids may be lost very fast. In most cases the presence of gases, vapors or liquids must guarantee the transport of matter, necessary for reaction. Even in HIPping solid-gas and solid-liquid interactions play a predominant role /19/.

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## MECHANISMS INVOLVED IN CHEMICAL VAPOR DEPOSITION AND EVAPORATION OF CERAMICS AT HIGH TEMPERATURE.

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Ceramics can be obtained by many techniques and mainly by powder processes such as sintering. They can also be grown from vapor phase. This technique where the molecules react at a heated surface, is called Chemical Vapor Deposition (CVD). Numerous attempts have been made to obtain a better understanding of the mechanisms involved in such a process but direct evidence is still lacking. Many reviews have dealt with this subject [1-5] and general trends used in modelizing the various steps of the process are presented and compared.

Most of the models used to represent the species fluxes, and thus the growth rate, assume the stagnant gas layer hypothesis. In this case the diffusion layer, the thermal boundary layer and the stagnant layer are supposed to be the same. The various hypotheses concerning the distribution of temperature and gas velocity only give minor changes in the results of the calculation [6]. Determination of the boundary layer thickness is obtained either from hydrodynamic calculation [7] or from experimental results through adimensional equations [8]. More complicated models take into account gas phase reactions [9-11] and the variation of the physical properties of gases with temperature and pressure in the neighbourhood of the substrate but many data concerning these quantities are still lacking.

A simple theoretical model [12] gives a good understanding of the influence of two important parameters in CVD : temperature and supersaturation of reactive species which both control surface phenomena. Building of ceramics from the surface involves adsorption, diffusion and growth with or without nucleation. The basic modes of growth are reviewed in the literature [13] and have been extrapolated to CVD surface processes. Mechanisms based on surface coverage concept with two adsorbed species (Langmuir-Hinshelwood) or one adsorbed species and a molecular gas (Rideal-Eley) have been used to explain variations in growth rate [14]. Inorganic precursors can adsorb onto a surface at some appreciable fraction of their saturated vapour pressure and give multilayer adsorption. A liquid may also be present on the surface and crystals are in this case grown by the VLS (Vapour-Liquid-Solid) mechanism [15].

Modern theories on nucleation and growth [16] are supposed to be applicable to the CVD process [16]. In practice if we exclude homoepitaxial growth for electronic devices these models have not been used and in the case of heteroepitaxial growth of ceramics only general trends are admitted. With respect to temperature and supersaturation the morphology of deposits can range from amorphous to epitaxial growth but a polycrystalline structure with columnar grains is the most common form for structural applications.

Without any assumption as to the mechanisms the thermodynamic calculation of the overall equilibria, whether they are kinetically or diffusionally controlled, can provide valuable information on the composition of the deposit as well as on the interactions with the substrate [18-19]. Some examples are given in the case of titanium carbide or nitride deposition [20-21]. These compounds are always obtained under almost stoichiometric composition although they exist over a wide range of C(or N)/Ti ratios. This behavior and the interactions with the substrate are explained from a thermodynamic point of view.

The general trends on non-reactive evaporation mechanisms of ceramics at high temperature are presented, and the main experimental techniques with respect to the information obtained are described. In the case of Langmuir evaporation three classes of mechanisms can be defined [22] which are illustrated with several compounds [23,24]. The main feature of vacuum evaporation is the coefficient necessary to represent the departure from the ideal process under equilibrium. Some physical interpretations of this coefficient are given.

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# REACTIONS OF CERAMIC OXIDES WITH AQUEOUS SOLUTIONS (INCLUDING DISSOLUTION)

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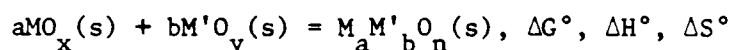
Traditional ceramic oxides are in general very resistant to attack by water and aqueous solutions; new materials however are not always impervious to the attack from water solutions, and the ensuing degradation places a limit to their durability.

Thermodynamics. For the case of simple binary oxides  $MO_n$ , three different categories of chemical reactions must be considered to take into account possible corrosive attack: a) hydrolysis behavior of  $M^{2n+}$  ions, and solubility of the oxidic phases; b) redox chemistry of  $M^{2n+}$ ; c) complexation chemistry of  $M^{2n+}$  (by ligands other than  $OH^-$  and  $H_2O$ ).

The thermodynamics of the first two types of reactions are usually summarized in the form of Pourbaix's diagrams that show the stability field of various oxides as a function of solution pH and redox potential. Attack (dissolution) may take place when aggressive conditions are established by changing pH and/or  $E_H$ .

In principle, the influence of complexation chemistry can be described also by Pourbaix-type diagrams if information is available regarding the stability of different complex species. For each ligand, the complete description requires the explicit consideration of one more variable, the ligand concentration.

For mixed oxides  $M_aM'_bO_n$ , a fourth type of chemical reaction must be considered. This category includes the formation from the binary oxides:



and any other possible phase transformation yielding other ternary phases. As the complexity of the oxide is increased, the manifold of reactions becomes very large, and in many cases there is no detailed experimental information. The mixed oxides of high  $T_c$  are a good example of these complexities.

Kinetics. Many oxides may be reasonably stable in contact with water even outside the range of thermodynamic stability, because of sluggish chemical kinetics. Attack of the oxide by solution constituents is a heterogeneous process implying: a) diffusion of attacking species to the surface; b) surface chemical reactions; c) diffusion of metal ions and other species to solution bulk. Any of these stages may control the overall rate. Diffusion control, in the case of ceramic oxides, is associated with phase transformation reactions that give rise to a surface layer of a second, more passive, solid phase. In the case of highly reactive oxides, the pretreatment to yield such a passive layer may be required;  $CrO_2$  is a good example.

Surface chemical reactions of various types may be involved in corrosive attack. In general, they may be classified in the same three groups mentioned before: acid-base attack, redox reactions and attack by complexing agents. The inertness of M-O bonds to acid attack (outside the thermodynamic range of stability) is governed by the oxidation state of M, by the coordination

number ( $O^{2-}$  ions of high coordination number are in general more resistant), and, of course, by the defect structure of the sample (in bulk and in surface). Redox attack or redox catalysis is often responsible for corrosive behavior under conditions where acid attack per se would not be severe; in fact, the more resistant oxides are those of metal ions not very likely to get engaged in electron exchange reactions (e.g., zirconium (IV)). Corrosive attack by complexing ions may be a serious problem for certain uses, such as solar energy transduction. Particularly aggressive are in many cases halide ions (fluoride, chloride) or certain organic reagents that form very stable complexes. The well-known case of hydrofluoric acid attack on silica is a good example. On the other hand, complexing agents of larger molecular size may passivate the surface through irreversible adsorption (e.g. oligomers and polymers with carboxylic groups).

The sol-gel route to ceramics. In a sense, the above corrosive processes are the reverse of the sequence of reactions involved in the preparation of ceramic precursors in aqueous media. Because of the drastic changes in the coordination sphere of the metal ions in either case, the more stable ceramic oxides cannot in general be prepared directly from aqueous solution, without intervention of metastable phases. In particular, amorphous hydrous oxides are usually first precipitated through olation and oxolation reactions, and only later evolve to crystalline varieties. The more sluggish oxides (e.g. amorphous  $Cr_2O_3 \cdot x H_2O$ ) require drastic conditions for crystallization, whilst in other case dissolution-recrystallization mechanisms in aqueous media are conducive to crystalline materials.

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## IONIC CONDUCTIVITY AND THE ROLE OF SURFACES AND INTERFACES IN CERAMIC ELECTROLYTES

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A large variety of functional properties of ceramic materials has been discovered during the past two decades. Several new types of practically important devices appear to be possible and many existing may be improved by better materials. Among the most interesting properties are extraordinarily electrical transport phenomena of fast predominantly ionic and mixed electronic-ionic conductivity. The applications that appear to be possible include solid state batteries (primary and secondary type), fuel cells (oxygen and hydrogen), high temperature water electrolysis cells, chemotronic elements (timers, memory elements), electrochromic displays and sensors.

Practical reasons require the application of polycrystalline materials, either as bulk phases or as thin films. In addition, all applications require the application of electronic leads or electrodes. Even in the case of open circuit voltage measurements, an electrical current has to pass across the interfaces which includes oxidation and reduction processes.

The transport of ionic species across and along grain boundaries shows resistances which are typically of a similar order of magnitude as in the bulk as long as major chemical changes (e.g., by segregation) may be excluded. The impedance depends strongly on the preparation and treatment. The process of ionic transport across hetero-interfaces is frequently strongly impeded. The often activated transport generally requires temperatures much higher than those expected from the point of view of bulk and grain boundary resistance. A general description and understanding of the details of the electrode/electrolyte interface processes is presently missing, even in the case of technologically important applications such as gas sensors. The available experimental data will be presented and the various models will be discussed.

## SURFACE DETERMINED PROPERTIES IN SILICATE GLASSES

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It is normally assumed that glass surfaces are inert, this is why glass is frequently considered as the container material of choice. However, anyone that has ever worked with a vacuum line or looked at the chemical or biological activity of glasses knows otherwise. Furthermore, when treated in specific ways, glass surfaces can be rendered extremely reactive. This presentation will deal with particular treatments which have been shown to greatly modify the activity and properties of glasses.

A problem with the understanding of glasses is that their structures are typically poorly defined. As an amorphous solid the surface is much less regular and more difficult to describe, than crystalline solids. Results of various analytical techniques will be presented so as to offer a better characterization of the glass surface.

Mechanical failure of this brittle material has been attributed to the existence of Griffith—Flaws and the associated free ion diffusion concepts used to model crack growth. However, this theory has consistently failed to provide complete agreement with the experimental results. This dilemma coupled with the reports of single-valued strengths in fibers cannot be rationalized by the modification of the intrinsic Griffith-flaw distribution to essentially a delta function.

It is for these reasons that the field-enhanced ion diffusion model has been introduced. The inclusion of a term for the electrostatic potential in the thin-film solution of Fick's second law has been shown to be consistent with the experimental results. Therefore, the effects on alkali ion migration as a consequence of the local variations in charge density that occur on the solution side of the glass/water interface play a direct role on the chemical corrosion mechanism. Thus chemistry which can modify the surface potential can alter the rate of ageing of glass.

