Synthesis and Pyrolysis of Novel Polymeric Precursors to TiC/Al_2O_3, TiN/Al_2O_3, and AlN/TiN Nanocomposites

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The reaction between furfuryl alcohol (FuOH) and the products obtained by hydrolyzing a mixture of $Ti(O\text{-}n\text{-}Bu)_4$ and $Al(O\text{-}sec\text{-}Bu)_3$ resulted in the formation of soluble polymeric solids. Pyrolysis of these polymers in argon yielded TiC/Al_2O_3 composites at 1250-1375 °C; further heating the precursors to 1500 °C in argon led to the formation of a new phase due to the reaction between C, Al_2O_3, and TiC. When these polymers were pyrolyzed in ammonia or nitrogen, a TiN/Al_2O_3 or TiN/AlN nanocomposite was formed, depending on the concentration of FuOH in the polymers. All these composites exhibited a fine-grained microstructure and excellent homogeneity. Furthermore, the structure and pyrolysis chemistry of these polymeric precursors, as well as the microstructure of the pyrolysis products, were studied by FTIR, TGA, GC, XRD, SEM, TEM, STEM, Auger electron spectroscopy (AES), and elemental analyses.

Introduction

Ceramic matrix composites offer a method for improving the reliability of structural ceramics and are expected to have a promising future. It is well-known that the ceramic composites have exhibited superior mechanical properties and have potential applications as cutting tools or wear-resistant parts.[1-7] Preparation of these composites usually is achieved by typical powder processing procedures, including mixing, milling, drying, and subsequently requires sintering at elevated temperature, often under hot-pressing conditions. The grain sizes in these materials typically are larger than 1 μm. As performance requirements for advanced ceramics increase, controlling the distribution of phases and their grain sizes will become more important. For example, fabricating composites with controlled composition, nanosized grains,[8] or interpenetrating ceramic phases[9] will require developing new materials synthesis and processing techniques.

Various methods are currently being investigated to prepare ceramic-ceramic composites with finer grains and better homogeneity than can be achieved by mechanical mixing of commercially available ceramic powders. One approach to simplify the processing and improve composite properties is to use a composite powder. An aluminothermic method has been used to prepare a TiC/Al_2O_3 composite from a mixture of TiO_2, C, and Al.[10] A recent publication described an approach for synthesizing Al_2O_3/SiC composite powders by adding a source of carbon to aluminosilicates.[11] Chaklader et al. reported that the Al_2O_3/SiC composite powders could be hot pressed to obtain composites with >95% relative densities.

Even more versatile synthetic approaches are needed to prepare nanocomposites and multiphase coatings and fibers with controlled compositions and microstructures. Nanocomposites are materials where at least one of the phases has grain sizes in the nanometer range. Materials with nanosized grains are expected to have unusual and interesting properties. For example, they are expected to exhibit superplastic behavior[7] and have improved mechanical properties.[12] Sintered ceramics which have grain sizes less than 0.1-0.2 μm are difficult to prepare by powder processing methods and preparing such materials requires new materials synthesis and processing approaches.

Sol-gel methods have been used to produce materials with finer grains than can be obtained by powder processing methods. For example, a sol-gel processing method has been developed to prepare Al_2O_3/TiN, AlON/TiN, and AlN/TiN composites using a mixture of boehmite, TiO_2, and a particulate carbon source. The composites had fine-grained (100-200 nm) microstructures, good hardnesses, and excellent abrasive properties.[6]

An approach for preparing nanocomposites, where ideally at least one component has grains smaller than 100 nm, involves the synthesis, processing, and pyrolysis of preceramic polymers. Many preceramic polymers have been synthesized and studied as precursors for single phase ceramics, such as SiC,[13] and are currently being investigated as precursors for nanocomposites.[14,15] They also offer an approach for improving control over composition, grain size, and homogeneity as well as the potential for forming ceramics by polymer-processing methods.[16] In addition, polymeric precursors can be used to prepare powders, monoliths, fibers, and coatings at low processing temperature.

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Synthesis of ceramic/ceramic composites using polymeric precursors has been reported for systems such as SiC/SiO_2,[17] SiC/TiC,[18] SiC/Al_2O_3,[17], SiC/AlN,[19] Si_3N_4/AlN,[20] TiN/TiB_2,[15] BN/Si_3N_4,[21] and TiN/AlN.[14] Pyrolysis of these precursors has resulted in the formation of composites with fine-grained microstructures. Although precursors for TiN, TiC, and AlN have been reported,[22–25] no studies on the preparation and pyrolysis of metalloorganic precursors for TiC/Al_2O_3 or TiN/Al_2O_3 composites have been reported. The TiN/AlN composite has been previously prepared by pyrolysis of a titanium aluminum polyimide.[14] Jaschek and Rüssel[14] reported that a (Ti,Al)N solid solution formed upon pyrolysis of the polyimide. Preparation of the (Ti,Al)N solid solution from a polymeric precursor indicates their potential for forming materials which are difficult to prepare by conventional processing methods.

