Pyrolytic Conversion of Precursors Prepared in Ti(NMe$_2$)$_4$–Diamine Systems

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Precursors possessing Ti–N bonds were prepared by the reactions between Ti(NMe$_2$)$_4$ and each of three diamines H$_2$NCH$_2$CH$_2$NH$_2$, Me(H)NCH$_2$CH$_2$N(H)Me, HN(CH$_2$CH$_2$)$_2$NH (Ti(NMe$_2$)$_4$:diamine = 1:2), and were converted into ceramics by pyrolysis. The reactions with H$_2$NCH$_2$CH$_2$NH$_2$ and HN(CH$_2$CH$_2$)$_2$NH led to the formation of insoluble solids, whereas a soluble oil was obtained by the reaction with Me(H)NCH$_2$CH$_2$N(H)Me. The pyrolyses under argon gave carbon-rich Ti(N,C,O) phases, but those under NH$_3$–N$_2$ resulted in the formation of Ti(N,C,O) phases with higher nitrogen contents. Despite the difference in precursor structures the pyrolysis behavior of three precursors under argon was rather similar, suggesting that the precursor obtained from Me(H)NCH$_2$CH$_2$N(H)Me was effectively cross-linked during pyrolysis. © 1998 John Wiley & Sons, Ltd.

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INTRODUCTION

Titanium nitride (TiN) exhibits excellent properties, such as high hardness, high melting point, corrosion resistance and high electrical conductivity.[1] It has been used for various applications, including wear-resistant coatings and solar control coatings for windows.[2–4] Also, TiN has attracted increasing attention because of its use as diffusion barriers in integrated circuits.[5,6] Traditional synthetic procedures for TiN are the nitridation of titanium metal and carbothermal reduction of TiO$_2$ under nitrogen, but recent studies on TiN synthesis have focused on chemical vapor deposition (CVD) processes for film preparation.[1] TiN films have been prepared mainly in TiCl$_4$–NH$_3$[7] and Ti(NR$_2$)$_4$–NH$_3$ systems,[8,9] and a variety of compounds possessing Ti–N bonds[10] other than Ti(NR$_2$)$_4$ can also be used as precursors.

Another synthetic route to TiN is the pyrolysis of inorganic and organometallic compounds possessing Ti–N bonds. This chemical route is capable of TiN-film preparation, if precursors are soluble or spinnable.[11] Insoluble polymeric precursors were prepared by the ammonolysis of Ti(NMe$_2$)$_4$, and were converted into TiN powders via pyrolysis.[12,13] Aminolysis of Ti(NMe$_2$)$_4$ led to the formation of soluble polymers which appeared to have ladder-like structures,[14–16] and such precursors were converted into TiN powder and film via pyrolysis.[15,16] TiN precursors were also prepared by the reactions between Ti(NMe$_2$)$_4$ and diamines (R(H)NCH$_2$CH$_2$N(H)R, R = H, Me, Et).[16] If R = H, the product was an insoluble polymer, whereas the use of diamines with R = Me and Et resulted in the formation of soluble precursors. TiN precursors can also be prepared electrochemically using titanium metal as a starting material.[17,18]

This paper describes the preparation of TiN via reactions between Ti(NMe$_2$)$_4$ and three different kinds of diamines [H$_2$NCH$_2$CH$_2$NH$_2$, Me(H)NCH$_2$CH$_2$N(H)Me and piperazine (HN(CH$_2$CH$_2$)$_2$NH)]. Precursors were characterized spectroscopically, and were pyrolyzed under argon and NH$_3$–N$_2$ atmospheres. Emphasis is placed upon the pyrolyzed products, which were characterized by compositional analysis and X-ray powder diffraction (XRD).

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EXPERIMENTAL

All the procedures were performed under a protective nitrogen atmosphere using a standard Schlenk technique or a globe box filled with nitrogen. Benzene and diamines (except piperazine) were freshly distilled using appropriate drying agents before use. Piperazine was dried under reduced pressure before use. Tetrakis(dimethylamino)titanium, $Ti(NMe_2)_4$, was used as received.

