New x-ray nondestructive evaluation techniques for studying microstructural homogeneity of green ceramics

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New x-ray nondestructive evaluation techniques for studying microstructural homogeneity of green ceramics

by

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A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Materials Science and Engineering

Major Professors: Chris Schilling and Joe Gray

Iowa State University

Ames, Iowa

1998
This is to certify that the Doctoral dissertation of

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ACKNOWLEDGEMENTS

I would like to acknowledge the assistance of several graduate students during the course of my dissertation research. Bryan Hinzie, Vivekanand Kini, Huafu Lu, and Victor Garcia have all been indispensable to me in this endeavor.

I would also like to thank the Office of Basic Sciences at the US Department of Energy and the National Science Foundation Industry-University Cooperative Research Program for supporting this work.
INTRODUCTION

A number of applications requiring high temperature stability, high strength, corrosion resistance, and relatively low density exist in the aerospace, automotive, and power generation industries. High-tech structural ceramics are ideally suited to meet many of these mechanical properties requirements. However, the inability of industry to form reliable, crack free parts from ceramics prevents these materials from being more widely used. In structural ceramics, both high processing costs and low fracture toughness are inherently linked to the evolving green microstructure during ceramic processing. Heterogeneities introduced prior to or during green consolidation ultimately become the defects which limit the mean fracture toughness and reliability statistics of the fired component. Specifically, packing density gradients in monolithic ceramics and composition gradients and texturing of asymmetric particles in composite ceramics ultimately become trapped porosity, cracking, and warping in the final part. Two strategies have been used by the ceramic community to overcome these difficulties: i) to reduce the incorporation of heterogeneities into the microstructure and ii) to make the microstructure more resilient to the presence of these heterogeneities.

In the last decade, suspension processing techniques have shown considerable promise in addressing the first of these strategies by producing more uniform, defect free green bodies. By controlling interparticle potential in the suspension, agglomerates can be eliminated before consolidation. As a result, both monolithic and composite ceramic materials prepared by the drained shaping of ceramic suspensions have demonstrated lower sintering temperatures and tighter strength distribution data than their dry pressed
counterparts. However, reliable parts are still out of reach for the majority of high tech ceramic compositions. Several key questions about the evolving green microstructure remain unanswered: What effects do processing variables have on the degree of spatial uniformity in the green state? What pore size in the green state will yield a given flaw size in the sintered part? To what extent will density or composition gradients in the green state yield unacceptable warpage in the final part? The first of the questions is the focus of this dissertation. Serious drawbacks in traditional characterization techniques make them unsuitable for such an investigation.

Central to exploring the relationship between interparticle potential and the evolving green microstructure is the development of nondestructive evaluation techniques and microstructure descriptors to image and characterize this microstructure directly. In this dissertation, the development of two such techniques, energy dispersive x-ray line scanning and x-ray computed tomography density mapping are presented. The latter technique is used to explore microstructure uniformity in centrifuged ceramic suspensions as a function of suspension chemistry and compaction stress in the particle network.

**Dissertation Organization**

To provide sufficient context for this study a literature review of work done to understand relationships between interparticle potential, effective stress, and green microstructure is provided. A discussion of current characterization techniques and their limitations is also included in this review. Following these background sections are two papers prepared for submission to scholarly journals. A section of general conclusions is included following these two papers. At the end of the work, two previously published
proceedings papers which deal with the techniques described here are included in the appendices.

Background

In the first of the following background sections, a dominant factor influencing microstructural homogeneity during ceramic processing, interparticle potential, is described and followed with a discussion of various treatments of density and composition gradients in suspension processed ceramics. The limitations of traditional green ceramic characterization methods are then discussed followed by a review of x-ray transmission techniques and x-ray computed tomography for the study of ceramics.

Microstructural Heterogeneities in Suspension Processed Ceramics

Interparticle potential

An in depth discussion of surface forces, their nature, and their experimental confirmation is provided by Horn. In ceramic suspensions, the well-known Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of colloidal stability describes a balance of forces acting on ceramic particles immersed in a polar medium. Ions in the liquid preferentially adsorb on the surface of the ceramic particle. Oppositely charged ions are then attracted to the surface and form a diffuse layer, or double layer, around the particle. Like particles are surrounded by double layers of like charge and so the resultant coulombic force between any two like particles is repulsive. The range and strength of the repulsive force is controlled by the extent of the double layer, which is, in turn, governed by the ionic strength of the suspension, the valence of electrolyte ions in suspension, and a host of other variables. A
strongly repulsive potential leads to a dispersed, or stable condition in the ceramic suspension.

An attractive van der Waals force is the result of induced dipole interactions between like particles and the suspending medium. The strength of this attractive interaction is a strong function of the difference between refractive indices of the ceramic particles and the suspending medium.\textsuperscript{5} When this attractive interaction is dominant in the suspension, the suspension is said to be flocculated.

A third potential, dubbed the hydration potential, which is responsible for the unique rheological behavior of clay slurries, is also present in oxide ceramic suspensions. This short range, repulsive potential was directly observed by Israelachvili, et al. between mica surfaces.\textsuperscript{6} It has been described as a structural ordering of water molecules in the vicinity of the ceramic surface. More recently Velamakanni, et al. have generated this potential in aqueous alumina slurries.\textsuperscript{7} This potential has also been used to generate weakly flocculated suspensions.\textsuperscript{8}

The addition of long-chain polymeric molecules to the ceramic slurry can also be used to generate short-range repulsion or attraction in ceramic suspensions. For example, if the added polymer molecule is polar, one end of the molecule may form an ionic bond with the surface of the ceramic particle, while the other end extends into the liquid medium forming a so-called micellar structure around the particle. Depending upon the interaction of the liquid medium with the polymer, and the nature of the bonding between the polymer and ceramic particle surface, these coated particles can be made to attract or repel one another yielding a dispersed, flocculated or weakly flocculated suspension.
The summation of the all of these surface interactions can produce local maxima or primary and/or secondary minima in the interparticle-potential separation distance curve. The exact form of this curve determines the distance of closest approach before, during, and after consolidation. It has further been shown that the slope of this curve (the force required to bring neighboring ceramic particles together) is related to the inherent compressibility and plasticity of the compact.

**Density gradients**

Packing density gradients that arise during slip casting, pressure casting, and centrifugal casting are controlled by two main factors: (i) spatial variations in compaction stress (effective stress) that are inherent in the method of consolidation, and (ii) the response of the particle network to these stresses (the drained compressibility), a response which is heavily dependent upon the surface forces outlined above between ceramic particles in the suspension.

Fluid mechanics modeling indicates that nonuniform local stresses during slip casting and pressure casting result from two primary components: (i) the buoyed weight of the particle network, which is transmitted through interparticle contacts and accumulates in the downward direction, and (ii) cumulative drag forces, which originate at particle-fluid interfaces and are transmitted through interparticle contacts such that the local stress increases in the downstream direction. A third component of nonuniform stress arises during centrifugal casting, since the applied centripetal force is proportional to the square of the distance from the center of rotation. If the particle network is compressible, these spatially-variable effective stresses cause nonuniform densities in the green body.
In efforts to relate compaction stress to the resultant packing density there have been continuum and non-continuum approaches. The approaches are fundamentally different in both their conceptualization and application.

The continuum approach of examining empirical compressibility in ceramic suspensions relies on the concept of a compressible particle network as the mechanism for compaction. Recently, Buscall, et al. established a comprehensive model of flocculated network consolidation. Buscall’s model proposes a compressive yield stress for the flocculated network which is an increasing function of ceramic particle volume fraction. In this model, the flocculated particle network can support loads elastically until a critical load value, $P_y(\phi)$ is reached. Above this load, the network irreversibly consolidates until reaching a higher, elastically stable volume fraction. This behavior can be expressed using the following equations:

\[
\frac{D\phi}{Dt} = 0, \left( P_p \leq P_y(\phi) \right) \tag{1}
\]

\[
\frac{D\phi}{Dt} = \kappa(\phi) \left[P_p - P_y(\phi)\right], \left( P_p > P_y(\phi) \right) \tag{2}
\]

where $D$ is a material differential, $t$ is time, $P_p$ is the applied load, $P_y(\phi)$ is the volume fraction dependent yield stress and $\kappa(\phi)$ is the compressibility. Consolidation occurs at this yield stress. The model has been solved numerically in one dimension for settling for filtration. Extensive experimental work has been performed to explore the concept of a compressive yield stress in the context of interparticle potential. In electrostatically modified
systems, dispersed suspensions exhibit nearly incompressible behavior at very low effective stresses, while strongly flocculated suspensions remain highly compressible over the entire compaction stress range. A transition from compressible to incompressible behavior has also been observed in weakly flocculated suspensions. An indifferent electrolyte can be used to suppress double repulsion leading to a balance between short range hydration repulsion and van der Waals attraction.

Similar transitions in compressibility have been demonstrated in sterically modified suspensions. Bergstrom, et al. studied compaction in a decalin-alumina system modified by fatty acids of varying chain length. In this work, the authors calculated the two-particle steric interaction energy as a function of distance between particles and related these curves to experimentally measured compressibility curves. They found that the compressibility behavior of the sterically modified suspensions could be modeled using a modified power law with the pre-exponential factor directly related to the minimum interparticle interaction energy.

The utility of the empirical measure of compressibility is in its ability to predict the severity of density gradients in a suspension processed ceramic given an apriori knowledge of the applied stress distribution. However, it is important to note that the continuum model and the experimental work to date have predicted smoothly varying gradients in packing density in a specimen as a result of changes in compaction stress. Abrupt changes in packing density or 'pockets' of locally distinct density are not predicted.

While these studies of compressibility may provide a useful starting point for weighing the benefits and drawbacks of different suspension processing variables, they have,
to date, been exclusively concerned with the one dimensional compaction behavior of ceramic suspensions. No clear picture of the spatial extent of the packed flocculated network is provided by such analysis. In an important study which illustrates the potential drawbacks of a one dimensional compressibility picture, Shen et. al used a microfocus x-ray computed tomography (CT) system to observe time-dependent microstructure evolution in consolidating silica gels. Of his more notable findings is the evidence for macroscopic fracturing and radial density gradients during the consolidation of stiff gels. Both of these phenomena are not accounted for by a unidimensional, purely plastic yield stress model of consolidation.

Noncontinuum approaches, including real and idealized dry pressing experiments and micromechanical simulations based on individual particle and agglomerate interactions have been used to study density gradient evolution in dry powder compacts. In these methods, some fundamental interparticle friction is assumed to occur between particles. Systems of particles are then stressed or allowed to settle under gravity, and the system is studied under equilibrium. Much of this work can be found in several volumes of the series, Powders and Grains.

In an idealized system of photoelastic cylinders, Kuhn, et al. studied two dimensional compaction behavior as it related to stress networks in the compact. A so-called 'push-through-buckle' micromechanical mechanism was proposed to account for changes in compressibility of the network as a function of stress.

Studies of packing density evolution in dry compacts of alumina as function of die wall stress distribution were performed by Aydin, et al. Using a constitutive model of
compaction based on nonlinear elasticity, the researchers predicted the axial and radial
density distributions in uniaxial alumina powder compacts using a finite element method.
These results were then compared directly to data from a projection radiography technique to
measure internal compact strains. The findings show a good qualitative agreement between
the numerical and experimental results in terms of predicting high and low density values
near the edges of the compact. However, marked differences between experiment and
simulation were found to exist in predicting density variations along the axial centerline of
the compact. The authors believe this discrepancy to be the result of internal friction effects
not accounted for by the numerical model.

Simulations of the compaction process have also been used to explore microstructure
evolution. Cundall, et al. has used a moving boundary condition simulation of spherical
particle collisions and compaction.\(^{25}\)

These approaches are beginning to provide a more realistic picture of the effects of
such processing variables as particle size distribution, interparticle friction, and wall effects
on the 2 and 3 dimensional density distributions in dry ceramic compacts. The direct
comparison between model in experiment in some of these studies is a necessary process for
improving our understanding of density gradient evolution. However, all of these studies
have involved dry powders or dry powder agglomerates. No incorporation of interparticle
potential in a suspending medium has been explored.

