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Chromium nitrides (CrN, Cr_2N) from solid state metathesis reactions: effects of dilution and nitriding reagent

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The solid state metathesis (SSM) reaction of $CrCl_3$ with Li_3N in a sealed evacuated Pyrex ampoule at 445 °C produces a propagation wave and enables phase pure Cr_2N to be isolated. The SSM reaction of $CrCl_2$ and Mg_3N_2 at 350–500 °C with dilutant $MgCl_2$ under similar conditions produces single phase CrN. Reaction of chromium oxide with Li_3N at 500 °C produces CrN after 2 h and Cr_2N after 60 h. This is the first report of a metal nitride being formed in a SSM reaction using an oxide starting material. The SSM nitrides were shown to have superior bulk nitridation levels (combustion analysis) and equivalent microscopic compositions (EELS, XRD) to commercial materials. The phases of chromium nitride produced were correlated with reaction enthalpy, dilution conditions and nitriding agent. The products were analysed by X-ray powder diffraction, FTIR, combustion microelemental analysis, SEM/EDAX, XPS and ELNES.

Transition metal nitrides have a number of properties; abrasive resistance, reflectance, hardness, electrical conductivity, inertness and diffusion resistance that make them useful for technological applications.[1] These applications include high temperature structural ceramics,[2] catalysts,[3] solar control coatings,[4] hard phases in steels,[5] drill bits, tool coatings, interconnects and diffusion barriers in microelectronics[6] as well as decorative coatings and jewellery.[7] Most transition metals form nitrides with the exception of the platinum group metals.[1] The early transition metal nitrides are refractory and non-stoichiometric. For example Ti forms cubic nitrides with stoichiometry $MN_{1.1}$ through to $MN_{0.45}$.[8] In these materials, the nitrogen occupies interstitial vacancies within a close packed metal array. Somewhat surprisingly all the early transition metals have a predominant mononitride phase MN_x (x *ca.* 1.1–0.7) which has the NaCl structure.[9] Later transition metal nitrides tend to be thermally unstable and are less well defined and utilised. The change over in nitride properties occurs at the Group VIa elements where the nitrides have intermediate stability; this has been grandly termed the ‘Chromium Enigma’.[10] For this group of elements CrN and the heminitrides Mo_2N, W_2N have the fcc structure whilst Cr_2N and the mononitrides WN, MoN are hexagonal. Small variations around the ideal stoichiometry are tolerated in the structures. For example the Cr_2N phase is stable with a nitrogen atom% from *ca.* 27.5–33%. However, CrN has a very narrow equilibrium range (47.5–50 atom% N).[11] Both CrN and Cr_2N are important as secondary metallurgical phases in refractory alloys, special steels and as dispersion strengtheners.[11] Interestingly, the presence of chromium nitride in high chromium steels can be deleterious, leading to chromium embrittlement. However, if the nitride is widely dispersed, it can be used for strengthening applications.[11]

Nitrides are traditionally synthesised by high temperature combination of metal and ammonia or nitrogen–hydrogen mix for prolonged time periods.[8–11] Problems can result from incomplete nitridation, incorporation of metal and oxygen in the final product, high energy costs and lack of control in crystallinity and particle sizes. Chemical vapour deposition routes to metal nitrides have employed molecular precursors such as homoleptic metal amides and ammonia, although notably, in some cases, the nitrogen in the final nitride comes from the ammonia and not the carefully tailored nitrogen containing precursor.[12] Sputtering based routes to nitrides are also common[13] and together with reactions of volatile anhydrous metal halides with ammonia, form the basis of most industrial routes to nitride coatings.[14] Bulk nitride materials have also been prepared by reactions of lithium amide and anhydrous metal chlorides,[15] by using carbon free precursors[16] and by self-propagating high temperature synthesis (SHS).[17] The latter reactions involve reacting the elements under pressure in a continuous flow reactor. The reaction temperature is maintained by the heat produced in the chemical reaction and not from an external source. A sub-class of SHS reactions, known as solid state metathesis (SSM) reactions, involving the reactions of anhydrous metal halides and lithium and sodium pnictides and chalcogenides was initially reported by Kaner and co-workers.[18] The scope of these reactions has been expanded to the formation of a vast array of inorganic ceramic materials from nitrides[19] to sulfides,[20] from dielectric insulators to super conductors.[21] The formation of nitrides has been of considerable focus both in synthesising a variety of phases and in helping to determine a mechanistic and empirical evaluation of the SSM reaction pathway and propagation velocity. All of the SSM reactions have a common theme. The reactions are exothermic, self propagating, self energetic with rapid heating and cooling rates sometimes accompanied by a propagation wave (also termed thermal flash, solid flame or synthesis wave[17]). As such, the reactions can give rise to unusual phases and stoichiometries that are difficult to obtain by traditional methods. For example, crystalline cubic TaN is formed in seconds from reaction of Li_3N and $TaCl_5$; conventionally high nitrogen pressures (20–160 atm), long time periods and temperatures in excess of 1600 °C are required.[22]