Precursors possessing Ti–N bonds were prepared on the basis of a previous report[16] by the reactions of $Ti(NMe_2)_4$ with diamines (DAs) with $Ti(NMe_2)_4$:DA = 1:2. For ethylenediamine and its dimethyl derivative (N,N'-dimethylethylenediamine), an ideal reaction can be expressed by Eqn [1];
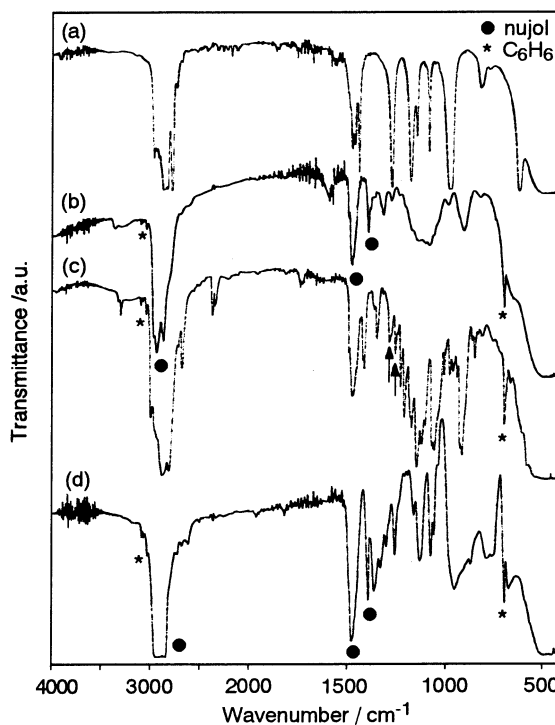
$$Ti(NMe_2)_4 + 2R(H)NCH_2CH_2N(H)R$$
$$\longrightarrow 1/n[Ti(RNCH_2CH_2NR)_2]_n + 4Me_2NH \quad [1]$$
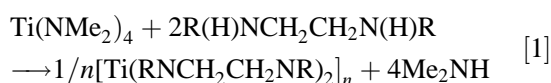
where R = H or Me. About 4 g of liquid $Ti(NMe_2)_4$ was dissolved in 50 ml of benzene in a 200-ml three-necked flask. DA dissolved in 20 ml of benzene was dropped slowly into a $Ti(NMe_2)_4$ solution at room temperature with stirring. Then the resulting solution was gradually heated, and finally refluxed at 78 °C for 20 h.

When $Ti(NMe_2)_4$ was reacted with $H_2NCH_2CH_2NH_2$ and $HN(CH_2CH_2)_2NH$, insoluble yellow precipitates were collected after the removal of the solvent and the volatile components under reduced pressure. By reaction between $Ti(NMe_2)_4$ and $Me(H)NCH_2CH_2N(H)Me$, however, a viscous black solution was obtained with the formation of a small amount of an insoluble precipitate, which was removed by filtration. The removal of the solvent gave a black oily product.

The precursors were characterized by IR spectroscopy (Perkin-Elmer FTIR-1640), and ^1H NMR (270 MHz, C_6D_6) spectroscopy was also applied for a soluble precursor. Thermogravimetric (TG) analyses of the precursors were carried out with a Shimadzu TGA-50 thermobalance at a heating rate of 10 °C min^{-1} under a helium flow.