In his Ph.D. thesis, J. C. Kim developed a three stage compaction simulation which
first considers the agglomeration process and then proceeds to simulate sedimentation of
spherical particles or agglomerates of particles.\(^{26}\) During the agglomeration phase DLVO
theory is used to provide a centrally acting force for agglomeration. During the subsequent settling steps, only gravity is considered to act on the agglomerates. These larger particles are allowed to move through energy minimization until 3 contacts with neighboring particles are made. While most of Kim’s results were qualitative, one can imagine a series of experiments to probe real microstructures for experimental confirmation of the model’s results.

In order to improve our understanding of the mechanism behind density gradient evolution during suspension processing, simulations such as Kim’s need to be applied to ceramic shape forming processes such as slip casting, pressure filtration and centrifugation. Descriptions of the simulated microstructure need to be compared to those resulting from similar experiments with real ceramic suspensions. In this way, the assumptions about the nature of interparticle interactions and the continuum-based compressibility of ceramic particle networks can be tested.

**Composition gradients**

In efforts to make the ceramic microstructure more resilient to strength limiting defects, reinforcement phases such as fibers have been added. Green microstructural uniformity is also critical to the fabrication of these ceramic composite materials. In addition to density gradients, phase segregation during processing can lead to reduced mechanical properties or the prevention of successful fabrication altogether. Singh, et. al. noted that the fracture toughness of continuous SiC fiber reinforced mullite specimens was greatly reduced by the presence of mullite rich regions in the microstructure. Hoffman, et al. illustrated the effect of phase segregation and misorientation at the container wall during slip casting of SiC whisker reinforced Si$_3$N$_4$.  

There are very few systematic studies of suspension chemistry-composition gradient relationships in suspension processed ceramic composites. One such study involved the centrifugation of zirconia particle reinforced alumina. In this work, Chang, et al. centrifuged composite compacts at three different suspension conditions: dispersed, strongly flocculated, and salt coagulated. The authors used Scanning Electron Microscopy together with EDAX analysis to monitor the composition profile in the axial direction of the centrifuge compacts. They found that both the strongly flocculated and salt coagulated suspension conditions were adequate to prevent centrifuge induced segregation of the larger and heavier zirconia particles. This type of study has also been extended to discrete fiber reinforced composites with similar findings. That is, both the strongly flocculated and salt coagulated suspension conditions could successfully prevent gravity induced segregation of the larger SiC fiber phase during pressure filtration.

A more in depth study of the effects of interparticle potential on the overall spatial distribution of phases in ceramic composites would be valuable for a wide range of compositions and applications.

Characterization Techniques

Much of the previously sited work has found that interparticle potential and varying compaction stresses can act to create spatially varying, three dimensional density and compositional variations. In order to better understand how these variables control these microstructures, the ceramic community needs 1) better tools to probe the intact microstructure and 2) better means to evaluate the data and link this data to processing variables. Traditional characterization techniques suffer from two main limitations: they
provide volume averaged information or they are destructive to the microstructures they seek to describe.

**Traditional characterization techniques**

The bulk packing density is often used as a means of characterizing the green microstructure.\textsuperscript{30} Alone, this information is insufficient to predict ceramic reliability, since it cannot account for spatial variations in the microstructure within a given sample. Samples with the same green density may exhibit different plastic shaping behavior, different drying behavior, and ultimately different post-firing fracture toughness statistics as a result of different spatial features between the two samples.

Rheological characterization of ceramic slurries has been used extensively to explain settling behavior, the kinetics of floc formation, and even the surface interaction of new additives. However, the rheology of a given suspension, while relevant to the packing behavior of a suspension, is not directly linked to the evolving microstructure and does not yield information about the spatial make-up of the microstructure during or following compaction.

Only those techniques which are capable of directly imaging the affected green microstructure can provide the spatial statistics we need to relate interparticle potential and homogeneity. Traditionally, various forms of microscopy have been used.\textsuperscript{31} These methods are problematic for suspension processed green bodies, since they involve some sort of destructive process for sample preparation. Since the microstructures of interest are extremely delicate in the green state, the value of such techniques is in question.
Mercury porosimetry provides another option for obtaining density distribution data. In a study on the effects of green density and sintering temperature on the evolution of pores in dry pressed agglomerates, Zheng, et al. used mercury porosimetry to show the demonstrate a relationship between critical pore size and pore shrinkage. However, as with microscopy, mercury porosimetry is inherently destructive to the microstructure being examined, and is not directly applicable to water saturated green bodies. In addition, mercury porosimetry suffers from inherent systematic errors due to pore neck entry effects.

**X-ray techniques**

It is apparent from the above discussion that the ideal method to examine a suspension processed green ceramic microstructure is a nondestructive one. Many techniques offer a means to nondestructively probe the microstructure: ultrasonic transmission, focused probe acoustic-microscopy, thermography, x-ray computed tomography, x-ray radiography. Among these, x-ray computed tomography (CT) is uniquely suited to provide high resolution 3 dimensional spatial details of the examined microstructure. Current, state-of-the-art x-ray CT is capable of resolving 10 to 100 micron sized features in small ceramic specimens.

A review of the basic principles of computed tomography can be found elsewhere. For the purposes of this discussion, it is necessary to appreciate that CT image resolution can be separated into two major components: spatial resolution and contrast sensitivity. Spatial resolution represents the smallest detectable length-increment of an object perpendicular to the x-ray beam, and is determined by the spatial sampling frequency of the field of view. For example, if a 1 cm specimen is magnified and imaged across a detector array with 500 elements, the spatial resolution is nominally equal to 1 cm divided by 500, or 20 microns.
Contrast sensitivity represents the smallest detectable length-increment of an object parallel to the x-ray beam and is governed by the x-ray counting statistics, noise characteristics and overall dynamic range of the detector. For example, if a one-cm-thick ceramic specimen is examined by an image intensifier system having a typical contrast sensitivity of 5%, the smallest detectable change in the thickness of the specimen would be 5% of one cm or 500 microns.

In the past decade, several researchers have used high performance x-ray CT to study microstructure evolution during ceramic processing. For example, Sawicka et al. combined a high energy, mono-energetic x-ray source with a single, solid-state detector and observed density variations as small as 1 volume % in sintered alumina specimens having an overall size of 10 cm. The spatial resolution of this system was limited by the collimation of the incident beam, reported at approximately 0.7 mm. Since then, significant increases in spatial resolution and significant reductions in acquisition time have been made possible by the introduction of two-dimensional, solid-state diode detector arrays in conjunction with either a microfocus x-ray generator or a synchrotron photon source. For example, Phillips et al. used a commercially available CT system consisting of a high energy x-ray source and a solid state detector array to observe density gradient evolution during dry powder compaction as a function of binder content and compaction pressure. Features as small as 200 microns were observed in compacts of ZnO, measuring 0.5 inches in diameter. Higher resolutions were reported by Kinney et al. using a synchrotron based x-ray CT microscope. In that study, the microstructure evolution of chemical vapor infiltrated composite samples was analyzed at different stages of the fabrication process at a voxel resolution of 15.8 microns.
It is important to note that the above work entails use of either a synchrotron or an array of solid-state detectors. The high cost of this research equipment generally limits its use as a process-development tool by ceramic manufacturers, and such equipment is unavailable to our research group. A key focus of this dissertation, therefore, is the development of affordable nondestructive techniques which may be used by the ceramic community at large to explore these microstructural phenomena.

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Abstract

A new x-ray computed tomography technique for mapping 3 dimensional variations of packing density in suspension processed green ceramics is introduced. The technique is used to measure the drained compressibility of two ceramic suspensions prepared at different extremes of interparticle potential: a strongly flocculated suspension and a weakly flocculated, salt coagulated suspension. Regions of low and high effective stress in both samples are then explored with the computed tomography technique. Both the spatial and statistical differences in microstructural features of both samples reveal unexpected trends in homogeneity.

Introduction

Consolidating dilute suspensions into dense, homogeneous ceramic green bodies is the basis for colloidal processing of ceramics. Since microstructural heterogeneities during the formation of the green body can ultimately lead to cracks and warpage during the final stages of processing, microstructural uniformity must be carefully controlled during the
drained shaping process. However, different stages of processing may require different levels or measures of uniformity. Often, a compromise must be struck between a dense, highly uniform green body which allows reduced sintering temperatures and higher final density and a more open, high strength green body to speed consolidation and reduce drying stresses\textsuperscript{1,2}.

Many processing parameters control the mechanical properties and resultant microstructure of the suspension during consolidation. Of particular importance is the role of interparticle potential on the bulk microstructure and mechanical properties of the suspension. Several researchers have empirically related the compressive yield stress of a suspension to the degree of flocculation\textsuperscript{3-5}. In addition, this kind of analysis has been taken further by measuring or calculating the pair potential between ceramic particles in suspension and comparing it directly to the compressive yield stress and green body plastic behavior\textsuperscript{3,6-8}. These measurements and theoretical results indicate that an attractive, or strongly flocculated particle network yields a very compressive, highly plastic green body while a repulsive, stable suspension of particles yields a largely incompressible, brittle compact. A third type of suspension, the weakly flocculated suspension, said to be the result of a superposition of long range attractive forces and short range repulsive forces, has been shown to yield and intermediate, highly dense and plastic green body\textsuperscript{35,9}. Theoretical and experimental treatments of the effects of interparticle potential on the bulk density and the compressive yield strength have been explored; however, very little attention has been focused on the microstructural origins of these mechanical phenomena. In all previous work, the assumption is made that the suspension processed ceramic green body may exhibit density gradients from top to bottom, but that it remains completely uniform in every other aspect. The question
remains, "how does interparticle potential control the spatial uniformity of packing density in the suspension processed compact?"

The significance of density gradients in the suspension processed green body has not been fully explored, most likely due to the lack of techniques available to image the spatial extent and severity of density gradients in the liquid saturated microstructure. In order to answer these questions, we need better tools to examine the in-situ microstructure of the suspension processed compact. In general, existing destructive techniques are ill-suited to examine the microstructure of a water saturated body, since any sample preparation adversely alters the microstructure of interest. Of the many nondestructive techniques available to probe the green microstructure, X-ray computed tomography (CT) stands out as the only technique capable of providing 3D microstructural information of 10 micron to 100 micron sized features in the green compact.

In this paper, we introduce an X-ray computed tomography technique to study the 3 dimensional variations of packing density in suspension processed green bodies. After bench-marking the performance and repeatability of the technique, we use it to construct a quantitative density map of two types of centrifugally compressed aqueous alumina suspensions at two different regions of effective stress. The raw density maps as well as their 2 and 3 dimensional density distributions are analyzed and related to interparticle potential and effective stress. The objective of this research is to introduce this technique to perform an initial study of the microstructural uniformity as a function of interparticle potential and compaction stress.
CT - Background

Previous research

In the past decade, several researchers have used high performance x-ray CT to study microstructure evolution during ceramic processing. For example, Sawicka et al. combined a high energy, mono-energetic x-ray source with a single, solid-state detector and observed density variations as small as 1 volume percent in sintered alumina specimens having an overall size of 10 cm. The spatial resolution of this system was limited by the collimation of the incident beam, reported at approximately 0.7 mm. Since then, significant increases in spatial resolution and significant reductions in acquisition time have been made possible by the introduction of two-dimensional, solid-state diode detector arrays in conjunction with either a microfocus x-ray generator or a synchrotron photon source. For example, Phillips et al. used a commercially available CT system consisting of a high energy x-ray source and a solid state detector array to observe density gradient evolution during dry powder compaction as a function of binder content and compaction pressure. Features as small as 200 microns were observed in compacts of ZnO, measuring 0.5 inches in diameter. Higher resolutions were reported by Kinney et al. using a synchrotron based x-ray CT microscope. In that study, the microstructure evolution of chemical vapor infiltrated composite samples was analyzed at different stages of the fabrication process at a voxel resolution of 15.8 microns.

