

MATERIALS SCIENCE RESEARCH • Volume 21

CERAMIC MICROSTRUCTURES '86

Role of Interfaces

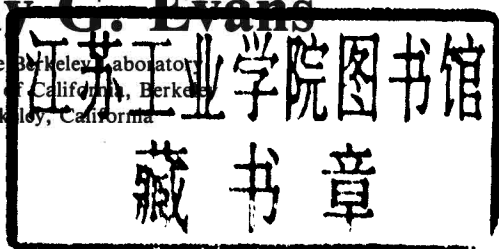
Edited by

Joseph A. Pask

and

Anthony G. Evans

Lawrence Berkeley Laboratory
University of California, Berkeley
Berkeley, California



PLENUM PRESS • NEW YORK AND LONDON

Library of Congress Cataloging in Publication Data

University Conference on Ceramics (22nd: 1986: University of California, Berkeley)
Ceramic microstructure '86: role of interfaces / edited by Joseph A. Pask and
Anthony G. Evans.

p. cm.—(Materials science research; v. 21)

“Proceedings of the 22nd University Conference on Ceramics, and the International
Materials Symposium, held July 28–31, 1986, at the University of California, Berkeley,
Berkeley, California”—T.p. verso.

Includes bibliographical references and index.

ISBN 0-306-42681-1

I. Ceramic materials—Congresses. I. Pask, Joseph Adam, 1913– . II. Evans,
Anthony G. (Anthony Glyn), 1942– . III. International Materials Symposium (1986:
University of California, Berkeley) IV. Title. V. Series.

TP815.U65 1986

620.1'4—dc19

87-22758

CIP

Proceedings of the 22nd University Conference on Ceramics, and the
International Materials Symposium, held July 28–31, 1986, at the
University of California, Berkeley, Berkeley, California

© 1987 Plenum Press, New York

A Division of Plenum Publishing Corporation
233 Spring Street, New York, N.Y. 10013

All rights reserved

No part of this book may be reproduced, stored in a retrieval system, or transmitted
in any form or by any means, electronic, mechanical, photocopying, microfilming,
recording, or otherwise, without written permission from the Publisher

Printed in the United States of America

MATERIALS SCIENCE RESEARCH

Volume 21

**CERAMIC
MICROSTRUCTURES '86
Role of Interfaces**

MATERIALS SCIENCE RESEARCH

Recent volumes in the series:

- Volume 12 **BORATE GLASSES: Structure, Properties, Applications**
Edited by L. D. Pye, V. D. Fréchette and N. J. Kreidl
- Volume 13 **SINTERING PROCESSES**
Edited by G. C. Kuczynski
- Volume 14 **SURFACES AND INTERFACES IN CERAMIC AND
CERAMIC-METAL SYSTEMS**
Edited by Joseph Pask and Anthony Evans
- Volume 15 **ADVANCES IN MATERIALS CHARACTERIZATION**
Edited by David R. Rossington, Robert A. Condrate,
and Robert L. Snyder
- Volume 16 **SINTERING AND HETEROGENEOUS CATALYSIS**
Edited by G. C. Kuczynski, Albert E. Miller, and Gordon A. Sargent
- Volume 17 **EMERGENT PROCESS METHODS FOR HIGH-TECHNOLOGY
CERAMICS**
Edited by Robert F. Davis, Hayne Palmour III,
and Richard L. Porter
- Volume 18 **DEFORMATION OF CERAMIC MATERIALS II**
Edited by Richard E. Tressler and Richard C. Bradt
- Volume 19 **ADVANCES IN MATERIALS CHARACTERIZATION II**
Edited by R. L. Snyder, R. A. Condrate, Sr., and P. F. Johnson
- Volume 20 **TAILORING MULTIPHASE AND COMPOSITE CERAMICS**
Edited by Richard E. Tressler; Gary L. Messing,
Carlo G. Pantano, and Robert E. Newnham
- Volume 21 **CERAMIC MICROSTRUCTURES '86: Role of Interfaces**
Edited by Joseph A. Pask and Anthony G. Evans

A Continuation Order Plan is available for this series. A continuation order will bring delivery of each new volume immediately upon publication. Volumes are billed only upon actual shipment. For further information please contact the publisher.