The purpose of the present study is to illustrate a flexible synthetic method for controlling the composition of ceramic nanocomposites. The method involves combining alkoxide-derived polymeric precursors with a polymeric carbon source and converting the mixture to ceramic composites by pyrolysis. In this paper, we report the synthesis of polymeric precursors for TiC/Al_2O_3, TiN/Al_2O_3, or TiN/AlN and study the precursors' pyrolysis chemistry and the microstructure of the ceramic products. These studies also indicate that easily prepared alkoxide-derived polymers can be used for preparing homogeneous, non-oxide/oxide, and non-oxide/non-oxide composites, instead of the more difficult to synthesize organometallic precursors. However, when the alkoxide precursors are used, first the oxides are produced and then reduced to form the non-oxide. Since TiO is an expected intermediate in the carbothermic reduction of TiO_2 and it has a cubic structure, solid solutions between TiO and TiN, TiC, and TiC_xNi_{1-x} are expected over a wide range of concentrations.[14,25,26]

Experimental Procedure

General Methods. All of the synthesis and manipulations of the precursors were carried out in a N_2-filled glove box or in Schlenk glassware under N_2. Titanium butoxide (Ti(O-*n*-Bu)$_4$) and furfuryl alcohol were purified by distillation. Aluminum butoxide (Al(O-*sec*-Bu)$_3$) and THF were used as received.

Synthesis and Pyrolysis of the Precursors. A solution of 0.45 g of H_2O in 10 mL of THF was added dropwise to a 50 mL THF solution containing 3.40 g of titanium butoxide and 2.46 g of aluminum butoxide under vigorous stirring at −30 °C (Al:Ti:H_2O = 1:1:2.5), yielding a clear, colorless solution. Then a solution of 0.735 g of furfuryl alcohol in 10 mL of THF was added dropwise to the above solution (Ti:FuOH = 1:0.75), resulting in a yellow solution. After this solution was refluxed for 1 h, the volatile components were removed at 120 °C under vacuum, leaving a yellow solid. On the basis of a similar procedure, precursors with Ti:FuOH ratios of 1:1, 1:1.25, 1:1.5, 1:2, 1:2.5 and 1:3 were prepared, and all these precursors were soluble in hydrocarbon solvents.

Pyrolysis of the precursors was performed in a carbon furnace in argon (ultrahigh purity) or an alumina tube furnace under anhydrous ammonia or nitrogen (ultrahigh purity) at a flow rate of 200 mL/min. When ammonia was used, the precursors were first heated in argon to 600 °C and then heated to higher temperatures under ammonia. A heating rate of 200 °C/h was used for all the pyrolysis experiments.

Characterization. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) studies were performed with a Nicolet PC/IR (Model 44) infrared spectrometer. Samples were prepared by mixing precursors or pyrolysis products with dry KBr in the glovebox. The ground mixture was loaded in the IR sample holder in the glovebox and quickly transferred to the sample chamber of the spectrometer, which then was flushed with N_2 for 10 min before data collection. Thermogravimetric analysis (TGA) of the precursor was carried out with a Perkin-Elmer TGA7 thermal analysis system at a heating rate of 10 °C/min. The TGA atmosphere was argon that had been passed through a BTS catalyst (BASF CO.) and a molecular sieve column to remove O_2 and H_2O, respectively. X-ray powder diffraction patterns were measured with a Rigaku 300 diffractometer employing Cu Kα radiation and a Ni filter at a scanning rate of 10 °C/min. The XRD peak assignments were carried out using the Rigaku Software JCPDS peak indexing programs. Gas chromatography (GC) measurements were performed on a Hewlett-Packard 5890 gas chromatograph with a 6-ft Carbopack B column using He carrier gas at a flow rate of 25 mL/min. The morphologies of the pyrolysis products were observed using a Hitachi S-530 scanning electron microscope with a beam voltage of 20–25 kV. Transmission electron microscopy (TEM) was performed on a TOPCON EM002B operating at 200 kV accelerating voltage. X-ray fluorescence elemental analyses was performed on a VG HB5 STEM (scanning transmission electron microscope) operating at 100 kV accelerating voltage. Auger analysis was recorded on a Perkin-Elmer 660 scanning Auger microscope with a working voltage of 15 kV. Elemental analyses were obtained from E+R Microanalytical Laboratory (Corona, NH).

Results and Discussion

It is well-known that mixed metal alkoxides have provided successful methods for preparing homogeneous metal oxide ceramics, glasses, or composites in various forms.[27,28] Therefore, adding an organic carbon source to the Al and Ti alkoxide systems in a suitable concentration should form precursors to TiC/Al_2O_3, TiN/Al_2O_3, or TiN/AlN, since these composites can be formed from the oxides by the following reactions:

$$2TiO_2 + Al_2O_3 + 6C \rightarrow 2TiC/Al_2O_3 + 4CO \quad (1)$$

$$2TiO_2 + Al_2O_3 + 2C + 2NH_3 \rightarrow 2TiN/Al_2O_3 + 2CO + 2H_2O + H_2 \quad (2)$$

$$2TiO_2 + Al_2O_3 + 4C + 4NH_3 \rightarrow 2(AlN/TiN) + 4CO + 3H_2O + 3H_2 \quad (3)$$

In the present study, soluble alkoxide-derived polymeric precursors to TiC/Al_2O_3, TiN/Al_2O_3, and TiN/AlN were prepared by partially hydrolyzing Ti and Al alkoxides.

Synthesis and Characterization of Precursors. It is well-known[29–32] that furfuryl alcohol or polyfurfuryl

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Table 1. Elemental Analyses of the Precursor and of Pyrolysis Products Obtained under Argon

no.	FuOH:Ti	T (°C)	Ti	Al	C	H	O[a]
1	1.5:1	room temp[b]	18.77	11.11	39.42	5.23	25.4
2	1:1	650, 6 h	29.65	16.68	21.70	0.29	31.68
3	1.25:1	1250, 6 h	46.52	23.64	12.39	0.1	17.35
4	1.5:1	1250, 6 h	47.87	25.20	18.22	0.17	8.54
5	1.5:1	1500, 6 h	72.04	5.59	14.82	0	7.55

[a] By difference. [b] The as-synthesized precursor.

alcohol gives good yields of carbon upon pyrolysis and can serve as a soluble polymeric carbon precursor in the alkoxide-derived polymers. Therefore, if the precursor has the desired ratio of furfuryl alcohol to metal alkoxides, TiC/Al_2O_3, TiN/Al_2O_3, or TiN/AlN can be formed from reaction 1, 2, or 3, respectively.

