Low-temperature Routes to Early Transition-metal Nitrides

Jonathan C. Fitzmaurice, Andrew L. Hector and Ivan P. Parkin *
Department of Chemistry, The Open University, Milton Keynes MK7 6AA, UK

Thermal initiation of the reaction of lithium nitride with anhydrous transition-metal halides produces crystalline transition-metal nitrides of various compositions M_xN_y (M = Y, La, Ti, Zr, Hf, V, Nb, Ta, Cr or Mn) *via* an exothermic solid-state metathesis reaction. Reaction of anhydrous late transition-metal halides with lithium nitride produces the metal (M = Mo, W, Fe, Co, Ni, Cu, Pt, Zn or Cd), dinitrogen and lithium halide. The metal nitrides were purified by tetrahydrofuran trituration and characterised by X-ray powder diffraction, scanning electron microscopy, energy dispersive analysis with X-rays, magnetic moment measurements, FTIR spectroscopy and microanalysis.

Transition-metal nitrides are hard, durable, abrasive-resistant refractory materials with thermal and electrical conductivities similar to those of metals.[1,2] Titanium nitride has a number of industrial uses ranging from reflectance and hardness coatings to microelectronic devices.[3,4] Transition-metal nitrides are also used as catalysts for foam-glass productions,[5] Fischer–Tropsch processes,[6] oxygen–nitrogen cleavage[7] and hydrogenation–coal gassification.[8] Conventionally, transition-metal nitrides have been made at high temperature (> 1000 °C) by the reaction of ammonia or dinitrogen with the pure metal or metal hydride.[9] Industrially, they have been deposited as coatings for steels and electronic devices by the reaction of a metal halide with ammonia at high temperature (600–800 °C).[10] One common feature of metal-nitride preparations is the sintering and annealing required to yield a crystalline product; for example, using a molecular precursor route, TaN has required[11] annealing for three days at 820 °C to induce crystallinity.

A current focal point in the development of new routes to novel and existing ceramic materials is the use of 'chemical molecular precursors'. Generally these are either a single compound that contains high amounts of the chosen elements, which under thermal degradation produce the required pre-ceramic material, or double-source compounds. In the case of metal nitrides double-source precursors normally involve use of ammonia and metal amides.[12] Such routes to metal nitrides have been studied for thin-film deposition[13] and bulk solid synthesis;[14] unfortunately they often suffer from sample contamination, either in the form of an oxide (from the reactor walls), or a carbide resulting from competitive decomposition pathways.[15]

Solid-state routes to metal sulfides and phosphides have been developed by Kaner and co-workers by reaction of anhydrous metal halides with sodium sulfide[16] and phosphides.[17] Such reactions have provided a rapid versatile method of producing minimum oxygen- and carbon-containing materials; once initiated the reaction is highly exothermic.

We report here an alternative solid-state route to crystalline early transition-metal nitrides *via* a rapid 'low temperature' initiated precursor approach.

Experimental

All reactions and preparations were carried out *in vacuo* or in a dinitrogen-filled dry box. Glass ampoules were made of either Pyrex, borosilicates or quartz glass and were either flame-dried under vacuum or heated to 400 °C for 6 h prior to reaction. All solvents were degassed with dinitrogen; tetrahydrofuran (thf) was distilled from sodium–benzophenone and stored over 4 Å molecular sieves prior to use. Metal halides were purchased from Aldrich and lithium nitride from Strem Chemicals and used as supplied. X-Ray powder diffraction patterns were obtained with a Siemens D5000 diffractometer using nickel-filtered Cu-Kα (λ = 1.5406 Å) radiation. Scanning electron microscopy (SEM) and energy dispersive analysis with X-rays (EDAX) data were determined using a JEOL JSM 820 instrument equipped with the Kevex system (Quantum detector Kevex delta 4 and Quantex 6.2 software). FTIR spectra, using pressed KBr discs were recorded on a Nicolet 205 (CsI) spectrometer and gas chromatography data on a Pye Unicam 204 chromatograph with a 5 Å sieves column using a thermal-conductivity detector and helium carrier gas, whilst magnetic-moment measurements were determined both by a Johnson Matthey balance and an Oxford Instruments resistive Faraday balance. Microanalyses were determined under fierce combustion conditions (powdered Sn, maximum O_2, 1800 °C) by MEDAC, Brunel University. Thermal initiation was achieved using a Lenton Thermal Design tube furnace.

