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# NMR imaging of slipcast SiC whisker-reinforced alumina

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Application of nuclear magnetic resonance (NMR) imaging, with analysis of grey levels in the images, provides a semi-quantitative non-destructive estimation of the extent of whisker distribution in the green state composites. Regions with large physical flaws caused by hard particles or open pores may be identified. Examination of the composite after sintering, by scanning electron microscopy (SEM) and energy dispersive analysis of X-rays, confirmed that the areas of high grey levels in the NMR images were mainly caused by whisker bundles. However, individual flaws smaller than the detection limit (100 μm) of the NMR imaging technique were also observed during the SEM analysis of the sintered sample.

## 1. Introduction

Ceramic matrix composites reinforced with fibres or whiskers show considerable potential as high-temperature structural materials [1, 2]. However, their practical applications in fabricating reliable components depend on a homogeneous distribution of the whiskers or fibres in the matrix and the reduction or elimination of all types of physical flaws [3]. Most of these physical flaws originate in the forming of the green compact. In addition, local variations in the distribution of fibres or whiskers in the matrix affect the densification behaviour of the green compact, and may cause large flaws in the material due to differential sintering. Therefore systematic inspection of the composite material in the green state is essential for the production of reliable components.

Recent reports [4, 5] have described the application of non-destructive nuclear magnetic resonance (NMR) imaging to slipcast samples of SiC fibre-reinforced ceramics for detecting physical flaws such as fibre agglomerates and open pores. Spatial resolutions of $70 \times 70\ \mu m^2$ were achieved in this study by using high-field instrumentation and suitably selected signal acquisition and echo times. The present paper describes the use of NMR imaging to obtain quantitative information regarding the bulk distribution of SiC whiskers in whisker-reinforced ceramics, in addition to detecting other physical flaws such as open pores or hard inclusions, that may inadvertently be included during sample preparation.

## 2. Experimental procedure

Samples were fabricated by slipcasting slurries of alumina (Reynolds RC-HP-DBM) containing 20 vol % SiC whiskers (Tateho SCW 1-S-1, diameter 0.5–1.5 μm and length 5–20 μm). These whiskers were washed with HCl to remove metallic impurities and were added to an alumina slip to give a total solids content of 60 wt %. Before casting the samples, the slurry was homogenized using a sonicator and the pH was adjusted to 4.5 to obtain a slip with a viscosity of about 200 cP.

Slipcasting was carried out using plaster moulds. The cast samples, of cylindrical shape (0.9 cm diameter and 2 cm high), were sealed in 1 cm o.d. NMR tubes as soon as they released from the mould. A moist atmosphere was maintained over the samples to prevent further loss of water and some water was added before imaging.

NMR imaging was carried out using a 200 MHz spectrometer (Bruker MSL NMR Spectrometer) equipped with a micro-imaging accessory. Scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDX) were carried out using an electron microscope equipped with an X-ray analysis system.

## 3. Results and discussion

As in all NMR techniques, nuclei of a single isotope are observed selectively in NMR imaging [6]. The isotope $^1H$ was chosen in this experiment in order to observe the distribution of water in the sample. A typical examination [4, 5] involved the imaging of the distribution of $^1H$ present in water in the ceramic samples examined.

Representative images obtained from samples of alumina and SiC whisker-reinforced alumina fabricated by slipcasting are shown in Figs 1 and 2. These images reflect the relative amont of $^1H$ spin density (i.e. the amount of water) across a transverse cross-section or a scanning slice through the sample. Therefore the areas with higher amounts of water appear brighter than areas with lower water content.

The NMR images were obtained with a soft 90°/soft 180° echo sequence, with TE = 5.3 ms and TR = 1 s (see [4] for details). Sixteen scans were obtained at

