SOLID STATE METATHESIS

PREPARATIONS

OF

HARD REFRACTORY CERAMICS

A thesis presented by:

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Abstract

This thesis presents the synthesis of binary and ternary transition metal borides, carbides, nitrides and silicides the solid state metathetical processes. The reactions were initiated both in bulk and in the propagation modes.

Rapid solid state metathetical reactions of Group 3-5, 13 and rare earth metal halides with nitriding agents such as Li$_3$N, Mg$_3$N$_2$, Ca$_3$N$_2$ and NaN$_3$ lead to formation of crystalline nitrides and co-product salts of Group 1 or 2 metals. Similarly, crystalline transition metal borides, carbides and silicides of Groups 4-8 have been synthesised using the halides and AlB$_2$, CaC$_2$, SrC$_2$, Al$_4$C$_3$, Li$_2$Si, Mg$_2$Si or CaSi$_2$. The rates of these reactions and their final product crystallinity were related to the reagents used and the mode of reaction initiation. Thermally unstable transition metal nitrides of Group 6 transition metals, manganese, iron and cobalt have been synthesised using their halides and magnesium nitride with the aid of magnesium chloride as an inert heat sink.

This work also reports the SSM (Solid State Metathesis) synthesis of highly crystalline transition metal carbides and silicides from the transition metal oxides and CaC$_2$, SrC$_2$, Li$_2$Si, Mg$_2$Si, CaSi$_2$.

All the co-products from the various reactions were removed using solvents such as THF, methanol, water or dilute acids. The final products were analysed using X-ray powder diffraction, FT-IR and SEM/EDXA. A selected group of carbides and nitrides were analysed using TEM and PEELS/ELNES (photoelectron energy loss spectroscopy/energy loss near-edge structure). Besides the identification of the final products, the main objectives in these analyses were to determine the elemental composition (and oxygen contamination) of these interstitial compounds. The compounds formed by SSM processes were shown to be useful in standardising ELNES measurements.
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CHAPTER 1

INTRODUCTION

1.1 WHAT ARE CERAMICS?

The word ceramic originates from keramos (in Greek meaning ‘burned earth’). Some define it as a ‘general term applied to the art or technique of producing articles by a ceramic process, or to articles so produced’,¹ Ceramics are all inorganic and nonmetallic materials, which are prepared and/or used at high temperature (which in this context is any temperature above the red heat, ca. 540 °C).² A ceramic material can be a ‘metal oxide, boride, carbide, or nitride, or a compound of such materials.’ Therefore it is ‘a glazed or unglazed object of crystalline or partly crystalline structure, produced from essentially inorganic, nonmetallic substances’.³ Ceramic substances can be made from a molten mass which then solidifies. Extra heat may be used to mature the material either before or after it material is solidified.⁴

1.1.1 History of ceramics

The physical properties of ceramics were discovered and utilised as far back as 12,000 years ago⁵.⁶ The earliest written evidence for the use of ceramics was around 7000 to 8000 years ago in the Near East, in the form of pottery.⁷ Fired clay bricks and tiles for use in buildings, water supply and sewer systems were employed at Mohenjo-daro around 2000 B.C.⁸

In ancient times the Chinese developed the most advanced and extensive production of ceramics. During the Shang dynasty (1500-1025 B.C.) they changed from Neolithic earthenware to a fine grained white stoneware.⁹ In the Mediaeval Ages the Song and Ming dynasties started to use a more hard paste porcelain formulae. These were prepared in an egg shaped kiln, which utilised pinewood for fuel.¹⁰
In Europe the first civilisation to utilise ceramics extensively was the ancient Greeks. A local illitic clay was used and its colour determined between red or black by applying reducing or oxidising conditions. Europe saw a great rise in demand and technology of production of ceramics throughout 14th century until the late 18th century. These included the production of salt-glazed stoneware and soft-paste porcelain.

In recent decades consumer demands have ‘pushed’ for wide range of advanced ceramics.

1.1.2 Classification of ceramics

Any discussion or survey covering ceramics must start from distinguishing traditional and advanced ceramics. A Traditional ceramics is a ware, which is either composed of unrefined clay or a number of refined clays with powdered or granulated nonplastic materials.

One of the earliest problems in making ceramic ware was the high-shrinkage cracking of clay. Adding other ingredients such as crushed stone, sand or crushed shell reduced this tendency. In traditional ceramics clay provided the plastic and dry bonding properties required for shaping and handling.

Advanced ceramics are made from highly refined natural or synthetic compositions, which have characteristic properties. These find increasing use as key components in many fields of industry including electronics, optical-communication, cutting-tools, high temperature reactors, wear-resistant parts, medical implants etc. Physical, compositional and structural properties of advanced ceramics play an important role in their characteristic capabilities and new roles. Advanced ceramics may require special electromagnetic properties, relative chemical inertness, hardness, strength or a range of temperature capabilities. Thus they can be classified most conveniently by their functions. These include:

- electric functions: insulation materials (Al₂O₃, MgO); semiconductors (BaTiO₃); ferroelectric materials (SrTiO₃); piezoelectric materials (PZT)
- magnetic functions: soft ferrite, hard ferrite
- optical functions: translucent alumina or magnesia, PLZT ceramics
• chemical functions: gas sensors (ZnO, SnO₂); humidity sensor (MgCr₂O₄-TiO₂)
• thermal functions: TiO₂ ceramics
• mechanical functions: cutting tools (TiC, TiN, Al₂O₃); wear resistant materials (ZrO₂); heat resistant materials (SiC, Al₂O₃).
• biological functions: alumina ceramics implantation
• nuclear functions: nuclear fuels (UO₂); cladding material (SiC, B₄C); shielding material (SiC, B₄C, Al₂O₃)

1.2 PROPERTIES AND UTILISATION OF CARBIDES AND NITRIDES

As briefly mentioned in section 1.1 there are 4 main groups of compounds, which fall into the classification of ceramics: metal borides, carbides, nitrides and oxides. The work in this thesis covers metal borides, carbides and nitrides. Because of very strong similarities in properties and applications we also chose to work with some silicides. This section will concentrate on carbides and nitrides. Properties and uses of borides and silicides are outlined in sections 1.3 and 1.4.

Carbides and nitrides are applied very widely in industry and it would be very difficult to discuss every single use for them. General and most apparent properties and applications of some nitrides and carbides are outlined in Table 1.1.

1.2.1 Properties

Carbides and nitrides have a very rich chemistry. Their properties determine their usefulness. Transition metal carbides can adopt various stoichiometries. Figures 1.1 and 1.2 show the transition metal carbide and nitride blocks in the Periodic Table.

Melting points. Melting points of nitrides have to be measured under raised nitrogen pressures. This is due to many nitrides decomposing on melting to yield nitrogen gas. The pressure of nitrogen used in measuring the melting points must equal to the nitrogen equilibrium pressure of the nitride at its melting
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</tbody>
</table>
| Figure 1.1 | Known phases of transition metal carbides as observed in a form of the Periodic Table.¹⁸
Table 1.1  Principal applications of metal carbides typified by several examples.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Principal Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC</td>
<td>cemented carbides</td>
</tr>
<tr>
<td>TiC</td>
<td>cemented carbides, base for formation of solid solutions with other carbides, formation of ferro-TiC alloys</td>
</tr>
<tr>
<td>NbC</td>
<td>reduction of Nb$_2$O$_5$ to yield Nb metal, hardmetals, cemented carbides</td>
</tr>
<tr>
<td>B$_4$C</td>
<td>abrasive material, wear resistant engineering components, nuclear industry (control rod material, neutron poison, neutron shielding), steel hardening</td>
</tr>
<tr>
<td>TiN</td>
<td>wear resistant layers for hardmetal tools, hardmetals</td>
</tr>
<tr>
<td>$\beta$-BN</td>
<td>machining, drilling, hard steels, superalloys, crucibles for melting glass</td>
</tr>
</tbody>
</table>

Point. Highest melting points occur for Group 4 and tantalum nitrides and approach 3000 °C, and in the case of hafnium nitride, HfN, 3330 °C. Many nitrides decompose on melting giving off nitrogen gas. Transition metal carbides have even higher melting points and Group 4 carbides reach near to 4000 °C as illustrated in Table 1.2.

Colour. A number of nitrides possess a bright metallic colour. Their colour is related to their composition (the N/M ratio). Their role in terms of colours in thin films for ornamental purposes is already advanced.

Thermal and electrical properties. One of the most characteristic properties of transition metal nitrides and carbides is that their heat conductivities increase with temperature. Group 4 transition metal nitrides possess much higher heat conductivity than the isotypic carbides. The electrical conductivities of carbides and nitrides are related to the N/M and C/M ratios, and are optimised when these ratios are close to unity. An increase in temperature decreases the electrical conductivities for both carbides and nitrides. Generally transition metal carbides have a lower conductivity than the corresponding transition metal nitrides.
<table>
<thead>
<tr>
<th>ScN</th>
<th>TiN&lt;sub&gt;0.3&lt;/sub&gt;</th>
<th>Ti&lt;sub&gt;2&lt;/sub&gt;N</th>
<th>TiN&lt;sub&gt;0.9&lt;/sub&gt;</th>
<th>TiN</th>
<th>V&lt;sub&gt;2&lt;/sub&gt;N</th>
<th>V&lt;sub&gt;2&lt;/sub&gt;N</th>
<th>VN</th>
<th>Cr&lt;sub&gt;2&lt;/sub&gt;N</th>
<th>CrN</th>
<th>Mn&lt;sub&gt;4&lt;/sub&gt;N</th>
<th>Mn&lt;sub&gt;2&lt;/sub&gt;N</th>
<th>Mn&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Fe&lt;sub&gt;4&lt;/sub&gt;N</th>
<th>Fe&lt;sub&gt;3&lt;/sub&gt;N</th>
<th>Fe&lt;sub&gt;2&lt;/sub&gt;N</th>
<th>Co&lt;sub&gt;3&lt;/sub&gt;N</th>
<th>Co&lt;sub&gt;2&lt;/sub&gt;N</th>
<th>Ni&lt;sub&gt;3&lt;/sub&gt;N</th>
<th>Cu&lt;sub&gt;3&lt;/sub&gt;N</th>
<th>Zn&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>YN</td>
<td>ZrN</td>
<td>Nb&lt;sub&gt;4&lt;/sub&gt;N&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Nb&lt;sub&gt;2&lt;/sub&gt;N</td>
<td>NbN</td>
<td>NbN&lt;sub&gt;0.95&lt;/sub&gt;</td>
<td>Mo&lt;sub&gt;2&lt;/sub&gt;N</td>
<td>MoN</td>
<td>TcN&lt;sub&gt;0.75&lt;/sub&gt;</td>
<td>TcN</td>
<td>TcN&lt;sub&gt;0.75&lt;/sub&gt;</td>
<td>TcN&lt;sub&gt;0.75&lt;/sub&gt;</td>
<td>TcN&lt;sub&gt;0.75&lt;/sub&gt;</td>
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<td>TcN&lt;sub&gt;0.75&lt;/sub&gt;</td>
<td>TcN&lt;sub&gt;0.75&lt;/sub&gt;</td>
</tr>
<tr>
<td>LaN</td>
<td>Hf&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Ta&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;5&lt;/sub&gt;</td>
<td>Ta&lt;sub&gt;2&lt;/sub&gt;N</td>
<td>TaN</td>
<td>TaN&lt;sub&gt;0.8&lt;/sub&gt;</td>
<td>TaN&lt;sub&gt;0.1&lt;/sub&gt;</td>
<td>W&lt;sub&gt;2&lt;/sub&gt;N</td>
<td>WN</td>
<td>Re&lt;sub&gt;2&lt;/sub&gt;N</td>
<td>ReN</td>
<td>ReN</td>
<td>ReN</td>
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<td>ReN</td>
<td>ReN</td>
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</table>

Figure 1.2 Known phases of transition metal nitrides as observed in a form of the Periodic Table.¹⁹
### Table 1.2

Melting/decomposition points of selected hardmetals compared with their parent metals, °C.

<table>
<thead>
<tr>
<th>Transition metal melting point /°C</th>
<th>Carbide/nitride melting point °C (all are cubic and stoichiometric unless stated)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti = 1667</td>
<td>2.940/2.950</td>
<td></td>
</tr>
<tr>
<td>Hf = 2222 (or 2467)</td>
<td>3.820/3.330</td>
<td></td>
</tr>
<tr>
<td>V = 1915</td>
<td>2.684/2.350</td>
<td></td>
</tr>
<tr>
<td>Ta = 2980</td>
<td>3.825/2.950 (hex)</td>
<td></td>
</tr>
<tr>
<td>Cr = 1900</td>
<td>1.810 (orth)/1.080°</td>
<td></td>
</tr>
<tr>
<td>W = 3380</td>
<td>2.720 (hex)/650 (hex W2N)</td>
<td></td>
</tr>
</tbody>
</table>

* at 0.1 Mpa (14.5 psi).