Transition-metal Nitride Preparation.—Lithium nitride (50–100 mg) and an anhydrous metal halide MX_n (M = Y, La, Ti or V; X = Cl; $n = 3$; M = Ti, V, Zr or Hf; X = Cl; $n = 4$; M = Nb or Ta; X = Cl; $n = 5$; M = Cr; X = Cl; $n = 2$ or 3; M = Mn; X = I; $n = 2$) were ground together using an agate pestle and mortar. The powder was added to a thick-walled glass ampoule, sealed under vacuum and sonicated with an ultrasonic gun for 10 min. The ampoule was then wrapped in glass wool and placed in a conventional oven at 400 °C for 5–10 min. After a variable induction time of a few seconds to 5 min (dependent on the sample), a red glow emanated from the ampoule for 2–3 s, during which time a white solid sublimed onto the reactor walls, whilst the main bulk of the product was contained in a fused grey-black solid. The ampoule was removed from the oven, allowed to cool to room temperature, and then broken open in a N_2-filled glove-box. Trituration of the grey-black solid with thf (3 × 20 cm^3) for 10 h produced a fine black precipitate and a cloudy thf layer. Evaporation of the thf filtrate produces crystals of a white solid identified as LiCl (LiI when MnI_2 is used) by X-ray powder diffraction, a lithium flame test and EDAX. The black powders were identified as transition-metal nitrides by X-ray powder diffraction (Table 1), EDAX, magnetic-moment measurements and nitrogen microanalysis. Ceramic yields, based on the metal after thf trituration varied from 50% (TiN) to 90% (HfN) dependent on the sample (Found: C, < 0.2; H, < 0.2; Cl, < 0.25; Li, < 0.25; N, 6.40. Calc. for HfN: N, 7.25%. Found: C, < 0.3; H, < 0.2; Li < 0.25; N, 5.80. Calc. for Mn_4N: N, 6.00%).

These reactions were also studied by gas chromatography in a sealed ampoule with a gas adaptor (Table 1).

Table 1 X-Ray powder diffraction and gas chromatography data on the reaction of lithium nitride with anhydrous transition-metal halides

MX_n	Product	a_{obs}/Å	c_{obs}/Å	a_{lit}[a]/Å	c_{lit}[a]/Å	N_2 Detected (expected) (%)
YCl_3	YN	4.89	—	4.89	—	0 (0)
$LaCl_3$	LaN	5.33	—	5.30	—	0 (0)
$TiCl_3$	TiN	4.23	—	4.23	—	
$TiCl_4$	TiN	4.23	—	4.23	—	
$ZrCl_4$	ZrN	4.57	—	4.56	—	20 (25)
$HfCl_4$	HfN	4.51	—	4.51	—	20 (25)
VCl_3	VN	4.10	—	4.14	—	
	V_2N[b]	4.34	4.54	4.36	4.56	
VCl_4	VN	4.10	—	4.14	—	
$NbCl_5$	Nb_4N_3	4.38	4.32	4.38	4.32	45 (60)
	Nb_2N	4.67	4.93	4.68	4.95	
$TaCl_5$	Ta_2N	3.04	4.91	3.04	4.91	45 (60)
	TaN	3.37	—	3.37	—	
$CrCl_3$	Cr	2.88	—	2.88	—	
	Cr_2N[b]	4.17	4.44	4.17	4.44	55 (66)
$CrCl_2$	Cr_2N	4.17	4.44	4.17	4.44	
	Cr[b]	2.88	—	2.88	—	
$MoCl_3$	Mo	3.15	—	3.15	—	
	Mo_2N[b]	4.18	8.08	4.16	8.06	
$MoCl_5$	Mo	3.15	—	3.15	—	90 (100)
WCl_4	W	3.16	—	3.16	—	90 (100)
MnI_2	Mn_4N	3.84	—	3.85	—	
	Mn[b]	8.91	—	8.91	—	75 (80)
$FeCl_3$	Fe	2.87	—	2.87	—	
$NiCl_2$	Ni	3.53	—	3.53	—	
K_2PtCl_4	Pt	3.92	—	3.92	—	100 (100)
$ZnCl_2$	Zn	2.67	4.96	2.67	4.95	
$CdCl_2$	Cd	2.98	—	2.98	—	

