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Needs Assessment for Nondestructive Testing and Materials Characterization for Improved Reliability in Structural Ceramics for Heat Engines

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CERAMIC TECHNOLOGY FOR ADVANCED HEAT ENGINES

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Metals and Ceramics Division

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D. R. Johnson, R. W. McClung, M. A. Janney,
and W. M. Hanusiak

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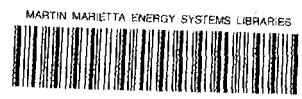

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NEEDS ASSESSMENT FOR NONDESTRUCTIVE TESTING AND MATERIALS CHARACTERIZATION FOR IMPROVED RELIABILITY IN STRUCTURAL CERAMICS FOR HEAT ENGINES*

D. R. Johnson, R. W. McClung, M. A. Janney, and W. M. Hanusiak†

ABSTRACT

A needs assessment was performed for nondestructive testing and materials characterization to achieve improved reliability in ceramic materials for heat engine applications. Raw materials, green state bodies, and sintered ceramics were considered. The overall approach taken to improve reliability of structural ceramics requires key inspections throughout the fabrication flowsheet, including raw materials, green state, and dense parts. The applications of nondestructive inspection and characterization techniques to ceramic powders and other raw materials, green ceramics, and sintered ceramics are discussed. The current state of inspection technology is reviewed for all identified attributes and stages of a generalized flowsheet for advanced structural ceramics, and research and development requirements are identified and listed in priority order.

EXECUTIVE SUMMARY

INTRODUCTION

Traditionally, the role of nondestructive evaluation (NDE) in structural materials has been to detect and characterize flaws. Flaw detection and characterization are particularly difficult in structural ceramics, however, because of the extreme sensitivity of ceramics to flaws and because of the very small size (20–50 μm) of critical flaws.

The flaw sensitivity of ceramics and the typically wide variation in flaw sizes result in the situation illustrated in Fig. 1, which is a frequency distribution of fast fracture strengths for a hypothetical structural ceramic with characteristic strength of 350 MPa and Weibull modulus

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of 5. The strength requirement, 250 MPa, for a particular application is shown. In this illustration, a significant fraction of the population of ceramic parts, 17%, has a strength below the 250-MPa requirement.

The situation illustrated in Fig. 1 is typical of structural ceramics today: although in many cases the average properties of a specific ceramic may be suitable for the intended use, a significant fraction of the parts made of that material will be unsuitable. The unacceptable parts are, of course, very difficult to distinguish from the rest of the population.

Deming[35] and others have developed systematic procedures over the past 40 years with the goal of manufacturing defect-free parts. These procedures include the systematic inspection of key attributes during the processing of the parts, maintaining statistical quality control of the process, and systematically seeking out and eliminating the sources of flaws.

The goal of our program is illustrated by Fig. 2. This drawing shows the frequency distribution from Fig. 1 with a superimposed desired distribution. The desired distribution, in this case, has a characteristic strength of 450 MPa and a Weibull modulus of 20. It is obvious from inspection of the drawing that virtually no parts from this distribution will fall below the design requirement of 250-MPa strength.

A general ceramic processing flowsheet and inspections at each stage of the flowsheet are shown in Fig. 3. The inspections shown were identified as potentially important in the development of highly reliable ceramics. There is no suggestion that all of these inspections be performed in a given product line. The inspections shown were all considered in our assessment of the relative priorities for the development of inspection techniques. It is anticipated that a limited number of key inspections will be identified for any given product line. The following sections review the status and needs for inspections in raw materials, green bodies, and dense ceramics.

DEVELOPMENT STATUS AND NEEDS ASSESSMENT

Raw Materials

Ceramic powder characterization is usually the first task in raw material qualification because ceramic powders represent the largest

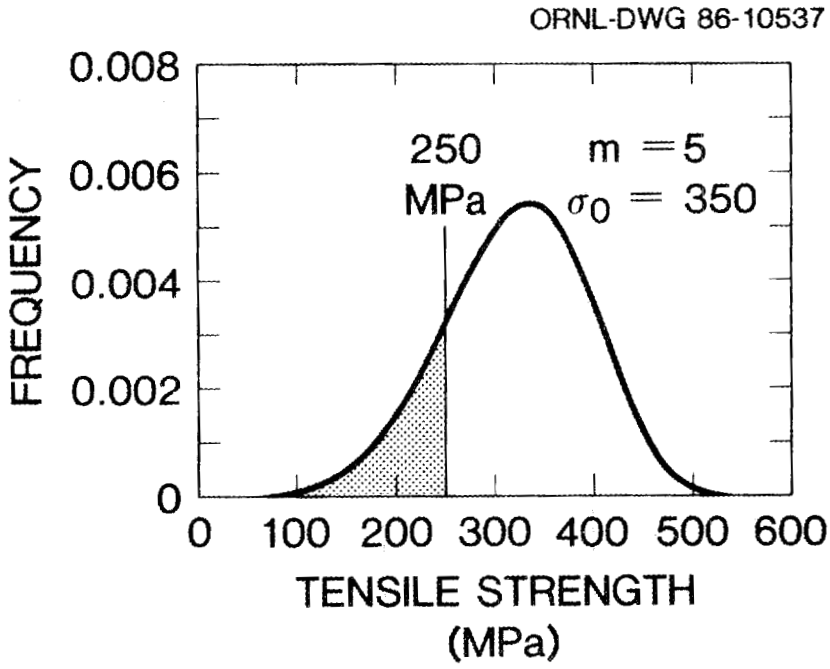

Fig. 1. Weibull frequency distribution for hypothetical ceramic material with characteristic strength σ_0 of 350 MPa and Weibull modulus of 5.

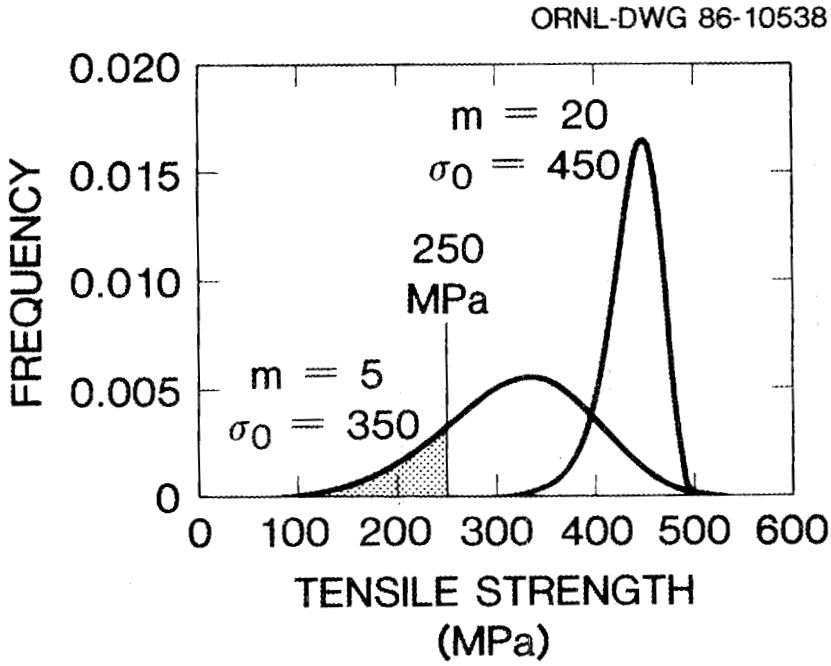

Fig. 2. A desired alternative distribution, resulting from improved processing with σ_0 = 450 MPa, m = 20.

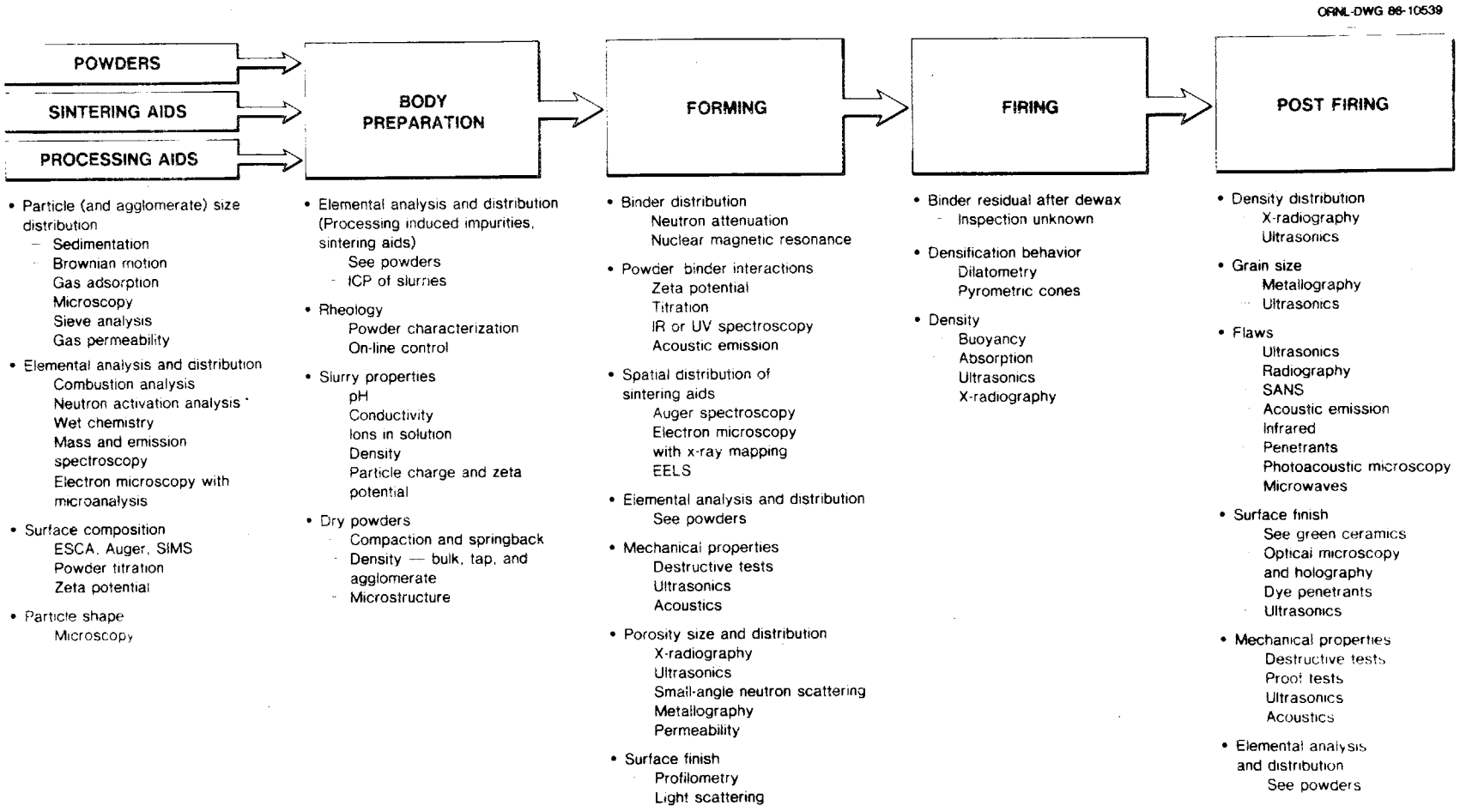

Fig. 3. General processing flowsheet and inspections considered.

fraction of the raw materials. The attributes that are typically determined (see Fig. 3) are particle size distribution (PSD), chemistry, crystallographic phase(s), morphology, and physical properties. PSD analysis techniques are generally well established, but interpretation of results is sometimes difficult. Applying multiple analyses such as light scattering, sedimentation, and specific surface area can often be helpful in sorting out agglomeration and porosity effects. Direct observation by scanning and transmission electron microscopy should not be ignored. We must determine which of the following chemical analyses are critical: (1) bulk vs surface, (2) soluble vs insoluble, (3) combined elements vs free elements (especially important for carbides and nitrides), and (4) distribution (particle to particle, and within particles). The precision of analysis must be specified (e.g., is oxygen analysis by combustion analysis or neutron activation analysis needed in a carbide or nitride?). Phase constitution is often critical in a starting material (e.g., α/β ratio in SiC, α content in Si_3N_4, and tetragonal/monoclinic ratio in ZrO_2). This is most often determined by X-ray diffraction. Other techniques, including Raman spectroscopy, optical microscopy, differential thermal analysis, differential scanning calorimetry, and electron diffraction can also be useful. Of the characterization techniques, particle shape analysis has received the least attention probably because few clear correlations have been demonstrated with processing or fired properties. The advent of whisker-reinforced ceramics will probably change this situation; methods to quantify whisker-aspect ratio, straightness, and roughness may be needed in the future.

