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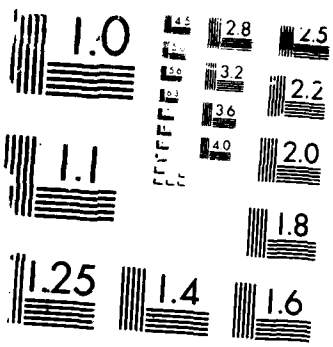

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THE PREPARATION OF TITANIUM NITRIDE AND TITANIUM CARBONITRIDE BY THE PRECERAMIC POLYMER ROUTE

by

Dietmar Seyferth and Gerard Mignani

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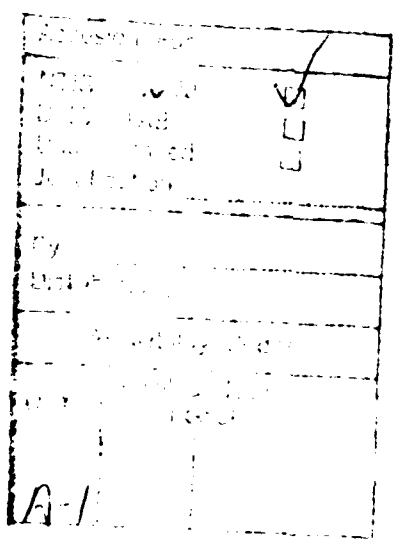

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FIELD	GROUP	SUB-GROUP	titanium nitride; titanium amides; titanium carbonitride; ceramics

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

The pyrolysis of selected titanium amides in a stream of ammonia gives titanium nitride. In a stream of argon titanium carbonitride is produced.

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titanium nitride, titanium [illegible]
titanium carbonitride, ceramics

19 ABSTRACT (Continue on reverse if necessary and identify by block number)
[illegible] polymeric titanium [illegible] in a stream of [illegible] gives titanium [illegible] in a stream of [illegible] titanium carbonitride is produced.

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The Preparation of Titanium Nitride and Titanium Carbonitride by the Preceramic Polymer Route

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Titanium nitride, TiN, is a very thermally stable (mp 2950°C) and a very hard (8 - 9 on the Moh scale) material. It is not attacked by acids (except hot aqua regia), but boiling alkalies decompose it. It is rapidly oxidized at high (~1200°C) temperatures by O_2, NO and CO_2 [1]. The conventional routes for the preparation of titanium nitride all involve high temperature chemistry [1].

The thermal decomposition of simple mononuclear titanium amides has been reported as an alternate route to titanium nitride [2]. Eq. 1 gives one example. Also, the ammonolysis of $[(CH_3)_2N]_4Ti$ in liquid ammonia resulted in dimethylamine displacement and formation of a solid product of idealized formula $Ti_3(N)_3(NH_2)_2[N(CH_3)_2]$ whose pyrolysis gave titanium nitride [3].

$$(R_2N)_4\,Ti \xrightarrow{300\text{-}500°C} TiN + \text{organic products} \qquad (1)$$

(R = C_2H_5, C_3H_7, C_4H_9)

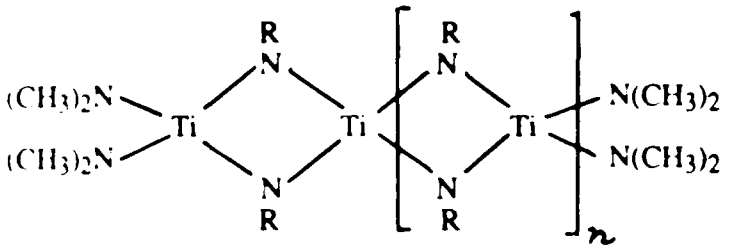
We have developed useful routes for the preparation of silicon [4] and boron [5] carbonitrides and nitrides by the pyrolysis of suitable polymeric precursors, and we were interested in developing such an approach for the synthesis of titanium carbonitride and nitride. We report some preliminary results.

The amine exchange reaction of $[(CH_3)_2N]_4Ti$ with various primary amines, RNH_2 (R = n-C_4H_9, n-C_6H_{13}, n-C_8H_{17}, $CH_3OCH_2CH_2$) occurs in benzene solution at reflux, a reaction described by Bradley and Torrible in 1963 [6].

* Author to whom inquiries should be addressed.

** On leave from Rhône Poulenc Recherches, 1986.

With the unbranched primary amines the products are waxy red solids, average molecular weight greater than 1100, which are soluble in organic solvents. The IR and proton NMR spectra as well as the elemental analyses of these products could be rationalized in terms of Bradley's formulation of such materials as shown in formula I,



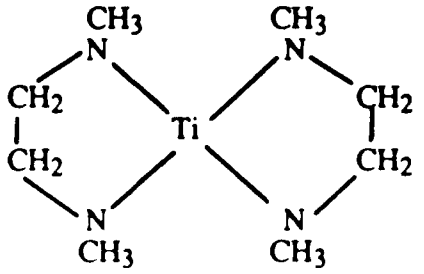
I

although the presence of some cyclic structures could not be excluded. Pyrolysis of the red solid obtained when n-butylamine was the primary amine used in a stream of dry ammonia (room temperature to 250°C at 10°C per min.; hold for 0.1 hr.; 250°C to 1000°C at 5°C per min., hold for 0.3 hr.) gave a golden-yellow solid residue (the color typical of TiN) in 32.3% (by weight) yield (calcd. for conversion of I, i.e., of $[(C_4H_9N)_2Ti]_x$, to TiN: 32.6%). The analysis of the ceramic residue (76.7% Ti, 22.1% N, 0.26% C, 0.9% O, 0.08% H) was in fairly good agreement for that required for TiN (77.4% Ti, 22.6% N).

