PROTON NMR IMAGING OF GREEN STATE CERAMICS

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INTRODUCTION

High performance ceramic materials in advanced technology applications are becoming of increasing importance. As a result, the necessity of finding new quantitative non-destructive evaluation (QNDE) methods for ceramics is becoming increasingly apparent. This paper explores the applicability of proton NMR imaging to the QNDE of ceramic materials. While proton NMR imaging is clearly well developed in the area of medical applications (1), only a few experiments have been performed to determine the applicability of this technique to the analysis of ceramic bodies (2). Compared to the NMR imaging of soft tissues for medical applications, the magnetic interactions of protons in solids or semi-solids make high resolution image generation more difficult. These interactions both broaden the proton NMR lines and shorten the spin-spin relaxation times. As a result, larger encoding magnetic field gradients and faster gradient switching are required of a NMR imaging system to produce high resolution, high signal-to-noise ratio images of solids.

In the plastic forming of ceramics, a wax or polymeric binder system is mixed with the dry ceramic powder, which is then molded, extruded, or rolled. After forming the green state ceramic piece, the binder is removed by thermal vaporization or pyrolysis. The physical and chemical homogeneity of the powder/binder mix has effects on the rheology, physical properties, and pyrolysis chemistry of the mix. Variations in these characteristics can produce defects in the ceramic piece during the fabrication steps. It would be valuable to be able to detect such inhomogeneities. While techniques such as computer X-ray tomography produce density maps of the green state ceramics, NMR proton imaging has the potential for producing maps of the proton's chemical state, in addition to maps of the proton density. The chemical map may provide information on the local viscosity of the binder and on the chemical interactions among the binder components and ceramic powders. That type of knowledge is very pertinent to development studies in ceramic processing. In the longer term, NMR imaging for that chemical information may also be
usable for process monitoring in a production situation. It is this potential which motivated this preliminary study of NMR imaging of green state ceramics.

GENERATION OF PROTON NMR IMAGES

The images of the different types of ceramic samples were generated on either Fonar Corporation Beta-3000 or Beta-3000M proton NMR imaging systems. The Beta-3000 system uses a permanent magnet to produce the external static magnetic field of 0.3 Tesla (3000 gauss), while the Beta-3000M system uses a non-superconducting magnet to provide a magnetic field of the same strength. The resonant frequency of protons in this magnetic field is 12.7 MHz. Gradient coils produce switchable magnetic fields which are used both to select a region for imaging and to code the locations from which the NMR signals originate. This imaging system uses a processor which reconstructs and scales a digital 256 pixel x 256 pixel image in 8 seconds. An image with 2000 digital intensity levels is displayed at the conclusion of each scan.

Images of the ceramic disks were produced using a two-dimensional Fourier transform multi-slice spin echo technique, using echo delay times of 14 or 28 ms. The gradient multiplier feature of the imager was used to continuously vary the slice thickness down to 2 mm, with an interslice gap of 1 mm. In this technique, the slope of the magnetic field gradient normal to the selected plane of the slice was scaled up from its nominal value of 0.1203 Gauss/cm, which corresponded to a slice thickness of 7 mm for the standard bandwidth radio frequency pulse. The nominal 512 Hz difference between the center frequency of the transmitted rf pulses exciting adjacent slices remained unadjusted, allowing a proportional scaling of the slice separation. A similar scaling of the frequency encoding (read-out) gradient allowed high resolution image acquisition on a 256 x 256 matrix with the nominal pixel size of 1 mm being reduced to as small a value as 0.2 mm.

Scan times varied from 2 to 30 minutes depending on the number of signal averages, the number of phase-encoding levels, and the specific pulse sequence repetition time chosen. Selection of the slices in the sample was accomplished with an oblique multi-slice cursor. This software feature overlays a translatable and rotatable set of parallel lines on a displayed image from an already completed scan. The lines can then be adjusted to choose the orientation and positioning for the slices in the subsequent scan.