Experiments in our laboratory have shown that furfuryl alcohol readily replaces the alkoxy groups of metal alkoxides via an alcohol exchange reaction. For example, a white solid material formed instantly when Al(O-*sec*-Bu)$_3$ and furfuryl alcohol were mixed at room temperature in THF; the FT-IR spectrum of the isolated solid product derived from the reaction of Al(O-*sec*-Bu)$_3$ and FuOH in a 1:1 molar ratio indicated that almost all the –*sec*-BuO– groups in Al(O-*sec*-Bu)$_3$ were replaced by FuOH groups, indicating the solid product was probably Al(FuO)$_3$. Our previous study[30,31] showed that furfuryl alcohol also readily replaces the butoxy groups of Ti butoxide.

Both Ti(O-*n*-Bu)$_4$ and Al(O-*sec*-Bu)$_3$ hydrolyze easily to form oligomeric or polymeric species depending on the amount of H_2O added to the alkoxides.[29] To obtain soluble precursors, a low H_2O:M ratio (1.25:1) and a low reaction temperature (−30 °C) were chosen for the hydrolysis reaction. GC analyses of the distilled components after hydrolysis of Ti and Al alkoxides (H_2O:Ti:Al = 2.5:1:1) indicated that more *sec*-butyl alcohol than *n*-butyl alcohol was present (the ratio of *sec*-C_4H_9OH:*n*-C_4H_9OH was 1.45:1), suggesting that the hydrolysis of Al(O-*sec*-Bu)$_3$ was greater than that of Ti(O-*n*-Bu)$_4$.

To control the amount of carbon available for reduction of the oxides, furfuryl alcohol was added to the hydrolyzed alkoxides. When the FuOH:Ti ratio was less than 2, the precursors could be described as a polymer such as $[\mathrm{Ti(O\text{-}}n\mathrm{\text{-}Bu)}_x\mathrm{Al(O\text{-}}sec\mathrm{\text{-}Bu)}_y\mathrm{(FuO)}_z\mathrm{O}_{2.5}]_n$ ($x + y + z = 2$) assuming that the hydrolysis reaction of the alkoxides and subsequent condensation, as well as the FuOH–butanol exchange reaction, were complete. Here, z is the amount of furfuryl alcohol added; the ratio of x and y depends on the relative stabilities and exchange rates for Ti and Al alkoxides. Therefore, the precursor with a FuOH:Ti ratio of 1.5:1 should give an empirical formula of $TiAlO_{4.5}C_{9.5}H_{12}$, which is relatively close to the actual empirical formula of $TiAl_{1.05}O_{4.05}C_{8.36}H_{13.32}$ obtained from the elemental analyses (no. 1, Table 1). The precursors were yellow or brown depending on the relative concentration of furfuryl alcohol in the starting materials.

Figure 1 shows the FTIR spectra of precursors synthesized with various FuOH:Ti ratios. The existence of O-*n*-Bu and O-*sec*-Bu groups are represented by the strong C–H stretching region (2959, 2933, and 2875 cm^{-1}) and C–H bending vibrations (1463 and 1375 cm^{-1}). These assignments were confirmed by comparing these spectra with the FTIR spectrum (Figure 1e) of the hydrolysis product resulting from Ti(O-*n*-Bu)$_3$–Al(O-*sec*-Bu)$_4$–2.5H_2O. As for the furfuryl alcohol groups, they are indicated by the absorption band at 3119 cm^{-1}, which is attributed to the C–H stretching vibration of the olefinic H on the furan rings. The sharp absorption bands at 1600 and 1506 cm^{-1} were assigned to the furfuryl alcohol C═C stretching vibrations. As expected, the spectra of Figure 1 also indicate that the relative intensity of the absorption bands for furfuryl alcohol groups increases as the amount of furfuryl alcohol increases in the precursors. In addition, the strong absorption band at 3630 cm^{-1} was attributed to the OH stretching vibration. The broad bands below 900 cm^{-1} were assigned to the Ti–O–Ti, Al–O–Al, and Al–O–Ti units.

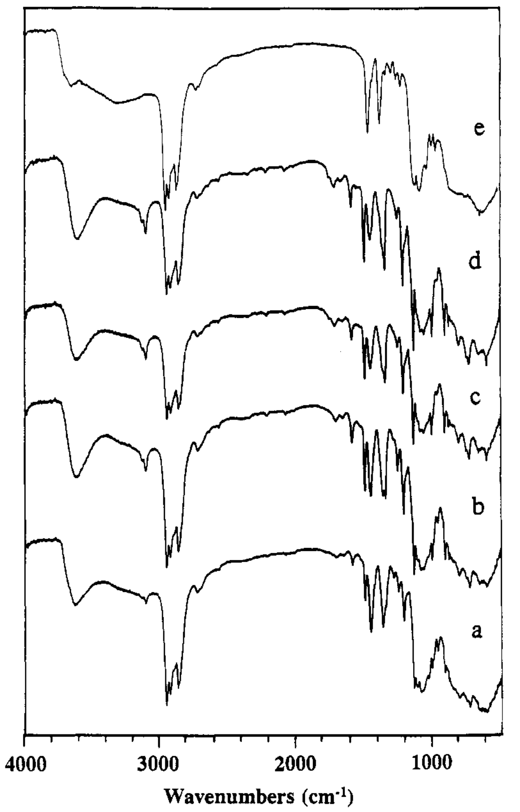

Figure 1. IR spectra of the as-synthesized precursors with a FuOH:Ti ratio of (a) 0.75:1, (b) 1.5:1, (c) 2:1, (d) 3:1, and (e) 0 (no FuOH in the system).