All f.c.c. nitrides of Groups 4 and 5 metals and molybdenum are superconductive at near absolute zero temperatures with $\delta$-NbN$_{1-x}$ having in 1960 one of the highest superconducting transition temperatures known (17 K). Only a few transition metal carbides are superconducting, the transition temperatures of which are much lower than the corresponding nitrides, for which the highest $T_c$ value is for $\delta$-NbC at 11.1 K.

**Thermal expansion.** Generally transition metal nitrides show very small (even negative) thermal expansions at low temperatures and large thermal expansions at high temperatures. For transition metal carbides this is an important property since carbides are mostly used in composites in which the difference in the thermal expansion coefficients of the components is crucial. In general, the thermal expansion of transition metal carbides is higher than that of the pure metal.

**Diffusivities.** In the case of transition metal nitrides, nitrogen diffusion occurs via a vacancy mechanism in the nonmetal sublattice. The nitrogen diffusivity is also dependent upon the N/M ratio. In the most recent studies of nitrogen diffusivities in $\delta$-HfN$_{1-x}$ and $\delta$-TiN$_{1-x}$ it has been shown that this dependence may vary strongly in terms of its magnitude. Similar principles are at work in the case of carbon diffusion in transition metal carbides.
Young' Modulus. All transition metal carbides and nitrides possess high Young's moduli (higher than those of the corresponding transition metals).\textsuperscript{29-30} In most cases an increase in the N/M or C/M ratio is accompanied by a linear rise in Young's moduli (e.g. $\delta$-TiC$_{1-x}$, $\delta$-TiN$_{1-x}$, $\delta$-ZrC$_{1-x}$).

Microhardness. Transition metal carbides are, in general, very hard materials. In the case of $\delta$-TiC$_{1-x}$ microhardness increases when the C/M ratio approaches unity. This is probably due to the valence electron concentration (VEC), where the maximum stability is at VEC = 8 when $x = 0$. Other values for selected carbides are in Table 1.3. Group 4 and 5 carbides are by far the hardest.

Table 1.3 Microhardness properties of selected transition metal carbides.\textsuperscript{18}

<table>
<thead>
<tr>
<th>Carbide</th>
<th>Microhardness, kg/mm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>3000</td>
</tr>
<tr>
<td>ZrC</td>
<td>2700</td>
</tr>
<tr>
<td>VC</td>
<td>2900</td>
</tr>
<tr>
<td>WC</td>
<td>1200-2500</td>
</tr>
</tbody>
</table>

Transition metals nitrides are also among the hardest materials known. For Group 5 nitrides the hardness decreases with increasing N/M ratio.\textsuperscript{27,29,31} Presumably, the generation of anti-bonding states causes electronically induced lattice softening. Band structure calculations show that in f.c.c. transition metal nitrides containing more than 8 valence electrons anti-bonding states are successively being occupied. Lattice softening then occurs for nitrides with more than 8 valence electrons. The best example is $\delta$-TiN$_{1-x}$ for which the maximum microhardness is obtained when $x = 0.33$ (7.3 valence electrons).\textsuperscript{27}

1.2.2 Application

The best way of describing the uses of carbides and nitrides is with reference to the particular properties required for a specific application. Therefore this section will often refer back to some of the previously outlined physical and
chemical characteristics of these materials. To express the magnitude of
application of these materials the production scales of various carbides and nitrides
have been illustrated in Table 1.4.

Table 1.4 Worldwide (unless stated) consumption of carbides and nitrides (1990 figures unless stated).\(^{18,19}\)

<table>
<thead>
<tr>
<th>Material</th>
<th>Production (tonnes/annum)</th>
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<tbody>
<tr>
<td>B(_2)C</td>
<td>500(^{a})</td>
</tr>
<tr>
<td>SiC</td>
<td>500 000(^{a})</td>
</tr>
<tr>
<td>WC</td>
<td>15 000-18 000</td>
</tr>
<tr>
<td>CaC(_2)</td>
<td>943 000 (1960), 308 000 (1975)(^{b})</td>
</tr>
<tr>
<td>TiC</td>
<td>1200-1500</td>
</tr>
<tr>
<td>TaC</td>
<td>350-450 (increase in world consumption predicted due to requirements to raise the TaC and NbC content in cemented carbides used for steel cutting from 3-5% to 7-18%).</td>
</tr>
<tr>
<td>BN</td>
<td>180-200</td>
</tr>
<tr>
<td>AlN</td>
<td>50-100</td>
</tr>
<tr>
<td>Si(_3)N(_4)</td>
<td>100-200</td>
</tr>
<tr>
<td>SiC</td>
<td>790 000 (1988)</td>
</tr>
</tbody>
</table>

\(^{a}\) non-communist countries only, \(^{b}\) USA only

High strength and hardness. Most applications of transition metal carbides and nitrides stem from the strength and hardness properties. Most carbides, carbonitrides and nitrides are useful as cemented hard metals. This is due to their wear resistant properties. In machining of hard metals and superalloys hot pressed cemented TaN-ZrB\(_2\) hard metals are better than cemented carbides.\(^{32}\)

Spinodal decompositions of quarternary carbonitrides into isotypic phases, one of which may consist of nearly a single metal nitride and the other being nearly a single metal carbide, has been used in production of cemented carbonitride alloys with less wear. An example of such phase is (Ti,Mo)(C,N).\(^{33}\)
Another use related to these properties is for coating of, for example, cemented carbides. A new technique involves multilayer coating of TiC, then Ti(C,N) and then TiN layers giving superior wear resistance.\(^{34}\)

The most commercially important transition metal carbide is hexagonal tungsten carbide. It is used as the hard constituent in WC-Co, WC-Ni or WC-Co/Ni hardmetals. These materials have attributes of great hardness, very high modulus of elasticity, good thermal and electrical conductivity, and good wear resistance. Other commonly used carbides for manufacture of hardmetals, especially for use in cutting tools, are TiC, NbC, and TaC. They show distinguished high temperature performance and wear resistance. The main factor which affects the extent of application of various carbides for the manufacture of hardmetals is whether or not they are too brittle. For example, TiC-based hardmetals have never been widely used since they are more brittle than WC-Co hardmetals.\(^{26}\) Still, such materials can be used as additional carbides in tungsten based cemented carbides, for example, in cutting tools. Titanium carbide is the most commonly used carbide for cutting tools. It is the hardest of all carbides and although its addition to a hard metal reduces toughness of the mixture a little, the hardness, and more importantly, the heat resistance are greatly increased. Similar properties apply to some pseudobinary systems such as Nb-TiC or NbN-NbC. The material most similar to WC-Co, with respect to its behaviour, is the quaternary solution, \((\text{Mo},\text{W})(\text{C,N})\) sintered with cobalt or nickel. It is common to observe that solid solutions of carbides and nitrides have properties superior to their separate phases in hardmetals applications. Ti(C,N) in many applications outperforms even WC coated hardmetals. Its advantages over conventional hardmetals are high chemical resistance and low frictional welding tendency.\(^{26}\) Nitrogen alloyed steels are an example where transition metal nitrides are used to improve hardness while retaining toughness.\(^{35}\)

Outside the transition metal block the most important carbide is boron carbide.\(^{36-39}\) It is used as an abrasive grit or powder and has applications in cemented hardmetals and fine ceramics industry. Wear resistant engineering components such as sand-blasting nozzles are most commonly made of boron carbide. Boron carbide materials are characterised by minimal scale of wear even with silicon carbide grit. Other engineering tools that use this material are cutting
tools, and pestles and mortars for grinding hard materials without contamination from the grinding equipment. The wear resistance and hardness properties of boron carbide are also exploited in protection from armour-piercing bullets in helicopters and monolithic breastplates.

Aluminium nitride has high thermal and chemical stability making it useful in thermocouple protecting tubes, nozzles and crucibles if it is well sintered.

**Colour.** The gold metallic shine of TiN make it extremely useful in the jewellery industry due to its hardness. Also Ti(C,N,O) layers are also used.

**Nuclear applications.** Carbides of $^{235}$U and thorium have been used for a long time as nuclear fuels and breeder materials for gas-cooled, graphite moderated reactors. Their nitrides have not been used yet for such purposes but this has already been proposed. The advantage of these nitrides over the oxides is the high chemical stability required for these applications.

Boron carbide is also used in nuclear industry. Its applications are as a shielding material, neutron poison and as an absorber for fast breeder reactor control material. Doors, windows and walls in laboratories containing radioactive matter are routinely screened with boron carbide plates.

**Solid electrolytes.** A very useful saltlike nitride is lithium nitride. It has a very high ionic conductivity for a solid and could be used as an electrolyte in lithium-sulfur batteries. Lithium nitride is also used as a catalyst in the preparation of cubic boron nitride.

**Refractories.** Hexagonal boron nitride is an electrical insulator. It has found some uses as a refractory material. Its advantages are low density, easy workability, good heat resistance, high thermal conductivity and stability to thermal shock. It also has high corrosion resistance.

Silicon nitride has high strength and resistance to oxidation at raised temperatures. This is crucial in the refractories industry. Research has begun in trying to develop silicon nitride turbine blades for automotive engines. It also possesses a capability for nonmetallic nitrides of forming alloys with other refractory materials such as aluminium oxide.
Silicon carbide is amongst the most useful carbides for application in a wide range of refractories. It has very high thermal conductivity and has high resistance to thermal shock damage. It is used for chemical tanks, kiln furniture, abrasion resistant linings, blast furnace and furnace linings etc. Incinerators and power generation plants use this material on a wide scale. Other carbides tend to have poor resistance to oxidation at high temperatures. Transition metal carbides of Group 4, 5 and 6, and boron carbide, have potential application in the technical ceramics and aerospace industry if used under neutral or reducing conditions.

**Abrasives.** At high pressures (4-6 Gpa, 40-60 kbar) and temperatures (1400-1700 °C) a graphitic form of boron nitride can be transformed into a diamond-like form in the presence of lithium nitride or magnesium nitride. Cubic boron nitride has hardness in the region of diamond and is used as an abrasive in the steel industry. The material is used already for some grinding equipment and competes with diamond in grinding operations involving high alloy steels.

Boron carbide powder is used to incorporate boron into the surface layers of steels. This occurs via the diffusion of boron into the surfaces forming a wear resistant layer of iron boride, Fe$_2$B.

**Catalysis.** High surface area porous Mo$_2$N and W$_2$N have interested a number of scientists for their potential catalytic applications. These nitrides when pure are very pyrophoric in air. The nitrogen can be replaced in the metal lattice by boron, carbon or metals producing high surface borides, carbides or metals. Catalysis of ammonia formation, ethane hydrolysis, CO hydrogenation and a number of other important processes can be performed with the aid of molybdenum nitride, γ-Mo$_2$N.

**Electronics.** Aluminium nitride has high thermal conductivity and electrical resistivity. Its thermal expansion coefficient matches that of the semiconducting silicon. This makes it useful for manufacture of, for example, semiconductor chips and sintered heat sinks.

**Diffusion barriers.** Transition metal carbides and nitrides have properties, which make them suitable for their use as diffusion barriers in multilayer
metallization schemes for integrated circuits.\textsuperscript{64,65} Their chemical inertness, high electrical conductivity and ease of deposition as layers makes them apt materials for this role. The most commonly used ones are the carbides of Group 4 due to their superior chemical stability.

### 1.3 TRANSITION METAL SILICIDES

The industrial utilisation of transition metal borides and silicides is limited by their low resistance to oxidation. Metal silicides have varied resistance to oxidation but mostly oxidise easily.