Process-related characterization refers to those techniques that are specific to a particular forming or processing method. Such techniques are often used as both qualification tests and in-process control tests. For example, bulk powders (as-received) and prepared powders (granulated, spray dried, etc.) are often characterized with respect to their ability to be dry pressed to size and weight; tests include bulk and tap densities, flow time, angle of repose, compaction curves, and springback. Other tests include green strength and abrasion resistance, green microstructure, and porosimetry or permeability as a function of forming pressure or green density. Slurries (including extrusion and injection

molding mixes) may be characterized with respect to their solution properties – pH, conductivity, ions in solution (and their slurry properties) – density, settling tendencies, viscosity and elasticity, and particle charge and zeta potential. Firing a test powder or powder mix determines its sinterability and its ability to produce a good microstructure. Recently, some investigators have used dilatometry to characterize lot-to-lot variations in powders or mixes. Finally, fired properties can be used to determine initial powder properties. As an example, the cemented tungsten carbide industry uses a magnetic saturation measurement on fired parts (related to the carbon content of the cobalt phase) to very accurately determine the need for more or less carbon in the starting powder; the magnetic measurement is far more sensitive than standard carbon analysis by combustion.

Organic additives need to be characterized with respect to purity and contamination, effectiveness (i.e., does a standard amount in a standard batch perform to a standard level?), and ash content. Carriers are often underanalyzed or not analyzed at all, which is dangerous because they can represent a major source of contaminants. Solvents and water may carry dissolved substances and particulates, and compressed gases can be contaminated with oil, water, and dust; filtering of carriers is a must if ultimate properties are to be attained. Recycling of solvents poses a major contamination problem; if solvents are to be recycled, they should be scrupulously cleaned and then analyzed to verify their purity.

Establishing cause-and-effect relationships among the various characterization techniques, processing parameters, and the green and fired properties may be the key to improving product quality and uniformity. In practice, powder and process specifications do not, in many cases, adequately ensure product quality. As a result, raw materials may be adequately qualified only by making the product in a laboratory or pilot-scale process.

Green-State Ceramics

At the stage of component forming, many conditions may be introduced that subsequently lead to less-than-optimum material properties and performance. Discovery and elimination of the sources of these conditions through process optimization are required for production of reliable

ceramics. Key inspections are needed in this process. Figure 3 shows several inspectable characteristics of green-state bodies that have been identified. Distribution of the binder is an important parameter, but no inspection system is available. Techniques involving neutron scattering and nuclear magnetic resonance (NMR) are being considered. Possible evaluation of powder/binder interactions may be done by colloid chemistry analysis (e.g., zeta potential and powder titration) and spectroscopy using infrared, ultraviolet, or other phenomena. The surface physical interaction may be amenable to measurement by techniques from soil-mechanics analyses. Elemental composition and distribution may best be accomplished by wet chemistry techniques or X-ray analytical techniques on the green-state bodies. Mechanical properties are conventionally determined by destructive tests. Acoustic and ultrasonic techniques offer significant promise for the measurement of elastic properties that may be related to mechanical properties. Several laboratory studies have been conducted to determine initial feasibility for nondestructive detection of flaws and density variations in green ceramics, including radiography, ultrasonics, NMR, and small-angle neutron scattering (SANS). Optical techniques and light-scattering techniques are considered potentially useful for evaluating surface finish.

Sintered Ceramics

A number of critical characteristics that affect the service performance of sintered ceramics have been identified: elemental composition, microstructure, local density variations, bulk material and mechanical properties, physical properties, flaws, and surface properties. For some of these characteristics, methods of evaluation and measurement are readily identified, and some are in place for application; some of the certain characterization needs are not as well in hand, although potential solutions may be identified (and laboratory studies may have been performed). Measurement of elemental composition and distribution can be accomplished by wet chemical and X-ray analytical techniques. Microstructures can be evaluated by techniques of microscopy. Ultrasonics offers the potential of providing useful information about grain size and grain size distribution. Both ultrasonic and X-ray techniques have shown

feasibility for detection and measurement of localized variations in density. Destructive testing and proof testing are currently used to determine mechanical properties and will undoubtedly continue until acceptable alternatives are available. However, neither approach provides direct data on actual components as they are being put into service. Acoustic and ultrasonic techniques show the ability to measure elastic properties and have promise as a powerful tool for the potential prediction of serviceability of a newly fabricated component or determination of residual life for a component after a period of operation.

Many NDE methods and techniques have been investigated and/or applied to the detection and evaluation of flaws in sintered ceramics with varying degrees of success. Major emphasis has been given to the various techniques of ultrasonics and radiography, and the encouraging results in laboratory studies indicate that these techniques should continue to receive significant attention in creating methods to be used in materials development and in product certification. Ultrasonics will require the use of higher-than-conventional frequencies (e.g., 25–100 MHz) and sophisticated signal processing for analysis of velocity, attenuation spectra, and reflections for flaw characterization. Microradiographic techniques (e.g., using microfocus X-ray tubes) have shown good resolution and sensitivity for small flaws and should be pursued with both film and non-film techniques. The benefits of tomographic techniques for three-dimensional localization of flaws and density gradients (in both green and sintered ceramics) should be further investigated. SANS shows promise as a research tool for materials research and development (R&D) but is not anticipated to be practical for product characterization, in part because of the expense of the limited facilities. Acoustic emission techniques have been studied for monitoring of flaw growth during destructive testing and, as such, are beneficial for product development and testing. Such techniques depend on stress wave emission (e.g., from a growing flaw), and no literature was discovered on applications to detect the presence of fabrication flaws. Infrared techniques that monitor temperature profiles are anticipated to have limited usefulness for flaw detection in ceramic bodies. Limited work in microwave methods has demonstrated a capability to detect internal flaws, but the limitations on resolution observed to

date are not encouraging. Liquid dye penetrants are used as a simple tool for surface-flaw detection, and little further engineering development is expected, except of methods of calibration and standardization. Photoacoustic microscopy shows promise as a high-sensitivity and high-resolution technique for surface and near-surface flaws but, in its current stage, is rather slow and may be limited to materials development and sampling.

Optical methods of examining the surfaces of sintered ceramics are anticipated to continue to be an important part of the evaluation, probably with little need for sponsored, noncommercial development. A possible exception is the use of laser-assisted optical examination for higher speeds and automated interpretation. A related area, optical holography using lasers, has shown promise for surface and subsurface detection of flaws. It may justify further investigation for applications in materials development and, for limited quantities, statistical sampling of production lots. Various ultrasonic techniques (e.g., surface acoustic waves and critical-angle reflectivity) have shown good sensitivity to surface flaws and properties in laboratory studies, and further investigations and technique development should be made.

Evaluations of these various flaw detection techniques have concentrated on resolution of discrete flaws or estimation of an average flaw dimension. The statistical frequency distribution parameters for the flaws are likely correlated with the corresponding strength distribution parameters (e.g., Weibull modulus). However, estimation of the Weibull modulus or other descriptors of the scatter in strength data has not been done successfully by nondestructive analysis.

RECOMMENDATIONS AND CONCLUSIONS

Our preliminary assessment of the R&D priorities for NDE and materials characterization are as follows:

1. Develop standard reference powders for powder characterization. We found that test development does not seem to be a problem with respect to powder characterization. Many techniques have been developed, and test apparatus are commercially available. However, the interpretation of the data from these tests remains a problem, and

appropriate standard materials are not generally available. Although standards are available for calibrating various instruments (e.g., National Bureau of Standards particle size standards), standard "real" materials are still needed. Standard powders should be in large lots, and multiple properties should be carefully characterized. Representative samples should be available to laboratories at cost. A first attempt at developing one such standard (Si_3N_4) is planned as part of the current IEA Annex II program in advanced ceramics.* It would be advantageous to have standard reference powders for all the major classes of ceramic powders.

2. Develop instrumentation, hardware, and procedures for determining volumetric and surface properties of green and dense ceramics by using ultrasonics. Properties include density, grain size, elastic and mechanical properties, and flaw detection and characterization. The laboratory studies conducted to date suggest that ultrasonics may be very versatile in characterizing both green and dense ceramics and in material characterization and flaw detection.
3. Develop instrumentation, hardware, and procedures for inspection of statistical samples for density and flaw detection and characterization by microfocus radiography techniques, including tomography. Advanced X-ray techniques, including microfocus, real-time imaging, and tomography, should be pursued for the determination of density variations and flaws; the ultimate planned applications should be for statistical sampling on large volume production and 100% examination on complex and expensive components where very extensive examination may be warranted.
4. Conduct an extensive, carefully controlled processing-improvement program in concert with one or more (simple) product lines. To accomplish this, a generic system such as slip casting or injection molding should be chosen for study. (If funding were available, parallel studies of multiple material/process/shape systems would be justified.) Key inspection parameters should be identified by means of a series of exhaustively documented experiments in which extensive

*International Energy Agency (IEA) Annex II, Cooperative Programme on Ceramics for Advanced Engines and Other Conservation Applications.

inspections should be conducted at each stage of the process to learn the effects of the measured properties on the performance of the finished product. As experience is gained in identifying precursors of flaws, the process or raw materials should be modified to eliminate the source of the flaws.

5. Develop instrumentation, hardware, and procedures for characterizing green ceramics for binder distribution by NMR. Although this NDE method will require equipment development to achieve the resolution and sensitivity sufficient for beneficial use on structural ceramics, it is currently the most promising method available for characterizing proton-rich material such as ceramic binders.

INTRODUCTION

Traditionally, the role of nondestructive evaluation (NDE) in structural materials has consisted of flaw detection and flaw characterization (e.g., detection of cracks in pressure vessel steel, cracks or voids in castings and welded heat exchanger tubes and headers, and surface cracks in structural members). Flaw detection and characterization are particularly difficult in structural ceramics, however, because of the extreme sensitivity of the material to flaws and the very small size (20–50 μm) of critical flaws in structural ceramics.

The mechanical behavior of structural ceramics under most conditions can be described as classical Griffith-Orowan[88,97] behavior,

$$\sigma = A \left(\frac{E\gamma}{c}\right)^{1/2} , \qquad (1)$$

where σ is the fracture stress, A is a constant that depends on specimen geometry, E is the elastic modulus, γ is the interplanar fracture energy, and c is the critical flaw size, typically 20 to 50 μm.

Analysis of the crack tip by fracture mechanics leads to a description of the fracture in terms of stress intensity factor. For failure in tension (load perpendicular to the crack), the critical stress intensity (K_{IC}) that leads to failure can be described as follows:[98]

$$\sigma_1 = \frac{K_{Ic}}{Y c^{1/2}} , \tag{2}$$

where σ_1 is the critical fracture stress, Y is a geometry dependent constant called the stress intensity factor coefficient, and c is one-half the critical flaw dimension. The value of K_{Ic} is typically 3 to 6 MPa $m^{1/2}$ for structural ceramics, leading to a critical flaw size of 50 to 20 μm for corresponding strengths of 350 to 700 MPa. The K_{Ic} value is usually interpreted in terms of "fracture toughness."

The frequency distribution of flaws (and thus of mechanical strength values) in ceramics can often be described by the Weibull[129,162] statistical frequency distribution, which assumes a weakest-link theory: a given volume of ceramic under a uniform stress will fail at the most severe flaw. The probability of failing as a function of volume is given by

$$F(\sigma) = 1 - \exp[-\int_V (\sigma/\sigma_0)^m dV] , \tag{3}$$

where $F(\sigma)$ is the failure probability distribution function; σ is the tensile stress; σ_0 is a material constant, the stress at which the probability of failure is 0.632 for a unit volume of material; and m is the Weibull modulus. The Weibull modulus for structural ceramics is typically 5 to 10, indicating a large amount of variation among strength values. The Weibull equation also predicts that the strength of structural ceramics will decrease as a log-log function of stressed volume, v,

$$\ln \sigma \propto - 1/m \ln v . \tag{4}$$

The flaw sensitivity and the typically wide variation in flaw sizes of ceramics results in the situation illustrated in Fig. 1. Figure 1 is a frequency distribution of fast fracture strengths for a hypothetical structural ceramic with a characteristic stress of 350 MPa and a Weibull modulus of 5. The strength requirement, 250 MPa, for a particular application is shown in Fig. 1. In this illustration, a significant fraction of the population of ceramic parts, 17%, has a strength below the 250-MPa requirement.

The situation illustrated in Fig. 1 is typical of structural ceramics today. The specific values chosen for illustration are somewhat arbitrary, but not unreasonable. The illustration is of fast fracture strength at

one fixed temperature when, in fact, the mechanical behavior must be expressed in terms of several time-, temperature-, and chemical-atmosphere-dependent parameters to be definitive.[8] Nonetheless, Fig. 1 is conceptually typical of state-of-the-art structural ceramics: although, in many cases, the average properties of a specific ceramic may be suitable for the intended use, a significant fraction of the parts made of that material will be unsuitable. The unacceptable parts are, of course, very difficult to distinguish from the suitable parts.