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## PHYSICAL AND CHEMICAL PROPERTIES OF SILICATE MATERIALS

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Both crystalline and vitreous silicate materials are interesting substances from the point of view of basic research as well as technological application. This is also true for geological and geophysical applications.

Until now, only few model systems for simple crystalline materials are well understood: the orthosilicates. The available data on their crystal chemistry and thermodynamic behaviour will be used to model their defect thermodynamics. Experimental values from thermodynamic measurements and spectroscopic information together with computer simulations serve to reduce the number of possible point defects.

On the basis of these ideas, ionic and electronic transport phenomena will be discussed. Interdiffusion reactions, formation of new phases in the solid state and high temperature creep can be interpreted.

For vitreous silicates the situation is more complex. For some simple pseudo-binary glasses, thermodynamic and transport data are available which can be interpreted on the basis of current structural models. For many reasons the chemical reactions between glasses and aqueous media are most important. Recent results on the different stages of these complicated reactions in a model system are interpreted. Special emphasis is given to the early stage of corrosion of fracture surfaces. As a further example bioglasses are considered in some detail.

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## CHARACTERIZATION, PROPERTIES AND PROCESSING OF CERAMIC POWDERS

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The interfaces that ceramic powders present to the outside world is very important in controlling their properties during processing. There are two types of fundamental inter-particle forces : attractive and repulsive. The summation of induced dipole forces in two particles was first performed by Hamaker giving an attractive force called "Van der Waals force". There are two other type of forces, electrostatic and steric. In some cases electrostatic and steric forces can be attractive or repulsive. When the particles have the same charge, caused by the adsorption of ions from solution, the electrostatic force between the particles is repulsive. When the particles have different charges, the electrostatic force is attractive. The exact form that this electrostatic force takes is still under debate. However with some simplifications electrostatic solutions exist. They take the form of a scaled exponential where the scalling parameter, the Debye Length, depends on the ion concentration in solution. Therefore to alter electrostatic forces it is necessary to adjust the ionic strength in solution and control the amount of the adsorption of potential determining ions. The last type of force is a steric force controlled by the adsorption of polymers at the surfaces of ceramic particles. Depending upon the interaction energy between the polymer and the solvent, you can have either attractive or repulsive steric forces. When the polymer likes itself better than the solvent, flocculation results between the particles, which is the result of an attractive force. When the polymer likes the solvent better than itself, steric stability of suspension is obtained with a strong repulsive core interaction energy. To effect the steric force you must control the adsorption of polymer from solution (i.e. the surface coverage) and the interaction energy between the polymer and the solvent. In principle, this is done by minor modifications in the structure of the polymer, the molecular weight of the polymer and the functional groups within the polymer and solvent. In some processes, it is desired that a suspension be stable. A clay and water suspension is stable as a result of its very strong electrostatic forces, only under high salt concentrations does a clay/water system coagulate. This technology is used all over the world to manufacture terracata and China ware. In more exoctic systems, colloidally unstable systems are used. For exemple with alumina and zirconia, if the particle size distributions are very different it is

better to flocculate the system; thereby locking into the particle structure of the flocs the well mixed structure of the suspension of two different types of particles than to let the particles segregate. This technique is also practiced in the production of aluminum nitride/titania reaction sintered material composites. The discussion of the effects of colloid chemistry on the processing of ceramics will include specific examples of coagulation kinetics and adsorption isotherms. In addition to providing control over ceramic suspension, colloid chemistry is also important in the synthesis of ceramic powders.

To precipitate powders from solution, it is necessary to control the size distribution. To do this it is necessary to control the relative rates of nucleation, growth and agglomeration. Using colloid chemistry the agglomeration can be controlled. Using the various reaction kinetics, the rates of nucleation and growth can be controlled. An in-depth discussion of the population balance that measures the formation of ceramic particles inside both batch and continuous plug flow crystallizers will be given. The final analysis of this shows that to make monosized particles with a batch reactor or a continuous plug flow reactor, it is necessary to have a single burst of nucleation followed by growth of the particles with a rate limiting step of diffusion in solution boundary layer. In this case the particle size distribution of the particles produced narrows as it grows, forming a narrow size distribution powder. In a plug flow reactor it is necessary to have the dispersion intensity for this reactor as low as possible thus giving the most narrow residence time distribution for the particles. Narrow residence time distribution can be obtained with turbulent flow or packing in a tubular reactor. In these types of reactors, agglomeration must be prevented to produce a narrow size distribution. In a continuous stirred tank reactor we must have a very large amount of nucleation continuously and very small rates of growth with a large amount of agglomeration. In this case, the particles grow by agglomeration primarily giving them a very narrow size distribution. After the reaction is completed, the particles must be stabilized colloidally to prevent further agglomeration after they leave the reactor. Narrow size distribution ceramic powders have been shown to provide very small grain size after sintering. During sintering the kinetics are much faster with a narrow size distribution ceramic powder.

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SOME CURRENT ISSUES ON GRAIN GROWTH IN SINTERED CERAMICS

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ABSTRACT

In polycrystalline ceramics, grain growth which is driven by the reduction of the solid-solid interfacial energy content of the system, is as yet insufficiently understood phenomenon with very important practical implications. Most of the mechanical, chemical, physical or thermal service properties of sintered ceramics are directly related to the structure and composition of grain boundaries and, in general, when theoretical models are developed which aim at relating the properties of materials to their microstructures, the so-called average grain size is very often explicitly taken as the key structural parameter. In practice, a rather limited control can be exerted on grain size in sintered ceramics via the duration of high temperature heat treatments, and to a lesser extent, via well-chosen impurity doping and/or adjustments to the gas atmosphere in the firing furnace. In contrast to metals, ceramics so far exhibit but limited intragranular ductility up to rather high temperatures, which prevents the recourse of primary recrystallization as a grain refining procedure. Such a limitation has had an important effect during the past 30 or 40 years in motivating a significant part of ceramic research programs, due to the fact that in the overwhelming majority of cases property improvements could only be obtained through grain size reductions. The race toward finer and finer grain sizes (at zero or minimal residual porosities) has intensified in recent years, in connection with and as a consequence of progress in powder processing in general. Rather spectacular results have thus been obtained in a number of cases and it is now becoming customary to produce fully dense sintered bodies with average grain sizes well in the submicron range. Interestingly however, several cases have arisen recently where an ultra fine equiaxed isotropic grain structure is no more synonymous of superior material properties. For example, the mechanical behavior of sintered silicon nitride (and for that matter of other ceramics and ceramic composites as well) has been shown to be improved when a fibrous-like structure is produced with individual grains having well defined geometries. Also, it is now recognized that the achievement of practically acceptable current densities in the modern high  $T_c$  ceramic superconductors necessitates the development of strong textures with probably as large an individual grain size as can be tolerated. Challenges such as these undoubtedly raise problems that are new to many professional ceramists and for the solution of which, very little directly useful information is yet available.

This presentation will consist of three parts. First, the geometry of ideal single phase isotropic polycrystals will be reviewed, from both metric and topological points of views. Particular attention will be given to recent research describing local changes in such structures and their overall stability toward grain growth. A brief historical account will also be given of the modelling of the classical parabolic grain growth kinetic law, from the early work of C.S. Smith (1952) and D. Turnbull (1952), through M. Hillert (1965) and W.W. Mullins (1986), to the present.

The second part will present and discuss results obtained in recent years on the computer simulation of the normal grain growth process. For obvious reasons, most studies actually producing synthetic structures have been performed in two dimensions. The three dimensional case therefore will only be alluded to very briefly. Most of the discussion will be centered on comparing simulations based on deterministic versus stochastic approaches respectively, and on discrete versus quasi continuous dynamics.

The third part finally will be devoted to some important physico-chemical aspects of grain growth in real ceramic systems for which still little experimental and theoretical information is available. In such a context, effects on grain boundary mobility associated with chemical heterogeneities and applied stresses respectively, will be of special concern. In conclusion, some suggestions will be made for future research.

## MICROSTRUCTURE OF GRAIN BOUNDARIES IN CARBIDE CERAMICS

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Grain boundaries play an important role in thermomechanical properties of ceramic carbides. Different models in creep tests such as dislocation or diffusional creep are based on the geometric and chemical structures of the grain boundaries. The aim of this paper is to present two different ceramic carbides (SiC and WC) where studies on grain boundaries between carbide crystals have been undertaken. These materials are prepared by sintering of refractory carbide powders and binders. Silicon carbide is sintered with aluminium base additives and tungsten carbide with the cobalt phase. The two carbides crystallize in hexagonal system, but their structure is quite different. Silicon carbide is characterized by numerous polytypes with a large  $\frac{c}{a}$  ratio. This  $\frac{c}{a}$  ratio is nearly equal to 1 for tungsten carbide and consequently a typical shape of the WC crystals is observed. It is based on triangular pyramids limited by the (0001) basal plane and the  $\{10\bar{1}0\}$  prismatic planes.

Orientation relationships between adjacent carbide grains can be described by using the coincidence site lattice (C.S.L) model already established for hexagonal metals. Experimental results show an important difference between these two materials. In tungsten carbide these orientation relationships are close to coincidence orientations with low  $\Sigma$  values. By contrast very few coincidence orientations are observed for silicon carbide. An explanation based on the growth conditions is proposed. It is worth noticing that tungsten carbide exhibits a particularly low value of the  $\Sigma$  coincidence index ( $\Sigma = 2$ ). High resolution image of such a grain boundary shows how the misfit between the a and c parameters can be accommodated by steps in the  $\{10\bar{1}0\}$  boundary plane. The majority of the coincidence orientations observed for the two carbides are described by rotations around  $\langle 10\bar{1}0 \rangle$  or  $\langle 11\bar{2}0 \rangle$  axis with symmetric or asymmetric grain boundary planes.

In silicon carbide faceted interfaces have been extensively observed in high temperature deformed materials. The occurrence of faceting suggests a decrease in the overall energy of the interface. In many cases the grain boundary tends to be parallel to a basal plane in one grain although no coincidence orientation is observed. Therefore a majority of asymmetric grain boundary planes are formed.

These observations illustrate how coincidence site lattice theory can predict the grain boundary plane in WC while the nature of the covalent bonding of SiC imposes asymmetric configurations associated with local minima in the free energy of the grain boundary.