Transition metal silicides have a metallic appearance and conductivity, and are very hard. Binary transition metal silicides have been illustrated in a form of the Periodic Table (Figure 1.3). They are mostly insoluble in acids, even aqua regia. All dissolve in HF and most in molten KOH. They have high melting points mostly in the range 1500-2500 °C (Table 1.5).\textsuperscript{66}

<table>
<thead>
<tr>
<th>Silicide</th>
<th>Melting point, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$_3$Si</td>
<td>1750</td>
</tr>
<tr>
<td>Cr$_2$Si</td>
<td>1606</td>
</tr>
<tr>
<td>CrSi</td>
<td>1630</td>
</tr>
<tr>
<td>CrSi$_2$</td>
<td>1500</td>
</tr>
<tr>
<td>MoSi$_2$</td>
<td>2030</td>
</tr>
<tr>
<td>W$_5$Si$_3$</td>
<td>2320</td>
</tr>
</tbody>
</table>

As was previously stated, metal silicides have low resistance to oxidation. A number of silicides, though, form SiO$_2$ coatings at high temperatures. These coatings are often viscous and retard further oxidation. Molybdenum disilicide forms a film of oxide at 1700 °C, which protects it. It is used as an electrical heating element.\textsuperscript{68-72} It has a thermal expansion coefficient similar to commercially available niobium alloy.\textsuperscript{73} This makes it useful as a coating material both for Mo-
| Ti$_3$Si$_3$ | V$_2$Si$_3$ | Cr$_3$Si | Mn$_3$Si | Co$_2$Si | Ni$_3$Si |
| TiSi | V$_2$Si | Cr$_2$Si | Mn$_2$Si | Fe$_2$Si | Ni$_2$Si |
| TiSi$_2$ | VSi$_2$ | CrSi | MnSi | FeSi | NiSi |
| TiSi$_3$ | VSi | CrSi$_2$ | MnSi$_2$ | FeSi$_2$ | NiSi$_2$ |

| Zr$_4$Si | Nb$_4$Si | Mo$_3$Si | Ru$_3$Si$_2$ | Rh$_5$Si$_3$ | Pd$_3$Si |
| Zr$_2$Si | Nb$_3$Si$_3$ | Mo$_2$Si$_3$ | RuSi | Rh$_3$Si$_2$ | Pd$_2$Si |
| Zr$_3$Si$_3$ | Nb$_2$Si$_2$ | Mo$_3$Si$_2$ | MoSi$_2$ | Rh$_3$Si | PdSi |
| Zr$_4$Si$_2$ | NbSi | ZrSi | Ru$_2$Si$_3$ | Rh$_2$Si$_3$ | |
| ZrSi | ZrSi$_2$ | RhSi | RhSi$_3$ | |

| Hf$_4$Si$_2$ | Ta$_5$Si | W$_3$Si | Re$_3$Si | Os$_3$Si$_2$ | Ir$_3$Si |
| Hf$_3$Si | Ta$_4$Si | W$_3$Si$_3$ | Re$_3$Si$_3$ | OsSi | Ir$_3$Si$_2$ |
| Hf$_2$Si$_2$ | Ta$_3$Si | WSi$_2$ | ReSi | OsSi$_2$ | IrSi |
| Hf$_2$Si | Ta$_2$Si | ReSi$_2$ | |
| HfSi | TaSi | |
| HfSi$_2$ | TaSi$_3$ | |
| TaSi$_2$ | |

**Figure 1.3**  Known phases of transition metal silicides as observed in a form of the Periodic Table.\(^6\)
as well as Nb-based alloys. It has a moderate density (6.24 g/cm$^3$) and a high melting point (2020 °C). It is better at resisting oxidation at high temperatures than most other disilicides. Another very useful property of this material (and other disilicides) is the high creep resistance at temperatures up to 1400 °C, which is due to strong ordering in the silicides making diffusion difficult. The major drawback is its low temperature ductility. However incorporation of niobium, WSi$_2$ and CrSi$_2$ improves the ductility of molybdenum disilicide.$^{66,74}$ It has been shown that molybdenum and tungsten disilicides act as a pseudobinary system with solid solutions being far more resistant to oxidation by air, for example at 1500 °C a 30% : 70%, WSi$_2$ : MoSi$_2$ solid solution shows no weight change over a 4 hour period.$^{75}$

The Fe-Si system is very important in the steel industry. Four binary iron silicides exist:

<table>
<thead>
<tr>
<th>Silicide</th>
<th>Structure</th>
<th>Cell Parameters</th>
<th>Density (g/cc)</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$Si</td>
<td>cubic</td>
<td>$\alpha$, $a = 5.64$</td>
<td>7.23</td>
<td></td>
</tr>
<tr>
<td>Fe$_5$Si$_3$</td>
<td>hexagonal</td>
<td>$D_6h$, $a = 6.73$, $c = 4.70$</td>
<td>6.55</td>
<td></td>
</tr>
<tr>
<td>FeSi</td>
<td>cubic</td>
<td>$T^4$, $a = 4.438$</td>
<td>6.37</td>
<td>1410</td>
</tr>
<tr>
<td>FeSi$_2$</td>
<td>tetragonal</td>
<td>$a = 2.68$, $c = 5.18$</td>
<td>4.79</td>
<td>1220</td>
</tr>
</tbody>
</table>

The main use of ferrosilicon is in deoxidising steel, especially low carbon content steels. Silicon steel is used for manufacture of the laminated magnetic cores of a.c. electrical equipment (e.g. transformers, motors etc.).

Other transition metal silicides are of little industrial importance but some ternary combinations of aluminium chromium (or manganese) silicides are present in alloys and chromium silicon carbides are useful in high-tensile steel. Copper forms a number of ternary silicides with magnesium, which are used as precipitation hardeners in aircraft alloys.

Silicides of Group 2 are less well exploited commercially. They are highly reactive with water releasing hydrogen gas and leaving metal hydroxides and silicon dioxide. In dilute acids they dissolve evolving silanes:

\[
\text{Mg}_2\text{Si} + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{MgSO}_4 + \text{SiH}_4 \quad \text{eqn. 1.1}
\]
Magnesium silicide can be used in aluminium alloys. Precipitation of silicon and magnesium silicide under controlled conditions hardens and strengthens the metal. Calcium silicides, Ca₂Si, CaSi, CaSi₂ are potent reducing agents. They are used for the final deoxidation of high-grade steel.⁵⁶

1.4 TRANSITION METAL BORIDES

Transition metal borides are a class of materials that are grouped together with carbides, nitrides and silicides and termed refractory hard metals.⁶⁶ Most metal borides do not resist oxidation above 1000 °C. One unusual feature of metal borides is their range of stoichiometries with compositions corresponding to at least 24 metal to boron ratios starting from 5 : 1 and ending on 1 : 66. Most common are:

\[ \text{MB, MB}_2, \text{MB}_4, \text{MB}_6, \text{MB}_{12}, \text{MB}_{66} \]

Binary borides of transition elements have been illustrated in the form of a transition metal block of the Periodic Table in Figure 1.4.⁷⁶,⁷⁷ The most attractive properties of transition metal borides, especially the diborides, are the high melting points, the high microhardness, the excellent wear resistance and the favourable chemical inertness. A major drawback is their brittleness. It can be observed that boron rich transition metal borides (MBₙ, \( n \geq 2 \)) have mostly higher melting points than their parent transition metals. This has been illustrated in Table 1.6 for some selected examples. Metal rich metal borides have melting points equivalent to their parent metals. The most stable binary borides at high temperatures are the diborides of the titanium group. Their melting points are above 3000 °C. They are extremely hard and often have high thermal conductivity, reasonable corrosion resistance and high thermal shock resistance compared to that of oxide ceramics. Borides have interesting electrical properties spanning from semiconductors, MB₆₆, MB₆ and MB₁₂ phases of Be, Mg, Ca, Eu, Al and Si, through metallic conductors in most transition metal borides, to superconductors, NbB, YB₆ and ZrB₁₂.
### Figure 1.4

Known phases of transition metal borides as observed in a form of the Periodic Table.⁷⁶,⁷⁷
Table 1.6  
*Principal properties of selected metal borides. Melting points of the parent metals are in brackets next to the melting points for their borides. All data were taken from references [201 and [76].*

<table>
<thead>
<tr>
<th>Boride</th>
<th>Melting point, °C</th>
<th>Density, g/cm³</th>
<th>Microhardness, kg/mm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaB₆</td>
<td>2230(839)</td>
<td>2.46</td>
<td>2750</td>
</tr>
<tr>
<td>TiB₂</td>
<td>2980(1667)</td>
<td>4.52</td>
<td>3250</td>
</tr>
<tr>
<td>HfB₂</td>
<td>3250(2222 or 2467)</td>
<td>11.20</td>
<td>2900</td>
</tr>
<tr>
<td>W₂B₅</td>
<td>2200(3380)</td>
<td>13.10</td>
<td>2650</td>
</tr>
<tr>
<td>ThB₄</td>
<td>2200(1750)</td>
<td>8.45</td>
<td>2650</td>
</tr>
</tbody>
</table>

Nonoxidising acids do not readily attack borides except for those of Groups 1 and 2. Metal borides are mostly inert in hydrogen and nitrogen atmospheres at high temperatures. Fluorine and chlorine react vigorously with all borides at 400 °C. In the presence of air metal borides are also attacked by oxidising molten salts such as nitrates or carbonates.

The most important application of borides is as a material for crucibles for nonferrous metals. Titanium diboride is used for the electrolytic production of aluminium. The high inertness to molten aluminium together with high electrical conductivity make titanium and zirconium diborides potential quality materials in aluminium metallurgy, for example, as cathode leads or electrodes. The most important use for titanium diboride is for the manufacture of resistance-heated boats used in continuous evaporation of aluminium metal for vacuum metallizing. This constitutes the primary consumption of TiB₂ of which ~ 100 tonnes/annum are produced.

Calcium hexaboride is used for deoxidising copper. Colmonoy alloys based on nickel, chromium and boron are produced from the corresponding diborides. Borides are often used for coating metal surfaces. In this way they increase hardness and wear resistance properties.

Lanthanide and actinide borides are among the best known high temperature electron emitters. Lanthanum hexaboride is used as a high-current-density electrode in electron microscopes, electron beam furnaces and many other
instruments requiring very high electron emission.\textsuperscript{84,85} Present research is focused on growing and shaping crystals of this material.\textsuperscript{86}

1.5 COMMERCIAL PREPARATION OF BORIDES, CARBIDES AND NITRIDES

Preparations of all these materials require high temperatures. One of the main challenges in their syntheses is obtaining a high level of purity. Highly specific conditions are required to produce pure products. Use of a protective gas atmosphere is usually required.\textsuperscript{19,76,77}

From the many possible precursor manipulations in use three main approaches emerge:

(i)  \textit{Direct combination of the elements.}

In this type of combination the reactions forming borides are promoted by melting or by reaction sintering below the melting points of the precursors. Carbides and nitrides are prepared at very high temperatures (up to 3000 °C) but below the melting points of the compounds to avoid decomposition.\textsuperscript{26,27} This approach frequently faces difficulties due to the high volatility of the metals and in some cases their reactivity towards oxygen. Therefore these procedures often have to be carried out inside sealed vessels under vacuum or in an inert gas atmosphere.\textsuperscript{76,87,88}

\begin{align*}
\text{W} + \text{C} & \longrightarrow \text{WC}, \quad 1400-1600 \, ^{\circ}\text{C}, \text{H}_2 \\
\text{Al} + \text{N}_2 & \longrightarrow \text{AlN}, \quad 800-1000 \, ^{\circ}\text{C} \\
\text{Cr} + \text{B} & \longrightarrow \text{CrB}, \quad 1150 \, ^{\circ}\text{C}
\end{align*}
(ii) *Reduction of metal oxide.*

These pathways require different reaction conditions for various preparations. In general borides require vacuum conditions with a temperature above at least 1000 °C. Both the diborides and hexaborides can be prepared using this method.

For nitrides, this approach has disadvantages arising from carbon and oxide impurities remaining throughout the syntheses. The reaction proceeds via several intermediates where carbon is the reducing agent. The oxides and carbon are difficult to remove especially when oxygen and carbon phases form a solid solution with the nitride. Most transition metal nitride syntheses suffer from this problem. Low reaction temperatures help to prevent carbide formation. High temperatures enable the more stable carbides to form.

$$\text{WO}_3 + 4\text{C} \rightarrow \text{WC} + 3\text{CO}, \quad 1400-1600 \, ^\circ\text{C}, \text{H}_2, \text{CO}$$

$$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 \rightarrow 2\text{AlN} + 3\text{CO}, \quad 700-1000 \, ^\circ\text{C}$$

$$\text{Sc}_2\text{O}_3 + 7\text{B} \rightarrow 2\text{ScB}_2 + 3\text{BO}, \quad 1800 \, ^\circ\text{C}$$

(iii) *Reduction of metal halides*

These syntheses require a hydrogen atmosphere. Borides of Group 4 and only some transition metal nitrides can be prepared using this method. Preparation of carbides often involves use of a graphite carrier or high melting point metals. Here the halides are reduced with hydrogen-hydrocarbon mixtures. This method is used for production of layers and coatings on other materials by chemical vapour deposition (CVD).

$$\text{HfCl}_4 + \text{CH}_4 \rightarrow \text{HfC} + 4\text{HCl}, \quad 2400-2800 \, ^\circ\text{C}, \text{H}_2, \text{W-wire}$$

$$2\text{TiCl}_4 + 4\text{BCl}_3 + 10\text{H}_2 \rightarrow 2\text{TiB}_2 + 20\text{HCl}, \quad 1300 \, ^\circ\text{C}$$

$$2\text{NbCl}_5 + \text{N}_2 + 5\text{H}_2 \rightarrow 2\text{NbN} + 10\text{HCl}, \quad 1340-1360 \, ^\circ\text{C}, \text{W-wire}$$
Other methods used are difficult to generalise. Use of metal halides to react with ammonia is one of the prominent ones in nitride syntheses. The ammonia-halide complexes form which are then thermally decomposed. Metals, metal oxides, hydrides or oxyhalides can also be reacted with ammonia to form nitrides of variable purity. Ammonia is often preferred as a nitrogen precursor since in many cases it reacts at lower temperatures. Work of Laffitte and Grandadam showed that nitrogen does not react with tungsten below 900 °C. However ammonia starts to react at 140 °C.\textsuperscript{90,91}

Borides can also be prepared by the reduction of boron oxide or boron halides by metals. This process is used industrially to prepare, for example, calcium hexaboride.\textsuperscript{77} Recent interest is concentrated on production of borides by fused-salt electrolysis, which can be performed at 1000-1300 °C using a mixture of alkali halide, metal oxide and a borate. However obtaining high purity products is challenging.

