ADVANCED CERAMIC PROCESSING AND TECHNOLOGY

Volume 1

Edited by

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Preface

Advanced ceramics and ceramic matrix composites are finding increasing use in modern technological applications as ever more stringent demands are placed upon material's properties. This has led to a significant expansion over the past two decades, in terms of research and development into optimising the properties of these generally brittle and unforgiving materials. However, whilst advanced ceramics and ceramic composites have many potentially useful properties, they can be extremely difficult to fabricate into usable artefacts. This has resulted in an ever increasing emphasis being placed on advanced ceramic processing and technology.

As long ago as 1972 Stuijts emphasised the need for precise control of microstructure as a means of achieving control of the properties of the final component. This approach, which is strongly reflected throughout the current book, must begin with the precursor powders and continue through to green body formation and the densification of the body via some sintering mechanism. Not only must accidental variations in the microstructure be avoided, but the design of the microstructure must be optimised with the final application of the component in mind—and then achieved.

This book, the first of two volumes, contains a series of independent chapters, each focussing on a different aspect of ceramics processing. It is not intended that these chapters should form a complete portfolio of all the possible techniques currently available for fabricating ceramics; such an approach would be more at home in a ceramics encyclopedia. Rather the aim is to offer the views of leading experts as to the current state-of-the-art of a number of ceramics processing options and, most importantly, the future directions which they see their fields taking. The two volumes, then, are aimed at the materials engineer who already has a grasp of the fundamentals underlying ceramic science and engineering and who is now looking to expand his or her knowledge of processing techniques and their underlying philosophies.

For a number of reasons this text has been a long time in the making and I would like to extend my heartfelt thanks to all the authors (and the publisher) who, without exception, have shown great patience. In particular, I should like to thank those authors who met the original manuscript deadlines and then found themselves, some time later, having to significantly update their chapters. Finally, I should like to thank Pam and Elaine for their excellent help in typing some of the incoming manuscripts.

This volume is dedicated to the memory of Professor Bill Knapp, former member of the Department of Materials Science and Engineering at the University of California at Los Angeles. Originally to be Bruce Kellet's co-author for the first chapter, Bill was tragically killed in a hit-and-run accident whilst out jogging one morning in late 1985. Bill was a very fine ceramist, but more importantly, he was a very special man.

Nottingham, England
June, 1990

Jon G.P. Binner

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NOTICE

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Contents

1

Advanced Processing Concepts for Increased Ceramic Reliability

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1. INTRODUCTION

Man's skill in processing functional ceramics dates back many millennia, preceding the introduction of more formable and less brittle materials, viz. metals, that have since received more economic, technological and scientific attention due to their deserved engineering importance. Ceramic materials, with their multiplicity of elemental combinations and structural arrangements, produce a multitude of unique properties, which are still being uncovered. Today, advanced ceramics are finding potential applications ranging from advanced heat engines to communication and energy transmission and they are emerging as the leading class of materials needed to implement many advanced technologies.

Engineering implementation of advanced ceramics is still hindered by their formability and brittle nature; however ceramic processing technology has advanced little beyond the needs associated with functional, traditional ceramics. Such traditional approaches inherently lack a clear methodology for controlling microstructural heterogeneities and uniformity. This lack of processing control leads to property variability and consequent uncertain engineering reliability.

The objective here is to review new approaches to powder processing that minimize heterogeneities common to this 'many bodied' problem. The review will start by outlining other approaches to ceramic processing. New thinking concerning densification will set the stage for discussions concerning new approaches to powder preparation and consolidation that emphasize the colloidal approach.

2. PROCESSING METHODS

Although powder methods dominate ceramic forming, ceramics can also be formed by glass-ceramic and gelation methods.

2.1 Glass-Ceramic Methods

Glass-ceramic methods can be used for compositional systems with relatively small free energies of crystallization (e.g. silicates) so that solidification occurs before crystallization. Direct crystallization from the melt must be avoided because very large grains result which produces a relatively friable material. Shapes are formed by conventional high temperature glass processing to take advantage of Newtonian rheology. Crystallization is induced by a two-step nucleation/growth process at moderate temperatures; however complete crystallization is rarely (if ever) achieved. Hence ceramics produced by the glass-ceramic method contain a residual glass phase which degrades the mechanical properties at high temperatures. Calculations(1,2) suggest that residual glassy pockets within a polycrystalline material can be thermodynamically stable. Many advanced structural ceramics (e.g. silicon nitride and carbide) decompose before melting, whereas others crystallize too readily for use of this method. The glass-ceramic process is thus limited to materials that melt and do not readily crystallize.