It is important to note that the above work entails use of either a synchrotron or an array of solid-state detectors. The high cost of this research equipment generally limits its use as a process-development tool by ceramic manufacturers, and such equipment is
unavailable to our research group. However, our efforts with a relatively low-cost CT system have yielded image resolution sufficient to detect small variations in ceramic suspensions. A summary of this work and its effects on image quality are given in the Experimental Procedure section of this paper.

**Image resolution**

To evaluate x-ray CT's capability to resolve the homogeneity of ceramic suspensions, it is necessary to appreciate that CT image resolution can be separated into two major components: spatial resolution and contrast sensitivity. Spatial resolution represents the smallest detectable length-increment of an object perpendicular to the x-ray beam; it is determined by the spatial sampling frequency of the field of view. For example, if a 1 cm specimen is imaged across a detector array with 500 elements, the spatial resolution is nominally equal to 1 cm divided by 500, or 20 microns. There are several ways this spatial resolution limit can be improved, for example, moving the specimen or detector array to increase sampling frequency, or by increasing the number of detector elements. However, this comes at the expense of acquisition time and equipment cost. The second component, contrast sensitivity, represents the smallest detectable length-increment of an object parallel to the x-ray beam and is a measure of the noise in the x-ray detector system. This limit is governed by the x-ray counting statistics, the noise characteristics, and the dynamic range of the detector. For example, if a one-cm-thick ceramic specimen is examined by an image intensifier system having a typical contrast sensitivity of 5%, the smallest detectable change in the thickness of the specimen would be 5% of one cm or 500 microns. For a high
resolution system such as the one used in this work, contrast sensitivity, not spatial resolution, is the limit of image resolution.

Experimental Procedure

X-ray System

The real time x-ray system used to measure compressibility and to perform computed tomography is illustrated in Figure 1. It consists of a bremsstrahlung microfocus x-ray source (FXE-200.50, Feinfocus, Germany) a series of positioning stages (Daedal, Harrison City, PA) allowing 5 degrees of sample movement, an image intensifier system (p600, Precise Optics, bay Shore, NY), an 8-bit digital charge coupled device (CCD) camera (Sony), a frame grabber card (DT 2867, Data Translation, Marlboro, MA) and a personal computer. The source spot size is roughly 1 to 5 microns allowing significant geometric magnification.

Image Artifact Removal

In order to improve upon the contrast sensitivity limits of our image intensifier detector system, we used techniques to increase the dynamic range of the output signal. These methods, frame averaging and grayscale subranging, are described elsewhere and effectively expand our 8-bit signal to an 11-14-bit signal. This, in turn, improves the contrast sensitivity from slightly better than 5% for a single frame to better than 1%. For example, shown in Figure 2 are projection images of a single layer of 300 micron diameter soda-lime silicate spheres that were positioned on a quarter-inch-thick plate of the same material. The diameter of each sphere is approximately 3% of the thickness of the glass plate. Therefore, a contrast sensitivity of better than 3% is required to resolve this thickness
change and image a single sphere. The left side of Figure 2 illustrates use of a standard acquisition scheme (i.e., no adjustment to the 8 bit signal) where the glass spheres are simply not visible; however, the spheres begin to take shape in the image on the right side of Figure 2, obtained by integrating multiple frames of an 11-bit subranged signal.

An additional source of artifacts in the CT images obtained from this system are the nonuniform responses of the image intensifier and CCD camera. The origin and extent of these variations is discussed in detail elsewhere\(^\text{16}\) and essentially amount to significant variations in the pixel grayscale output for a constant x-ray flux. As a result, as multiple projections are joined during the CT reconstruction process, these pixel variations become ring artifacts in the final image. To minimize the effects of these artifacts, we fit the response of each pixel element to x-ray flux using a quadratic equation. The coefficients of all of the quadratic fits of all pixel elements are then normalized to their average values. The results of this artifact removal process are shown in Figure 3. The images on the right side of the figure represent the raw, reconstructed CT data of two types of samples: a calibration suspension and a centrifuged compact. In both images, the grayscale variations associated with the rings dominate the image contrast. Images on the right side of Figure 3 show the effects of ring artifact removal. While remnants of the rings are still present in these images, they are reduced enough to allow the homogeneity of the calibration suspension and the individual features of the centrifuged compact to be visible.

**Density Mapping**

Grayscale images, such as the ones shown in Figure 3, do not provide a quantitative description of the packing density variations within a compact. To do so, we need a means to
convert the grayscale images to packing density maps. The technique must determine the relative amounts of two different materials (i.e., ceramic powder and liquid suspending medium). To accomplish this, the Beer-Lambert law is employed with two assumptions: i) the overall thickness of the sample and the container, \( L \), remains constant during the measurement, and ii) the smallest pixel or voxel resolved is composed of a combination of both materials (ceramic and water in our case). With these assumptions, the volume fraction of solids, \( \phi \), of the ceramic suspension is seen to be linearly related to the logarithm of the image grayscale value:

\[
\begin{align*}
I &= I_0 \exp(\mu_c x_c + \mu_w x_w) \\
G &= I \\
G &= C \cdot \exp(\mu_c x_c + \mu_w x_w) \\
G &= C \cdot \exp(\phi (L \mu_c + L \mu_w) + L \mu_w); L = x_c + x_w, \phi = \frac{x_c}{L} \\
\phi &= \frac{1}{L(\mu_c + \mu_w)} \cdot \ln G - (\ln C + L \mu_w) \\
\phi &= A \cdot \ln G + B
\end{align*}
\]

where \( G \) is the image grayscale, \( I \) is the transmitted x-ray intensity, \( I_0 \) is the incident x-ray intensity, \( \mu_c \) is the linear x-ray attenuation coefficient of the ceramic material, \( x_c \) is the path length of ceramic material, \( \mu_w \) is the attenuation coefficient of water, \( x_w \) is the path length of water, \( L \) is the thickness of the container, and \( A, B, \) and \( C \) are constants.

By preparing a series of calibration slurries of known volume fraction solids, \( \phi \), a calibration curve must be generated to convert an unknown grayscale value into packing density. This process can be repeated for each pixel in a projection or CT image, thereby
minimizing the systematic errors associated with pixel to pixel variations on the image intensifier. A typical calibration curve for a single image pixel using 5 calibration slurries is shown in Figure 4 below.

These calibration suspensions were made by mixing the appropriate amounts of alumina powder (A16 Superground, Alcoa, Pittsburgh, PA) with water to obtain five distinct volume fractions. The volume fraction of each slurry was confirmed using a pycnometer. HCl was used to maintain suspension pH at 4.0 to ensure dispersion. The suspensions were poured into tubes of the same size as the ones used for the centrifuged specimens (see below).

**CT Resolution Summary**

As a result of the contrast sensitivity improvements, artifact removal methods, and packing density conversion, we have established a level of confidence in detecting changes in packing density in ceramic suspensions. Specifically, we are able to detect features larger than 40 microns in size which represent density variations as small as 2 percent.

**Suspension Preparation**

Two types of aqueous alumina suspensions were prepared for centrifugation. Using the same procedures and reagents described elsewhere strongly flocculated (pH 8.6) and weakly flocculated (pH 4, 1.75 M NH₄Cl) aqueous slurries containing 0.20 volume fraction of α-alumina were prepared. These slurries were centrifuged in plastic tubes (10 mm in diameter and 75 mm in length) with hemispherical bottoms. The specimens were centrifuged for 4 hours at 1350 RPM. Measurements of slurry height as a function of time in the centrifuge were recorded to ensure adequate time to achieve equilibrium consolidation.
Compressibility Measurements

A projection image of the vertical centerline of each calibration suspension was taken with the x-ray system to create a series of linear calibration curves for points along the vertical centerline of the image intensifier. Both of the centrifuged suspensions were scanned in the same manner. Using the calibration data for each pixel along the centerline, the projection images of the centrifuged specimens were converted into packing density profiles. These profiles were then converted into plots of effective stress (see Figure 5) as a function of packing density using the relationship described by Buscall. Similar to the method employed by Chang et al., our technique allows the rapid determination of compressibility curves for a wide range of suspension conditions. After calibration suspensions are scanned, an entire compressibility curve may generated in a few minutes.

Computed Tomography Density Maps

CT images of the calibration suspensions were used to make calibration curves for each pixel in the CT images of the centrifuged specimens. A total of ten CT slices were used from each calibration specimen. These same ten horizontal slices of the image intensifier were used to build up 100 slice CT data sets of the two centrifuged samples (see Figure 6) by successively moving the specimen in the z direction. Two regions of each specimen were scanned in this manner. The position of these 100 slice data sets is shown in Figure 7. These locations were chosen to explore both a high and low effective stress region for each of the two suspension processing conditions. All four of the 100 slice data sets as well as the repeated set and the CT slices of the calibration suspensions were then converted into density
maps using the calibration curves generated from the calibration suspensions. In addition, the calibration suspension CT datasets were also converted into density maps to determine the extent of systematic error in the density map data. Histograms of all of the CT slices were also generated. The mean density and standard deviation of each of these distributions were tabulated.

Results

Density Profiles and Compressibility Measurements

The linear density profiles of the two specimens are illustrated in Figure 7. As expected, the weakly flocculated condition yielded a suspension which consolidated to a much higher overall density than the compact prepared from the strongly flocculated condition. Also shown in the figure are the mean density data from all of sample CT datasets. The values of mean packing density from the CT slices agree well with the independently measured 1 dimensional density profiles, with at most 1 percent differences. The compressibility profiles generated from the linear density profiles are shown in Figure 8. Here, also as expected, the strongly flocculated condition yielded a more compressible compact over the entire range of effective stress probed. In contrast, the weakly flocculated suspension exhibited a quick transition from compressible to nearly incompressible behavior in the top 1 mm of the specimen. Also shown on the figure are the locations of the four CT datasets in terms of effective stress. These four regions will be referred to as FT for the top of the strongly flocculated specimen, FB for the bottom of the strongly flocculated specimen.
WT for the top of the weakly flocculated specimen, and WB for the bottom of the weakly flocculated specimen.

**CT Density Measurements**

A typical CT density map of the strongly flocculated specimen is shown adjacent the map of a calibration suspension in Figure 9. While the mean densities of the two slices are roughly equivalent (0.392 and 0.397), the standard deviation of the specimen’s density distribution is larger than that of the calibration suspension, indicating a broader density spread in the specimen. In addition, examination of the images reveals the presence of large (200-500 μm) low and high density regions in strongly flocculated specimen not present in the calibration suspension. A direct comparison of the histogram data between the FB region and the calibration suspension of approximately the same density reveals similar behavior (see Figure 9). While the density data are noisy, these images demonstrate the presence of real density gradients in the sample specimens.

A further measure of repeatability is provided by the images in Figure 10. Here, duplicate CT slice density maps are directly compared with one another. The images show repeated large, low density regions. The mean values are within 1 percent of each other while the standard deviation values are in agreement to 0.1 percent.

The large volume of data associated with several 100 slice density map datasets requires several different methods of visualization to fully appreciate trends in the centrifuged specimens’ microstructures. We present, for each region examined, two orthogonal planes of the 3 dimensional data set (see figure 6) to give a sense of trends in the z direction (centrifuge axis.) In addition, two example x-y plane slices for each region are shown together with their
respective density histograms to reveal specific microstructural features in the dataset. Figures 11 and 12 represent the CT data from the FT region of the strongly flocculated sample. Figures 13 and 14 show CT data for region WT, figures 15 and 16 show CT data for region FB, and figures 17 and 18 show CT data for region WB. Finally, the standard deviations of all CT slices are plotted as a function of effective stress in the particle network in Figure 20. In this way, general trends for both suspension conditions can be observed. These trends include i) a general increase in packing density with applied stress, ii) a larger standard deviation of packing density for the weakly flocculated condition than for the strongly flocculated condition for both stress regimes, and iii) opposite trends in the standard deviation of packing density as a function of compaction stress for both specimens.

Discussion

The density profiles and compressibility curves generated from projection line scans yielded expected trends in both of the specimens. In particular, the strongly flocculated sample packed to a lower overall density more gradually with position than did the weakly flocculated suspension. As a consequence, the strongly flocculated sample exhibited a higher compressibility than the weakly flocculated sample over the entire stress range.