In virtually all synthetic studies for the formation of metal nitrides, oxygen contamination can be a problem. This can arise from surface oxidation of individual nitride grains through to intrinsic oxygen incorporation throughout a material, in effect an oxynitride solid solution. The SSM reactions to form AlN[19] have suffered from significant oxygen incorporation which has been traced to the purity of the initial nitriding reagents. Further, transition metal nitrides produced from

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SSM reactions are often deficient in nitrogen. This deficiency could be illusionary and due to the difficulties of getting good combustion microanalysis on such refractory materials, or be real and due to either intrinsic substoichiometric nitride or the presence of an oxynitride. One method that that has been shown to be sensitive to the degree of nitridation is measurement of the lattice parameter, shrinkage of which occurs with lower nitrogen levels.[9–11]

Initial survey work revealed that it was possible to form single phase nitrides by SSM reactions for the Group IIIa, IVa and Va elements.[19,20] However, for the chromium group, nitrides were difficult to form and at best constituted a minor phase alongside elemental metal. This was attributed to the fact that the reaction temperature produced in the SSM reaction exceeded the decomposition point of the Group VIa nitrides. Here we report the synthesis and characterisation of phase pure CrN and Cr_2N by SSM reactions using dilutant effects and alternative nitridation reagents to moderate the reaction temperature. We also report, for the first time, a detailed investigation of the purity and degree of nitridation in SSM reactions from both 'bulk' combustion microanalysis and 'nanoscaled' electron energy loss spectroscopy (EELS) analysis with associated energy loss near edge fine structure (ELNES).

Experimental

All reagents were handled under a nitrogen or argon atmosphere using either a Saffron Scientific glove box or Schlenk line techniques. Anhydrous chromium chlorides ($CrCl_2$, $CrCl_3$), magnesium and calcium nitrides were obtained from Strem Chemicals or Aldrich Chemical Co. and used as supplied. Lithium nitride was prepared from the reaction of lithium metal with nitrogen in molten sodium (350 °C) by Dr M. Barker of the University of Nottingham. All reagents were checked for phase and elemental purity by X-ray powder diffraction (XRD) and energy dispersive X-ray analysis (EDXA) prior to use. Methanol was distilled over magnesium and iodine and degassed with nitrogen prior to use. A Lenton Thermal Designs programmable tube furnace was used to initiate the reactions. Quartz or Pyrex ampoules (typically made with 2 mm thick walls and an internal volume of 15 cm^3) were annealed prior to use and thoroughly dried by flame under vacuum. XRD measurements were performed on a Siemens D5000 Diffractometer in transmission mode using germanium monochromated Cu-Kα_1 ($\lambda = 1.5406$ Å) radiation. Samples were indexed using TREOR or Metrix LS programmes. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 205 instrument using pressed KBr discs. Combustion microanalysis was performed by the UCL chemistry departmental service by vapourisation of an accurately weighed nitride sample containing tin powder (combustion aid), under an oxygen flow. The resultant nitrogen oxides, water and carbon dioxide contents were analysed by GC.[19] XPS measurements were performed with a VG ESCALAB 220i XL using focussed (300 μm spot) monochromatised Al-Kα radiation at a pass energy of 20 eV. Scans were acquired with steps of 50 meV. A flood gun was used to control charging and the binding energies were referenced to an adventitious C 1s peak at 284.8 eV. EELS (electron energy loss spectroscopy) samples were prepared by crushing in a pestle and mortar, dispersing the resultant powder in propan-2-ol followed by deposition onto a holey carbon film on a Cu grid. All of the samples were prepared in air. EELS spectra from the CrN and Cr_2N produced by the SSM reactions were recorded using a GATAN 666 PEELS spectrometer on a Philips CM20 transmission electron microscope with a field emission gun operated at 200 keV while those from commercial CrN and Cr_2N powders (Alpha Chemicals) were recorded using a similar spectrometer system on a VG Microscopes HB5 scanning transmission electron microscope operated at 100 keV. EELS gives an accuracy at best on the order of 1–2%. Both the CrN and Cr_2N commercial standards showed oxide contamination and mixed phases (the CrN sample contained about 5–10% Cr_2N by X-ray powder diffraction; CrN indexed with $a = 4.146$ Å; the Cr_2N sample showed *ca.* 5% CrN and the Cr_2N indexed with $a = 4.799$ Å, $c = 4.483$ Å). Significant surface oxide contamination was observed for the commercial samples (by EELS). However, this oxide material did not show up on the X-ray powder diffraction patterns and was assumed to be amorphous. Combustion elemental microanalysis of CrN and Cr_2N commercial samples gave N = 4.43 wt.% for CrN and N = 4.19 wt.% for Cr_2N; CrN requires N = 21.22 wt. % and Cr_2N requires N = 11.87 wt.%. These apparent discrepancies are considered below.

