sistent with $x = 1.04$ and $y = 0.96$.

Preparation of $[NP(OC_6H_4C_6H_5\text{-}p)_x(OC_6H_4Et\text{-}3)_y]_n$ (28). This polymer was prepared with use of the technique described for **27**. The side groups were present in the proportions $x = 1.06$ and $y = 0.94$.

Preparation of $[NP(OC_{10}H_7\text{-}2)_x(OC_6H_4Et\text{-}3)_y]_n$ (29). Polymer **29** was prepared in the same way as **27**. The side groups were present in the proportions $x = 1.10$ and $y = 0.90$.

Preparation of $[NP(HNPh)_2]_n$ (30). Aniline (150 mL) was distilled from $Ca(OH)_2$ and was added to dry dioxane (50 mL). A solution of **19** (5.0 g) in warm dry dioxane (200 mL) was prepared and was added to the aniline solution. The reaction mixture was stirred and refluxed for 96 h. The mixture was concentrated by means of a rotary evaporator and was then precipitated into deionized water. The particulate solids were isolated by suction filtration and were vacuum dried. The polymer was reprecipitated from THF into deionized water (4×), methanol (3×), and then hexane (3×) to give the white powdery product.

Procedure for Solution Sulfonation of Polymers with Concentrated or Fuming H_2SO_4. All sulfonation reactions were carried out under a dry nitrogen atmosphere in order to exclude moisture. Glassware was dried in an oven. The acid was heated in an oil bath to the specified temperature before the addition of the phosphazene. If the material to be sulfonated was added as a solid, it was first crushed into a powder and then added to the acid over a 5-min period. The volume of acid used varied from polymer to polymer, depending mainly on the ease of stirring. In all instances, the acid was present in a large excess. When a solvent was used, a 2% (g/mL) concentration of the polymer was employed. Solvent was also added to the acid, and the mixture was heated to the appropriate temperature. Each mixture was stirred and heated for a specific time and was then neutralized by pouring into a large excess of aqueous Na_2CO_3. The resulting solution was concentrated on a rotary evaporator. All polymer solutions, even if solid polymer was present, were placed in dialysis tubing (12000–14000 MW cutoff) and were dialyzed against deionized water for 5 days. The polymer was then isolated by evaporation of water from the contents of the dialysis tubing. The progress of a typical macromolecular sulfonation is illustrated by Figure 2.

Procedure for Solution Sulfonation of Cyclic Trimers with Concentrated or Fuming H_2SO_4. The trimers were treated in the same way as the polymers. Sulfonated trimeric compounds were isolated by dialysis. The neutralized solutions were placed in flasks, and the mouths of the flasks were covered with several layers of dialysis tubing (1000 MW cutoff). The solutions were then dialyzed against deionized water for 7 days. The contents of the flask were then evaporated to dryness and the residues analyzed.

Preparation of Films 31–35. The polymers were dissolved in dry distilled solvents (THF, dioxane, and or toluene). The solutions were filtered and films were then cast in a dust-free inert-atmosphere glovebox on a clean, level, glass surface. The samples were covered with small loose fitting covers to slow the evaporation rate. After at least 1 week, the films were removed from the casting chamber and were placed in the vacuum oven for 48 h at 80 °C. Films were then peeled from the glass plate.

Radiation Cross-Linking of 32–35. Films were dried under vacuum for 24 h and then sealed in an evacuated glass container. The samples were then exposed to ^{60}Co γ-rays at a dose rate of 0.3 Mrad/h.

Procedure for Sulfonation of Films with Fuming H_2SO_4. Films were rinsed in water, ethanol, and hexane and then dried before sulfonation. The film samples were held by Teflon forceps and immersed in the sulfonating agent for a limited period of time (typically 10–60 s), before being rinsed quickly in cold concentrated H_2SO_4 and then in cold deionized water. The sodium salt form of the active sites was generated by placing the films in deionized water and then gradually neutralizing with aqueous Na_2CO_3. The protonated variant was obtained by immersion of the neutralized films in 0.1 M HCl. All the films were rinsed with deionized water and were then stored in the same medium.

Procedure for Sulfonation of Films with $ClSO_3H$. A 20% solution of $ClSO_3H$ in 1,2-dichloroethane was used. The films were immersed in the solution for 60 s and were then rinsed quickly with fresh 1,2-dichloroethane under an atmosphere of argon. The films were subsequently exposed to condensed NH_3 (0 °C), n-butylamine in Et_2O (50%, 0 °C), or $LiAlH_4$ in Et_2O (0.5 M, 0 °C) for 12 h. Each film was then rinsed and soaked in deionized water and in ethanol.

Ion-Exchange Reactions. Sulfonated films were soaked in 1 M salt solutions for 24 h at room temperature and were then rinsed and soaked for 48 h in deionized water.

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Preparation of TiN and TiC from a Polymeric Precursor

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Hydrolysis of the $Ti(O\text{-}n\text{-}Bu)_4$/furfuryl alcohol mixture resulted in the formation of a polymeric solid. Pyrolysis of the polymer at 1150 °C under argon yielded metallic, gray TiC. When the pyrolysis was carried out in an atmosphere of anhydrous ammonia, pure TiN containing less than 0.8 wt % carbon was obtained at 1000 °C. The structure and pyrolysis chemistry of the precursor were studied by Fourier transform infrared spectroscopy (FT-IR), thermal gravimetric analysis (TGA), gas chromatography (GC), elemental analyses, and X-ray diffraction (XRD).