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## INTERFACES IN DIRECTIONALLY SOLIDIFIED OXIDE-OXIDE EUTECTICS

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Because of their potentially interesting anisotropic properties, many directionally solidified eutectic materials have been studied in the past two decades. Mostly metallic systems have been investigated, with the main purpose being the improvement of mechanical properties, particularly in the field of turbine blade alloys. More recently, and with similar applications in mind, various ceramic eutectic systems have been considered because of their high melting points, high strength-to-weight ratios at high temperature and resistance to oxidation [1,2].

During the same twenty year period, impressive developments of studies of grain boundaries in both metals and ceramics were observed because of the role played by interfaces in controlling properties of solids.

This growing interest for both ceramic eutectic materials and grain boundaries has naturally led to the examination of the nature and characteristics of the interfaces separating the two phases of oxide-oxide eutectic structures. These studies have been reviewed by several authors [3-5].

In our presentation, which will be a general overview of the subject, we shall firstly discuss the main techniques used to grow aligned oxide-oxide structures and then show the different types of microstructures which may be obtained by directional solidification. We shall continue by examining the crystallographic relations existing between the two phases of these structures. Finally, results of HREM observations of eutectic interfaces will be presented and discussed with respect to models.

In addition, we shall report recent results concerning metal-oxide interfaces obtained by selective chemical reduction of lamellar oxide-oxide eutectic structures [6].

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## THE ROLE OF SURFACES IN CERAMIC PROCESSES

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The preparation of ceramic materials is a process with a large number of independent steps. The way from the ores to the final product is effected by the presence, the number and the chemical and physical constitution of surfaces. Since ceramic manufacturing is basically the consolidation of powder particles which contact each other via their surfaces, the control of the process is based on the control of the surfaces. The importance of surfaces for technical manufacturing but also the difficulties will be reported. Powder preparation ( $ZrO_2$ ), shaping processes ( $Si_3N_4$ ) and the final thermo-electrical properties ( $ZrO_2$ ) will be used for examples.

## SEGREGATION AT CERAMIC SURFACES AND EFFECTS ON MASS TRANSPORT

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Impurity segregation to free surfaces and internal interfaces in ceramic materials can, in general, be described in terms similar to those developed for metals and semiconductors<sup>(1,2)</sup>. Broadly speaking, a particular element will tend to accumulate at the boundary if its binding energy at the boundary site is greater than that in the bulk of the crystal; the effect should generally be more pronounced at lower temperatures where configurational entropy contributions are of less importance. Interactions among segregating ions may lead to 2-dimensional phase separation<sup>(3)</sup> or even precipitation in the near surface region. There are, however, special features of ceramic materials that must be given consideration. The main, distinguishing property of ceramic crystals is the low density of free or mobile charge. Local disturbances in the lattice thus produce long range effects, i.e. they have long screening lengths. In ceramic materials, the interfaces will generally have electrically charged double layers associated with them with characteristic Debye lengths in the range  $10^2 - 10^4$  Å. The densities of defects may therefore be disturbed to a considerable depth below a ceramic surface; this may have important consequences for the near surface ionic transport properties.

The origin of ionic space charge regions near surfaces of ceramic crystals can most easily be understood in terms of the occupation of sites at the surface with binding energies different from those in the crystal interior<sup>(4)</sup>. The relative energies of the surface sites and the ionic chemical potentials determine the surface site occupancy, and hence the surface charge density and potential. A brief discussion of the details of this model will be given and illustrated with recent calculations of the temperature variations of surface potential, surface charge and impurity profile near the surface of  $\text{Al}_2\text{O}_3$  doped with MgO.

Recent results<sup>(5)</sup> from our laboratory on the temperature variation of the composition of the (0001) and (1010) surfaces of  $\text{Al}_2\text{O}_3$  doped with Mg by ion implantation will be discussed. The results can be compared with recent computations of segregation energies by Tasker and coworkers<sup>(6)</sup> and interpreted in the light of the space charge model. Interesting correlations have also been found in the surface concentrations of Ca and Mg, (- both divalent ions).

The effects of the surface segregation of Mg on the mass transport properties of alumina are being studied through the use of the surface sine-wave decay technique<sup>(7)</sup>. An enhancement of mass transport rate has been found for the situation when precipitates are present in the near surface region; at low surface Mg concentrations the effects are small within the temperature range investigated.

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## GROWTH AND MASS TRANSPORT IN CERAMIC TYPE PROTECTIVE SCALES ON METALS

W.W. SMELTZER

A survey is presented of growth and mass transport in ceramic type protective scales on metals and alloys at high temperatures by the short-circuit diffusion of metal and oxygen through low resistance diffusion paths in oxide boundaries. A methodology based on correlating phenomenological theory of oxidation with reactant short-circuit diffusion across reaction product layers is discussed in some detail for  $\text{Cr}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  scales on iron and nickel alloys because independent measurements of diffusivities by isotopes are available to confirm the oxidation models.

The point defect structure of  $\text{Cr}_2\text{O}_3$  which behaves as an intrinsic semiconductor has not been completely<sup>2,3</sup> elaborated but probably consists of cation interstitials, cation and anion vacancies. At  $1000^\circ\text{C}$ ,<sup>4</sup> chromium diffusion by low angle boundaries and dislocations is  $\sim 10^4$  more rapid than lattice diffusion. The parabolic oxidation rate constants governing scale growth from different investigators vary as much as three orders of magnitude, a behavior believed to be associated with variations in scale adherence, oxide grain size and porosity. Metal diffusion along the oxide grain boundaries will be shown to play a pivotal role in the growth of the scales.

The point defect structure of  $\alpha\text{-Al}_2\text{O}_3$  which behaves intrinsically as an ionic conductor is largely determined by the nature of impurities in the host lattice. Both Al and O are mobile, the diffusion coefficient of Al is approximately one order of magnitude greater than that of O in polycrystalline oxide. Diffusion of oxygen is structurally sensitive, its diffusivity in polycrystalline oxide being  $10^2$ - $10^4$  larger than for single crystal oxide. In the case of  $\text{Al}_2\text{O}_3$  layer growth, outward aluminum and inward oxygen transport<sup>3</sup> occur predominantly by grain boundary diffusion to a degree dependent on the type of alloy but the prevailing species appears to be oxygen.

$\text{SiO}_2$  is a network type oxide often existing at high temperatures for long<sup>2</sup> exposures in the vitreous state. Diffusion and permeation measurements indicate that interstitial oxygen is the prevailing point defect and that this species interacts and exchanges with network oxygen during growth of  $\text{SiO}_2$  scales on pure Si at high temperatures. The problem with the formation of protective  $\text{SiO}_2$  films on alloys is that the Si content required for its exclusive growth is very high and corresponds to alloys with poor mechanical properties. Silicon as a minor alloying element in Fe-Cr alloys does lead to growth of healing passive type barriers beneath protective  $\text{Cr}_2\text{O}_3$  scales.

Isotope studies using sequential oxidation in  $\text{O}^{16}$  and  $\text{O}^{18}$  have been definitive in describing mechanisms of oxide nucleation and growth within protective  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  scales on transition metal alloys. Mechanisms involved in the formation of new oxide within these protective scales are open to speculation and to discussion at the Workshop.

## INVESTIGATION OF THE FRACTAL STRUCTURE OF THE PORE-GRAIN INTERFACE IN ALUMINA CERAMICS<sup>+</sup>

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### ABSTRACT

At low frequency the conductivity of fluid saturated porous media varies with porosity as  $\phi^m$  where  $m$  is the Archie's exponent. At higher frequencies, the real part of the conductivity exhibits a dispersive (non Gaussian) behaviour characterized by the power law  $\sigma'(\omega) \propto \omega^x$ . The real part of the dielectric constant which can attain very large value at low frequency varies in the dispersive region as  $\epsilon'(\omega) \propto \omega^{-y}$  with  $x + y = 1$ . We obtained the values of these exponents from data in brine saturated porous alumina ceramics presented in previous papers.

The conclusion of our analysis is that the low frequency conductivity of porous alumina ceramics saturated with saline water yields an Archie's exponent compatible with the theory of percolation. The conductivity frequency exponents in the dispersive region are consistent with the model of anomalous conduction on fractals and the high value of the real part of the dielectric constant can be accounted for if the microgeometry of the grain-pore interface and multipole effects are incorporated into the Maxwell-Garnett theory of composite media.

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**MODELING OF METAL-OXIDE INTERFACE BEHAVIOUR DURING OXIDE SCALE GROWTH CONTROLLED BY CATION DIFFUSION.**

**B. PIERAGGI, R.A. RAPP**

The growth of cation-diffusing scales on pure metals is described from a modelling of metal/oxide interface in terms of intrinsic dislocations for an epitaxial metal-scale interface. This model is consistent with the experimental observations of high local deformation and intimate contact, and epitaxial relations between the innermost grains of the scale and the underlying metal.

The annihilation of metal-vacancies at the metal-scale interface occurs by the climb into the metal of some fraction of the intrinsic misfit interface dislocations, a process which generates tensile stress in the metal and compression in the scale. Above a critical interfacial strain, the glide of dislocations in the metal, in combination with dislocation glide in the scale, recreates or resupplies the interface dislocations. These processes provide plastic deformation in both phases near the interface and permit the retention of epitaxy during metal recession.

The model may explain the origin of stresses arising during the growth of cation-diffusing scales on an extensive flat surface and the influence of surface orientation and surface preparation on the oxidation kinetics, etc. The epitaxial growth of NiO scale on pure Ni is described as a typical example.

## SMALL PARTICLES AND THIN FILMS OF METALS ON CERAMIC OXIDES

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The growth of small particles or very thin films of metals on ceramic oxides can lead to new interesting properties. The systems where selected metals are dispersed on specific oxides are known to give very efficient results in catalysis. More generally, growth mechanisms, morphology and properties of very thin metallic films on ceramic oxides are investigated from the point of view of the basic research and for electric, electronic as well as optical or decorative applications.

In this lecture, the attention will mainly be focussed on well-defined oxide surfaces, preferably pure and monocrystalline of ceramic oxides which can be considered both as the most representative and the most studied, i.e.:  $\text{Al}_2\text{O}_3$  (corundum structure),  $\text{TiO}_2$  (rutile structure),  $\text{MgO}$  and  $\text{NiO}$  (rock-salt structure). The following points will be developed:

### A/ Definition and specific properties

Here we are concerned only with metallic films (or small particles) having their thickness (or their size) low enough to give unusual properties when compared to those of massive metals. The role played by the particle size, the dispersion state and the structural relationship at the metal-substrate interface will be discussed.