The traditional approach in the United States to the problem illustrated in Fig. 1 is to inspect or proof-test 100% of the components made from the hypothetical material and to reject the defective components for discard or later rework. This approach can be shown to be impractical over the long term for two reasons. First, the NDE technology readily available today has difficulty with the inspection of complex parts with cross sections of more than a few millimeters for internal 20- to 50-μm flaws. There is reason to believe that such inspections, if they become commercially feasible, will always be slow and expensive. Although proof-testing will work in principle for truncating the low-strength tail of the distribution, structural ceramics that are susceptible to slow crack growth may be a problem. A subcritical flaw may grow during the proof test to a nearly critical size and then result in rapid failure during service. Second, it can be shown that this approach is prohibitively expensive.[35] The extensive inspection and rejection of components may be considered as an attempt to "inspect-in" the quality of the parts. Although this approach may be necessary for making prototype parts in the near term for research and development (R&D) or demonstration programs, the only way to manufacture quality ceramic components is to make them correctly from the beginning. Complete (100%) inspection and proof-testing will probably be required in the near term for a different reason: until the structural ceramic community overcomes the stigma of poor reliability, some assurance of quality will have to be provided to our customers and improved NDE techniques will be required. Even after significant improvements in manufacturing quality, NDE (at least on a sampling basis) will, of course, be required as part of the necessary quality assurance.

Deming[35] and others have developed systematic procedures over the past 40 years with the goal of manufacturing defect-free parts. These procedures include systematically inspecting key attributes during the processing of the parts, seeking out and eliminating the sources of flaws, and maintaining statistical quality control of the process. An excellent example of such a system is that used by Microcomputer Memories, Inc. (MMI).[9] MMI, a manufacturer of computer storage devices such as tape and disk drives, has implemented a closed-loop quality control system that spans the entire use cycle – from suppliers of components to final users. Along the way, a documented train of controlled procedures is maintained, allowing a failure at any point to be fed back and the system to be adjusted accordingly. The component vendors are also required to follow documented closed-loop quality control and to supply defect-free components to MMI. The practice of manufacturing 1200 components to deliver 1000 is not acceptable to MMI. This standard of quality requires a change of philosophy on the part of MMI vendors. Internally, MMI has implemented a quality control system that starts with design and continues through manufacturing, packaging, and shipping. After delivery, field failures are evaluated by the quality control department for feedback into the system for fine-tuning or a change in procedure. The current assessment considers NDE and other material characterization inspections from the point of highly controlled manufacturing processes incorporating a systematic program for eliminating defects.

The advocated approach to reliable ceramics should not be construed as a plan to inspect the product at each step in the process and then reject the defects earlier in the manufacturing process when the components represent a lower value added and, thus, lower invested cost. Although this approach has some appeal compared to rejecting finished parts, it still represents an attempt to inspect-in quality. Instead, the role of inspections in the advocated procedure is to maintain and ensure control of the process and to systematically locate and eliminate the source of flaws.

The goal of our program is illustrated by Fig. 2. This drawing shows the frequency distribution from Fig. 1 with a superimposed desired distribution. The desired distribution, in this case, has a characteristic strength (450 MPa) and a Weibull modulus of 25. It is obvious from

inspection of the drawing that virtually no parts from this distribution will fall below the design requirement of 250-MPa strength. Although the specific values in this illustration are also arbitrary, they are not unreasonable and are similar to the material development goals of several of our program subtasks and associated tasks in related programs.[155,156]

The relationship between the character of starting materials for ceramic powder processing and the reliability of the resulting ceramic parts has been accepted in concept for many years.[22,26,58,82,128,157] Also conceptually obvious is the relationship between processing variables and final product quality.[18,22,25,47,68,69,82,117,158,159,160,161] That is, defects or defect precursors may be introduced along with the original starting materials or at many points along the process flow path. Defects introduced into the process may be in the form of foreign particles, for example, or particle agglomerates. The first of these is an extrinsic defect, whereas the second is an intrinsic defect. A defect precursor may be an unwanted element or phase that either inhibits sintering or causes exaggerated grain growth, thus creating a defect as processing proceeds. This is an example of an extrinsic defect precursor. An example of an intrinsic defect precursor is an improperly distributed additive or second Phase that would inhibit sintering and/or result in localized large pores.

The derivation of these relationships by empirical means has been very slow and difficult. Many researchers have analyzed material properties such as microstructure,[19,26,53,73,83,94,127] size distributions,[19,74,76,82,95] shape distributions,[22,74,76,82,88,135] surface area,[76,128] tap density,[76] bulk and microstructural chemistry,[12,29,33,41,47,49,53,76,81,88,93,96] crystal structure,[33,74,95,118] and residual stress.[108] Chemical analysis of additives[20,21,127,132] and process variables such as time-temperature-pressure cycles[32,84,86,93,126,134] have also been investigated and correlated with final properties. In general, these efforts have always fallen short of our ultimate goal – the identification of the necessary and sufficient variables controlling product reliability. The reason is twofold: (1) ceramic powder processing is a multivariable synergistic problem and (2) quality control has not been effectively applied. Control of only a few variables at a time results in inconsistent correlations between

characterization and final component reliability. In principle, to truly exert complete control over the properties of the final product, control of every variable in the process cycle simultaneously would be necessary. Because this may not be possible as a result of the magnitude of the number of variables, identification and control of the most significant variables will have to be sufficient to maintain an acceptable range of properties for the final product.[27,35,61,85,89] (It is envisioned that "expert" systems can be developed and implemented to provide simple on-line control of key variables. Introduction of artificial intelligence could assist in identifying critical variables or allow control of more variables.)

For example, many critical flaws have been traced to the powder from which the corresponding ceramic was made.[82] The ultimate solution to the problem of flaws or flaw precursors preexisting in the powder will be to develop a better source of powder that does not contain the defects. Flaw precursors in powders can be inadvertent impurities, such as lint, hair, or dust, or particles of material introduced in milling or handling the powder. Foreign matter or impurities may be introduced in binders, lubricants, liquid carriers, dispersants, and other processing aids. The degree of cross-linking in a polymeric material, for instance, can affect its reactivity as well as its thermomechanical behavior. Chemical contaminants can inhibit or catalyze desired and undesired reactions, respectively, with the powder and/or the other additives.

The flaw sources also include defects that may be characteristic of powders made by certain processes — for example, discrete large particles or agglomerates or impurities that are uniformly distributed throughout, and characteristic of, the powder. An assessment of inspection requirements for manufacturing highly controlled, reproducible ceramics should, therefore, include a study of the inspections now available for powders and processing aids, the capabilities and limitations of those inspections, the relative importance of the inspections with regard to process control and material characterization, and the future needs and priorities. The current effort attempts to accomplish these goals.

Similarly, it can be shown that flaws may be introduced during green-body preparation and handling, and during firing, grinding, metalizing,

and other processing of dense ceramics. It follows that appropriate inspections during these fabrication steps will be required in a reliable ceramic manufacturing process. This assessment considers the status, needs, and priorities of nondestructive inspections and characterization techniques for all phases of ceramic processing: (1) raw material characterization, (2) in-process characterization, and (3) final product characterization.

RAW MATERIALS CHARACTERIZATION AND QUALIFICATION

INTRODUCTION

Inspection and qualification of the raw materials are the most important step in manufacturing a high-quality ceramic part. The reason for this is clear: it is difficult (and sometimes impossible) to engineer around bad starting materials. For example, if a ceramic powder cannot be formed into the desired part by the selected processes, it is worthless. The practicing ceramic engineer has a real problem at this point. A meaningful set of specifications must be written that will ensure a given level of performance in terms of fired properties and size and shape control. Ensuring such level of performance requires defining, and then controlling, a critical set of attributes (chemistry, particle size, etc.) for the raw materials. (Standards for similar materials may already exist.[7]) An iterative process evolves in which specifications are set, problems in control arise, new specifications are set, new problems arise, and so on. This process is most often driven by the need (1) for tighter control of fired properties, (2) for additional qualified raw materials vendors, or (3) to deal with variations in the quality of raw materials received from current vendors.

Inspection and qualification activities take at least three forms: (1) pure analytical procedures such as determining chemical and physical properties; (2) processing-related procedures such as determining formability and green-state properties; and (3) developing cause-and-effect relationships among raw material properties, processing, and fired properties. We stress the importance of establishing true cause-and-effect relationships, and not simply correlations, between characterization, processing, and fired properties. One must establish why changes in input

variables (raw materials) create changes in the final properties. This is especially true in regard to lot-to-lot variations in materials from a given supplier. For a given problem, it will take considerably longer to find out "why" than simply to establish "what" and fix it; in the long run, however, the knowledge gained by such process research will pay for itself many times over when related problems are encountered.

ANALYTICAL POWDER CHARACTERIZATION TECHNIQUES

Ceramic powder characterization is usually the first task in raw material qualification because ceramic powders represent the largest fraction of the raw materials. The attributes that are typically determined are particle size and particle size distribution (PSD), chemistry, crystallographic phase(s), morphology, and physical properties.

Particle size and PSD analysis techniques are generally well established; several excellent reviews exist,[3,6,16,17,57,116] and a description of specific techniques will not be addressed here. It should be noted, however, that each of the standard methods, such as light scattering, sedimentation, electrical zone sensing, permeability, and specific surface area, measures a different attribute of a powder; hence, each tends to yield different information about the powder. For a raw powder, the main concerns are its ultimate PSD and its degree of agglomeration. The degree of agglomeration can often be determined by comparing the average particle size determined from a surface area measurement such as BET[163] gas adsorption, d_{BET}, with that determined by sedimentation, light scattering, or electrical zone sensing, $\bar{d}$. A major difference between $\bar{d}$ and d_{BET} indicates either agglomeration or internal porosity in the particles. Several investigators have taken this technique a step further to define various "agglomeration numbers," which describe the average number of primary particles per agglomerated particle. These are reviewed by Adair et al.[3] If an incoming powder is agglomerated, then one must determine what degree of treatment is necessary to achieve complete deagglomeration. For example, time-of-milling experiments with particle size analysis performed periodically are often performed. Typically, these analyses must be coupled with an in-process test, such as slurry viscosity or die compaction, to ensure that the powder is neither undermilled nor overmilled.

Direct observation by scanning electron microscopy and transmission electron microscopy should not be ignored. Another example is the use of surfactants and/or Stokes' Law sedimentation to eliminate agglomerates. Slurry properties such as zeta potential and pH can be important.

When qualifying a new supplier, one must be especially careful because the new supplier's material will be different from that of the current supplier. The differences may be small, but they must be documented and quantified. Thus, the particle size of 2.6 μm of material from the current supplier may be equivalent to that from the new supplier of 2.2 or 3.2 μm because of shape or agglomeration differences; yet both may process equally well. Obviously, the specifications for one material cannot be applied to the other material.

Chemical analysis of ceramic powders and other raw materials presents numerous choices, problems, and challenges for the ceramist: (1) For which elements does one analyze? (2) Is there a mass balance (i.e., do the elements sum to 100%)? (3) Are there special considerations (e.g., oxygen in nitrides, carbides, or borides; free vs combined carbon in carbides; and light-element analysis)? It is necessary to determine which types of analysis are critical: bulk vs surface, soluble vs insoluble species, combined vs free vs total, and distribution. Also, one must specify the precision needed (e.g., oxygen analysis can be performed by combustion analysis for a rough analysis or by neutron activation analysis if greater precision is required).

Phase constitution of a starting powder is often critical to ceramic performance, yet it is sometimes overlooked or improperly characterized. Examples of systems in which phase constitution represents an important parameter include sintered SiC (α/β ratio), Si_3N_4 and sialons (α content of starting powder, amount of β or β' phase in final product, glassy phase devitrification), and ZrO_2 (tetragonal/monoclinic ratio).

Phase constitution is most often determined by X-ray diffraction.[62] Other crystallographic techniques, such as Raman spectroscopy, optical petrography, and electron diffraction, may also be used. Thermal analysis techniques, such as differential thermal analysis, differential scanning calorimetry, and thermal gravimetric analysis, are employed less frequently in ceramics.

Bulk chemical analysis is a necessary part of powder characterization. A variety of techniques can be used depending on whether the analysis is for major or minor elements.[44] Typical examples include spark-source mass spectrometry, dc-arc spectroscopy, inductively coupled plasma, and atomic absorption techniques, as well as classical wet chemistry techniques. Instrumental techniques are desirable because of their speed and ability to be automated. However, the more time consuming, traditional methods of gravimetric and volumetric analyses are often desirable or even necessary.

Several areas of concern exist with respect to specifying the chemical composition of a ceramic powder. The first is the need for a mass balance. This is especially difficult when dealing with nonoxide materials. Using B_4C (ref. 2) as an example, to fully specify its chemistry, one must determine total, free, and combined boron; total, free, and combined carbon; oxygen [as B_2O_3 on the B_4C surface and as adsorbed H_2O (ref. 40)]; and various cation and anion impurities such as Al, Ca, Co, Cr, Fe, F, and Cl. Each determination is based on a different technique with varying degrees of precision, which makes attaining a 100% mass balance quite difficult. SiC, Si_3N_4, and sialons pose similar problems.

Surface chemistry of ceramic powders has recently received much attention. It is widely recognized that impurities that reside on powder surfaces often are concentrated at grain boundaries in the fired material. Also, the types and concentrations of surface species play a critical role in the processing behavior of powders.

