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New Molecular Precursors from the Reaction of Hydrazine and Aluminum Alkoxide for the Synthesis of Powders in the Al−O−N System

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A novel low-temperature sol−gel-based process has been developed for the synthesis of amorphous and crystalline powders in the Al−O−N system. The process involves reacting aluminum tri-*sec*−butoxide with anhydrous hydrazine using a solvent mixture of acetonitrile (ACN) and chloroform (at ≈60 °C) to result in solid precursors. The as-prepared precursors have been pyrolyzed in nitrogen and in anhydrous ammonia to yield amorphous and crystalline oxynitride or nitride powders. The powders have been characterized using X-ray diffraction (XRD), fourier transform infrared (FTIR), and ^{27}Al magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy techniques. Results of the structural spectroscopic analyses conducted on the pyrolyzed powders obtained at 800 °C indicate the formation of an amorphous or nanocrystalline aluminum oxynitride containing Al bonded to O in buta-, penta-, and hexacoordination. Evidence is also presented suggesting the influence of hydrazine in facilitating replacement of the butoxy groups during heat treatment and creating molecular species containing Al−N linkages in the solid precursor. Continued heat treatment of these precursors in NH$_3$ at 1300 °C leads to the formation of crystalline AlN. The role of hydrazine in the formation of the nitride was also verified by conducting the reaction using controlled amounts of deionized (DI) water. The addition of water competes with the nitridation ability of hydrazine leading to the formation of either oxides or oxynitrides of aluminum. The approaches thus developed demonstrate the potential and flexibility of alkoxides for synthesizing precursors that lead to either single phase of AlN or molecularly mixed composites of Al$_2$O$_3$, AlON, and AlN, in the Al−O−N system.

Introduction

The use of alkoxide chemistry has become an attractive method for synthesizing oxide materials especially with the success of sol−gel science and technology to synthesize refractory and difficult to melt glass and ceramic phases.[1] Similar chemical routes for the synthesis of non-oxide materials, such as the sulfides and nitrides, remain somewhat unexplored largely due to the formidable problems in the chemistry of precursors suitable for the non-oxidic compounds, especially the known reactivity of −OH moieties with the precursors. The reactive metal centers in the alkoxides are prone to nucleophilic attack (by H$_2$O, RSH, H$_2$S, and R$_2$NH) leading to the formation

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of metal—anion bonds at very low temperatures in solution. As a result, these compounds are extremely attractive for the synthesis of nonoxide ceramics, particularly nitrides and sulfides. We have demonstrated the applicability of these compounds for the synthesis of sulfides of reactive metals, such as the rare earths, and recently we have also developed a thio–sol–gel process and demonstrated its potential for the synthesis of transition metal sulfides.[2,3] We have also shown the ability of the thio–sol–gel process to alter the stoichiometry, morphology, and microstructure of the evolved sulfide ceramic.

The unique strength of the thio–sol–gel process is the excellent control of stoichiometry, morphology, and microstructure of the sulfide obtained by heat treatment of a single precursor derived from the alkoxide. However, in the case of nitride ceramics, apart from some reports on the reactions of the alkoxide-derived gels of silica with ammonia as indicated above, there has not been any study related to the direct reaction of alkoxides with nitrogen-containing reagents in solution with the aim of forming precursors containing either directly bonded metal-nitrogen linkages or a uniform molecular distribution of nitrogen. The introduction of nitrogen into the alkoxide-derived gel network provides unique opportunities for synthesizing amorphous and crystalline oxynitride and nitride ceramics. At the same time, the approach also provides the flexibility to synthesize either composites containing distinct glass and ceramic phases or a glass—ceramic composite containing an internally nucleated crystalline nitride phase well distributed in the amorphous oxynitride structural framework.

There has been considerable interest in recent years on the processing of multianion oxide glasses formed by substituting oxygen with nitrogen and/or carbon, mainly to increase the stability, oxidation resistance, and high-temperature mechanical properties.[4–7] The refractory properties of these glasses arise because of the more covalent nature of metal—nitrogen and metal—carbon bonds. As a result, these glasses are known for their improved hardness and abrasion resistance.[8] However, the refractory nature of the nitrides and carbides coupled with the inert nature of nitrogen makes it extremely difficult to process the amorphous or crystalline forms of these materials at moderate (≈1000 °C) temperatures.[9] Conventional approaches to synthesize these non-oxides consist of reacting the metal oxides, carbides, and nitrides at elevated temperatures (>1700 °C). A further reduction in processing temperatures (to 900–1000 °C) has been achieved in the case of silicon oxynitride glasses. In this process, nitrogen is incorporated by mainly reacting porous oxide glasses[10] and high-surface-area alkoxide-derived gels[11] with ammonia. Brinker et al.[11] have discussed the reaction of silica gels with ammonia and have found that the presence of B and/or Al promotes the incorporation of nitrogen in these gels at temperatures below 1000 °C.[11]

In recent years, alternate chemical routes based on modification of the traditional sol—gel process have also evolved which offer much improved flexibility with regard to the synthesis of these materials. For example, Zhang et al.[12] have synthesized glasses in the Si—O—C system by pyrolyzing gels derived from hydrolysis and condensation of alkyltrimethoxysilanes. They have shown that in their reactions only the methoxy groups participate in the hydrolysis and condensation processes ensuring the presence of the silicon-alkyl bonds in the gel stage. The presence of these directly bonded silicon-alkyl links in the room temperature-derived precursors promotes the formation of Si—C bonds in the Si—O—C glass network during subsequent pyrolysis. Silicon—oxycarbide glasses have also been reported to be synthesized by pyrolysis of commercially available resins.[13]