The CT data reveal several interesting and non-intuitive trends in the specimen microstructures. The first of these is the spatial extent of the density gradient at the top of the strongly flocculated sample (see Figure 11). While the overall density gradient is expected, the radial density difference is opposite to what might be expected from drag near the edge of the sample. However, this result is consistent with the radial stress distribution present during centrifugation. A second interesting result is the spatial extent of low and high density
areas in both regions of the strongly flocculated sample. Features ranging in size from 100 to approximately 900 microns represent areas of 2 to 4 percent change in packing density. Considering the size of the starting alumina particles, roughly 0.5 microns, these results suggest the interaction of large flocs containing hundreds of individual particles. While such flocs have been proposed and directly visualized in dilute ceramic slurries, these CT data represent the first direct evidence of these type of features in a saturated consolidated ceramic suspension.

Images of the weakly flocculated microstructure are decidedly more subtle. Large features seen in the strongly flocculated sample are, for the most part, absent from the CT data of the weakly flocculated sample. Most of the periodic density patterns in the x-z and y-z slices can be attributed to the patterns observed in the CT images of the calibration suspensions (see Figure 19). However, histograms of the density slices reveal that the standard deviation of densities throughout the weakly flocculated microstructure are significantly higher than those of the strongly flocculated microstructure. This result is entirely unexpected. The traditional view of the dispersed and weakly flocculated microstructures is that they are more highly packed and more uniform than the strongly flocculated microstructures. While the mean densities are more uniform, and the spatial extent of density variations is small, the overall breadth of the density range is larger for the weakly flocculated compact than for the strongly flocculated compact.

Examination of the tabulated standard deviation data in Figure 20 reveals an additional non-intuitive trend in the microstructural uniformity as a function of stress. During the transition from low to high stress the two suspensions exhibited opposite trends in
the standard deviation data. The standard deviation of the weakly flocculated density data was reduced from approximately 0.033 to 0.026 as the effective stress in the network increased from 0.011 to 0.058 MPa. In contrast, the standard deviation of the strongly flocculated density data increased from approximately 0.020 to 0.022 as the stress increased from 0.0001 to 0.010 MPa and to 0.023 at 0.050 MPa. Just as the individual microstructural features have been shown to be repeatable, so too are these general trends in standard deviation of density. Figure 21 compares the standard deviation data for all of the CT dataset in the FT region with the repeated 100 slice dataset taken of the same region. The values are within 0.001 of each other at every point.

A possible explanation for these trends may lie in the difference in compaction behavior between individual particle units (as in the weakly flocculated case) and large interconnected particle flocs (as in the flocculated case). One would expect an increase in space filling efficiency as stress is increased in the weakly flocculated system if particles behave as individual packing units. A highly interconnected network of large flocs, on the other hand, may yield a coalescence of more open, low density parts of the network during the application of stress.¹⁹

Conclusions

Overall, we have demonstrated the ability to generate 3 dimensional density maps of saturated ceramic green bodies using X-ray computed tomography in conjunction with a series of well-characterized calibration suspensions. With our CT system, the technique is capable of providing 40 micron feature resolution at better than 2% sensitivity to changes in packing density.
Results from the two alumina centrifuged compacts demonstrate the need for a 3 dimensional exploration of the consolidated microstructure. Trends in the mean density as a function of stress are in agreement with those previously obtained in the literature. However, the images evidence profound differences in the compacted microstructures as a function of suspension chemistry. Specifically, the strongly flocculated condition yields regions of low and high density which extend spatially for hundreds of microns. In contrast, the weakly flocculated condition yields a microstructure which appears spatially homogeneous to the 20 micron level.

The standard deviation data reveal opposite trends for both of the suspension chemistry conditions as a function of effective stress. Our explanation of these differences is speculative, and will require a more systematic and intensive study of the microstructure as a function of interparticle potential and network stress.

In summary, our initial CT study of suspension processed green ceramics has revealed new microstructural details and trends. These trends lead us to conclude that the concept of microstructural homogeneity with regards to these suspension processed ceramics must be expanded to include the 3 dimensional spatial extent and severity of density gradients.

References


Figure 1 - This digital photograph of the X-ray CT system shows all of its major components with the exception of the computer operated by the system user which resides outside of the X-ray vault.
Figure 2 - Digital x-ray projection images of 300 micron diameter soda-lime silicate spheres. The image on the left obtained from an unprocessed 8-bit signal from the CCD camera. The image on the right was obtained by accumulating 60 frames of an 11-bit subranged signal.
Figure 3 - The effects of ring artifact removal are shown on CT images of a calibration slurry and a the strongly flocculated sample. Note the features on the right side of the corrected CT image of the strongly flocculated sample (bottom left) are more clearly visible after artifact removal.
Figure 4 - A plot of a typical calibration curve showing the logarithm of grayscale values as a function of volume fraction solids, $\phi$. 
1) Real Time Projection  

2) Density Profiles

3) Buscall's Relationship  

4) Compressibility Curves

\[ \sigma'(z) = \Delta \rho \omega^2 \int \phi(z)zdz \]

\( \sigma' \) - effective stress  
\( \rho \) - density  
\( \omega \) - angular velocity  
\( z \) - distance to center of rotation  
\( \phi \) - volume fraction solids

Figure 5 - Schematic diagram detailing the steps used to generate compressibility curves for each of the centrifuged specimens.
Figure 6 - 100 CT slices of the x-y plane of each sample were converted into 100 slice density datasets. Two orthogonal planar cuts of these datasets, the y-z and x-z planes, were made to view density trends.
Figure 7 - Density profiles of the two centrifuged suspensions reveal a higher packing density for the weakly flocculated condition. The mean density values of the CT data are shown to be in good agreement with the line scan values.
Figure 8 - Buscall’s relationship was used to convert density profiles into compressibility curves. The four regions of the centrifuged samples chosen for CT are shown as FT, FB, WT, and WB.
Figure 9 - A CT slice density map of the strongly flocculated sample (left) is compared with the same slice of a calibration suspension with approximately the same mean packing density (right). The large low and high density regions in the strongly flocculated slice demonstrate that these observed features are not a function of the calibration process.
Figure 10 - Repeated density maps of the same sample region. Large, low density features are repeated in images 1 and 1a and in 2 and 2a. Repeated features are surrounded by geometric outlines.
Figure 11 - The x-z planar cut (top) and y-z planar cut (bottom) of the FT 100 slice density map dataset. Both images show a steep density gradient in the z direction and a low density 'capping' near the top of the scanned region.
Figure 12- Two density map x-y slices from the dataset shown in the previous figure (left) illustrate the contrasting features at the top and bottom of the FT region. The histograms (right) of these slices reveal a 4 percent increase in mean density and a slight increase in the standard deviation of density.
Figure 13 - The x-z planar cut (top) and y-z planar cut (bottom) of the WT 100 slice density map dataset. Both images show a relatively homogeneous region peppered with small areas of high and low density.
Figure 14 - Two density map x-y slices from the dataset shown in the previous figure (left) illustrate similar features at the top and bottom of the WT region. The histograms reveal no change in the mean or standard deviation of packing density.
Figure 15 - The x-z planar cut (top) and y-z planar cut (bottom) of the FB 100 slice density map dataset. Both images reveal several extensive regions of relatively low density throughout the region.
Figure 16 - Two density map x-y slices from the dataset shown in the previous figure (left) show the large spatial extent of low density regions in both the top and bottom of the FB region. The histograms reveal no change in the mean and very little change in the standard deviation of packing density.
Volume Fraction Solids

Figure 17 - The x-z planar cut (top) and y-z planar cut (bottom) of the WB 100 slice density map dataset. A periodic pattern of low and high density regions characterizes both images.
Figure 18 - Slice 1 from the previous figure (top left) contains a few small, relatively low density regions. Slice 2 (bottom left) appears similar with a slightly higher overall packing density. The histograms reveal a small change in the mean and no change in the standard deviation of packing density.
Figure 19 - The x-z planar cut of repeated calibration suspension CT images (top) is shown next to the same cut of the FB region of the strongly flocculated sample (bottom). The periodic patterns in the calibration suspension data help reveal the nature of image artifacts which exist in the sample data.
Figure 20 - The tabulated standard deviation data for all four regions reveal two opposite trends between the two suspension processing conditions.
Figure 21 - The tabulated standard deviation data as a function of position for the strongly flocculated sample and the repeated dataset of the same sample.
ENERGY DISPERSIVE X-RAY LINE SCANNING OF COMPOSITE MATERIALS

A paper to be submitted to the Review of Scientific Instruments

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Abstract

We introduce a new technique for using transmitted x-ray spectra to obtain quantitative phase distribution information in composite materials. In the technique, incident and transmitted x-ray intensities are collected and used in conjunction with the energy dependent linear x-ray attenuation coefficients to determine the path length of each phase as a function of position in a composite material. Key parameters affecting the accuracy of this method are discussed in detail, including counting statistics, attenuation coefficient accuracy, and compositional contrast. A computer simulation of this technique was written to compare it with a previous method and to optimize scanning variables. Results from the simulator were experimentally verified using an ideal metal composite composed of an aluminum step-wedge and a copper sheet. The technique was also used to map spatial variations of composition and porosity in a fiber reinforced, ceramic matrix composite.

Background

The performance of a composite material critically depends on the spatial distribution of the constituent phases in this material. In turn, a knowledge of how different processing
variables affect this spatial distribution is necessary to improve or optimize the design of composite microstructures.

Techniques to examine composite microstructures can be classified according to several different criteria such as speed, cost, and the size of the smallest detectable feature. In many composite systems, there is a need for quantitative phase distribution data at the 100 micron to 1 mm size range. For example, in the case of graphite epoxy composites, a one volume percent increase in porosity can lead to a three percent reduction in shear strength. Since compositional variations on the order of 10 percent are not uncommon in candidate composite materials for aerospace applications, quantifying these variations is important.

For fully processed samples, destructive methods are capable of obtaining this kind of information, but generally involve some kind of metallography and microscopy, and are time consuming as a result. In addition, these methods may not be feasible for composite materials during the early stages of processing. For example, green ceramic matrix composites cannot themselves be sectioned for microscopy without first modifying the microstructure of interest. A final drawback to destructive techniques is that they do not generally allow the examination of a single specimen through various stages of its processing. Nondestructive techniques are needed which can overcome this problem.

Energy dispersive x-ray analysis provides a means to examine spatial variations of composition and porosity nondestructively. The technique takes advantage of the fact that x-ray attenuation in a given material is a function of both the composition and the energy of incident photons according to the following relation:
In this equation, \( I(E) \) and \( I_0(E) \) are the energy-dependent intensities of the transmitted and incident x-ray beams, respectively. \( x_i \) is the thickness of constituent \( i \) in the path of the x-ray beam, and \( \mu_i \) is the linear x-ray attenuation coefficient of constituent \( i \).

By irradiating a specimen at two (or more) energies, and collecting the incident and transmitted x-ray intensity (see Figure 1,) the above relationship can be solved explicitly for the material path lengths, \( x_i \), of each constituent material in the composite. For example, for a two constituent composite, equation (1) can be solved explicitly at two separate energies yielding

\[
x_1 = \frac{\xi(E_1)\mu_2(E_2) - \xi(E_2)\mu_2(E_1)}{\mu_1(E_1)\mu_2(E_2) - \mu_1(E_2)\mu_2(E_1)}
\]

\[
x_2 = \frac{\xi(E_2)\mu_1(E_1) - \xi(E_1)\mu_1(E_2)}{\mu_1(E_1)\mu_2(E_2) - \mu_1(E_2)\mu_2(E_1)}
\]

where \( x_1 \) and \( x_2 \) are the path lengths of material 1 and 2, \( \mu_1 \) and \( \mu_2 \) are the attenuation coefficients of material 1 and 2, and \( \xi \) is the logarithm of the incident to transmitted x-ray intensity.

