Conference Reports

Better High-Tech Ceramics by Improved Processing

The 90th Annual Meeting of the American Ceramic Society from 2-6 May in Cincinnati was, with more than 4000 participants, once again the most exciting congress event of the year for the ceramic community. The general trend towards obtaining better high-tech ceramics by improved processing resulted in a noticeable emphasis on processing steps such as powder production methods, powder handling, and on forming and sintering. In this report some special aspects illustrating the general trends will be discussed.

Powder Synthesis

The sessions on powder synthesis showed the efforts being made to produce powders of higher purity and smaller, controlled particle size. *G. M. Crosbie* et al. (Ford Motor Company, Dearborn, Michigan) reported on the synthesis of Si_3N_4 powder of outstanding purity by the reaction of $SiCl_4$ with liquid NH_3 at 0°C. The intermediate reaction product was described as "$Si(NH)_2$" which reacted further to Si_3N_4 at elevated temperatures. An optimized method to obtain a homogeneous distribution of yttria in a Si_3N_4 powder matrix yielding homogeneous densification and microstructural development was described by *A. K. Garg* and *A. L. C. DeJonghe* (University of California, Berkeley). The beneficial effect of Y_2O_3 additions to Si_3N_4 itself is well known. The additive forms a liquid phase at temperatures between 1500 and 1800°C, which results in the benefits of fast densification and satisfactory microstructural development of Si_3N_4. In the work described, a better distribution of the additive was obtained when yttrium hydroxycarbonate was precipitated from a liquid suspension on to the Si_3N_4 matrix powder and transformed into Y_2O_3 during calcining. A number of speakers described other methods which are particularly suitable for the synthesis of highly pure, monosized submicron powders, namely sol-gel technique, hydrothermal synthesis and emulsion techniques. All of them expected an enhanced sinterability and improved mechanical and physical properties due to the high purity and narrow size distribution of powders produced by these methods.

An entire session was devoted to AlN, which has a considerable potential for technical applications where its outstandingly high thermal conductivity can be used. A new method of AlN powder production was proposed by *L. D. Silverman* (Engelhard Corporation, Edison, NJ). An Al_2O_3 sol is embedded in a polymer matrix and heated in nitrogen. During heating the pyrolysis of the polymer matrix provides free carbon, which reacts at still higher temperatures with Al_2O_3 in a carbothermic reaction. In the presence of nitrogen the reacting Al_2O_3 forms AlN.

Interesting possibilities for controlled texture formation in ceramics were reported, which also have implications with regard to the anisotropy of critical currents in the new ceramic superconductors. Precursor powders consisting of faceted cubic MgO particles were converted into textured MgO ceramics by cold pressing and sintering. The existence of texture was established by a new application of EPR spectroscopy showing that after sintering the MgO $\langle 111 \rangle$ cubic axes are preferentially oriented along the cold pressing direction. EPR spectroscopy seems to be an important new tool for studying texturing effects in a wide range of ceramics.

Nanocrystalline Ceramics

Nanocrystalline solid bulks of strongly covalent ceramics such as SiC, Si_3N_4 and BN were synthesized and consolidated by *G. D. Soraru* et al. (University of California, Los Angeles) by the pyrolysis of organometallic polymers. The initially amorphous powders transformed into the nanocrystalline solid bulks during tempering. No information was available at the conference on the properties of these nanocrystalline materials.

Forming

D. J. Rhee and *I. A. Aksay* (University of Washington, Seattle) presented an improved understanding of the debindering of injection molded ceramic parts, which is one of the potential future methods for producing high-tech ceramics with complex shapes. Debindering in ceramic-polymer composites not only determines the properties of the residual matrix, but also the required debindering time has a decisive influence on the economic viability of the method.