The methods of analysis for determining surface chemistry include (1) vacuum electron beam and X-ray methods, such as Auger electron spectroscopy, electron spectroscope chemical analysis, and secondary ion mass spectrometry to determine elemental composition; (2) colloidal methods, such as particle electrophoresis (zeta potential) and potentiometric titration to determine electrical double-layer properties; and (3) infrared spectroscopy to identify surface species, degree of hydration, and organic contaminants.

Particle shape analysis has received the least attention of the characterization techniques, probably because few clear quantitative relationships have been demonstrated with processing or firing behavior. Also, shape is probably the most difficult parameter to specify, and shape

analysis is very time consuming. For most ceramic systems, the payback in improved performance is not justified in terms of the time and effort invested. The existence of quantitative relationships between shape and performance has only recently been demonstrated in other areas of technology. An example is the work of Vetter and Swanson,[125] which showed that abrasive wear resulting from size and shape could be distinguished.

The advent of whisker-reinforced ceramics may result in more emphasis on particle shape analysis. Methods to quantify the aspect ratio, straightness, roughness, etc., of whiskers may be needed in the future.

PROCESS-RELATED POWDER CHARACTERIZATION TECHNIQUES

Process-related characterization refers to those techniques that are specific to a particular forming line or processing scheme. Often, such techniques are used both as qualification tests and as in-process control tests. Techniques that yield slurry-viscosity and powder-compaction curves fall into this category.

Bulk powders (as-received) and prepared powders (granulated, spray dried, etc.) are often characterized with respect to their ability to be dry pressed to size and weight; tests include bulk and tap densities, flow time, angle of repose, compaction curves, and springback. Bulk and tap density are critical with respect to loading the proper amount of powder into a die. Flow time and angle of repose can be related to the speed with which a die can be filled and the uniformity of the die fill. Compaction and springback curves determine the pressures needed to achieve a given green density and the deviations of the as-pressed dimensions from the die dimensions. Other tests that may be performed on dry powders include green strength and abrasion resistance of pressed parts, determination of green microstructure (by infiltrating with a low-viscosity epoxy resin, then polishing), and porosimetry or permeability as a function of forming pressure or green density to determine the pore structure of the pressed part. Permeability measurements are potentially of use in real-time control because they can be performed rapidly.

Slurries of powders (and other processing aids) may be characterized with respect to their solution and slurry properties. Solution properties that can be measured include pH, conductivity, and ions in solution.

Conductivity and pH are easily measured on-line; ion concentration may also be measured if an appropriate specific ion electrode is available (e.g., Br^-, Ca^{++}, $CO_3^=$, Cl^-, Pb^{++}, O_2, K^+, and Na^+). Slurry properties that can be measured include density, settling tendency, viscosity and elasticity, and particle charge and zeta potential. Density and viscosity are easily measured on-line. Most often only a few of these analyses are conducted for a given slurry line.

Firing a test powder or powder mix determines its ability to sinter to density and produce the desired microstructure. Some investigators have found dilatometry to be valuable in characterizing sinterability.[99] Dilatometric analysis of powders provides maps of the sintering paths in terms of density, time, and temperature. It provides a tool for adjusting the sintering schedule in response to lot-to-lot variations in the incoming powders.

Fired properties can also be used to determine initial powder mix properties. As an example, the cemented tungsten carbide industry uses the measurement of magnetic saturation on fired parts (magnetic saturation is related to the carbon content of the cobalt phase) to accurately determine the need for more or less carbon in the starting powder mix. The magnetic saturation measurement is far more sensitive than standard carbon analysis by combustion.

OTHER RAW MATERIALS CHARACTERIZATION

Raw materials for ceramics include processing aids in addition to the ceramic powders. These processing aids include organic additives, such as binders, dispersants, and lubricants, as well as acids and bases. Often overlooked in terms of characterization are the carrier vehicles, which include water, solvents, and gases such as compressed air.

Organic additives should be characterized, and the manner in which they interact in the processing system should be determined. The organics may be characterized with respect to purity, contamination (especially particulates), molecular weight, viscosity, percent active, and ash content on pyrolysis. They may also be characterized in terms of "effectiveness" in the system, such as slurry viscosity for a standard powder that has a standard amount of dispersant and/or binder added.

Carriers are often underanalyzed or not analyzed at all, which is dangerous because they represent a major source of contamination. Solvents and water may carry with them both dissolved species and particulate contaminants. The use of chemically pure (not technical grade) solvents or high-purity deionized water is often justified; filtering is essential if ultimate performance is to be achieved. Recycling of solvents poses severe contamination problems. If solvents are to be recycled, they should be scrupulously cleaned and analyzed to verify their purity; special attention should be paid to particulate contamination, water pickup, and processing-aid carryover.

CAUSE-AND-EFFECT RELATIONSHIPS

Establishing cause-and-effect relationships among the various characterization techniques, processing, and green fired properties is the key to improving product quality and uniformity. In practice, ceramic engineers frequently make their final go/no-go decisions regarding the acceptability of raw materials by running a laboratory- or pilot-scale processing line. This is done because it is often the only way to ensure that the ceramic powders and processing aids will actually make good product. The following industrial situations often occur: (1) a new lot of raw materials passes every qualification test currently in use; (2) a test of the materials is made on the pilot line and poor-quality product is produced, resulting in a "mad scramble" in the quality assurance (QA) and R&D labs to determine a cure for the problem; (3) after the cure (and the cause) are identified, a new specification is added to the existing set of specifications; and (4) this proves sufficient until the next crisis arises. As this cycle is repeated, the set of specifications becomes more restrictive and, at the same time, more cumbersome.

Writing specifications for ceramic powders and other raw materials is very difficult because of the complexity of these materials systems. Fully characterizing a given raw material, such as a powder, require an enormous effort. Usually, only a small fraction of the total attributes is specified for characterization. As the requirements for control of final properties are raised, the required degree of control of the raw

materials is also raised and more attributes must be characterized. In addition, greater understanding of the materials and processes used to make a specific product is required. At this point, processing R&D becomes important. The object of processing R&D is to understand the physics and chemistry of a ceramic particulate system. The benefits to be derived from such an understanding include the ability to cure and anticipate processing problems, the determination of the sensitivity of a process to changes in procedures or raw materials, and the potential to improve current processes and to develop new processes.

STANDARDS

Standards for the characterization of ceramic powders are desperately needed in the ceramics community. Although standards are available for calibrating various instruments [e.g., National Bureau of Standards (NBS) particle size standards], there is a need for nonideal powders having a known set of properties. This set might include PSD (by several methods); specific surface area; bulk, surface, and solution chemistries; bulk, tap, and true solid densities; titration behavior and zeta potential as a function of pH; and various other characteristics. Such materials would be invaluable for interlab comparisons and as standards for QA and production labs. A first attempt at developing one such standard (Si_3N_4) is planned as part of the current International Energy Agency (IEA) Annex II program in advanced ceramics.* It would be advantageous to have standard reference powders for all the major classes of ceramic powders. Similar standard materials are common in other industries, especially with respect to chemical analysis. Examples include glasses (both major and trace elements), mineral areas, and cements. These standard reference materials are available through the U.S. National Bureau of Standards.[55]

RECOMMENDATIONS

Our preliminary recommendations regarding raw materials characterization and qualification are as follows:

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*International Energy Agency (IEA) Annex II, Cooperative Programme on Ceramics for Advanced Engines and Other Conservation Applications.

1. Develop standard reference powders with an exhaustive set of established properties to include chemical and physical properties and, perhaps, forming and firing behavior. Such a material would probably best result from a standard round-robin test procedure.
2. Develop relationships between analytical and process-related characterization techniques and real system performance. To accomplish this, a generic system such as slip casting, injection molding, dry pressing, or tape casting would be chosen for study. Critical input parameters and their effects on final product quality would be identified through a series of well-controlled, exhaustively documented experimental test runs. Such a program would have to be a long-term one to justify capital costs and to allow for learning curve behavior.
3. Develop and publish guidelines for writing meaningful specifications for ceramic raw materials. The practicing ceramic engineer often must start at the beginning when asked to write raw material specifications because of a lack of appropriate guidelines in the public domain. This document could help companies accelerate their learning curves and reduce needless duplication of effort.
4. Investigate various basic problems in materials characterization, such as applications of porosimetry and permeametry to powders and green bodies; addressing the problem of obtaining a mass sum to 100% on a reported chemical analysis; examining the interactions of binders, dispersants, solvents, and powder surfaces; examining the effects of particle morphology on processing and fired properties; establishing quantitative relationships between laboratory analytical techniques and on-line control measurements; and applications of dilatometry to determining optimum sintering schedules.

GREEN-STATE CERAMICS

INTRODUCTION

An intermediate step in the processing of structural ceramics is the fabrication of green-state bodies. It is at this first stage of actual component shaping (e.g., through powder compaction) that many conditions

are introduced which subsequently lead to less-than-optimum material and component properties and/or performance. Discovery and elimination of these conditions through process optimization, rejection, or repair of the green bodies, or other appropriate means, could lead to significant cost savings. The current high rejection rate for structural ceramics, nominally 25 to 75% (ref. 23), is sufficient cause for concern, particularly when the value added to the raw materials at this point is largely in the form of raw material, overhead, and labor costs.

Several characteristics of green-state bodies have been identified that are important to the production of reliable structural ceramic components. The sections that follow describe these characteristics, as well as the means of distinguishing critical parameters or features. These include selection and composition of binders and sintering aids, as well as methods of removal and interactions with powders; elemental composition; mechanical properties; and discontinuities such as porosity and surface condition. For some of these characteristics, methods of measurement and evaluation may be readily identified and may in fact be in use. In other cases, methods may be identifiable, but little or no application has been done; in still others, there may be no currently identifiable approach.

BINDERS

The binder holds the powder in the desired shape prior to sintering and is a key material in the fabrication of acceptable ceramic parts. Among the major considerations is selecting the optimum binder material for a fabrication process to match the ceramic powders and ensuring the correct chemistry (cations and anions) for proper interaction. Although it is not obvious that characterization tools are needed for this specific item, limited parametric studies of these features as a part of materials and process development could provide useful insight into this important step. Characterization of attained properties would then be done on the resultant green-state or sintered ceramics (as discussed subsequently in this report).

The distribution of the binder is an important parameter because the binder is removed by firing and variations could result in excessive voids

in the finished ceramic. Consideration has been given to nondestructive methods of determining the binder distribution, and limited experiments have been conducted.[77] The low atomic number of the constituents causes the organic binder to have insufficient attenuation relative to the matrix for X-ray absorption techniques to be considered feasible. The hydrogen-rich composition appears to offer promise for neutron attenuation or scattering techniques because of the relatively high neutron cross section. However, preliminary experiments with neutron radiography on samples with and without binders yielded inconclusive results apparently because of other attenuation differences. Experiments using a pulsed-neutron source showed a small (2%) difference between specimens with and without a binder; this may have promise for further investigation (Kupperman et al., private communication, 1984). The expense of neutron-source facilities would probably limit their application to materials development. Another method sensitive to the presence of hydrogen in the binder is nuclear magnetic resonance (NMR). Changes in the spin (and magnetic moment) of proton-rich nuclei in the presence of external magnetic fields allow the presence of the proton-rich material to be detected. Preliminary experiments conducted with a commercial medical NMR tomographic system showed inadequate response to the binder. However, water-doped SiC showed the feasibility for detection of water-filled pores.[77] Modification of the equipment would be necessary to enhance the resolution and sensitivity sufficient for beneficial use on structural ceramics. For determining porosity, water tracers would probably be used in materials and processing development rather for production components.

After the binder has been removed by firing, the efficiency of the removal should be determined, as well as the distribution of any potential residues. Whether the removal can be accelerated and, in turn, whether this acceleration can be measured should also be determined. As noted in the preceding discussion on determining binder distribution, detection and measurement of the initial binder is difficult and techniques are not yet in hand. Detection and measurement of distribution of any small amount of residual binder will be even more difficult, and potential approaches are currently not obvious. Consideration should be given to the potential of "tagging" or doping the binder to enhance detection of the residue by some

method. It has been suggested that one approach for determining residual binder is thermal gravimetry and gas analysis.

POWDER/BINDER INTERACTIONS

During the formation of the green-state body, interactions between the powder and binder occur that can affect the properties of the green state and, subsequently, the properties of the finished component. For example, such phenomena as agglomerate generation, modification of the surface chemistry of the powder phase, and effects on surface physical properties can occur. Because the agglomerate is generally a clump of particles having the same chemical composition as the rest of the matrix, detection and evaluation will probably depend on the effect on other properties such as porosity and density. (See "Discontinuities and Surface Finish" section.) Changes in the surface chemistry of the powder phase influenced by the binder may be detectable by techniques such as colloid chemistry analysis (e.g., zeta potential and powder titration) and spectroscopy using infrared, ultraviolet, or other phenomena. The surface physical interaction of powder particles and binder during forming and consolidation of the green-state body can influence subsequent properties. Measurements of internal and external friction may be possible using techniques from soil mechanics analyses. It is postulated that measurements of acoustic noise (acoustic emission) produced during powder/binder interaction could offer additional diagnostic information.