Reaction of $CrCl_n$ ($n = 2, 3$) with Mg_3N_2 and Ca_3N_2

Magnesium or calcium nitride (1–2 mmol), anhydrous chromium chloride (1 : 2 ratio of alkaline earth metal to chloride) and anhydrous magnesium chloride (1.5 molar equivalents) were ground together in an agate pestle and mortar and placed in a Pyrex ampoule which was sealed under vacuum. The ampoule was placed in a furnace at room temperature and rapidly brought to 300 °C (5–10 min) then raised from 350–500 °C over 1 h and kept at 500 °C for 1.5 h as detailed in Table 1. The ampoule was allowed to cool (*ca.* 10 °C min^{-1}) to room temperature. This produced a fused black-grey solid which was opened in air and the contents washed with methanol (2 × 30 ml) and dried *in vacuo*. The products were identified by XRD (Table 1), SEM/ EDXA and FTIR. Selected samples (Table 1) were also analysed by XPS and ELNES. Combustion microanalysis of the product from the reaction of $CrCl_2$ and Mg_3N_2 revealed N = 16.2 wt.%; $CrN_{0.72}$ requires N = 16.2 wt.%.

Reaction of $CrCl_3$ with Li_3N

Lithium nitride (0.070 g, 2 mmol) and anhydrous $CrCl_3$ (0.317 g, 2 mmol) were lightly ground together in an agate pestle and mortar and placed in a Pyrex ampoule which was sealed under vacuum. The reagents were spread out along the bottom of the ampoule (*ca.* 12 cm strip) and the temperature raised to 500 °C over 30 min; at *ca.* 445 °C an orange thermal flash was observed. The ampoule was then allowed to cool (*ca.* 10 °C min^{-1}) to room temperature, opened in air and the black contents washed with methanol (2 × 30 ml) and dried *in vacuo*. The products were identified by XRD (Table 1), SEM/ EDXA, FTIR and ELNES as Cr_2N. Combustion elemental microanalysis revealed N = 8.8 wt.%; $Cr_2N_{0.72}$ requires N = 8.8 wt.%.

Reaction of Cr_2O_3 with Li_3N

Chromium oxide (0.154 g, 1 mmol) and lithium nitride (0.070 g, 2 mmol) were ground together in an agate pestle and mortar in a nitrogen filled glove box and placed in a Pyrex ampoule that was sealed under vacuum. The ampoule was placed in a furnace at 500 °C and heated for 2 h. This produced a black-grey solid. The solid was washed with water (10 ml), methanol (2 × 10 ml) and dried *in vacuo*. The resultant solid was identified by X-ray powder diffraction (Table 1), FTIR and SEM/EDAX as CrN. Combustion elemental microanalysis observed N = 15.9 wt.%; CrN requires 21.21%; $CrN_{0.7}$ requires 15.8 wt.%. Reaction of the same reagents for 60 h at 500 °C in an evacuated ampoule produced single phase Cr_2N (Table 1).

CAUTION

Self propagating reactions are by nature very exothermic and, on occasion, produce large amounts of dinitrogen gas. If the reactions are contained within a small ampoule an explosion can occur. It is recommended that all reactions be carried out

Table 1 Initial reagents, reaction conditions, colour of products and observed lattice parameters obtained by solid state metathesis reactions

reagents	conditions[a]	phase observed	observed lattice parameters/Å (0.002)	literature lattice parameters/Å[9–11]
$CrCl_3 + Li_3N$	$T_{int} = 445$ °C	Cr_2N[b]	$a = 4.772$, $c = 4.452$	$a = 4.805$, $c = 4.479$[c]
$CrCl_3 + Li_3N$	$T_{bulk} = 300$ °C, 2 h	CrN (Cr)	$a = 4.148$	$a = 4.150$
$CrCl_2 + Li_3N$	$T_{int} = 250$ °C, 2 h	Cr_2N (Cr,CrN)	$a = 4.776$, $c = 4.454$	$a = 4.805$, $c = 4.479$[c]
$CrCl_3 + Mg_3N_2$	$T_{bulk} = 350$ °C, 1 h; 500 °C, 1.5 h; 1.5 equiv. $MgCl_2$	CrN (Cr_2N)	$a = 4.147$	$a = 4.150$
$CrCl_2 + Mg_3N_2$	$T_{bulk} = 350$ °C, 1 h; 500 °C, 1.5 h; 1.5 equiv. $MgCl_2$	CrN[b,d]	$a = 4.150$	$a = 4.150$
$CrCl_2 + Mg_3N_2$	$T_{int} = 380$–430 °C	CrN (Cr_2N)	$a = 4.151$	$a = 4.150$
$CrCl_3 + Ca_3N_2$	$T_{bulk} = 325$ °C, 1 h; 490 °C, 6 h	CrN (Cr_2N)	$a = 4.149$	$a = 4.150$
$CrCl_2 + Ca_3N_2$	400 °C, 2 h	CrN (Cr_2N)	$a = 4.150$	$a = 4.150$
$Cr_2O_3 + Li_3N$	500 °C, 2 h	CrN	$a = 4.145$	$a = 4.150$
$Cr_2O_3 + Li_3N$	550 °C, 60 h	Cr_2N	$a = 4.800$, $c = 4.469$	$a = 4.805$, $c = 4.479$[c]