From the IR spectra, we noticed that all the investigated precursors (with a FuOH:Ti ratio from 0.75:1 to 3:1) showed the presence of M–OH groups, indicating that the condensation reaction was not complete. Therefore, the precursors can be described as a polymer of $[\mathrm{Ti(O\text{-}}n\mathrm{\text{-}Bu)}_x\mathrm{Al(O\text{-}}sec\mathrm{\text{-}Bu)}_y\mathrm{(OFu)}_z\mathrm{O}_a\mathrm{(OH)}_b]_n$ ($a = 2.5 - b$). Furthermore, even when the ratio of FuOH:Ti was larger than 2, the IR spectra of the precursors indicated that *n*-BuO and *sec*-BuO groups were still present, which suggested that the FuOH exchange reaction was not complete. The furfuryl alcohol, which did not bond to the Al or Ti atoms, probably polymerized to polyfurfuryl alcohol.

Preparation of TiC/Al_2O_3. The TGA curve (Figure 2) of the precursor with a FuOH:Ti ratio of 0.75:1 in argon indicated several weight-loss steps; the weight loss below 300 °C was attributed to the condensation of M–OH and decomposition of both O-*n*-Bu and O-*sec*-Bu groups, presumably forming H_2O and other volatile organics; the

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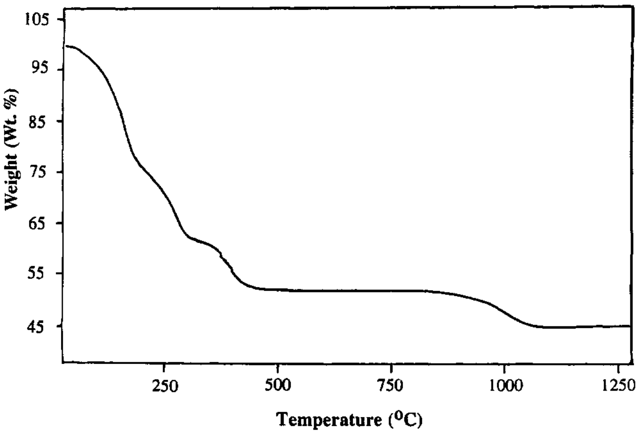

Figure 2. TGA curve (in argon) of the precursor with a FuOH: Ti ratio of 0.75:1.

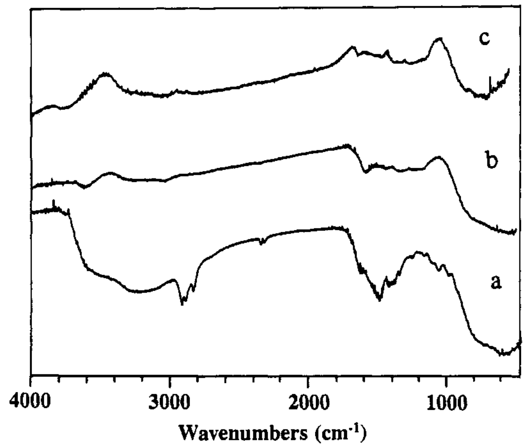

Figure 3. FT-IR spectra of the precursor (FuOH:Ti = 1.5:1) heated in argon at (a) 300 °C, 1 h; (b) 600 °C, 1 h; and (c) 800 °C, 6 h.

FuO groups decomposed between 300 and 450 °C, yielding carbon. By 500 °C, no organics remained in the precursors. These assignments were supported by the IR spectra of the pyrolysis product. For example, the IR spectrum (Figure 3a) of the precursor heated at 300 °C for 1 h in argon indicated that the absorption bands corresponding to the OH or butyl groups had decreased compared with those (Figure 1b) of the as-synthesized precursor. In addition, the absence of the C–O stretching vibration around 1200 cm^{-1} and the C–H vibration at 3110 cm^{-1} also suggested that the FuO groups had begun to decompose at 300 °C. In fact, the strong absorption at 1600 cm^{-1} was assigned as the C=C stretching vibrations, which was the major structural unit resulting from the decomposition of polyfurfuryl alcohol to carbon.[33] Further heating the precursor to 600 °C resulted in the disappearance of this C=C absorption band (Figure 3b). The broad absorption band between 500 and 1000 cm^{-1} observed in the spectrum was attributed to the Ti–O and Al–O stretching vibrations.

The weight loss observed between 850 and 1170 °C in the TGA was attributed to the carbothermic reduction of TiO_2, which resulted in the formation of TiC. The XRD patterns of the pyrolysis products indicated that the product obtained after heating to 800 °C for 6 h in argon was amorphous. The IR spectrum (Figure 3c) of this product showed the relative intensity of the Ti–O absorption band had decreased, which indicated that the carbothermic reduction of TiO_2 had begun. Further heating the precursor resulted in the formation of TiO_xC_{1-x} at 1000 °C, and α-Al_2O_3 at 1150 °C. The XRD pattern (Figure 4a) of the same precursor heated to 1250 °C for 12 h in argon indicated that TiC and α-Al_2O_3 were the only crystalline phases. In addition, a weight loss of 48.4%, 59.8%, and 63.2% was observed for the precursor heated at 800, 1150, and 1250 °C, respectively.