### B/ Preparation and characterization of small particles and thin films

Nucleation and growth mode of chemically and physically formed films will be compared in relation with section A. In very thin films or small particles of metals formed by solid state chemical reduction, the influence of the structural properties at interfaces is often favoured whereas, in films formed by condensation from vapour phase, better dispersion can be obtained on homogeneous substrate.

Some specific experimental techniques to characterize crystal structure, chemical composition and interfacial properties of these different types of films will be outlined.

### C/ Films grown by chemical reduction

The mechanism of nucleation and the growth modes of nickel particles from the  $\text{NiO}(001)$  surface will be presented as an example of chemically formed films. Relation between stacking mode, structural orientation of metallic particles and quality of films as evidenced by structural analysis

(reflection high energy electron diffraction) and Auger electron spectrometry will be discussed.

D/ Films formed by vapour condensation.

Microtopographical arrangement, wettability and, therefore, morphology of physically formed films will be discussed for different classical systems, particularly Ni-TiO<sub>2</sub>. Parameters such as evaporation flux, surface stoichiometry and purity and metal-substrate interaction will be presented as important factors in that case.

E/ From several examples, the problems of stability will be discussed. Also the interest of selecting and studying different specific very thin metallic film-oxide systems will be summarized.

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## THE ROLE OF GRAIN BOUNDARIES AND INTERFACES ON SUPERCONDUCTIVITY

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The recent discoveries of cuprate based ceramic materials having superconducting transition temperatures well in excess of those exhibited by the A15 compounds and the Chrevel phases have not only heralded a resurgence of interest in the phenomenon of superconductivity around the world but also have spurred interest in the materials aspects. At the same time the discovery that the critical current densities of polycrystalline yttrium barium cuprate films and bulk materials are orders of magnitude lower than those exhibited by single crystals has caused a re-examination of the role of internal interfaces, such as grain boundaries and twins, on superconducting properties.

Recent experiments in which the critical current density of individual grain boundaries in yttrium barium cuprate have been measured directly clearly show that values for the grain boundary are significantly lower than those of the grains on either side. Thus, it has been argued that grain boundaries do not act as pinning centers in these materials. This is in seeming contrast to the conventional wisdom in the metallurgical superconductors where the critical current density increases with decreasing grain size as in  $\text{Nb}_3\text{Sn}$ , or in heavily drawn NbTi where the critical current density increases with deformation and the formation of thin Ti platelets.

After an introduction to the principles of superconductivity in polycrystalline materials we will present, in this tutorial lecture, the experimental evidence for the effect of internal interfaces on superconducting properties. We will then discuss the possible role of interfaces both in terms of flux pinning by dislocations and in terms of the local reduction in potential. The behavior of grain boundaries as Josephson junctions, their behavior in magnetic fields and the problems for materials design when dealing with the percolative flow of supercurrents across boundaries having a variety of misorientation, and hence coupling, will also be discussed.

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## STRUCTURE AND PROPERTIES OF GRAIN BOUNDARY IN MgO BICRYSTALS

by Etichi YASUDA

Researches of grain boundary structure in ceramics are more complicated comparing with metals, because of the difficulty to obtain pure materials without secondary phases at the boundary. Many experimental and theoretical efforts have been devoted to study the structure and properties of grain boundaries in ceramic materials, however, their characterizations have not been clarified sufficiently.

In this paper, some problems in boundary energy and diffusion will be discussed. At the meeting, fabrication techniques of MgO bicrystals, the chemical properties of MgO grain boundaries will be reviewed.

### 1. Grain Boundary Energy of MgO

After many researches have been experimentally confirmed the model proposed by Read-Shockley, it was cleared that the small angle boundaries are composed by an array of dislocations[1]. (001) and (110) low angle tilt boundaries in MgO were also confirmed from observation by TEM[2].

The energy of high angle grain boundary have been widely interpreted by using the geometrical models based on the CSL theory. Around the CSL misorientation, the tilt boundary was identified to be dislocation arrays from the TEM observation[3]. When twist boundaries were slightly deviated from CSL misorientation, secondary grain boundary dislocation arrays were found near the CSL misorientation[4] of  $\Sigma = 1, 5, 13, 17, 25, 29$  and 53.

The relationships between the relative boundary energy and the (100) tilt angle at various temperatures were nearly the same and no cusps were observed. The relative boundary energies as a function of temperature were shown in Fig.1 for 5.4° and 69° inclined (100) tilt boundary. Since the temperature dependency of surface energy is not clear, it is difficult to calculate the boundary energy. However, the temperature dependency (entropy) of boundary energy will be larger than that of the surface and the value of enthalpy will be smaller at high angle tilt boundary than that of small tilt boundary.

### 2. Estimated Structure from Boundary Energy and Diffusional properties

Strong anisotropy of diffusion was observed up to 10° in (100) tilt boundary. The anisotropy was the results of pipe diffusion in dislocation arrangement, however the anisotropy disappeared above 10°[5]. On the other hand, Read & Shockley relationship suggests that the (100) tilt boundary is constructed by dislocation array up to 22°[2]. The discrepancy of the tilt angle in (100) boundary might suggest the differences in dislocation arrangement. When (100) small angle tilt boundary is composed by (100) dislocation arrangement, all of the burgers vectors are parallel in each other, then dislocations arrange in the same distance and never crosses. In metals, minimum distance of dislocations arrangement with the same sign of the burgers vector is thought to be about 5 lattices. This distance corresponds to 11.3°.

Dislocations are generally inserted into (110) in MgO and dislocation core passes into  $\langle 001 \rangle$  because of the slip systems, then the dislocations of (100) can be substituted by (110) dislocations. When (100) tilt boundary is composed by (110) dislocation, the burgers vectors are normal in each other, then the dislocations attracted and are able to crisscross. Looking at the sphere model of MgO deeply, not only the dislocation core passes through in the direction of  $\langle 100 \rangle$ , but also passes through  $\langle 110 \rangle$  direction. This arrangement is one of the type of arranged jog. Figure 2 is (020) dark field image of low angle tilt boundary. There are many crisscrossed dislocations and it supports the existence of the arranged jog. Considering above, the isotropic diffusion observed above  $10^\circ$  will depend on the crisscrossed edge dislocations with jogged arrangement.

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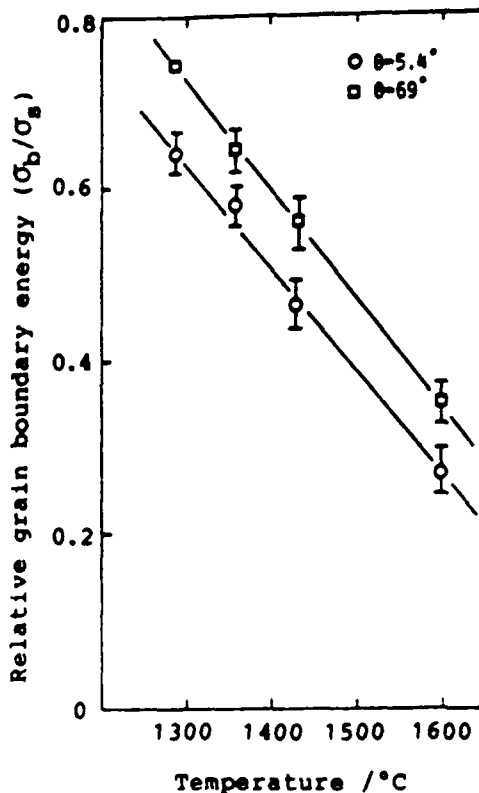


Fig.1 Relative grain boundary energy of (100) tilt boundary of MgO as a function of temperature.

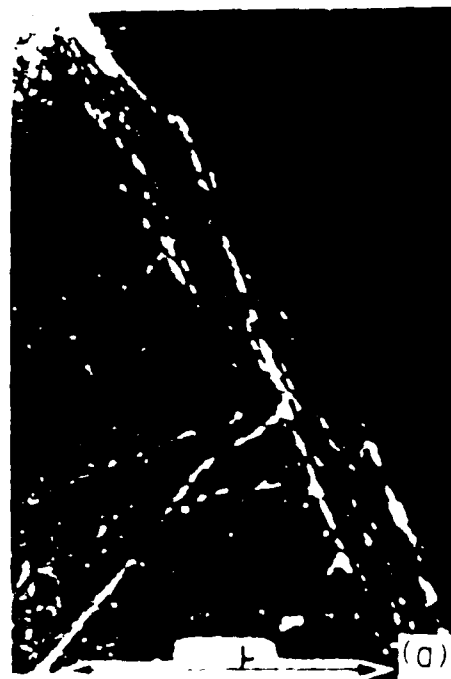


Fig.2 (020) dark field image of 6.8° inclined (001) tilt boundary of MgO bicrystals.

## DISSOLUTION MECHANISMS OF OXIDES AND TITANATE CERAMICS - ELECTRON MICROSCOPE AND SURFACE ANALYTICAL STUDIES

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Despite substantial research, there is not yet a full understanding of the mechanisms controlling dissolution of simple oxides in aqueous acid solutions (see, eg, the review by Segall et al 1988). The mechanisms involved in reactions of ceramics are even less certain, with the added complexity of distinguishing between "leaching" reactions (incongruent attack with preferential release of some species from the solid) and "dissolution" (congruent attack, with all species released at equal rates). For some classes of problem, such as the prediction of very long term rates of release of ions from ceramic matrices for immobilization of high level radioactive waste products (eg Synroc), it is essential that the processes and mechanisms be fully understood in order to establish predictive models (see eg review by Myhra et al 1988). Early studies of oxide dissolution often involved only solution parameters - pH, temperature, ionic concentrations - with geometric estimates of surface areas. More recently, the critical importance of the solid side of the reactive interface has been recognised, through the use of surface analytical methods (XPS, SIMS, AES) and electron microscopy ((S)TEM/SEM, EDXS, EELS).

Although many of the materials of practical interest are in the form of polycrystalline multiphase solids (eg Synroc) - with microstructural characteristics such as grain size and orientation, intergranular films, etc, which can affect reactivity - it is necessary to study the individual phases in pure, single crystal form in order to establish the fundamental mechanisms. (We are not concerned here with (semi-)conducting oxide or ceramic electrode kinetics, under applied potentials).