[a] All products were black. [b] EELS measurements were performed. T_{int} = temperature of initiation of propagation wave; T_{bulk} = temperature of oven for bulk reaction, below propagation temperature. Minor phases (typically 5–10%) are shown in parentheses and were not indexed. [c] The 'Cr_2N' phase has reported literature parameters from $a = 4.759$ Å, $c = 4.438$ Å at $Cr_2N_{0.76}$ to $a = 4.805$ Å, $c = 4.479$ Å for $Cr_2N_{1.00}$.[9] [d] XPS was carried out on this sample.

behind a blast proof safety screen and the maximum pressure calculated.

Results and Discussion

Synthesis and characterisation

Reactions of Li_3N, Ca_3N_2 and Mg_3N_2 with $CrCl_3$ and $CrCl_2$ were investigated under a variety of conditions. Mixtures of CrN, Cr_2N and Cr were normally produced (Table 1). It was possible by tailoring the conditions to produce single phases of CrN or Cr_2N [eqn. (1), (2)].

$$2CrCl_3 + 2Li_3N \xrightarrow{445\,^{\circ}C} 6LiCl + Cr_2N + 1/2N_2 \qquad (1)$$

$$3CrCl_2 + Mg_3N_2 \xrightarrow{350\,^{\circ}C\ 1\ h,\ 500\,^{\circ}C,\ 1.5\ h;\ 1.5\ equiv.\ MgCl_2} 3CrN + 3MgCl_2 \qquad (2)$$

Products were identified by X-ray powder diffraction, microanalysis, FTIR, XPS, SEM and ELNES. Pretriturated powders showed a rounded morphology by SEM which on trituration became sharp angles and faces corresponding to agglomerates of dimension *ca.* 1 µm. EDXA of the triturated material showed only chromium metal, whilst the untriturated material showed, dependent on the sample, chromium, magnesium, calcium and chlorine. (The detector window prevented analysis of elements with atomic number <11.)

FTIR analysis of the triturated powders was not particularly diagnostic but did show a broad band at *ca.* 600 cm^{-1} corresponding to a Cr—N stretch. XPS of a triturated CrN sample (Table 1) showed only the presence of chromium, nitrogen and some oxygen. On sputtering, the oxygen content decreased, indicating that it was mainly surface oxide, but was never completely removed (typically material was sputtered to a depth of 1–2 nm). The chromium and nitrogen concentrations increased with depth. The XPS chemical shift values for nitrogen (396.7 eV; lit.,[23] 396.8 eV) and chromium (576.3 eV; lit.,[23] 576.6 eV) in the sputtered material were consistent with the formation of CrN.

The untriturated material from all the SSM reactions did show some crystalline coproduced salt ($MgCl_2$ and $CaCl_2$) in addition to the nitride peaks by powder X-ray diffraction. On trituration either a single phase of nitride was observed by powder X-ray diffraction [eqn. (1), (2)], or a mixture of CrN, Cr_2N and Cr was observed (Table 1). X-Ray powder diffraction patterns of the triturated single phase CrN and Cr_2N are shown in Fig. 1 and 2. The CrN sample indexed with $a = 4.150(2)$ Å, this compares very favourably with previous literature measurements of 4.150 Å[11] and 4.149 Å.[9] The *a* parameter of cubic nitrides has been shown to be very sensitive to nitridation levels, decreasing by as much as 2% as substoichiometry increases.[9] Literature data[9,11] on CrN suggest that it is stable only over a narrow composition window (*ca.* CrN—$CrN_{0.95}$)[24] unlike most other early transition metal nitrides and no variation of lattice parameter with composition is reported.[11] The Cr_2N phase is stable over a wider composition range; $Cr_2N_{0.76}$ to Cr_2N.[24] It has an hexagonal structure in which the chromium atoms are arranged in an hexagonal close packed lattice whilst the nitrogen atoms are dispersed in the interstices. The Cr_2N lattice parameters vary from $a = 4.759$ Å and $c = 4.438$ Å to $a = 4.805$ Å and $c = 4.479$ Å at the nitrogen rich end.[9] The Cr_2N produced in the metathesis