These results indicate that during the pyrolysis in a stream of ammonia an amine displacement reaction takes place, with amido (NH_2) functions replacing C_4H_9N and terminal $(CH_3)_2N$ substituents. At those temperatures and as the temperature is increased, thermal condensation processes then convert the intermediate titanium amides and imides to titanium nitride.

Similar reactions of $[(CH_3)_2N]_4Ti$ with diamines were examined as well. Such reactions, carried out either in benzene solution at 80°C or with no solvent at 100-120°C using $CH_3NHCH_2CH_2NHCH_3$, $C_2H_5NHCH_2CH_2NHC_2H_5$ and a commercial 85/15 mixture of $CH_3NHCH_2CH_2NHCH_3$ and $CH_3NHCH_2CH_2NH_2$ gave red, waxy solid products of low (225-350) average molecular weight (cryoscopy in benzene). A similar reaction with $C_2H_5NH(CH_2)_3NHC_2H_5$ gave a red oil. Analyses of these products by fast atom bombardment mass spectrometry showed them to be a mixture of mainly the monotitanium species, II, but with also some higher oligomers, i.e., di, tri, etc. nuclear

species, present as well. All of these products were soluble in organic solvents. In contrast, such reactions of ethylenediamine itself did not give soluble products.



II

Pyrolysis of these titanium compounds derived from diamines under a stream of ammonia again gave fairly pure TiN. The example of the $CH_3NHCH_2CH_2NHCH_3$ reaction product is typical. The red solid obtained in 61% yield (MW 234) in the reaction of 17.7 mmol of $[(CH_3)_2N]_4Ti$ and 39.8 mmol of the diamine in 60 ml of benzene for 18 hr. at reflux was pyrolyzed in a stream of ammonia (temperature program as previously noted). A yellow ceramic residue was obtained in 26.7% yield (calcd TiN yield for this product, 28.1%). The analytical data (74.2% Ti, 23.5% N, 1.4% C, 0.5% O) indicated the formation of fairly pure TiN. A product of somewhat higher molecular weight (325) was obtained in a similar reaction of the 85/15 $CH_3NHCH_2CH_2NHCH_3/CH_3NHCH_2CH_2NH_2$ mixture with $[(CH_3)_2N]_4Ti$ (MW for Ti species is 220; for the Ti_2 species, 440). Pyrolysis to 1000°C under ammonia gave a yellow residue which contained 75.2% Ti, 22.5% N and only minor amounts of carbon and oxygen. Pyrolysis to 1500°C gave crystalline material whose powder X-ray diffraction lines matched those of authentic TiN.

When the pyrolysis of this precursor was carried out in a stream of argon to 1000°C, a black solid remained which contained 30.9% C in addition to Ti (45.5%) and N(9.9%). Obviously, a titanium carbonitride had been formed. The decomposition of the organonitrogen substituents provided carbon as well as nitrogen.

The approach which we describe is indeed a route to titanium nitride. The diamine-derived precursors at best are oligomeric, but the primary amine-derived materials are in the "preceramic polymer" molecular weight range and these merit further, more detailed investigation. A major drawback of these materials is the fact that their potential TiN content is quite low. For instance, in the case of the n-butylamine

product, 67.4% of the initial weight must be lost in the reaction with NH_3 in order to obtain the theoretical amount of TiN. Ideally, on the basis of ceramic yield considerations, similar products with methyl- or ethylamine would be better, but these appear to be insoluble in organic solvents (hence not readily processable) although they may find some application in TiN synthesis.

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REFERENCES

1. J. Whitehead in "Kirk-Othmer Encyclopedia of Chemical Technology", Wiley, New York, Third Edition, vol. 23, pp. 135-136.

2. (a) K. Sugiyama, S. Pac, Y. Takahashi and S. Motojima, J. Elecctrochem. Soc., 122 (1975) 1545.
(b) V.V. Kutyreva, V.A. Varyukhin, O.N. Suvorova, B.A. Nesterov and G.A. Domrachev, Zh. Neorg. Khim., 15 (1979) 1692.
(c) L.M. Dyagileva, V.P. Marin, E.I. Tsyganova, I.L. Gaidym and Yu. A. Aleksandrov, Zh. Obshch. Khim. 54 (1984) 609.

3. G.M. Brown and L. Maya, Advanced Ceram. Mat., in press; see also L. Maya, in "Better Ceramics Through Chemistry II", C.J. Brinker, D.E. Clark and D.R. Ulrich, editors, Material Reserach Society: Pittsburgh, 1986, pp. 401-406.

4. (a) D. Seyferth and G.H. Wiseman, J. Am. Ceram. Soc., 66 (1983) C-13.
(b) D. Seyferth and G.H. Wiseman, J. Am. Ceram. Soc., 67 (1984) C-132.
(c) D. Seyferth and G.H. Wiseman, U.S. patent 4,482,669 (Nov. 13, 1984).

5. W.S. Rees, Jr. and D. Seyferth, J. Am. Ceram. Soc., in press.

6. D.C. Bradley and E.G. Torrible, Can. J. Chem. 41 (1963) 134.

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