The precursors were pyrolyzed in a tube furnace. About 0.5 g of precursor was placed in an Al_2O_3 boat, which was then introduced into an Al_2O_3 tube filled with argon or NH_3. For pyrolysis under argon, the precursor was heated at 600, 1000, and 1500 °C for 2 h with a flow rate of 100 ml min^{-1}. For pyrolysis under $NH_3–N_2$, the precursor was first heated at 600 °C under NH_3 (30 mL min^{-1}), and cooled to room temperature. Then, the product

Figure 1 IR spectra of (a) $Ti(NMe_2)_4$, and of the reaction products of $Ti(NMe_2)_4$ with (b) $H_2NCH_2CH_2NH_2$(PreH), (c) $Me(H)NCH_2CH_2N(H)Me$(PreMe) and (d) $HN(CH_2CH_2)_2NH$(PreP); the spectra (a) and (c) were obtained in the neat state, and the spectra (b) and (d) were obtained in Nujol.

pyrolyzed under NH_3 was heated again at 1350 °C for 8 h under N_2 (100 ml min^{-1}). The heating and cooling rate was 5 °C min^{-1}.

The pyrolyzed residues were analyzed by XRD (CuKα Mac Science MXP^3 diffractometer). The lattice parameters of the pyrolyzed residues were calculated by the non linear least-squares method. The amounts of nitrogen, oxygen and carbon in the pyrolyzed residues were measured with LECO TC-436 and CS-444LS instruments. The pyrolyzed residues were dissolved by treatment with aqua regia in a Teflon decomposition vessel at 130 °C for 24 h, and the amounts of titanium were determined by inductively coupled plasma emission spectroscopy (ICP; Nippon Jarrell Ash ICAP-575 II).

RESULTS AND DISCUSSION

The precursors prepared with $H_2NCH_2CH_2NH_2$ and piperazine [$HN(CH_2CH_2)_2NH$] (hereafter PreH

and PreP, respectively) were obtained as insoluble solids, implying that they possess cross-linked structures. However, the average molecular weight should be much lower for the liquid precursor obtained from $Ti(NMe_2)_4$ and $Me(H)NCH_2CH_2N(H)Me$ (PreMe).

The IR spectra of the precursors, as well as that of $Ti(NMe_2)_4$, are shown in Fig. 1. After the reactions with each of the DAs, the v(Ti-N) band intensities[19] of $Ti(NMe_2)_4$ (at 588 cm^{-1}) decrease dramatically, and new bands appear at 558–650 cm^{-1}. Bradley and Gitlitz studied the IR spectra of $Ti(NMe_2)_{4-x}$ $(N^nPr_2)_x$, and reported that mixed species showed two v(Ti-N) bands near the position for Ti-NMe$_2$ and that for Ti-N^{n}Pr$_2$.[19] Since only one v(Ti-N) band is observed for each of PreH and PreP, we assume that most of the NMe$_2$ groups are lost during the syntheses of PreH and PreP. This is further supported by the fact that the δ(CH$_3$) band[19] of the NMe$_2$ groups ($\sim$1250 cm^{-1}) is hardly detected in the IR spectra of these two precursors. In the IR spectrum of PreMe, a few bands assignable to v(Ti-N) are observed at 558, 584, and 650 cm^{-1}. In addition, bands attributable to the (CH$_3$) mode are observed at 1242 and 1274 cm^{-1} (as shown by arrows). Thus, PreMe appears to contain a small proportion of unreacted NMe$_2$ groups.

In the IR spectrum of PreH, weak bands due to (N-H) and δ(NH$_2$) modes are observed. The number of H atoms attached to N (i.e. the number of NH) is twice the number of the NMe$_2$ groups in the $Ti(NMe_2)_4$–$H_2NCH_2CH_2NH_2$ system (in the other two systems, the number of NH is equal to that of the NMe$_2$ groups). Hence, the NH groups should be present even after the complete removal of the NMe$_2$ groups (which can be achieved with the equivalent number of NH groups; see Eqn [1] in the Experimental section). Based on the loss of most of the NMe$_2$ groups and the nominal NH$_2$: NMe$_2$ ratio (1:1), the presence of δ(NH$_2$) bands indicates that some nitrogen atoms should be present as imido bridges (Ti-N-Ti), which partly accounts for cross-linked structure formation. Imido-bridge structures have also been proposed for the precursors prepared between Ti(NR$_2$)$_4$ and primary amines, RNH$_2$.[14–17] It should also be expected that some of the $H_2NCH_2CH_2NH_2$ acts as a chelating agent[16] and forms bidentate ligands bridging two titanium atoms (**A**).