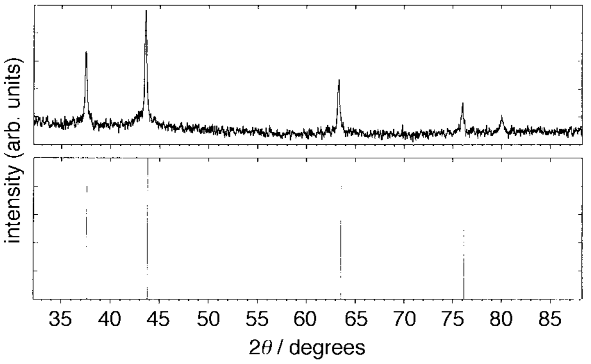

Fig. 1 Top trace: X-ray powder diffraction pattern obtained from the reaction of $CrCl_2$ and Mg_3N_2. Bottom trace: standard stick pattern for CrN.

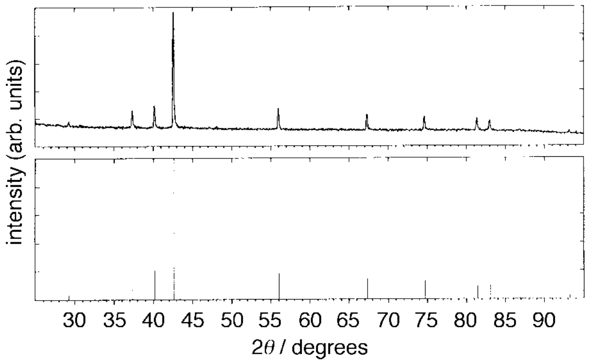

Fig. 2 Top trace: X-ray powder diffraction pattern obtained from the reaction of $CrCl_3$ and Li_3N. Bottom trace: standard stick pattern for Cr_2N.

reaction had $a = 4.772(2)$ Å, $c = 4.452(2)$ Å which corresponded to a mid range composition of $Cr_2N_{0.82}$ assuming Vegard's law.[25] Combustion microanalysis of the single phase CrN and Cr_2N samples revealed slight nitrogen deficiencies corresponding to $CrN_{0.72}$ and $Cr_2N_{0.72}$, respectively. It is unlikely that these low values are due to the difficulty of getting good combustion analysis as commercial NbN and MoN samples which have similar decomposition temperatures[11] gave excellent nitrogen combustion analysis (within 0.1 wt.% N). Commercial CrN and Cr_2N powders gave extremely poor nitrogen combustion analysis ($CrN_{0.17}$ and $Cr_2N_{0.32}$, respectively) as they contained significant amounts of oxygen. The low bulk nitrogen content from the SSM samples could be due to incorporation of some oxygen within the nitride lattice, and/or some surface oxidation of the chromium nitride particles as indicated by the XPS analysis. Oxygen incorporation in nitride samples is well documented and leaves many literature assignments uncertain.[9–11]

EELS analysis; determination of nanoscaled nitrogen content

Further information on the composition and oxygen content of the nitrides was obtained from electron energy loss spectroscopy (EELS). EELS has the advantage of being able to investigate very small sample volumes (*ca.* 5 nm transverse dimension) enabling selective analysis of nitride rich areas. Thus even though the commercial samples contained significantly more oxide than the SSM samples, EELS would enable an assessment of oxygen contamination within the nitride lattice thus largely avoiding the problems of surface oxidation. Even though the commercial samples had multiple nitride phases (CrN contained some Cr_2N and *vice versa*), unlike the SSM materials, it was possible by EELS to select information from grains which represented the majority nitride phase.

Although the SSM samples and commercial powders were examined in different microscopes, the operating conditions were such that the ratio of N K edge to Cr $L_{2,3}$ edge excitation cross-sections could be expected to be comparable. However, stray scattering in the electron gun contributes a background to the electron spectrum from the CM20. After correction for this background a small contribution is left and this causes a small but detectable perturbation to the shape of some of the ionisation edges. The effect of this perturbation is noted below.

Fig. 3 compares the EELS spectrum from the CrN prepared by SSM with that from the commercial CrN and shows a close match. The mean compositions of the material can be determined by integrating the number of counts under the edges and using relevant cross-sections. Ignoring the small oxygen content, this gave compositions of $CrN_{0.90}$ and $CrN_{0.94}$ for the SSM CrN and the commercial CrN respectively. These values, which are in reasonable agreement with the equilibrium composition range of $CrN_{0.95}$ to $CrN_{1.00}$ given by Frisk,[24] were obtained using the Hartree–Slater cross-sections provided by the Gatan EL/P software used to collect and analyse the spectra. EELS indicates that the particular region of the commercial CrN sample analysed had an oxygen content estimated at about 4 atom% of the nitrogen content while the SSM sample had a slightly higher oxygen fraction. The electron energy loss near edge fine structure (ELNES) is sensitive to the site symmetry and the lattice parameter of the material. The N K edges in both samples are very similar exhibiting the same shape and thereby showing that the SSM sample has the same structure as the face centred cubic CrN standard.[26] For both samples, the peaks in the ELNES on the N K edge occur at the same energies indicating that the compounds have similar lattice parameters and hence similar compositions. The shapes of the Cr $L_{2,3}$ edges differ slightly. The two sharp peaks at the thresholds (known as white lines) are slightly higher in the commercial CrN and there is more detail in the structure immediately after the white lines. These differences are likely to be related to differences in the oxygen content and suggest that Cr is present in more than one atomic environment. Thus, overall, the SSM CrN is consistent with the commercial CrN standard. It should again be stressed that the regions studied by EELS have been selected for minimum oxygen content. Thus the large amount of amorphous chromium oxide found in the commercial sample will not figure prominently in the analysis although it can clearly play a minor role as a thin surface layer.