Introduction

Titanium nitride and titanium carbide have many desirable properties such as high melting point, extreme hardness, and strength at high temperatures.[1,2] At present, both TiN and TiC are used predominantly as cutting materials, although TiN layers also can be used as conductors for electronic applications. Previous studies indicated the addition of TiC to SiC[3,4] and TiN to BN[5]

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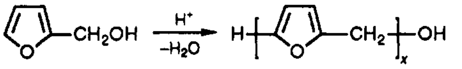
resulted in improvements in toughness, sinterability, and other specific properties, implying that both materials have excellent potential for use as components of high-temperature composite materials.

Current commercial methods for producing TiC powders include direct reaction of Ti metal with carbon and the carbothermic reduction of TiO_2.[1] TiN powders are produced by direct nitridation of metallic titanium, by carbothermic reduction and nitridation of TiO_2, or by the reaction of titanium halides or hydrides with anhydrous ammonia or nitrogen/hydrogen mixtures.[1,6] The above methods generally require high temperatures and cannot be used to prepare TiN or TiC thin films or fibers.

Recently, metalloorganic Ti compounds have been used as precursors to TiC or TiN in various final forms. In general, these precursors can be divided into two categories based on the type of structural units bonded to Ti. The first one, which possesses Ti–N or Ti–C bonds, is either a dialkylamide of titanium,[7,8] $Ti(NR_2)_4$, and electrochemically formed polymeric imides of titanium,[9] $Ti[(NR)_2]_x$, or tetraalkyltitanium,[10,11] TiR_4. TiN (thin films and powders) and TiC (thin films) have been produced from these precursors by pyrolysis at temperatures below 1100 °C. The second category, which possesses Ti–O bonds, is made either by transesterification of common titanium alkoxides with bifunctional acetates[12] or by alcohol exchange reactions between $Ti(OR)_4$ and organic compounds containing one to three hydroxyl groups.[13,14] These oxygen-containing precursors yield TiN or TiC, with a considerable amount of carbon and/or oxygen contamination, at higher temperatures than those required to produce TiN or TiC by pyrolyzing the Ti–N or Ti–C metalloorganic compounds (especially for the latter, where the temperature exceeds 1300 °C).

It is well-known that acid catalysis of furfuryl alcohol (FuOH) forms a polymeric resin by the following dehydration reaction:[15]



(1)

Furthermore, pyrolysis of this polymeric resin under inert atmosphere leads to the formation of carbon.[16,17] Pyrolysis of poly(furfuryl alcohol) mixed with SiO_2[18,19] or Al_2O_3[20,21] gels has been used to prepare SiC or AlN, respectively, representing a new strategy for preparing non-oxide ceramics from oxygen-containing metalloorganic precursors. In these systems, the furfuryl alcohol group (–OFu) decomposes to carbon to provide a carbon source for the carbothermic reduction of the metal oxide and for the formation of metal carbides upon pyrolysis.[13]

In the present study, TiN and TiC were prepared at low temperatures by pyrolysis of a polymeric precursor formed by hydrolysis of a $Ti(O\text{-}n\text{-}C_4H_9)_4$/furfuryl alcohol mixture. Furthermore, the pyrolysis processes involved in the formation of TiN and TiC were studied by various methods, resulting in a better understanding of the chemistry of the above precursor system.

Experimental Section

General Methods. All of the syntheses and manipulations were carried out in a N_2-filled drybox or in Schlenk glassware under N_2, because titanium butoxide, $Ti(O\text{-}n\text{-}C_4H_9)_4$, and its derivatives are moisture-sensitive. Titanium butoxide and furfuryl alcohol (FuOH) were purified by vacuum distillation. THF (AR grade) was used as received. Poly(furfuryl alcohol) was obtained from Polysciences, Inc.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) studies were performed with a Nicolet PC/IR (Model 44) infrared spectrometer. Samples were prepared by mixing the precursor or pyrolysis products with dry KBr in a drybox. The ground mixture was quickly transferred into the sample holder in air and immediately transferred to the sample chamber which was flushed with N_2 for a minimum of 10 min before data collection. 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. Thermal gravimetric analysis (TGA) of the compounds was carried out with a Perkin-Elmer TGA7 thermal analysis system at a heating rate of 10 °C/min. The TGA atmosphere was either argon that had been passed through a BTS catalyst (BASF Co.) and a molecular sieve column to remove O_2 and H_2O, respectively, or electronic grade ammonia. X-ray powder diffraction (XRD) patterns were measured with a Rigaku 300 diffractometer employing Cu Kα radiation and a Ni filter at a scanning rate of 10°/min. The X-ray peak assignments were carried out using the Rigaku Software JCPDS peak indexing program. Elemental analyses were obtained from E+R Microanalytical Laboratory, Inc.