In the present paper, we demonstrate another potential of metal alkoxides for synthesizing non-oxide nitrides of reactive metals such as aluminum. Accordingly, we have shown that the alkoxide can be reacted with nitrogen-containing reagents, such as hydrazine, in solution to facilitate the formation of molecular species containing Al—N linkages in the solid precursor leading to the formation of oxynitride (Al—O—N) glasses and AlN ceramics. Hydrazine (N_2H_4) is a strong nucleophile and has a tendency to form adducts with several metalorganic compounds. Bains and Bradley[14] in the past have studied the reactions of aluminum, titanium, and zirconium alkoxides with hydrazine and they have identified adducts of the type $Al(OR)_3 \cdot xN_2H_4$ ($1 \leq x \leq 2.5$) in the case of the reaction of aluminum alkoxides with hydrazine. However, these reactions have not yet been investigated further with regards to the formation of nitride and oxynitride glasses and ceramics. In the present study, we have investigated the reaction of aluminum tri-*sec*-butoxide [$Al(OC_4H_9)_3$] with hydrazine (N_2H_4) and have studied the pyrolysis of the precursors formed in ammonia and nitrogen atmospheres. The reactions have also been monitored by controlled addition of water to study the influence of hydrazine on the formation of nitride and oxynitride phases. X-ray diffraction (XRD), fourier transform infrared (FTIR), and ^{27}Al magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy have been used to identify the evolved phases and to aid in the understanding of the molecular changes occurring in the precursors during nitridation.

Experimental Section

I. Powder Synthesis. Two different processes were employed for synthesizing the solid precursors. The first process (process I) consisted of reacting aluminum alkoxide (aluminum tri-*sec*-butoxide) with hydrazine, while the second process (process II) involved the addition of controlled amounts of water to enable the observation of its influence on the nitridation potential of hydrazine.

Process I. All of the reactions in this process were conducted in the absence of air and moisture. On the other hand, the second process involved conducting reactions with the addition of controlled amounts of water in the absence of air in order to aid in the understanding of the role of hydrazine as a nitriding agent. *It must be noted that hydrazine is a very toxic chemical and its vapors could be explosive if brought in contact with air, and therefore, extreme care must be exercised in handling it.* The experimental procedure followed is described below.

Aluminum tri-*sec*-butoxide ($Al(OC_4H_9)_3$, Aldrich, 97%) was dissolved in a mixture of acetonitrile (HPLC grade) and chloroform (HPLC grade) and heated to ≈60 °C for 30 min. Anhydrous hydrazine (N_2H_4, Aldrich, 98%) was then added dropwise to the solution to achieve a hydrazine:butoxide molar ratio of 5:1. After few minutes, a turbid solution resulted owing to the precipitation of a solid. (The reaction of the butoxide with hydrazine was also conducted in benzene and in tetrahydrofuran using similar conditions. However, no precipitate was observed, even after refluxing the solution for 40 h). The reaction was allowed to continue at the same temperature for 6–12 h after which the liquid was distilled under flowing ultrahigh purity nitrogen (UHP-N_2). The precipitate was dried under vacuum at ≈120 °C. This powder was still highly reactive and hence could not be exposed to air to prevent oxidation and loss of nitrogen. In addition, exposure to air could cause the release of hydrazine due to hydrolysis of the solid. Extreme precautions were therefore taken while handling the precursor powders to prevent any exposure to moisture.

Powder Synthesis in the Al−O−N System

J. Phys. Chem. B, Vol. 101, No. 24, 1997 **4691**

This dried powder was further heated at 800 °C for 10 h in flowing NH_3 (labeled as "HZ-NH_3-800") and in flowing UHP-N_2 (labeled as "HZ-N_2-800"), employing a heating rate of 2 °C/min. The powders pyrolyzed in NH_3 were gray and those pyrolyzed in UHP-N_2 were black in color. The precursor was also heat treated at 1300 °C for 15 h in flowing NH_3 using a heating rate of 5 °C/min up to 800 °C and 1 °C/min up to 1300 °C and has been labeled as "HZ-NH_3-1300". The temperature of 1300 °C was chosen in order to ensure complete crystallization of the resultant phases.

Process II. In the second approach, three different precursors were generated using excess anhydrous hydrazine, DI water, and a mixture of anhydrous hydrazine and water, respectively. Water was chosen in this approach to initiate hydrolysis and thereby allowed the observation of its effect on the nitridation reaction of hydrazine. A series of these reactions were selected mainly as a control experiment to test the role of hydrazine as a nitriding agent in its reaction with alkoxide and to also demonstrate the flexibility of this process to synthesize oxide, oxynitride, and nitride ceramics. All the precursors in these experiments were generated using aluminum tri-*sec*-butoxide. Similar to process I, the alkoxide was first dissolved in a mixture of distilled acetonitrile (HPLC grade) and chloroform (HPLC grade) and heated to ≈60 °C for 30 min. The first precursor was then synthesized by adding excess anhydrous hydrazine to the solution employing a hydrazine:butoxide molar ratio of 5:1 in order to initiate precipitation. This precursor is denoted as "HZ" (hydrazine) in all the discussion hereafter. The second type of precursor referred to as "HZ+WT" (hydrazine and water) in the subsequent discussion was generated by introducing a small amount of DI water to partially hydrolyze the alkoxide, while maintaining the same molar ratio of hydrazine:butoxide (5:1) that was used to obtain the first type of precursor. The molar ratio of water:butoxide was set at 1:5 in this approach.

The third type of precursor was synthesized by adding only excess water to the solution of alkoxide in a mixture of acetonitrile and chloroform in order to initiate the hydrolysis and condensation reactions and to yield a solid gel similar to the well-known solution sol−gel process.[15] A water:butoxide molar ratio of 10:1 was used to generate this precursor, which is referred to as "WT" (water) in the discussion to follow. In all three processes, the reaction was allowed to continue at the same temperature after addition of anhydrous hydrazine or a mixture of hydrazine and water for 6−12 h, following which the liquid was distilled under flowing ultrahigh purity nitrogen. The precipitates were then dried under vacuum at ≈120 °C.

All the three precursors were heat treated in flowing NH_3 at 1300 °C for 15 h (referred to as "HZ-NH_3-1300", "HZ+WT-NH_3-1300", and "WT-NH_3-1300") using a heating rate of 5 °C/min up to 800 °C and 1 °C/min up to 1300 °C in flowing NH_3.

