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THREE-DIMENSIONAL NUCLEAR MAGNETIC RESONANCE AND X-RAY
MICROTOMOGRAPHIC IMAGING OF COMPOSITE MATERIALS

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ABSTRACT

This paper presents a new three-dimensional nuclear magnetic resonance (NMR) imaging technique for nondestructive evaluation of green-state ceramic composite materials. The technique is based on a 3-D backprojection protocol for data acquisition combined with a Radon reconstruction technique. Particularly for NMR of solid materials, this imaging protocol can provide higher three dimensional spatial resolution than is possible with commonly applied slice-selection protocols. The applicability of this 3-D NMR imaging technique was demonstrated using whisker-reinforced Si₃N₄/Si₃N₄ ceramic composites. While NMR is a sensitive and unique method for spatial discrimination of chemical properties (e.g., organic distributions), X-ray CT is a sensitive and proven technique for determining variations in density (i.e., voids and inclusions) within an object. The complementary nature of these two techniques was shown by imaging a piece of green ceramic

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composite material by both NMR and X-Ray microtomography techniques.

INTRODUCTION

Development of techniques for mass production of high performance structural ceramics and ceramic composites requires a detailed understanding of the component macro- and microstructural characteristics as effected by process conditions. The origin, nature and effect of flaws (such as voids, cracks, inclusions, density variations, etc.) on component reliability must be understood for the continuing technological development of advanced processing techniques. Nondestructive evaluation techniques (such as nuclear magnetic resonance (NMR) imaging and x-ray computed tomography (CT)) can play a key role in this development by providing detailed diagnostic measurements on selected specimens before, during and after various processing steps.

Application of x-ray CT techniques to study of advanced structural materials has been under development in recent years [1]. The utility of 3-D X-ray CT for interrogation of ceramic components has been demonstrated and has quickly become an accepted NDE method. Being sensitive to local density variation throughout the specimen, x-ray CT can provide information on internal voids, cracks, inclusions, and density gradients. However, for heterogeneous materials (of differing atomic number), conventional x-ray CT techniques may not be able to distinguish between local compositional differences and density variations.

NMR imaging, however, is sensitive to local chemical compositions and the NMR imaging techniques currently under

development can provide spatially dependent measurements of a sample's chemical or physical properties in three dimensions. Several applications of two-dimensional NMR imaging techniques to ceramics have been demonstrated including qualitative evaluation of open porosity in debinderized ceramics by using filler fluids [2,3], measurement and determination of binder distributions in green-state ceramics [2-5], and evaluation of mold-slip performance in slip-cast ceramics [6].

While two-dimensional NMR imaging has been demonstrated on a variety of materials including geological specimens [7], polymeric materials [8,9], and ceramics [2-6], difficulty persists in obtaining information in three (spatial) dimensions. A true 3-D method based on backprojection protocol has been previously demonstrated and applied to solutions [10,11]. In this work, a similar backprojection protocol was applied along with a 3-D Radon transform reconstruction technique, to obtain 3-D images of solids. Application of this method to solids has demonstrated by measurement of low concentration organic distributions in Si_3N_4 whisker reenforced Si_3N_4 composites with good sensitivity and high spatial resolution.

The NMR imaging system used in this work consisted of a Bruker CXP-100 solids NMR spectrometer fitted with a custom home-built (designed at Argonne National Laboratory (ANL)) imaging accessory (described in detail elsewhere [4]). The accessory, designed specifically for imaging solid materials, consists of a versatile home-built IBM/PC based pulse programmer, three (X,Y,Z) Techron audio range 1KW gradient amplifiers, a RF shaping unit, and a home-built singly tuned imaging probe capable of operating at 1KW radio frequency levels. The probe also contains forced air cooled gradient coils which are capable of operating with duty

cycles in excess of 20% while producing a highly linear magnetic field gradient of approximately 60 G/cm over a sphere of 30mm in diameter.

In a conventional 2-D NMR backprojection tomographic experiment, one applies a linear magnetic field gradient in a plane at numerous projection angles. For each angle, the Fourier transform of the data represents a planar integral of the proton density normal to the gradient vector. Similarly, in the 3-D backprojection experiment, by varying the gradient vector so as to sample the entire 3-D space, one obtains 3-D Radon transform of the proton density. Let $Rf(P)$ be the Radon transform of the object function $f(M)$, where P and M are discrete points in the Radon and object space, respectively (Figure 1):

$$Rf(P) = \int_{(OP, OM)=0} f(M) dM \quad (1)$$

The inversion of this transform can be obtained by double differentiation and backprojection. Marr et. al.[12] have shown that the fastest way to invert the Radon transform is to use two sets of backprojections, one along the meridian planes and the other along planes of constant latitude. The inversion can then be written as (Figure 2):

$$f(M) = \frac{1}{4\pi} \int_{\theta=0}^{\theta=\pi} \int_{\phi=0}^{\phi=\pi} \frac{\partial^2 Rf}{\partial \rho^2}(\rho(M, \theta, \phi), \theta, \phi) \sin \theta d\theta d\phi \quad (2)$$

where; ρ, θ, ϕ are the classical parameters of spherical coordinates; and $\rho(M, \theta, \phi) = OM \cdot n$ where O is the origin and n is the unit vector in the direction (θ, ϕ) .

Fig. 1. Definition of the 3D Radon transform. The value of the 3D Radon transform in P is the Integral of the value of the points M in the plane defined by $OP \wedge MP$.

Fig. 2. Decomposition of the integral over a sphere in two series of backprojections.