Carbides can also be prepared by chemical separation occurring from carbon-saturated ferroalloys. High melting point metals can be carburized and separated by treatment with acids. This is the most commonly used approach to prepare oxygen- and nitrogen-free carbide solid solutions.\textsuperscript{92}

Transition metal silicides are usually prepared by heating elemental powders for several hours or co-reducing silicon dioxide with carbon.\textsuperscript{75,93,94} Mechanical alloying and solid state displacement methods can also be applied.\textsuperscript{95-97} Also in Russia silicides are at present more and more commonly prepared using SHS processes.\textsuperscript{98,99} These processes will be discussed in the next section.

## 1.6 SHS REACTIONS

### 1.6.1 Background and history

Self-propagating High-temperature Synthesis (SHS) is a controlled combustion process. The process proceeds by a synthesis wave which propagates through the reagents via an exothermic chemical exchange to form the final products. The origins of SHS stemmed from the discovery of the solid flame phenomena in 1967.\textsuperscript{100} In the SHS processes the initial solid substances undergo
combustion forming solid products without a change of state occurring throughout the reaction even at high temperatures.\textsuperscript{101-103} SHS is characterised by high reaction rates and high temperatures, attained due to internal heat release. The key contribution to the rapid progress in the development of SHS were the studies on the mechanism and theory of combustion in gasifying condensed systems coupled with experience acquired in the combustion of thermites.\textsuperscript{101} The first research into SHS outside the former USSR was in the US. Industrial SHS production started in 1979 at the Kirovakan Plant of High-Temperature Heaters. There application of the new SHS methods lead to a decrease in workspace required, increase in labour productivity and increase in product quality.\textsuperscript{101} To date companies in the former USSR, USA, Spain, UK and Japan utilise SHS preparations on an industrial scale.

The first thorough studies of SHS, performed in 1969-1971, concentrated on optimising final product purity. Borides, carbides, nitrides and silicides of transition metals were prepared.\textsuperscript{104,105} Throughout the seventies a lot of attention has been drawn to acquiring knowledge of the mechanisms in complex SHS reactions and identification of intermediate products and stages.\textsuperscript{106,107}

The first large-scale production of SHS powders were initiated in 1972 in Chernogolovka (near Moscow) using a 20 l reactor. The first powders produced there were TiC, TiN, Ti(C,N), TiB\textsubscript{2}, AlN, Si\textsubscript{3}N\textsubscript{4} and MoSi\textsubscript{2}. It was observed that an increase in volume of reactants improved product quality.

It was thought until recently that SHS can only be used for the preparation of large particles. Now it is known that finely dispersed products can be obtained by controlling structure and improving the dispersion procedure (ingots or cakes). The minimal particle size presently obtainable via SHS is approximated 0.1 micron. Such powders are suitable for sintering. Various methods of treating the final products to obtain dispersions were suggested.\textsuperscript{107,108} One of them, suggested by Borovinskaya et al., and named the ‘chemical dispersion technique’ involves placing the SHS product in a liquid of specific composition at a specific temperature. This in effect dissolves defect layers at the crystallite boundaries leaving undissolved single, fine crystalline particles.

The opposite problem is in trying to increase the final product particle size. One of the most common methods in use is via a decrease in the cooling rate for combustion products, which enhances the extent of crystallization. When 1 ton of
reagents were reacted to form TiC single crystal particles of 1 mm in size were obtained.\textsuperscript{107}

1.6.2 Synthesis of pore-free materials, items and coatings by SHS

Since 1975 SHS has been used to produce consolidated, pore-free materials and items. This was performed by forced pressing of the still hot SHS products. The success in performed shaping, structuring and synthesis functions in a single step process has advantages. In the past the powders first had to be synthesised and then treated by powder metallurgy.\textsuperscript{109} Many scientists started to follow this new work by studying different methods of consolidating the SHS products which include extrusion, explosive shock, pressing, high pressure effects etc.

Another direction in SHS investigations was made to develop the deposition techniques of high temperature SHS melts to produce coatings. One such work lead to the development of centrifugal casting of large-scale pipes.\textsuperscript{110} For years SHS studies concentrated on producing homogenous products to prove that these processes are equivalent to those using furnaces. Recently the preparation of SHS materials with a preset inhomogeneity became more commanding.

At the end of the 1970s, work on deposition of coatings was initiated. Two processes were studied:

(i) The formation of SHS melts on the surface of subject to be coated (SHS surfacing).

(ii) Transferring reactants via a gas phase to the surface of the subject in the combustion wave (gas-transport SHS coatings).

Other processes then followed:

(iii) Induction SHS surfacing.

(iv) Deposition of coatings in chain flames at low temperatures.

(v) Formation of coatings in chemical furnaces.
6.3 Industrial applications of SHS products, materials and items

SHS products were commercialised in 1973 when SHS prepared TiC was found to have suitable abrasive properties required for grinding powders and pastes. Around 1500 plants in USSR used such powders and pastes prepared from this abrasive material. For the first time economic significance of SHS has been demonstrated.

To date SHS products are commonly used in mechanical engineering, metallurgy, the chemical industry, aerospace engineering, electronics and medicine. The development of commercial production lines for SHS has proved to be the rate-determining step. In Japan production of titanium nickelide has been set up, a material with shape memory.

1.7 WHAT ARE THE SSM REACTIONS?

1.7.1 Background

The discovery of Solid State Metathesis reactions (SSM) has been motivated by the desire for alternate straightforward and rapid routes to crystalline solid state compounds. Scientists search for new routes to materials that will produce the desired products more rapidly, with less energy input and obtaining purer phases of controlled particle size.

Currently SSM reactions are more and more frequently placed under the umbrella of SHS. They are also very rapid and the energy for the process also comes from the reaction enthalpy. SSM reactions involve elemental exchange (metathesis meaning exchange from Greek) between two reagents. In most cases two products are formed, the desired ceramic and a salt like co-product. The formation of the co-product is the driving force for the process providing anything up to 90% of the total reaction enthalpy. In most cases to date such co-products are the Group 1 or 2 salts which can be conveniently removed after the reaction is complete, by washing with water.
1.7.2 **Initiation and product formation**

Most SSM reactions, in order to initiate, require initial energy input. In some cases they may react on contact but in most cases grinding the reagents, applying a hot filament or flame (the temperatures of the flame and filament can be controlled), or heating the mixture is required. All these modes of initiation are characterised by a different magnitude of energy input. The minimal energy input required to initiate SSM processes is dependent on the ease by which the solid state diffusion barrier is overcome. All solid state metathesis reactions require a phase change to initiate and propagate. Such phase change is either the melting of one of the reagents or decomposition or structural (phase) rearrangement. The minimum energy input for initiation to occur is related to the phase change. The lower the melting point of transition metal halide the less energy is required to initiate the reaction. Therefore it is always going to be more convenient to use TiI$_4$ than TiCl$_3$ for the formation of TiN using Li$_3$N for the nitrogen supply as shown in the following reactions:

\[
\begin{align*}
\text{TiCl}_3 + \text{Li}_3\text{N} & \rightarrow \text{TiN}_x + 3\text{LiCl} + 1-x/2\text{N}_2 & T_m = 420 \, ^\circ\text{C} \\
\text{TiI}_4 + 4/3\text{Li}_3\text{N} & \rightarrow \text{TiN}_x + 4\text{LiI} + (1/6 + 1-x/2\text{N}_2) & T_m = 180 \, ^\circ\text{C}
\end{align*}
\]

m. pt. TiCl$_3$ = 440 °C, m. pt. TiI$_4$ = 155 °C

1.7.3 **Comparison of SHS and SSM processes**

SHS and SSM processes share a lot of characteristics but also can be discerned from each other. SHS processes draw their energy from the inbuilt chemical energy of the reaction. Only the initiation requires outside energy input. The maximum combustion temperatures reached vary in the range between 1000 °C and 4000 °C. These are reached within seconds after initiation and cooling normally being rapid can be controlled by varying the reaction scales. In most SHS reactions a fuel source and an oxidiser are required. The reactions are of a redox type.
SSM processes usually have lower combustion temperatures (700–1400 °C cf 1400–4000 °C). However the velocity, initiation power and initiation duration are comparable for both reactions. The mechanistic pathways in SSM have been postulated as either a direct ionic metathesis or a reduction-recombination (elemental) mechanism (Scheme 1.1). The particular mechanism adopted varies between different reactions.

![Scheme 1.1 Ionic (i) and reductive-recombination (elemental) (ii) mechanisms in SSM reactions.](image)

1.7.4 **Future and advantages of SSM reactions**

In recent years research has been progressing in order to control SSM synthesis and produce small particle size powders. Reactions performed in solvents were most successful yielding nanoparticulate products such as pnictides of gallium and indium. The narrow size distribution desired was obtained. The particle size can be manipulated by altering the solvents or co-ligating molecules used.

Solid state metathesis reactions provide a new route to many materials. One such group is the electroceramic materials such as barium titanate, produced using barium peroxide and titanium trichloride in a process, which involves solid state metathesis. All groups of ceramic materials have been researched with substantial success. Metal nitrides, silicides, borides and many others have been synthesised. Formation of solid solutions has also been successful.

Products obtained from SSM reactions are also usually characterised by their high purity. The high reaction enthalpy in SSM processes due to the
formation of Group 1 or 2 halide allows formation of compounds inaccessible using conventional methods at parallel temperatures. Conventional preparations also require much longer periods for heating.

One cannot ignore the advantages that a self-propagative process such as SSM provides, where no heating is required in most cases, except for the initiation, for example, with a hot filament. This eliminates the requirement of high temperature furnaces for the procedures. The propagation wave is a more rare phenomenon than most may think. Very few other processes can self propagate without any external heat input. This is due to the presence of high activation barriers in most reagent combinations. One example of that is the industrial preparation of layered-form hexagonal boron nitride:

\[
3\text{CaB}_6 + \text{B}_2\text{O}_3 + 10\text{N}_2 \rightarrow 2\text{0BN} + 3\text{CaO} \quad \text{eq. 1.2}
\]

\[T_{ad} = 3400 \, ^\circ\text{C}^{128}\]

This process is highly exothermic yet h-BN can only be obtained at temperatures above 1500 °C using this approach.\(^{36}\)

The most outstanding characteristic of the SSM processes is their reaction rate, reaching completion and cooling to room temperature in a matter of seconds. This is incomparable with most conventional preparations. The high reaction rates also mean that contact time with the vessel at raised temperature is short and contamination from this source is reduced. Conventional methods that have long periods of heating often suffer from high levels of contamination and in order to reduce this have to be performed at a larger scale. SSM processes can be envisaged to produce products of unusual microstructure. A typified crystallite size of an SSM prepared powder, obtained from the Scherrer equation, is within 200-800 Å. SEM studies revealed presence of agglomerates of crystallites. Previously work has been performed to determine microstructure by SEM and using SSM methods to manipulate the crystallite size using a solvent heat sink.\(^{123}\) These studies have been very beneficial in raising interest in potential applications of SSM processes for industrial scale preparations of a wide range of ceramic materials.
The high temperatures of SSM reactions have also promoted crystalline phases of products such as hexagonal boron nitride. Conventionally even the highly explosive reaction of caesium and $\beta$-trichloroborazine produces amorphous rather than crystalline boron nitride. Work of Kaner et al. has proved that crystalline boron nitrides can be prepared using SSM reactions without any additional annealing.

SSM reactions can be envisaged to yield phases, which can only be conventionally prepared using extreme conditions, for example, cubic TaN requires prolonged periods of heating above 1600 °C and a pressure of 20-160 atm. Solid state metathesis processes can prepare this product by reacting TaCl$_5$ with Li$_2$N (or Ca$_3$N$_2$, Mg$_3$N$_2$, Sr$_2$N and Na$_3$N) at 200-250 °C within 2-5 seconds without any additional external pressure applications. Crystallinity can be controlled by changing the nitrogen precursor. Some control over the level of nitridation is also possible.

A whole group of reactions which are a combination of solid state metathesis and a molecular precursor route have also been studied. One example of such approach is the reaction between lithium amide and metal halides at 300-350 °C occurring with a thermal flash producing a material rich in nitrogen which is then annealed at temperatures around 700 °C to produce a metal nitride. This approach is less exothermic and is very useful in obtaining thermally unstable materials without applying raised pressures.

In summary, solid state metathesis reactions provide a new route to materials. They provide a lot of advantages over conventional preparations. The reactions are faster, produce generally purer products of high crystallinity, give high yields affected only by mechanical sources, are very straightforward to perform and need little external energy input. These advantages are accompanied by retaining some important characteristics of conventional methods such as the ability to control the particle size. SSM processes still need more developing but have a very promising scope.
1.6 AIMS OF THIS WORK

Prior to this work SSM processes have been used to prepare metal borides, nitrides, silicides, pnictides and chalcogenides. These reactions were studied in some detail focusing on obtaining a variety of pure phases using metal halides and main group element precursors. Also some nitride phases have been prepared using metal oxides as precursors.\textsuperscript{133,134}

The main aim of this work was to dedicate itself to discovering new metathesis reactions to form phases of carbides, nitrides and carbonitride solid solutions. Some previously studied formations of nitrides were also repeated to study their products more widely using highly sophisticated analytical techniques such as TEM, PEELS and ELNES.

