Surfaces and Interfaces of Ceramic Materials

Edited by

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and Georgette Petot-Ervas

NATO ASI Series

Surfaces and Interfaces of Ceramic Materials

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PREFACE

This book contains the proceedings of the NATO Advanced Study Institute on Surfaces and Interfaces of Ceramic Materials, held on the Oléron island, France, in September 1988. This Institute was organized in nine months after receiving the agreement of the NATO Scientific Affairs Division. Despite this very short time, most of the lecturers contacted have accepted our invitation to prepare a specific talk.

The meeting was held at "La Vieille Perrotine" on the Oléron island. This holiday village of the French CNRS is located near the Ocean in a natural area which contributed to create a very pleasant atmosphere favourable to develop interaction between the 91 participants in this Institute.

First of all, the Institute was aimed at diffusing the foremost results on the characterization of and the role played by surfaces, grain boundaries and interfaces in preparation and overall properties of ceramic materials, mainly of oxide ceramics. Through its interdisciplinary character, the Institute was also aimed at developing interaction between scientists and engineers interested in basic and practical aspects of processing and use of ceramics. Lastly, the Institute has emphasized the fundamental importance and the key role of the external and internal surfaces in the advanced technology of these materials. 42 hours of courses were given by 23 lecturers and 13 additional hours on more limited subjects by 13 invited lecturers. 8 hours were devoted to three round table discussions on segregation, ceramic-metal bonding and sintering processes. Moreover, a poster session, preceded by a short oral introduction by the authors, enabled the students to present their own works.

Most of the lectures and papers presented during this Advanced Study Institute are gathered in this book which is divided in six sections according to the following description:

1/ STRUCTURAL AND MICROSTRUCTURAL ASPECTS OF SURFACES AND INTERFACES OF CERAMIC MATERIALS, INCLUDING ELECTRONIC AND CHEMISORPTION PROPERTIES. Although progress is still needed, many theoretical calculations are now available and reliable to predict the thermodynamical stability of both free and doped surfaces and interfaces *. Modern high resolution spectroscopy and microscopy make it possible to explore and understand the crystallographic, electronic and chemical structure of surfaces and interfaces on an atomic scale. These investigations reveal the fundamental role played by defects and additives or impurities in the properties of surfaces and interfaces of these materials. Also the theory of fractals is considered a very interesting mathematical approach to treat some specific problems, particularly wetting, elaboration by sol-gel route or sintering of ceramics **.

2/ SEGREGATION PHENOMENA AND TRANSPORT PROPERTIES. One important point emphasized here concerns the role of segregation now better analyzed and controlled in the equilibrium conditions. After thermal treatment, this phenomenon is often involved in modifying, sometimes drastically, the expected behaviour of the ceramic materials and its study therefore is to be considered a priority. Recent approaches on the role of both surface and grain boundary diffusions in the overall properties of ceramic protective layers, solid electrolytes, sensors and electrical ceramics, including new high T_c oxide superconductors, are presented.

3/ THERMODYNAMIC AND STRUCTURAL ASPECTS OF CERAMIC-METAL INTERFACES. Another question largely involved in many industrial applications concerns the ceramic-metal bonding. The way to improve the bond strength of ceramic-metal interfaces by subtle changes in chemical composition or stoichiometry at interfaces is discussed. Recent data on preparation and properties of small particles and very thin films of metals on oxides is also presented.

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* For instance , see references in: (a) Henrich V.E., *The surfaces of metal oxides*, Rep. Prog. Physics, 48 (1985) 1481-1541; (b) Egdell R.G. and Mackrodt W.C., this book ; (c) the papers published by Stoneham A.M., Tasker P.W. and coworkers (*e.g.* , ref. in the chapter 1, *The theory of ceramic surfaces*, in 'Surface and Near-Surface Chemistry of Oxide Materials', Nowotny J. and Dufour L.C., (Eds), Elsevier, Amsterdam, 1988)

** Some references in this field may be found in: (a) Mandelbrot B., 'The Fractal Geometry of Nature', Freeman, San Francisco, 1982; (b) Cherbit G. (Ed.), 'Fractals, Dimensions Non Entières et Applications', Masson, Paris, 1987; (c) Feder J., 'Fractals', Plenum Pub. Corp., New York, 1988; (d) Botet R. and Julien R., *A theory of aggregating systems of particles: the clustering of clusters process*, Ann. Phys. Fr., 13 (1988) 153-221

4/ ROLE OF SURFACES AND INTERFACES IN ELABORATING CERAMIC MATERIALS. Current issues on processing of ceramic powders, particularly from monosized particles and on grain growth in sintered ceramics are analysed in this section.

5/ INTERACTION OF CERAMIC MATERIALS WITH ENVIRONNMENT, INCLUDING SOLID-GAS AND SOLID-LIQUID REACTIONS. Several chapters present the most recent development on the role of surfaces and interfaces in the interactions of ceramics with gas at high temperature and with liquids such as acidic solutions. The key role of the surface defects as well as the formation, in specific conditions, of thin protective amorphous films is discussed in the processes of dissolution of ceramic oxides.