Synthesis of Precursors. A solution of 0.54 g of 1 N H_2SO_4 (corresponding to 0.03 mol of H_2O if the amount of H_2SO_4 is neglected) in 20 mL of THF was added dropwise to 30 mL of a THF solution containing 6.8 g (0.02 mol) of titanium butoxide and 1.96 g (0.02 mol) of furfuryl alcohol under vigorous stirring. The resulting light brown solution was refluxed under nitrogen for 12 h, leaving a deep brown solution. The product, after removal of solvent under vacuum at 100 °C, was a reddish brown solid (3.28 g) which was slightly soluble in hydrocarbon solvents. On the basis of a similar procedure, precursors with Ti:FuOH ratios of 1:1.3, 1:0.75, 1:0.6, 1:0.5, and 1:0.25 were prepared.

When the hydrolysis was carried out using less than 2 equiv (relative to Ti) of pure water (no sulfuric acid), the products obtained were either polymeric viscous liquids or solids depending on the ratio of Ti:H_2O; all of them were soluble in hydrocarbon solvents after removal of solvent by vacuum distillation. After hydrolysis, the solvent was removed by distillation, and the distillate was analyzed by GC to determine the ratio of butanol and furfuryl alcohol present. The sensitivity of the flame ionization detector was determined by analyzing solutions containing known amounts of butanol and furfuryl alcohol.

Pyrolysis of Precursors. Samples of the isolated precursors were broken into pieces, placed into alumina boats, and transferred to a tube furnace. The tube furnace was fitted with an alumina tube with gastight fittings on each end. The samples were pyrolyzed in the tube furnace (Pt heating element) under a flow of either argon (ultrahigh-purity grade) or anhydrous ammonia at a flow rate of 300 mL/min at atmospheric pressure. The temperature was increased from room temperature to 1300 °C at a heating rate of 200 °C/h, held at the desired temperature for a period of time (3–12 h), and then cooled to room temperature.

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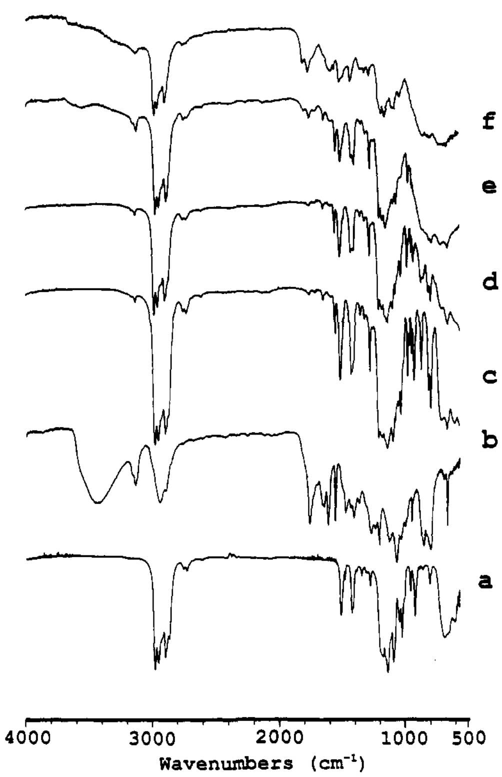

Figure 1. FI-IR spectra of (a) $Ti(O\text{-}n\text{-}Bu)_4$, (b) poly(furfuryl alcohol), (c) $TiOFu(O\text{-}n\text{-}Bu)_3$, (d) hydrolysis product of $TiOFu(O\text{-}n\text{-}Bu)_3$ with 0.5 mol of H_2O, (e) with 1.5 mol of H_2O, and (f) with 1.5 mol of H_2O and acid catalyst.

The ceramic residues obtained under ammonia were cooled in a flow of argon gas.

Results and Discussion

Preparation of Precursors. Furfuryl alcohol derivatives of titanium alkoxides were prepared by adding furfuryl alcohol to $Ti(O\text{-}n\text{-}Bu)_4$ at room temperature. As furfuryl alcohol was added to $Ti(O\text{-}n\text{-}Bu)_4$, the light-yellow titanium butoxide turned to a dark-yellow liquid, indicating the following alcohol exchange reaction had occurred:

$$FuOH + Ti(O\text{-}n\text{-}Bu)_4 \rightarrow TiOFu(O\text{-}n\text{-}Bu)_3 + HO\text{-}n\text{-}Bu \quad (2)$$

Any unreacted FuOH and the n-BuOH produced were transferred to a cold trap by vacuum distillation at 50 °C [any unreacted $Ti(O\text{-}n\text{-}Bu)_4$ and the $TiOFu(O\text{-}n\text{-}Bu)_3$ are not volatile enough to be distilled under the above condition]. GC analysis of the distillate indicated the ratio of butanol to furfuryl alcohol was 100:2.8, indicating reaction 2 is almost quantitative.

Figure 1c shows the IR spectrum of the product from reaction 2. The absence of –OH absorption bands in this spectrum agrees with the GC analysis of the distillate and indicates approximately all (>97%) of the furfuryl alcohol molecules reacted with $Ti(O\text{-}n\text{-}Bu)_4$ to form $TiOFu(O\text{-}n\text{-}Bu)_3$. The existence of the furfuryl alcohol groups in the product is indicated by the small peak at 3112 cm^{-1}, which is assigned to the C–H stretching vibration of the olefinic H on the furan rings; the sharp absorption bands at 1597 and 1504 cm^{-1} are assigned to the C=C stretching vibrations, and the absorption band at 1223 cm^{-1} is assigned to the C–O stretching vibrations on the furan rings.[22] As for the n-Bu groups, they are represented by the strong C–H stretching region (2958, 2932, and 2872 cm^{-1}) and C–H bending vibrations [1464 and 1371 cm^{-1}; refer to the spectrum of $Ti(O\text{-}n\text{-}Bu)_4$, Figure 1a].