MEMBERS OF INTERNATIONAL ADVISORY COMMITTEE

H.K. Bowen - M.I.T., U.S.A.
D.G. Brandon - Technion, Haifa, Israel
R.J. Brook - Leeds University, U.K.
L.E. Cross - Penn. State University, U.S.A.
H.E. Exner - Max-Planck-Inst., Stuttgart, F.R.G.
A.H. Heuer - Case Western Reserve, U.S.A.
J.T. Klomp - Philips Res. Labs., Netherlands
F.F. Lange - Rockwell Science Center, U.S.A.
M.G. Nicholas - AERE Harwell, U.K.
K. Okazaki - Nat. Defense Academy, Japan
M. Rühle - Max-Planck-Inst., Stuttgart, F.R.G.
S. Somiya - Tokyo Inst. of Tech., Japan
M.V. Swain - C.S.I.R.O., Australia
R.R. Tummala - I.B.M. Corporation, U.S.A.
T.S. Yen - Academia Sinica, China

MEMBERS OF ARRANGEMENTS COMMITTEE

S.C. Carniglia, Kaiser Aluminum & Chemical
Corp., Pleasanton, CA
L.C. DeJonghe, MMRD, LBL, Berkeley
J.J. Gilman, CAM, LBL, Berkeley
A.M. Glaeser, Univ. of Calif., Berkeley
R.L. Landingham, LLNL, Livermore, CA
R.E. Loehman, Sandia, Albuquerque, NM
F.R. Monforte, Ampex Corp., Sunnyvale, CA
N.E. Phillips, MMRD, LBL, Berkeley
A.W. Searcy, Univ. of Calif., Berkeley
P.W. Smith, GTE Wesgo, Belmont, CA

PROGRAM CHAIRMAN

Joseph A. Pask, U.C. Berkeley

PROGRAM CO-CHAIRMAN

Anthony G. Evans, U.C. Santa Barbara

TECHNICAL EDITOR

Richard E. Albert, Jr.

CONFERENCE COORDINATOR

Peggy Little, LBL

SUPPORT

The financial support of the following government agencies for the Ceramic Microstructures '86 Symposium is greatly appreciated:

Defense Advanced Research Projects Agency, Materials Sciences Division
National Science Foundation, Ceramics and Electronic Materials Program

The financial support of the following industrial establishments for the Symposium is also greatly appreciated:

Allied-Signal Inc., Morristown, NJ
Aluminum Company of America, Alcoa Center, PA
GTE Wesgo, Belmont, CA
Industrial & Consumer Sector/3M, St. Paul, MN
Kyocera Corporation, Kyoto, Japan
Martin Marietta Corp., Baltimore, MD
Norton Company, Northboro, MA
Sohio Engineered Materials Co., Niagara Falls, NY

PREFACE

The Proceedings of the International Materials Symposium on Ceramic Microstructures '86: Role of Interfaces presents a comprehensive coverage of the past decade's advances in ceramic science and technology related to microstructures. The term microstructure is used in the broad sense and is synonymous with character. Character is defined as a complete detailed description of chemical and physical characteristics of a material.

This symposium is the third in a series, held every ten years, on ceramic microstructures. The first symposium, in 1966, had as a subtitle "Their Analysis, Significance and Production" and emphasized the need and importance of characterization in order to fully understand the chemical and physical properties of materials. The second Symposium, in 1976, placed emphasis on the exploration of characters most suited and needed for "Energy-Related Applications." By the time of that conference, the sequence of processing--characterization--properties was fully accepted. It was recognized that characterization was the basis of materials science; the objective of processing was to produce a desired character that was considered necessary to realize a given property or behavior. To further emphasize the importance of character, the symposium dealt primarily with the property/character coupling.