SSM reactions are a very new preparative route to ceramic materials. Therefore this study also aimed at improving preparations formerly already reported in order to gain more control over them. This would be of benefit in obtaining powders of particular particle size while gaining or retaining high phase purity. This was accomplished by using new reagents not utilised previously in the SSM processes.
CHAPTER 2

PREPARATIONS OF METAL NITRIDES

2.1 INTRODUCTION

A wide range of nitriding reagents are available for solid state metathetical preparations of transition metal nitrides. Previous work has studied the reactions of anhydrous metal halides with lithium nitride, calcium nitride, magnesium nitride and sodium azide (equation 2.1).\textsuperscript{116,117,130,135-137} Despite this work a vast range of potential nitriding reagents have not been investigated. A number of nitriding reagents are listed below in section 2.1.1; the species that are represented in bold are those that have been previously studied.

\[
\text{TiCl}_3 + \text{Li}_3\text{N} \rightarrow \text{TiN} + 3\text{LiCl} \quad \text{eqn. 2.1}
\]

2.1.1 Potential nitriding reagents

1. **Alkaline and alkaline earth main group binary metal nitrides:**

   \(\text{Li}_3\text{N}, \text{Na}_3\text{N}, \text{Rb}_3\text{N}, \text{Cs}_3\text{N},\)

   \(\text{Be}_3\text{N}_2, \text{Mg}_3\text{N}_2, \text{Ca}_3\text{N}_4, \text{Ca}_{11}\text{N}_8, \text{Ca}_3\text{N}_2, \text{Ca}_2\text{N}, \text{Sr}_3\text{N}_4, \text{Sr}_2\text{N}, \text{Sr}_3\text{N}, \text{Ba}_3\text{N}_2,\)

   \(\text{Ba}_3\text{N}.)

2. **Alkaline and alkaline earth main group ternary metal nitrides:**

   \(\text{CaMg}_2\text{N}_2, \text{LiMgN}, \text{Mg}_2\text{CaN}_2.)

3. **Alkaline and alkaline earth metals azides:**

   \(\text{LiN}_3, \text{NaN}_3, \text{KN}_3,\)

   \(\text{Mg(N}_3)_2, \text{Ca(N}_3)_2, \text{Sr(N}_3)_2, \text{Ba(N}_3)_2.)

\[\text{49}\]
4. **Alkaline and alkaline earth metal amides:**

LiNH₂, NaNH₂, LiNMe₂, LiNEt₂, Mg(NH₂)₂, Ca(NH₂)₂.

Some of these potential nitriding species cannot be used due to their poor thermal stability, for example Na₃N slowly decomposes at room temperature and rapidly at 150 °C.¹³⁸ Some surveys on nitrides, however actually doubt the existence of sodium nitride.¹⁹,¹³⁹,¹⁴⁰ Many nitrides are also difficult to isolate as pure phases and exist as a mixture of two or more stoichiometries, making them undesirable as regents for the formation of stoichiometric products. Isolation of pure phases of such precursors is usually time-consuming and expensive.

Some transition metal nitrides are thermally unstable especially those from the latter transition metals. Since solid state metathesis reactions give rise to highly exothermic reactions, thermally unstable nitrides cannot be isolated, as the formed nitride will decompose to nitrogen and metal at the reaction temperatures. Nitrides of Groups 6-10 are thermally unstable (have a decomposition point below 600 °C) and more sophisticated methods have been used to recover the nitride from SSM reactions. These methods can include the addition of an inert heat sink such as an alkali metal halide or by increasing nitrogen gas partial pressures. The phenomena of low thermal stability for the latter transition metal nitrides is known as the ‘chromium enigma’, as chromium nitride is significantly less refractory than the Group 4 and 5 rock salt type nitrides.¹⁴⁰ **Figure 1.2** shows the Periodic Table of nitrides.

There are other precursors, which can in principle be used for the preparation of transition metal nitrides. These include the ternary lithium group 13 nitrogen precursors, such as Li₃AlN₂ and Li₃GaN₂. Other transition metal precursors that can be utilised for metathesis reactions include some of the transition metal oxides (equation 2.2).¹³³,¹³⁴

\[
\text{LiTaO}_3 + \frac{5}{3}\text{Li}_3\text{N} \rightarrow \text{TaN} + 3\text{Li}_2\text{O} + \frac{1}{3}\text{N}_2 \quad \text{eqn. 2.2}
\]
2.1.2 Aims and background

This chapter discusses new reactions of anhydrous metal halides with alkaline or alkaline earth metal nitrides and sodium azide. This work builds on the quite extensive metathesis literature for the formation of nitrides, which has been reported by Kaner et al.\textsuperscript{136,141} and Parkin et al.\textsuperscript{116,117,135,137,142-147} It was reported previously that lithium nitride can be used to form $\text{S}_4\text{N}_4$ by solution phase metathesis.\textsuperscript{148} The aim of the work presented in this chapter is to provide an enhanced view on analysis of the products formed rather than necessarily producing new nitride phases. New manipulations with control over the experiments were performed and the oxidative stabilities of some SSM prepared nitrides are reported. In particular, the work focussed on producing for the first time a range of non-stoichiometric transition metal nitrides. This was of particular relevance for the characterisation of these materials by the ELNES (energy loss near edge structure) technique. One new synthetic extension to the metathesis reactions developed in this chapter is the metathesis formation of Group 3 nitrides.

One of the major interests in the syntheses of ceramic materials is the formation of ternary solid solutions. These can include the bimetallic nitrides such as $(\text{Ti},\text{V})\text{N}$, the bimetallic carbides such as $(\text{Mo},\text{W})\text{C}$ and transition metal carbonitrides such as $\text{Ti}(\text{C},\text{N})$.

There are many known binary nitrides and carbides. However the number of mixed metal carbides and nitrides, $\text{MM}'\text{C}$ and $\text{MM}'\text{N}$, is comparably more restricted.\textsuperscript{19,26,27,149-152} This is because the formation of such intimate solutions is dependent on the lattice constants of the binary compounds and is related to the Hume-Rothery rule.\textsuperscript{153} It has been reported that some methods of preparation result in poor solid solutions, which then require heating at high temperature, to form anything like a solid solution. Preparation of mixed metal species often requires very high temperatures and addition of small quantities of other metals to initiate diffusion (e.g. to form $(\text{Ti},\text{Ta})\text{C}$ the conditions required are 2000 °C and Ni metal). Solid solutions of transition metal nitrides include: $(\text{M}_x\text{M}'_y)$\text{N} where $x + y = 1$ (e.g. $\text{Mo}_2\text{Co}_3\text{N}$), $(\text{M},\text{M}')\text{N}$ (e.g. $\text{FeNiN}$), $(\text{M}_2,\text{M})\text{N}$ (e.g. $\text{Ti}_2\text{AlN}$ or $\text{Ti}_2\text{SnN}$), $(\text{M}_3\text{M}'\text{N})$ (e.g. $\text{Fe}_3\text{NiN}$ or $\text{Fe}_3\text{PtN}$), $(\text{M}_3,\text{M}')\text{N}_4$ (e.g. $\text{Ta}_3\text{MnN}_4$), $(\text{M}_3,$
Section 2.4.4 discusses the results from the reactions where homogeneous bimetallic transition metal nitrides were the desired products. This work builds up on some previous studies performed by Parkin et al.\textsuperscript{116,117,119} Some work has also been reported on forming ternary sulfides using solid state metathetical routes by reacting transition metal halides with sodium sulfide, Na\textsubscript{2}S.\textsuperscript{157} Materials such as (Mo,W)S\textsubscript{2} have been prepared using this combination. The reactions where bimetallic transition metal carbides and transition metal carbonitrides were the desired products are discussed in chapter 3. In the next section the results of the synthetic work discovered in this thesis in forming metal nitrides are presented.

2.2 SYNTHESIS

(i) Reactions performed inside ampoules (bulk reactions)

Reactions of transition metal halides of Group 3 to 5 with Group 1 and 2 nitrides and sodium azide inside an evacuated ampoule at various temperatures between 190 °C and 550 °C produce transition metal nitrides and Group 1 or 2 halides (Tables 2.1-2.2). The reactions often proceed with a thermal flash and cease within seconds of their initiation. The black solids produced were triturated with dried and degassed methanol. The products were mostly annealed at 550 °C to induce greater crystallinity. The products obtained from the direct reactions without annealing were often poorly crystalline. The schematic equations 2.3-2.5 typify the SSM reactions discussed in this chapter.

The yields obtained from the reactions of transition metal halides with Group 1 and 2 nitride were generally high (70-90% by weight). The losses with respect to the transition metal used were usually attributed to mechanical handling. In more violent reactions such as all the reactions where sodium azide was used as a nitriding agent the products were spread over the ampoule walls. Some solids produced were not collected off the ampoule walls. It can be generally accepted that increasing the reaction scale will decrease such losses in yields. The yields with respect to the amount of nitrogen used were much lower.
since some of it escaped as a gas. This can be observed in the products from the reactions of titanium and vanadium trichlorides with nitriding agents where the products formed possessed substoichiometry (MN_x, where x > 1) despite the fact that there was enough nitrogen in the reagents to form MN_x (where x = 1).

Scheme 2.1  Schematic equations typifying the SSM reactions discussed in this chapter.

for the reactions in which Group 1 metal nitride precursor was used,

\[ MX_n + n/3Li_3N \rightarrow MN_x + nLiX + [(n/3-1) + (1-x)]/2N_2 \quad \text{eqn. 2.3} \]

for the reactions in which Group 2 metal nitride precursor was used,

\[ MX_n + n/6A_3N_2 \rightarrow MN_x + n/2AX_2 + [(n/3-1) + (1-x)]/2N_2 \quad \text{eqn. 2.4} \]

for the reactions in which sodium azide precursor was used,

\[ MX_n + nNaN_3 \rightarrow MN_x + nNaX + [(3n-1) + (1-x)]/2N_2 \quad \text{eqn. 2.5} \]

where, A = Mg, Ca, Sr, Ba; M = transition metals of Groups 3, 4 and 5; X = Cl, Br, I.

(ii) Reactions initiated with a flame or a filament (propagation reactions)

Reactions of Group 4-6 transition metal halides with lithium nitride and calcium nitride can also be initiated with flame or filament. These were also performed under an inert atmosphere. The reactions of magnesium nitride with these halides did not propagate with the exceptions for niobium and tantalum pentachlorides, which propagated slowly, when initiated with flame. All reactions of Group 3 transition metal halides and lanthanide halides with Group 1 and 2 nitrides and sodium azide failed to propagate. In all the reactions that could be initiated with flame or filament the propagation was accompanied by a yellow to orange flame with some of the co-product subliming away or separating as a white layer around the edges of the black nitride product. Most of these reactions
have not been represented in the X-ray diffraction results tables since most of their products were poorly crystalline and their lattice parameters could not be calculated accurately.

X-ray powder diffraction patterns, FT-IR, and SEM/EDXA were performed for both crude and triturated samples from all the reactions. A selected group of triturated products was also analysed using TEM, PEELS/ELNES, electron probe and microanalysis. Details regarding the instruments used are included in the experimental section.

2.3 CHARACTERISATION

2.3.1 X-ray powder diffraction

(i) Bulk reactions

All reactions of Group 3-5 transition metal halides and rare earth halides with lithium nitride yielded crystalline powders with crystallite size of the order of 250-1200 Å, as calculated from XRD line broadening using the Scherrer equation using Formula 2.1 below:

\[
L = \frac{k \lambda \cos \theta}{\sqrt{(B^2 - b^2)}}
\]

where, \( L \) = crystallite size, \( k \) = constant \((0.89 < k < 1.1)\), \( \lambda \) = X-ray wavelength, \( \theta \) = diffraction angle, \( B \) = halfwidth of reflection for sample, \( b \) = halfwidth for standard peak ([101] of zinc)

Crude and triturated products showed that purification using solvent washing completely removed the co-formed salt (figure 2.1). (continued on page 56)
Figure 2.1 XRD patterns of crude (a) and triturated (b) product from bulk reaction of yttrium trichloride with lithium nitride. Bottom stick patterns are for yttrium nitride (c), lithium chloride hydrate, $\text{LiCl.H}_2\text{O}$ and lithium chloride (dashed lines) (d).
Table 2.1  Selected reactions of metal halides with lithium nitride or sodium azide initiated with flame (fl), filament (fil) or performed in bulk under vacuum (bkv) or nitrogen pressure (b kp). *