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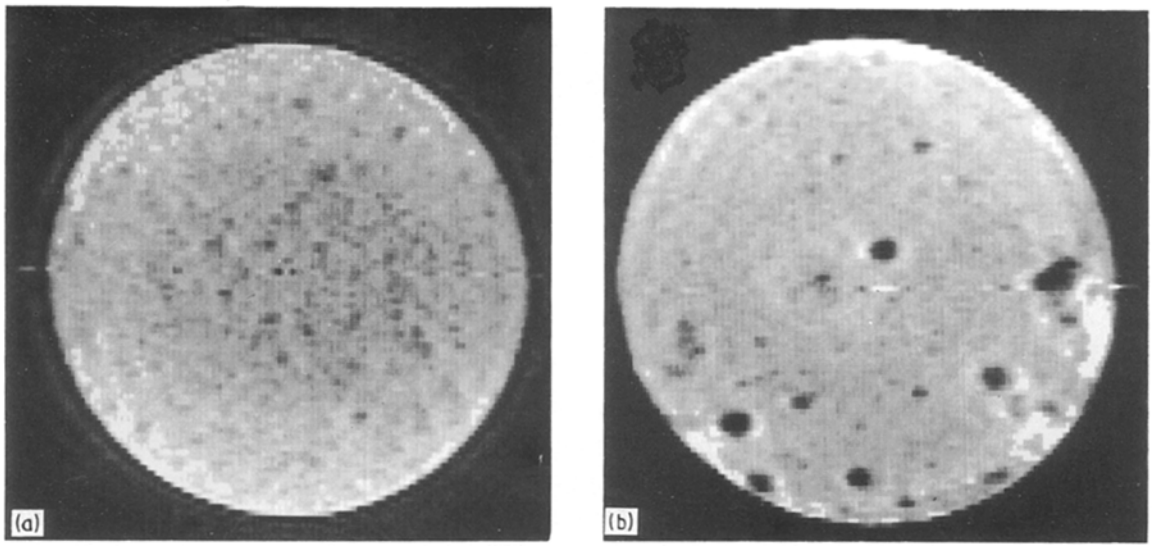


*Figure 1* NMR images of alumina slices, thickness = 2.5 mm: (a) slice with no detectable flaws, (b) slice with large pores; the diameter of these pores is in the range 120–860 μm.

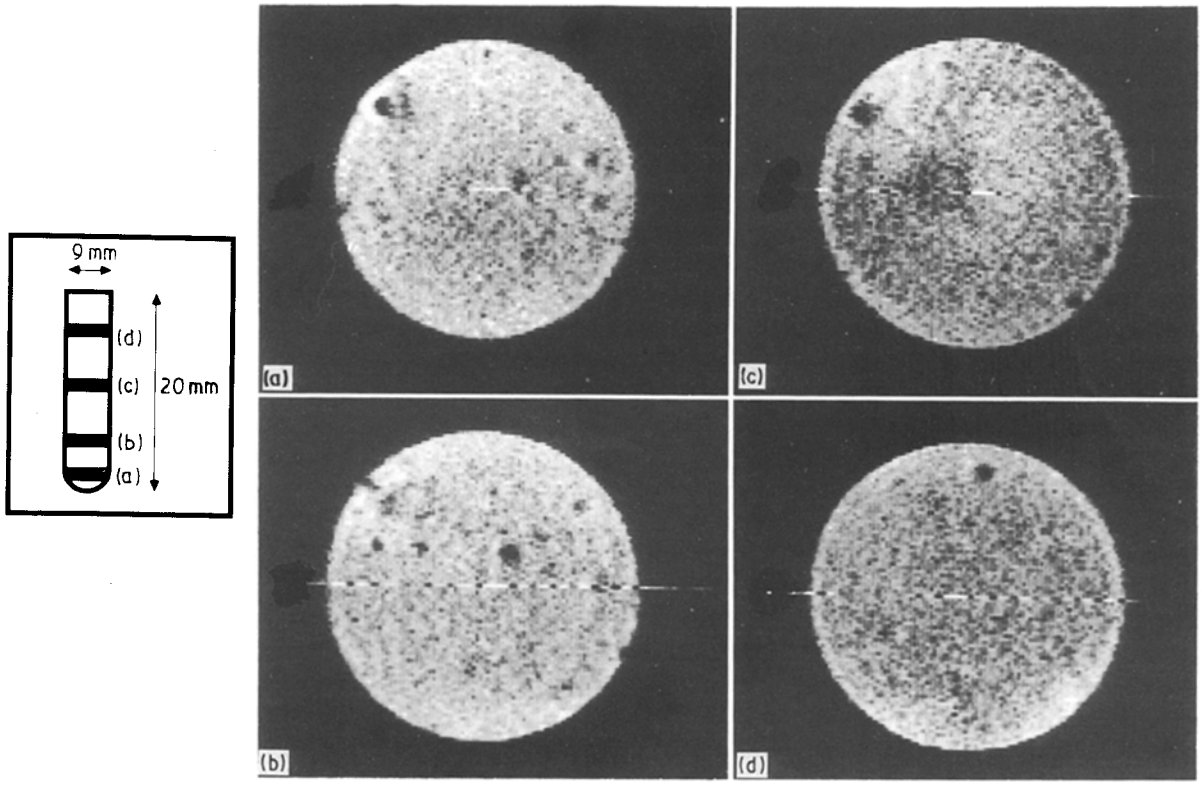


*Figure 2* NMR images of SiC whisker-reinforced alumina. Thickness of scanning slice = 2.5 mm. The location of each slice is marked on the left-hand side.

each of 128 increments of the phase-encoding gradient. The spatial resolution of these images is 100 × 100 $\mu m^2$ for a 2.5 mm thick slice examined.