II. Characterization. Infrared (IR) spectroscopic analyses were conducted on all the precursors generated using the first process. Transmission infrared spectra (using a Mattson Galaxy Series 5000 FTIR spectrometer) were collected on the dried precursor, HZ-NH_3-800 and HZ-N_2-800 samples in the 4000−400 cm^{-1} spectral range using the KBr pellet technique. These three powders were also chemically analyzed by Galbraith Laboratories (Knoxville, TN) for Al, N, C, and H contents.

All the precursors generated using the two different approaches, as well as the powders obtained after the respective heat treatments mentioned above, were studied for their phase evolution and crystallization characteristics using X-ray diffraction. The X-ray diffraction patterns were obtained on the heat-treated samples using a Rigaku θ/θ diffractometer (Cu Kα radiation, $\lambda = 1.5418$, equipped with a diffracted beam graphite

TABLE 1: Results of Chemical Analysis of the As-Prepared Precursor and Products Pyrolyzed at 800 °C

wt %	Al	N	C	H
precursor	2.4	48	40.5	7.1
N_2-800 (black)	36.7	7.6	10.1	0.6
NH_3-800 (pale gray)	38.0	1.3	1.8	1.9

monochromator). X-ray analysis was not conducted on the as-prepared precursors obtained using hydrazine, owing to its reactivity and potential hazards on exposure to moisture.

^{27}Al MAS-NMR spectra were obtained on the HZ-NH_3-1300, HZ-NH_3-800, HZ-N_2-800 samples as well as on a commercial AlON sample manufactured by Raytheon for comparison, (labeled as "AlON-R"). The spectra were recorded at 104.3 MHz with a Chemagnetics CMX-400 spectrometer and a sample probe configured for 4 mm o.d. rotors. The MAS rates were about 17 kHz. No significant [27]Al background was observed for this configuration.

The spectra were obtained with single-pulse excitation under quantitative run conditions with pulse widths of 0.5 μs, where the nonselective 90° pulse was 12 μs. Recycle delays varied from 0.5 to 10 s, depending on the relaxation rate, which varied widely between samples.

The MAS-NMR spectra contain center bands and spinning sidebands (SSB) arising from the central transition ($^1/_2$, $-^1/_2$), in addition to satellite transition SSBs (primarily the transitions $\pm(^3/_2, ^1/_2)$). The central peaks are shifted upfield from the isotropic chemical shift by an amount proportional to the square of the ratio of quadrupolar coupling constant (C_q) to Larmor frequency, in relative units (parts per million, ppm). The peak positions correspond to those observed at 104.3 MHz with the understanding that these values differ slightly from the isotropic chemical shifts.

Results and Discussion

Results of the chemical analysis conducted on the precursor powders obtained by the reaction of the alkoxide with anhydrous hydrazine in the first process are shown in Table 1. It can be seen that the precursor contains significant amounts of nitrogen (48 wt %) and carbon (40.5 wt %) probably originating from hydrazine, acetonitrile, chloroform, and the unreacted *sec*-butoxy groups. It should be noted that the detection of only 2.4 wt % of Al is a reflection of the large amounts of nitrogen and hydrocarbons contained in the as-prepared precursor. The precursor can therefore be considered as a metalorganic complex of Al containing N, H, C, and O. However, the presence of these molecular units play an important role in the transformation of the precursor to form the nitride.

In order to identify the nature of bonding of nitrogen, the precursor was analyzed using IR spectroscopy. The IR spectrum of the precursor in the range of 4000−400 cm^{-1} (Figure 1) shows NH_2 bending vibrations[16−18] at 1650 cm^{-1} (which could include contributions from δ_{N-H}) and 1540 cm^{-1}, ν_{N-H} at 3444 cm^{-1}, and δ_{N-N} around 970 cm^{-1}. The absorption around 2350 cm^{-1} arises due to CO_2, while the vibration centered around 760 cm^{-1} has been assigned to the ν_{Al-N} vibration as reported by Paterson and Onyszchuk.[18] The observation of Al−O vibrations[19] at 480 and 600 cm^{-1} could be due to the presence of unreacted butoxy groups still bonded to Al. On the basis of IR and chemical analysis (presented in Table 1) results of the precursors and the work of Bains and Bradley,[14] it appears that the precipitate has resulted due to the formation of adducts $[Al(OC_4H_9)_3 \cdot N_2H_4]$ of hydrazine with the butoxide. However, it is difficult to ascertain the exact formulas of the adducts on the basis of the chemical analysis due to the presence of
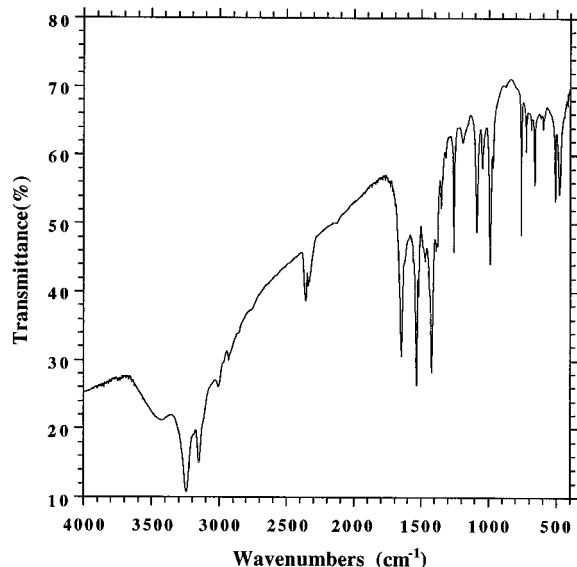
Figure 1. IR spectrum of the as-prepared precursor prepared by reacting aluminum tri-*sec*-butoxide with hydrazine. The spectrum shows N$-$H (1650 and 1540 cm^{-1}) and Al$-$N (760 cm^{-1}) vibrations. (See text for more details.)

acetonitrile in the as-prepared precursor, which leads to high N (48 wt %) and C (40.5 wt %) contents as listed in Table 1. The formation of such adducts should facilitate the replacement of the alkoxy groups by hydrazide species during subsequent heat treatment, leading to the formation of oxynitride and nitride ceramics. The occurrence of such a replacement reaction during heat treatment is very plausible mainly because of the large amounts of nitrogen (48 wt %) contained in the precursor. Thus, the reaction of hydrazine with aluminum alkoxide offers the possibility of generating new molecular precursors for the synthesis of oxynitride and nitride materials. The present paper illustrates the potential of these new molecular precursors.