In this lecture, two examples will be considered - dissolution kinetics of the ionic oxide MgO in dilute acid electrolytes, with particular emphasis on the initial stages of attack; and the durability of the titanate ceramic  $\text{CaTiO}_3$ , which is the least resistant of the phases of Synroc.

It is well established theoretically and by gas-phase reactions that the {100} faces of MgO are quite unreactive, and yet MgO single crystals (essentially {100} faced cubes) dissolve at the same rate as highly faceted sintered particles of the same surface area (as measured by gas adsorption), after an initially slower starting rate. Recent results from precision computer-controlled rate measurements of initial and advanced MgO kinetics will be presented, and the importance of associated TEM imaging to develop a consistent model of the mechanisms will be emphasized.

In the case of  $\text{CaTiO}_3$ , different mechanisms are involved for the dissolution of the titanate lattice and for the calcium ions. Recent results show that perovskite dissolves congruently, under a restricted range of pH and  $[\text{Ca}^{2+}]$ , over a range of temperature (20°C - 200°C), with the formation of a protective, amorphous titanaceous film at temperatures <60°C. The establishment of the conditions under which perfect single crystal perovskite dissolves has enabled us to explain the complex observations from solution and surface analyses of polycrystalline perovskite and the multiphase Synroc ceramics.

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## SOME ASPECTS OF THE INFLUENCE OF GRANULOMETRY ON PROPERTIES AND BEHAVIOUR OF A DIELECTRIC MATERIAL : EXAMPLE OF BARIUM TITANATE

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Anybody agrees with the idea that granulometry is playing an important role in the behaviour of a polycrystalline material but very few studies are giving precise information about this role.

In this lecture we will present some experimental results making possible to illustrate the importance of this physico-chemical parameter.

- Physical role of granulometry In this part we will show the influence of granulometry on the crystalline structure of the BaTiO<sub>3</sub> grains and, then, on the dielectric properties of the material.

- Chemical role of granulometry In this part we will show that granulometry is able to apparently modify the reactivity of BaTiO<sub>3</sub> and, consequently, the dielectric properties of the resulting material.

- Granulometry in solid way synthesis of BaTiO<sub>3</sub> In this last part of the lecture we will show how both granulometry and crystalline quality of BaTiO<sub>3</sub> are controlled by the granulometry of one of the two precursor materials, TiO<sub>2</sub>.

**STUDY OF NON STOICHIOMETRIC PURE AND Zr-DOPED YTTRIA SURFACES  
BY X-RAY PHOTOEMISSION AND SCANNING ELECTRON MICROSCOPY**

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Surfaces of oxygen-deficient yttrium oxide, pure or Zr-doped, have been studied by means of X-ray photoemission and scanning electron microscopy.

The local geometrical structure of these non-stoichiometric compounds was previously determined around the Y atom by an EXAFS (Extended X-ray absorption fine structures) study.

In order to get insight into the change in the chemical environment of the Y and the O atom respectively, the evolution of the Auger parameter (measured on an X-ray photoemission spectrum) was followed. The Auger parameter indeed is an accurate probe of the partial transfer of the electronic distribution between the anion and the cation.

Coupling of these experiments with microscopic observations leads to the following results :

- in the oxygen-deficient samples, the oxygen vacancies concentration appears to be increased in the grain boundaries.
- the Auger parameter shows an evolution of the Y-O bond towards a more covalent one, this evolution being modulated with the presence of the  $ZrO_2$  concentration.

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SEGREGATION ASPECTS IN THE  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  CERAMIC SYSTEM

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In solid solutions often a difference is present in chemical composition between bulk and interface of the materials which is due to segregation of impurities or main components to the interfaces. The composition of grain boundaries and surfaces often control phenomena like sintering, grain growth, wear resistance and corrosion behaviour.

Ultrafine grained Y-PSZ powders (with a composition ranging from 4 - 31 mol%  $\text{YO}_{1.5}$ ) were prepared by means of hydrolysis of a metal chloride solution. The powders were isostatically pressed at 4000 bar and afterwards sintered to full density (95% or more) at temperatures ranging from 1100-1400°C.

The specimens were polished, ultrasonically cleaned and subsequently submitted to a thermal treatment at either 600 or 1000°C during 5 hours.

Surface analysis were performed using AES (Auger electron spectroscopy) and XPS (X-ray photoelectron spectroscopy).

The analysis showed that the specimens which were heat treated at 600°C had a surface composition which was similar to their bulk composition. On the contrary all the specimens which were heat treated at 1000°C showed a surface composition which was about 34 mol%  $\text{YO}_{1.5}$ . The thickness of this surface layer was 2-4 nm.

In the calculations of the AES results correction for possible Silicon segregation was applied. It could be shown that the relative increase of the 76 eV line was only due to the segregation of Yttrium, and not of Silicon.

DEMIXING TENDENCY UNDER CHEMICAL POTENTIAL  
GRADIENTS IN OXIDE SOLID SOLUTIONS

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At sufficiently high temperature oxide solid solutions are often not in thermodynamical equilibrium with their surrounding atmosphere. The constituents are then mobile and a transport of matter occurs in the oxide solid solution which yields to an oxidation or reduction of the material. Depending of the mobilities of the different species this may give rise to a demixing tendency of the impurities or of the constituents of the solid solution. This demixing tendency modifies the reaction kinetic and can lead in some cases to the decomposition of compounds or to the formation of new phases dispersed near the interface or forming a continuous layer as is often observed in alloy oxidation scales at the metal/oxide interface.

Chemical potential gradients arise when the surfaces of the material are exposed to different oxygen partial pressures due to metal/oxide or oxide/gas equilibrium. The more known examples are of course the growth of oxide scales or the oxido-reduction reactions of oxides. These last reactions which take place within the range of stability of the oxide solid solution can lead to the formation of new phases responsible in some cases of the ageing of the material.

This survey concerns particularly the behavior of p-type semiconducting oxides under an oxygen potential gradient. Among them transition metal oxides have received great attention due to their technological applications but also from a fundamental point of view. A number of results are then available for these materials. On the basis of general equations of oxidation or reduction kinetic the demixing tendency of these materials will be discussed and illustrated with experimental examples.



Silicon Nitride/carbon steel joining by HIP technique

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Joining of  $\text{Si}_3\text{N}_4$  with carbon steel is a huge problem in the development of this ceramic for high temperature applications. HIP technique can provide strong mechanical strengths ( $\sigma = 690\text{MPa}$ ) with a good reliability (Weibull modulus 9.9)

The behaviour at high temperature is excellent since the bending strength remains up to  $600^\circ\text{C}$  after, this one decreases swiftly and the fracture occurs at the interface.

Even if nitrides formation is possible, such compounds can't be revealed by XR diffraction or EPM analysis but the  $\text{Si}_3\text{N}_4$  decomposition happens with a rather large iron diffusion in the ceramic, especially in the grain boundaries; on the other hand a very small diffusion of Silicon is observed into steel. The roughness doesn't affect the bending strength, even as sintered surfaces can be acceptable. The biggest problem remains the difference between the metal and the ceramic coefficients of thermal expansion; in the case of  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joining using iron solder sheet, the bending strength decreases drastically from 0.4mm metal thickness.

In the case of  $\text{Si}_3\text{N}_4$ /steel joining, a Tungsten buffer is used to avoid residual stresses in the ceramic.

Bonding using Nickel joint show a different behaviour: nickel silicides are formed at the metal-ceramic interface, lower mechanical resistance is observed ( $\sigma < 250\text{MPa}$ ), ceramic roughness affects the mechanical properties.

## COPPER-CORDIERITE COSINTERING

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The copper-cordierite ( $2\text{MgO}, 2\text{Al}_2\text{O}_3, 5\text{SiO}_2$ ) system is of great interest for microelectronic packaging. Its main advantages are low dielectric constant and low thermal expansion for the ceramic, high conductivity and low cost for the metal. Using a sol-gel processed cordierite precursor whose sintering temperature is about  $900^\circ\text{C}$  allows cosintering of the two materials.

Green ceramic pellets were coated with a copper-ink layer by screen printing. Cosintering conditions appear to be determining to obtain high quality interfaces, associating high adhesion with low metal diffusion. Optimal properties are reached when cosintering is achieved according to the following three-step thermal treatment :

- heating in air at  $500^\circ\text{C}$  for several hours to eliminate the organic constituents of the ceramic and of the ink,
- reduction in hydrogen at  $250^\circ\text{C}$  of the cupric oxide formed during the first step,
- cosintering at  $1070^\circ\text{C}$  in wet argon (dew point  $20^\circ\text{C}$ ).

This last step, derived from the eutectic bonding technique used for sealing copper on alumina, results in a strong bonding of the copper layer. The density of the ceramic is then close to the theoretical one (95%th.d.).

To throw some light on the mechanisms occurring at the copper-cordierite interfaces during these thermal treatments, thin copper layers were sputter-deposited on green ceramic samples and cosintered under various conditions. Three types of interfaces were then studied by ESCA and SEM : (a) cosintered in hydrogen, leading to poor metal adhesion, (b) cosintered in wet argon with heating conditions so that copper diffuses strongly into the bulk of the ceramic, (c) cosintered in the above mentioned conditions. Green and sintered cordierite samples are used as references to characterize the changes in composition at the different interfaces. Concentration and bonding state depth profiles are obtained by ion sputtering in combination with XPS analysis. From these results and from those obtained by X-ray analysis, clear correlations can be drawn between macroscopic properties on one hand and chemical composition and bonding state at the interface on the other hand. Mean conclusions concern the particular behaviour of Mg and Al for high adhesion interfaces, accounting for strong interfacial interaction and decisive role of the cosintering conditions.

## SINTERING OF $\text{Nd}_2\text{O}_3$ AND CERAMIC STABILITY TO HYDRATION

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Sintering of lanthanide oxides has not been studied extensively, especially since the first sesquioxides of the series are extremely sensitive to hydration. The present paper deals with a first study of the sintering of neodymium oxide and the influence of hydration. It is possible to achieve high final densities but the compacts show a very poor resistance to humidity. This is mainly due to the (A) hexagonal structure. In 1968 CARO [1] gave a new description of rare earth oxides structures, revealing the layered nature of the (A) lattice. According to this scheme one can observe two types of cleavages, one of which is of chemical nature. It corresponds in fact to water penetration between  $(\text{NdO})_n^{n+}$  layers and the oxygen planes. Such defects -cleavages- appear clearly on SEM observations of sintered samples and explain their rapid decomposition.

