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Diffuse-Reflectance Fourier Transform Infrared Spectroscopic Studies of the Stability of Aluminum Nitride Powder in an Aqueous Environment

James G. Highfield* and Paul Bowen¹

Laboratoire de Chimie Technique, Ecole Polytechnique Fédérale de Lausanne, Lausanne, CH-1015 Switzerland

Diffuse-reflectance infrared Fourier-transform spectroscopy (DRIFT) is applied to monitor the degradation process that occurs when AlN ceramic powders are suspended in water at 25 °C. By virtue of its ability to obtain optical absorption data from amorphous and bulk materials, DRIFT has certain advantages over alternative techniques such as X-ray photoelectron spectroscopy and X-ray diffraction in this case. An amorphous oxy-hydroxide shell, of probable formula AlO(OH), initially forms and grows on a shrinking AlN core. Later, the shell crystallizes to bayerite, Al(OH)₃. The quantitative capability of DRIFT is demonstrated by good linear calibration of OH stretch band area vs O content, before crystallization, with a correlation coefficient of 0.995 and a standard error on the slope of ±7% at the 95% confidence level. The method appears insensitive to the inhomogeneous (shell/core) structure of the samples.

INTRODUCTION

Diffuse-reflectance infrared Fourier-transform (DRIFT) spectroscopy can be considered as one of a versatile range of analytical tools now available for the study of infrared absorption in solid materials (1, 2).

Diffuse reflectance (DR), along with a growing family of calorimetric techniques of which photoacoustic spectroscopy (PAS) is arguably the most popular (3, 4), offer the means to investigate samples directly in powdered form and are finding increasing application in such fields as catalysis, corrosion science, and materials characterization (1-10).

Although such techniques were originally established for application in the UV-visible region (11, 12), their recent extension to the valuable infrared region has been possible with the advent of Fourier-transform infrared (FTIR) spectrophotometers. Here, the multiplexing advantage of FT methods is exploited to offset the traditional sensitivity problem due to low source power as compared to the UV-visible region.

While DR and PAS are clearly complementary in applications where the latter technique's calorimetric mode of detection becomes important, as in studies of, e.g., photochemical and luminescent systems (13), DRIFT tends to be the preferred choice in the infrared by virtue of its superior signal-to-noise ratio for equivalent analysis times (2). However, whereas there is good evidence that PAS can yield quantitative data in this spectral region (5, 6, 9, 10, 14), the same cannot yet be said of DRIFT. The major sources of measurement error have been under intense investigation, notably by Griffiths et al. (1, 2, 15-19), and shown to be related to, inter alia, irreproducible packing (pressing) of the powdered sample bed, incomplete rejection of the specular (surface)-reflection component, nonideal optical properties of the diluent matrix and geometric factors such as sample positioning,

etc. If such problems can be overcome, or at least well-controlled, DRIFT should soon take its place alongside other established techniques in analytical spectroscopy.

In this paper, we wish to illustrate the power of DRIFT in its application to monitor and elucidate some details of the degradation process occurring when finely divided AlN is exposed to an aqueous environment. AlN is one starting material in the preparation of TiN/Al₂O₃ ceramic composites, according to the displacement reaction



This route is designed to introduce fine microstructure into the final product with benefits in terms of superior mechanical properties (20). Attention in this laboratory has recently focused on the stability of the nitride precursor in the suspending agent of preference, i.e. H₂O (from economic considerations), and of the effect of its controlled hydrolysis on the quality of the resulting composite (21). A detailed study of kinetic aspects of the reaction and implications for the ceramic process will be reported elsewhere (22).

In this work we place emphasis rather on the advantage that the DRIFT technique, supplemented by elemental analysis, holds over alternative methods of characterization, viz. X-ray photoelectron spectroscopy (XPS) and X-ray powder diffraction (XRD), for such studies. These benefits arise largely from the nature of IR photometric methods in general, i.e. the ability to probe the *bulk* of the sample and to yield spectral details on *amorphous phases*.

From the spectroscopic viewpoint the AlN/H₂O reaction, in which the kinetics are best treated in terms of a *core-shrinkage* approximation (22), also serves as a possible model system to address the question of surface selectivity in DRIFT measurements, evidence for which has been reported elsewhere (1, 2).

EXPERIMENTAL SECTION

Sample Treatment. The AlN starting material was of commercial origin (H. C. Starck, grade C) with a stated density of 3.26 g·cm⁻³, and a median particle size (*d_v*) of 1.2 μm. Powder samples (20 g) were mixed with deionized water (100 cm³) and treated with an ultrasonic horn (20 kHz) for 2 min. The suspension was then stirred for 2-24 h at 25 °C. In the drying step, samples were washed successively with 2-propanol (400 cm³) and then filtered. The resulting paste was dried to constant weight in a forced-air oven at 60 °C. Dried powders were stored in air-tight containers for subsequent investigations. Samples are designated S_x, where *x* represents the exposure time in hours.