Samples designated HZ-NH$_3$-800 and HZ-N$_2$-800 generated from precursors using the first approach show X-ray diffraction patterns characteristic of amorphous materials as shown in Figure 2. Table 1 also shows the results of chemical analyses conducted on these powders. The HZ-NH$_3$-800 sample shows a lower carbon content in comparison to that of HZ-N$_2$-800 (due to the reducing nature of ammonia which causes the removal of carbon by the formation of HCN: NH$_3$ + C $\rightarrow$ HCN).[20] Another observation that can be made from the results of the chemical analysis is that the heat treatment in NH$_3$ also yields a product with a significantly lower nitrogen content. This reduction (along with the nature of C, H, and N bonding in the powders) can be explained on the basis of IR spectroscopic analysis of these powders (shown in Figure 3). The assignment for the peaks observed in Figure 3 and the corresponding references are listed in Table 2.

The IR spectra obtained on the HZ-NH$_3$-800 and HZ-N$_2$-800 samples shown in Figure 3 indicate four interesting features: 1. In the range of 3500 to 2500 cm^{-1}, spectra for both the HZ-N$_2$-800 and HZ-NH$_3$-800 samples show a broad vibration at 3440 cm^{-1} which corresponds to the stretching vibration of N$-$H bonds.[16,17] In addition, the spectrum for HZ-NH$_3$-800 exhibits C$-$H stretching vibrations at 2920 and 2860 cm^{-1} (as observed in the IR spectra of films prepared by plasma polymerization of acetylene[21]), which is not present in the spectrum collected on the HZ-N$_2$-800 sample. The observation of stretching vibrations due to bonded hydrogen in the samples heat treated in NH$_3$ is consistent with a larger hydrogen content detected in these samples by chemical analysis. The samples
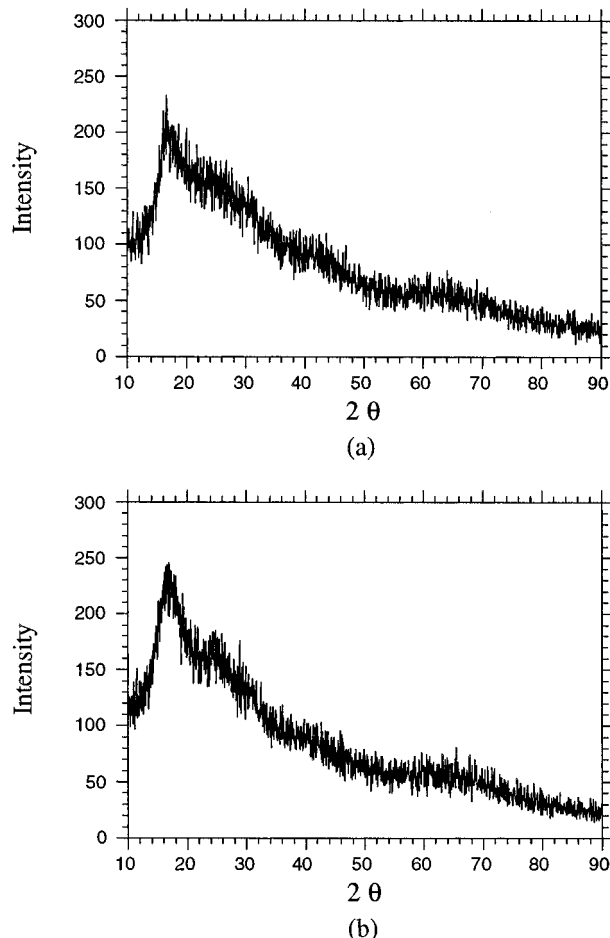

(a)

(b)

Figure 2. X-ray traces collected on the powders obtained from the reaction of aluminum tri-*sec*-butoxide and hydrazine (a) pyrolyzed in NH$_3$ (HZ-NH$_3$-800) and (b) in UHP-N$_2$ (HZ-N$_2$-800) at 800 °C for 10 h.
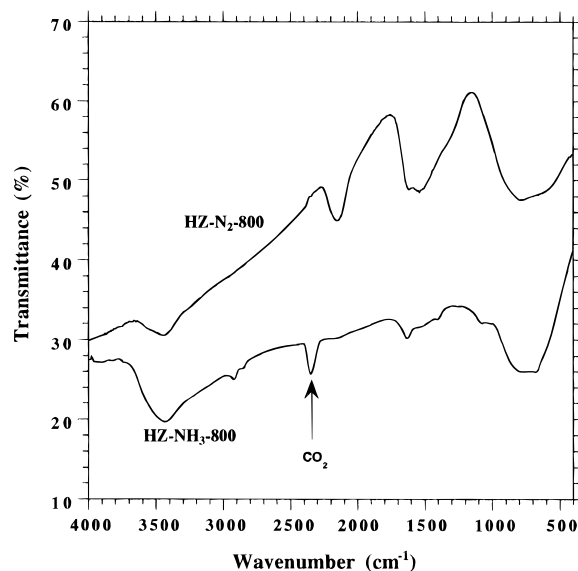

Figure 3. IR spectra collected on the powders obtained from the reaction of aluminum tri-*sec*-butoxide and hydrazine pyrolyzed in NH$_3$ (HZ-NH$_3$-800) and UHP-N$_2$ (HZ-N$_2$-800) at 800 °C for 10 h. (See text for assignment of various peaks.)

heat treated in NH$_3$ also show $-$CH$_3$ bending vibrations in the lower frequency range of the spectrum as explained below.