This third Microstructures Symposium emphasizes the "Role of Interfaces," which falls within the coverage of the processing/character coupling. New analytical tools and procedures, and development of greater sophistication in research approaches, have emphasized the importance and provided the impetus for exploring the nature and role of grain boundaries and interphase interfaces. In addition, this development has also sparked the initiation of studies in processing or microstructure production, with emphasis on uniformity and homogeneity, which are controlling factors in the realization of reliability.

Much progress has been made during the past ten years toward an understanding of all aspects of ceramic microstructures. The objectives of this Symposium were to explore this progress as well as to assess current activities and understanding. Major areas of discussion were the nature of interfaces and the role that they play in the production of ceramic microstructures, their characterization, and the correlation and relationship of their character with electrical and mechanical properties and behavior. Also, a group of papers dealt with reactions and adherence of dissimilar materials at interfaces that are important in designing and developing composites.

The editors have benefited from the cheerful help and assistance of many people. Special thanks are extended to David A. Shirley, Director of Lawrence Berkeley Laboratory, for his welcoming remarks; Peggy Little, for her invaluable assistance as Conference Coordinator; Tony Tomsia, for his

general assistance particularly in organizing the Poster Session; and Rich Albert, for his assistance with the editing of the manuscripts.

We particularly appreciate the financial assistance provided by the Materials Science Division of the Defense Advanced Research Projects Agency, and the Ceramics and Electronic Materials Program of the National Science Foundation. Also, the financial assistance of Allied-Signal Inc., Morristown, NJ; Aluminum Company of America, Alcoa Center, PA; GTE Wesgo, Belmont, CA; Industrial & Consumer Sector/3M, St. Paul, MN; Kyocera Corp., Kyoto, Japan; Martin Marietta Corp., Baltimore, MD; Norton Co., Northboro, MA; and Sohio Engineered Materials Co., Niagara Falls, NY contributed to the overall operations of the Symposium.

The editors also extend their thanks to the speakers and authors. This volume would not have materialized without their participation. Because of the indicated advances that have occurred in the past twenty years, it is anticipated that the next ten years will be most productive and that the Ceramic Microstructures '96 Symposium will bring forth interesting and productive results.

Joseph A. Pask
Anthony G. Evans

Berkeley, California
December, 1986

CONTENTS

Progress in the Understanding of Ceramic Microstructures and Interfaces since 1976	1
H.F. Fischmeister	
Ceramic Microstructures: The Art of the Possible	15
R.J. Brook	

DESIGNING MATERIAL STRUCTURES

Purposive Design of Nanocomposites: Entire Class of New Materials	25
Rustum Roy	
Design of High Thermal Expansion Glass-Ceramics Through Microstructural Control	33
R.E. Loehman and T.J. Headley	
Microdesigning of Ceramic-Metal Composites	45
A.J. Pyzik, I.A. Aksay, and M. Sarikaya	

CHARACTERIZATION OF MICROSTRUCTURES

Grain Boundaries and Interfaces: Some Applications of Electron Microscopy and Microanalysis	55
Gareth Thomas	
Quantitative Characterization of Microstructural Geometry of Interfaces	73
Hans Eckart Exner	
Gas Transport as a Tool for Structural Characterization of Interfacial Phases	87
James F. Shackelford	
Unit Cell Distortion of $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ by $\text{Pb}(\text{Co},\text{Nb})\text{O}_3$	95
Jeon Kook Lee and Hyung Jin Jung	
Electron Microscopy Studies of BaTiO_3 - NaNbO_3 Ceramics	103
Z. Xu and D.A. Payne	