[a] Ref. 18. [b] Minor phase, typically less than 20%.

Mixed-metal Nitrides.—Attempts at making mixed-metal nitrides were investigated under the same reaction and work-up conditions as above, except equimolar quantities of the starting metal halide powders were ground together before adding the lithium nitride.

Transition Metal Preparations.—The reactions of lithium nitride with other transition-metal halides MX_n (M = Co, Ni, Cd or Zn; X = Cl; $n = 2$; M = Mo or Fe; X = Cl; $n = 3$; M = W or K_2Pt; X = Cl; $n = 4$; $MoCl_5$ or CuI_2) were identical to those of the early transition-metal halides except that evacuated glass ampoules sealable with Teflon taps and an adaptor suitable for gas chromatography were used. After the reaction had been initiated and allowed to cool to room temperature, the ampoule was opened to an argon line for a few seconds to equalise the pressure and the gases chromatographed. This showed the presence of dinitrogen in excess of that of the initial argon and quantified as 0–100% (depending on the sample) of the nitrogen in the initial lithium nitride, as illustrated in Table 1.

The reaction of hydrated metal halides with lithium nitride invariably leads to an uncontrollable exothermic reaction which results in explosion of the ampoule. The reaction with anhydrous metal halides is also extremely exothermic and can cause ampoules to explode. The use of a safety screen around the oven and suitable tongs to handle the ampoule is advisable. No reaction was observed between the anhydrous metal halides and lithium nitride on manually grinding the reagents together. However caution must be exercised with reactions of liquid $TiCl_4$ or VCl_4 with Li_3N where some samples spontaneously self-initiated on addition of the metal halide to Li_3N with no external heating or grinding.

Results and Discussion

Crystalline powders of early transition-metal nitrides are produced in seconds using a thermally-initiated solid-state metathesis reaction of lithium nitride and anhydrous metal halides [equations (1)–(4)].

$$MCl_3 + Li_3N \xrightarrow{\text{ignition}} MN + 3LiCl \qquad (M = Y, La, Ti \text{ or } V) \qquad (1)$$

$$3MCl_4 + 4Li_3N \xrightarrow{\text{ignition}} 3MN + 12LiCl + \tfrac{1}{2}N_2 \qquad (M = Ti, Zr, Hf \text{ or } V) \qquad (2)$$

$$MCl_5 + \tfrac{5}{3}Li_3N \xrightarrow{\text{ignition}} MN_y + 5LiCl + xN_2 \qquad (M = Nb \text{ or } Ta) \qquad (3)$$

$$2CrCl_2 + \tfrac{4}{3}Li_3N \xrightarrow{\text{ignition}} Cr_2N + 4LiCl + \tfrac{1}{6}N_2 \qquad (4)$$