Hydrolysis of $TiOFu(O\text{-}n\text{-}Bu)_3$ in THF with less than 2 mol of H_2O (relative to Ti) produces a soluble Ti–OR polymer. It is well-known that as more H_2O is added, more hydrolysis occurs, followed by condensation reactions which result in the subsequent formation of a polymer. Furthermore, some furfuryl alcohol molecules also can be produced through hydrolysis of Ti–OFu groups, even though Ti–OFu is more resistant to hydrolysis than Ti–O-n-Bu. GC analysis of the distillate from the hydrolysis reactions with 0.5, 1.0, and 1.5 mol of H_2O (relative to Ti) indicated the ratios of butanol to furfuryl alcohol in these three distillates were 100:4.6, 100:9, and 100:22.5, respectively.

To prevent the loss of FuOH, a catalytic amount of H_2SO_4 was added to catalyze the hydrolysis of TiO-n-Bu groups and the polymerization of any FuOH molecules produced from the hydrolysis of TiOFu groups. GC analysis showed that the ratio of butanol to furfuryl alcohol in the distillate in the case where 1.5 mol of H_2O (with acid catalyst) was used was 100:3, indicating the addition of acid is effective in preventing the loss of FuOH. After hydrolysis, we assume that the precursor consists of some poly(furfuryl alcohol) plus a molecular precursor with the approximate formula $O_{1.5}Ti(OFu)_{1-x}(O\text{-}n\text{-}Bu)_x$.

The IR spectra of the products after hydrolysis with H_2O (Figure 1d,e) are similar to that of the starting material, $TiOFu(O\text{-}n\text{-}Bu)_3$, (Figure 1c), except that the sharp bands below 900 cm^{-1} in the starting material become broader after hydrolysis, indicating Ti–O–Ti units formed upon hydrolysis. Figure 1f shows the IR spectrum of the product obtained after hydrolyzing $TiOFu(O\text{-}n\text{-}Bu)_3$ with 1.5 mol of H_2O (with acid catalyst). Compared with the IR spectrum of the hydrolysis product without acid (Figure 1e), most absorption bands in Figure 1f are broader, indicating the structure of the product was more polymeric in nature. Furthermore, the sharp bands corresponding to the furfuryl alcohol groups have almost disappeared; instead, two bands are observed at 1762 and 1718 cm^{-1}, which are attributed to the poly(furfuryl alcohol) [refer to the spectrum of poly(furfuryl alcohol), Figure 1b] formed by the acid-catalyzed condensation polymerization of furfuryl alcohol. In addition, this spectrum also indicates the relative concentration of butanol groups decreased considerably compared with that in the uncatalyzed hydrolysis product (Figure 1e). This decrease in butanol groups occurred because the addition of acid during hydrolysis also catalyzed hydrolysis of Ti–OBu groups, resulting in more butanol molecules produced from the hydrolysis reaction.

We observed that the addition of acid greatly decreased the solubility of the product, making the further structural characterization of the product difficult. The elemental analyses of the hydrolysis product with 1.5 mol of H_2O and acid catalyst indicated C 36.50%, H 4.67%, and Ti 27.86, corresponding to an empirical formula of $TiC_{5.4}H_{8.1}O_{3.6}$. The elemental analysis, GC analysis of the distillate, an IR spectrum, and an NMR spectrum indicated hydrolysis was not quantitative and some O-n-Bu groups remained in the product.

Thermal Decomposition of Precursors. Figure 2a shows the TGA curve of the 1:1 Ti:FuOH precursor with nominal composition $[O_{1.5}Ti(OFu)_{1-x}(O\text{-}n\text{-}Bu)_x]_n$ (product obtained after hydrolysis with 1.5 mol of H_2O and with acid catalyst) under argon from 40 to 1260 °C. The data indicate the precursor underwent three weight-loss processes: one at 150–270 °C, the second at 270–480 °C, and the third at 760–1250 °C. The first one is attributed to the con-

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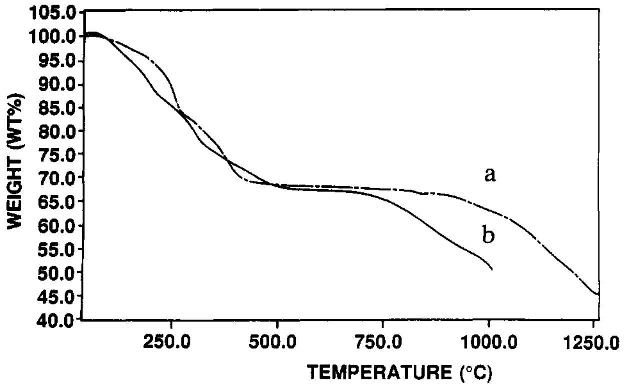

Figure 2. Thermal gravimetric analysis of the hydrolysis product of $TiOFu(O\text{-}n\text{-}Bu)_3$ with 1.5 mol of H_2O and acid catalyst ($O_{1.5}Ti(OFu)_{1-x}(OBu)_x$) under (a) argon and (b) ammonia.