Stabilization against hydration was attempted by coating the  $\text{Nd}_2\text{O}_3$  grains. Sintering of samples doped with  $\text{TiO}_2$  leads to the hexagonal oxide which is constituted of  $\text{Nd}_2\text{O}_3$  particles surrounded by an intergranular phase, identified as  $\text{Nd}_2\text{TiO}_5$  by use of microprobe analysis. Unfortunately, this compound itself is sensitive to water and then the resistance to hydration of (A)  $\text{Nd}_2\text{O}_3$  improves only by a factor 4.

[1] P.E. CARO. " $\text{OM}_4$  tetrahedra linkages and the cationic group  $(\text{MO})_n^{n+}$  in rare earth oxides and oxysalts". J. Less Common Metals 16 (1968) 367-377

## FT-IR ANALYSIS OF THE SURFACE OF A CORDIERITE AEROGEL

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Cordierite is prepared by a sol-gel process and hypercritically dried. It is obtained with a high specific surface-area ( $400 \text{ m}^2 \text{ g}^{-1}$ ) needed for infrared (IR) surface studies. We have investigated the FT-IR transmission spectra, the cordierite aerogel being pressed in fine pellets in a grid supported and then introduced inside a vacuum heatable cell. The samples were activated under vacuum by heating up to  $450^\circ\text{C}$  for two hours and cooled down. Several adsorbates ( $\text{D}_2$ ,  $\text{CO}_2$ , pyridine, methanol...) were admitted to the cell and the I.R. spectra recorded in situ at different temperatures and pressures.

### Results

After activation, we have noted that the silanol surface groups ( $\text{SiOH}$ ) are all free and completely removed by isotopic exchange. The adsorption of methanol caused the methylation of silanols which is characterized by a shift of CH stretching bands. The physisorption of pyridine adsorbed on the silanols was featured by H bonds.

No  $\text{AlOH}$  vibration was observed in the IR spectra, as usual in compounds including both aluminium and silicon atoms. Nevertheless, these atoms are present on the surface, and we have evidenced their Lewis acidity by interaction with pyridine. Moreover the  $\text{CO}_2$  adsorption has not given rise to carbonate species; we have only observed physisorbed  $\text{CO}_2$ . The behaviour of methanol on cordierite surface seems to be quite different from that on alumina.

The spectra displays neither  $\text{MgOH}$  nor carbonate vibrations while usually these last are spontaneously formed on magnesium oxide after adding  $\text{CO}_2$ . This means that Mg atoms are either inaccessible or not enough active.

### Conclusion

The Si atoms almost have the same behaviour as in pure silica. Not all the active sites present on alumina surface exist on cordierite. The surface reactivity of cordierite aerogel is also different from that of silica-alumina. No activity of magnesium atoms has been evidenced so far.

## CHARACTERIZATION, BEFORE SINTERING, OF HIGH SURFACE AREA SILICON NITRIDE AND CARBIDE, USING FT-IR

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Technologies of Si<sub>3</sub>N<sub>4</sub> and SiC, advanced engineering ceramics, involve sintering of powders which are influenced by the chemical state of the surface. The Fourier Transform Infrared spectroscopy is one of the few techniques available to study the surface species and reactivity of low-particle-sized materials which were, in this case, prepared by a laser driven gas-phase reaction. The pure powders prepared as fine grid-supported pellets are activated by heating under vacuum, and put into contact with different atmospheres of adsorbates.

Si<sub>3</sub>N<sub>4</sub> should only expose silicon and nitrogen atoms on its ideal surface. The observed surface sites are :

- free surface **silanol** SiOH groups and possible Si(OH)<sub>2</sub> geminal groups characterized by their band frequencies (3742, 4540, 3720 cm<sup>-1</sup>), their progressive disappearance upon adsorption of basic molecules, and isotopic exchange with D<sub>2</sub> and D<sub>2</sub>O.
- **imido** groups Si-NH-Si with stretching and bending frequencies at 3355 and 1550 cm<sup>-1</sup>, partially deuterated, available to reaction with methanol and acetic acid and so accessible to adsorbates, at least partly. We also observed small amounts of amide SiNH<sub>2</sub> groups and hypothesized Si<sub>3</sub>N ones, reacting in wet atmosphere
- **silane** SiH and SiH<sub>2</sub> groups, exchangeable with deuterium and perturbed by water and acetic acid adsorption.

SiC at high surface area was studied for different stoichiometry and crystallinity, using deuterium exchange and several probe molecules. From the i.r. absorption bands surface sensitive, we have characterized the main surface species : SiOH (3740cm<sup>-1</sup>); SiH<sub>x</sub> (2280-2120 cm<sup>-1</sup>), CH<sub>x</sub> (3000-2850cm<sup>-1</sup>), C=O (1720 cm<sup>-1</sup>) and Si-C-Si.

Treatments at different temperatures and atmospheres were applied to these powders, among which **calcination** in dry or wet oxygen. This causes perturbations of several of the above mentioned strong surface bands, which suggests that **sintering** may involve, for Si<sub>3</sub>N<sub>4</sub> condensation and exchange reactions between Si<sub>2</sub>O and Si<sub>3</sub>N. So, to preserve the surface from growing silica layers, heating in wet atmospheres must be avoided, at the very time when water is naturally present in the intergranular volume, because of desorption of H<sub>2</sub>O from the surface. A preliminary treatment for removing adsorbed water should be needed. On the other hand, the silicon carbide surface is far more reactive towards oxygen, with formation of silica layers, even in the absence of water. Therefore SiC technology should require heating in drastic inert atmosphere.

## A VIBRATIONAL STUDY OF TETRACYANOETHYLENE ADSORBED ON MAGNESIA.

J. J. HOAGLAND AND K. W. HIPPS

During the last several years there have been several studies conducted on the adsorption of tetracyanoethylene (TCNE) on metal oxide surfaces. Most of these studies used electron spin resonance (ESR) to characterize the reaction products<sup>1</sup>. However, recent studies of TCNE adsorbed on alumina using Fourier transform infra-red (FTIR) and inelastic electron tunneling spectroscopy (IETS) have shown that there are many products formed that are not detected by ESR<sup>2,3</sup>.

We present, for the first time, a combined FTIR and IET spectroscopy study of the chemisorption of TCNE on magnesia. Vibrational spectral data will be used to characterize the redox products formed during TCNE adsorption on high surface area magnesia. Included in the presentation will be a discussion of the TCNE induced variation in magnesia surface OH population. A model for product formation will be discussed.

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## NICKEL DEPOSITION ON TiO<sub>2</sub> (100): CHARACTERIZATION BY AES AND SIMS

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The first stages of the growth of a nickel deposit onto the (100) face of TiO<sub>2</sub> was investigated using mainly Auger Electron Spectroscopy (AES) and Secondary Ion Mass Spectrometry (SIMS).

Auger intensities of both adsorbate (Ni) and substrate (Ti, O) were followed as a function of deposition time. The growth of three nickel layers in the layer-by-layer growth mode was initially observed. It was followed by a nucleation stage. The attenuation coefficients for both adsorbate and substrate Auger peaks through a monolayer of adsorbate were calculated.

In dynamic SIMS experiments, secondary ion intensities of both deposit and substrate were measured during sputtering. By using the Sequential Layer Sputtering (SLS) model for the sputtering process, the morphology of the nickel deposit obtained by AES was confirmed.

INTERFACIAL TENSION AND CONTACT ANGLE IN IMMISCIBLES  
SYSTEMS BY CAPILLARY PRESSURE MEASUREMENTS.

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The recent development of experimentation in space, under microgravity conditions, makes it possible to measure the interfacial tension ( $\sigma$ ) between immiscible fluids (organic compounds, liquid alloys etc.) by a straightforward application of the Laplace equation in its simplest form.

The method we present here, which has been selected to fly on the Sounding Rocket MASER-4 of ESA, consists, essentially, in measuring the pressure difference across a liquid-liquid (immiscibles) or liquid-vapour interface as a function of its radius of curvature, using the simplified boundary conditions provided by the  $\mu$ -gravity environment. In fact, when the product  $\Delta\rho g = 0$ , the drop's shape is exactly spherical so that the capillary pressure is linear versus  $1/R$  (where  $R$  is the drop's radius) with a slope of  $2\sigma$ . This slope is calculated by a linear fit of experimental  $P$  and  $1/R$  data. In spite of the simple theoretical approach, measuring  $\sigma$  by using capillary pressures, requires very high instrumental sensitivities and experimental care.

This method, apart from measurements under equilibrium conditions, is particularly useful under dynamic conditions, when adsorption phenomena or some mass transfer across the interface take place.

Moreover, this method can be successfully used to measure, nearly simultaneously, the interfacial tension and the contact angle of the liquid-liquid interface with a solid substrate.

We present here the experimental apparatus and the first results obtained on test liquids with the same density ( $\Delta\rho=0$ ) to assess the precision and the accuracy of the method.

ROLE OF CARBON - SILICATE INTERFACE AREA  
IN THE ELABORATION OF SIMON POWDERS.

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Our work is a comparative study of the elaboration of ceramic powders of the SIMON family (M = Al, Mg, Y) from three classes of precursors:

(i) Intercalation compounds of swelling clays ( montmorillonite, hectorite) with acrylonitrile. Prior to intercalation, the clay is doped by cation exchange with yttrium, sodium, or hexylammonium ions. After intercalation, acrylonitrile is polymerized in the interlayer space of the clay, yielding a layered clay-polyacrylonitrile nanocomposite material in which the clay-organic interface area is extremely high, of the order of  $800 \text{ m}^2/\text{g}$ .

(ii) Colloidal microcomposites obtained by sedimentation in water of two colloids: the clay, eventually doped with the same ions as before, and graphitic oxide, obtained by oxidation of graphite with  $\text{KClO}_4$  in concentrated nitric acid. This type of material is characterized by an estimated carbon-silicate interface area of the order of  $80 \text{ m}^2/\text{g}$ .