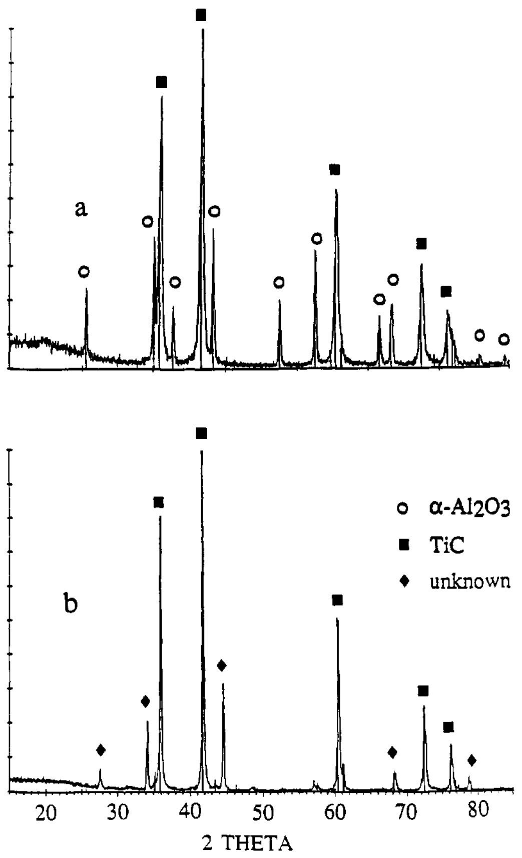

Figure 4. XRD patterns of the precursors heated in argon at (a) 1250 °C for 6 h; (FuOH:Ti = 1.5:1) and (b) 1500 °C for 6 h (FuOH:Ti = 1.5:1).

To determine the appropriate amount of furfuryl alcohol for the carbothermic reduction of TiO_2, it is necessary to know how much carbon will be derived from the pyrolysis of each mole of FuOH. The precursor with the FuOH:Ti ratio of 1:1, when pyrolyzed at 650 °C for 6 h in argon, had a composition of $TiAlC_{2.92}H_{0.47}O_{3.19}$ based on the elemental analyses (no. 2, Table 1), indicating that pyrolysis of each mole of FuOH will lead to 2.92 mol of carbon if we assume that all the carbon in the product is contributed from furfuryl alcohol.

On the basis of the above analysis, pure TiC/Al_2O_3 will result from the precursor with a Ti:FuOH ratio of approximately 1:0.92 according to reaction 1 if the carbothermic reduction is complete.[34] In agreement with this estimate, we observed that the precursors with a FuOH:Ti ratio of 1.25:1 and 1.5:1 gave products (obtained by heating the precursors in argon at 1250 °C for 12 h) containing excess C (no. 3 and 4, Table 1), even though TiC and Al_2O_3 are observed as the only crystalline phases in the XRD patterns. Under the same condition, the

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(34) Since 1 mol of FuOH will lead to 2.92 mol of C, 0.92 mol of FuOH will result in 2.69 mol of C which is used for the formation of TiC (1 mol) and CO (1.69 mol); the latter is obtained by substrating the total oxygen amount (2.92 mol) from the oxygen needed for the formation of Al_2O_3 (1.5 mol).

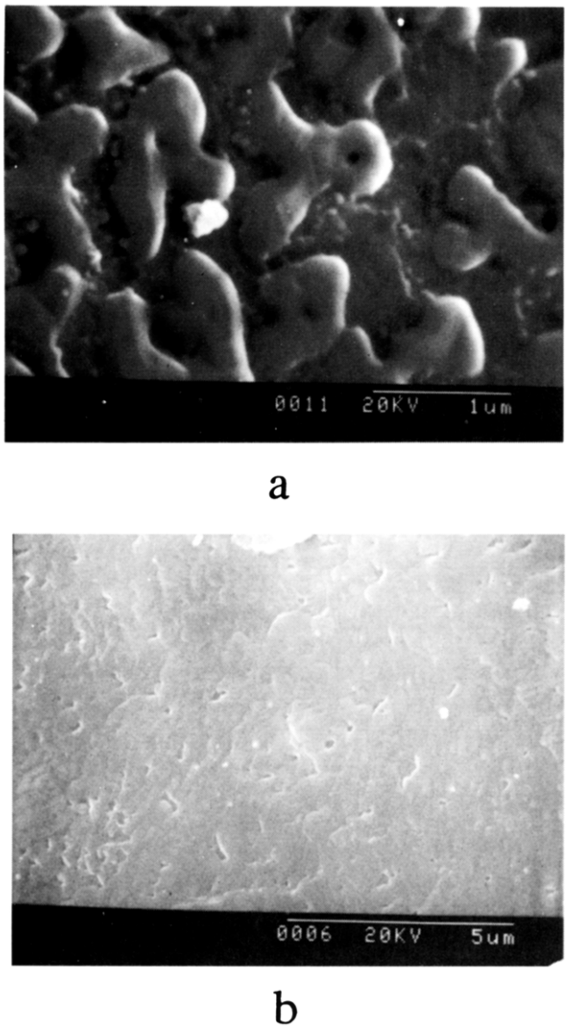

Figure 5. SEM micrographs of the precursor for Al_2O_3/TiC heated in argon at (a) 1250 °C, 6 h (FuOH:Ti = 1.25:1), and (b) 1250 °C, 6 h (FuOH:Ti = 1.5:1).

precursor with a FuOH:Ti ratio of 1:1 gave a product containing two crystalline phases (TiC_xO_{1-x} and Al_2O_3), which indicated that the carbothermic reduction was not complete at 1250 °C. Further heating the precursor to 1375 °C resulted in the formation of TiC and Al_2O_3 as the only crystalline phases. As for the precursor with a Ti: FuOH ratio of 0.75:1, it gave a product containing three crystalline phases (Ti_2O_3, α-Al_2O_3, and TiO_xC_{1-x}) at 1250 °C, further heating to 1375 °C resulted in Al_2O_3, TiC, and TiO.