The SSM prepared Cr_2N and commercial Cr_2N spectra are shown in Fig. 4. Overall the ELNES on both the N K edges and Cr $L_{2,3}$ edges are very similar showing that SSM Cr_2N has the same structure as the hexagonal Cr_2N standard. There is a slight excess of intensity from the N K edge of the SSM material relative to that in the commercial material but the difference between the two shapes is smooth and so is likely to be a residual effect from the stray background noted above. In both samples the oxygen content is about 10 atom% of the nitrogen content. Compositions of $Cr_2N_{1.12}$ and $Cr_2N_{0.96}$ were obtained for the SSM Cr_2N sample and the commercial Cr_2N respectively. Thus the SSM Cr_2N appears to contain *ca.* 14% more nitrogen. However, it is likely that this apparent high nitrogen content is a result at least in part of the edge shape perturbation.

The compositions of the Cr_2N samples may be estimated from the lattice parameters obtained by XRD using the composition range given in Toth[10] assuming Vegard's Law. As discussed above the SSM Cr_2N has the composition $Cr_2N_{0.82}$ from X-ray data. Compositions of $Cr_2N_{0.96}$ and $Cr_2N_{1.02}$ were obtained for the commercial Cr_2N from the lattice parameters of $a = 4.799(2)$ Å and $c = 4.483(2)$ Å. Thus, the commercial

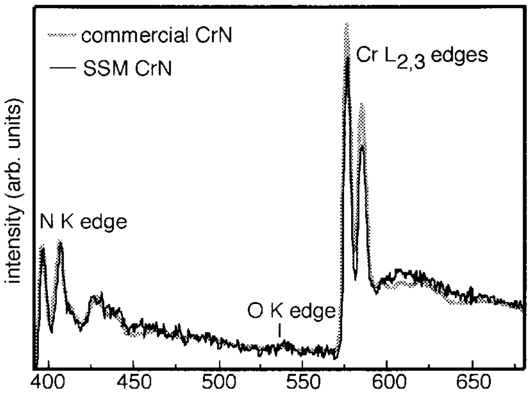

Fig. 3 EELS spectra of N K edge and Cr $L_{2,3}$ edges in commercial CrN and SSM CrN

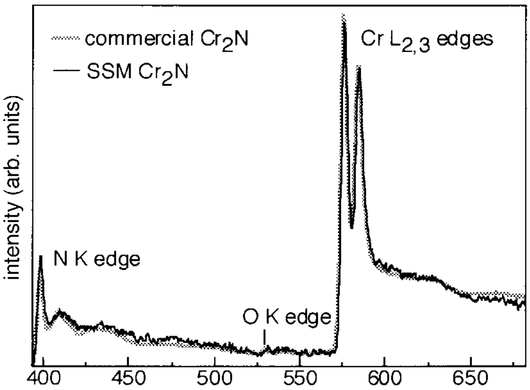

Fig. 4 EELS spectra of N K edge and Cr $L_{2,3}$ edges in commercial Cr_2N and SSM Cr_2N

Cr_2N standard appears to be consistent with it being $Cr_2N_{0.99}$. Both commercial and SSM Cr_2N samples give XRD composition values between the known limits for the Cr_2N phase ($Cr_2N_{0.72}$–$Cr_2N_{1.00}$).