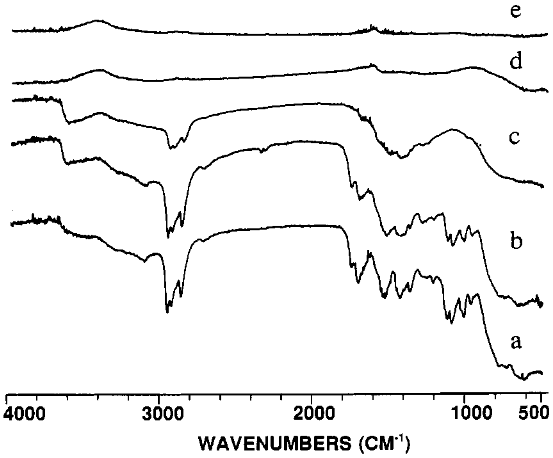

Figure 3. FT-IR spectra of pyrolysis products of the same precursor in Figure 2 at (a) room temperature and heated under argon at (b) 200 °C for 3 h, (c) 300 °C for 3 h, (d) 600 °C for 3 h, and (e) 800 °C for 3 h.

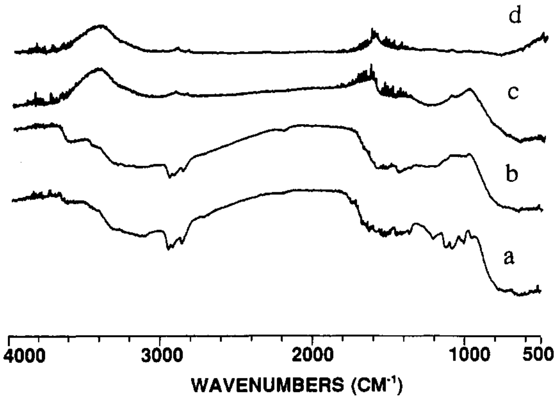

Figure 4. FT-IR spectra of $O_{1.5}Ti(OFu)_{1-x}(OBu)_x$ heated under ammonia for 3 h at (a) 200, (b) 300, (c) 600, and (d) 800 °C.

densation polymerization of furfuryl groups and the decomposition of O-*n*-Bu groups attached to Ti atoms. The second weight-loss step presumably corresponds to the decomposition of furan fings. These assignments are supported by the fact that similar decomposition temperatures have been observed for poly(furfuryl alcohol) and polymeric $TiO_x(O\text{-}n\text{-}Bu)_y$.[23] However, unlike the O-*n*-Bu groups, the decomposition of furan rings results in the formation of carbon. The weight loss starting at around 760 °C and ending at 1250 °C is assigned to the carbothermic reduction of TiO_2, which is consistent with the previous results obtained for the thermal decomposition of organotitanium compounds.[12]

The TGA curve (Figure 2b) of $[O_{1.5}Ti(OFu)_{1-x}(O\text{-}n\text{-}Bu)_x]_n$ when heated under a flow of ammonia shows a different curve shape than it does when heated under argon, indicating different pyrolysis mechanisms are involved for this precursor under the two atmospheres. The weight loss below 520 °C in Figure 2b is attributed to reaction 3, possibly accompanied by the decomposition

$$TiOR + NH_3 \rightarrow TiNH_2 + ROH \qquad (3)$$

processes previously discussed concerning the TGA obtained under argon (Figure 2a). This type of reaction is known to occur for organosilicon compounds[25] and also in reactions of metal alkoxides with amine groups.[26] The weight loss around 680–1000 °C is attributed to the following reaction:[1,27]

$$TiO_2 + C + NH_3 \rightarrow CO + TiN + H_2O + 0.5H_2 \qquad (4)$$

Further investigation into the pyrolysis process under argon and ammonia was carried out with infrared spectroscopy. The IR spectrum for the precursor heated at 200 °C for 3 h under argon (Figure 3b) indicates the absorption peaks attributed to the furan rings are unchanged and the relative intensities of the absorption peaks contributed from the O-*n*-Bu groups have decreased, presumably due to the decomposition of some O-*n*-Bu groups into volatile organics during the heat treatment. These observations are consistent with the TGA results. That is, the O-*n*-Bu groups begin to decompose at 200 °C, but the furan rings are still stable at this temperature.

Parts c–e of Figure 3 show the IR spectra of precursors heated at 300, 600, and 800 °C for 3 h under argon, respectively. After heating to 600 °C (Figure 3d), the only detectable absorption bands (1000–500 cm^{-1}) in the spectrum are due to Ti–O units, even though carbon remains in the precursor at this stage. The IR spectrum illustrated in Figure 3e indicates the Ti–O absorption disappeared after heating at 800 °C, presumably due to the carbothermic reduction of Ti–O units (TGA indicates the reduction starts at 760 °C). However, both TGA and XRD (vide infra) results indicate some oxygen remains in the product, since the carbothermic reduction is not complete at 800 °C.