$$(TiNCH_2CH_2NTi) \qquad (A)$$

The IR spectrum of PreP shows the absence of
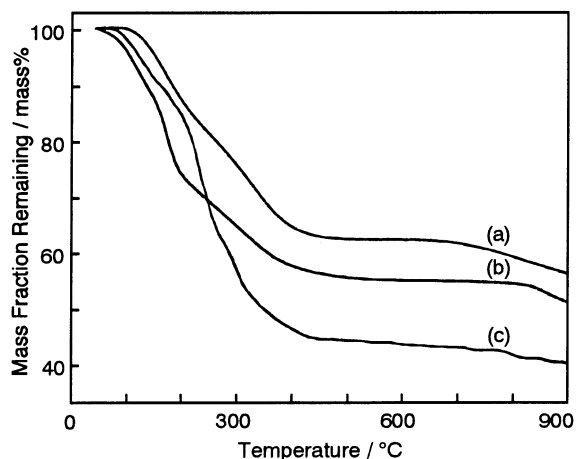
Figure 2 TG curves of the reaction products of $Ti(NMe_2)_4$ with (a) $H_2NCH_2CH_2NH_2$(PreH), (b) $HN(CH_2CH_2)_2NH$(PreP) and (c) $Me(H)NCH_2CH_2N(H)Me$(PreMe) under He at a heating rate of 10 °C min^{-1}.

NH groups, which is consistent with the loss of most of the NMe$_2$ groups. Since piperazine cannot act as a chelating reagent, piperazine should bridge two Ti atoms to form a cross-linked structure.

Oily PreMe is the only product that can be analyzed with ^{1}H NMR. Many sharp signals were observed at 2–5 ppm (not shown), indicating the presence of various environments for the methyl groups. It should also be noted that no broad signals were observed, suggesting that the product is not highly polymeric. Seyferth and Mignani prepared TiN precursors in the same and very similar systems, and observed the formation of monomeric $[Ti(RNCH_2CH_2NR)_2]$ with oligomers.[16] Therefore we assume that PreMe consists of mixtures of monomeric and oligomeric species. The IR spectrum of PreMe shows the presence of a v(N-H) band at 3290 cm^{-1}, consistent with the presence of remaining NMe$_2$ groups.

The pyrolysis behavior of these three precursors was investigated by TG analyses (Fig. 2). All the precursors showed a two-step mass loss (room temperature to $\sim$500 °C and $\sim$700 °C upwards). The ceramic yield of PreMe is the lowest based on the TG results (40%, up to 900 °C), and the other two precursors show quite high ceramic yields of over 50% (the ceramic yield of PreH is higher than that of PreP).

When the precursors were pyrolyzed at 1500 °C under argon, black residues were obtained. The ceramic yields of the precursors (Table 1) are between 20 and 30%, and these values are much

Table 1 Ceramic yields and characteristics of the pyrolyzed products for pyrolysis under Ar at 1500 °C for 2 h

| | Precursor | | |
	PreH	PreMe	PreP
Ceramic yield (mass%)	26	21	27
Loss of Ti (mass%)	33	44	31
Elemental analysis (mass%)[a]			
Ti	76.0 (1)	67.5 (1)	52.7 (1)
N	2.1 (0.09)	4.2 (0.21)	5.4 (0.35)
C	18.7 (0.98)	25.2 (1.49)	34.7 (2.63)
O	1.5 (0.06)	1.6 (0.07)	7.0 (0.40)
Total (mass%)	98.3	98.5	99.8
Lattice parameter (nm)	0.4321	0.4314	0.4285

[a] Molar ratio in parentheses.