Sintering and Hot Isostatic Pressing

During the Annual Meeting the three day symposium "Sintering of Advanced Ceramics" effectively summarized the present knowledge in this field. A book containing the papers presented orally or as posters will be published soon by the American Ceramic Society. The symposium was also intended to honor Professor *Robert L. Coble* (Massachusetts Institute of Technology), who has made outstanding contributions to the field of ceramic materials development (LUCALOX). In the mid-1970's, *R. L. Coble* had stimulated a series of questions about an ideal approach to powder processing, from which the proposal for optimized programs for sintering single phase ceramics evolved. *K. Bowen* (Massachusetts Institute of Technology) summarized some of the experimental results that were subsequently obtained and concluded that the sintering programs have been a necessary stage in structuring the problem of improving the sintering process. This improves the reliability of ceramics, which is essential for the broader application of structural ceramic components. *A. G. Evans* (University of California, Santa Barbara) explained how reliability enhancement may be achieved by combining control of defects with high toughness microstructures, a problem which includes topics such as defects caused by differential densification and grain growth in the presence of pores and second phases. In electronic ceramics the reliability of the products is considerably affected by impurities which influence processing and the final properties. *P. Morris* (Bellcore, Red Bank, NJ) pointed out that most of the present ceramic materials typically contain at least several thousand ppm of impurities, due to chemical inhomogeneities present in the powdered starting materials or introduced during processing.

Impurity and Additive Control

Unintentional impurities or intentional additives were shown to result in complex chemical reactions, often involving liquid phases, which frequently cause discontinuous grain growth (see Fig. 1). A quite surprising effect of the particle size distribution on liquid phase sintering of alumina was found in the case of three alumina powders with equivalent purity levels but varying particle size distributions, which were sintered using a calcium-magnesium-aluminum silicate glass additive. Although the samples sintered to essentially identical densities, radical differences in the fired microstructure were observed. Alumina powders having a bimodal particle size distribution were observed to have the most uniform fired microstructure. Questions regarding the role of a liquid phase (often a glass) in sintering of technologically important ceramics, and also on tungsten when cofired with ceramics in multilayer ceramic packages were generally thought to be of considerable practical importance. Controlled use of impurities and additives can improve the production of, for example, electronic ceramic-metal composites. Tungsten, for example, is commonly used to form conductors in ceramic multilayer packages. During cofiring in hydrogen, densification of the tungsten was shown to be promoted by a silicate liquid that forms either in the ceramic body (typically 90% alumina) or from glass forming components added to the tungsten screen printing paste. In lead perovskite systems a controlled small change in the cation stoichiometry can lead to a substantial reduction of the sintering temperature. This is thought to be due to the formation of a liquid phase during sintering, which would be detrimental to the electronic properties if allowed to remain in the material. However, as some components of the liquid phase have relatively high vapor pressures, the liquid phase can be removed by the evaporation process. Thus, a single perovskite phase is obtained by liquid phase sintering at low temperatures.

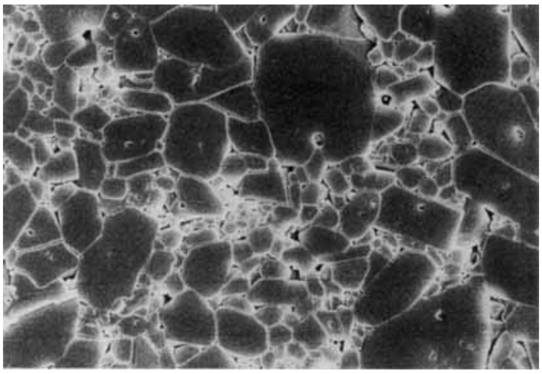
Fig. 1. Uncontrolled abnormal grain growth during sintering of MgO-doped alumina due to the presence of a small amount of liquid phase.

A considerable number of presentations dealt with sintering and hot isostatic pressing of nanoscale powders of Si_3N_4 and Si_3N_4/AlN, obtained by pyrolysis of organometallic precursors in ammonia, or described the effects of sintering aids on densification and microstructural development of SiC, Si_3N_4 and oxide ceramics. Major emphasis was put on the advantages of rare earth oxides which are increasingly used as sintering aids in high performance ceramics. The chemical stability of these oxides should theoretically result in very little oxidation reaction with the host material. In addition, the eutectic mixtures of rare earth oxides with silica have unusually high melting points, which provide a decreased tendency towards uncontrolled grain growth.