The pyrolysis of the precursor under ammonia was also studied by FT-IR. The IR spectrum (Figure 4a) for the precursor heated at 200 °C under ammonia shows two broad bands around 3200 and 1600 cm^{-1}, which are attributed to the NH_2 stretching and bending vibrations, respectively;[28] these NH_2 groups are presumably generated from reaction 3. Furthermore, the IR spectrum indicates the relative absorption intensities contributed by the O-*n*-Bu groups (C–O and C–H stretching vibrations) are much less than is observed when the same precursor is heated under argon (compare Figure 4a with Figure 3b), which is expected if reaction 3 is involved during the pyrolysis. The IR spectrum obtained after heating to 300 °C under NH_3 (Figure 4b) is similar to that obtained after

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[24] The same alumina tube was used in this work, when pyrolyses under both argon and ammonia were performed. In the latter case, an AlN layer could be formed on the ceramic tube, which reacts with any water produced during the decomposition of furfuryl alcohol to form alumina and NH_3 when the pyrolyses were carried out under argon. The contamination of the products with nitrogen presumably resulted from the following reaction: $NH_3 + TiO_2 + 2C \rightarrow TiN + 2CO + 1.5H_2$.

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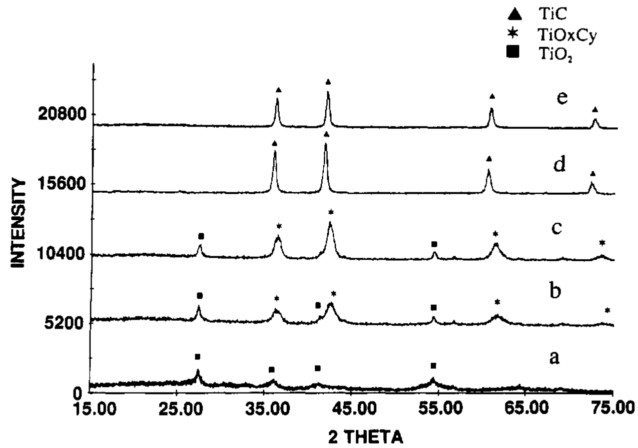

Figure 5. X-ray diffraction patterns for $O_{1.5}Ti(OFu)_{1-x}(OBu)_x$ after heating under argon for 12 h at (a) 800, (b) 900, (c) 1000, (d) 1150, and (e) 1300 °C.

Table I. Elemental Analyses of Pyrolysis Products Heated under Argon for 12 h

Ti:FuOH	T, °C	no.	wt % Ti	wt % C	wt % H	wt % N
1.3	1300	1	57.94	39.60	0.00	0.69
1.0	1300	2	69.25	28.74	0.00	0.88
1.0	1150	3	69.72	28.24	0.00	1.25
0.75	1300	4	78.03	17.62	0.00	2.73
TiC (calcd)			79.95	20.05		

heating to 300 °C under argon (Figure 3c) except for the extra NH_2 absorption bands. The IR spectrum in Figure 4c indicates some organics (represented by the broad band around 1220 cm^{-1}) remain after heating the precursor at 600 °C in ammonia. The Ti–O stretching vibrations still present at 600 °C (Figure 4c) disappear after the precursor is heated at 800 °C under ammonia (Figure 4d).

Formation of TiC under Argon. XRD analysis of the pyrolysis products in argon (Figure 5a) shows that TiO_2 is the only crystalline phase which remains after the precursor is heated at 800 °C for 12 h, even though both TGA and IR studies suggest that carbothermic reduction has already started at this temperature. At 900 °C, some new peaks (36.40°, 42.55°, 61.75°, and 73.85°, labeled with asterisks) emerge in addition to the TiO_2 peaks (Figure 5b), and the relative intensities of these new peaks increase with heating of the precursor at 1000 °C (Figure 5c, 36.36°, 42.35°, 61.45°, and 73.56°, labeled with asterisks). Figure 5d shows that the TiO_2 phase disappears and only four peaks (35.92°, 41.72°, 60.52°, and 72.40°, labeled with solid triangles) are observed after heating the precursor at 1150 °C for 12 h under argon. Further heating of the precursor at 1300 °C gives a similar XRD pattern (Figure 5e, 36.00°, 41.84°, 60.60°, and 72.48°, labeled with solid triangles), except that these four peaks are a little sharper. Both products at 1150 and 1300 °C are shiny, gray solids.

Table I shows the elemental analyses of precursors with various Ti:FuOH ratios heated under argon for 12 h. (Note: these results indicate some nitrogen contamination in all the products even though the pyrolyses were performed under argon of ultrahigh-purity grade; the reason is explained in ref 24.) On the basis of these results and the assumption that all the titanium in the starting material transforms into TiN and TiC around 1300 °C and that no furfuryl alcohol molecules added to the reaction were lost in the distillation step, we determined the total amount of carbon contributed by the furfuryl alcohol in each system, which includes the carbon consumed by reactions 5 and 6, and the excess carbon represented by xC

$$TiO_2 + 3C + xC \rightarrow TiC + 2CO + xC \qquad (5)$$

$$TiO_2 + NH_3 + 2C \rightarrow TiN + 2CO + 0.5H_2 \qquad (6)$$

in reaction 5 in the final product. In this way, the yield of carbon from each furfuryl alcohol molecule was obtained. The calculation from analyses 1, 2, and 4 in Table I indicates a carbon yield of 44.6, 44.8, and 46.5 wt %, respectively. Therefore, the theoretical Ti:FuOH ratio for the formation of pure TiC through reaction 5 is proposed to be approximately 1:0.80.