The reactions between the anhydrous metal halides and lithium nitride were initiated by heating in a conventional oven at 400 °C. After a variable induction period, ranging from a few seconds to five minutes, a red glow emanated from the sealed ampoule, with the reaction lasting two to three seconds. Invariably the walls of the ampoule were coated in a white solid while the bulk of the material was contained in a fused black lump. For the chlorides the white solid analysed as lithium chloride (using X-ray powder diffraction, lithium flame test and EDAX) while the black lump comprises predominantly of metal nitride with a small percentage of lithium chloride. The metal nitrides were purified by trituration with thf to remove lithium chloride. The isolated products (after thf trituration) from the reaction of anhydrous $LaCl_3$, YCl_3, $TiCl_3$, $TiCl_4$, VCl_4, $HfCl_4$ or $ZrCl_4$ with Li_3N were all phase pure binary nitrides (MN) as determined by X-ray powder diffraction, Table 1.

The FTIR spectra of the metal nitrides showed only a broad band centred at 450 cm^{-1} assignable to M–N vibrations. SEM micrographs of the initial metal nitrides all showed a smooth surface coating of lithium chloride; this coating was removed on thf trituration and micron-sized particles with sharp angles and faces were resolved. The Scherrer equation[19] (based on the X-ray diffraction linewidths) gives an average crystallite size of 320–380 Å for the triturated nitride products. EDAX data for the thf-washed nitrides showed the presence of only metal and nitrogen with no chlorine or oxygen evident (2–3% detection limit).

The magnetic moments of the metal nitrides were consistent with those observed in the literature;[9] however the degree of nitrogen vacancy and degree of crystallinity slightly alters the measurements (±0.2), which corresponds with previous findings for metal nitrides.[9,10] For example, HfN was found to have a room temperature magnetic moment (μ) of 1.73 at 0.4 T compared to a spin-only value ($S = \frac{1}{2}$) based on hafnium of $\mu = 1.76$. Interestingly the sample displayed an unusual field-dependent magnetisation.

Microanalysis of the triturated metal nitrides revealed only metal and nitrogen, no lithium or chlorine was present (less than 0.1%). Unfortunately, the refractory nature of metal nitrides and their resistance to oxidation even at high temperatures meant that conventional combustion analysis always indicated a low level of nitrogen in these samples. For example, the material identified as VN by X-ray powder diffraction and compositionally confirmed by step EDAX revealed only 10.1% nitrogen (expected 21.5%) by conventional microanalysis. Improvements to the microanalytical technique by using maximum oxygen flow, powdered tin and 1 800 °C combustion temperatures revealed nitrogen levels in HfN at close to the predicted value (6.41 compared to 7.26%).

The reaction of lithium nitride with early transition-metal halides is very exothermic and, once initiated, extremely rapid. Hess' law calculations[20] indicate that the enthalpy of formation for equation (1), M = La, is −300 kJ mol^{-1}, and for equation (2), M = Ti, is −900 kJ mol^{-1}. The observation of a red glow from the reaction is indicative of temperatures in excess of 750 °C. The temperature may be much higher as metal nitrides made by molecular precursor routes[21] often require annealing at 900 °C for 12 h to induce crystallinity and characterisation by powder X-ray diffraction. The crystallinity of lanthanide nitrides formed from low-temperature amide precursor routes has been found to be improved by the judicial addition of lithium amide or lithium chloride.[22] The lithium chloride coproduct in this reaction may help to induce order in the solid and coupled with the high temperatures generated, induce crystallinity even with a reaction time as short as a few seconds. Initiation by heating in a conventional oven at temperatures up to 300 °C did not stimulate any reaction in the samples under test, indicating that a critical induction temperature quantified at 375–425 °C is required for sufficient localised reaction to proliferate through the whole material. It is possible that the presence of a small amount of free lithium, generated either by thermal decomposition of lithium nitride, or present as a common impurity in commercial lithium nitride, may initiate the reaction.