2.2 Gelation Methods

Gelation methods are analogous to the glass-crystallization method in that processing starts with a metastable system. With this method, soluble metal-organic precursors are 'gelled' (e.g. hydrolysis of alkoxides). After the liquid is removed, organic residuals are removed by heat treatment preceded by crystallization and densification. Unlike the glass-ceramic method, compositions are not restricted to those that are glass formers at high temperature, viz. crystallization is induced by heating and not cooling.

One of the major attributes of the gelation method is that multi-element, metastable systems (intimately mixed at the molecular level) can be produced at low temperatures. Phase partitioning from these metastable systems can be used to control microstructures by heat treatment at higher temperatures.

Removal of the liquid is one major limitation of the gelation method. Capillary pressure causes the low density network to shrink during drying(3). Shrinkage initiates at the surface and generates stresses that usually cause the drying system to break apart into small granules (analogous to the mud crack pattern observed on a drying lake bed). The shrinkage stresses can be reduced by extremely slow drying to produce sound, monolithic bodies, but these drying periods (of the order of weeks) are not practical. Surface tension and thus capillary pressures on the network can be completely eliminated by removing the fluid phase at temperatures and pressures above the fluid's critical point (i.e. super critical drying)(4). Super critical drying (used for more than 40 years to produce aero-gels) results in very low density networks (relative densities <0.2) and thus a large degree of shrinkage occurs during heat treatments that produce crystallization and densification. Low densities and hence large shrinkages are the second major drawback of the gelation method. A third, but lesser problem is the elimination of the organic radicals bound to the polymer networks which must be carefully controlled to avoid gas entrapment, etc. These limitations become greater with component size.

Gelation methods are generally limited to the processing of thin films, fibres and powders.

2.3 Powder Methods

Powder methods are used to fabricate most advanced ceramics. They involve powder manufacture, preparation of the powder for consolidation, consolidation of the powder into a shape and densification (elimination of the void phase). Post-densification heat treatments can develop specific microstructures to optimize certain properties.

Although powder methods are much less restrictive than those discussed above, its 'many-bodied' nature makes it prone to heterogeneities. One of the major causes of these heterogeneities is the powder itself. Nearly all current powders are agglomerated, i.e. groups of either weakly or strongly bonded particles. Agglomerates pack together during consolidation to produce compacts with differentials in packing density leading to poor densification and the formation of crack-like voids which can be a major strength degrading flaw population(5).

It is common practice to reduce agglomeration size by attrition milling. Studies(6) have shown that milling has a low probability of eliminating all agglomerates. It also introduces contaminates and large inclusions not acceptable for the fabrication of reliable, advanced ceramics. Various organics can be added as helpful binders and/or lubricants during consolidation. For rheological consolidation methods (e.g. slip casting, tape casting of thin sheets, extrusion and injection moulding), the non-volatile residual polymer content of the system can be between 40 and 50 volume percent. Elimination of this polymer (e.g. through pyrolysis) is not only time consuming (days) but can also produce disruptive phenomena.

The most common method of consolidating powders is via dry pressing in which forces are applied to powder contained within a die. Since dry powders are naturally agglomerated and the consolidation of agglomerates must be avoided to produce reliable ceramics, this technique is undesirable. In addition, since dry, fine powders do not flow to uniformly fill pressing dies, powder slurries with polymer additions are currently spray dried to produce large, flowable particles (>50 μm agglomerates). These massive particles (agglomerates) produce larger separating forces due to differential acceleration which can overcome attractive (e.g. Van der Waals) forces during flow. Thus, although spray drying is helpful in producing a flowable powder, it can introduce large agglomerates and thus produce large crack-like voids during densification.

Powders are also consolidated from slurries. Current methods include: filtration (slip casting), electrophoresis, evaporation (casting of thin sheets, i.e. tape casting), extrusion and injection moulding. Although these slurry state consolidation methods are adaptable to new colloidal methods