The elemental analyses in Table I indicate 0.8–1.8 wt % oxygen remains in the products if we assume that the rest of the weight belongs to residual oxygen due to incomplete carbothermic reduction. Preparing pure titanium carbide is extremely difficult, and Krainer and Konopicky[29] have reported that titanium carbide made from a thermal reduction process at 2100 °C contained at least 2 wt % oxygen. Therefore, even with these levels of nitrogen and oxygen contamination, the TiC prepared in this study is purer than that obtained with other metalloorganic precursors[12,13] or by conventional carbothermic processes.

After comparison of the XRD pattern (36.00°, 41.84°, 60.56°, and 72.50°) of pure commercial TiC with those in Figure 5d,e, it is clear that TiC is the only crystalline phase obtained above 1150 °C. Furthermore, the elemental analyses indicate the products obtained at 1150 and 1300 °C have almost the same composition, suggesting that the carbothermic reduction is complete by 1150 °C. We observe that TiO_2 is present at 800 °C and an intermediate phase appears at 900 °C, labeled with solid squares in Figure 5b,c, and the diffraction peaks for this phase tend to shift to lower 2θ angles with increasing temperature until they reach the positions of TiC, as shown in Figure 5d.

It is well-known that TiO is soluble in TiC over a wide range of concentrations to form a solid solution of TiO_xC_y, due to the similar cubic structures of TiC and TiO, which have lattice constants of 0.433 and 0.417 nm, respectively. Therefore, the X-ray diffraction peaks obtained after pyrolysis at 900 (Figure 5b) and 1000 °C (Figure 5c) are attributed to titanium oxycarbide. Judging by the diffraction peak positions, the solid solution phase obtained at 900 °C has higher oxygen and lower carbon contents than does the product obtained at 1000 °C.

To study the reduction process in more detail, precursors with Ti:FuOH ratios of 1:0.25, 1:0.5, and 1:0.6 were heated at 1250 °C for 12 h under argon. These X-ray diffraction patterns (Figure 6) indicate no pure TiC phase forms in the three systems and that the only crystalline phases observed are TiO_2, Ti_2O_3, Ti_3O_5, and TiO_xC_y, as expected from the previous experiments. Figure 6b,c indicates that the relative intensities of the TiO_xC_y phase peaks increase with increasing amounts of FuOH in the system; moreover, the TiO_xC_y phase (36.08°, 41.92°, 60.78°, and 72.80°, Figure 6c) obtained using 0.6 FuOH/Ti has a higher carbon content and a lower oxygen content than the product obtained using 0.5 FuOH/Ti, based on their X-ray diffraction peak positions (36.40°, 42.32°, 61.44°, and 73.66°, Figure 6b).

Formation of TiN under Ammonia. X-ray diffraction studies (Figure 7) of the pyrolysis products of the precursor with a Ti:FuOH ratio of 1:0.75 under ammonia indicate a crystalline phase emerges at 700 °C; moreover, the peaks of this phase shift to lower angles and become sharper with increasing calcination temperature, as shown in Figure 5 for TiO_xC_y. On the basis of the peak positions of the products, these phases in the X-ray diffraction patterns in Figures 7a–c are attributed to titanium oxynitride solid solutions (TiO_xN_y).

The elemental analysis of the precursor heated at 800 °C under ammonia for 5 h (Table II) shows that about 10

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(29) Krainer, H.; Konopicky, K. *Hüetlenmaenn. Monatsh. Montan. Hochschule Leoben* **1947**, *92*, 166.

Table II. Elemental Analyses of Pyrolysis Products Heated under Ammonia

Ti:FuOH	T, °C	no.	wt % Ti	wt % N	wt % C	wt % H
0.75[a]	1000 (12 h)	1	77.64	22.28	0.76	0.00
0.75[a]	800 (5 h)	2	64.74	18.64	6.87	0.23
0.75[b]	1000 (12 h)	3	77.81	21.98	0.55	0.00
TiN (calcd)			77.38	22.62		
1.0[c]	600 (3 h)	4	70.67	4.27	23.52	0.00

[a] Heated under NH_3 to T (°C). [b] The precursor was heated at 600 °C for 3 h under argon, then further heated to 1000 °C under ammonia, and held for 12 h at that temperature. [c] The precursor was heated at 600 °C for 3 h under ammonia, then further heated to 1300 °C under argon, and held for 12 h at that temperature.

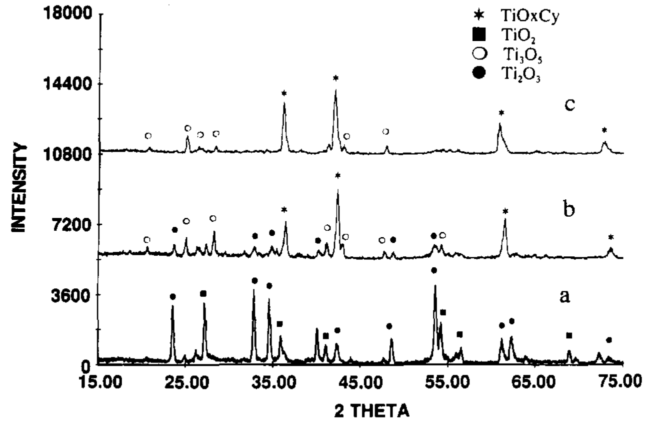

Figure 6. X-ray diffraction patterns for the hydrolysis products heated at 1250 °C for 12 h under argon with Ti:FuOH ratios of (a) 1:0.25, (b) 1:0.5, and (c) 1:0.6.