Analytical Electron Microscopy of the Glassy Phase in Mullite/Zirconia Composites	111
K. Srikrishna, G. Thomas, and J.S. Moya	
Microstructure Characterization of Basalt Glass-Ceramics	117
M. Hidalgo, P. Callejas, and J. Ma. Rincón	
Interfacial Reaction Between Bioactive Glass and Synthetic Physiological Solution	127
Panjian Li and Feipeng Zhang	
Oxidation and Microstructure of Sintered Silicon Nitride	137
H. Sakai, T. Soma, M. Matsui, and I. Oda	
Origin of Cracking Phenomena Observed in Decomposition Reactions	145
M.G. Kim, U. Dahmen, and Alan W. Searcy	

CHARACTERIZATION OF INTERFACES

Oxide Interfaces: Theory of Oxide-Oxide and Oxide-Metal Interfaces	155
A.M. Stoneham and P.W. Tasker	
Green Function Method for Calculation of Atomistic Structure of Grain Boundary Interfaces in Ionic Crystals	167
V.K. Tewary, E.R. Fuller, Jr., and R.M. Thomson	
Comparison of the Energies of Symmetrical and Asymmetrical Grain Boundaries	177
D. Wolf	
The Structure of a Natural Grain Boundary in a Magnetite Bicrystal Studied by XRD Technique	187
S. Stock, S. Ahn, and J.B. Cohen	
Interface Morphology in Ceramics	195
M. Backhaus-Ricoult and H. Schmalzried	
HREM Study of a Tetragonal $\rightarrow$ Monoclinic Martensitic Interface in a Y_2O_3 -Stabilized ZrO_2 Alloy	203
R. Chaim, P.A. Labun, V. Lanteri, and A.H. Heuer	
Control of the Tetragonal to Monoclinic Phase Transformation of Yttria-doped Tetragonal ZrO_2 Polycrystals by Annealing in Water	215
T. Sato, T. Endo, and M. Shimada	
Grain Boundary Energy of Twisted MgO Bicrystals on (100)	223
Eiichi Yasuda, Shiushichi Kimura, Minji Sakaki, Hyo Joon Kim, and Yusuke Moriyoshi	
T.E.M. Statistical Characterization of Grain Boundaries in Polycrystalline NiO Scales Obtained by High Temperature Oxidation of Nickel	231
Abdel Marrouche, Françoise Barbier, and Michel Déchamps	
Structure of High-Angle Grain Boundaries in NiO	241
K.L. Merkle, J.F. Reddy, C.L. Wiley, and David J. Smith	

High-Angle Grain Boundaries in Sheet Silicates (Biotite/Chlorite): A TEM Study	249
Richard Wirth	
HRTEM Analysis of Ordered Grain Boundaries in High Purity Alpha-SiC	255
Hideki Ichinose, Yoshizo Inomata, and Yoichi Ishida	
Atomic Structure of Interfaces in Sialon Ceramics	263
A. Thorel, J.Y. Laval, D. Broussaud, G. Teste de Sagey, and G. Schiffmacher	
CHARACTERIZATION OF IMPURITY SEGREGATIONS	
Atomistic Lattice Simulations of the Structure, Energetics and Impurity Segregation Behaviour of Ceramic Boundaries	271
W.C. Mackrodt	
Distribution and Influence of Minor Constituents on Ceramic Formulations	281
W. David Kingery	
CHARACTERIZATION OF INTERPHASE INTERFACES	
Diffusion Bonding of Metal/Ceramic Interfaces--A Model Study at the Nb/Al ₂ O ₃ Interfaces	295
M. Rühle, M. Backhaus-Ricoult, K. Burger, and W. Mader	
Ceramic-Metal Reactions and Their Effect on the Interface Microstructure	307
J.T. Klomp	
The Influence of Surface Roughness on Interface Formation in Metal/Ceramic Diffusion Bonds	319
Brian Derby	
A Reappraisal of Wetting in the System Al-Al ₂ O ₃ from 750-1000°C	329
D.A. Weirauch, Jr.	
Microstructural Characterization of Ni/Al ₂ O ₃ Diffusion Bonds	341
J.A. Wasynczuk and M. Rühle	
Bonding Ceramic-Metal Interfaces and Joints	349
M.G. Nicholas	
Copper-Glass-Ceramic Interfaces and Composites: Reactions, Microchemistry, and Electrical Properties	359
Subhash H. Risbud, Gregory D. Allen, and Janet E. Poetzing	
The Study of Microstructures for Pt-Silicide Interfaces after Nd:YAG Laser Irradiation by XRD, SEM, XPS, and RBS	369
Shen Zhongxin	
High Resolution Electron Microscopy of Silicon Nitride-Metal Bonded Interfaces	379
Yoichi Ishida, Hideki Ichinose, and Shun-ichiro Tanaka	