The pyrolysis products from precursors with a FuOH: Ti ratio from 1:1 to 1.5 obtained at 1250 °C were composed of large (0.1–1 mm), metallic-gray, irregular shaped pieces. The SEM micrograph of the pyrolysis product from the precursor with a FuOH:Ti ratio of 1.25:1 (Figure 5a) showed a morphology consisting of two phases; that is, one phase consisting of large grains (0.7–1 μm) and the other consisting of small grains (0.05–0.1 μm). Auger analyses indicated that the large grains contained only Al and O elements; Ti and C were the major components of these small grains with small amounts of Al. These results suggested that the large and small grains were to α-Al_2O_3 and TiC, respectively. In addition, the SEM micrograph indicated that the α-Al_2O_3 and TiC grains were homogeneously distributed, presumably due to the intimate mixing between Al and Ti components in the precursor. Figure 5b shows the SEM micrograph of the product from the precursor with a FuOH:Ti ratio of 1.5:1, which indicated that excess C obscured the grains of both α-Al_2O_3 and TiC, which resulted in a flat, featureless surface.

The XRD patterns for all the precursors with a FuOH: Ti ratio of 0.75:1 to 1.5:1 heated to 1500 °C under argon indicated that the XRD peaks were much sharper than those of the pyrolysis products obtained at 1250 °C. Furthermore, a substantial weight loss (5–32%) was observed upon heating from 1250 to 1500 °C, indicating some material was lost during the treatment. Also, an unidentified crystalline phase was observed in the XRD patterns of these products in addition to the phases we observed before (α-Al_2O_3, TiC, and TiO_xC_{1-x}).

As this new phase formed, the intensity of α-Al_2O_3 diffraction peaks decreased. Furthermore, the concentration of this new phase relative to that of α-Al_2O_3 was dependent on the concentration of carbon; as the concentration of C in the system increased, higher concentrations of this new phase were observed. For example, the XRD pattern of the pyrolysis product with a FuOH:Ti ratio of 1.25:1 indicated that some α-Al_2O_3 crystalline phase still remained in the product, but the XRD pattern (Figure 4b) of the product with a FuOH:Ti ratio of 1.5:1 indicated that almost all the crystalline α-Al_2O_3 phase had disappeared; instead, TiC and this new phase were the major crystalline compounds present.

Pyrolysis of the precursor with a FuOH:Ti ratio of 1.5:1 from 1250 to 1500 °C resulted in a weight loss of 32.5%; the elemental analyses (no. 5, Table 1) of this product indicated the relative content of Al, C, and O has significantly decreased as compared with that heated at 1250 °C. We also observed that excess C plays an important role in the formation of this new phase, since this phase was not observed in the product obtained by heating a mixture of TiC and Al_2O_3 (Ti:Al = 1:1) powders at 1650 °C. This reaction resulted in the disappearance of Al_2O_3 as well as the formation of another unidentified phase. In addition, Ti also appears to be indispensable for the formation of this phase since pyrolysis of the precursor derived from Al(O-*sec*-Bu)$_3$–H_2O–FuOH only leads to α-Al_2O_3 and Al_3C_4.

The above results indicate the unidentified phase formed in the present system could be the reaction product of TiC, Al_2O_3, and C. Kim et al.[27] briefly mentioned that an unidentified compound containing Al, Ti, C, and O, was present in the product of the reaction between Al_2O_3, TiC, and C. However, since no detailed data were given for this unidentified compound in their study, it could not be compared with the new phase in the present system.

Preparation of TiN/Al_2O_3. The formation of TiN/Al_2O_3 was achieved by the pyrolysis of the precursor (with a FuOH:Ti ratio of 0.75:1) in argon at 600 °C and then further heating to higher temperature in NH_3. The XRD patterns of the pyrolysis products indicated that TiO_xN_{1-x} was the only crystalline phase at 1000 °C; the crystalline α-Al_2O_3 phase emerged at 1150 °C. Further heating the precursor to 1250 °C for 12 h resulted in the formation of α-Al_2O_3 and TiN. The SEM micrograph (Figure 6a) of this product showed a microstructure consisting of fine grains. TEM analyses of the same product revealed the grain sizes were in the range 150–400 Å. The elemental analyses (no. 1, Table 2) of the product agreed closely with the stoichiometry of TiN/Al_2O_3. Figure 6b showed the STEM micrograph of the product, which indicated that the images of Ti and Al were similar to that of N and