SINTERING AIDS

During the forming of the green-state body, sintering aids are also integrated to promote the desired product. Two principal concerns are the homogeneity or spatial distribution of the sintering aid and the bonding between the sintering aid and the matrix particle. Little analysis has been done on the problem of spatial distribution of sintering aids. Techniques that are probably applicable include Auger spectroscopy, electron microscopy using X-ray mapping, and electron energy loss spectroscopy (EELS). Some of the questions to be addressed relate to the attainable or necessary resolution and sensitivity and whether the data need to be qualitative or semiquantitative. Techniques for evaluation of bonding between the sintering aid and matrix particle have not been identified.

ELEMENTAL COMPOSITION AND DISTRIBUTION

As discussed in the section on powder characterization, the elemental composition and distribution are important parameters that can affect the performance of sintered ceramics. Confirmation of the compositional distribution at the green state could be an important aspect of ensuring process control and determining the suitability of the represented batch for further processing. The anticipated methods will be destructive, thus making them applicable for materials development or for statistical sampling of production quantities. Wet chemistry techniques with standard procedures can be applied to determine composition, as well as compositional changes that may have been introduced since the powder stage. On prepared surfaces of the green-state bodies, mass spectrometry and X-ray analytical techniques (peripheral to electron microscopy) can be applied for determination of distribution.

DIMENSIONS

The dimensions of green ceramics contain information about the green density and uniformity of green density and may contain information about the status of forming equipment (e.g., wear of dies or molds and setting of die-fill depth). Control of the green dimensions and green density are, of course, essential to the control of the final dimensions of a part. Existing automated inspections for dimension, such as pneumatic and laser optical techniques, appear to be adequate in terms of speed, sensitivity, and accuracy and should be modified and applied to ceramics.

MECHANICAL PROPERTIES

Determination of the mechanical properties of green-state ceramics could, in some instances, provide statistical insight into the ultimate performance of the final sintered product. Strength and fracture properties are commonly determined by essentially standard techniques that use destructive-testing specimens, such as three- and four-point bending specimens, notched-beam specimens, etc. These, coupled with fractographic analysis, can provide insight into the mechanical properties of the green-state component and the site-specific sources of failure. Being destructive, these tests remove specimens from the production stream and rely on

statistical techniques to correlate with ultimate product properties and as a tool for process control. Acoustic and ultrasonic techniques offer significant promise for the measurement of elastic properties that can be related to mechanical properties. Kupperman[77] demonstrated the feasibility of measuring acoustic velocity and anisotropy in SiC and other ceramics in the green state. With contact ultrasonic techniques, care must be taken to prevent the mechanical pressure of the transducer from affecting the data or damaging the specimen. However, the potential for ultrasonic nondestructive assessment of mechanical properties makes possible the correlation of green-state measurements with properties and performance of the sintered product. Such techniques can be applicable for materials development and for process control. (For additional discussion, see "Sintered Ceramics" section.)

DISCONTINUITIES AND SURFACE FINISH

Internal and external discontinuities, such as porosity and surface irregularities, can affect the quality of the final product.

Porosity and Other Flaws

The green-state body has much lower density than the final sintered product because of its distributed porosity. Variations in properties of the finished component may result from variations in the spatial distribution and size distribution of pores and the attendant effect on the density uniformity in the green state. Characterization of the size and spatial distribution of porosity (as well as detection and analysis of other discontinuities) and attendant density variations is considered important as a part of process control toward fabrication of acceptable components. Several laboratory studies have been conducted to determine initial feasibility for nondestructive flaw detection in green ceramics, including radiography, ultrasonics, NMR, and small-angle neutron scattering (SANS). Except for the special care that may be required in handling the more fragile green-state shapes, the radiographic and microradiographic techniques may be essentially the same as for sintered ceramics, and the discussion of radiography in the section on sintered ceramics is applicable here. Of course, details of X-ray energy, effects of scattering, etc., may be different. Radiography that has been reported[77] on

green-state ceramics indicates that flaws of less than 50 μm can be detected if the contrast to background is sufficient. Baaklini and Roth[143] found that the statistical reliability for detection of implanted internal voids using microfocus radiography is approximately 2.5% of thickness in the green-state and approximately 1.5% of thickness in the sintered state of both SiC and Si_3N_4. Computed tomographic techniques[101] in green ceramics demonstrated the capability to detect gradients in density (caused by porosity gradients) and inclusions; localization in three dimensions was achieved by means of the display of computer-selected slices through the specimen.

Ultrasonic techniques have been studied for application to green ceramics with moderate success despite several difficulties.[77] It was determined that the low-density, porous nature of the green state limits the applicable frequencies to less than 10 MHz (depending on specimen thickness) because of attenuation. The wavelength associated with the range of frequencies limits the sensitivity to discrete flaws to sizes approaching 1 mm. However, correlation was observed between measurements of ultrasonic velocity and specimen density. Ordinary ultrasonic couplants (e.g., water or glycerol) are generally absorbed by the green-state ceramics, losing the coupling effect and potentially affecting subsequent fabrication. In some instances, application of pressure to the transducer without supplementary couplant has allowed adequate transmission into the specimen. However, care must be taken to avoid damage to the specimen; velocity data were also shown to vary with transducer pressure. An alternate coupling technique by Roberts et al.[101] in which the green ceramic is placed in an evacuated Mylar film enclosure has shown success. Through-transmission, immersed ultrasonic techniques using a 10-MHz transducer allowed detection of isolated inclusions with diameters on the order of 500-μm and mapping of velocity differences that were attributed to density differences that were correlated with X-ray tomography.

SANS that uses multiple scattering and beam-broadening techniques[51] has shown variations in green ceramics to be a function of compaction pressure and degrees of sintering. This is attributed to differences in porosity and specimen density. Density values determined by SANS were

within 1% of values determined by weight and volume measurements. Optimum neutron wavelength is different for green-state and sintered ceramics because the average size of porosity is smaller in sintered materials.

Ackerman et al.[146] demonstrated the capability of NMR to image internal volume on the order of 300 μm in a green-state ceramic body using filler fluids (e.g. benzene) to provide NMR signal intensity.

Of course, metallographic and microscopic techniques are applicable and are used for the observation of porosity; however, these techniques are used with difficulty in green-state ceramics because of the potential for damage or alteration to the structure. Such techniques are destructive, removing material from the production line, and can be applied only on a statistical sampling basis and during materials development.

Surface Finish

As with many other properties, the quality of the surface finish in the green state can affect the surface finish in the finished component and its ultimate performance and serviceability (or need for supplementary expensive processing such as grinding to attain desired surface properties). The surface finish is also one of the attributes that can provide information about the green state processing and, as such, offers a tool for process control. Because observation or measurement of surface quality can be nondestructive, each lends itself to either statistical sampling or (if rapid, inexpensive tools can be devised and implemented) to examination of a large proportion of production batches. Techniques for measuring the surface finish include profilometry and light scattering using lasers or other sources. The light-scattering optical techniques lend themselves to engineering development for rapid automated scanning of consistent shapes that would be typical of production. For further discussion about such optical techniques, see "Sintered Ceramics" section.

RECOMMENDATIONS FOR CHARACTERIZATION OF GREEN-STATE CERAMICS

Improved methods of nondestructive characterization of green ceramics should be developed, and correlations should be established between the characterization and the subsequent properties of the sintered ceramic and its service performance or performance-related property. Attention should be given not only to discontinuities and density variations (e.g.,

resulting from porosity distribution) but also to homogeneity (e.g., of binder and sintering aids), mechanical properties, and sintering aids. Many of the potential characterization techniques would be impractical to apply to entire production quantities but could have significant value for statistical process control and for material development. No single method seems to be dominant for potential process control examinations, although ultrasonics and radiography show significant promise for certain aspects of green ceramics as well as for sintered ceramics (see "Sintered Ceramics" section).

Further investigations should be made into the use of NMR for determining binder distribution. This will require improvements in the sensitivity and resolution over current commercial NMR systems. Neutron techniques may have long-range potential, but relative inaccessibility of neutron facilities may limit the interest. If initial binder distribution can be determined, the more difficult problem of assessing the presence of residual binder (after binder removal) should be investigated. Application studies should be made using instrumented chemical analytical techniques (e.g., zeta potential, infrared spectroscopy, etc.) to see if there are detectable changes in surface chemistry of the ceramic powder influenced by the binder.

Investigations should be undertaken to ascertain the applicability of techniques such as Auger spectroscopy, EELS, etc., for determining the spatial distribution of sintering aids.

Development studies in ultrasonics should be conducted to establish correlations with mechanical properties. Both radiographic (including tomography) and ultrasonic techniques should be further developed for the evaluation of discontinuities, porosity distribution, and density.

Advanced light-scattering optical techniques should be further investigated and developed for rapid scanning of surface finish of production components.

SINTERED CERAMICS

INTRODUCTION

Sintering is the final fabrication stage for many ceramic components. In some specimens, a grinding operation may be employed for minor surface

preparation or sizing. Because sintering is often the culmination of the fabrication process before the component is used, proper characterization is important to ensure that the desired integrity and quality have been attained and maintained. This characterization is necessary to improve the confidence that the component will perform in accordance with design expectations. A number of critical characteristics have been identified that affect the service performance. In brief, these include local density variations, microstructure, mechanical properties, physical properties, surface properties (as affected by machining), and elemental composition and distribution. For some of these characteristics, methods of evaluation and measurement are readily identified and, in some instances, are in place for application; some of the other needs for characterization cannot be met as easily, although potential solutions may be identified (and laboratory studies may have been performed). In the following sections, the characteristics to be evaluated and the methods (current or potential) of examination will be expanded. Some of the evaluation methods may be applicable to large numbers of production parts; others may be better suited for sampling inspection as part of process control or for use during process development. Recognition must be given to the necessity for further developments of techniques that are or may become applicable to idealized configurations to allow beneficial use on components having complex shapes. This may require complex programmed mechanical systems or robotics to accomplish the desired controlled movements.

ELEMENTAL COMPOSITION AND DISTRIBUTION

As discussed in the section, "Raw Materials Characterization and Qualification," the elemental composition and distribution are important parameters that can affect the performance of sintered ceramics. Although the determination will be destructive of the specimen, these analyses have application in material development; sampling could be beneficial during production fabrication. The elemental composition would be known (and measured) at earlier fabrication stages; measurement at the sintered stage would allow determination of any changes introduced during the various fabrication processes and, with special techniques, could determine

distribution or segregation. Wet chemistry involves standard procedures and can be applied to determine composition and compositional changes. On ground surfaces, mass spectrometry and X-ray analytical techniques as an adjunct to electron microscopy can provide the additional details of elemental distribution.[109]

MICROSTRUCTURE

Microstructural properties of ceramics that affect service performance include several variables, including grain size and shape, porosity (distribution, shape, and orientation of pores), phase distribution, anisotropy, inclusions, agglomerates, and cracks or voids. Lange[82,158,159,160,161] discusses several common flaws that result from agglomerates, organic matter, inclusions, large grains, and surface cracks; how the flaws are produced; and new fabrication methods to reduce the effect of flaws on strength. Most of the investigations of nondestructive testing (NDT) for structural ceramics have emphasized the detection of discrete flaws (e.g., pores, voids, and cracks) and will be discussed herein. Less effort has been directed toward NDE of the parameters related to grain structure. Because average strength is often inversely proportional to grain size,[82] knowledge and control of this property is important to ceramic performance. The most direct way (although destructive) for observation and measurement of grain size is microscopy of sectioned specimens. This also offers the capability to observe phase distribution and, with peripheral capabilities related to electron microscopy, to determine elemental distribution and segregation. Advanced high-frequency ultrasonic techniques can be affected by the grain size and offer the potential for a nondestructive method for determining grain size. Further investigations in these latter techniques should be made because of their potential for nondestructive characterization. Study should be made of the correlation between the failure mechanisms (caused, for example, by multiple microscopic variables) and the NDT characterization.

DENSITY

Sintering of the preformed (green-state) ceramic bodies at high temperatures reduces (or eliminates) void space and increases density. The

rate at which densification occurs (and subsequent specimen quality) is affected by several variables, including the sintering aids, elemental composition, temperature, heating rate, etc. Control of these variables and the subsequent densification rate is necessary for reproducibility of product and optimization of ceramic quality. Dilatometry[99] is the primary method used in measuring the densification rate. Pyrometric cones[1] traditionally have been used to monitor the completeness of firing, which is related to density if other factors remain constant.