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products (after trituration)*</th>
<th>( a_{obs} / \text{Å} +/- 0.001 )</th>
<th>( a_{ref} / \text{Å} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{ScCl}_3 + \text{Li}_3\text{N} ) (bkv)</td>
<td>ScN</td>
<td>4.488</td>
<td>4.45</td>
</tr>
<tr>
<td>( \text{ScCl}_3 + \text{Li}_3\text{N} ) (fil)</td>
<td>No reaction</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \text{ScCl}_3 + \text{Na}_3\text{N} ) (bkv)</td>
<td>ScN</td>
<td>4.491</td>
<td>4.45</td>
</tr>
<tr>
<td>( \text{TiCl}_3 + \text{Li}_3\text{N} ) (bkv)</td>
<td>TiN(_{0.84})</td>
<td>4.238</td>
<td>TiN(_{0.84}) - 4.238</td>
</tr>
<tr>
<td>( \text{TiCl}_3 + \text{Li}_3\text{N} ) (fil)</td>
<td>TiN(_{0.69})</td>
<td>4.231</td>
<td>TiN(_{0.69}) - 4.231</td>
</tr>
<tr>
<td>( \text{TiCl}_3 + \text{Na}_3\text{N} ) (bkv)</td>
<td>TiN(_{0.81})</td>
<td>4.236</td>
<td>TiN(_{0.81}) - 4.236</td>
</tr>
<tr>
<td>( \text{TiCl}_3 + \text{Li}_3\text{N/Na}_3\text{N} ) (bkv)</td>
<td>TiN(_{0.90})</td>
<td>4.240</td>
<td>TiN(_{0.90}) - 4.240</td>
</tr>
<tr>
<td>( \text{ZrCl}_3 + \text{Li}_3\text{N} ) (fil)</td>
<td>ZrN(_{0.00})</td>
<td>4.577</td>
<td>ZrN(_{0.00}) - 4.577</td>
</tr>
<tr>
<td>( \text{ZrCl}_3 + \text{Na}_3\text{N} ) (bkv)</td>
<td>ZrN(_{0.95})</td>
<td>4.570</td>
<td>ZrN(_{0.95}) - 4.570</td>
</tr>
<tr>
<td>( \text{HfCl}_3 + \text{Li}_3\text{N} ) (bkv)</td>
<td>HfN(_{0.83})</td>
<td>4.520</td>
<td>HfN(_{0.83}) - 4.520</td>
</tr>
<tr>
<td>( \text{HfCl}_4 + \text{Li}_3\text{N/Na}_3\text{N} ) (bkv)</td>
<td>HfN(_{0.09})</td>
<td>4.516</td>
<td>HfN(_{0.09}) - 4.516</td>
</tr>
<tr>
<td>( \text{VCl}_3 + \text{Li}_3\text{N} ) (bkv)</td>
<td>VN(_{0.89})</td>
<td>4.111</td>
<td>VN(_{0.89}) - 4.111</td>
</tr>
<tr>
<td>( \text{VCl}_3 + \text{Li}_3\text{N} ) (fil)</td>
<td>VN(_{0.88})</td>
<td>4.098</td>
<td>VN(_{0.88}) - 4.098</td>
</tr>
<tr>
<td>( \text{VCl}_3 + \text{Na}_3\text{N} ) (bkv)</td>
<td>VN(_{0.93})</td>
<td>4.112</td>
<td>VN(_{0.93}) - 4.112</td>
</tr>
<tr>
<td>( \text{NbCl}_3 + \text{Li}_3\text{N} ) (bkv)</td>
<td>NbN(_{1.06})</td>
<td>4.399</td>
<td>NbN(_{1.06}) - 4.399</td>
</tr>
<tr>
<td>( \text{TaCl}_3 + \text{Li}_3\text{N} ) (bkv)</td>
<td>TaN ([\text{TaN}_3\text{N}])</td>
<td>(TaN) 4.294</td>
<td>TaN 4.294</td>
</tr>
<tr>
<td>( \text{CrCl}_3 + \text{Li}_3\text{N} ) (bkv)</td>
<td>Cr(_2\text{N}) (hex)</td>
<td>(Cr(_2\text{N})) (a = 4.772, c = 4.454)</td>
<td>a = 4.805, c = 4.479</td>
</tr>
<tr>
<td>( \text{CrCl}_3 + \text{Li}_3\text{N} ) (bkv)</td>
<td>Cr(_2\text{N}) (hex)</td>
<td>a = 4.772, c = 4.479</td>
<td>a = 4.805, c = 4.479</td>
</tr>
<tr>
<td>( \text{CrCl}_3 + \text{Li}_3\text{N} ) (bkv)</td>
<td>CrN, Cr</td>
<td>(CrN) 4.148</td>
<td>CrN 4.150</td>
</tr>
<tr>
<td>( \text{MoCl}_3 + \text{Li}_3\text{N} ) (bkv)</td>
<td>Mo</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \text{LaCl}_3 + \text{Li}_3\text{N} ) (bkv)</td>
<td>LaN</td>
<td>5.295</td>
<td>5.30</td>
</tr>
<tr>
<td>( \text{LaCl}_3 + \text{Na}_3\text{N} ) (bkv)</td>
<td>LaN</td>
<td>5.277</td>
<td>5.30</td>
</tr>
<tr>
<td>( \text{EuCl}_3 + \text{Li}_3\text{N} ) (bkv)</td>
<td>EuN</td>
<td>4.99</td>
<td>5.01</td>
</tr>
<tr>
<td>( \text{EuCl}_3 + \text{Na}_3\text{N} ) (b kp)</td>
<td>EuN</td>
<td>5.01</td>
<td>5.01</td>
</tr>
<tr>
<td>( \text{AlCl}_3 + \text{Li}_3\text{N} ) (bkv)*</td>
<td>AlN(hex), Al</td>
<td>(AlN) (a = 3.109, c = 4.972)</td>
<td>a = 3.110, c = 4.975</td>
</tr>
<tr>
<td>( \text{AlCl}_3 + \text{Li}_3\text{N/Na}_3\text{N} ) (bkv)*</td>
<td>Al</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \text{AlCl}_3 + \text{Li}_3\text{N/Na}_3\text{N} ) (b kp)*</td>
<td>AlN(hex)</td>
<td>(a = 3.110, c = 4.979)</td>
<td>a = 3.110, c = 4.975</td>
</tr>
<tr>
<td>( \text{LiAlCl}_4 + \text{Li}_3\text{N} ) (bkv)*</td>
<td>AlN, Al</td>
<td>(AlN) 7.927</td>
<td>a = 7.913</td>
</tr>
<tr>
<td>( \text{LiAlCl}_4 + \text{Li}_3\text{N/Na}_3\text{N} ) (bkv)*</td>
<td>Al</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \text{LiAlCl}_4 + \text{Li}_3\text{N/Na}_3\text{N} ) (bkv)*</td>
<td>AlN</td>
<td>(a = 7.935)</td>
<td>a = 7.913</td>
</tr>
<tr>
<td>( \text{InCl}_3 + \text{Li}_3\text{N} ) (bkv)</td>
<td>InN(hex), In</td>
<td>(InN) (a = 3.49, c = 5.61)</td>
<td>a = 3.54, c = 5.70</td>
</tr>
</tbody>
</table>

*All the reaction mixtures were always heated to 550 °C within 30 minutes and then cooled down ready for trituration. Most of these reactions initiated at temperatures below 500 °C. In the reactions performed under vacuum it is has been assumed that no nitrogen is lost from the reaction mixture. In the reactions where lithium nitride and sodium azide were used together the standard molar ratio applied was 3 : 1 \((\text{Li}_3\text{N} : \text{NaN}_3)\).

*all nitride products cubic unless stated.

*a reaction required annealing for 24-36 hours.

[ ] - minor phases present.
The products from the reactions of transition metal halides and various nitriding reagents were highly crystalline considering the reaction timescale. This is due to two factors, which participate in the SSM reactions:

(i) High reaction enthalpies as demonstrated by the examples in equations 2.11-2.16 in section 2.5. The theoretical maximum reaction temperatures as calculated assuming adiabatic processes are expected to be close to the temperatures reached in practice due to the short timescale of the SSM processes.

(ii) Formation of molten salts which may catalyse crystallisation of SSM products. Lower melting point salts will remain molten for longer allowing more time for recrystallization of the product.

Table 2.2  Selected reactions of metal halides with Group 2 nitrides performed using flame (fl) or filament (fil) initiation or as a bulk reaction under vacuum (bk). * Literature lattice parameters were taken from references [152] and [159].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products after trituration and annealingb</th>
<th>(a_{\text{obs}}/\text{Å} \pm 0.005)</th>
<th>(a_{\text{theo}}/\text{Å})</th>
</tr>
</thead>
<tbody>
<tr>
<td>ScCl₂ + Mg₃N₂ (bk)</td>
<td>ScN</td>
<td>4.933</td>
<td>4.45</td>
</tr>
<tr>
<td>ScCl₂ + Ca₃N₂ (fil)</td>
<td>No reaction</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>YCl₃ + Mg₃N₂ (bk)</td>
<td>YN</td>
<td>4.862</td>
<td>4.89</td>
</tr>
<tr>
<td>YCl₃ + Ca₃N₂ (bk)</td>
<td>YN</td>
<td>4.897</td>
<td>4.89</td>
</tr>
<tr>
<td>TiCl₃ + Mg₃N₂ (bk)</td>
<td>TiN₀.₉₂</td>
<td>4.224</td>
<td>TiN₀.₉₂ = 4.224</td>
</tr>
<tr>
<td>VCl₃ + Mg₃N₂ (bk)</td>
<td>VN₀.₉₂</td>
<td>4.117</td>
<td>VN₀.₉₂ = 4.117</td>
</tr>
<tr>
<td>VCl₃ + Ca₃N₂ (fil)</td>
<td>VN₀.₈₉, V₃N</td>
<td>(VN) 4.110</td>
<td>VN₀.₈₉ = 4.110</td>
</tr>
<tr>
<td>VCl₃ + Mg₃N₂ (bk)</td>
<td>VN₀.₉₇</td>
<td>4.121</td>
<td>VN₀.₉₇ = 4.121</td>
</tr>
<tr>
<td>VCl₃ + Mg₃N₂ (fil)</td>
<td>No reaction</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>TaCl₅ + Ca₃N₂ (fil)</td>
<td>TaN</td>
<td>4.31</td>
<td>4.33</td>
</tr>
<tr>
<td>TaCl₅ + Ca₃N₂ (fil)</td>
<td>TaN</td>
<td>4.28</td>
<td>4.33</td>
</tr>
<tr>
<td>TaCl₅ + Mg₃N₂ (fil)</td>
<td>No reaction</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>TaCl₅ + Mg₃N₂ (fil)</td>
<td>TaN, Ta₂N²</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>CrCl₂ + Mg₃N₂ (bk)</td>
<td>CrN [Cr₂N(hex)]</td>
<td>(CrN) 4.151</td>
<td>4.150</td>
</tr>
<tr>
<td>CrCl₂ + Mg₃N₂ (bk)</td>
<td>CrN, Cr₃N(hex)</td>
<td>(CrN) 4.150</td>
<td>4.150</td>
</tr>
<tr>
<td>CrCl₂ + Ca₃N₂ (bk)</td>
<td>CrN, Cr₃N(hex)</td>
<td>(CrN) 4.150</td>
<td>4.150</td>
</tr>
<tr>
<td>CrCl₂ + Ca₃N₂ (bk)</td>
<td>CrN, Cr₃N(hex)</td>
<td>(CrN) 4.149</td>
<td>4.150</td>
</tr>
<tr>
<td>MoCl₅ + Mg₃N₂ (bk)</td>
<td>Mo</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>MoCl₅ + Mg₃N₂ (bk)</td>
<td>Mo</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>AlCl₃ + Ca₃N₂ (fil)</td>
<td>AlN(hex) [Al]</td>
<td>(a = 3.114, c = 4.984)</td>
<td>(a = 3.110, b = 4.975)</td>
</tr>
<tr>
<td>LaCl₃ + Mg₃N₂ (bk)</td>
<td>No reaction</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>LaCl₃ + Ca₃N₂ (bk)</td>
<td>No reaction</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

*All bulk reaction mixtures were brought to 550 °C and cooled down for trituration. Most of the bulk reactions initiated below 400 °C. Products from the reactions initiated with flame or filament were not annealed. [ ] – minor phases present, "sample poorly crystalline and the lattice parameter was not calculated, 'all nitride products cubic unless stated.
The lattice parameters calculated for the products from the metathesis reactions were correlated with the level of nitridation. Goldschmidt determined that the lattice parameter is sensitive to the degree of nitridation where a decrease in the amount of nitrogen in the product corresponds to a decrease in the $a$-parameter in cubic nitrides. These can be correlated with the Vegards Law and shows a linear relationship.

Reactions of Group 6-9 transition metal halides with alkaline or alkaline earth metal nitrides yielded only pure metal phases with nitrogen gas being released. This is due to the fact that the reaction temperatures generated are above the nitride decomposition point. The reactions of chromium halides were the only exception yielding mixed or single nitride phases and often chromium metal (Tables 2.1 and 2.2). Group 3-5 nitrides have much higher decomposition temperatures than group 6-9 nitrides. This has been referred to as the ‘Chromium enigma’.

(ii) Propagation reactions

Reactions initiated using a filament form solids of smaller particle size than those initiated using flame. Figure 2.2 shows the products obtained from the reaction of zirconium tetrachloride and lithium nitride in bulk and filament initiated processes. The zirconium nitride formed in the bulk reaction was more crystalline. The crystallite sizes of the solids prepared using propagation reactions, calculated using the Scherrer equation, were of the order of 50-600 Å.