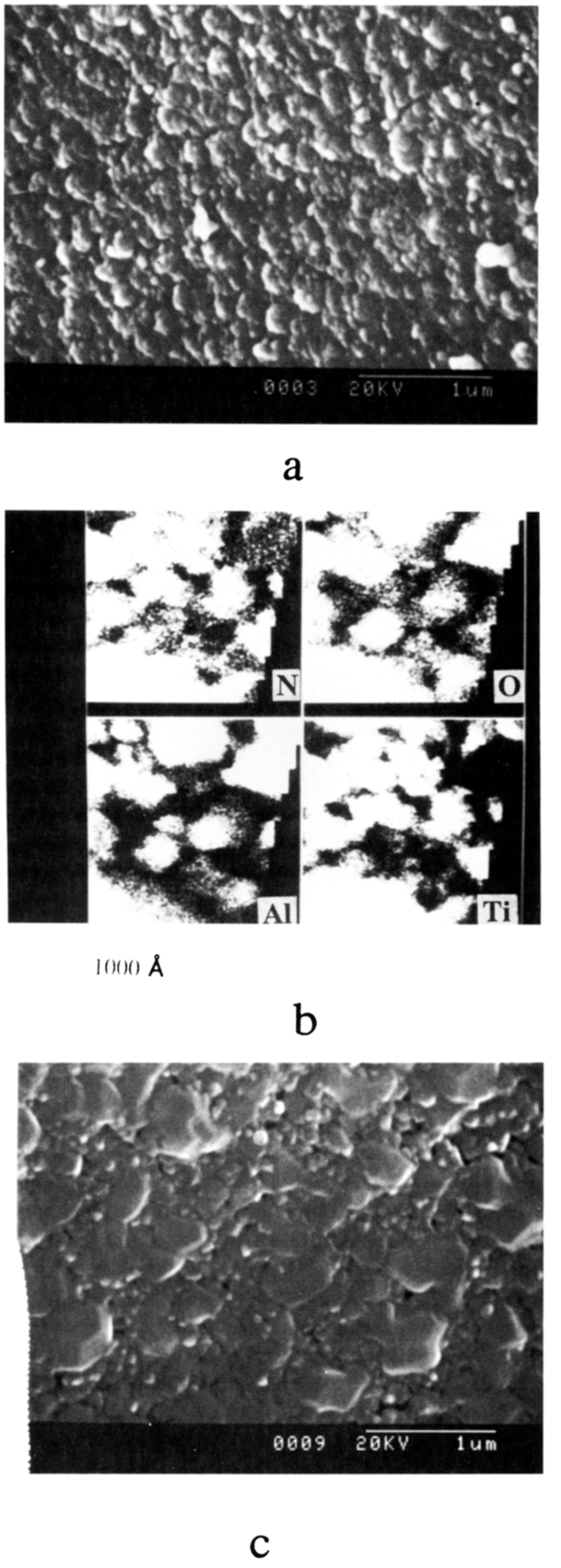

Figure 6. SEM micrographs of (a) the precursor for Al_2O_3/TiN (FuOH:Ti = 0.75:1) heated in ammonia at 1250 °C for 6 h, (b) the STEM micrograph for the same product at (a), and (c) the SEM micrograph of the same product at (a) further heated at 1500 °C under N_2 for 6 h.

O, respectively, suggesting that TiN and α-Al_2O_3 were the only components in the system and homogeneously dispersed.

Both XRD and TEM results of the product resulting from 1250 °C indicated the presence of some amorphous material in the system. Further heating of this product to 1500 °C under N_2 increased the crystallinity of both TiN and α-Al_2O_3 based on the XRD study. Furthermore, no weight loss or gain was observed during this treatment, indicating no reaction was involved. The SEM micrograph (Figure 6c) of the resulting product showed that the grain sizes of the product had increased, and two sizes of grains were present which corresponded to the α-Al_2O_3 (the large grains) and TiN (the small grains), respectively.

Table 2. Elemental Analyses of Pyrolysis Products TiN/Al_2O_3 and TiN/AlN

no.	FuOH:Ti	*T* (°C)	Ti	Al	C	H	O[a]	N
1	0.75:1	1250,[b] 6 h	41.31	24.83	0.21	0.10	11.25	22.30
2	2.5:1	1250,[b] 6 h	43.3	26.46	0.42	0.20	12.93	16.69
3	3:1	1250,[b] 6 h	44.22	26.69	0.95	0.21	11.13	16.80
4	3:1	1500,[c] 6 h	45.83	27.78	0.40	0.10		26.54
5	2:1	1250[d]	42.68	27.60	4.42	0.18	5.55	19.67

[a] By difference. [b] Pyrolyzed below 600 °C in argon, then in ammonia at high temperatures. [c] Pyrolyzed in nitrogen. [d] Pyrolyzed in nitrogen at 1500 °C for 6 h, then in ammonia at 1250 °C for 6 h.

The formation of the TiN in the present study could result from two different reactions. The first one was the carbothermic reduction of TiO_2 and subsequent nitridation, which was proposed in reaction 2; the second one is the direct reduction and nitridation of TiO_2 by ammonia. In fact, recent studies[35,36] indicated that TiN fibers and thin films can be made by reacting NH_3 with a Ti alkoxide-derived polymer. In our system, pyrolysis of a precursor prepared from Ti(O-*n*-Bu)$_4$, Al(O-*sec*-Bu)$_3$ and H_2O in a molar ratio of 1:1:2.5 (no FuOH) at 1250 °C for 6 h in ammonia yielded crystalline α-Al_2O_3, TiN, and Ti_2O_3. This result indicated that both reaction 2 and the direct reaction with NH_3 are involved.

Preparation of AlN/TiN. The formation of AlN/TiN was achieved by heating the precursors with a FuOH:Ti ratio of 2.5:1 or 3:1 in ammonia. The XRD patterns of these pyrolysis products indicated the presence of cubic TiO_xN_{1-x} at 1000 °C; hexagonal AlN and cubic TiO_xN_{1-x} at 1150 °C; hexagonal AlN and cubic TiN at 1250 °C. The SEM micrograph (Figure 7a) of the latter pyrolysis products showed a morphology consisting of small grain sizes (15–40 nm by TEM); furthermore, the STEM study of the products revealed that both Al and Ti components were homogeneously dispersed. However, elemental analyses (no. 2 and 3, Table 2) of the products indicated significant amounts of oxygen were present; furthermore, both products had similar compositions, even though different amounts of carbon were provided. The similar compositions produced by both precursors could be due to the fact that NH_3 reacts with C forming HCN and removed the carbon before the carbothermic reduction of Al_2O_3 was complete.[37,38] Furthermore, the results indicate that the direct nitridation of Al_2O_3 was much more difficult than the nitridation of TiO_2.