Researchers in soil chemistry initially reported a so-called dual-energy technique, where they simultaneously irradiated binary soil mixtures with two mono-energetic
radioisotopes to measure the bulk density and water content of soils. An advantage of this isotope based technique is that the energy bands of the incident photons are very narrow, resulting in a high degree of confidence in the choice of attenuation coefficients. In addition, fast, non-energy discriminating x-ray detectors can be used to make these intensity measurements. However, the technique provides very little flexibility in terms of energy choice, and can therefore have limited applicability to a wide range of composite materials.

Instead of using radioactive isotopes with fixed energies, we employ a brehmsstrahlung x-ray source and an energy discriminating, solid-state detector (see Figure 2). An advantage of having a brehmsstrahlung source is that we can enhance detectability by optimizing the choice of energies based on the accuracies of measured attenuation coefficients. Work by Ting, et al., (1991 and 1993) demonstrated this optimized energy dispersive technique (hereby referred to as the explicit solution technique) on carbon-prepreg composites to measure variations in the concentrations of the fiber and resin. Ting et al. (1991) also used this method to measure the thickness of alumina corrosion films on aluminum.

We introduce here a new technique for using the transmitted x-ray spectrum to obtain phase distribution information. Rather than solving the Beer-Lambert relationship explicitly at i different energy ranges for an i constituent composite, we make use of the entire experimentally captured transmitted spectrum, \( I_{\text{exp}} \). For example, for a two material composite, an initial estimate of the values of the material path lengths, \( x_1 \) and \( x_2 \), is made. These estimates are then used to generate an estimate transmitted spectrum, \( I_{\text{est}} \). The two spectra, \( I_{\text{est}} \) and \( I_{\text{exp}} \), are then compared using a chi squared function:
where $R_i$ and $S_i$ are two binned data sets, such as $I_{exp}$ and $I_{ext}$.

Next, by setting $x_1$ and $x_2$ as independent variables in the chi squared function, the path lengths are iterated using Powell's multi-dimensional minimization until the chi squared difference between the spectra is minimized. An example of this minimization is shown in Figure 3. The values of the material path lengths, $x_1$ and $x_2$, which yield this minimum are the closest approximation to the real values. We will hereafter refer to this technique as the spectrum fitting technique.

**Measurement Sensitivity**

Many different factors control the overall accuracy and speed of both techniques. The most important are Poisson counting statistics, attenuation coefficient accuracy, and attenuation coefficient contrast. All three of these factors are related, and the impact of each can vary greatly depending on the specific composite system under investigation.

**Poisson Statistics**

Poisson counting statistics result from the nature of x-ray photon production which follows a Poisson distribution. Since the first standard deviation of the Poisson distribution is equal to the square root of the mean, the accuracy of the transmitted photon counts increases as the square root of the number of counts, or the time elapsed. For our system (see
Experimental Procedure,) the ultimate limit on the counting rate is not the x-ray source, but rather the saturation limit of the solid state detector. A concern with earlier work using the explicit solution technique is that it required long acquisition times (up to 24 hours per point) to achieve sufficient counting statistics needed for good measurement sensitivity. This extended acquisition time requirement is related to the two other major factors controlling technique accuracy: attenuation coefficient accuracy and attenuation coefficient contrast.

**Attenuation Coefficient Accuracy**

Ting et al. established through extensive error propagation analysis that the accuracy of the constituent attenuation coefficients would have a dominant effect on the overall measurement accuracy provided sufficient counting statistics were achieved. For this reason, relatively narrow energy ranges were used in the explicit solution analysis, so that the particular attenuation coefficient value for a given energy range could be chosen with a high degree of confidence.

There are several ways to arrive at an effective attenuation coefficient, $\mu_{\text{eff}}$, for the energy band chosen. One method is to simply use the attenuation coefficient at the mid-point of the energy range. However, this average energy value may lead to a grossly inaccurate value for attenuation coefficient depending upon the slopes of both the attenuation coefficient vs. energy curve and the transmitted spectrum vs. energy curve. One way to account for any rapid changes in the transmitted spectrum would be to weight the attenuation coefficient according to the transmitted intensity in each energy bin:
where \( \mu_i(E) \) is the linear attenuation coefficient for energy bin \( i \) and \( I_i(E) \) is the transmitted intensity for energy bin \( i \). Such a weighting technique would require capturing the binned energy spectrum for the energy ranges being used and weighting the attenuation coefficient for each measurement.

The effects of widening the energy ranges on the accuracy of the explicit solution technique have not yet been quantitatively explored. The assumption has been that as the range was widened, the accuracy of the chosen attenuation coefficient would diminish proportionally.

**Compositional Contrast**

The necessary accuracy and precision of the attenuation coefficients is also heavily dependent upon the contrast in x-ray attenuation between the constituent materials. For example, in a Cu- Al composite system, the difference in attenuation coefficient over the entire energy spectrum is sufficiently large as to make the composition measurement relatively insensitive to small systematic errors in linear attenuation coefficients. However, as shown in Figure 4 for the alumina- SiC system, many composite constituents posses attenuation coefficients much nearer to one another. In these systems, small systematic errors may have significant effects on the overall accuracy of the final measurement.
Often, a sensitivity to attenuation coefficient accuracy may necessitate an empirical measurement of the attenuation coefficients before performing energy dispersive analysis. There are several reasons for this. First, if the attenuation coefficients are close together as in the example in Figure 4, the level of precision needed might not be attainable by making use of standard tables for attenuation coefficient calculation. As an example, compare the resulting attenuation coefficient curves for a typical SiC fiber obtained through i) calculation from standard tables and ii) empirical measurement both shown in Figure 5. The mean variation between the two curves is 11 percent over the displayed energy range. A second reason for empirical measurement arises when exact composition of a given constituent may not be well known, and can only be measured.

**Empirical Measurement of Attenuation Coefficients**

In many cases, an empirical measurement of the linear attenuation coefficient of a given constituent is straightforward. All that is required is a known, easily measured thickness of the constituent material. The incident and transmitted x-ray spectra are collected as with the energy dispersive technique, and equation (1) is solved explicitly for the attenuation coefficient as a function of energy, \( \mu(E) \).

However, in the case of fiber reinforced composite materials, the fiber phase is not generally available in a bulk, solid form. This is also true of green ceramic composites made from crystalline powder precursors. In these cases, the thickness of the constituent material is not readily attained. Two techniques to overcome these difficulties, a powder packing technique and a slurry technique, are discussed in detail elsewhere. Depending upon the
technique used, different aspects of the empirical measurement may control the overall precision of the measured attenuation coefficients.

Simulation of Energy Dispersive Techniques

As is evident from the previous discussion, many different variables can impact the accuracy of both the explicit solution and spectrum fitting techniques. Each of these variables depends heavily upon the specific material system being examined and the experimental system being used to perform the measurement. In order to better understand the significance of each of these variables and to optimize a given set of scanning conditions, a simulation program of the energy dispersive technique was conceived.

Experimental Procedure

A computer program which simulates both the explicit solution technique and the spectrum fitting technique was written. This code facilitates the optimization of scanning variables by allowing the user to alter the composition and thickness of constituent materials, the accuracy and precision of the constituents' attenuation coefficients, and the incident x-ray spectra. Additionally, the code allows the user to control which portions of the incident spectra are used for each of the two analysis techniques.

A material system upon which both the simulation and actual experiments could be performed was devised. A small step-wedge of aluminum was joined to a thin sheet of copper for this purpose. Each run of the simulation code simulated a line scan across the step-wedge yielding five separate percentages of Cu (see Figure 6). In the simulations, six step-wedge line scans, corresponding to a total of thirty path length calculations, were
performed. Results from the simulation code were directly compared to the known percent Cu values to predict the accuracy of both techniques under various scanning conditions. For each scanning condition, the average deviation from the actual percent Cu was tabulated.

Many of the simulated runs on the Al-Cu step-wedge were then experimentally verified using an X-ray line scanning system. This system has been described in detail elsewhere and consists of a brehmsstrahlung x-ray source (HOMX 161), several high precision sample positioning motors (Daedal, Harrison City, PA), and a high purity Ge detector (GL0510R, Canberra Industries Inc., Meriden, CN) all linked to a personal computer (see Figure 2).

First, the effects of Poisson counting statistics on the average deviation were studied. Transmitted spectra ranging from 100 thousand to 7 million counts were simulated with both calculation techniques. In these simulations, the energy range of the spectrum fitting technique was 30 KeV to 60 KeV. The energy ranges of the explicit solution technique were 30 to 37 KeV for the low range and 53 to 60 KeV for the high range. A 2 percent systematic error in both attenuation coefficients was introduced in addition to a 1 percent random fluctuation in the attenuation coefficient values. The effects of both averaging and weighting the attenuation coefficients over the energy range were simulated. These simulations were then experimentally verified using a real x-ray line scanning system.

The effects of broadening the energy ranges in the explicit solution technique were examined with both the simulator and actual experiment. In the simulator, the energy range was broadened from a single bin (approximately 0.073 KeV) to 200 bins (approximately 14.6 KeV) using the explicit solution technique. This was done both without the effects of
Poisson statistics (or virtually infinite acquisition time) and using a typical scanning time corresponding to approximately 50,000 overall transmitted photon counts at a bin width of 0.737 KeV and 1,000,000 overall transmitted photon counts at a bin width of 14.6 KeV. During these simulations, the systematic error of both attenuation coefficients was kept at 2 percent and the random attenuation coefficient error at 1 percent. These experiments were also duplicated on the real system.

Next, the effects of systematic imprecision in the attenuation coefficients of each constituent were examined with the simulation code. Simulated experiments of 0, 2, 4, 8, and 16 percent positive adjustment in the attenuation coefficient of Cu in the Al-Cu system and of SiC fiber in the alumina-SiC fiber system. These two systems were chosen to test the influence of compositional contrast on the sensitivity of the techniques to attenuation coefficient inaccuracy.

Finally, given the results of the compositional contrast simulations, the spectrum fitting technique was chosen to examine a small region of a dense alumina-SiC fiber composite. A 2 dimensional 25 point by 20 point scan of this composite was performed at a step increment of 0.02 inches (508 microns.) Since the composite possessed a rectangular solid geometry with well-characterized, machined surfaces, caliper measurements of the overall composite thickness were made. By subtracting the total material thickness derived from the line scan from this caliper measurement, a value of the local porosity could be obtained. In this way, maps of spatial variations of porosity and compositional were obtained and compared.
Results and Discussion

Figure 7 illustrates the effects of Poisson counting statistics on the accuracy of both the explicit solution and spectrum fitting technique using the simulator. In these simulations, weighted attenuation coefficients were used for the explicit solution technique (see equation 4.) The ordinate represents the mean deviation from the actual percent copper values. Both techniques show an increasing level of accuracy with increasing counts. Simulations of the results at infinite counts (no Poisson errors) show the ultimate limit of accuracy for both techniques on this material system given the initial 2 percent systematic error and 1 percent random error in the attenuation coefficients. These limits are 0.85 percent and 0.36 percent for the explicit solution and spectrum fitting techniques, respectively.

When the attenuation coefficients are averaged over the separate energy ranges, the results are slightly different for the explicit solution technique. Figure 8 reveals roughly the same ultimate limit on accuracy for the explicit solution technique. However, the explicit solution technique results seem much less dependent on transmitted counts than with the weighted coefficients. In both situations, the spectrum fitting technique appears to be more accurate than the explicit solution method above 500 thousand counts. Below this value, the spectrum fitting technique appears very inaccurate.

Results of the experimental tests of the previous simulations are shown in figures 9 and 10. In both figures, there is some discrepancy in the absolute values of deviation from the ideal percentage of copper between the simulations and experiments. However, this discrepancy is never more than a few percent, and may be explained by an inaccurate estimate of the precision of material attenuation coefficients in the simulator.
Widening the energy range width is shown to have a significant, negative effect on the accuracy of the explicit solution technique. Figure 11 below shows the marked change in accuracy as a function of energy range width in scans with averaged attenuation coefficients and scans with weighted attenuation coefficients. These simulated effects are confirmed by experiments in Figure 12.