2.3.2 SEM/EDXA analysis

SEM measurements of the ‘as prepared’ solids from all modes of initiation showed large agglomerates with smooth morphologies. Triturated samples were typified by having smaller size agglomerates with sharper angles and faces (figure 2.3). Some crystals within agglomerates were of significantly large dimension. An example of this is the reaction of transition metal halides with lithium nitride and sodium azide (ratio 3 : 1). Figure 2.4 shows large crystallites on the face of an agglomerate of the product from the reaction of titanium trichloride with lithium nitride and sodium azide. Transition metal nitrides
obtained from the reactions of transition metal halides with Group 1 and 2 nitrides or sodium azide showed narrow particle size distributions within the samples.

EDXA analysis of pretriturated products showed the presence of transition metal (or rare earth metal), Group 1 or 2 metal and halogen (nitrogen was below the threshold of the EDXA system used). However it was found that most of the surface of the particles was layered with the co-product salt. Triturated product analysis showed only metal present.

The morphology of products prepared at different reaction temperatures showed little variation across the whole transition metal block. The most visible distinction observed in the numerous products analysed was associated with the mode of initiation. Products prepared using a filament for initiation were less pure and had smaller aggregates than those isolated from bulk reactions. A non-uniform product particle size was frequent. Higher quality products were obtained from bulk reactions. An increase in the reaction scale assisted an improvement in product quality.

Figure 2.2  Triturated products from the reactions of zirconium tetrachloride with lithium nitride performed inside ampoule (a) or initiated with a filament (b). Bottom stick pattern is for rocksalt zirconium nitride, ZrN.
Figure 2.3  SEM micrographs of triturated products from the reactions of titanium trichloride with lithium nitride and sodium azide (a), vanadium trichloride with lithium nitride (b), titanium trichloride with lithium nitride (c), hafnium tetrachloride with lithium nitride and sodium azide (d), and surface of particle shown in (d), (e).
Figure 2.4  Crystallites on the face of an agglomerate of titanium nitride prepared by the bulk reaction of titanium trichloride with a lithium nitride/sodium azide mix (molar ratio 3 : 1 respectively).

On selected samples linescan measurements using an instrument with a thin-window detector were observed. This system allowed semi-quantification of nitrogen. Figure 2.5 shows the results obtained from linescan tests performed on hafnium nitride prepared in a bulk reaction of hafnium tetrachloride and lithium nitride under nitrogen pressure. Figure 2.5a shows the surface of the sample as seen in the EDXA system, monitored with a line, across which, the measurement was performed. Figure 2.5b shows plots of linescan lengths against the intensities for nitrogen and hafnium in arbitrary counts. The patterns obtained show clearly a match between hafnium and nitrogen indicating their relationship as part of one compound. The presence of oxygen has also been tested and the results showed that the sample surface is somewhat contaminated with oxygen. This is expected with this class of compounds since they readily form an oxide layer on their surface. Similar results have been obtained for the other transition metal nitrides analysed.

2.3.3 TEM analysis

This technique has not been used previously to analyse products prepared by SSM reactions. The main objective in these analyses was to study the microstructure of selected samples and cross-analyse the results with reference to
Figure 2.5  
Linescan test of hafnium nitride prepared by a bulk reaction of hafnium tetrachloride with lithium nitride under a nitrogen pressure, showing (a) the region scanned and plots of linescan length against the intensity for nitrogen (b) and hafnium (c) in arbitrary units.

the reaction conditions. Investigations using TEM have given more in depth knowledge about the product structure, crystallography and physical appearance. Useful information has also been obtained about grain sizes and distributions.

As is shown in Table 2.3 two samples of AlN (AlN(1), AlN(2)) have been prepared using lithium aluminium chloride, LiAlCl₄, and lithium nitride at 550 °C
followed by annealing for 36 hours. The samples were highly oxidised. One of
the samples, AlN(1), was prepared and annealed under a nitrogen pressure of ca.
1.5-2 atmospheres and the other, AlN(2), under vacuum. The structure of both
these samples could not be determined from the electron diffraction patterns
obtained from the TEM analysis due to the lack of individual diffraction spots.
This is due to the presence of randomly orientated polycrystalline grains (figure
2.6).

Table 2.3  
*Samples analysed using EELS/ELNES and TEM techniques.*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction/annealing temperature and time</th>
<th>Generalised TEM results</th>
</tr>
</thead>
<tbody>
<tr>
<td>ScN</td>
<td>ScCl₅ + Li₃N/550 °C</td>
<td></td>
</tr>
<tr>
<td>TiN(1)</td>
<td>TiCl₃ + Li₃N/550 °C</td>
<td></td>
</tr>
<tr>
<td>VN(1)</td>
<td>Commercial</td>
<td></td>
</tr>
<tr>
<td>VN(2)</td>
<td>VCl₃ + Li₃N/550 °C</td>
<td></td>
</tr>
<tr>
<td>VN(3)</td>
<td>Commercial</td>
<td></td>
</tr>
<tr>
<td>VN(4)</td>
<td>Commercial</td>
<td></td>
</tr>
<tr>
<td>CrN(1)</td>
<td>CrCl₂ + Mg₃N₂/350 °C (1hr),</td>
<td></td>
</tr>
<tr>
<td></td>
<td>500 °C (1.5 hr), 1.5 equiv. MgCl₂</td>
<td></td>
</tr>
<tr>
<td>Cr₂N</td>
<td>CrCl₃ + Li₃N/445 °C</td>
<td></td>
</tr>
<tr>
<td>TiVN</td>
<td>TiCl₄/VCl₄ + Li₃N/r.t.</td>
<td></td>
</tr>
<tr>
<td>AlN(1)</td>
<td>LiAlCl₄ + Li₃N/550 °C, 36 hrs</td>
<td>Structure not determined using electron diffraction patterns, randomly orientated polycrystalline grains present</td>
</tr>
<tr>
<td>AlN(2)</td>
<td>LiAlCl₄ + Li₃N/550 °C, 36 hrs, 2.5 atm N₂ pr.</td>
<td>Structure not determined using electron diffraction patterns, randomly orientated polycrystalline grains present</td>
</tr>
</tbody>
</table>
Figure 2.6 TEM analyses of triturated products (cubic AlN) obtained from the reactions of lithium aluminium tetrachloride, LiAlCl₄, with lithium nitride under vacuum, samples AlN(1) (dark field image) (a), (bright-field image) (b) and under a ~2 atmosphere nitrogen pressure, sample AlN(2) (c). Note the larger crystallites in the second sample.
The sample of AlN, which was annealed under nitrogen pressure, possessed larger grains, by an averaged factor of 3, than the sample annealed under vacuum. The difference in the nitrogen pressure used in the two reactions was only ~1.5–2 atmospheres. This demonstrates that changes in pressure can modify the particle size of the product. Microanalytical results outlined in the experimental section also suggest that introduction of nitrogen pressure into solid state metathetical preparations helps to produce more nitrogen rich samples. Further investigative experiments performed to control SSM product particle size and the level of nitridation are discussed in chapter 7.

2.3.4 ELNES/PEELS analysis

Recently electron energy loss spectroscopy (EELS) has been applied as a characterisation technique for determining lattice parameters and chemical compositions of conventionally prepared carbides and nitrides.\textsuperscript{164,165} Ionisation edges obtained from EELS possess electron energy loss near edge structure (ELNES) which is sensitive to deviations from stoichiometry, site symmetry, lattice parameter and elemental composition. Modifications in the crystal structure give rise to systematic changes in both the absolute and relative energies of features in the ELNES. The ELNES technique utilises the fine structure present on the ionisation edges of EELS spectra. It is related to XANES, which results from the interference caused by the backscattering of the ejected electrons from the surrounding atoms. The N K and metal L\textsubscript{2,3} edges were determined on a number of samples prepared by metathesis in this project. Separation of the peaks and their heights were the primary features of interest in these spectra. The samples tested and the methods of their preparation are outlined in \textbf{Table 2.3}.

\textbf{Figure 2.7} shows the N K edges of samples of CrN(1), VN(1) and TiN(1). Sample CrN(1) was prepared using chromium trichloride and magnesium nitride with magnesium chloride (ratio of 1.5 : 1, MgCl\textsubscript{2} : Mg\textsubscript{3}N\textsubscript{2}) used as a diluent. The reaction initiated at 350 °C and the products were annealed at 550 °C for 90 minutes. VN(1) was a commercial sample prepared by arc melting process. TiN(1) was prepared from the reaction of titanium trichloride with lithium nitride, which initiated at ~300 °C. The temperature was raised to 550 °C and then the products were taken out and triturated. The first two samples have similar peak
separations while TiN has a more compact spectrum. This is consistent with the larger lattice parameter of TiN than of the former two species. This study demonstrates that decrease in lattice parameter is assisted by a proportional increase in peak separations on the N K edge. This phenomenon has been studied in more detail previously.\textsuperscript{164}

![Graph showing energy loss/eV vs. arbitrary intensity for CrN, VN, and TiN](image)

**Figure 2.7**  \textit{N K edges for nitrides of chromium (CrN(1)), titanium (TiN(1)) and vanadium (VN(1)).}

Apart from the effect of substitution of the metal nitrides the second primary feature in the ELNES studies was to investigate its changes with stoichiometries of the nitrides. Since the lattice parameter increases with the increase of nitridation then the peak separations should decrease. Samples VN(1), VN(2), VN(3) and VN(4) were investigated (figure 2.8, Table 2.3). Samples VN(1), VN(3) and VN(4) were commercial materials produced by arc melting process. Sample VN(2) was prepared using vanadium trichloride and lithium nitride with annealing at 550 °C for 1-2 hours. The results show that there is only a small change in peak separation, which is consistent with a small difference in the lattice parameters. The main changes are in the peak heights. Increasing the nitrogen content of VN\textsubscript{x} increases the height of P4 relative to P1 and makes P5 more distinct.
Figure 2.8  

*N K edges of vanadium nitride samples, VN(1-4), with peaks assigned at the top.*

A number of other nitride samples formed in this project have also been analysed using the ELNES technique. These include nitrides of titanium with varied stoichiometry, TiVN, ScN and Cr$_2$N (figure 2.9). Many have been compared with corresponding commercially prepared samples. Detailed studies of chromium nitrides have been performed and are discussed in section 2.3.5. This technique has also been used in this project to test samples for oxygen content.

2.3.5 ELNES of CrN and Cr$_2$N

This project has shown that via manipulation of reagents and reaction conditions it is possible to obtain various phases of chromium nitride. The reactions of chromium halides with lithium nitride or magnesium nitride under specific conditions are outlined in Table 2.3. The combination of magnesium nitride and chromium dichloride in the presence of magnesium chloride yielded cubic chromium nitride, CrN, and the combination of lithium nitride with chromium trichloride yielded hexagonal chromium subnitride, Cr$_2$N. These two samples have been further analysed using EELS and ELNES and compared with commercial samples as standards.
Figure 2.9 shows the spectra of commercial and SSM prepared Cr$_2$N samples. The N K edges and Cr L$_{2,3}$ edges are similar which is consistent with the same hexagonal structures determined for both samples using XRD. The mean compositions of the samples were determined from integration of the counts under the edges applying the relevant cross-section corrections. Both samples contained some oxygen (about 10 atom. % of nitrogen content) with the nitrogen to metal stoichiometries of Cr$_2$N$_{1.12}$ for the SSM prepared sample and Cr$_2$N$_{0.96}$ for the commercial sample. This high level of nitridation in the SSM prepared sample (~14 % more than in the commercial sample) was unexpected. The commercial sample also contained an oxide layer on the surface of the grains with the nitride present within them.

The N K edges of commercially prepared and SSM prepared cubic chromium nitrides resembled each other showing agreement in structure and lattice parameter. The level of oxidation in cubic SSM chromium nitride was significantly lower (only 5 atom. % of the nitrogen content). EELS spectra obtained from both samples matched closely with the compositions at CrN$_{0.90}$ for the SSM sample and CrN$_{0.94}$ for the commercial sample, not taking into account some small oxygen contamination present. Frisk et al. has reported that the equilibrium composition range for cubic chromium nitride is CrN$_{0.95-1.0}$. Therefore these samples show a good fit when the oxidation is taken into account.

Figure 2.9 N K edges and Cr L$_{2,3}$ edges for commercial and SSM prepared CrN (a) and Cr$_2$N (b) samples.
There are more distinct disparities between the two samples in their Cr L\textsubscript{2,3} edges. The main two peaks are a little higher in the spectrum of the commercial sample and show more detail after the so-called white lines. The depth of study performed and presented in this work does not allow elucidation of such dissimilarities but the most probable causes are the differences in the level of oxygen contamination and variation of the chromium environment.

2.4 DISCUSSION

Solid state metathesis reactions of anhydrous transition metal halides with alkali or alkaline earth metal nitrides initiate at temperatures, which are related to a phase change of one of the materials (melting or decomposition point). These reactions were performed inside of sealed evacuated ampoules. Often the reactions were accompanied by a thermal flash and produced grey/black solids, which are spread over the ampoule walls. Notably some co-produced salt condenses onto the cooler parts of the ampoule. Two examples where the initiation temperatures are directly correlated with phase changes of the reagents used are shown in equations 2.6-2.7.