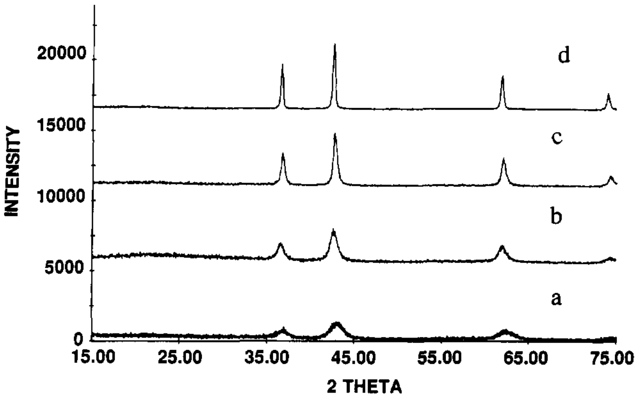

Figure 7. X-ray diffraction patterns for the hydrolysis product with a Ti:FuOH ratio of 1:0.75 after heating under ammonia at (a) 700 °C for 5 h, (b) 800 °C for 5 h, (c) 900 °C for 5 h, and (d) 1000 °C for 12 h.

wt % oxygen (determined by difference) still remains in the product. The pyrolysis product obtained at 1000 °C is a gold-colored solid, typical of TiN, and it contains 0.76 wt % carbon (Table II). Furthermore, on the basis of the combined percentages (100.68 wt %) of Ti, N, and C, the oxygen content of this product necessarily must be quite low. Finally, it is clear that ammonia can function as a nitrogen source for the pyrolysis product under both low and high temperature through reaction 3 and reaction 4, respectively.

It is important to know how much nitrogen is contributed by reactions 3 and 4 to the final product in order to better understand the pyrolysis chemistry of the precursors in ammonia. The elemental analysis of the 1:1 Ti:FuOH precursor heated at 600 °C for 3 h under ammonia and then heated to 1300 °C for 12 h under argon shows that the product has low nitrogen content (4.27 wt %) and high carbon content (23.52 wt %; no. 5, Table II), indicating reaction 3 is of minor importance and most of the butanol and furfuryl groups survive this reaction. On the basis of the XRD peak positions of this product (36.08°, 41.90°, 60.80°, and 72.78°), the crystalline phase of the product is TiN_xC_y solid solution. On the other hand, the elemental analysis of the 1:0.75 Ti:FuOH precursor heated at 600 °C for 3 h under argon (at this stage all the furfuryl alcohol has converted to carbon) and then heated to 1000 °C for 12 h under ammonia (no. 3, Table II), indicates pure TiN forms containing only 0.55 wt % carbon.

This result confirms that reaction 3 is not an important source of nitrogen, and pure TiN still can be obtained through reaction 4. However, only 1 equiv of carbon is consumed in reaction 4 rather than 3 equiv of carbon as in reaction 5. Pyrolysis of the 1.0:0.75 Ti:FuOH precursor under argon gave a product with the empirical formula $TiC_{0.9}N_{0.1}$, indicating 0.75 equiv of FuOH should yield approximately 2.9 equiv of carbon. Therefore, if reaction 4 is the only reaction involved in removing carbon, there should be a large excess (~1.9 equiv) of carbon left in the product. Evidently, the excess carbon reacts with ammonia at high temperatures to form volatile compounds. The above proposal is also supported by the fact that no residue was left when 0.1 g of the poly(furfuryl alcohol) was pyrolyzed at 600 °C for 3 h under argon and then 1000 °C for 12 h under ammonia. Furthermore, the reaction between carbon and ammonia was also observed in Maya's recent work.[30] However, the detailed reaction mechanism between ammonia and carbon is unknown at present.

Conclusions

Furfuryl alcohol derivatives of titanium *n*-butoxide were prepared and then hydrolyzed to obtain polymers $[O_{1.5}Ti(OFu)_{1-x}(OBu)_x]$ which were characterized by elemental analysis and spectroscopic methods. The value of x depends on the relative hydrolytic stability of the OR groups and was estimated to be less than 0.3 based on the analytical results. To improve the hydrolysis reactions and decrease the loss of furfuryl alcohol from the system, trace amounts of sulfuric acid were added to catalyze the hydrolysis of the titanium alkoxide and the polymerization of furfuryl alcohol.

Since furfuryl alcohol is known to be a good precursor for glassy carbon, these titanium polymers could be thermally converted to an intimate mixture of titanium oxides and carbon. When the polymer was pyrolyzed under ammonia, we observed that the oxynitride, TiO_xN_y, began to form at temperatures as low as 700 °C and that TiN was completely formed by 1000 °C. Ammonia also removed carbon from the system and almost pure TiN was obtained. When the polymer was pyrolyzed under argon, TiO_xC_y was observed to form at 900 °C and TiC was completely formed by 1150 °C. The temperatures observed for the formation of TiN and TiC in this research are lower than those reported for the formation of TiN and TiC by the conventional carbothermic reduction method.

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Registry No. TiC, 12070-08-5; TiN, 25583-20-4; NH_3, 7664-41-7; $(BuO)_4Ti$, 5593-70-4; FuOH, 98-00-0.

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(30) Maya, L.; Richards, H. L. *J. Am. Ceram. Soc.* **1991**, *74*, 406.