lower than the corresponding values obtained by TG analysis up to 900 °C. The ratios of Ti lost during pyrolysis are estimated from the amounts of Ti in the precursors and those in the 1500 °C pyrolysis residues (Table 1). PreMe shows the lowest ceramic yield and the highest Ti loss (consistent with TG results), but these values (yield and Ti loss) are not very different from those of the other precursors. Based on the difference in the precursor structures, PreMe, which appears to consist of monomeric and oligomeric species, is expected to show a much lower yield than those of the other cross-linked precursors. In addition, as shown in Fig. 2 the TG curve profile of PreMe is similar to those of the other two precursors, and no sharp mass loss (indicative of volatilization) is observed. Thus, we assume that the pyrolysis of PreMe leads to the formation of a cross-linked structure without considerable volatilization, and is finally converted into ceramic residue with a reasonable yield. Thus, PreMe is the most attractive precursor among the three examined because of its solubility.

The pyrolyses of the precursors under argon at 1500 °C resulted in the formation of well-crystallized single-phase rock-salt-type products. The XRD pattern of the product from PreH is shown in Figure 3 (c) and the lattice parameters of all the products are listed in Table 1. TiN is known to possess a rock-salt-type structure, and can form solid solutions with TiC and TiO.[20–23] The observed lattice parameters are close to that of TiC (0.4327 nm)[20] rather than those of TiN (0.4240 nm)[20] and TiO (0.4178 nm).[24] The compositions of the products (Table 1) also reveal that the N:Ti ratios are very low [0.10:1 (PreH),0.21:1 (PreMe) and 0.35:1 (PreP)], and considerable amounts of carbon are present. The presence of

carbon remaining in the residues obtained by pyrolysis under argon has also been reported previously.[16,17]

It should be noted that the initial N:Ti ratios in the precursors should be 4:1 for PreMe and PreP [since the NMe_2 groups in $Ti(NMe_2)_4$ are replaced by the same number of -NMe (PreMe) or = N (PreP) groups, the N:Ti ratio should be maintained during the precursor synthesis] or equal to or above 2:1 for PreH [the N:Ti ratio ranges from 4:1 (the value for the 1:1 reaction) down to 2:1 (assuming that one NH_2 group reacts with two NMe_2 groups to form each imido bridge)]. Thus, it should be concluded that large amounts of nitrogen are lost during pyrolysis. In order to obtain further information, PreH was pyrolyzed at lower temperatures (600 and 1000 °C). After the pyrolysis at
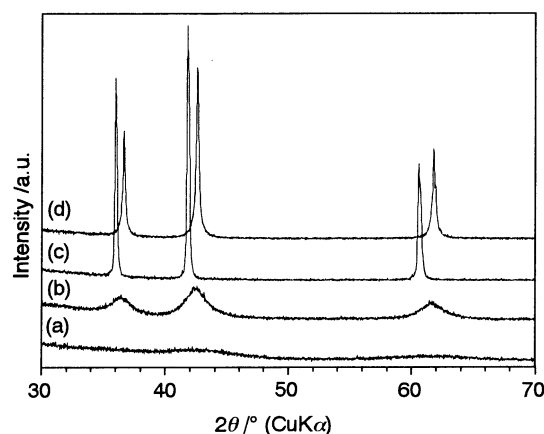
Figure 3 XRD patterns of the reaction product of $Ti(NMe_2)_4$ with $H_2NCH_2CH_2NH_2$(PreH) pyrolyzed under argon at (a) 600 °C, (b) 1000°C, (c) 1500°C; and (d) pyrolyzed under NH_3–N_2 (for conditions see the Experimental section).

Table 2 Compositional characteristics of the reaction product of $Ti(NMe_2)_4$ with $H_2NCH_2CH_2NH_2$(PreH) pyrolyzed under argon

Pyrolysis temp.(°C)	Elemental analysis (mass%)					Empirical formula
	Ti	N	C	O	Total	
600	50.7	13.0	20.0	13.7	97.4	$TiN_{0.88}C_{1.58}O_{0.81}$
1000	51.4	8.5	20.9	9.9	90.7	$TiN_{0.57}C_{1.63}O_{0.58}$