DRIFT spectra from 4000 to 800 cm⁻¹ at 4 cm⁻¹ resolution (Hamming apodization) were obtained on a Bomem DA3.002 FTIR spectrophotometer equipped with a Harrick DRA-2CO diffuse-reflectance accessory. Spectral signal to noise was routinely improved by coaddition of 500 scans, resulting in a data acquisition time of 3 min. All spectral data manipulation, e.g. conversion to Kubelka-Munk units, base-line correction, peak integration, and deconvolution, was done with the standard software supplied by Bomem, Inc. Curve fitting was performed by using simple linear regression statistics.

Due to the high intensity of most of the IR spectral bands of interest, samples were routinely ground with an excess of KBr

¹ Laboratoire de Ceramique, Département de Matériaux, Ecole Polytechnique Fédérale de Lausanne, Lausanne, CH-1007 Switzerland.

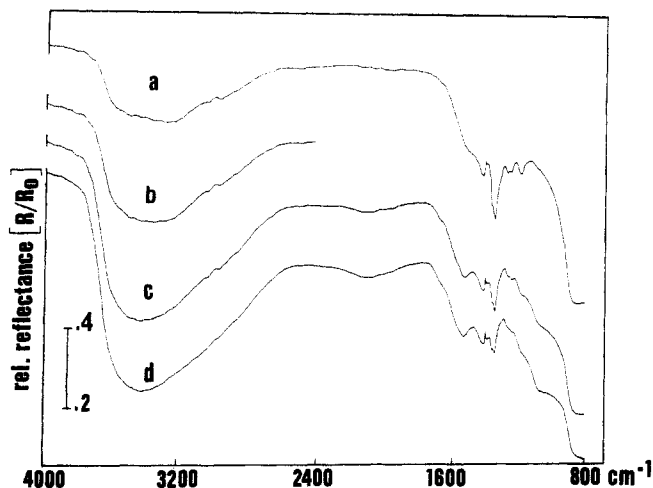


Figure 1. DRIFT spectra of AlN powder after treatment in water for (a) 0 h, (b) 2 h, (c) 4 h, and (d) 8 h.

($\times 10^{-40}$). This served to enhance spectral definition and, in the case of quantitative work, to provide a range of reflectance values (typically 0.2–0.8) for analyte peaks where the photometric precision is good (11). Spectra are presented in the form of relative reflectance (vs pure KBr) or in Kubelka–Munk units. The latter is established practice in quantitative measurements of optical absorption in powders. Sample loading was performed with particular attention being given to the packing procedure. The cup was overfilled, and the sample layer pressed and flattened as reproducibly as possible with the aid of a spatula. In this way, preliminary (100%) base-line checks using pure KBr were typically good to within $\pm 5\%$ relative.

Alumina reference compounds, including boehmite ($\text{AlO}(\text{OH})$), bayerite, and gibbsite ($\text{Al}(\text{OH})_3$) were kindly donated by Alusuisse.

X-ray photoelectron spectroscopy (XPS) data were collected with a Perkin-Elmer PHI 590-550 XPS spectrometer. Gold ($\text{Au } 4f_{7/2}$) and copper ($\text{Cu } 2p_{3/2}$) lines at 84.0 and 932.6 eV were used for calibration and the carbon 2s peak at 284.6 eV as an internal standard to compensate for any charging-up effects.

X-ray powder diffraction (XRD) analyses of the crystalline phases found in the treated AlN samples were made with a Siemens D500 X-ray diffractometer.

Elemental analysis (CHN) was made with a Perkin-Elmer Model 2400 CHN elemental analyzer. Values of oxygen content were generally estimated by material balance from Al analyses (obtained by firing in air at 1400 °C for 4 h) together with the respective nitrogen data. Some O values thus obtained were also checked by direct analysis (H. Starck, LECO TC316 oxygen analyzer) and found to be consistent (to $\pm 5\%$ relative) with those obtained by material balance.