6/ PROPERTIES RELATED TO SURFACES AND INTERFACES OF SPECIFIC CERAMIC MATERIALS AND COMPOSITES, INCLUDING MECHANICAL PROPERTIES. Here attention is more particularly concentrated on the relationship between microstructural properties of the interfaces and strength of composites, on the surface properties of vitreous silicates and the elaboration of ceramic membranes.

The aim of an Advanced Study Institute is to collect the knowledge gained in a scientific field and to make this information easily accessible to those interested. We trust that this book will show that the subject treated is timely and important for basic research as well as in the development of modern technology for ceramic materials. This research area is now in fast expansion and has an ever increasing impact on the way to improve ceramics and composite materials for catalysis, metallurgy, energetics, electronics, space science,.. No doubt that, in short future, this scientific branch becomes one of the most active and rapidly developing of contemporary Materials Science.

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Claude Monty
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THE MATERIALS SCIENCE OF CERAMIC INTERFACES

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ABSTRACT. The significance of surfaces and interfaces for the processing and application of ceramics has long been recognised. In this review attention is given to phenomena where the existence of surfaces is responsible for important phenomena in processing (free surfaces and the sintering of powders) and properties (surface cracks and the influence on mechanical strength). Attention is also given to two subject areas where an improved understanding of interface behaviour would be beneficial. The first relates to the significance of segregation at grain boundaries and at free surfaces for the development of ceramic microstructures; the second relates to the structure and behaviour of grain boundaries in the presence of second phases, a factor important both for the processing and for the high temperature properties of ceramic materials.

1. Introduction

As preliminary to a conference where much of the discussion will involve close analysis of the chemical and physical properties of surfaces and interfaces in ceramic materials, it may be helpful to review the subject from the point of view of the ceramist, namely from the point of view of someone wishing to fabricate and use this set of materials for applications and seeking to understand surfaces and interfaces as a means of improving product performance. This approach has the potential benefit that it allows identification of the critical questions as seen from the viewpoint of someone working with the processing or use of ceramics; it should also be helpful to the wider community in revealing any prejudices or preoccupations that may have arisen among those working with the development of ceramics.

In the opening section a brief review is given of certain topics where the ceramist has long recognised that interfaces or surfaces play a critical role. These include the densification of powders by sintering and the mechanical properties of ceramics at ambient temperatures. In subsequent sections two topics are treated where the current understanding of grain boundary or surface structure is incomplete and where further progress should prove rewarding for the processing or application of these materials. The two themes are the segregation of dopants or impurities at grain boundaries in single phase ceramic materials and secondly the

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distribution and properties of second phases in the grain boundaries of multiphase ceramics. The two themes therefore relate directly to the structure and behaviour of solid/solid grain boundaries and of solid/liquid/solid boundaries.

2. Surfaces and Interfaces and the Processing, Properties and Application of Ceramics

One approach to materials science and engineering is to recognise a causal sequence between processing, the resulting microstructure, and the properties that are then associated with this microstructure; applications must then be satisfied on the basis of the properties that have been developed. Recognition of this logical sequence allows one to argue that a given application will require a given set of material properties which must then be attained by specific processing designed to achieve a microstructure capable of yielding these properties. The significance of surfaces and interfaces in each of these stages has long been recognised by the ceramics community[1].

The processing of ceramics is most commonly based upon the heat treatment of powders. The energy present in a powder as a consequence of its high surface area provides a driving force for structural change which results in the densification of the powder and the production of a finished solid component. The central importance of this sintering process in the fabrication of ceramics has made it a much studied subject.

At the macroscopic level, a requirement for successful densification is that the surface energy in the powder be greater than the interfacial energy of the resulting polycrystalline material. This then ensures that densification, the removal of porosity and the replacement of free surfaces by grain boundaries is favourable. One explanation, e.g., for the difficulties in the sintering of SiC lies in the view[2] that this energy change may be insufficient to drive densification. At the microscopic level, it is important to recognise and control the atom movements that provide the mechanism for the microstructural change. Here attention is given to the role of curved surfaces (Fig. 1) in establishing the chemical potential gradients in the system which then drive the atom diffusion. The argument is that since the diffusion of atoms from point to point in the powder bed is likely to be the slow process in the sequence of events leading to microstructural change, all other steps in the sequence can be considered to be at virtual equilibrium. Where curved surfaces occur in the system, the ability of the surfaces to act as rapid sources or sinks for atoms ensures that they are in equilibrium with the local partial pressures in an adjacent gas phase or with the local point defect concentration in an adjacent solid phase.

The local pressures and concentrations are readily calculated[3]. The first step is to recognise the pressure difference, ΔP, that occurs across a curved surface at equilibrium. The energy balance for an infinitesimal volume change dV undergone by a spherical pore of radius r in a solid is

$$\Delta P \, dV = \gamma dA \qquad (1)$$

where γ is the specific surface energy and dA the change in pore surface area. For the spherical geometry, therefore,