The algorithm of the 3-D Radon transform was implemented in the following steps:

- (1) computation of the second derivative $d^2 R_f / dp^2$
- (2) weighting of all the points of the space by $\sin(\theta)$
- (3) backprojection at ϕ constant
- (4) backprojection at z constant

The 3-D X-ray microtomograph system used in these experiments was designed and constructed at ANL. The system consists of a IRT HOMX 161 microfocus source, a Precise Optics tri-field image intensifier, a Sony XC-57 CCD (512^2) camera, Daedal Precision Components manipulation stages (X, Y, θ), and an IBM/PC/AT compatible computer with frame grabber and accelerator boards. The image reconstruction was performed on a local VAX 8700, using either one of two analytical codes (Radon [13] or Feldcamp [14]). For small apertures, it has been shown that both codes provide similar results in reconstructed images [15].

Si_3N_4 -whisker-reinforced Si_3N_4 matrix composites were prepared by conventional ceramics processing techniques. Si_3N_4

powder (UBE Chemical Ind. UBE-SN-E10, α), 2.5% w/w MgO (in form of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), and Carbowax 400 (Union Carbide - polyethylene glycol), were suspended in ethyl alcohol and ball milled for 16 hours. Si_3N_4 whiskers 10% W/W (UBE Chemical Ind. UBE-SN-WB β) were added and ball milling was continued for 3 hours. The sample was pan-dried to remove the alcohol before pressing. The pressed specimens were stored under desiccant until the imaging experiment. The sample chosen for examination in this work was 7mm*7mm*3mm.

The x-ray data of the composite specimen were acquired using x-ray source settings of 39KV, and 0.9mA of flux. The number of projections equaled 185 over 2π , and 128 averages were acquired per projection. A final spatial resolution of $124x*124y*124z \mu\text{m}^3$ per volume element (voxel) was achieved in the reconstructed image. Three-dimensional NMR imaging data was acquired using 128 complex data points, and a total of 1024 projections (16 theta angles over $\pi/2$ radians * 64 phi angles over 2π radians). Gradient strength of 35 G/cm and a sweep width of 100 KHz were used. One hundred twenty eight averages were acquired using an approximate 90° pulse, and a recycle delay time of 0.25 S. A spectroscopic resolution of $175x*175y*175z \mu\text{m}^3$ was achieved.

RESULTS AND DISCUSSIONS

Photos of three-dimensional representations of the (A) NMR and (B) x-ray results reconstructed via surface rendering techniques are presented in Figure 3. Surface rendering is performed by applying a user adjusted threshold intensity to define a minimum intensity which is used to calculate the

contiguous surface. With the particular threshold chosen, the rendered x-ray image resulted in an accurate representation of the sample's morphology. The NMR surface was however was reconstructed with a minimal threshold intensity chosen to suppress structure arising from low proton density near the surface of the sample. This threshold level essentially eliminated two corners of the sample from the rendered object (a). Note however that the remainder of the object's morphology is very similar (b) to that of the x-ray acquired surface.

A narrow two-dimensional section ("a slice") of three-dimensional (A) NMR and (B) X-ray CT reconstructed image from identical spatial locations obtained on the composite specimen is shown in Figure 4. Given that the NMR and x-ray signals arise from completely different mechanisms and thus have different filtering functions, scaling constants, signal-to-noise ratios, and intrinsic image contrast, image analysis is most appropriately performed by comparing localized intensity variations within each image. Given the complementary nature of the two techniques, intensity indications from identical geometric positions in both images can then be discussed. Three types of localized intensity indications can be observed in Figure 4: (a) areas of low NMR and low x-ray intensity, possibly stemming from a void or low density non-protonated inclusion; (b) areas of low NMR intensity (low organic concentration) and high x-ray intensity (high sample density); and (c) areas of high NMR intensity (high organic concentrations) and low x-ray intensity (low sample density). Effort are being made to calibrate image intensities with appropriate proton density or actual density using appropriate standards. Dual-modality experiments performed in this manner will allow NDE of flaws (voids, cracks, etc.), as well as map

binder and density interdependency throughout the green component, and thus significantly impact the product development process.

While the experimental NMR imaging times are perhaps lengthy, significant reductions in data acquisition time can be expected for commercial components. Given that the concentration of binder used in the composite specimen (2.5% w/w) is approximately a factor of five to seven less than of commercial green-state injection-molded materials, significant (factor of five to seven) increases in signal-to-noise ratios can be expected when examining commercial components. Additionally, given that the sensitivity increases approximately as frequency^{7/4} an additional factor of ≈ 12 in sensitivity is expected (disregarding possible changes in spin-lattice relaxation rates constants) by increasing the experimental field strength from 2.3T (100MHz) to 9.2T (400MHz). Thus an increase of perhaps a factor of 80 might be expected under these conditions allowing reduction of imaging time, while improving signal-to-noise ratio throughout the image.

Figure 3. Three-dimensional surface reconstruction of (A) 3-D NMR image and (B) 3-D X-ray CT data obtained on a green-state $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ whisker reinforced composite specimen.

Figure 4. Narrow two-dimensional section "a slice" of three-dimensional (A) NMR image and (B) X-ray CT data obtained on the green-state $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ whisker reinforced composite specimen.

CONCLUSIONS

We have demonstrated the feasibility and practicality of performing three-dimensional (spatial) microtomographic NMR imaging on solid materials. Specifically, using a 3-D dual back-projection protocol combined with a 3-D Radon reconstruction technique, low concentration (2.5% w/w) organic additive distributions have been measured in green-state Si_3N_4 -whisker-reinforced Si_3N_4 matrix composite specimens. Additionally, three dimensional density variations have also been determined of the specimen via x-ray microtomography. We have demonstrated that results obtained from 3-D NMR (derived from proton density) and those from 3-D x-ray microtomography (derived from absolute sample density) are complementary, and thus can provide a more thorough nondestructive evaluation of the sample than provided by a single technique alone.

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