RESULTS AND DISCUSSION

DRIFT spectra (in relative reflectance) of samples reacted with water for up to 8 h (S_0 through S_8 , 10% in KBr) are presented in Figure 1. The main features are the systematic growth of strong bands characteristic of OH stretching and (weaker) bending fundamentals centered at 3300 and 1060 cm^{-1} , respectively, a new band at 1510 cm^{-1} , and erosion of the band at 1330 cm^{-1} . From O analysis, the AlN starting material already has a small oxide component (2.6% O), which probably stems from the preparation and/or slow reaction with the atmosphere. This explains the immediate presence of the OH band in Figure 1a. In other respects the spectrum, when extended down to 500 cm^{-1} (not shown), resembles quite closely the reference spectrum of AlN from the literature (23). The very strong Al–N stretching fundamental centered at $\sim 700 \text{ cm}^{-1}$ can be seen along with a group of features around 1400 cm^{-1} , the strongest of which (1330 cm^{-1}) is almost certainly an overtone of this fundamental. The major difference between the DRIFT spectrum reported here and that in the literature, obtained in transmission, is the selective enhancement of the overtone region; i.e. there is an apparent

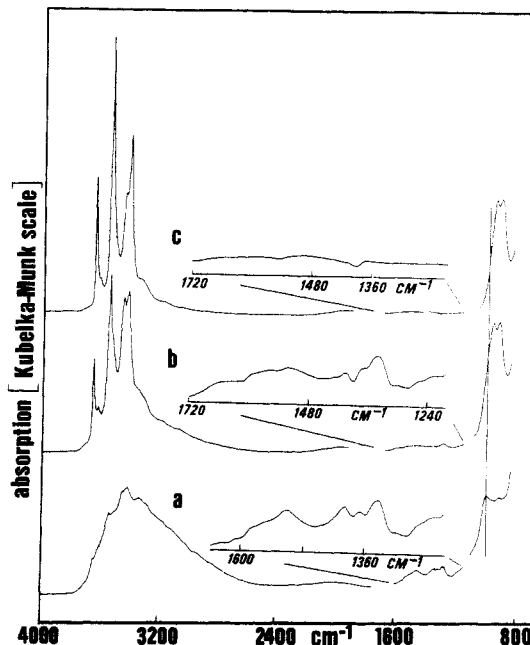


Figure 2. DRIFT spectra (Kubelka–Munk scale) of AlN powder after treatment in water for (a) 16 h and (b) 24 h. Spectrum c is bayerite, included for comparison.

reduction in dynamic range across the spectrum. This somewhat illusory effect is a common observation in DRIFT measurements on mineral or inorganic compounds. It arises from the intrinsic sensitivity of the technique, coupled with the presence of strong absorption bands and the use of the relative-reflectance plotting mode. A more faithful representation of the variation in absorption coefficient with spectral frequency is in terms of Kubelka–Munk units (11), which will be used hereafter. Nonetheless, it is worth emphasizing here that DRIFT conveniently offers the overtone region for analytical purposes when the fundamental region is effectively excluded due to the strong, broad, band structure often encountered there. The band that develops at 1510 cm^{-1} is assigned as the first overtone of an Al–O stretching fundamental of the growing oxy-hydroxide phase, the latter generally occurring in the range 700–800 cm^{-1} (24, 25). No evidence is found for the familiar deformation band of molecular or crystal H_2O at 1640 cm^{-1} (26). Throughout this series, no correspondence is seen with reference spectra or literature data (23, 25, 27, 28) of hydrated aluminas ($\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$), boehmite ($\text{AlO}(\text{OH})$), bayerite, gibbsite, or nordstrandite (all different structural forms of $\text{Al}(\text{OH})_3$).

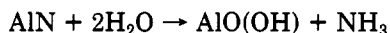
For the same range of samples, XRD shows the systematic erosion of the lines of AlN but no new features, confirming that the oxy-hydroxide phase is *amorphous*.

XPS is limited in this study due to its shallow analytical depth, which is generally accepted to be of the order of $\sim 70 \text{ Å}$ (29). Between 2 and 4 h of reaction, the N 1s signal suddenly drops, by roughly an order of magnitude, to a vestigial level and thereafter remains low. Similarly, the growth of the O 1s signal is detectable up to $\sim 4 \text{ h}$, and then remains constant. This result nevertheless provides spectroscopic evidence that the process occurring can be envisaged in terms of a *shrinking-core model*, i.e. the amorphous product overlayer forms a coherent outer-shell that grows progressively thicker with time in a predictable way (30). This is discussed in detail elsewhere (22).