Localized variations in the attained density of ceramic shapes after sintering are undesirable because of the effects on structural performance. Radiographic and ultrasonic methods of NDT offer potential for the detection and measurement of density variations, and studies have been performed to determine applicability. The attenuation of X or gamma radiation through material is affected by the thickness, chemical composition, and density of the material. If thickness and chemical composition are uniform, the transmission of radiation can be directly related and quantitative correlation can be established for density measurement. Film radiographic techniques have the capability to detect and display density changes of less than 2%; quantitative nonfilm radiation detection systems[43] offer up to an order-of-magnitude improvement (0.2%) in sensitivity. In radiographic examination of modulus of rupture bars, Klima[71] showed unique patterns of density variations decreasing from the exterior surface to the interior. Sanders and Baaklini[142] demonstrated improvements in strength of silicon nitride achieved through systematic changes in powder processing and sintering parameter guided by iterative radiography to characterize structural (density) uniformity.

Sawicka et al.[148,149] conducted investigations with a first generation (single-source, single-detector) gamma-ray computer tomographic system with ^{60}Co and ^{192}Ir sources on several ceramic materials and shapes. In 14-mm-diam alumina cylinders, the pixel-to-pixel density error was in the 0.7 to 0.9% range; by averaging data from concentric annuli, measurement of density variation across the radius was made to 0.1%. In 6-mm and 23-mm tiles of alumina, the average density measurement in a pixel was determined with an accuracy better than 1%; average densities over

several pixels were determined with an accuracy of 0.2%. Cracks were also noted relative to density gradients but were not observed as well as on 70-kV contact radiographs. When polychromatic radiation is used, it is preferentially attenuated by the material as a function of photon energy resulting in beam hardening (BH), i.e., preferential decrease of lower-energy radiation relative to higher-energy radiation. This can adversely affect contrast sensitivity and spatial resolution. Segal et al.[151,152] have conducted studies in ceramics of correction methods for BH using either fitted added material around the structure or beam filters before the radiation enters the specimen, both to reduce the BH effect. A third option studied by Segal corrects the nonlinear preprocessed data with algorithms that take the specific material and energy spectrum into effect. A reduction of the BH effect to about 1% is anticipated.

Klima[72] investigated the feasibility of using measurements of ultrasonic velocity as an approach to determining bulk density of sintered α SiC with densities varying from 2.8 to 3.2 g/cm^3. Using 20-MHz ultrasound and commercial equipment, the bulk nominal density could be estimated within 1%.

Based on the experimental work reported, it appears that both ultrasonic and X-ray techniques have shown feasibility for detection and measurement of localized variations in density. Further study and technique development are recommended.

DIMENSIONS

The dimensions of sintered ceramics contain information about the green dimension and green density of the parts; the uniformity of the green density and dimensions; and the density, shrinkage, and uniformity of shrinkage of the parts. The uniformity of shrinkage from the green dimensions is an indication of the temperature uniformity in the part during sintering. Existing automated inspections for dimensions, such as pneumatic and laser optical techniques, appear to be adequate in terms of speed, sensitivity, and accuracy and should be modified and applied to ceramics.

BULK MATERIAL AND MECHANICAL PROPERTIES

Current practice for determining the mechanical properties (e.g., strength, fracture toughness) of sintered ceramics (and other materials) is to perform destructive tests on large numbers of specially prepared specimens (e.g., three- and four-point bending specimens for strength determination and short-rod, notched-beam specimens for fracture toughness) or performance proof-tests on specimens that represent actual components. This practice represents the state of the art and will undoubtedly continue until acceptable alternatives are available. However, to provide sufficient statistical data that may be applied to material being developed or to components being produced, the destructive tests are expensive and time consuming. The proof-testing of actual components removed from the production cycle has the same limitations and, in addition, may eliminate components from potential service. Neither approach provides direct data on the actual components as they are being put into service. However, modification of the destructive testing or proof-testing in conjunction with NDE may have merit. For example, NDE of selected specimens at intervals after subcritical static or dynamic proof-testing could provide insight into material quality, stress analysis, and flaw formation or propagation. In some instances, real-time application of NDE (for example, acoustic emission) during low load stress tests may be beneficial for component screening. The acceptable performance of a ceramic material in service may depend as much (if not more) on the basic bulk material and mechanical properties of the individual specimen as on the presence of discrete discontinuities. For that reason, NDE of these properties on the actual item to be used would be a very powerful tool for the potential prediction of serviceability of a newly fabricated component or determination of residual life in a component after a period of operation. Some of the NDE technology for the detection and evaluation of discontinuities has the potential, with modifications, for measurement of such properties or for the measurement of parameters that can be correlated with the desired material properties (e.g., the measurement of density, see "Density" section). One of the most promising methods is the use of various aspects of acoustic or ultrasonic interrogation. The ultrasonic velocity is a function of the elastic constants and elastic

properties of the material. Ultrasonic attenuation can be related to bulk microstructure, as well as to defect structure (both microscopic and macroscopic). Laboratory studies by several investigators confirm the promise and feasibility of techniques for making such measurements.

Gogotski et al.[46] used ultrasonic attenuation over the frequency range of 1.8 to 5.0 MHz to observe the effects of various degrees of thermal shock damage in specimens of Si_3N_4. The ultrasonic spectra clearly distinguished various degrees of thermal shock damage; the change in frequency response correlated well with a decrease in ultimate tensile strength of the ceramic specimens. Iwasaki[59] measured ultrasonic longitudinal and transverse wave velocities in different directions in hot-pressed Si_3N_4. Anisotropy was observed with velocities perpendicular to the hot-pressing direction being about 5% higher than velocities parallel to the hot-pressing direction. Ultrasonic attenuation measured with both longitudinal and transverse waves in the 30- to 130-MHz frequency range exhibited a frequency-dependent characteristic proportional to the square of the frequency. Work at Argonne National Laboratory[10] in siliconized SiC tubes indicated that the velocity of sound changed as a function of the volume fraction of silicon; this may offer a technique for indicating silicon content. Rey[100] used ultrasonic velocity measurements for determination of elastic moduli used in the analysis of fracture stress as an integral part of mechanical strength testing on sintered specimens of high-alumina ceramics. Vary[123,124] demonstrated the laboratory feasibility of the use of ultrasonic methods to measure elastic moduli, microstructure, hardness, fracture toughness, and strength for a wide range of materials, including metals, ceramics, and fiber composites. He indicated that the ultrasonic methods are particularly useful because they involve mechanical elastic waves that are modulated by the same morphological factors that govern mechanical strength and dynamic failure processes.

Johnson[60] studied the feasibility of high-frequency (32-MHz) ultrasonic electromagnetic techniques for the evaluation of Si_3N_4 and SiC. Although the technique was limited in its defect detection ability, variations were observed in signals that seemed to reflect variations in electrical and dielectric properties, possibly as a result of variations in microstructure or chemistry.

Another of the property characteristics of structural ceramics that can impact serviceability is residual stress. Ultrasonic techniques have been studied to determine residual stress in metals, but no references to ceramics were found. X-ray diffraction techniques have also been used for determination of stress, and work by Ruud and Gazzaro[141] showed a correlation between stress and X-ray diffraction in alumina and silicon carbide.

PHYSICAL PROPERTIES

The physical properties (e.g., the thermal, elastic, and electrical properties) of a sintered ceramic can have an effect on its performance and serviceability and would be a factor in the design of a structural ceramic component. For that reason, a quantitative knowledge of the values of the parameters in as-fabricated components would be desirable to ensure that the manufacturing process is being adequately controlled for good quality. The thermal properties (thermal expansion and conductivity) can be measured in specimens by established techniques. Application to complex shapes, if desired, would require development. The thermal expansion of a given material is not expected to vary significantly with processing; the conductivity could be affected by changes in the microstructure and serve as an indirect indicator of the microstructural condition. Acoustic and ultrasonic techniques are useful for the measurement of the elastic moduli. Application to prepared specimens at room temperature is readily performed; application to complex shapes and at elevated temperatures is more difficult and could require special development. Although the electrical properties of sintered ceramics (e.g., resistivity and dielectric constant) are normally not of direct interest for application of structural ceramics, variations of these properties could be an indirect indicator of variations in microstructure, composition, or phase distribution. As noted before, these properties directly influence structural performance. Therefore, if correlations could be established between the electrical and structural properties (or even directly to performance), such measurements would be important.

FLAWS (POROSITY, INCLUSIONS, CRACKS, AND VOIDS): DETECTION AND EVALUATION

Several NDE methods have been studied for potential application to the detection and evaluation of flaws in sintered ceramics. These include

ultrasonics and radiography, SANS, acoustic emission, infrared, penetrants, photoacoustic microscopy, and microwaves. The detectable size of discrete flaws or distributed discontinuities varies significantly between the various approaches. The degree of difficulty or complexity and sophistication of the various methods is also significantly different.

Ultrasonics

Ultrasonic techniques for flaw detection vary from traditional pulse-echo techniques to detect and evaluate reflections from discrete flaws to measurement of attenuation and/or velocity of ultrasound as a function of ultrasonic frequency with correlation to distributed flaw size. The ultrasonic frequencies for application to ceramics are somewhat higher than those conventionally applied to metals because (in ceramics) the ultrasonic velocity is greater and the typical grain size and critical flaw size is smaller. For metals, the frequencies generally range from 1 to 10 MHz; work to date in sintered ceramics has generally found that frequencies ranged from 20 MHz to 50 or 100 MHz. Special techniques and equipment are required for these (and higher) frequencies. Chou et al.[30,31] constructed a 50-MHz C-scan imaging system for flaw detection in Si_3N_4. A high-frequency (150- to 450-MHz) A-scan system was used for flaw characterization (and matrix evaluation). Signal processing schemes included temporal and spatial averaging, filtering, and corrections for diffraction and attenuation. Difficulties were encountered in flaw characterization with single backscattering measurements. Encouraging preliminary results were obtained using synthetic aperture-imaging techniques. Kino et al.[70] and Khuri-Yakub et al.[65] later reported on continued studies with the 150- to 450-MHz and the 50-MHz systems, respectively. For the higher-frequency system, special transducers and filtering techniques were developed that allowed comparison of time-domain backscattered signals from inclusions with calculations from theory. Good agreement was observed for 100-μm inclusions in Si_3N_4. Synthetic aperture-imaging at 50 MHz was studied to obtain three-dimensional images of flaws. Computer simulations based on theoretical flaw models were conducted. Derkacs[36,39] investigated longitudinal and shear wave ultrasonic pulse-echo techniques in Si_3N_4 and SiC ceramics at frequencies between 25 and 45 MHz for detection of pores and inclusions in the range of 10 to 130 μm. Shear wave techniques were more

sensitive than longitudinal wave techniques. Sensitivity to flaws as small as 25 μm was demonstrated. Specimens that had subsequent failure at detected flaws showed lower strengths. Kessler and Yuhas[63,64,136,137] used 100-MHz acoustic waves in a scanning laser acoustic microscope (SLAM) to detect and display flaws in ceramics and other materials. Pores and inclusions (50–100 μm) were detected in Si_3N_4 disks. Distributed porosity smaller than 50 μm was detected because of its effect on ultrasonic attenuation rather than by discrete indications. This work (and that of others) has observed that specimens seeded with intentional inclusions exhibit unintentional porosity and lower density. Roth et al.[144,145] conducted statistical studies to determine the probability of detection of surface and internal voids using 100 MHz SLAM in sintered specimens of silicon carbide and silicon nitride. Surface voids as small as 100 μm in diameter were detected in polished specimens. If they were close to the surface, internal voids as small as 30 μm in silicon nitride and 60 μm in silicon were detected. Larger voids were detected with confidence at greater depths. Kupperman[78,79,80] investigated the feasibility and applicability of ultrasonic techniques (including SLAM) for the examination of SiC heat exchanger tubes and silicon nitride gas turbine rotor components. A boreside 22-MHz ultrasonic probe demonstrated detection of 125-μm-deep notches on both the outer and inner surface of SiC tubing. The SLAM modified for 30-MHz operation detected the same size notch. Frequencies up to 35 MHz were required for wall thickness measurements and the detection of laminar flaws. Knoop indents having depths in the surface as small as 25 μm that were not detected at 10 MHz were clearly resolved at 75 MHz. Schuldies and Derkacs[112] applied ultrasonic techniques of up to 45 MHz and showed the potential for detecting clusters of subsurface flaws in the 25-μm range in hot-pressed Si_3N_4. Similar studies in reaction-bonded Si_3N_4 showed the potential for detecting clusters in the 125-μm range. Silicon-rich inclusions were difficult to detect when they were less than 250 to 500 μm in size. Srinivasan et al.[115] applied 36-MHz pulse-echo ultrasonic techniques and SLAM to the detection of intentionally seeded defects in the range of 50 to 125 μm and 150 to 250 μm in SiC disk thicknesses ranging from 2.5 to 127 mm (0.1 to 5 in.). The seeded defects (as well as others) were observed. Critical strength-limiting flaws were complex-shaped, three-dimensional voids 75 to 200 μm

in size and two-dimensional surface cracks less than 150 μm deep. Kunerth and Walter[138] developed an acoustic microscopy technique using high-frequency (50 MHz) focused ultrasonic transducers and fast signal processing techniques to rapidly scan SiC heat exchanger tubes for flaws and to display the results in real time. The system can acquire data as fast as 2800 data points per second and has demonstrated the ability to detect and image seeded flaws as small as 0.050 mm in size.