High Temperature Creep

Special sessions treated sintering and creep of two phase materials as a subject of growing importance with regard to understanding ceramic processing and improving the reliability of ceramic materials at elevated temperatures. Again, trace amounts of a second phase at grain boundaries were shown to have disastrous effects on component lifetime, since cavities that form during creep tend to propagate as cracks. The viscosity and Poisson's ratio of sintering glass/ceramic and metal pastes used in multilayer substrates can be used to predict stresses and strains produced by differential strain during sintering of composites. Methods of measuring and avoiding these strains were described by a number of authors, emphasizing the enormous amount of recent research activity in the USA in the field of ceramic composites.

The Long Road of Materials Research

A most illuminating example of the subtle and complex chemical and physical problems involved in research on existing and emerging advanced materials was presented by *M. P. Harmer* (Lehigh University, Bethlehem, PA) when he gave the keynote lecture on the perennial topic "Alumina". He commented: "Twenty-seven years have elapsed since *R. L. Coble* reported that small additions of magnesia promote the sintering of alumina to full density—the LUCALOX invention. A steady succession of papers have subsequently appeared concerning the role of the additive, and a considerable amount of controversy has surrounded this topic until today. After critically reviewing what progress has been made over that twenty-seven year period in understanding the role of MgO in the sintering of alumina, I have to conclude that, although we have come a long way in understanding the phenomenology of this classic additive effect, much still remains to be done to understand the detailed mechanisms involved at the atomic level".

Many of the talks at the 90th Annual Meeting of the American Ceramic Society suggested that *Harmer*'s statement is equally applicable to most of the other major topics of current research on the processing of advanced ceramics.

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Advanced Concepts for Ceramic Toughening

A workshop on Advanced Concepts for Ceramic Toughening was held on 14–17 April 1988 at Schloss Weitenburg, FRG. The objective of the workshop was to clarify current understanding of toughening mechanisms in ceramics and to identify future patterns of work needed for the development of materials with the mechanical properties required for applications.

The meeting was divided into four sections concerned respectively with the theory of toughening mechanisms, with the role of interfaces in toughened microstructures, with the requirements of processing and with the transfer of these concepts into industrial practice. An additional discussion session was devoted to the significance of toughness for the acceptability of ceramics.

It was recognized that different sectors of the subject were at very different levels of development. Thus, work on transformation toughening had been brought to a level of maturity where significant issues remained but where the basic understanding was now sound. In contrast, work on fiber and whisker reinforcement was at a very preliminary level in terms of the understanding of the desired interface structure between the reinforcing phase and the matrix. There was in particular concern that high temperature events in toughened microstructures had received little attention and were not well understood.

Toughness and Microstructure

The majority of contributions in this session were concerned with transformation toughening and this subject was also emphasized in the discussion. The common opinion expressed in the summary was that the understanding of transformation toughening is already very high; we have a good understanding of the microstructural contributions (grain size, grain shape, glassy phase, inclusions, etc.) to the toughness. In general it is possible to tailor a microstructure towards a desired toughness.

In selecting particular items from the session, ceria-stabilized tetragonal zirconia (Ce-TZP) is seen as a new material in the group of transformation toughened zirconias. The strongly nonlinear crack diffraction curve will be a subject for many investigations in the future. The origin for the curve is the unusual transformation zone which reaches far ahead of the crack tip and whose shape and elongation are not yet understood. The crystallographic origin of this shape is probably the related transformation tensor, which is not known and which has to be investigated. The scatter of the mechanical properties, especially that of the K_{Ic} values, is dramatic and reaches from just 5 MPa m^{-1} to over 30 MPa m^{-1}. There is strong evidence for a microcrack mechanism in this material; however, the microscopic proof for this is still missing. For this material, the fracture mechanical description using only a K_{Ic} value is no longer valid and has to be replaced by a set of R-curves.

Interfaces

Compared to transformation toughening, the understanding of the role of interfaces is pretty weak. The audience agreed that experiments on the characterization of interfaces in model systems and, of course, in practical systems are missing. For most materials the fracture energies