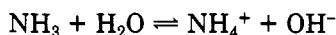
DRIFT spectra of samples S_{16} and S_{24} are presented in Figure 2. After 16 h (Figure 2a), the OH bands and the Al–O overtone at 1510 cm^{-1} (see inset) are yet stronger, but signs of the onset of a phase transformation are also discernible. Weak, sharp features at 3656, 3548, and 3440 cm^{-1} can be seen

in the OH stretching region and a new peak at 980 cm^{-1} , all bands characteristic of bayerite $\text{Al}(\text{OH})_3$ included for comparison (Figure 2c). After 24 h, the spectrum (Figure 2b) indicates that the crystallization process is essentially complete. This result is generally in line with the extensive literature available on the chemical complexity of aluminas (24, 31). For example, a recent paper on the gelation of aluminum hydroxide sols from the *sec*-butoxide, under similar conditions, also reports the initial formation of an amorphous oxyhydroxide which undergoes dissolution-crystallization to bayerite upon aging (32).

According to the elemental analysis data, the first hydrolysis product encountered here has an Al:O ratio very close to 1:2, e.g. $S_4 = 1:2.1$, $S_8 = 1:1.9$, indicating an elemental formula of $\text{AlO}(\text{OH})$. The H analyses do not correlate so precisely, probably on account of sensitivity problems. However, all the indications from the IR spectra are that there is a simple accumulation of a monophasic product up to the point where the transformation to bayerite ensues, i.e. above 8 h of reaction. Thus, the first stage of the degradation process can perhaps be represented as



As the NH_3 accumulates and raises the pH via the secondary reaction



the crystallization step to bayerite becomes favorable.

In view of the steady growth of the OH stretching band with reaction degree, as indicated by O content, it was considered appropriate to assess the potential of the DRIFT technique for quantitative analysis. Under normal circumstances, the OH band is of limited use in this respect due to its susceptibility to H-bonding effects as manifested in peak shifts and, often, dramatic changes in extinction coefficient (33). In this case, however, the OH band shape remains remarkably stable, showing only a slight change for reaction times up to 8 h.

Peak integration from 3800 to 2400 cm^{-1} , incorporating a minor base-line correction, was performed on three replicate samples (10% in KBr) at each stage up to 8 h of reaction time and plotted against percent O content. The resulting curve, fitted by using simple linear regression statistics, shows good linearity, with a correlation coefficient of 0.995 (taking mean values of peak area) and a standard error on the slope of $\pm 7\%$ (95% confidence level). The linear fit is not entirely satisfactory as there is a small negative intercept at the origin. This may arise from the nonideality of the peak area values at high O levels, as chemical intuition suggests an increasing molar extinction for the OH stretch would be quite likely from H-bonding considerations.

The spread of successive measurements on each sample was relatively high at $\pm 10\%$. In the opinion of these authors, by far the major contributory factor to the analytical error is sample loading and packing. This inference is drawn from the fact that when two different samples at equivalent O content were compared, i.e. those taken through the entire process of weighing, grinding, and mixing etc., the mean values obtained were typically consistent to better than 5% relative. In contrast, the precision of six measurements on any one sample (obtained by successive emptying and reloading) was always of the order of $\pm 10\%$.

The inhomogeneous nature of the samples, i.e. the existence of an outer shell of hydrolysis product surrounding an inner core of unreacted AlN, also provides a model system to assess the effect, if any, of such a distribution on the optical (IR) response. It has already been reported elsewhere that the sensitivity advantage for the detection of a surface-deposited species is roughly 4 times that for the same amount distributed evenly through the bulk (2). This has been interpreted in

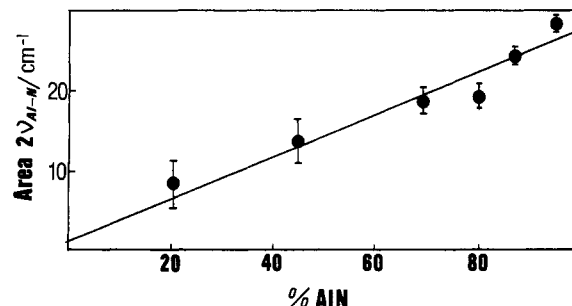


Figure 3. Plot of Al-N stretch overtone peak area (1330 cm^{-1}) vs residual AlN content.

terms of an effective multipassing of the exciting light due to external, and possibly internal, reflection phenomena. From similar considerations, it can be envisaged that the outermost layer (or layers) of the ingrowing monohydroxide shell might show a surface-specific enhancement in response. The corollary of this picture is that the core material may become progressively "hidden" due to specular reflection at the solid-solid interface. As this specular component is a function of differences in, inter alia, the mean angle of incidence (which should in turn be a function of angle of curvature at the interface), the "hiding power" of the shell may be expected to increase with the degree of reaction, i.e. a calibration plot of analyte band absorption vs residual AlN would be a curve which deviates positively from linearity.