Comparison of EELS, XRD and elemental analysis to determine nitrogen content

The lack of agreement from the composition determined by quantitative combustion analysis, XRD and EELS can almost certainly be explained by the nature of the techniques. The combustion technique analyses the whole sample including all the oxidised material present. Thus its N : Cr ratio will appear low by an amount determined by the oxygen content. If this oxide is amorphous, then it will not show up in the XRD traces. Oxygen incorporation in nitride samples could occur during their initial preparation, in which case it would typically be well dispersed within the material forming in essence an oxynitride solid solution. An oxynitride solid solution would modify the lattice parameter because the XRD traces average over all the lattice parameters. Alternatively, oxidation could occur during storage of the samples in which case it would be largely surface limited, decrease with depth and depend on storage conditions. If the oxidation proceeds from the surface it is likely that the individual crystals have a graded composition also giving rise to a modified lattice parameter. The very fine grained nature of the SSM product may render it more susceptible to such oxidation. However, based on bulk chemical analysis, the SSM materials appear to have far superior levels of nitridation to commercial standards however this may reflect storage conditions. The nanometer scale EELS analysis reveals that the SSM materials and commercial materials are more comparable. The XRD and ELNES techniques can be seen to give similar results for the CrN sample. The XRD lattice parameters obtained for both the commercial CrN and the SSM CrN are similar and consistent with the narrow equilibrium composition range reported for CrN. The XRD data suggest that the SSM CrN has a slightly higher N : Cr ratio while the EELS data suggest the opposite. The EELS data can be viewed from two limits. The first is that the material is homogeneous so that the sample is an oxynitride with an approximate sample of formula $CrN_{0.90}O_{0.04}$. The other limit is a core nitride phase containing no oxygen overlayed by an oxide phase containing no nitrogen. In the latter limit, the lower average N:Cr ratio and the higher average O : N ratio in the SSM CrN is the result of a larger fraction of the material under the beam being oxide, this may be related to the fact that the SSM material has finer grains, with higher surface areas. If the Cr in the oxide is discounted, the N : Cr ratio in the nitride will approach that in the commercial CrN and both will probably approach unity. Bearing in mind that the specimen analysed is only *ca.* 40 nm thick, an O : N ratio of *ca.* 0.04 means that the oxide layer on each surface is only 0.5–1 nm thick. Even freshly fractured material is likely to gain such an oxide layer in the TEM specimen preparation process. Such a layer is certainly thinner than that observed by XPS where the material was not freshly fractured.

Table 2 Bulk combustion, EELS and X-ray powder diffraction compositions of commercial and SSM prepared CrN and Cr_2N

sample	combustion composition	EELS	X-ray[a]
commercial CrN	$CrN_{0.17}$	$CrN_{0.94}$	CrN
commercial Cr_2N	$Cr_2N_{0.32}$	$Cr_2N_{0.96}$	$Cr_2N_{0.99}$
SSM CrN[b]	$CrN_{0.72}$	$CrN_{0.90}$	CrN
SSM Cr_2N[c]	$Cr_2N_{0.72}$	$Cr_2N_{1.14}$	$Cr_2N_{0.84}$

[a] X-Ray compositions determined using Vegard's law. [b] Prepared from the SSM reaction of $CrCl_3$ and Li_3N. [c] Prepared from the SSM reaction of $CrCl_2$ and Mg_3N_2.

One previous study at comparing bulk (combustion analysis) with microscopic (XPS) analysis has been attempted for SSM prepared AlN. In this case the nitride samples were shown to be vastly inferior to the chromium nitride samples prepared here with typical atomic ratios for AlN from $AlN_{0.3}O_{0.7}$ to $AlN_{0.06}O_{0.94}$.[19]

Variations in reaction conditions, thermodynamic considerations

Various different reaction conditions were employed: temperature, time of heating, rate of temperature rise, spread of reagents within the ampoule and use of a dilutant salt in order to produce a single phase of SSM material. The optimum conditions for CrN formation involved the reaction of $CrCl_2$ with Mg_3N_2 using 1.5 equivalents of $MgCl_2$ and adopting a rise from 350–500 °C over 1h followed by heating at 500 °C for 1.5 h. Use of Mg_3N_2 with $CrCl_3$ or $CrCl_2$ without a dilutant $MgCl_2$ heat sink resulted in a mixed phase material; CrN (*ca.* 75%) and Cr_2N (*ca.* 25%). From the Cr–N phase diagram,[24] Cr_2N is more thermally stable than CrN although both are very sensitive to pressure. The reaction of Mg_3N_2 with $CrCl_2$ is less exothermic based on Hess's Law (-210 kJ mol^{-1}) than corresponding reactions of Li_3N and $CrCl_2$ (-430 kJ mol^{-1}) or Ca_3N_2 and $CrCl_2$ (-370 kJ mol^{-1}). This reduction in reaction exothermicity coupled with the use of a dilutant salt to soak up some of the reaction energy and subsequently reduce the reaction temperature to below 1080 °C enabled a single phase of CrN to be isolated from the reaction of Mg_3N_2 with $CrCl_2$. Formation of CrN by solid state metathesis reactions has not been reported before.[20] Previous work on the reaction of $CrCl_3$ and Li_3N in a sealed ampoule produced Cr with a small amount of Cr_2N.[19] This was attributed to the high reaction temperature (1400 °C) which exceeded the decomposition point of CrN (1080 °C, 1 atm N_2).