Kunerth and Telschow[139] demonstrated the ability of different ultrasonic techniques to characterize the distribution of porosity in SiC. Acoustic microscopy and measurements of ultrasonic attenuation, velocity, and backscatter provided complementary information about the size and spatial distributions of porosity of mean size 0.002 mm in a hot-pressed SiC plate.

Singh et al.[153] used focused ultrasonic surface wave backscattering, through-transmission ultrasonics, and low-kV radiography to detect intentionally introduced iron inclusions in Si_3N_4. Comparison with NDE results and fractography indicated that the ultrasonic backscattering provided better correlation because of the preferential sensitivity to near-surface flaws.

X Rays

Several approaches [e.g., quantitative measurement and qualitative imaging (radiography)] are used in the application of penetrating radiation (X and gamma rays, beta radiation, and neutrons) for flaw detection; predominance is given to radiography. Because of the small critical flaw size typical of most structural ceramics, special techniques for improved resolution and sensitivity have been investigated, including contact microradiography, projection microradiography (with microfocus X-ray units), image enhancement, and tomography. Contact microradiographic techniques[90,91] can use near-conventional techniques and equipment to make radiographs of ceramic materials using magnified viewing to allow examination of microscopic flaws. With thin specimens, low energies, and high-resolution film, image detail of a few micrometers is possible. To aid in detection of surface-connected flaws (e.g., cracks), liquid penetrants containing a constituent ("dye") that is more opaque to the X rays than is the object material can be applied to provide an enhancement of the flaw

indication on the radiograph. (Now the flaw will appear lighter than the object material rather than darker.) The method has been applied successfully to a variety of materials, including metals, graphite, and ceramics. Kupperman et al.[78] applied the technique (using silver nitrate) to SiC heat exchanger tubes and Si_3N_4 rotors and indicated that the dye-enhanced radiographic techniques were capable of detecting tight cracks missed by conventional techniques. The advent of microfocus X-ray tubes (with focal spots measured in tens of micrometers rather than a few millimeters) has improved the sharpness of radiographic images and the detectability for small flaws. The very small focal spot also allows the use of projection radiographic techniques in which the specimen is placed near the X-ray tube and at a distance from the film to allow geometric magnification (e.g., 10×) of the image of the specimen (and flaws) at the film. This improves the image quality by dissipating some of the secondary radiation before it reaches the film and decreasing the dependence on the image resolution of the detector (e.g., granularity of the film). Goebbels[65] described the use of an 80-kV unit having a focal spot of 15 μm. Projection magnifications of 10 to 20× were used. As an indication of the attained sensitivity and resolution, a 150-μm-wide slot having a 21-μm depth was imaged in a projection microradiograph of a 5-mm-thick Si_3N_4 specimen. Pores and seeded defects (inclusions of iron and carbon) were also observed, but their sizes were not mentioned. Schuldies[111,113] used a microfocus (50-μm focal spot) X-ray unit and projection magnification on Si_3N_4 specimens containing selected inclusions. Some difficulty was encountered in observing inclusions with radiation attenuation properties near that of the base material, but high-density inclusions (50 μm tungsten and 25 μm iron) were detectable. Computer-based image-enhancement techniques used on the radiographic film did not significantly change the detectability but offered improvements for visualization of details and flaw characterization. Srinivasan et al.,[115] using a 100-μm focal spot size in an X-ray unit operating at 30 kV, examined voids and known carbide and carbon inclusions in disk specimens of SiC. Detection capability with this system seemed to be for flaws ~4% as large as the section thickness (e.g, 110-μm voids in 2.5-mm disk thickness). Baaklini[11] determined relative detectability limits for seeded voids in green and sintered SiC and Si_3N_4 and reported a sensitivity of 1.5% of

specimen thickness using projection microfocus radiography and 2.5% using conventional contact radiography in 4-mm-thick sintered material. Feldkamp[42,75,164] used a microfocus (150-μm focal spot) X-ray unit, projection magnification, and a video-based real-time imaging system. Successive radiographic images taken at small increments of specimen rotation and stored in computer memory allow subsequent processing with computerized tomographic algorithms to reconstruct image detail in three dimensions through selected cross sections. Resolution of ~50 μm in 1-cm specimens has been demonstrated. Aiba et al.[5] investigated the use of a Japanese-developed 120-kV computer tomography system for examining ceramic nozzles for continuous steel casting. Resolution limited by the size of the detecting elements was shown to be from 0.1 to 0.75 mm. Demonstrated application included detection of defects, oxidation, or other damage caused by service, density, ingress of foreign material, etc. Taylor et al.[150] used a first-generation (single-source, single-detector) gamma ray (^{60}Co) computer tomographic system in a preliminary evaluation of flaw detection in ceramics. Spatial resolution of about 0.13 mm was demonstrated in silicon nitride block (approximately 1 mm thick) on machined grooves that extended through the 1-mm thickness. Contrast resolution was about 2.4%. In several thicker sections of ceramics, cracks with a calculated width (separation between faces) of 0.16 mm were observed; a detection limit of 0.05 to 0.07 mm was estimated for the images.

Small-Angle Neutron Scattering

Hardman-Rhyne et al.[50,51] have studied the application of SANS for the detection and measurement (and determination of size distribution) of distributed flaws (e.g, microcracks, voids, inclusions, porosity) in ceramic materials such as Al_2O_3, SiC, $MgAl_2O_4$, and $YCrO_3$. (Agglomerates of the same material as the matrix are generally not detectable in the absence of voids.) With diffraction techniques, information is obtainable in the 2- to 200-nm size range; using multiple refractive scattering, the size range increases to about 10 μm. It has been suggested that the latter approach can overlap the resolution limits observed with high-frequency ultrasonics and could be used for correlation or calibration.

Acoustic Emission

Acoustic emission (AE) techniques (i.e., the detection and evaluation of stress waves emitted during stressing of specimens and generated by

deformation or initiation and propagation of flaws) have been considered or examined for the evaluation of sintered ceramics.[15,45] In some early experimental work, Romrell and Bunnell[102] investigated and demonstrated the applicability of AE to detect crack initiation and growth resulting from thermal shock in thorium-yttrium oxide and alumina. Iwasaki and Izumi[59] studied AE associated with slow crack growth in torsion tests and observed a close relationship between AE patterns and fracture surface structure. Correlations were noted between AE count rate and crack growth velocity. Schuldies[110] showed that AE techniques can be applied to detect the onset of catastrophic failure. Acoustic emission response from four-point-bend lithium-aluminum-silicate specimens exhibited a precursor to final failure, implying a transition from microcracking to unstable macrocracking.

Infrared

The flow of heat through a ceramic body can be affected by inhomogeneities in the internal and surface structure, and variations in resultant surface temperature profiles may be detected by infrared technology. Several investigators have studied infrared applicability, especially for the evaluation of materials intended for heat transfer. One of the early studies by Maley[87] demonstrated the feasibility of determining variations of material conditions and properties by measuring the heat transfer within metals and ceramics and by measuring and recording the emitted infrared radiation. Deininger and Kupperman[34] applied heat to one end of SiC heat exchanger tubing and monitored the axial heat flow pattern using a commercially available infrared camera. Computer modeling predictions and experimental data were in fair agreement on changes in heat flow related to variations in physical properties.

Microwaves

The ability of microwave energy at frequencies of 100 GHz and above to penetrate some types of ceramics materials has led to feasibility studies to determine the use of microwave techniques to detect and locate voids and inclusions. Bahr[13,14] reported that microwave technology can detect inclusions as small as 125 μm (0.005 in.) in seeded plates of Si_3N_4 using frequencies in the range of 80 to 100 GHz. Cross-polarized C-scan images of inclusions were obtained with a resolution of about one

wavelength (3 mm). Some distinguishing features for different types of flaws could be discerned.

Penetrants

Several researchers have used the application of penetrants (usually a dye-bearing liquid material) to detect surface-connected flaws. This relatively simple method provides an enhancement for visual examination and has been a principal industrial practice. For example, Cassidy,[28] in assessing several techniques (pre-1977), found that visual examination, radiography, and penetrants were the principal selected techniques for the detection of defective Si_3N_4 gas turbine rotors at various stages of fabrication. McLean et al.[92] also applied liquid penetrant techniques prior to hot spin testing of ceramic rotors in a high-temperature gas turbine project. Sines and Okada[114] used fluorescent liquid penetrant techniques to make direct observations of early stages of crack extension from preexisting inherent flaws on the surface of an alumina specimen during an eccentrically loaded column test. A proposed model for delayed fracture indicated that better prediction of fracture times could be made based on assembly and coalescence of microscopic cracks, which were more detrimental than a single macroscopic crack.

Bubble testing,[154] a modification of the penetrant process in which surfactant-treated water is impregnated into the flaws, has yielded moderate success on surface-connected flaws. The fluid trapped in the flaws appears as bubbles when the part is immersed in a hot fluorocarbon oil.

Photoacoustic Microscopy

Photoacoustic microscopy (PAM) (and related thermal wave imaging techniques)[103,119,120] is an emerging method of NDE for the detection and imaging of macroscopic and microscopic discontinuities on or beneath the surface of a sample. A frequency-modulated beam of energy (e.g., a laser or electron beam) is focused and scanned across the surface of a sample. Surface heating occurs within the same period as the excitation and with a penetration of one to two wavelengths. The periodic thermal wave is scattered from the structural features with different thermal characteristics. These perturbations may be detected by the subsequent alteration of the local surface temperature (e.g., by a microphone to detect the generated

acoustic signal in a gas cell surrounding the probed point, by infrared detection, or by a change in the optical index of refraction in contiguous air as a result of the thermal gradient). An alternate method is the detection of the thermoacoustic signal generated in the bulk of the sample. Raster scanning of the heat-producing beam allows imaging of localized variations in the specimen. The method is slow but offers high resolution (a few microns) near the surface. Inglehart et al.[56] used a mechanically chopped laser beam at a frequency of 1200 Hz and a focal spot of 50 μm to examine Si_3N_4 test bars. The sample was enclosed in a gas cell, and a microphone detected the periodic gas pressure variations from the periodic heating. The effective depth of penetration was about 12 μm, and surface and subsurface features as small as 150 μm were detected. Comparison with SLAM was made with good agreement on surface and near-surface features. Srinivasan et al.[115] applied scanning PAM (SPAM) to detect surface flaws introduced by Knoop indentations with loads from 1 to 3.5 kg on sintered alpha SiC. The Knoop flaws and similar-sized natural flaws were observed. However, SPAM background from the as-fired surface was considerable in many instances. Wong and Thomas[133] demonstrated the detection of surface cracks (~50 μm × 100 μm) in sections of reaction-bonded Si_3N_4 removed from turbine blades.

Characteristic Vibration

Sonic vibration (resonance) techniques have been used for many years to establish overall integrity of a fabricated shape based on the characteristic resonance spectrum. Changes in the component caused by flaws, for example, can introduce changes in the resonance spectrum. Goebbels[140] investigated the method for ceramic turbine blades. A constant resonance frequency of 29.85 kHz was observed in the sample in the as-delivered state after oxidation treatment. Cracking led to a decrease in frequency to 18.02 kHz. Detection and tolerance limits have not been determined, but the technique should be further investigated.

Summary Comments on Flaw Detection and Evaluation

Many NDE methods and techniques have been investigated and/or applied to the detection and evaluation of flaws in sintered ceramics with varying degrees of success. Major emphasis has been given to the various techniques of ultrasonics and radiography; based on the encouraging results in

laboratory studies, these techniques should continue to receive significant attention for the creation of new methods to be used in materials development and in product certification. Ultrasonics will require the use of higher-than-conventional frequencies (e.g., 25–100 MHz) and sophisticated signal processing for analysis of velocity, attenuation spectra, and reflections for flaw characterization. Microradiographic techniques (e.g., both contact and with microfocus X-ray tubes) have shown good resolution and sensitivity for small flaws and should be pursued using both film and nonfilm techniques. The benefits of tomographic techniques for three-dimensional localization of flaws should be further investigated. SANS shows promise as a research tool for materials R&D but is not anticipated to be practical for product characterization, in part because of the cost of the limited facilities. AE techniques have been studied for monitoring of flaw growth during destructive testing and, as such, are beneficial for product development and testing. The technique depends on stress wave emission (e.g., from a growing flaw); no literature was discovered on applications to detect the presence of fabrication flaws. Infrared techniques that monitor temperature profiles are anticipated to have limited usefulness for flaw detection in ceramic bodies. Limited work in microwave methods has demonstrated a capability to detect internal flaws, but the limitations on resolution observed to date are not encouraging. Liquid dye penetrants are used as a simple tool for surface-flaw detection, and little further engineering development of this technique is expected, except for methods of calibration and standardization. Photoacoustic microscopy shows promise as a high-sensitivity and resolution technique for surface and near-surface flaws but, in its current stage, is rather slow and may be limited to materials development and sampling. Investigations should be continued. More work should be done to establish correlations between NDE results and fracture mechanics/reliability/performance of ceramics.