(iii) Mixed powders, obtained by mechanical mixing of a clay powder with graphite and charcoal. This yields a very low carbon-silicate contact area, of a few  $\text{m}^2/\text{g}$ .

Ceramisation was achieved in a nitrogen flux, between  $1000$  and  $1400^\circ\text{C}$ . As expected, the reaction temperature decreases drastically as the organic - mineral interface area increases.

COLLOIDAL FILTRATION OF CHEMICALLY MODIFIED ALUMINA

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Colloidal filtration (slip casting) with a porous mold is studied using suspensions of  $\alpha$ -alumina particles provided with an organic coating. These particles form stable dispersions in weakly polar organic solvents such as ethanol. The viscosity of the suspension remains constant and no 'aging' is observed on the time scale of filtration experiments (minutes to hours). However, in water the hydrofobic particles rapidly flocculate and settle subsequently as large agglomerates.

Filtration curves have been measured for suspensions in ethanol and flocculated suspensions in water. The curves (height  $h$  of the suspension versus square root of time  $t$ ) show deviations from a linear  $h - \sqrt{t}$  relationship. These deviations are due to the influence of the hydraulic resistance of the mold on the filtration kinetics and - in the case of flocculated suspensions in water - also to the sedimentation of agglomerates. These conclusions are corroborated by calculations based on solutions of Darcy's law for the appropriate boundary conditions.

The present work shows that after a simple organic surface modification, alumina particles form stable suspension in organic solvents. These suspensions can be handled more easily than 'conventional' suspensions of uncoated particles in water and the filtration kinetics in case of slip casting can be explained on the basis of Darcy's law.

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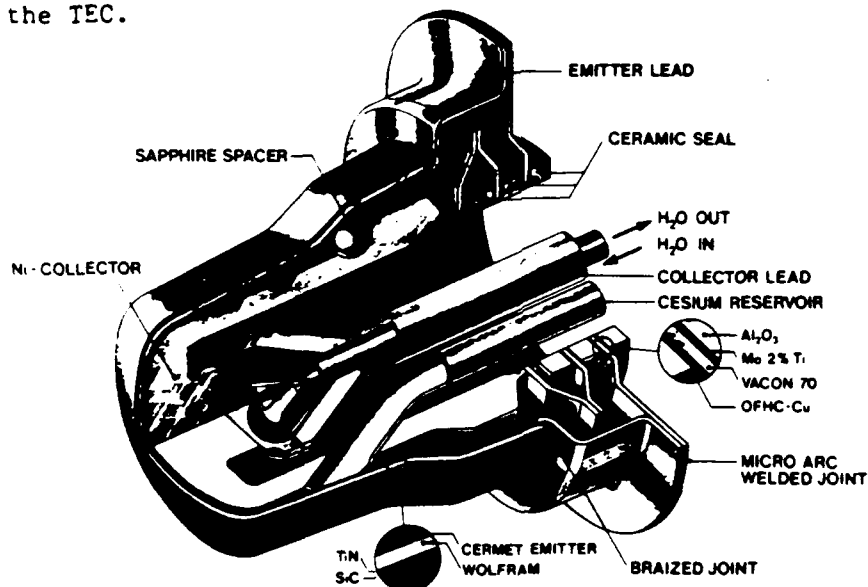
## W-TiN-SiC MATERIAL FOR HIGH TEMPERATURE APPLICATION

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In the course of a BRITE project of the European Communities, Eindhoven University's Center for Technical Ceramics (C.T.K.) together with dutch and italian partners, developed a trilayer material for application in a Thermionic Energy Converter (TEC). A TEC is a diode. One electrode is heated to 1400°C so it will thermally emit electrons. A cooled counterelectrode collects these electrons. Thus a potential difference develops which can be subjected to an external load. A TEC is a direct current power source producing a low voltage (.5 V) at a high current density (10 Amps/cm<sup>2</sup>).

In this BRITE project the CTK is developing materials for a combustion heated TEC which directly (without moving parts) converts heat into electricity (see fig.). The material which is subject of this presentation is the "hot shell" material of the TEC. The hot shell is the confinement of the TEC which is to protect it against the combustion environment at 1400°C. It also serves as an emitter electrode and as an electrical lead for the high currents that are generated by the TEC.



*Combustion heated  
Thermionic Energy  
Converter designed  
by the Center for  
Technical Ceramics  
of the Eindhoven  
University of  
Technology*

No monolithic material can meet the long list of requirements for this hot shell material. Therefore a composite material was designed in which W serves as emitter electrode and electrical lead. SiC is used for corrosion protection. TiN was selected as a diffusion barrier in order to prevent reaction between W and SiC.

A technology was developed for producing this composite material. W is given the desired shape by robotized plasma spraying. After reduction and sintering TiN and SiC are applied by Chemical Vapour Deposition (CVD). This W-TiN-SiC material was tested in a number of ways. The results reported in this presentation include thermoshock and thermal testing, Young's Modulus and thermal conductivity as a function of temperature.

STRUCTURAL DEGRADATION OF TZP CERAMICS AT LOW  
TEMPERATURES IN HUMID ATMOSPHERES

T.T. LEPISTÖ, T.A. MÄNTYLÄ

Structural degradation at low temperature, especially in humid atmosphere, is a serious disadvantage of TZP ceramics when these are considered for constructive applications. To date many contradictory mechanisms have been proposed for degradation but with no unanimously accepted solution of the problem. In our work various sintered and hot pressed TZP ceramics have been exposed at 150 °C both to water vapour and to water solutions to study the effect of the exposures on the structure and mechanical properties of the materials. It was found that the exposure to water vapour can cause the formation of transformed layer in the surface of the sintered materials but in the surface of the hot pressed materials no transformed layer was found and also the amount of transformed monoclinic phase was much smaller compared to that of the sintered materials. It was also found that surface finish has a remarkable influence on the phase transformation rate. We believe that the phase transformation is mainly due to chemical reactions between the surrounding water containing atmosphere and the grain boundaries where the degradation initiates. The process continues through the grain boundaries deeper into the material so that the thickness of transformed layer continuously grows with time.

## INTERFACES BETWEEN PIGEONITE, AMPHIBOLE AND AUGITE

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Many igneous and metamorphic rocks contain pyroxenes which may have exsolved during cooling. Depending on the chemical composition of the pyroxene, the temperature and the cooling rate the exsolution behaviour changes. Addition of water leads to alteration phenomena. In the present work pigeonite/augite and amphibole/augite interfaces have been studied by conventional and high resolution transmission electron microscopy. The precipitation of pigeonite and amphibole in augite has taken place under natural conditions.

The augite investigated ( $\text{Wo}_{45}\text{En}_{41}\text{Fs}_{14}$ ) shows two types of exsolution lamellae:

i) Pigeonite lamellae ( $\text{Wo}_2\text{En}_{55}\text{Fs}_{43}$ ):

- The lamellae are lying almost parallel to the (100) and (001) planes of augite. The deviation of the interphase boundaries from these planes is about  $15^\circ$ .
- With increasing width of the lamellae the interphase boundary becomes semicoherent. The misfit dislocations have  $[100]$  Burgers vectors.
- The nucleation of the precipitates is preferentially at dislocations.

ii) Amphibole lamellae (hornblende):

- The amphibole lamellae are lying parallel to the (010) plane of augite.
- Its formation is via stacking faults with  $1/2 [101]$  displacement vector. The stacking faults are bounded by partial dislocations with Burgers vectors of the same type. They most probably are the result of a dissociation of  $[001]$  dislocations according to  $[001] \rightarrow 1/2 [101] + 1/2 [\bar{1}01]$ .
- The minimum width of the lamellae is  $9\text{\AA}$ , that is one double chain. Broadening of the lamellae is by motion of partial dislocations (steps) along the interface.
- A broader, probably different generation of amphibole lamellae is semicoherent.
- The nucleation of these lamellae has taken place preferentially at augite/orthopyroxene interfaces.

The deviation of the pigeonite exsolution lamellae from (100) and (001) may be explained in terms of the differences in unit-cell parameters of the matrix and the precipitate phase. In order to minimize the resulting elastic strain energy between the two phases exsolution occurs on the plane of dimensional best fit between the two lattices, giving a generally irrational trace of the interphase boundary. The reason for the formation of amphibole lamellae along (010) planes in augite is given by the dislocation aided exsolution mechanism.

**RESIDUAL STRESSES IN POROUS PLASMA-SPRAYED ALUMINA COATING  
ON TITANIUM ALLOY FOR MEDICAL APPLICATIONS**

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Hip prosthesis fixation and stabilisation have been improved by biological anchorage. An alumina porous coating is obtained by plasma-spraying alumina on Ti-6Al-4V titanium alloy. In order to measure the mechanical properties of the coating and the residual stresses, an original method for removing the ceramic layer from the metallic substrate has been developed. The coating structure is predominantly metastable gamma alumina. The porosity has been determined by mercury porosimetry. The open porosity consists of two pore size domains: a macroporosity and a microporosity. The removed coating has the shape of a thin plate which is used as a cantilever beam for bending tests. Young's modulus of 14 and 10 GPa have been found for coatings with respective 30% and 40% porosity. When the coating is removed from the substrate, it gets significant curvature demonstrating residual stresses in the coating-substrate system. The mechanical stress necessary to straight back the removed curved thin ceramic plate leads to a calculated surface residual stress of 4GPa.

**MICROSTRUCTURE DEPENDENT TOUGHENING MECHANISMS IN Mg-PSZ**

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Three main toughening mechanisms are believed to operate in magnesia - partially stabilized zirconia (Mg-PSZ) ceramics during failure. These are transformation toughening, microcracking and crack deflection. In order that the transformation toughening contribution is maximised, the firing cycle must be carefully controlled to optimise the microstructure. Within this constraint the possibilities for varying other aspects of the microstructure, particularly those associated with crack deflection toughening mechanisms, are limited. However, by varying the concentration of trace level impurity additions within the ceramic, notably P, Ti, Ca, Si and F, it is possible to alter the kinetics of the decomposition reactions occurring during the heat treatment of the ceramic. By selecting impurities which segregate to the grain boundaries, it is possible to enhance or retard selectively the kinetics of second phase particle nucleation or growth in these regions.

An example of the complexity of fracture in Mg-PSZ is described and illustrated using microspot Raman spectroscopy, scanning electron microscopy and acoustic emission analysis.