Fig. 1, shows the NMR image of two scanning slices of alumina with and without open pores. Because the water molecules are evenly distributed in this monolithic material the image in Fig. 1a shows a very narrow band of grey levels. The slice in Fig. 1b shows dark spots in places occupied by open pores, and the rest of the image of this slice reflects similar grey level distribution as in Fig. 1a. The four NMR images (Fig. 2) of a whisker-reinforced alumina, however, show a broader distribution of grey levels indicating a higher degree of heterogeneity in water distribution in the composite caused by the difference in water retention by the "soft" alumina grains and the "hard" SiC whiskers. Therefore, the difference in the grey levels in different areas in these images reflect the extent of whisker distribution in the composite material.

As mentioned earlier, each of these images correspond to a scanning slice of 2.5 mm thickness of the green-state sample. The first slice examined (Fig. 2a) was located on the rounded bottom of the sample and therefore has a slightly smaller diameter. This was taken as reference plane (i.e. $h = 0$) to indicate the height of subsequent slices examined. The large dark

spots observed in the interior regions of these images indicate the presence of hard inclusions or open pores in the sample. However, the dark spots on the edges of the circular images 2a–c could be caused by surface damage which occurred during transfer of the wet sample from the mould to the NMR tube.

The image shown in Fig. 2c shows a large flaw close to the centre of the sample in which a small area of the cast appears to have partially separated from the rest of the sample. This is an evidence of the "cake clogging" effect caused by partial flocculation of the slip during the slip-casting process.

An analysis of the grey levels of images of the samples was carried out by measuring the amount of light passing through different areas of these images under the same conditions. Theoretically, a slice with a homogeneous distribution of water should show a very narrow band of grey levels in its image. The image in Fig. 1a showed grey levels in the range 30–50. In contrast, the images in Fig. 2 showed a wider distribution of grey levels. The average distribution of grey levels of images in Fig. 2a–d is summarized in the form of a pie-graph in Fig. 3. These values of grey levels are relative optical density values where the lowest value (i.e. zero) is assigned to the area which transmitted the maximum amount of light.

The highest optical density value of 200 detected in these images corresponds to the dark spots which take up about 6% of the area. This value corresponds to the total area, in the scanning slices examined, that is occupied by physical flaws such as hard inclusions picked up during the powder processing step, open pores caused by trapped air bubbles and surface flaws formed during the handling of the wet cast.

An explanation of the distribution of grey levels is provided by microscopic information about the whisker distribution in the ceramic matrix. The sample used for NMR imaging was dried in a humidity chamber to prevent formation of additional flaws due to rapid drying, and sintered in a vacuum furnace at 1600 °C. Physical slices of the sintered sample, obtained by cutting at locations previously analysed by NMR imaging, were analysed with SEM and EDX. Some open pores caused by trapped air during the casting process were observed in slices obtained in the area shown by image 2b. Scanning electron micrographs obtained at several locations in these slices showed pockets of whisker agglomerates mixed with the evenly distributed whisker-matrix network. As shown in Fig. 4 some of these pockets contain cage-like structures made by the whiskers with very little amount of alumina grains between them. These whisker cages enclose open pores creating strength degrading physical flaws in the material. Although the dimensions of small flaws like this are smaller than the resolution of NMR imaging technique adapted here, the absence of absorbed water in these pores will contribute to the formation of darker regions (higher optical density levels) in the NMR images.

EDX mapping of the sintered composite obtained by detecting X-rays from the element Si will show the distribution of SiC whiskers. Low-resolution ( × 50) Si X-ray maps obtained in a physical slice of the sintered sample detected an average of 45 whisker bundles with diameters of 10 μm or higher in the analysed area of 4 $mm^2$. Because these maps could not detect individual whiskers, most of which had diameters close to 0.5 μm, a further X-ray map of the element Si of an