SAMPLES

Green state disks were prepared with alpha alumina powder using a two component binder consisting of a 50/50 mixture of a proprietary mix of plasticizer and resin. Disks were prepared with binder contents varying from 5 to 30 wt.%, with most disks having a 25 wt.% binder content. The disks were pressed at 90°C and 10,000 psi. The sample cylinders to be imaged were prepared by epoxying several disks together. An example of one such sample is shown in Figure 1. In this case, the disks contain 25 wt.% binder. For two disks, glass beads 4 mm in diameter were included as sample "defects" of a known size, in the pattern shown in Figure 1. The disks containing these glass beads were formed by pressing half of the required alumina/binder mix into a thinner disk, pressing the glass beads on the surface in the desired pattern, and then adding the rest of the alumina/binder mix and repressing to form the complete disk.
In green state ceramics, proton NMR imaging occurs via the protons contained in the binder. For the green state ceramics discussed here, the use of the two component binder ensures that protons are present in a number of different chemical environments. Protons may also be present in material of differing viscosity, depending on the uniformity of solution of the resin in the plasticizer. At sufficiently high binder viscosity, the NMR properties of the binder will be those of a solid material, with broad proton NMR lines and short spin-spin relaxation times ($T_2$). Since medical NMR imaging systems are limited in both the pixel-to-pixel separation in NMR frequency and the shortness of the spin echo delay, obtaining high resolution, high signal-to-noise ratio images can be expected to be difficult.

To illustrate some of the problems that can be anticipated from the binder proton NMR properties, the proton NMR free induction decay (FID) spectrum of the resin/plasticizer solution at 300 MHz is shown in Figure 2. The NMR spectrum is composed of a number of lines, with the aliphatic lines falling near 1100 Hz (from the reference line of water), and the aromatic lines occurring near 3000 Hz. The width of each region is roughly 1200 Hz. For a proton spectrum obtained at 12.7 MHz, the frequency at which the imager operates, the frequency difference of the aliphatic and aromatic regions which scales with the NMR frequency, would decrease to almost 80 Hz. This difference is much less than the pixel frequency difference of 512 Hz. However, the widths of the aromatic and aliphatic regions will probably not decrease very much, as these widths are primarily determined by the proton NMR linewidths, which will not change much with the NMR frequency. As a result, image resolution will be limited to about two pixels if the pixel frequency separation is 512 Hz.

Proton NMR images of green state ceramics have been obtained under a variety of imager conditions with several different samples. The images discussed here are typical of those obtained for the samples. A typical sagittal image of the green state ceramic sample shown in Figure 1, is displayed in Figure 3a. This is an eight scan image with an echo delay...

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Fig. 1. Photograph of green state alumina disks, epoxied together.

Fig. 2. 300 MHz proton FID NMR spectrum of binder resin dissolved in the plasticizer.
time of 28 ms. The location of the glass beads in two of the four disks is apparent. Also clearly shown are the regions of epoxy between the disks and the presence of several regions of severe sample inhomogeneity. In the upper disk with glass beads, the region between the two halves of the disk can be discerned. A higher resolution axial image of the lower disk is presented in figure 3b. Again, a spin echo delay time of 28 ms was used. The cylinder axis is tilted with respect to the axial slice, so that the glass beads are visible on the right side of the disk, but less so on the left side. Other inhomogeneities are visible in the sample, particularly near the glass beads. This indicates that the technique by which the glass beads were incorporated into the sample introduced additional non-uniform regions.