2. An intense vibration at 2160 cm^{-1} is observed in the spectrum of the HZ-N$_2$-800 sample and is also seen with a considerably lower relative intensity in the spectrum of the HZ-

Powder Synthesis in the Al−O−N System

J. Phys. Chem. B, Vol. 101, No. 24, 1997 **4693**

TABLE 2: Assignment of Peaks Observed in the IR Spectra Collected on the Powders Pyrolyzed at 800 °C

wave number (cm^{-1})	assignment	HZ-NH$_3$-800	HZ-N$_2$-800	ref
750	Al−N (or Al−O)	s^a	s	20, 26
1330	D (carbon vibration in disordered graphite)	N^b	vw^c (shoulder)	24, 25
1410	−CH$_3$ (bending)	w^d	N	21
1530	G (carbon vibration in graphitic carbon network modified by N atoms)	vw	w	25
1625	C=C($\nu_{C=C}$)	w	s	21
2160	C≡N($\nu_{C≡N}$)	vw	s	22, 23
2860	C−H(ν_{C-H})	w	N	21
2920	C−H(ν_{C-H})	w	N	21
3440	N−H(ν_{N-H})	w	w	16, 17

^{a} s, strong intensity. ^{b} N, no intensity. ^{c} vw, very weak intensity. ^{d} w, weak intensity.

NH$_3$-800 sample. This absorption is due to the stretching vibration of the C≡N triple bond ($\nu_{C≡N}$),[22,23] suggesting the presence of terminal nitrogen bonds on the carbon residue within the structure obtained after pyrolysis. The low intensity of the C≡N vibration certainly indicates few terminal N atoms in the HZ-NH$_3$-800 sample, which is in agreement with a lower N content reflected in the chemical analysis of these powders.

3. The third feature is the set of broad bands in the range of 1700−1250 cm^{-1}. The vibration at 1625 cm^{-1} is observed in both the powders (with a lower relative intensity in the powder pyrolyzed in NH$_3$) and corresponds to $\nu_{C=C}$.[21] In the HZ-N$_2$-800 spectrum, there is also a peak at 1530 cm^{-1} with a shoulder at 1330 cm^{-1}. The absorption at 1330 cm^{-1} corresponds to carbon vibrations in disordered graphite,[24,25] and the one at 1530 cm^{-1} corresponds to the carbon vibrations in a graphitic carbon network modified by nitrogen atoms[25] (as observed in products obtained after pyrolysis of nitrogen containing hydrocarbons). In the spectrum of the HZ-NH$_3$-800 sample, the absorption at 1530 cm^{-1} is very weak and the absorption at 1330 cm^{-1} (due to disordered graphite) is absent. However, the absorption at 1410 cm^{-1} due to −CH$_3$ bending vibrations[21] implies bonded hydrogen consistent with the chemical analysis data discussed earlier and shown in Table 1.

4. The fourth feature is, of course, the broad band centered around 750 cm^{-1}, which could correspond to the presence of Al−N bonds, although both Al−O and Al−N vibrations occur in this region (as observed in γ-Al$_2$O$_3$ and γ-AlON).[19,26]

Thus, on the basis of the IR and chemical analysis results discussed above, it can be seen that pyrolysis of the precursor in N$_2$ generates an amorphous powder containing larger amounts of C and N in comparison to the precursor pyrolyzed in NH$_3$. Heat-treatment of the precursor in NH$_3$, on the other hand, also results in an amorphous powder, but with significant reduction in the carbon (461%) and nitrogen (484%) contents as expected. At the same time, there is a corresponding increase in the hydrogen content (~200%) consistent with the IR analyses. The results of chemical analysis supported by IR data suggest that the precursor is mostly formed as a result of the formation of adducts of the alkoxide with hydrazine and acetonitrile. Infrared analysis fails to unequivocally isolate the presence of Al−N vibrations due to their strong overlap with Al−O vibrations centered at 750 cm^{-1}. Hence, the exact role of hydrazine on the formation of Al−N linkages in the as-prepared precursor and in the powder obtained after heat treatment in N$_2$ at 800 °C could not be ascertained, although chemical analysis of the precursors and corresponding powders have revealed significant amounts of nitrogen. In order to further elucidate the role of hydrazine in determining the final pyrolysis product, ^{27}Al MAS-NMR spectra were obtained for HZ-NH$_3$-800 and HZ-N$_2$-800, HZ-NH$_3$-1300, and for comparison, a crystalline, optically transparent sample of γ-AlON (AlON-R). These spectra are shown in Figure 4. The AlON-R sample gives a peak for AlO$_4$
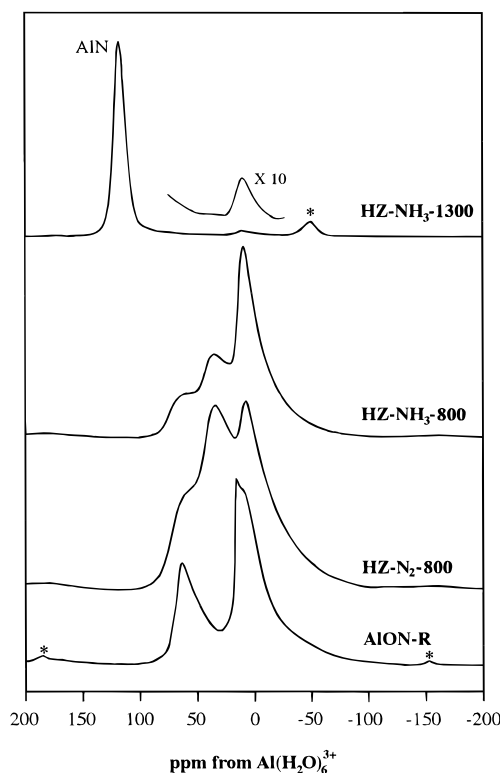