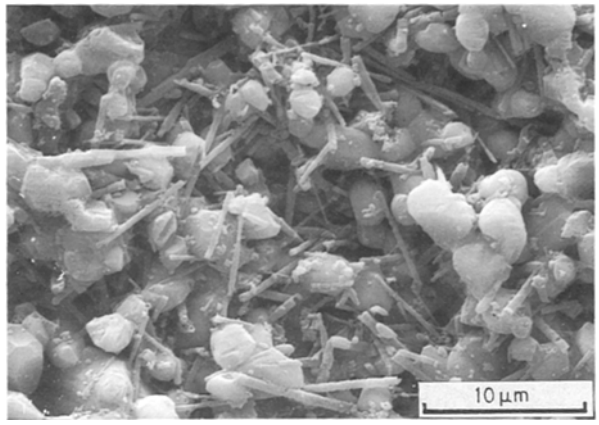


*Figure 4* "Whisker cage" enclosing open pore in the sintered composite (slice 2b).

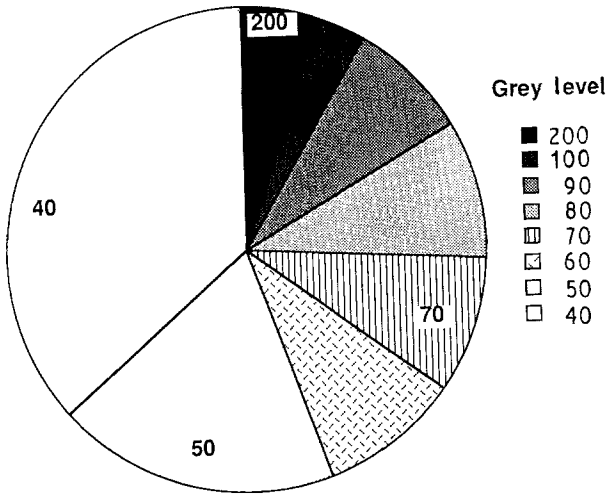


*Figure 3* Image analysis of the NMR images of SiC whisker-reinforced alumina shown in Fig. 2.

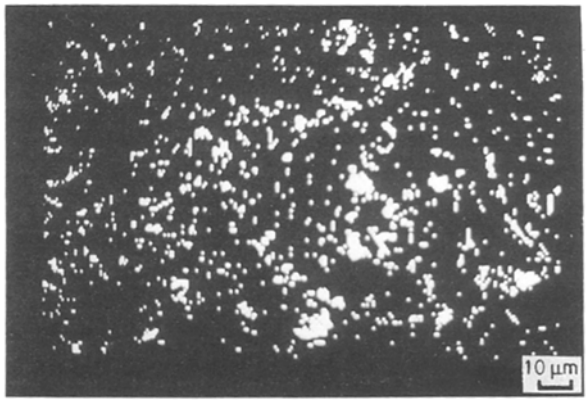


*Figure 5* Silicon X-ray map of an average area in slice 2c ($h$ = 9.5 mm in NMR image) after sintering of the composite. The area analysed (175 × 110 $\mu m^2$) is the maximum detectable in one analysis with adequate magnification to resolve individual whiskers in the SEM image.

average area was obtained at a magnification of × 600 (Fig. 5). This is low enough to examine the maximum possible area of the sample with a resolution high enough to detect individual whiskers.

The whiskers oriented perpendicular to the slice are observed as single spots in this image while those aligned parallel to the slice appear as long streaks. Large spots in this image are caused by bundles of whiskers. Allowing for the 15% shrinkage observed in the sample during the drying and sintering steps, the area shown in the EDX image corresponds to 205 × 130 $\mu m^2$ of the green sample.

X-ray and NMR imaging techniques used in this work are complementary to each other. The X-ray image which examines a smaller area of the physical slice shows that the area resolvable in the NMR image of the green composite may include both well-dispersed and agglomerated whiskers. In the green state composite, however, the presence of whisker bundles without any alumina grains between them would cause a significant decrease in the amount of water retained in the region. Therefore the brightness of each pixel in the NMR image, which is related to the amount of water in the region, would correspond to the average distribution of the whiskers in this region. The different grey levels observed in the NMR images could therefore be caused by the difference in the "net" whisker distribution within the area of resolution.

As described earlier, the whiskers were mechanically dispersed in the slip by using the high shear-rate field of an ultrasonic horn. These whiskers, however, rearrange after this dispersion process to form closed networks or bundles. The observation of cake clogging effect in one of the slices examined also suggests the instability of the slurry with respect to flocculation during the casting process.

## 4. Conclusion

Examination of the slipcast composites in the green state using NMR imaging provides information regarding the distribution of whiskers and detects other physical flaws. Development of this technique for practical applications should result in considerable savings in cost and increased reliability in components made from composite materials.


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