Interfacial Chemistry and Bonding in Fiber Reinforced Glass and Glass-Ceramic Matrix Composites	387
John J. Brennan	
Effects of Interfacial Diffusion Barriers on Thermal Stability of Ceramic Fibers	401
Neal R. Langley and Chi-Tang Li	
Solid State Bonding of Alumina and Steel by HIPING	409
M. Shimada, K. Suganuma, T. Okamoto, and M. Koizumi	
Thermochemical Analyses of Interface Reactions in Carbon-Fiber Reinforced Glass Matrix Composites	415
P.M. Benson, K.E. Spear, and C.G. Pantano	
Interfaces in Heterogeneous Dissolution of Oxides in Molten Ca-Al-Silicates	427
J. Lambert Bates	

MICROSTRUCTURE DEVELOPMENT

Powders, Interfaces, and Processing: Alumina as a Case Study	433
Andreas Roosen, Shigekazu Sumita, and H. Kent Bowen	
The Role of Powder Packing in Sintering	447
L.C. De Jonghe, M.N. Rahaman, and M. Lin	
Effect of Pores on Microstructure Development	455
Martin P. Harmer and Junhong Zhao	
Microstructure Development of Hydrothermal Powders and Ceramics	465
Shigeyuki Sōmiya, Masahiro Yoshimura, Zenjiro Nakai, Kazumitsu Hishinuma, and Takao Kumaki	
The Colloidal Chemistry of Growing Silica Spheres	475
G.H. Bogush and C.F. Zukoski IV	
Effects of Vapor Transport on Microstructure Development	485
D.W. Readey, T. Quadir, and J. Lee	
Controlling Grain Growth	497
F.F. Lange	
The Effects of Grain Growth on the Intergranular Porosity Distributions in Hot-Pressed and Swelled UO_2	509
Antai Xu and A.A. Solomon	
Effects of Solutes on the Grain Boundary Mobility of TiO_2	519
M.F. Yan and W.W. Rhodes	
Microstructural Development in Hot Pressed CaO: Density Decrease and Pore Growth During Post Sintering	533
E. Yasuda, K.S. Ramesh, Bao Q.L., and S. Kimura	
Diffusion Induced Interface Migration in Ceramics	541
John E. Blendell, Carol A. Handwerker, Cynthia A. Shen, and Ngoc-Duyen Dang	

Grain Boundary Diffusion Artefacts in Polycrystalline Nickel Oxide Grown by High Temperature Oxidation	549
Françoise Barbier, Hean Bernardini, Fernand Moya, and Michel Déchamps	
Variations in Grain Growth of Donor-Doped SrTiO_3 with Cation Nonstoichiometry	555
C.-J. Peng and Y.-M. Chiang	
The Wetting and Dewetting of Grain Boundaries	569
D.R. Clarke	
Anion Controlled Microstructures in the Al_2O_3 - AlN System	577
James W. McCauley, K.M. Krishnan, R.S. Rai, G. Thomas, A. Zangvill, R.W. Doser, and N.D. Corbin	