Figure 4. ^{27}Al-NMR spectra of γ-AlON (AlON-R), precursors pyrolyzed in NH$_3$ at 800 °C (HZ-NH$_3$-800) and at 1300 °C (HZ-NH$_3$-1300) and in N$_2$ at 800 °C (HZ-N$_2$-800). Data obtained with single-pulse excitation at 130.3 MHz with 10 kHz spinning rate. Spectra for all samples except HZ-NH$_3$-1300 display a broad unresolved central component. (Asterisks denote spinning sidebands).

environments near +66 ppm plus a signal for AlO$_6$ that comprised a narrow peak at +14 ppm plus a broader peak centered near +6 ppm, with a large tail toward low frequencies arising from a distribution of C_q values. These relatively narrow MAS peaks occur atop a broad, unresolved absorption that contains approximately 20% of the total signal. This broad component is due to distorted Al sites that exhibit C_q values greater than about 12 MHz. These results for γ-AlON are generally in agreement with previous results,[27,28] although we do not observe a peak due to AlN$_4$ environments (+113 ppm) that was reported in earlier studies but may have resulted from the presence of unreacted AlN. Conspicuously absent from this spectrum is any peak that can be attributed specifically to Al coordinated to N, even though such environments must be present, considering that the composition is 34 wt % AlN. Mixed anion environments (i.e., Al(O,N)$_4$) have been observed by ^{27}Al MAS-NMR in sialon materials,[27,29] but the present result suggests that, even in homogeneous oxynitrides, such Al sites might exhibit C_q values too large to produce a resolvable ^{27}Al MAS-NMR peak.

The samples HZ-NH$_3$-800 and HZ-N$_2$-800 display very similar ^{27}Al MAS-NMR spectra, showing distinct peaks for AlO$_4$ (+60 ppm), AlO$_5$ (+33 ppm), and AlO$_6$ (+6 ppm) environments, overlying a broad unresolved absorption arising from distorted sites. The spectra of these two samples differ primarily in the relative intensity of the AlO$_6$ peak, which is about twice as large as that in the HZ-NH$_3$-800 spectrum . All of these NMR peaks are asymmetrical, with the tail extending to low frequency as is typical for a distribution of C_q values, making determination of relative peak areas highly uncertain. In addition, although no peaks are observed that can be attributed to Al bonded to N, this result must be viewed as inconclusive, based on the data discussed above for AlON-R. Assignment of the peak at +33 ppm to AlO$_5$ environments can be based on similar chemical shifts observed for crystalline oxides whose crystal structures are known to contain pentacoordinated Al.[30−32] Peaks with similar chemical shifts have been observed for a variety of disordered materials.[33−35] However, aluminum alkoxides might provide a more relevant comparison because they form complexes containing pentacoordinated Al that exhibit five chemical shifts in this range.[36] In particular, aluminum tri-*sec*-butoxide contains a trimer composed of edge-linked AlO$_4$ and AlO$_5$, that exhibit five chemical shifts near 62 and 44 ppm, respectively. These isotropic shifts are consistent with peak positions we observe, because the quadrupolar coupling shifts the peak position for solids upfield from the isotropic (solution-state) value. The peak position for AlO$_6$ (+6 ppm) is similar to that observed previously for alkoxide complexes[36] and for spinel-type oxides and oxynitrides, but differs significantly from the position for α-Al$_2$O$_3$ at this field, +12 ppm.[27] The spectrum of HZ-NH$_3$-1300 contains a sharp peak for AlN at +113 ppm[27] plus a minor peak for AlO$_6$ and a much smaller one for AlO$_5$ at the same positions as for HZ-NH$_3$-800.

The failure to observe any resonance peaks associated with Al coordinated to N for the HZ-N$_2$-800 sample combined with the IR and Chemical analyses results clearly confirm that the reaction of the alkoxide with hydrazine at ≈60 °C in the presence of acetonitrile and chloroform leads to the formation of a significant fraction of adducts with minimal or no replacement of the butoxy groups with hydrazide species. Heat-treatment in nitrogen at 800 °C leaves most of the nitrogen (7.6 wt %) bonded to carbon as evidenced by the intense vibration at 2160 cm^{-1} seen in the IR spectrum (see Figure 3) collected on HZ-N$_2$-800 sample. However, heat treatment in NH$_3$ helps in the removal of carbon and nitrogen while promoting the reaction of ammonia with the unreplaced butoxy groups to form metal amide (−M−NH$_2$) type species, which can subsequently condense to form AlN.

The IR and MAS-NMR results of the precursor and pyrolyzed products, therefore, lend credence to the inference of Bains and Bradley.[14] In order to ascertain the potential of these adducts and verify the influence of hydrazine as a nitride former, water was used to initiate hydrolysis and compete with the reaction of hydrazine to form adducts. Three different precursors were therefore generated using a new batch of aluminum tri-*sec*-butoxide. The reactions were conducted in an identical fashion, except that some water was introduced during the reaction. Water was added in controlled amounts to induce hydrolysis and compete with the reaction of the alkoxide with hydrazine in order to observe its effect on the formation of AlN and aluminum oxynitride. Such a reaction could therefore serve as a control experiment and provide an indirect confirmation regarding the role of hydrazine to form non-oxide nitride ceramics.