SURFACE PROPERTIES (ROUGHNESS AND FLAWS): DETECTION AND EVALUATION

The integrity of the surface of sintered ceramics is extremely important for many reasons, including the small critical flaw size, the tensile stress concentrations possible on the specimen surface during service, and the potential for damage during fabrication (e.g., during grinding or

other machining). For these reasons, examination of the surface is an important aspect of ensuring the performance of the ceramic. Several different methods have been applied or studied for accomplishing the needed high-resolution, high-sensitivity examinations, including optical methods, ultrasonics, penetrants, etc. Some of the technology discussed in the preceding sections for detection of flaws as part of the microstructure are also applicable for surface examination.

Optical Methods

Visual examination of the surface of ceramics with the enhancement afforded by optical magnification is and will continue to be a significant factor in ensuring surface quality. The use of liquid dye penetrants also offers significant benefits to visual examination by improved contrast afforded by the dye material entrapped in the surface flaws (as discussed in preceding sections). The principles and practices of visual examination with supplementary lighting, magnification, or other aids are well known and documented and will not be discussed further in this report.

Limited work has been reported on the use of optical holographic techniques for the surface examination of ceramics. Roszhart et al.[107] conducted early studies in holography applying a pulsed ruby laser to a variety of ceramic testing problems. Live fringe interferometry was used to study static fatigue.[104] Holographic fringe patterns were observed continuously as the minute cracks propagated through the material, permitting detection of impending failure prior to fracture. Laser techniques were also studied for measuring surface roughness by analyzing the scattering of a laser beam from random surfaces.[105,106] Surface roughnesses on the order of 100 μ-in. were measured on Si_3N_4-bearing specimens. Kupperman et al.[78,80] performed preliminary studies on holographic interferometric techniques for the location of surface cracks in SiC heat exchanger tubes and Si_3N_4 rotors. Circumferential flaws, 125 μm deep by 250 μm long, were detected on the inner surface of SiC tubing (3-mm wall thickness). Holography was shown to be complementary to ultrasonic techniques and to improve the capability for crack sizing.

Ultrasonics

High-frequency ultrasonic surface waves (surface acoustic waves) have been studied by several investigators and shown to be applicable for the

detection of small surface flaws. Derkacs and Matay[37,38] developed a 45-MHz ultrasonic surface-wave technique for the detection of surface flaws less than 100 μm deep in Si_3N_4 and SiC. The technique was found to be sensitive to surface conditions such as grinding damage as well as to flaws. Flexural strength was correlated qualitatively with ultrasonic response to machining damage. Sensitivity to defects was limited by the depth of machining damage and the focal spot size of the ultrasonic beam. For the 580-μm (0.023-in.) focal spot, the smallest verified flaw was a 30-μm-deep semicircular crack. Khuri-Yakub et al.[66,67] also studied the use of surface acoustic waves in ceramics and demonstrated a technique to detect individual cracks having depths as small as 60 μm. The detectability is affected by the size distribution of adjacent background microcracks (e.g., caused by grinding). A preliminary correlation was observed between attenuation of the surface wave and the extremes of the crack size distribution. In the studies by Khuri-Yakub et al. particularly addressed to machining damage (suspected of being a major cause of specimen failure), a measurement technique was developed to find the microcrack, and a long wavelength scattering theory was proposed for predicting size. The techniques are affected by variations in the plastic zone and by the crack closure at the surface resulting from residual stresses. Fracture stress prediction may be possible if the long wavelength criterion is met and the size of the plastic zone is correctly assumed. The long wavelength (low frequency) showed good agreement between predicted and actual fracture stresses in Si_3N_4 specimens containing semicircular surface cracks with radii (depths) ranging from 51 to 274 μm (ref. 121). Tittman et al.[122] studied the scattered ultrasonic radiation patterns from surface cracks and found that modulation of the ultrasonic frequency spectrum is related to crack length and aspect ratio (geometric crack parameters important for failure prediction). The technique is similar to that developed by Whaley and Cook,[131] Whaley and Adler,[130] and Adler et al.[4]

The use of ultrasonic critical angle reflectivity has been used for surface evaluation of metals and has been examined by Brokowski[24] and Hildebrand[54] for potential feasibility in ceramics in evaluating near-surface properties such as surface layers, stress, defects, elastic properties, and other material variations.

Summary of Techniques for Surface Properties

Optical methods of examining the surfaces of sintered ceramics are anticipated to continue to be an important part of the evaluation, probably with little need for sponsored, noncommercial development. A possible exception is in the use of laser-assisted optical examination for higher speeds and automated interpretation. A related area, optical holography using lasers, has shown promise for surface and subsurface detection of flaws and may justify further investigation for applications in materials development and, for limited quantities, statistical sampling of production lots. Various ultrasonic techniques (e.g., surface acoustic waves and critical-angle reflectivity) have shown good sensitivity to surface flaws and properties in laboratory studies, and further investigations and technique development should be undertaken.

RECOMMENDATIONS FOR CHARACTERIZATION OF SINTERED CERAMICS

Increased emphasis should be given to improved methods of nondestructive characterization of sintered ceramics. Correlations should be established between the nondestructive characterization and the service performance or performance-related properties. Attention should be directed not only to the detection and evaluation of discrete and dispersed discontinuities, but also to the determination of bulk mechanical and structural properties such as density, strength, fracture toughness, grain size, etc. It is recognized that some of the examinations may be impractical to apply to 100% of the production quantities of large-volume items; but, in such cases, application of valid, proven methods and techniques can ensure control of the fabrication process and provide added confidence in the unexamined items.

Based on laboratory studies conducted to date, significant attention should be given to various ultrasonic techniques because of the potential for the determination of such volumetric and surface properties as density, flaws, strength, toughness, elastic properties, etc. Advanced X-ray techniques, including microfocus, real-time imaging, and tomography, should be pursued for the determination of density variations, flaws, inclusions, etc.; the ultimate planned applications should be for statistical sampling, except for the very complex and expensive components

that may warrant more complete examination. Photoacoustic microscopy, a relative newcomer among NDT methods, shows promise for high-resolution surface and near-surface examination and should be pursued. However, in its current stage, and even with anticipated developments, its slowness will limit its application to materials development and statistical sampling on relatively simple shapes. SANS shows promise as a research tool for microscopic determination of porosity, but the cost of neutron source facilities would seem to preclude its industrial application. Thermal, infrared, and microwave methods appear to have insufficient resolution for microscopic flaws but could have merit for material characterization if a quantitative correlation can be established between the measured property (e.g., thermal conductivity, dielectric properties) and a service property. Destructive mechanical tests are expected to continue to be used for direct measurement of mechanical properties during material development or on a statistical sampling basis from production material. Selective nondestructive characterization should be performed on the specimens before destruction to screen specimens with less-than-desired quality to aid in the interpretation of test results and to establish correlations between nondestructive characterization of properties and service properties. The latter could lead to replacement of the expensive destructive tests with nondestructive tests that could be applied to specimens intended for actual service. Liquid penetrant and optical techniques are expected to be used regularly for observation of surface conditions in sintered ceramics. Engineering development will be beneficial to increase the speed with which performance and interpretation can be made for inexpensive application to production quantities.

CONCLUSIONS AND RECOMMENDATIONS

An assessment has been made of the need for NDT and materials characterization for improved reliability in structural ceramics for heat engines. Using current fabrication practices, a significant fraction of manufactured ceramic parts may be unsuitable for use. Current NDE practices have difficulty distinguishing the unacceptable parts because of the very small size of critical flaws: even if properly identified, the loss

of a substantial fraction of production is economically undesirable. The established goal is to identify the material parameters and characterization techniques for process control that can be used in the fabrication process to achieve and ensure a high percentage of fully acceptable parts. The assessment has included the raw materials, green-state bodies, and sintered ceramics. The following recommendations for R&D priorities have considered the seriousness of a material parameter on the final product, the state of development of the identified measuring technique, and the expectation of success in development. As an integral part of the development of new technology, correlations should be established between the nondestructive characterization and the service performance or performance-related properties, and the reliability of the characterization technique must be established. It is recognized that some of the recommended examinations may be impractical to apply to 100% of the production quantities of large-volume items, but the application of proven methods and techniques on a sampling basis can ensure the control of the fabrication process. The NDE must be closely associated with design and stress analysis to enhance relevant accept/reject criteria and improve performance prediction capabilities.

Standard reference powders should be developed for powder characterization. The powders should have an exhaustive set of established properties, including chemical and physical properties and, perhaps, forming and firing behavior. Such a material would probably result from a standard round-robin test procedure. Many testing techniques have been developed for powder characterization, and test equipment is commercially available. However, the interpretation of the data from these tests presents a problem: appropriate standard ceramic materials are not generally available to establish a base of interpretation. Although generic standards are available for calibrating various instruments (e.g., National Bureau of Standards particle size standards), a need for standard "real" materials (i.e., actual ceramic powders similar to those intended for manufacturing) remains. The recommended standard powders should be in large lots in which multiple (all pertinent) properties have been carefully characterized. Representative samples should be available to laboratories (including those of ceramic manufacturers) at cost. This

should enhance the uniformity of equipment calibration and powder characterization and permit more realistic correlations of material parameters with final product quality. A first attempt to develop one such standard material (Si_3N_4) is planned as part of the current IEA Annex II program in advanced ceramics.* It would be advantageous to have standard reference powders for all the major classes of ceramic powders.

Significant attention should be given to the development of ultrasonic instrumentation, hardware, techniques, and procedures for the determination of volumetric and surface properties of green and dense ceramics. Properties include density, grain size, elastic and mechanical properties, and flaw detection and characterization. The laboratory studies conducted to date suggest that various techniques of ultrasonics may be very versatile in characterizing both green and dense ceramics for both material characterization and flaw detection. For dense ceramics, this will require the development of advanced technology for the use of ultrasonic frequencies up to 100 MHz.

Development efforts should be directed toward instrumentation, hardware, techniques, and procedures for advanced X-ray techniques to detect and characterize density variations, flaws, inclusions, and other internal discontinuities. Recommended approaches include microradiography (with both contact and microfocus technology) and real-time imaging for plan-view evaluations. High-resolution tomography should be pursued because of the benefits of three-dimensional interpretation capability. It is anticipated that the major applications would be for statistical sampling in large production lots, except for very complex and expensive components for which more complete examination may be warranted.

An extensive, carefully controlled processing-improvement program should be conducted with one or more (simple) product lines to develop relationships between analytical and process-related characterization techniques and real system performance (quality of produced components). To accomplish this, a generic system, such as slip casting or injection molding, should be chosen for study. (If funding considerations permit,

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*International Energy Agency (IEA) Annex II, Cooperative Programme on Ceramics for Advanced Engines and Other Conservation Applications.

parallel studies of multiple material/process/shape systems would be justified.) Critical input parameters and their effects on final product quality would be identical through a series of well-controlled, extensively documented experimental test runs. Extensive inspection and characterization parameters should be identified and conducted at each stage of the process to either learn or confirm the effects of the measured properties on the performance of the finished product. As experience is gained in identifying and measuring precursors of flaws, the process or raw materials should be modified to eliminate the source of flaws. This would be a long-term program to justify capital costs for equipment and to allow for learning curve behavior.

Further investigations should be made into the use of NMR for characterizing green ceramics for binder distribution. To accomplish this characterization, improvements to the sensitivity and resolution over that currently attainable by commercial NMR systems must be made. NMR is currently the most promising method recognized for characterizing proton-rich material such as ceramic binders. Development of instrumentation, hardware, techniques, and procedures will be required if the current promise is sustained.

The above items constitute the primary recommendation for development of material characterization and NDE technology for making significant improvements in reliability of structural ceramics. Several other important areas are recommended for developmental consideration as resources become available as noted herein (not in order of priority).

Guidelines should be developed and published for writing meaningful specifications for ceramic raw materials. Such documentation could help reduce needless duplication of effort and accelerate learning curves for material development.

Basic problems in materials characterization should be investigated, including applications of porosimetry and permeametry to powders and green bodies; obtaining a mass sum of 100% on reported chemical analyses; interactions of binders, dispersants, solvents, and powder surfaces; effects of particle morphology on processing and fired properties; applications of dilatometry to determine optimum sintering schedules; and establishing quantitative relationships between laboratory analytical techniques and on-line control measurements.

Photoacoustic microscopy shows promise for high-resolution surface and near-surface examination for flaws in sintered ceramics and should be further investigated. In its current stage, and even with anticipated developments, its slowness should limit its application to materials development and statistical sampling on relatively simple shapes.

Advanced light-scattering optical techniques should be further investigated and developed for rapid scanning and interpretation of surface finish for inexpensive application to production quantities of both green-state and sintered ceramics.

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