SINTERING

Sintering Theory for Crystalline Solids	591
Alan W. Searcy	
Selected Sintering Conditions for SiC and Si_3N_4 Ceramics	601
C. Greskovich and S. Prochazka	
Colloidal Consolidation and Sintering Behavior of CVD-Processed Mullite Powders	611
Yoshihiro Hirata and İlhan A. Aksay	
Sintering of Acicular NiZn -Ferrite Powder	623
Ken-ichi Omatsu, Toshio Kimura, and Takashi Yamaguchi	
Continuous SiC Fiber/Glass Composites	633
S.M. Johnson, D.J. Rowcliffe, and M.K. Cinibulk	

ELECTRICAL PROPERTIES

Electrical Conductivity in Ceramics: A Review	643
D.M. Smyth	
The Crystallographical and Chemical Relationship between Intergranular and Bulk Resistivity in Semi-Conductor Oxides	657
M.H. Pinet-Berger and J.Y. Laval	
Interface Effects in Zinc Oxide Varistors	665
Lionel M. Levinson, Herbert R. Philipp, and E. Sonder	
The Role of Interfacial Microstructure in ZnO Varistor Materials	679
E. Olsson, R. Österlund, and G.L. Dunlop	
Electrical Properties and Microstructure of $\text{ZnO-Nb}_2\text{O}_5\text{-MnO}$ Ceramics Sintered in the Liquid Phase	687
Kenya Hamano, Zenbe-e Nakagawa, Yoshiaki Okamoto, Akio Sayano, and Tatsuro Mitsudome	
New Composite PTC Materials Based on $\text{PbTiO}_3\text{-TiO}_2$	697
Masuo Okada, Takashi Iijima, and Motofumi Homma	

Effects of Microstructure Control on Ferroelectric Ceramics	707
K. Okazaki, H. Igarashi, K. Nagata, T. Yamamoto, S. Tashiro, and S. Kashiwabara	
Effect of Deviations from Stoichiometry on Microstructure and Magnetic Properties of Ferrites	719
Raúl Valenzuela	
Optical Effects of Grain Boundaries in PLZT Ceramics	727
Z.W. Yin	
Microstructures of High Dielectric Constant Materials	739
Helen M. Chan and Martin P. Harmer	
Interfaces Generated by Electronic Device Development in Beta SiC Thin Films	749
C.H. Carter, Jr., S.R. Nutt, and R.F. Davis	
Electrical Barriers at Grain Boundaries in Silicon Carbide Materials with BeO Addition	757
K. Maeda, Y. Takeda, A. Soeta, K. Usami, and S. Shinozaki	
Microstructural Analysis of Silicon Carbide Materials with BeO Addition	767
S. Shinozaki, J. Hangan, and K. Maeda	

MECHANICAL PROPERTIES AND BEHAVIOR

The New Generation of High Toughness Ceramics	775
A.G. Evans	
Influence of Microstructure on Creep Rupture	795
S.M. Wiederhorn, B.J. Hockey, and R.F. Krause, Jr.	
Mechanisms of Dynamic Failure in Debased Alumina	807
D.G. Brandon and Y. Yeshurun	
Some Interfacial Related Properties of Transformation Toughened Ceramics	819
M.V. Swain, R.H.J. Hannink, and J. Drennan	
Precipitation in a (Mg) Partially Stabilized Zirconia during Aging at 1000°C	831
K.H. Westmacott, U. Dahmen, A. Thorel, and J.Y. Laval	
High Temperature Mechanical Properties of ZrO ₂ -Based Ceramics	839
M.I. Osendi and D. Lewis	
Microstructure and Mechanical Properties of a Al ₂ TiO ₅ -Mullite-ZrO ₂ Composite Obtained by Reaction Sintering	847
P. Pena, S. de Aza, and J.S. Moya	
Interfaces in Ceramic Fiber Composites	859
D.B. Marshall	
Delamination Toughening from Interfacial Cracking in Ceramics and Ceramic Composites	869
M. Sakai, S. Takeuchi, D.B. Fischbach, and R.C. Bradt	