## TEMPERATURE MODELING OF SURFACE REACTIVITY WITH OXIDIZING-REDUCING MIXTURES ON RUTILE $\text{TiO}_2$ - $\delta$

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Oxygen transfer at a rutile surface by means of an oxidizing-reducing  $\text{CO}/\text{CO}_2$  mixture is a slow process even at high temperature (950-1150 °C). The oxygen transfer rate can be followed experimentally whilst a precise determination of the actual active area of the sample is considerably more difficult. Nonetheless, classical models can be handled, like those by Wagner or Grabke, in order to verify their sustaining hypotheses. At present, it seems more likely that the slow reaction step would not be between the gas phase and the oxide surface but rather between two different species at the oxide surface.

## THE ROLE OF GRAIN BOUNDARY MODIFICATIONS TO THE THERMAL DECOMPOSITION OF Mn-FERRITES

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Manganese ferrite samples with and without minor ( $< 1$  Wt%) additions of  $\text{SiO}_2$  and  $\text{CaCO}_3$  quenched in air from the sintering temperature yielded a single spinel phase. Thermogravimetric analysis in a magnetic field was used to determine Curie temperature of magnetic phases present. The Curie temperature provides a measure of the composition and cation distribution in the spinel grains. Samples with and without minor additions were subjected to an anneal at temperatures up to  $600^\circ\text{C}$  in argon and air. There was little or no change in the Curie temperature for samples annealed in nitrogen. However, samples annealed in air showed a significant change in Curie temperature indicating decomposition of the spinel. This decomposition was suppressed by  $< 1$  Wt%  $\text{SiO}_2$  or  $\text{CaCO}_3$  additions indicating that the thermal stability of manganese ferrite is enhanced by the suppression of grain boundary diffusion by minor dopants concentrated at the grain boundaries.

## ELECTRICAL PROPERTIES OF $\text{BaTiO}_3$ PTCR MATERIALS

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Doped  $\text{BaTiO}_3$  ceramic (with 0.3 atm % La and 0.05 atm % Mn) is an n-type semiconductor at 25°C which exhibits a dramatic increase in electrical resistance by 3 to 7 orders of magnitude when heated through the ferroelectric Curie point,  $\sim 130^\circ\text{C}$ .

The widely accepted Heywang mode (1) attributes this positive temperature coefficient of resistance, PTCR, behaviour to grain boundary phenomena. Catlow (2) has suggested segregation of dopants and vacancies to the grain boundaries to form n-i-n junctions.

The cooling treatment from the sintering temperature,  $\sim 1300^\circ\text{C}$  of doped  $\text{BaTiO}_3$  ceramics is crucial in determining the resistance at 25°C and the PTCR profile.

A study of the ac electrical response of doped  $\text{BaTiO}_3$  ceramics cooled under different conditions from the same sintering temperature has been undertaken. The results were analysed using the complex impedance ( $Z^*$ ) and electric modulus ( $M^*$ ) formalisms and by combined spectroscopic plots of the imaginary part of the impedance,  $Z''$  and electric modulus,  $M''$ , against frequency.

The results demonstrate the presence of at least two components in the sample, both of which exhibit PTCR behaviour. From the  $M^*$  plots, the less resistive element exhibits a temperature dependent capacitance, which obeys the Curie-Weiss Law whereas the more resistive component has a temperature independent capacitance. These results will be interpreted in terms of bulk and grain boundary contributions to the overall electrical response.

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## ELECTRICAL CONDUCTION IN POLYCRYSTALLINE COPPER MOLYBDATE

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Polycrystalline ceramic copper (II) molybdate ( $\text{CuMoO}_4$ ) was prepared by solid state reaction between  $\text{CuO}$  and  $\text{MoO}_3$ . X-ray diffraction patterns show that lattice parameters of the prepared sample are in good agreement with the lattice parameters of  $\text{CuMoO}_4$  (1). Temperature variations of electrical conductivity and thermoelectric power of  $\text{CuMoO}_4$  have been studied in the temperature range 300-1000 K, using pressed pellet of the powdered sample.

These studies show the semiconducting nature of  $\text{CuMoO}_4$ . Using electrical conductivity and thermoelectric power data, charge carrier mobility (2,3) and mean free path (4) of the charge carriers have been estimated. Low value of the mobility ( $\sim 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ ) and mean free path ( $0.1893 \text{ \AA}$ ) in the extrinsic region ( $T < 700 \text{ K}$ ) clearly indicate large interface effects and localisation of the charge carriers, which ultimately leads to small polaron formation (5). However intrinsic conduction is normal band conduction with the activation energy 1.53 eV, Mobility and mean free path of the charge carriers in intrinsic region are  $2.9 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$  and  $2.8591 \text{ \AA}$  respectively.

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"GRAIN BOUNDARY PHENOMENA IN THE EARLY STAGES OF SINTERING:  
MO OXIDES"

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*The linear Frenkel law of sintering<sup>1</sup> is briefly reviewed. Sintering of pure and doped ZnO and NiO was studied by using computer assisted dilatometry. The linear shrinkage law was observed during sintering of both oxides for low values of shrinkages. Its extent is changed by doping with  $Cr_2O_3$  additions.*

*The sintering kinetics is discussed on the grounds of the MO oxides grain boundary structure.*

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PREPARATION OF AN  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  SOL FOR PRODUCING MICROSPHERES

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It is well known that the microstructures developed during sintering are determined, to a large extent, by the powder characteristics : chemical and phase composition, particle shape, size and size distribution, presence of agglomeration (1,2). Recently it has been reported that it is possible to control the microstructure of a ceramic material: by closely controlling the chemical homogeneity of the powder, by using particles of spherical shape and sized between 0.1 and 1  $\mu\text{m}$ , by having a particle size distribution close to the average value ( $d_{\text{max}}/d_{\text{ave}} < 3$ ) and by avoiding agglomeration (3).

To achieve this goal in preparing ceramic powders of  $\text{Al}_2\text{O}_3$  doped by 10 % weight of  $\text{ZrO}_2$  a sol-gel process has been developed, by which microspheres having controlled size have been obtained. A gel of Al and Zr hydroxides was precipitated from the respective chlorides solution by adding  $\text{NH}_4\text{OH}$  up to  $\text{pH}=9$ . The precipitate was then washed until a  $\text{Cl}^-/\text{Al}^{3+}$  molar ratio of 0.35. Then the gel was peptized to a stable sol at 80 °C for 48 hours in hermetically sealed vessels by HCl addition : the final  $\text{Cl}^-/\text{Al}^{3+}$  molar ratio in the sol was 0.40. The sol was then concentrated at 80 °C under stirring till to an  $\text{Al}^{3+}$  ions concentration of about 4 M. The viscosity of the sol was about 7 P.

The concentrated sol has been used to feed a capillary tube ( $\phi=0.2$  mm) in a pilot plant, already described (4). The sol droplets are broken up by a stream of 1-octanol, containing 1% by volume of a surfactant, the flow rate of which determines the microspheres diameter. Furthermore the 1-octanol produces a slow dehydration of the sol preserving the microspheres whole. Due to the surfactant the microspheres do not agglomerate and can thus be collected and subjected to heat treatment for converting the hydroxides into oxides. Laser granulometry of the heat treated product shows that the microspheres average size is about 20  $\mu\text{m}$  and that the particle size distribution is close to the average value ( $d_{\text{max}}/d_{\text{ave}}=2.7$ ).

SEM observations confirm the granulometry results, show that the particles are spherical and uncracked, that no agglomeration phenomena are present and, on a fracture surface, that the microspheres are dense. The specific surface area of the powder heated at 1200 °C measured by the  $\text{N}_2$  method is 30  $\text{m}^2/\text{g}$ .

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## ELECTRICAL EVIDENCES IN Me-MeO SINTERING

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The Me-MeX biphasic coexistence electrodes are since long time used in solid state electrochemical devices to fix the chemical potential of the non-metal X at the electrolyte/electrode interface. From the thermodynamic point of view, if the condensed phase is strictly biphasic, the chemical potential of X in the gaseous phase can be easily calculated at a given temperature through the standard free energy change involved in the MeX formation. This implies that the Me and MeX particle are in thermal and thermodynamic equilibrium everywhere in the powder mixture. To obtain this, all particles have to equilibrate by a fast mass and heat transfer. To do this, the averaged distance among the particles must be as short as possible. Such a goal cannot be reached by simple compaction of the powders because this process doesn't join them and the void volume doesn't decrease. Sintering is the right process because produces bonding of the particles through mass transfer and, consequently, all the components in the particles have the same chemical and electrochemical potential.

A relevant aspect in the sintering studies is that to monitor the evolution of the process. We try to do this by measuring in an alternate automatic way, the ohmic resistance and the emf of the specimens vs time for two kinds of powder mixture compacts: Ni-NiO and Fe-FeO (wustite).

The measurements were carried out at 1293 K and 101.325 kPa in high purified argon in which the oxygen partial pressure didn't exceed  $1 \times 10^{-10}$  Pa.

The results obtained show that:

- a. The Fe-FeO(wustite) mixture resistance decreases on time up to a constant value. Its resistivity decreases of 43.5% starting from an initial value of 1.2 ohm x cm. The relative resistance change of the specimen obeys to the equation

$$\lg (R_0 - R)/R_0 = -(3.3 + 0.1) + (0.53 + 0.03) \lg t$$

where  $R_0$  and  $t$  are, respectively, the initial resistance of the specimen and time in seconds. It will be shown that this equation can be related, as a good approximation, to the specimen shrinkage through the Kuczynski's neck growth equation. The time dependence of the shrinkage is, approximately, according the square root as well known in the literature. The system emf was found to be zero during the experiments;

- b. The Ni-NiO mixture behaviour was very different showing initially a resistance of the same order of magnitude of the Fe-FeO(wustite) which rapidly increased after a short time at the temperature of the experiment. The maximum value was of about .3 Mohm which was practically constant for 43 hours (1st period), after which, in about two hours (2nd period), the specimen resistance became equal to 3 ohm (3rd period). During the first period the emf of the system slowly decreased from 95 to 6.5 mV and, successively, to zero in the second period. Current crossing the system was recorded in the 2nd period. It was an increasing trend but with oscillations up to the beginning of the 3rd period where its value became constant.

A tentative explanation of the results obtained will be given.