Table 3 Ceramic yields and characteristics of the products of pyrolysis under NH_3–N_2 (at 600 °C for 2 h under NH_3 and subsequently at 1350 °C for 8 h under N_2)

	Precursor		
	PreH	PreMe	PreP
Ceramic yield (mass%)	41	25	19
Loss of Ti (mass%)	1.0	27	34
Elemental analysis (mass%)[a]			
Ti	71.2 (1)	74.3 (1)	71.6 (1)
N	16.0 (0.77)	19.2 (0.89)	14.5 (0.69)
C	3.1 (0.17)	1.4 (0.08)	9.6 (0.54)
O	4.7 (0.20)	4.4 (0.18)	4.3 (0.18)
Total	95.0	99.3	100
Lattice parameter (nm)	0.4244	0.4243	0.4250

[a] Molar ratio in parentheses.

600 °C, the product was amorphous, as shown by its XRD pattern [Fig. 3 curve (a)]. Since the N:Ti ratio is 0.88:1 (Table 2), a considerable amount of nitrogen was lost during the pyrolysis up to 600 °C. After the pyrolysis at 1000 °C, a poorly crystalline rock-salt-type phase was detected by XRD [Fig. 3 curve (b)]. A lower N:Ti ratio (0.57:1) indicated a further loss of nitrogen at 600–1000 °C (Table 2); this may be ascribed to the loss of nitrogen during the crystallization from an amorphous phase. The much lower N:Ti ratio for the 1500 °C pyrolysis product (0.10:1) shows that additional loss of nitrogen occurred at high temperature, consistent with the lower ceramic yield for the 1500 °C pyrolysis.

The pyrolyses under NH_3–N_2 resulted in the formation of light-brown solids. The XRD pattern of the pyrolyzed residue obtained from PreH is shown in Fig. 3 curve (d); all the pyrolyzed residues were single-phase Ti(N,C,O). All the lattice parameters of the products listed in Table 3 are close to that of TiN (0.4240 nm).[20] The yields range from 41% (PreH) to 19% (PreP), and are comparable with the reported value for the precursor prepared in the $Ti(NMe_2)_4$-Me(H)NCH$_2$CH$_2$N(H)Me system in the same way.[16] The compositional analysis reveals that N:Ti ratios range between 0.69:1 and 0.89:1 (Table 3). It is also revealed that the carbon contents are much smaller than those of the corresponding products pyrolyzed under argon, consistently with the previous studies on TiN precursor pyrolysis.[16,17] For the AlN precursor prepared in an AlR_3–$H_2NCH_2CH_2NH_2$ system, the amine-exchange reaction during pyrolysis under an NH_3 atmosphere was reported; NH_3 reacted with $EtAlNCH_2CH_2NAlEt$ to release $H_2NCH_2CH_2NH_2$.[25] Thus, it appears that amine-exchange reactions also occur in the present systems, and the removal of DAs leads to the decrease in the carbon contents in the pyrolyzed products. The amount of Ti lost during the pyrolysis is very low for PreH (Table 3), which might be ascribed to the effective amine-exchange reaction and subsequent conversion into a highly cross-linked structure at lower temperature.

CONCLUSIONS

Precursors possessing Ti–N bonds have been prepared form $Ti(NMe_2)_4$–DA (diamine) systems using three different kinds of DAs [$H_2NCH_2CH_2NH_2$, Me(H)NCH$_2$CH$_2$N(H)Me, $HN(CH_2CH_2)_2NH$; $Ti(NMe_2)_4$:DA = 1:2], and their pyrolytic conversion processes and resultant ceramic residues were studied. The pyrolyses of these three precursors at 1500 °C under argon led to the

formation of carbon-rich products with ceramic yields of 20–30%. For all the precursors, the only crystalline phase was Ti(N,C,O), whose lattice parameters were close to that of TiC. Although the structure of the oily precursor using Me(H)NCH$_2$CH$_2$N(H)Me was very different from those of the other two cross-linked precursors, the pyrolysis results (TG curve, ceramic yield from 1500 °C pyrolysis and the amount of Ti lost during pyrolysis up to 1500 °C) were quite comparable with the corresponding values of the other two precursors; the precursor obtained from Me(H)NCH$_2$CH$_2$N(H)Me appeared to be converted into a cross-linked structure during pyrolysis. Pyrolysis under NH$_3$–N$_2$ effectively reduced carbon contents, and led to the formation of nitrogen-rich single-phase Ti(N,C,O).