Crystalline metals can also be produced from the reaction of some transition-metal halides MX_n (M = Co, Ni, Cd or Zn; X = Cl; $n = 2$; M = Mo or Fe; X = Cl; $n = 3$; M = W or K_2Pt; X = Cl; $n = 4$; $MoCl_5$ or CuI_2) with lithium nitride powder [equations (5) and (6)]. The metals are produced in a

$$MX_n + Li_3N \longrightarrow M + nLiX + N_2 \qquad (5)$$

$$3K_2PtCl_4 + 2Li_3N \longrightarrow 3Pt + 6KCl + 6LiCl + N_2 \qquad (6)$$

crystalline state but are contaminated with lithium halide by-product, which can be removed by washing with water or thf. The thermal stability of many of the binary nitrides of these metals is low (platinum group binary nitrides are unknown). The heat generated in the metathesis reaction is such that temperatures in excess of the decomposition points of the metal nitrides are generated with the subsequential formation of dinitrogen and reduction to the metal.

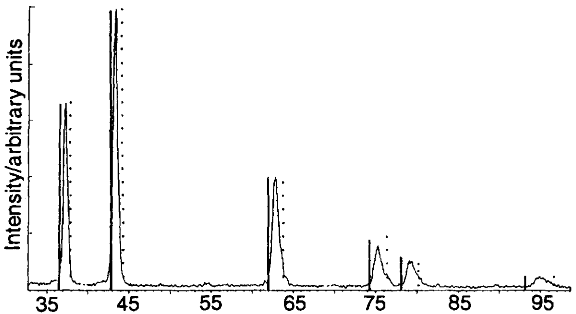

Fig. 1 X-Ray powder diffraction pattern of the reaction of equimolar quantities of $TiCl_4$ and VCl_4 with Li_3N. Standard patterns for TiN (——) and VN (· · · ·)

The phases of material detected by X-ray diffraction from the reaction of lithium nitride with anhydrous metal halides (Table 1) illustrate two points. First, as a period is traversed from left to right or on moving down a group the reaction produces more metal and dinitrogen and less metal nitride. Secondly, the oxidation state of the starting metal halide affects the phase of nitride produced. Metals in lower oxidation states are more likely to produce metal nitrides than undergo reduction to the metal as the reaction is less exothermic (less LiX is produced) and hence the decomposition temperature of any metal nitride formed is less likely to be reached (compare the products of the reaction of $MoCl_5$ with $MoCl_3$ and $CrCl_3$ with $CrCl_2$, Table 1).

Reaction of mixed anhydrous tantalum and hafnium chlorides with lithium nitride gives an X-ray powder diffraction pattern consistent with the formation of HfN, TaN and Ta_2N. The lattice *a* value observed for the hafnium nitride (4.52 Å) in the mixed-metal lattice is almost identical to that of the literature (4.51 Å).[18] Similarly, the tantalum nitride lattice remains unchanged, indicating that no Ta_xHf_yN species was formed. However, reacting mixed anhydrous hafnium and zirconium halides with lithium nitride produces a broader pattern, intermediate to those obtained for single HfN and ZrN patterns ($a = 4.54$, HfN $a = 4.51$, ZrN $a = 4.57$ Å) consistent with a solid solution. Similar results are obtained from the reaction of mixed $TiCl_4$ and VCl_4 with Li_3N, illustrated in Fig. 1. The step EDAX of the mixed nitrides Hf_xZr_yN and Ti_xV_yN shows constant values for the concentrations of the metals across the surface.

Conclusion

Solid-state methods offer a facile, rapid, low-energy, minimum-impurity route to crystalline transition-metal nitrides *via* metathesis reactions of Li_3N with anhydrous metal halides. These reactions require a heat source, but are exothermic or 'self-energetic' once initiated. The metathesis reaction to form transition-metal nitrides are most applicable to the early transition elements; for the late transition elements reduction to the metal and formation of dinitrogen occurs. This reaction can be used to form mixed-metal nitrides $M_xM'_yN$.