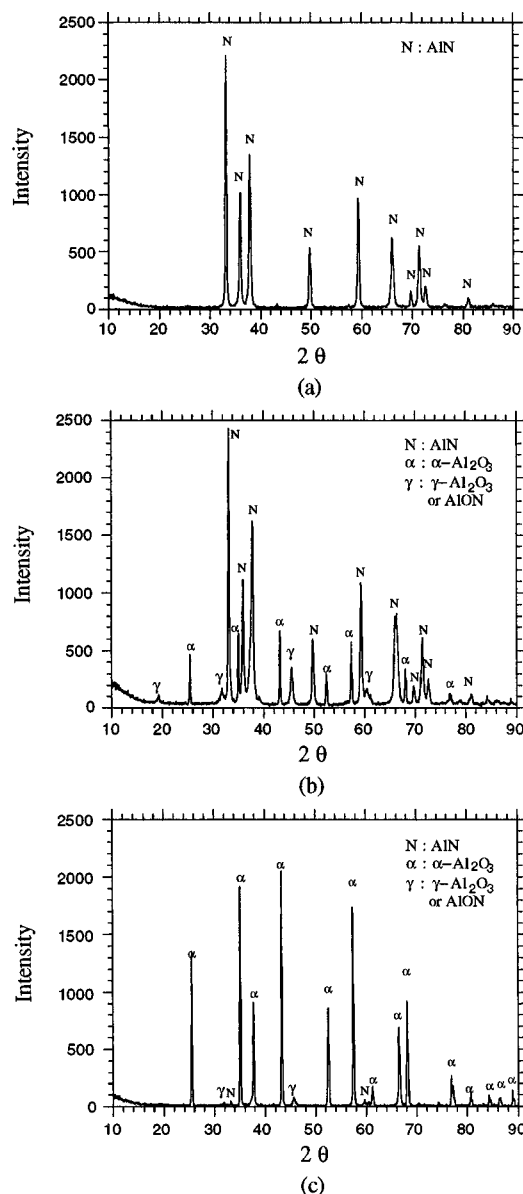Results of the XRD analysis conducted on the three different

Figure 5. X-ray traces of precursors heat-treated in NH$_3$ at 1300 °C for 15 h: (a) HZ-NH$_3$-1300, (b) HZ+WT-NH$_3$-1300, and (c) WT-NH$_3$-1300.

precursors generated with pure hydrazine, HZ, a mixture of hydrazine and water, HZ+WT, and pure water, WT heat treated in NH$_3$ at 1300 °C for 15 h, are displayed in Figure 5. Figure 5a shows the XRD pattern corresponding to single phase of hexagonal AlN from the HZ sample obtained by heat treatment of the precursor in NH$_3$ at 1300 °C. In the case of the HZ+WT sample synthesized using a mixture of hydrazine and water, the XRD pattern indicated a mixture of AlN and α-Al$_2$O$_3$ with a small amount of AlON or γ-Al$_2$O$_3$ after heat treatment of the precursors in NH$_3$ at 1300 °C for 15 h (Figure 5b). It is normally hard to distinguish AlON from γ-Al$_2$O$_3$ by X-ray diffraction since the peak positions of both phases are almost identical. However, it could be speculated that this phase (labeled as "γ" in Figure 5) is indeed AlON, which had not yet undergone decomposition to form AlN and α-Al$_2$O$_3$, since γ-Al$_2$O$_3$ is unstable at temperatures beyond 1000 °C. In the as-prepared precursors of the HZ+WT sample, some butoxy groups were replaced by hydroxyl groups from water, while the unhydrolyzed butoxy groups formed adducts with hydrazine. In this state, the precursor could be easily converted into AlON which undergoes decomposition into a mixture of AlN and α-Al$_2$O$_3$ at 1300 °C. Therefore, the phase labeled as "γ" in

Powder Synthesis in the Al−O−N System

J. Phys. Chem. B, Vol. 101, No. 24, 1997 **4695**

Figure 5 is probably the residual AlON phase which would undergo decomposition to AlN and α-Al$_2$O$_3$ on further heat treatment. On the other hand, the alumina precursor WT reveals the formation of α-Al$_2$O$_3$ as the major phase, obtained by heat treatment of the precursor under identical heat treatment conditions (Figure 5c). These results indicate that the addition of hydrazine and its reaction with the alkoxide alone must lead to the formation of Al−N linkages in the precursor during heat treatment in NH$_3$ that helps in its complete conversion into crystalline AlN.

The addition of excess water however, results in the formation of Al−O−Al linkages by the condensation of Al−OH groups in the precursor, which facilitates the crystallization of α-Al$_2$O$_3$ even after heat treatment of the precursor in NH$_3$ at 1300 °C for 15 h. Therefore, it can be concluded that addition of excess amounts of water results in the replacement of all or most of the butoxy groups with hydroxy groups in the WT sample, causing the formation of Al−O−Al bonds by condensation. These condensed units crystallize into α-Al$_2$O$_3$ during ammonia treatment at 1300 °C for 15 h. In the case of the HZ+WT sample, only partial amounts of butoxy groups could be replaced with hydroxyl groups by the addition of some water (butoxide: water molar ratio of 5:1). This leads to the formation of Al−O−Al linkages, while the addition of hydrazine (butoxide: hydrazine molar ratio of 1:5) could simultaneously result in the formation of adducts that promote the generation of Al−N linkages during heat treatment. Therefore, this sample reveals a mixture of both AlN and α-Al$_2$O$_3$ when heat-treated in NH$_3$ at 1300 °C.

It is interesting to note that the unreacted butoxy groups in the HZ sample were, however, almost completely converted into AlN when heat-treated in NH$_3$ at 1300 °C for 15 h, while the alumina precursor WT was not converted into AlN when heat-treated under similar conditions. A possible explanation for this observation is the characteristic linkage of oxygen with aluminum in the WT precursor that promotes the formation of the α-Al$_2$O$_3$ phase. In the case of the HZ sample, the only possible source of oxygen that could lead to formation of alumina is obviously the unreacted butoxy groups in the precursor. On the other hand, the alumina precursor WT has Al−OH linkages caused by the addition of water. Compared to the reactivity of the hydroxyl groups, the butoxy groups are much less conducive to condensation and formation of Al−O−Al linkages in the as-prepared powders. Thus, the HZ precursor generated by addition of only hydrazine contains unreacted butoxy group that probably do not condense to form Al−O−Al linkages in the precursors. The presence of these unreacted butoxy groups is better suggested by the AlO$_5$(Al(5)) NMR peak observed for the precursor heated at 800 °C. These Al(5) environments are likely to be remnant from the aluminum tri-*sec*-butoxide used in the reaction.[36] Furthermore, butoxy groups contain carbon, which helps in the removal of oxygen during ammonia treatments, facilitating the incorporation of nitrogen. The predominance of the AlO$_6$ (+6ppm) coordination in HZ-NH$_3$-800 is a reflection of the structural changes in the precursor due to nitrogenation since similar peak positions are observed in the cubic spinel forms of AlON.[27] On the other hand, the hydroxyl groups in the WT sample caused by the addition of water form strong Al−O−Al linkages during condensation which are more resistant to ammonia treatment at 1300 °C, leading to the formation of α-Al$_2$O$_3$ as the major phase.