The effect of systematic errors in attenuation coefficients on the accuracy of the composition measurement appears to be heavily dependent upon the attenuation coefficient contrast as described in the background section. Figure 13 shows a gradual decrease in accuracy as a function of attenuation coefficient error in the Al-Cu system. However, the mean deviation is low or both techniques, topping out at 2% for the explicit solution technique and 1% for the spectrum fitting technique, respectfully. In contrast, the deviation from the ideal composition line is much larger in the alumina-SiC fiber system. Figure 14 reveals no noticeable decrease in accuracy with increased systematic attenuation coefficient error. However, even with no systematic error, the 1 percent random error introduced in the simulation resulted in a 9-10% deviation for the explicit solution technique and a 2-3% deviation for the spectrum fitting technique.

Contrasting Techniques

From all of these simulations and confirming experiments, we find that the spectrum fitting technique is generally faster than the explicit solution since it allows more of the incident and transmitted spectra to be used, reducing the time required to achieve adequate counting statistics. In this step-wedge example, the data from the spectrum fitting technique shown in figures 7-10 above were taken in half the time of equivalent data from the explicit
solution technique. Widening the energy ranges to obtain better counting statistics and reduce scanning is not accomplished with the explicit solution technique without sacrificing technique accuracy. As illustrated in figure 11 and 12, when a broader portion of the energy spectrum is used for each energy range in the explicit solution technique (above approximately 7 KeV.) the accuracy of the technique is greatly reduced.

While overall the spectrum fitting technique appears more accurate than the explicit solution technique, this is not the case at low counting regimes as evidenced in figures 7-9. While the explicit solution to the Beer-Lambert relationship is simply shifted by Poisson statistical errors, the convergence of the minimization routine in the spectrum fitting routine is more drastically effected. The simulation code is certainly one means of determining how many counts a particular scan requires to reach a certain level of precision. However, for a given scanning result with the spectrum fitting technique, the chi-squared probability function provides a degree of confidence in the accuracy of the result. The chi-squared probability function, or p value, is defined as the probability that the observed chi-square for a correct model should be less than an observed value, chi-square. In our case, a low value often represents inaccurate convergence during minimization, and a low level of confidence in the result can be expected. For example, compare the chi squared functions obtained for a single point scan of the step-wedge. In the example given in Figure 3, 1 million counts were collected, a single peak in the function 1/(chi squared) is apparent, and the result yields a p value of 0.96. In the top of Figure 15, a total of 250,000 counts were collected, the resulting 1/(chi squared) function reveals many separate peaks rather than a single, obvious convergent point. In this example, the chi-squared probability function yields 0.70. Finally, in the
bottom of Figure 15, only 125,000 counts were collected, the $1/(\text{chi squared})$ function shows no legitimate convergent peak, and the $p$ value is 0.00.

**Application to a Composite Specimen**

The maps of porosity and composition as a function of position for the dense, alumina-SiC fiber composite are shown in Figure 16. Given the results of the simulation data in Figure 14, we can trust the relative compositional percentage to about 3 percent. The mean value of sample porosity from the scan of 10.2% is in excellent agreement with the value of 10% provided by the manufacturer. The mean composition of 44.8% alumina is about 10% lower than the range 55 to 75% given by the manufacturer. This discrepancy may be due to a number of factors. The composite actually contains a residual percentage of pure Al metal which may distort the transmitted spectra. In addition, the local composition in this specimen may vary substantially from the mean of the entire sample. Only destructive analysis of the exact region can confirm or refute these possibilities.

In both images of Figure 16, several similar spatial patterns are clearly evident. These suggest a strong correlation between regions of high porosity and high alumina content for this region of the specimen. Figure 17 confirms this correlation by plotting the porosity data against the compositional data at the same sample positions.

**Conclusions**

In summary, we have demonstrated two energy dispersive techniques to probe the internal distribution of phases in composite materials. Several parameters which were thought to directly control the accuracy of each technique were explored in detail using
simulations and experiments for an ideal composite system. The effects of these parameters depended heavily on the particular material system being examined. This dependence motivates the continued use of the simulator to optimize scans of other compositions. Overall, the spectrum fitting technique appears to be more accurate and less time consuming than the explicit solution technique. The reverse is true only at very low counting statistics.

The use of this technique on an actual alumina-SiC composite system has also been demonstrated. Two dimensional maps of the composite's porosity and composition were obtained with the spectrum fitting technique. The mean of these scans compared reasonably well with bulk sample data.

Being able to simultaneously probe spatial variations of porosity and composition in composite materials allowed us to elucidate a positive correlation between regions of high porosity and high alumina content. This capability makes the technique ideally suited as a process development tool.

In order to more accurately examine composites with more two constituents, the spectrum fitting technique needs to be modified to accommodate a three variable minimization. Simulations of a three material composite are currently being performed.

References


Figure 1 - The incident, $I_0$, and transmitted, $I$, intensities are collected at two energy ranges, $E_1$ and $E_2$, and used in conjunction with the attenuation coefficients of each constituent to solve equation (1) explicitly for $x_1$ and $x_2$. 

$$\ln\left(\frac{I_0(E)}{I(E)}\right) = \sum_i \mu_i(E) \cdot x_i$$

- $E$ - energy
- $I_0$ - incident intensity
- $I$ - transmitted intensity
- $\mu_i$ - linear attenuation coefficient of material $i$
- $x_i$ - path length of material $i$
Figure 2 - Schematic illustration of the real x-ray line scanning system used in real experiments.
Figure 3 - The point at which the $1/(X^2)$ function is maximized represents the closest approximation to the obtainable values $x_i$ and $x_2$. In this example, the transmitted counts were 500,000 and the $p$ value was 0.96.
Figure 4 - Linear x-ray attenuation curves for the Al-Cu system (top) and the alumina-SiC fiber system (bottom.)
Figure 5 - Linear attenuation coefficients of SiC fiber obtained through calculation from standard tables and through direct experiment.
Figure 6 - The Al-Cu stepwedge was used to verify simulated energy dispersive experiments. Five levels of the Al stepwedge allowed five separate percentages of Cu to be simulated and tested.
Figure 7 - The simulated effects of Poisson counting statistics on compositional accuracy for both techniques. In these data, weighted values of the attenuation coefficients were used in the explicit solution technique (see equation 4.)
Figure 8 - The simulated effects of Poisson counting statistics on compositional accuracy for both techniques. In these data, attenuation coefficients taken at the energy midpoint in each energy range were used in the explicit solution technique.
Figure 9 - The simulated effects of Poisson counting statistics on compositional accuracy for the spectrum fitting technique are compared against experimental data.
Figure 10 - The simulated effects of Poisson counting statistics on compositional accuracy for the explicit solution technique are compared against experimental data. Here, average values of the attenuation coefficients over the energy ranges were used.
Figure 11 - The effects of widening energy ranges on the compositional accuracy of the explicit solution technique are simulated. Both methods for obtaining attenuation coefficients are compared.
Figure 12 - The simulated effects of widening energy ranges on the compositional accuracy of the explicit solution technique are compared to experimental data. Here, average values of the attenuation coefficients over the energy ranges were used.
Effect of Attenuation Coefficient Error
Al-Cu System

Figure 13 - The simulated effects of gradually increasing the systematic error of the linear attenuation coefficient of Cu in the Al-Cu system on the accuracy of both the explicit solution and spectrum fitting technique are shown.
Figure 14 - The simulated effects of gradually increasing the systematic error of the linear attenuation coefficient of SiC fiber in the alumina-SiC fiber system on the accuracy of both the explicit solution and spectrum fitting technique are shown.
Figure 15 - Plots of the \(1/(X^2)\) function for a scan of the Al-Cu stepwedge at 250,000 transmitted counts (top) and 125,000 counts (bottom) are shown. The p values of the spectrum fitting minimizations are 0.70 and 0.00 respectively.
Figure 16 - Two dimensional scans of a small region of the dense, alumina-SiC fiber composite using the spectrum fitting technique are shown. A map of porosity (left) shows features which correlate to regions of high alumina content in the compositional map (right.)
Figure 17 - Porosity plotted against alumina fraction from Figure 16 illustrates a strong positive correlation between regions of high porosity and regions of high relative alumina content.
CONCLUSIONS

The inability of industry to produce reliable ceramic components for many structural applications stems from our lack of understanding of the underlying principles governing the evolving green microstructure. In order to better establish the link between processing variables and the resulting microstructure, we need to make use of improved nondestructive techniques to probe this microstructure. The development and application of two such techniques was given in this dissertation.

First, a technique for studying the 3 dimensional variations in packing density of a liquid saturated ceramic compact was developed from a low-cost x-ray computed tomography system. Improvements in the contrast sensitivity of this system combined with image artifact removal methods facilitated the ability to calculate quantitative variations in packing density. The technique is capable of providing 40 micron feature resolution at better than 2% sensitivity to changes in packing density in 1 cm diameter ceramic compacts. The technique was used to study the effects of suspension chemistry and compaction stress on the packing density uniformity of alumina centrifuged compacts.

The results of the CT examination of monolithic centrifuged suspensions pose more questions about microstructural uniformity: Why should a flocculated suspension yield larger regions of low and high density under higher stress? How does the weakly flocculated suspension posses a higher degree of spatial uniformity while simultaneously exhibiting a broader density distribution? To answer these questions, and to better understand these findings, more study needs to be done. In this case, only two regions of effective stress in two specimens were examined. To be more confident about overall trends with regards to
either processing variable (effective stress or interparticle potential) we need to look at a
wider range of suspension chemistries at many different stress regimes. In addition, a higher
resolution CT system with fewer systematic image artifacts could provide more insight into
the nature of the smaller density variations of smaller spatial extent. The advent of more
efficient 2 dimensional x-ray detectors promises to push the limits of feature resolution to
that of the current spatial resolution limit. Features on the order of 5 to 10 microns in
diameter should be resolvable in ceramic suspensions in the next few years.

The current CT study could be extended into later aspects of ceramic processing. By
allowing the suspension processed samples to dry, we could explore the effects of
interparticle potential, particle size, drying rate, and a host of other variables on the dried
microstructure. By pushing the microstructure investigation along, one processing step at a
time, we could begin to establish which variables at which stages of processing are critical to
obtaining the desired final microstructure and properties.

A new technique for using transmitted x-ray spectra to obtain quantitative phase
distribution information in composite materials was also introduced. Key parameters
affecting the accuracy of this method were explored in detail using a simulation of the
technique in addition to real experiments. The technique’s ability to distinguish variations in
composition and porosity as small as 2% was demonstrated on a dense, ceramic fiber
reinforced ceramic matrix composite.

The energy dispersive line scanning technique has an abundant, untapped potential for
investigating 2 dimensional compositional variations in green ceramic composites. Now that
scans can be optimized prior to experiment the user can obtain an apriori knowledge of the
expected precision of the results. One application of the technique would be to determine the effects of interparticle potential on phase distribution in discrete fiber reinforced ceramic composites in the green state. Such a study could be taken further by following the fiber-matrix distribution through the final densification process. In this way, not only could the effects of suspension chemistry on the green phase distribution be understood, but also its impact on the final, dense distribution of phases.

Both of the x-ray techniques discussed in this dissertation have demonstrated an ability to reveal aspects of the green microstructure which have not been previously examined. What these studies have shown is that there are definite, repeatable variations in the microstructure which occur at the 100 micron to 1 mm spatial scale as a result of changing interparticle potential. The value of these techniques lies in their potential to provide a necessary link of understanding in the processing variable-microstructure-properties relationship. By exploring the effects of processing variables such as interparticle potential on microstructural non-uniformity, we can begin to develop more sophisticated models to explain how these variables control the evolving microstructure.