Notably in all the reactions of Mg_3N_2 and Ca_3N_2 with $CrCl_3$ or $CrCl_2$ no thermal flash was observed. The reactions did, however, rapidly change colour to black on heating. Previously it has been shown that if $T_{ad,s}$ (the adiabatic temperature for salt formation only) is less than the melting point of the coproduced salt then the reaction fails to propagate with a synthesis wave (thermal flash).[27] In both Mg_3N_2 and Ca_3N_2 reactions with $CrCl_2$, $T_{ad,s}$ is less than the melting points of $CaCl_2$ and $MgCl_2$. Thus the reaction proceeded without an observable synthesis wave (thermal flash). The coformation of small amounts of Cr_2N in reactions involving Ca_3N_2 may be due to localised variations of heat in this reaction (Ca_3N_2 reactions are more exothermic than corresponding Mg_3N_2 reactions).

In this study the reaction of Li_3N and $CrCl_3$ was reinvestigated under different conditions. If the temperature is slowly ramped to 450°C a propagation wave (thermal flash) is observed at 445 °C for a well spread out mixed powder (note $T_{ad,s} >$ mp LiCl). This produces after trituration single phase Cr_2N. These results are at variance with our previous preliminary report[19] where reaction of densely packed $CrCl_3$ and Li_3N powders proceeded by a synthesis wave forming Cr and Cr_2N. It is probable that the reaction temperature produced in the propagation wave when the mixture is spread out in an ampoule is too high for CrN to be isolated (> 1080 °C, 1 atm N_2) but not too high to decompose Cr_2N (*ca.* 1350 °C, 1 atm N_2). Interestingly if the reagents are heated to 300 °C and maintained at this temperature for 2 h no thermal flash is observed. However a slower solid state reaction does occur producing CrN and Cr metal.

Reaction mechanism

Solid state metathesis reactions have been suggested to proceed by both elemental [reductive recombination, eqn. (3)] and ionic (metathesis) pathways [eqn. (4)].

$$Li_3N + CrCl_3 \xrightarrow{\text{reduction step}} Cr + N + 3LiCl \qquad (3)$$

$$\xrightarrow{\text{recombination step}} CrN + 3LiCl$$

$$Li_3N + CrCl_3 \rightarrow Cr^{3+} + N^{3-} + 3LiCl \rightarrow CrN + 3LiCl \qquad (4)$$

It is unlikely, at least in the chromium reactions studied here, that the reactions proceed by reductive recombination as nitrogen has limited solubility in chromium metal at the temperatures employed in these reactions and is not routinely used for the synthesis of chromium nitrides.[12] This would tend to favour an ionic metathesis pathway, the Cr and Cr_2N phases being obtained in a number of reactions by the thermal decomposition of CrN.

Reactions of Cr_2O_3 and Li_3N

Reaction of chromium oxide with lithium nitride was also investigated by combining the reagents in a sealed evacuated ampoule and heating to 500 °C for 2 h. The X-ray powder diffraction pattern of the untriturated product showed only $LiCrO_2$ (or Li_2O) and CrN; trituration with methanol enabled phase pure CrN to be isolated [eqn. (5)]. If the reaction was conducted at 550 °C for 60 h the predominant product after trituration was Cr_2N, presumably due to nitrogen loss from CrN. Metal nitrides are known to lose nitrogen on heating under vacuum[28] and in the case of CrN Cr_2N is the most likely product.[24]

$$2Cr_2O_3 + Li_3N \rightarrow CrN + 3LiCrO_2 \qquad (5)$$

As was commented on above, oxide contamination is a significant problem in solid state reactions to form metal nitrides. This normally arises from the purity of the starting materials and long reaction times encouraging oxygen incorporation. In the reactions to form CrN and Cr_2N from chromium oxide, the nitride product seems counter intuitive. Indeed it is to our knowledge the only reported method of forming a nitride product in a metathesis reaction using an oxide starting material.[20] The CrN indexed with $a = 4.145$ Å, a slightly lower value for the lattice parameter than for reaction (2); elemental microanalysis was also slightly lower corresponding to $CrN_{0.7}$. The Cr_2N formed in the metal oxide reactions indexed with $a = 4.800$ Å, $c = 4.469$ Å; which corresponds to a composition $Cr_2N_{0.92}$ assuming a Vegard's law relationship.[25]

Conclusions

Solid state metathesis reactions can be tailored by the use of diluent reagents, careful heating conditions and attention to sample packing to rapidly produce single phase chromium nitrides CrN and Cr_2N. Solid state metathesis reactions can also be made to proceed below the ignition temperature for the propagation wave, dramatically affecting the phases produced. Solid state metathesis reactions can use metal oxides as starting reagents for the formation of metal nitrides. Comparison of combustion microanalysis, X-ray powder diffraction parameters and ELNES enables both a bulk and microscopic examination of nitrogen content in metal nitrides. This indicates that SSM prepared CrN have better bulk purity and virtually equivalent microscopic purity to commercial materials.

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