REFERENCES

1. L. E. Toth, *Transition Metal Carbides and Nitrides*, Margrave, J.L. (ed.), Refractory Materials Vol. 7, Academic Press, New York, 1971.
2. W. Schintlmeister, O. Pacher, K. Pfaffinger and T. Raine, *J. Electrochem. Soc.* **123**, 924 (1976).
3. J. C. Haygarth, *Thin Solid Films* **72**, 51 (1980).
4. B. Karlsson, R. P. Shimshock, B. O. Seraphin and J. C. Haygarth, *Solar Energ. Mater.* **7**, 401 (1983).
5. M. Wittmer, *Appl. Phys. Lett.* **37**, 540 (1980).
6. C. Y. Ting, *J. Vac. Sci. Technol.* **21**, 14 (1982).
7. S. R. Kurtz and R. G. Gordon, *Thin Solid Films* **140**, 277 (1986).
8. R. M. Fix, R. G. Gordon and D. M. Hoffman, in *Chemical Vapor Deposition of Refractory Metals and Ceramics*, Besmann, T. M. and Gallois, B. M. (eds), Mat. Res. Soc. Symp. Proc. Vol. 168, Pittsburgh, PA, 1990, p. 357.
9. R. Fix, R. G. Gordon and D. M. Hoffman, *Chem. Mater.* **3**, 1138 (1991).
10. R. M. Fix, R. G. Gordon and D. M. Hoffman, *Chem. Mater.* **2**, 235 (1990).
11. C. K. Narula, *Ceramic Precursor Technology and Its Applications*, Marcel Dekker, New York, 1995.
12. G. M. Brown and L. Maya, *J. Am. Ceram. Soc.* **71**, 78 (1988).
13. D. V. Baxter, M. H. Chisholm, G. J. Gama, V. F. DiStasi, A. L. Hector and I. P. Parkin, *Chem. Mater.* **8**, 1222 (1996).
14. D. C. Bradley and E. G. Torrible, *Can. J. Chem.* **41**, 134 (1963).
15. H. Zheng, K. Oka and J. D. Mackenzie, in *Better Ceramics Through Chemistry V*, Hampden-Smith, M. J., Klemperer, W. G. and Brinker, C. J. (eds), Mat. Res. Soc. Symp. Proc. Vol. 271, Pittsburgh, PA, 1992, p. 893.
16. D. Seyferth and G. Mignani, *J. Mater. Sci. Lett.* **7**, 487 (1988).
17. C. Rüssel, *Chem. Mater.* **2**, 241 (1990).
18. C. B. Ross, T. Wade and R. M. Crooks, *Chem. Mater.* **3**, 768 (1991).
19. D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc. A.* 980 (1969).
20. H. J. Beattie, Jr. and F. L. VerSnyder, in *Trans. Am. Soc. Metals*, Bayless, R.T. (ed.), American Society for Metals, Cleveland, OH, 1953, p. 397.
21. P. Duwez and F. Odell, *J. Electrochem. Soc.* **97**, 299 (1950).
22. E. K. Storms, *The Refractory Carbides*, Margrave, J. L. (ed.), Refractory Materials Vol. 2, Academic Press, New York, 1969.
23. G. Neumann, R. Kieffer and P. Ettmayer, *Monatsh. Chem.* **103**, 1130 (1972).
24. M. E. Straumanis and H. W. Li, *Z. Anorg. Allg. Chem.* **305**, 143 (1960).
25. Z. Jiang and L. V. Interrante, *Chem. Mater.* **2**, 439 (1990).