When the pyrolysis products obtained at 1250 °C were further heated to 1500 °C in nitrogen, a weight loss of 11.1% was observed. The XRD pattern of the resulting product indicated that the crystallinity of both TiN and AlN had increased. Furthermore, the SEM micrograph

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(35) Kamiya, K.; Yoko, T.; Bessho, M. *J. Mater. Sci.* **1987**, *22*, 937.

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(38) On the basis of the reaction $TiO_2 + 0.5Al_2O_3 + 3.5C + N_2 =$ TiN/AlN + 3.5CO and the formula of $TiAlC_{2.92}H_{0.47}O_{3.19}$, the complete carbothermic reduction in this system will need 1.09 mol of FuOH.

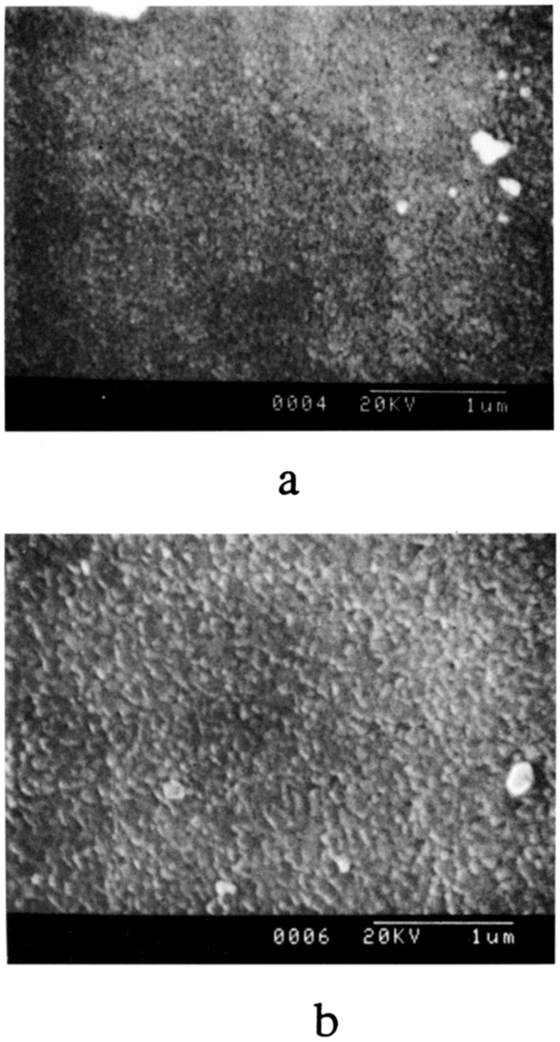

Figure 7. SEM micrographs of (a) the precursor for AlN/TiN (FuOH:Ti = 3:1) heated in ammonia at 1250 °C for 6 h and (b) the same product at (a) heated in nitrogen at 1500 °C for 6 h.

(Figure 7b) of the corresponding product showed that the grains grew to 50–100 nm. These grains are still an order of magnitude smaller than found in composites prepared using ceramic powders. In addition, the elemental analyses (no. 4, Table 2) revealed that almost pure TiN/AlN composite was obtained by such a treatment, presumably due to the nitridation of Al–O by N_2.

As mentioned earlier, we observed that even though much more carbon than needed for reaction 3 remained after pyrolysis, the carbothermic reduction was still not complete at 1250 °C, presumably due to the removal of C by the reaction with ammonia. It appears that one solution to this problem is to pyrolyze the precursors in nitrogen to 1500 °C and then treat the resultant product in ammonia at 1250 °C to remove any residual carbon. In this way, AlN/TiN can be formed with a lower FuOH:Ti ratio, since there is no significant reaction between carbon and nitrogen at 1500 °C. However, the XRD pattern of the pyrolysis product obtained by heating the precursor (FuOH:Ti = 1.25:1) in nitrogen at 1500 °C for 6 h indicated that some α-Al_2O_3 still remained in the product besides AlN and TiN, even though enough C was provided for the carbothermic reduction of Al_2O_3 and TiO_2.[29] With more C in the precursor (for example, the precursor with the FuOH:Ti ratio of 2:1), the α-Al_2O_3 phase disappeared after heating at 1500 °C (in nitrogen) for 6 h; however, the XRD result indicated that TiN_xC_{1-x} was formed besides AlN, indicating that some of the excess C has combined with TiN. Pyrolysis of the above product in ammonia at 1250 °C for 6 h resulted in a 8.5% weight loss, which was presumably caused by the reaction between ammonia and free carbon; however, the elemental analyses (no. 5, Table 2) of this product indicated that 4.42% of carbon still remained in the product. Furthermore, the XRD of this product showed the presence of TiN_xC_{1-x} besides AlN. Therefore, it appears that the carbon in TiN_xC_{1-x} is more difficult to remove than free carbon.

Jaschek and Rüssel reported that they obtained the (Ti,Al)N solid solution, and it decomposed around 1200 °C when hexagonal AlN began to appear.[14] The carbon content of their product was 4.7% when pyrolyzed in ammonia and 11.7% when pyrolyzed in nitrogen and are comparable to our results. In this effort, our product contained oxygen below 1200 °C, and, once the reduction was complete, we observed that hexagonal AlN began forming above 1250 °C. The X-ray evidence suggests that a cubic phase, such as a Ti–Al–N–O solid solution, was present in our product at lower temperatures.

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