Acknowledgements

We thank the Leverhulme Trust (J. C. F.), the Nuffield Trust, the Royal Society, the SERC and the Open University research fund (for a studentship to A. H.).

References

1 J. C. Bailar, H. J. Emeleus, R. Nyholm and A. F. Trotman (Editors), *Comprehensive Inorganic Chemistry*, Pergamon, Oxford, 1973, vol. 2, p. 233.

2 N. Nobuhiro, M. Kazuo, M. Atshushi, F. Sakae, T. Toshijuki and A. Kelichi, *Kenkyu Hokoku-Tokyo-Toritsu Kogyo Gijutsu Senta*, 1990, **19**, 33.

3 S. Koichi, T. Masashi, O. Takuji and S. Susmu, *Jpn. Pat.*, 01308 848, 1989.

4 O. Masafumi and Y. Kenji, *Jpn. Pat.*, 02 68 926, 1990.

5 A. McNeill and K. Russel, PCT INT. WO90/09355, 1990.

6 C. Masters, *Adv. Organomet. Chem.*, 1979, **17**, 16.

7 G. I. Panov and A. S. Kharitonov, *Proc. Int. Congr. Catal.*, 1989, **817**, 3111; G. I. Panov, *Kinet. Katal.*, 1985, **54**, 1623.

8 R. B. Levy and J. A. Gusumano, *Liq. Fuels Coal, Proc. Symp.*, 1976, 79.

9 R. T. Sanderson, *Chemical Periodicity*, Reinhold, New York, 1960, pp. 201–207; C. C. Anderson and B. M. Davies, *J. Chem. Soc. A*, 1969, 1822.

10 L. Toth, *Transition Metal Carbides and Nitrides*, Academic Press, New York, 1971, p. 176.

11 M. M. Banaszak Holl, M. Kersting, B. D. Pendley and P. T. Wolozanski, *Inorg. Chem.*, 1990, **29**, 1518.

12 R. M. Fix, R. G. Gordon and D. M. Hoffman, *J. Am. Chem. Soc.*, 1990, **112**, 7833; R. G. Gordon and D. M. Hoffman, *Chem. Mater.*, 1992, **4**, 68.

13 L. V. Interrante, W. Lee, M. McConnell, N. Lewis and E. Hall, *J. Electrochem. Soc.*, 1989, **136**, 472.

14 C. B. Ross, T. Wade and R. M. Crooks, *Chem. Mater.*, 1991, **3**, 768.

15 C. Russel, *Chem. Mater.*, 1990, **2**, 241; C. Russel and M. M. Seibold, *J. Am. Ceram. Soc.*, 1989, **72**, 1503.

16 P. R. Bonneau, R. F. Jarvis and R. B. Kaner, *Inorg. Chem.*, 1992, **31**, 2127.

17 R. E. Treece, G. S. Macala and R. B. Kaner, *Chem. Mater.*, 1992, **4**, 9.

18 B. R. Brown, *Mellors Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longman, London, 1964, vol. 8, suppl. I, Nitrogen, part I, section III, pp 150–237; R. W. G. Wyckoff, *Crystal Structures*, Wiley, New York, 2nd edn., 1963, vol. 1.

19 H. P. Klug and L. E. Alexander, *X-Ray Diffraction Procedure for Polycrystalline and Amorphous Materials*, Wiley, New York, 2nd edn., 1974.

20 D. D. Wayman, W. H. Evans, V. B. Parker, R. H. Schumm, J. Halow, S. M. Bailey, K. C. Chumey and R. L. Nuttal, *The NBS Tables of Chemical Thermodynamics Properties*, American Chemical Society, Washington, 1982.

21 M. H. Chisholm, V. Distasi and I. P. Parkin, unpublished work.

22 R. L. LaDuca and P. T. Wolczanski, *Inorg. Chem.*, 1992, **31**, 1313.

Received 5th *March* 1993; *Paper* 3/01301D