The utility of multislice proton NMR imaging to the QNDE of green state ceramic materials is displayed in the series of axial images shown in Figure 4. A one scan off-axis sagittal image of the sample is shown in Figure 4a, which displays the positions of the axial slices in the rest of Figure 4 by the position of the multislice cursor. The axial images in Figures 4b through 4h are sequential images of the green state ceramic starting with the slice at the bottom edge of the disk. A total of 25 minutes was required for the generation of the seven interleaved images. The appearance and tracking of the glass beads and other sample nonuniformities through the seven sequential images indicates how the locations of such inhomogeneities or "defects" in the green state ceramic can be located and characterized with a medical NMR imaging system.
Fig. 4. Multislice proton NMR images of green state ceramic disks with echo delay of 28 ms and recycle time of 0.5 sec. a) Off axis sagittal image of green state ceramic disks showing multislice cursor placement. b - h) Sequential axial images starting from the edge of the sample - 12 scans, 2 mm thick slice, slice center separation of 2.9 mm, 0.33 mm x 0.33 mm pixels.
The origin of the contrast difference or inhomogeneities in the images of these green state ceramic samples is of considerable importance in determining the utility of the proton NMR imaging technique for the QNDE of such materials. Visual inspection of the samples did not indicate the existence of any inhomogeneities or "defects" of the size indicated in the images (exclusive of the glass beads). However, with a two component binder, questions arise as to the uniformity of distribution of the plasticizer and resin, and the degree to which the resin is uniformly dissolved in the plasticizer. Spatial variations in the plasticizer/resin mix uniformity could effect the proton NMR properties, leading to spatial variations in the contrast of the image. To determine if the NMR properties of the binder depended on the exact conditions of component mixing and heat treatment during pressing the green state material, spin echo proton NMR spectra at 300 MHz were generated with different echo delay times for samples of differing homogeneity. Of particular interest is a comparison of a binder sample where the resin has been fully dissolved in the plasticizer, and a sample which is a physical mixture of the resin and plasticizer. Proton NMR spin echo spectra of these samples at different echo delay times are shown in Figure 5. The spectra of the solution are shown in Figure 5a, and the spectra of the physical mixture are shown in Figure 5b. The size of the NMR signal decays very rapidly with increasing echo delay time for the solution, while the signal of the physical mixture decays much more slowly. The change in the relative intensities of the various lines in the spectra with increasing echo delay, indicates that protons in chemically different environments will dominate the NMR signal and hence the image at longer echo delays. These spectra demonstrate that the images are $T_2$ selective, with the contrast possibly arising from plasticizer rich regions of the green state ceramic samples or regions where the resin has been poorly dissolved in the plasticizer.

To determine if the use of shorter spin echo delay times would alter the images of the green state ceramics significantly, proton NMR images

![Fig. 5. 300 MHz proton spin echo NMR spectra at the indicated echo delays. a) Solution of resin in plasticizer. b) Physical mixture of resin and plasticizer.](image-url)
were generated at echo delay times of 14 and 28 ms. The use of a 14 ms echo delay time required the use of thicker image slices and larger pixel size. In Figures 6a and 6b, sagittal image slices at 14 and 28 ms delay are compared. A similar comparison of two axial image slices is given in Figures 6c and 6d. In general, the spatial variation of the image intensity at a 28 ms delay appears to be greater than at 14 ms (exclusive of the glass beads), although, the differences are not dramatic. These results suggest that if an imaging system with a much shorter echo delay were used to image these samples, the resulting images would show much less contrast.

Fig. 6. Single scan proton NMR images of green state ceramic disks using either 14 or 28 ms echo delays with 0.75 mm x 0.75 mm pixels. 

a) Sagittal image with 14 ms echo delay - 7 mm thick slice.
b) Sagittal image with 28 ms echo delay - 7 mm thick slice.
c) Axial image with 14 ms echo delay - 4.9 mm thick slice.
d) Axial image with 28 ms echo delay - 5.0 mm thick slice.
CONCLUSIONS

The preliminary proton NMR images of green state alumina ceramics discussed here clearly indicate that proton NMR imaging can develop into a valuable advanced QNDE technique for such materials. Sample nonuniformities of 1 mm diameter or larger appear to be easily detectable, and smaller nonuniformities can probably be detected under certain conditions, using the Fonar Beta-3000 NMR imaging system. The decrease in signal size with increasing echo delay time for the green state ceramics, indicates the need for imager modifications to achieve shorter echo delay times. However, in $T_2$ selective images of the type presented here, longer echo delays may in some cases provide better contrast and easier "defect" detection.