Still, even without further study, this work has shown that interparticle potential has a definite effect on microstructural uniformity in both monolithic and composite specimens. Furthermore, the concept of microstructural uniformity itself has been shown to necessitate a three dimensional description. Models which describe the one dimensional compaction behavior of ceramic suspensions do not adequately account for the types of microstructural features observed during shape forming.
APPENDIX 1 - PROCEEDINGS PAPER 1

RECENT ADVANCES IN X-RAY CHARACTERIZATION OF COMPOSITES
AND TAPE CAST CERAMICS

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ABSTRACT

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* Ames Laboratory is operated by Iowa State University under the contract number W-7405-eng-82 with the U.S. Department of Energy.
We have recently developed two prototype x-ray techniques for the nondestructive evaluation of ceramic tapes and composites: (i) x-ray radiography of tape casting defects, including tape thickness variations, surface pits, cracks, pores, bubbles, and density gradients, and (ii) energy-dispersive absorption spectroscopy for simultaneous mapping of composition and porosity in ceramic composites. These methods can both function as two-dimensional area detectors (rather than conventional point- or line-detectors), providing rapid, statistical information on microstructure heterogeneities in flat sheets of ceramic material. Both techniques demonstrate the potential to serve as process development tools capable of inspecting both green and sintered materials.

I. BACKGROUND

Cracks and warpage that arise during drying, debinding, and sintering of ceramics are exacerbated by green-microstructure heterogeneities, e.g., agglomerates, packing-density gradients, composition gradients, isolated pores and bubbles, and so on. Earlier in this proceedings, we reviewed major problems associated with traditional methods of controlling these heterogeneities in ceramic production: (i) they provide insufficient information on the spatial- and temporal-evolution of green-microstructure defects from one unit operation to the next, (ii) they usually involve slow and costly trial-and-error procedures that are off-line and destructive in nature, and (iii) they also have limited value when attempting to sort through and optimize so many different processing variables that typically affect microstructure-defect evolution in a given production operation. To overcome these barriers, advances in
nondestructive (NDE) instrumentation are needed, advances not only for on-line inspection purposes but also for off-line process development.

The goals of this paper are to briefly summarize two prototype techniques that we have recently developed for characterizing green and sintered ceramics. These techniques include: (i) x-ray radiography of tape casting defects, including tape thickness variations, surface pits, cracks, pores, bubbles, and density gradients, and (ii) energy-dispersive absorption spectroscopy for simultaneous mapping of composition and porosity in ceramic composites. In the following sections we discuss design details, performance characteristics, and relevant background information for each technique.

II. AREA DETECTION OF TAPE-CASTING DEFECTS

Tape casting of microelectronic substrates and capacitors is a prime example of a high-value-added, ceramic-manufacturing process where new, on-line methods of defect sensing and process control are needed. Ceramic tapes are typically characterized by off-line techniques, such as visual inspections, transmission optical microscopy, reflection optical microscopy, and single-point thickness measurements. There are a few examples of nondestructive, on-line inspection of ceramic tapes, including surface analysis by the use of optical microscopy, and thickness gauging using measurements of x-ray transmission with a solid-state point detector.

We took advantage of recent improvements in image processing and x-ray microfocus radiography to develop a prototype apparatus that would allow area detection of thickness
variations, surface pits, pores, bubbles, and density gradients in tape cast ceramics\textsuperscript{3,4}. The apparatus was designed to incorporate several benefits over traditional characterization routes: (i) the system functions as a two-dimensional area detector (rather than a conventional point- or line-detector), providing rapid, statistical information on two-dimensional maps of microstructure heterogeneities in ceramic tapes; (ii) it is capable of detecting small bubbles, pores and surface pits on the order of 10 microns in size; (iii) it can also detect tape thickness variations on the order of 10 microns. Using standard equipment, it is also amenable to scale up for quantitative process monitoring in an industrial setting.

The operating principle entails irradiating a ceramic tape with a microfocus x-ray generator and digitizing the projected image, followed by image processing. The projected image can be obtained using x-ray film or an amorphous silicon array detector. We developed an off-line, prototype technique, i.e., it was applied to stationary pieces of ceramic tape that were removed from a tape casting apparatus. Figure 1 shows a schematic illustration of a scaled-up, on-line system that could be developed based on our prototype. We can envision use of a scaled-up, on-line system to monitor tape defects in a moving tape as a function of time and position immediately after casting and also during subsequent debinding and sintering.
We recently benchmarked the performance of a film-based, prototype system in a study of tape-cast alumina$^{3,4}$. In that study, our goal was to achieve maximum detectability of small pores, density gradients, and small tape-thickness variations through the proper selection of exposure parameters. Results of the radiography data were correlated with optical and scanning electron microscopy. First, we developed a protocol to quantitatively analyze image-blurring effects that are inherently produced by grains in the x-ray film. This protocol involved use of a charge-coupled-device (CCD) camera to digitize exposed pieces of x-ray film, followed by computerized image analysis. We also employed a bremsstrahlung x-
ray beam having a maximum voltage of 30 kV. This relatively low voltage increased the
detectability of small pores, density gradients, and small tape-thickness variations, as a result
of the higher degree of attenuation that naturally occurs with low-energy photons.

Figure 2 illustrates the application of this prototype to a 200 µm-thick piece of a green
tape that was cast using α-alumina powder (0.4 µm average particle size). The first thing to
notice is the original radiograph (a) in Figure 2, which appears brighter when passing from
the upper left to the lower right corner. This increase in brightness signals an increase in the
tape thickness. Thickness variations can easily be determined by digitizing the radiograph
and correlating the results with separate, digitized radiographs of controlled-thickness
specimens. Also shown in Figure 2, the digitized image of radiograph (a) was normalized in
order to mask the effects of tape-thickness variations and in turn improve the resolution of
discreet, isolated features, including bubbles, pores, and surface pits. The first part of this
normalization process involved calculating an average, background grayscale level in
radiograph (a), which was then subtracted from all pixels in this image to produce the
normalized image in radiograph (b). As shown in Figure 2, one-dimensional, grayscale
profiles (line scans) are easily generated from the digitized images, profiles that can be useful
in an industrial setting to analyze isolated defects. Grayscale levels in all pixels of this
resulting image were then thresholded to allow viewing of pixel clusters that represented
isolated regions where there was a loss of alumina (Figure 3). We then calculated a pixel
cluster size distribution in Figure 3, which collectively represents thresholded data from
radiographs of several different regions of the same alumina tape (not shown). This type of
analysis illustrates the technique's potential for statistical process control.
Figure 4 illustrates another example of this technique which was used to study the effects of the average particle size of alumina on tape microstructures before and after sintering. As expected, the larger-sized powder results in larger-sized defects. Figure 4 illustrates how bubbles that are introduced in the green tape (0.4 micron particle size) are also visible in the radiograph after sintering.

Figure 2. Radiographs (a) and (b) respectively show the same region of an alumina tape before and after background normalization. Line-scans along the same path in both radiographs (right) show how this normalization can enhance the detection of isolated spots where there is loss of alumina (pores, bubbles, or surface pits).
Figure 3. Radiograph (b) of Figure 2 is thresholded on the left. Black pixels indicate regions where there is a loss of alumina. A distribution of pixel-cluster sizes (right) was obtained by analyzing thresholded images from several radiographs of different regions of the same alumina tape.

Of course, one of the drawbacks of this method is that it does not reveal information on the location of a given defect in a direction normal to the surface of the tape. In other words, it is uncertain whether a given pixel cluster signals the occurrence of a surface pit or a sub-surface pore. We are currently exploring the use of stereography to overcome this problem.
Figure 4. Radiographs of tape-cast alumina showing effects of the average powder size. Images corresponding to each powder size were obtained at approximately the same region of each tape before and after sintering to 1550 °C.
III. COMPOSITION & POROSITY MAPPING WITH X-RAY ABSORPTION SPECTROSCOPY

The Center for Nondestructive Evaluation (CNDE) at Iowa State University has developed an x-ray absorption spectroscopy technique allowing quantitative, simultaneous mapping of both the composition and porosity of a broad range of ceramic, metal, and polymer composite materials. Much like the radiographic technique described above for tape casting applications, this technique involves a two-dimensional projection of a flat test specimen. It uses a single, solid-state detector or an array of detectors to capture the transmitted intensity. Coupled with a multi-channel analyzer, this configuration measures the transmitted intensity as a function of the x-ray photon energy.

Our procedure takes advantage of the fact that each constituent phase of a composite material tends to exhibit a unique x-ray attenuation coefficient as a function of the photon energy. This can be understood by recognizing that the x-ray attenuation coefficient primarily describes the degree of photon scattering by electrons and by the photoelectric effect in an irradiated material. In turn, this coefficient strongly depends on the energy of the incident photons and the electron density (or mass number) of the irradiated material. In order to obtain reliable maps of composition and porosity, it is essential to make an accurate determination of the x-ray attenuation coefficient as a function of the photon energy for each constituent phase in the composite. Theoretical calculations are useful in this regard, however, they require detailed information regarding the composition and mass density of each constituent phase. Laboratory measurements of x-ray attenuation coefficients are easily
performed by exposing calibration specimens of each constituent phase with white radiation
and then measuring forward attenuation with an energy-discriminating detector. Calibration
specimens can be in monolithic, fibrous, or powder forms. Figure 5 illustrates a set of such
measurements for α-alumina powder and SiC-based fiber.

![Experimentally Measured Linear Attenuation Coefficients](image)

Figure 5. Experimentally-measured x-ray attenuation coefficients (\(\mu\)) of alumina
powder and SiC-based fiber.

Once the attenuation coefficient as a function of the photon energy is known for each
constituent phase, the composite specimen is exposed to white radiation at various locations,
and the incident and transmission spectra are recorded. Maps of composition and porosity
are then calculated by substituting the incident and transmitted spectral intensities along with
measured attenuation coefficients into the Beer-Lambert law and mass conservation
equations:
In equation (1), $E$ is the photon energy. $I(E)$ and $I_0(E)$ are the energy-dependent intensities of the transmitted and incident x-ray beams, respectively. $x_i$ is the thickness of constituent $i$ in the path of the x-ray beam, and $\mu_i$ is the linear x-ray attenuation coefficient of constituent $i$. For a two-constituent composite (e.g., alumina + SiC fiber), Equation (1) can be solved knowing x-ray attenuation coefficients and x-ray intensity data at two photon energies. The thickness of each constituent, $x_1$ and $x_2$, can then be used together with an independent measure of total sample thickness, $x_m$, to calculate the fraction of porosity, $f_p$, the fraction of component 1, $f_1$, and the fraction of component 2, $f_2$, as shown in equation (2).

$$f_p = 1 - \frac{x_1 + x_2}{x_m}, \quad f_1 = \frac{x_1}{x_1 + x_2}, \quad f_2 = \frac{x_2}{x_1 + x_2}$$

Researchers in soil chemistry initially reported a so-called dual-energy technique, where they simultaneously irradiated soil mixtures with two mono-energetic radioisotopes to measure the bulk density and water content of soils. Instead of using radioactive isotopes with fixed energies, we employ a brehmsstrahlung x-ray source and an energy discriminating,
solid-state detector, which allows us to choose a wide range of photon energies. An advantage of having a brehmstrahlung source is that we can enhance detectability by optimizing the choice of energies based on the accuracies of measured attenuation coefficients. Early work by Ting, et al. demonstrated this optimized energy dispersive technique on carbon-prepreg composites to measure variations in the concentrations of the fiber and resin. Ting, et al. also used this method to measure the thickness of alumina corrosion films on aluminum. However, a concern with this early work is that it required long acquisition times (up to 24 hours per point) to achieve sufficient counting statistics needed for good measurement sensitivity. We have since improved the technique by analyzing a larger portion of the energy spectrum, which in turn increases the counting statistics and significantly reduces the measurement time (2.5 minutes per point).