Development of Structure in Silicon Nitride	
Grain Boundaries	877
Dawn Bonnell	
The Impact of Compositional Variations and	
Processing Conditions on Secondary Phase	
Characteristics in Sintered Silicon Nitride Materials	883
W. Braue, G. Wötting, and G. Ziegler	
Structure and Chemistry of Interfaces in Silicon Carbide-	
Containing Materials	897
R.F. Davis, C.H. Carter, Jr., S.R. Nutt, K.L. More,	
and S. Chevacharoenkul	
Interfaces in Alumina-SiC Whisker Composites	911
T.N. Tiegs, P.F. Becher, and L.A. Harris	
Creep Performance of Silicon Carbide	
Whisker-Reinforced Alumina	919
John R. Porter and Atul H. Chokshi	
Temperature-Dependent Toughening in	
Whisker-Reinforced Ceramics	929
M.C. Shaw and K.T. Faber	
Effect of High Temperature Oxidation on the	
Microstructure and Mechanical Properties of	
Whisker-Reinforced Ceramics	939
W.M. Kriven, G. Van Tendeloo, T.N. Tiegs, and P.F. Becher	
The Role of Interfacial Reactions on the	
Mechanical Properties of Ceramic Brazements	949
A.J. Moorhead, H.M. Henson, and T.J. Henson	
Fracture Energies of Ceramic-Metal Interfaces	959
R.M. Cannon, V. Jayaram, B.J. Dalgleish, and R.M. Fisher	
On the Fracture Behavior and Microstructure of	
Metal-to-Ceramic Joints	969
Martin Turwitt, Gerhard Elssner, and Günter Petzow	
Index	981

PROGRESS IN THE UNDERSTANDING OF CERAMIC MICROSTRUCTURES AND INTERFACES
SINCE 1976

H. F. Fischmeister

Max-Planck-Institut für Metallforschung
Stuttgart, FRG

INTRODUCTION: THE SCENE IN 1976

In reviewing this decade's progress, our base line will be the proceedings of the previous "Microstructures" conference¹; in addition, Kingery's papers² on "Concepts Plausible and Necessary for Interpretation of Grain Boundary Phenomena" of 1974, and Johnson's Review³ on "Grain Boundary Segregation in Ceramics" of 1977 will mark the position around the mid-seventies.

Firmly established at the time was the importance of grain boundaries for the elimination of pores during sintering⁴⁻⁷. The segregation of impurities to grain boundaries had been inferred from indirect evidence², and Auger spectroscopy (AES) had recently begun to provide direct quantitative data³. However, it had not been possible to prove the segregation of Mg in alumina which had been invoked to explain the rapid and complete densification of this material³, and the mechanism of this important dopant effect remained unexplained.

Beside AES, Transmission Electron Microscopy (TEM) and analytical Scanning Transmission Microscopy (STEM) were just beginning to make their impact on ceramics research. Their increasing application has been instrumental for the rapid progress during of the following decade. Glassy interlayers between the crystal grains in ceramics, previously inferred from high temperature behaviour, were demonstrated in TEM shortly after the '76 conference⁸.

In the mid-seventies, grain boundary structures were directly accessible only to the field ion microscope⁹. Despite the great effort needed for each specimen tip containing a grain boundary, a large volume of evidence had accumulated¹⁰ from such studies by 1976. Several speculative models of grain boundary structure had been developed. They stressed the importance of lattice site coincidences across the boundary and throughout both crystals ("CSL-model")¹¹, or the presence of energetically favourable configurations ("structural units") at the boundary itself¹², or matching of lattice plane spacings at the boundary ("plane matching model")¹³. TEM had revealed the existence of grain boundary dislocations in specific patterns, confirming that large angle boundaries have regular structure. Computer modelling had been recognized as a promising method of developing detailed ideas of the atomistic