The work of Kupperman, et al. (2), demonstrated the imaging of porosity in green state ceramics by proton NMR of water in the pores. However, Kupperman was not successful in imaging a green state ceramic with a polyvinyl alcohol binder. In contrast, our study demonstrates spatial image variations in a green state ceramic which contained a two component (resin/plasticizer) binder system. Preliminary analysis indicates that inhomogeneous solvation of the resin component by the plasticizer is a possible source of the observed image contrast.

The possibility of imaging binder chemistry variations in a green state ceramic opens up a new tool for ceramic processing studies. If the NMR response of the protons in an organic binder is modified by changes in solvation, chemical crosslinking, phase, composition, and viscosity, it may be possible to map the extent of those changes in the green state ceramic. Similar types of results should also be obtainable in polymer and composite materials.

REFERENCES

1. For a review of proton NMR imaging, particularly for medical applications, see, for example, T. F. Budinger and P. C. Lauterbur, Science 226, 288 (1984), or P. A. Bottomley, Rev. Sci. Instrum 53(9), 1379 (1982).


DISCUSSION

Mr. W. Friedman, Standard Oil: Have you compared these with x-ray C.T.'s and are the NMR images also susceptible to some of the artifacts that occur in more complicated shapes?

Mr. Welsh: We planned to compare with C.T., but don't have the results yet. We obtained the final images just before the conference, but did not have time to perform the C.T. experiments. What was the second part of the question?

Mr. Friedman: Whether you get artifacts if you have complicated flaw shapes.

Mr. Welsh: I think the main problem with artifacts is if you have anything metallic or conductive--
Mr. Friedman: But what about looking at high-aspect ratio things like blades?

Mr. Welsh: We haven't tried that. Images obtained so far are on model systems, to determine image quality from the present system.

From the Floor: Can you explain to me what is it that controls the slice thickness in this?

Mr. Welsh: The strength of the magnetic field gradient across the sample. As you increase the size of that gradient, you will get a thinner slice. What you are basically doing is spatially separating the resonance of protons in nearby spatial locations.

From the Floor: I see how that sort of affects your pixel size, but the slice thickness seems to be something other --

Mr. Welsh: Well, it depends on the bandwidth of the transmitter, but it also depends on the magnetic field gradient. So if you keep the bandwidth fixed and increase the magnetic field in the 2 directions you will get a thinner slice thickness.

Mr. D. Copley, G.E.: What do you see is the prospect for imaging fully-cured polymerical composite materials?

Mr. Welsh: I think, with the current medical imaging systems, that's a very tough problem. I think you generally have to go to multi-pulse methods.

Mr. Copley: Do you think that would be feasible?

Mr. Welsh: Certainly, several groups are putting a lot of effort into it and getting some positive results.

From the Floor: What's your minimum delay time?

Mr. Welsh: Minimum delay time for this imager was 14 milliseconds.

From the Floor: That's an instrumental factor?

Mr. Welsh: Yes. That relates to how fast you can switch the gradients. If you go to a smaller imager, you can probably switch a lot faster. And this is a large imager with a small object.

From the Floor: Do you consider that 1 millimeter or so resolution is sufficient to find what you want in green ceramics?

Mr. Welsh: We turned the question around the other way; that is, we wanted to see what kind of spatial information can be obtained by this technique. Right now, we are working with pixel sizes that are about 0.2 millimeters, and it may be possible to get down to that kind of resolution. For the samples that we imaged, I believe the resolution is closer to a half to 1 millimeter. A year from now, the resolution should be better.