Evidence for "surface sensitivity" should be manifested in the calibration curve already described. However, the simple linear plot indicates that such an effect, if present, does not contribute significantly to the measurement. As a check on the self-consistency of the spectral data, the second possibility of a "hidden-" or "suppressed-core response" was also examined. The Al-N stretching overtone at 1330 cm^{-1} was selected as the analyte band. Due to a certain loss of spectral definition at high reaction degree, i.e. for reaction times greater than ~ 16 h (or 50% conversion), a gentle deconvolution treatment was applied through the series. Over the spectral range 1800 – 800 cm^{-1} , the fitting parameters used were a Lorentzian line shape and a half-bandwidth of 20 cm^{-1} . Base-line correction was made from 1700 to 1270 cm^{-1} and peak integration from 1355 to 1275 cm^{-1} . The resulting curve (Figure 3) can be fitted to a straight line, as drawn, although it must be admitted that the most reliable points, i.e. those for high AlN content, tend to fall on a line of greater slope. In view of the nonideal fit (correlation coefficient = 0.95) and the band definition uncertainty, no strong conclusion can be made other than that if such an optical effect is present, then it does not markedly influence the analytical result. A more-definitive answer may ultimately be forthcoming from studies on simpler model systems.

It can be concluded that the utility of the DRIFT technique, as applied here to bulk analysis of inhomogeneous samples in the size range of $1\text{ }\mu\text{m}$, does not seem to be susceptible to artifacts such as those considered above. As the problem of inhomogeneity may often be encountered in the fields of, e.g. powder processing and corrosion, DRIFT would appear to be assured of an important future role in analytical science. The major limitation in its application to quantitative analysis is reproducibility of sample packing, but extensive investigations are under way in this laboratory (34) and elsewhere into gaining a better understanding and control of this problem.

ACKNOWLEDGMENT

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Registry No. AlN, 24304-00-5; Al(OH)₃, 21645-51-2; water, 7732-18-5; bayerite, 20257-20-9.

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Theoretical and Practical Aspects of Short Open Tubular Columns at Subambient Pressures in Gas Chromatography/Mass Spectrometry

Mark E. Hail¹ and Richard A. Yost*

Department of Chemistry, University of Florida, Gainesville, Florida 32611

Various theoretical and practical aspects of the use of short open tubular columns in gas chromatography/mass spectrometry (GC/MS) are discussed, including the advantages of low-pressure operation with short and/or wide-bore open tubular columns. It is shown that short columns with vacuum outlet require subatmospheric inlet pressures if optimum gas velocities are to be obtained. Since subatmospheric inlet pressures are not obtainable with most gas chromatographic inlet systems, a computer-controlled flow control system has been investigated that allows the injection port to be operated at subambient pressures with either split or splitless injections. Plate heights have been experimentally determined at subambient pressures and have been compared with theoretical predictions. The effects of extracolumn band broadening are evident in the experimental data and demonstrate the need for high-speed injection systems if maximum performance is to be obtained with short columns. The use of subambient inlet pressures is also shown to improve the sensitivity when short columns are used with electron ionization in GC/MS. Finally, it is shown that hydrogen carrier gas can be used to obtain the fastest analyses without altering the relative abundances of ions obtained with methane chemical ionization mass spectrometry.

Many of the chromatographic separation techniques currently in widespread use employ high inlet pressures, namely, high-pressure liquid chromatography (HPLC), supercritical fluid chromatography (SFC), and even high-resolution (open tubular) gas chromatography (HRGC). In contrast, research in the area of low-pressure separation techniques has been limited. More than 25 years ago, Giddings demonstrated that the minimum analysis times in gas chromatography (GC) can be obtained when the column outlet is connected to a vacuum (1). To date, a majority of the research done in high-speed GC has dealt with the use of small diameter columns and the development of high-speed injectors required for use with these columns (2-8). Recently, interest in vacuum outlet operation has been renewed, as Leclercq and co-workers have published a number of articles that have addressed the theory and advantages of vacuum outlet operation for improving the speed of analysis in open tubular GC (9-12).

Vacuum outlet operation in gas chromatography results in lower column pressures, which increases the diffusivity of the solute in the gas phase and leads to increased optimum carrier gas velocities and shorter analysis times (9). The advantages of vacuum outlet operation are inherently obtained when gas chromatography is combined with mass spectrometry (GC/MS), provided the column is inserted directly into the vacuum of the mass spectrometer. Consideration of the theory indicates that low outlet pressure operation has a more pronounced effect if wide-bore columns (14) and/or short columns (11) are used. Application of short columns with conventional

* Author to whom correspondence should be addressed.

¹ Current address: Finnigan MAT, 355 River Oaks Parkway, San Jose, CA 95134.