The above results therefore confirm that the reaction of aluminum alkoxide with anhydrous hydrazine results in the formation of a metalorganic solid complex containing nitrogen

largely bonded to carbon. Heat-treatment of this precursor in NH$_3$ promotes the formation of Al−N linkages, thereby leading to the generation of AlN. In order to characterize the nitride phase, ^{27}Al MAS-NMR was conducted. The MAS-NMR spectrum recorded on the HZ-NH$_3$-1300 sample is also shown in Figure 4. The spectrum clearly reveals the well-resolved resonance peak at 113 ppm, which is the characteristic shift for crystalline AlN.[27] The XRD pattern obtained on this powder also shows hexagonal AlN consistent with the MAS-NMR data (Figure 5a). However, as shown in the MAS-NMR spectrum in Figure 4 (HZ-NH$_3$-1300), there is also a small band at 6 ppm consistent with the presence of a small amount of γ-Al$_2$O$_3$ or AlON. Thus, it can be seen that even though the reaction of aluminum alkoxide with hydrazine does not lead to the formation of directly bonded Al-N linkages in the as-prepared precursor; it facilitates the replacement of the alkoxy groups during subsequent heat treatment in NH$_3$, leading to the formation of AlN. At the same time, controlled addition of water competes with the adduct formation ability of hydrazine, thereby promoting the formation of either α-Al$_2$O$_3$ or a composite mixture of α-Al$_2$O$_3$, γ-AlON, and AlN. The present approach thus illustrates the potential of hydrazine as a nitride former in sol−gel processing and demonstrates its use in the reaction with aluminum butoxide for the synthesis of oxides, nitrides, and oxynitrides in the Al−O−N system. Following this work, we have also observed that AlN could be crystallized from the amorphous precursor by heat treatment in Ar at 800 °C itself. These results suggest a possible replacement of −OR groups with −NHNH$_2$ species. Results of this work will be described in a subsequent publication.

In summary, it can be seen that the reaction of aluminum alkoxide with anhydrous hydrazine results in the formation of a metalorganic solid complex due to the formation of adducts. The NMR analysis conducted on the powder heat treated in inert atmosphere (HZ-N$_2$-800) combined with the IR and chemical analyses clearly confirm that the reaction of the alkoxide with hydrazine at ≈60 °C in the presence of acetonitrile and chloroform results in the formation of a significant fraction of adducts with minimal or no replacement of the butoxy groups with hydrazide species. Heat treatment of this precursor in N$_2$ at 800 °C leaves most of the nitrogen (7.6 wt %) bonded to carbon as evidenced by the intense vibration at 2160 cm^{-1} seen in the IR spectrum (see Figure 3). However, heat treatment in NH$_3$ helps in the removal of carbon and nitrogen while promoting the reaction of ammonia with the unreplaced butoxy groups to form metal amide (−M−NH$_2$) type species. These amide species can subsequently condense to form crystalline AlN at high temperatures of 1300 °C.

On the other hand, addition of controlled amounts of water combined with excess hydrazine during the reaction initiates preferential hydrolysis and condensation and results in the formation of α-Al$_2$O$_3$ even after heat treatment of the precursor in NH$_3$ at 1300 °C for 15 h. Therefore, it can be concluded that the formation of adducts due to the reaction of hydrazine with aluminum alkoxide promotes the replacement of butoxy groups with hydrazide groups during heat treatment, resulting in the formation of Al−N linkages which convert into crystalline NH$_3$ at high temperature. Thus, these results validate the potential of this process for the synthesis of nitrides and oxynitrides and verify the role of hydrazine as a nitride former in sol−gel processing of oxynitrides and nitrides of aluminum.

Conclusions

The reaction of hydrazine with aluminum tri-*sec*-butoxide in a mixture of acetonitrile and chloroform causes the precipitation

of a solid precursor. Chemical analysis and IR and ^{27}Al MAS-NMR spectroscopic analyses of the solid confirmed the formation of an adduct as reported by Bains and Bradley.[14] Pyrolysis of this precursor to 800 °C in UHP-N$_2$ and NH$_3$ resulted in an X-ray amorphous powder. Chemical analyses revealed that the amorphous powder obtained after pyrolysis in NH$_3$ had lower carbon and nitrogen contents in comparison with that pyrolyzed in UHP-N$_2$. At the same time, FTIR analysis indicated that some of the nitrogen was bonded to carbon as terminal bonds in the powder obtained after pyrolysis. The presence of Al−N bonds could not be directly ascertained in the pyrolyzed powders using IR spectroscopy; however, MAS-NMR spectroscopy proved to be an excellent tool to characterize the structural changes undergone by the precursors during heat treatment, and to determine the local coordination of Al with respect to N and O atoms in the pyrolyzed precursors. The heat treatment of this precursor at 1300 °C in NH$_3$ for 15 h resulted in the formation of the hexagonal phase of AlN. On the other hand, the addition of controlled amounts of water resulted in precursors that facilitated the formation of α-Al$_2$O$_3$ or composites of α-Al$_2$O$_3$, γ-AlON, and AlN, thereby confirming the role of hydrazine as a nitride former in sol−gel processing. The sol−gel based approach described herein therefore offers excellent potential for the synthesis of nitrides and oxynitrides of oxophilic metals such as aluminum. Although nitrogenation of the alkoxide has been demonstrated by careful handling of hydrazine, it should be also possible to achieve similar results using other nitriding agents such as primary and secondary alkyl amines. This work is currently in progress and will be reported in subsequent publications.

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