In Figure 6, the technique is used to map spatial variations of porosity in a SiC-fiber-reinforced mullite-matrix composite that was prepared from different shape-forming techniques in our laboratory: uniaxial pressing of a dry powder and pressure filtration of a strongly flocculated suspension. The Figure illustrates a 0.4 inch by 0.75 inch area that was sampled at an increment of 0.02 inches (508 microns). Both the scans and their respective histograms (Figure 7) reveal that while the overall porosity ranges are similar in both samples (a mean porosity value, $\rho$, of 0.41), more severe spatial variations of porosity are present in the dry pressed sample. These differences highlight the potential of this technique to be used as a process development tool by analyzing the effects of different processing variables (in this case, the shape forming technique) on the porosity distribution in the green state.
Figure 6. 2D porosity distributions of green ceramic samples obtained through energy dispersive x-ray measurements.
Figure 7. Histograms of the above porosity distributions show the same mean porosity value, $\rho$, for both samples. A larger standard deviation, $\sigma$, indicating a wider porosity range is observed in the dry pressed sample.

Figure 8 shows maps of composition and porosity of an alumina-matrix composite containing woven fibers of SiC. In this specimen, a 0.4 inch by 0.5 inch area was sampled at an increment of 0.025 inch (635 microns). The porosity and compositional data are plotted against one another in Figure 9 illustrating a strong positive correlation between regions of high porosity and regions of high alumina concentration in this sample. This type of analysis illustrates the technique's potential for statistical process control.

In the above examples, fairly coarse sample-positioning intervals were used (508 and 635 microns) in the interest of reducing the overall scan time. Much finer spatial resolution is possible by reducing the width of the detector collimator. We frequently demonstrate 30 micron spatial resolution with our system. With a single point detector, mapping out a reasonably sized area of $1 \text{ cm}^2$ at 30 micron intervals is overly time-consuming. However, for on-line applications, this trade-off between acquisition time and spatial resolution can be overcome by implementing 1D and 2D detector arrays.

The accuracy of the technique depends strongly upon the acquisition time and the accuracy of the attenuation coefficients of the constituent materials. While a full analysis is beyond the scope of this paper, we believe the overall accuracy of the data in the above
examples is acceptable (2% for porosity and 5% for composition) based on a comparison of mean values of porosity and composition that we obtained by independent measurements.

IV. SUMMARY

Two prototype x-ray techniques have been developed for the nondestructive evaluation of ceramic tapes and composites: (i) x-ray film radiography of tape casting defects allowing detection of tape thickness variations, surface pits, cracks, pores, bubbles, and density gradients and (ii) energy-dispersive x-ray spectroscopy which provides quantitative maps of both porosity and composition in green and sintered composites. We have used both techniques to relate processing variables such as starting powder size and shaping method to the green and sintered microstructures in ceramic tapes and composites. In addition, we are currently exploring the potential of examining multi-constituent (3 and up) ceramic composites using the energy dispersive technique.
Figure 8. 2D porosity and alumina distributions in a dense alumina-SiC fiber composite obtained through energy dispersive measurements.
Figure 9. Porosity plotted against alumina fraction from Figure 8 illustrates a strong positive correlation between regions of high porosity and regions of high relative alumina content.

ACKNOWLEDGEMENTS

This research is supported by the Office of Basic Energy Sciences at the U.S. Department of Energy and by the NSF Industry/University Cooperative research program.

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APPENDIX 2 - PROCEEDINGS PAPER 2

FINE SCALE RESOLUTION OF CERAMIC MICROSTRUCTURES BY X-RAY COMPUTED TOMOGRAPHY: AN ECONOMICAL APPROACH

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ABSTRACT

* Ames Laboratory is operated by Iowa State University under the contract number W-7405-eng-82 with the U.S. Department of Energy.
High-magnification, 3-dimensional imaging of ceramics by x-ray computed tomography (CT) typically requires use of a synchrotron and/or a massive array of solid-state detectors. The high cost of this research equipment generally limits its use as a process-development tool by ceramic manufacturers. In this paper, we demonstrate a more economical approach which produces image quality comparable to that of standard, high performance equipment. In this method we utilized an inexpensive image intensifier and applied techniques of frame averaging, gray-scale sub-ranging and other noise reduction and artifact removal methods in order to improve contrast sensitivity while maintaining low cost. After discussing critical factors affecting image quality, we discuss cost/performance tradeoffs associated with different CT equipment options.

I. BACKGROUND

In an earlier paper in this proceedings, we described two x-ray techniques capable of two dimensional imaging of green-body defects in ceramics. We also discussed the importance of gaining knowledge of the specific location and shape of these defects in order to improve our understanding of relationships between manufacturing variables and defect evolution. Microstructural features ranging from micron-sized pores to millimeter-scale density gradients are all critical to this understanding. While no technique yet exists to nondestructively image individual, submicron ceramic particles in a green body, current, state-of-the-art x-ray CT approaches this goal with an imaging capability of 10 to 100 micron sized features.
High Resolution CT of Advanced Ceramics: Previous Research

In the past decade, several researchers have used high performance x-ray computed tomography to study microstructure evolution during ceramic processing. For example, Sawicka et al. combined a high energy, mono-energetic x-ray source with a single, solid-state detector and observed density variations as small as 1 volume % in sintered alumina specimens having an overall size of 10 cm. The spatial resolution of this system was limited by the collimation of the incident beam, reported at approximately 0.7 mm. Since then, significant increases in spatial resolution and significant reductions in acquisition time have been made possible by the introduction of two-dimensional, solid-state diode detector arrays in conjunction with either a microfocus x-ray generator or a synchrotron photon source. For example, Phillips et al. used a commercially available CT system consisting of a high energy x-ray source and a solid state detector array to observe density gradient evolution during dry powder compaction. Features as small as 200 microns were observed in compacts of ZnO, measuring 0.5 inches in diameter. Higher resolutions were reported by Kinney et al. using a synchrotron based x-ray CT microscope. In that study, the microstructure evolution of chemical vapor infiltrated composite samples was analyzed at different stages of the fabrication process at a voxel resolution of 15.8 microns. We should also mention the work of Shen et. al who used a microfocus x-ray source and an array of solid-state detectors to observe time-dependent microstructure evolution in consolidating silica gels. Of his more
notable findings is the evidence for macroscopic fracturing during the consolidation of stiff
gels.

It is important to note that the above work entails use of either a synchrotron or an
array of solid-state detectors. The high cost of this research equipment generally limits its
use as a process-development tool by ceramic manufacturers. In this paper we wish to
discuss a more economical approach where the costs can be reduced by an order of
magnitude while still maintaining acceptable levels of image quality.

**Critical Factors Affecting Image Resolution**

It is necessary to appreciate that CT image resolution can be separated into two major
components: spatial resolution and contrast sensitivity. Spatial resolution represents the
smallest detectable length-increment of an object perpendicular to the x-ray beam, and is
determined by the spatial sampling frequency of the field of view. For example, if a 1 cm
specimen is magnified and imaged across a detector array with 500 elements, the spatial
resolution is nominally equal to 1 cm divided by 500, or 20 microns. There are several ways
this limit can be improved by moving the specimen or detector array to increase sampling
frequency, however, this is at the expense of acquisition time. Contrast sensitivity represents
the smallest detectable length-increment of an object parallel to the x-ray beam and is
governed by the x-ray counting statistics and the noise characteristics and dynamic range of
the detector. For example, if a one-cm-thick ceramic specimen is examined by an image
intensifier system having a typical contrast sensitivity of 5%, the smallest detectable change in the thickness of the specimen would be 5% of one cm or 500 microns.

**Current Equipment Choices**

Let us consider the current limits and equipment choices regarding spatial resolution. Prior to the availability of microfocus x-ray generators in the 1980's, high spatial resolution CT (i.e., capable of resolving features finer than 100 microns) was only possible at synchrotron ports where a stream of parallel x-rays could be used to image an object. In this parallel-beam configuration, the spatial resolution is limited by the pixel width of the detector surface. In the early 1980's, standard industrial x-ray generators possessed large spot sizes (>1 mm) prohibiting object magnification without severe image blurring. Since then, minifocus and microfocus x-ray tubes with respective spot sizes of less than 500 and 10 microns have enabled object magnification in the fan beam or cone beam configuration, thereby allowing previously untenable spatial resolution (down to a few microns).

One approach to reduce the cost of an x-ray CT system while retaining the ability to resolve fine-scale features is to implement a minifocus source rather than a microfocus source (or a synchrotron). Minifocus sources are available with a wide range of x-ray spot sizes and cost approximately half that of high-performance microfocus sources. We can demonstrate the magnification capability of a minifocus source by imaging a standard resolution gauge, which consists of a thin sheet of plastic coated with a thin, metal pattern (e.g., Au or W) of converging lines. Figure 1 illustrates digitized images of projection radiographs of such a
resolution gauge at 3x magnification using both a microfocus (5 micron spot size) and minifocus (200 micron spot size) source. The images reveal that the lines of the gauge are clearly resolvable up to at least 10 line pairs per millimeter, or 50 micron increments. As a result, one could expect to resolve 50 micron features in computed tomography using such a minifocus source.

Figure 1 - digitized radiographic images of a standard resolution gauge for both the minifocus (~200 micron spot size) and microfocus (~5 micron spot size) x-ray source.

Let us now consider the current limits and equipment choices regarding contrast sensitivity. While image intensifiers and linear arrays of charge-coupled device (CCD) detectors are fast and relatively inexpensive, the contrast sensitivity is low, typically between

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line pairs/mm
1 and 5%. Solid-state detectors provide much better contrast sensitivity (typically 0.1%), however, they are much more expensive, and they require prohibitively long acquisition times. Of course, the acquisition time can be reduced by implementing an array of solid-state detectors rather than a single detector, however, this significantly raises the equipment cost.

II. IMAGE-INTENSIFIER APPROACH

In order to overcome these problems our approach uses a microfocus generator and an inexpensive image intensifier with an 8-bit digital CCD camera. Using techniques of frame averaging, gray-scale sub-ranging and other noise reduction and artifact removal methods we significantly improved the contrast sensitivity to below 1%. For example, shown in Figure 2 are projection images of a single layer of 300 micron diameter soda-lime silicate spheres that were positioned on a quarter-inch-thick plate of the same material. The diameter of each sphere is approximately 3% of the thickness of the glass plate. Therefore, a contrast sensitivity of better than 3% is required to resolve this thickness change and image a single sphere. The left side of Figure 2 illustrates use of a standard acquisition scheme (i.e., no adjustment to the 8 bit signal) where the glass spheres are simply not visible. However, the spheres begin to take shape in the image on the right side of Figure 2, which was obtained by integrating multiple frames of an 11-bit subranged signal.

The effect of this frame accumulation and subranging is further demonstrated in Figure 3 by the CT images of 300 micron diameter soda-lime silicate spheres packed inside a 1.5 cm inside-diameter glass vial. The pixel size in this image is approximately 20 microns.
It is apparent that these signal processing techniques produce a major improvement in the quality of the image, allowing resolution of the individual 300 micron spheres.

Finally, we would like to mention that the current limits of spatial resolution depend not only on the x-ray equipment but also on the data handling capacity of the computers working with the images. It is important to consider that the storage capacity requirements for a given image are inversely proportional to the voxel volume. For example, an object measuring 1 cm$^3$ would require approximately 64 megabytes of memory if sampled at a voxel size of 25 microns and 64 gigabytes if sampled at a voxel size of 2.5 microns. It is only recently that advances in computer technology have made it possible to capture, display, and store these large images conveniently.
Figure 2 - Digital x-ray projection images of 300 micron diameter soda-lime silicate spheres. The image on the left obtained from an unprocessed 8-bit signal from the CCD camera. The image on the right was obtained by accumulating 60 frames of an 11-bit sub-ranged signal.

Figure 3 - X-ray CT images of 300 micron soda-lime silicate spheres in a 1.5 cm glass vial. The image on the left was obtained from an unprocessed 8-bit signal from the CCD camera. The image on the right was obtained by accumulating 60 frames of an 11-bit sub-ranged signal.
IV. SUMMARY

We augmented a relatively inexpensive image intensifier based CT system to reap the high spatial resolution inherent in a microfocus x-ray source. In turn, we have a practical system capable of achieving image quality comparable to that of the high performance CT systems (i.e., synchrotron or massive solid state detector array systems) without the high cost.

ACKNOWLEDGEMENTS

This research is supported by the Office of Basic Energy Sciences at the U.S. Department of Energy and by the NSF Industry/University Cooperative Research program.

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