Products obtained from the reactions of transition metal halides with Group 1 and 2 nitrides and sodium azide were analysed using various analytical techniques. One of the most important aspects in preparation of inorganic materials is the product particle size. SEM measurements showed that transition metal nitrides prepared using solid state metathetical pathways have, for the specific samples, narrow particle size distributions. Even more importantly, the products showed large differences in agglomerate sizes, which were directly related to the nitriding reagents.

\[
\begin{align*}
\text{TaCl}_5 + 5/3\text{Li}_3\text{N} & \rightarrow \text{TaN} + 5\text{LiCl}, \\
T_m & = 200-240 \degree\text{C} \\
\text{ScCl}_3 + \text{Li}_3\text{N} & \rightarrow \text{ScN} + 3\text{LiCl} \\
T_m & = 550 \degree\text{C}
\end{align*}
\]

m. pt. TaCl\textsubscript{5} 210 \degree C\textsuperscript{20}, dec. pt. Li\textsubscript{3}N 548 \degree C\textsuperscript{20,21}, m. pt. ScCl\textsubscript{3} = 939 \degree C\textsuperscript{21}
Analyses of products obtained from solid state metathetical reactions of transition metal halides with Group 1 and 2 nitrides or sodium azide show that highly pure phases of nitrides are obtained. All the reactions were performed on a very small scale (up to 0.01 moles of nitriding agents). The yields obtained in these reactions were essentially 90 %, or higher with respect to the amount of transition metal initially used. Mechanical handling constitutes the main reduction in yield.

Crude products, from the reactions discussed in this chapter, when analysed using XRD and EDXA have shown that the starting reagents are absent from the final mixtures. Since nitrogen was below the threshold of the EDXA system used (in most of the studies) it was difficult to assess this completely. One of the key points in analysing these reactions was to find out what gases escape from the reaction mixture, especially in those preparations, which were initiated with flame or filament in an open environment where the gases are free to escape from the reaction mixture. Tests have been performed to trap some of these gases by placing a glass plate over the initiated reaction mixture. Some of the metal halides were sublimed onto its surface and analysed by XRD. The results of repeated tests for a number of reactions have shown that some of the most volatile transition metal halides such as tantalum pentachloride or zirconium tetrachloride also escape in small proportions from the reaction mixture when reacted with lithium nitride or calcium nitride. This suggests that there is some excess nitride reagent available in the mixture, which has no halide to react with. No unreacted Group 1 or 2 nitrides were ever observed in the final products. This can be explained by the low thermal stability of these reagents, which are decomposed by the high temperatures reached in these reactions.

Some of the products formed by the reactions of transition metal halides and Group 1 and 2 nitrides were annealed at different temperatures for similar time periods. The results have shown that transition metal nitrides obtained in this way can be annealed at temperatures of 450-550 °C to induce greater crystallinity. Transition metal nitrides prepared using the syntheses discussed in this chapter undergo a slow colour change with an accompanying increase in crystallinity on annealing. Nitrides of vanadium and titanium turned brown (from black) while tantalum nitride turned from grey/black to grey.
Preparations of transition metal nitrides of Group 6-8 have proved to be challenging. These nitrides are thermally unstable and decompose during these highly exothermic metathesis reactions. When chromium trichloride is reacted with lithium nitride a subnitride, Cr$_2$N, forms as a result of partial decomposition of chromium nitride, CrN. Most other reactions between chromium chlorides and Group 1 and 2 nitrides lead to formation of impure phases of nitrides with some chromium metal. The reactions of other Group 6-8 transition metal halides with Group 1 and 2 nitrides lead to the formation of pure metal phases with all the nitrogen being released from the reaction mixture. The bulk reaction of molybdenum trichloride with lithium nitride has produced molybdenum with a very minor phase of molybdenum subnitride (Mo$_2$N). To overcome these problems in the solid state metathetical syntheses of these nitrides Group 1 and 2 salts such as magnesium chloride or lithium chloride were ground into the reagents mixtures to act as an inert heat sink, partly absorbing the energy released in the reactions. The effects of utilising lithium chloride and magnesium chloride were thoroughly investigated for these syntheses and are discussed in chapter 7. The most outstanding fact is that using magnesium chloride as an inert heat sink in these reactions enabled solid state metathetical syntheses of transition metal nitrides of Groups 6-8 to be successful. The following nitride phases have been isolated using this method:

\[ \text{CrN, Mo}_2\text{N, W}_2\text{N, Mn}_3\text{N}_2, \text{Mn}_4\text{N, Fe}_3\text{N(Fe}_2\text{N), Co}_2\text{N}_{0.67} \]

This has not been possible before.

The main drawback in the syntheses of transition metal nitrides using transition metal halides and Group 1 or 2 nitrides or sodium azide is the difficulty in containing the nitrogen gas released during the reactions. Using sealed evacuated vessels is one option but when performed on a large scale the best way to overcome the problem is to perform such reactions in an opened space. Experiments were performed in this project where some nitrogen containing species such as sodium azide was decomposed inside an evacuated ampoule at 500 °C together with the reagents required to synthesise a transition metal nitride using a solid state metathetical route. Therefore the reaction was performed with the following steps and initiated under an effective nitrogen pressure, which was
calculated at 2.0-2.5 atmospheres. The products formed in these syntheses were always characterised by larger particle sizes (of the order of 3 to 5 times).

2.4.1 Level of nitridation in transition metal nitrides prepared by SSM

Transition metal nitrides are interstitial in nature. They are characterised by a range of stoichiometries that are accessible without the need for structural rearrangement, for example, cubic TiN$_x$ is stable for $x = 0.38-1.2$. The work presented in this section discusses the possibilities of forming transition metal nitrides of various stoichiometries using solid state metathetical reactions.

The reactions of Group 4 and 5 transition metal halides with nitrides of Group 1 and 2 or sodium azide yield substoichiometric transition metal mononitrides, (MNN$_x$). This is despite the fact that the reagents used provide sufficient or even an excess of nitrogen over that required to produce stoichiometric mononitrides, MN. Solid state metathetical reactions in which nitrogen precursors are used can undergo three pathways. The first of these results in the formation of pure transition metal nitride, the second results in the formation of transition metal and dinitrogen and the third will result in partial decomposition of the nitride produced forming substoichiometric phases such as V$_2$N or Ta$_2$N. In practice, it is very common to observe the occurrence of a combination of these processes. The outcome of a particular reaction process is dependent on the relative thermal stability of the desired transition metal nitride product and the reaction enthalpy. Equations 2.8-2.10 represent three possible routes, which could occur in solid state reactions of vanadium trichloride with lithium nitride.

\[
\begin{align*}
\text{VCl}_3 + \text{Li}_3\text{N} & \rightarrow \text{VN} + 3\text{LiCl} \quad \text{eqn. 2.8} \\
2\text{VCl}_3 + 2\text{Li}_3\text{N} & \rightarrow \text{V}_2\text{N} + \frac{1}{2}\text{N}_2 + 6\text{LiCl} \quad \text{eqn. 2.9} \\
\text{VCl}_3 + \text{Li}_3\text{N} & \rightarrow \text{V} + \text{N}_2 + 3\text{LiCl} \quad \text{eqn. 2.10}
\end{align*}
\]

It is difficult to predict how much nitrogen is going to be lost as dinitrogen gas in a particular reaction. This is affected both by the thermal stability of the nitrides
used and to some extent the scale of the reaction. Reactions performed on a larger scale are more adiabatic.

Solid state metathetical reactions of the trichlorides of vanadium, scandium and titanium with various nitriding reagents yielded nitrides with varying stoichiometries. These are all outlined in Table 2.4. It can be observed that sodium azide is the most efficient nitriding reagent. This is probably because it provides a lot of excess nitrogen most of which escapes as dinitrogen gas thus providing a nitrogen gas overpressure and helping to prevent decomposition of the nitride product during the reaction. Using a mixture of sodium azide and lithium nitride as the joint nitrogen precursor mixture in the reactions with transition metal halides (TiCl₃, ZrCl₄, HfCl₄, TaCl₅) has yielded transition metal nitrides, which had the best overall properties considering both the crystallinity and the level of nitridation (figure 2.10). It is also worth noting that in the formations of the mononitrides of vanadium, niobium and tantalum using lithium nitride as the nitrogen precursor minor amounts of an M₂N phase were also formed. Using a mixture of lithium nitride and magnesium nitride as the nitriding reagents (molar ratio 1 : 1) with the tantalum halides yielded even larger quantity of this substoichiometric phase.

2.4.2 Decomposition of transition metal nitrides prepared using SSM routes

All transition metal nitrides undergo decomposition via nitrogen loss or oxidation. This becomes a major problem at elevated temperatures in the presence of moist air. Analyses of the solids prepared using solid state metathesis, discussed in this work, have shown evidence that many of them gain significant amount of oxygen on storage. All the solids prepared using these routes contain small particles. Therefore a large surface area is in contact with air. To investigate this a number of metal nitrides have been analysed using various techniques. Two points of interest are focused upon and discussed in this section, the first being the oxidation of metal nitrides and the second, nitrogen loss in aluminium nitride and yttrium nitride.
Figure 2.10  [200] reflections for tritiated products from the reaction of titanium trichloride with various nitriding reagents: lithium nitride and sodium azide inside ampoule (molar ratio 3 : 1) (a), lithium nitride inside ampoule (b), lithium nitride initiated with a filament (c), sodium azide inside ampoule (d), magnesium nitride inside ampoule (e).

(i) **Oxidation of metal nitrides prepared using SSM routes**

The oxidative stability of a number of SSM prepared metal nitrides has been investigated. These are all outlined in Table 2.4. All these products are labelled and referred to in this discussion as shown in the middle column. The right-hand-side column shows what conditions the products were subjected to and the length of the reaction. Normally the products were subjected to air at room temperature for a long time (weeks or months). The problem with this method is that the moisture content in air is variable throughout the time and so is the temperature. However considering the timelength and the ease with which these studies can be performed these investigations have been investigated and very interesting results have been obtained.

Scandium nitride prepared using the trichloride and lithium nitride analysed three times over a period of over three years showed systematic decomposition which appears to slow down with time. This result is explainable since oxidation is a surface phenomenon and a protective oxide crust overlays the
nitride product. Similar results have been obtained for a sample of yttrium nitride. However it decomposed completely within 8 hours. In figure 2.11 only one of the sample diffraction peaks has been repeatedly studied every 10 minutes. The results showed a similar trend. The diffraction peak lost its intensity indicating a loss of crystallinity with the decomposition as well as a slowing rate of decomposition, as can be observed from the decreasing shift of the peak throughout the time of analysis. Lanthanum nitride has also been studied in a similar way. However due to the much more rapid decomposition of this compound no new conclusions have been obtained from this analysis.

A sample of vanadium nitride prepared using a bulk reaction of vanadium trichloride with lithium nitride has been used to study its resistance to decomposition in water. The sample was divided into 2 parts, which were immersed in water for 5 hours, one at the temperature of 40-50 °C and the other at room temperature (Table 2.4). The results have showed that the nitride decomposes quite readily in any moist conditions regardless of the temperature.

![Figure 2.11](image)

**Figure 2.11** Changes in YN [111] reflection recorded at 10-minute intervals of storage in air.
Table 2.4  
Conditions used to test oxidative stability of a selection of transition metal nitrides prepared using solid state metathesis discussed in this chapter.

<table>
<thead>
<tr>
<th>Sample/reagent</th>
<th>Label</th>
<th>Conditions applied before analyses by XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>ScN/ScCl3, Li3N</td>
<td>ScN</td>
<td>Analysed immediately after trituration</td>
</tr>
<tr>
<td></td>
<td>ScN'</td>
<td>Kept at room temperature in air for 6 months before analysis</td>
</tr>
<tr>
<td></td>
<td>ScN''</td>
<td>Kept at room temperature in air for 38 months before analysis</td>
</tr>
<tr>
<td>VN/VCl3, Li3N</td>
<td>VN</td>
<td>Analysed immediately after trituration</td>
</tr>
<tr>
<td></td>
<td>VN'</td>
<td>Kept in water for 12 hours before analysis</td>
</tr>
<tr>
<td></td>
<td>VN''</td>
<td>Kept for 12 hours in warm water (ca. 40-50 °C)</td>
</tr>
<tr>
<td>YN/YCl3, Li3N</td>
<td>YN(1)</td>
<td>Treated to vacuum conditions (electric pump) for 5 minutes before analysis</td>
</tr>
</tbody>
</table>

Both samples showed great loss in crystallinity after the treatment (due to the probable formation of amorphous oxides). The sample, which was kept in warm water, VN'', became amorphous, showing only minor vanadium nitride diffraction peaks by powder XRD. However the comparable extent of oxidation in the two samples treated under varied conditions could not be judged.

(ii)  Nitrogen loss in nitrides of yttrium and aluminium

A sample of yttrium nitride prepared using calcium nitride and the trichloride has been tested for nitrogen loss when exposed to vacuum conditions for several minutes. During evacuation time the sample changed colour from brown to navy green and its a-parameter shifted from 4.897 Å to 4.886 Å. The lattice parameter is sensitive to the level of nitridation. Therefore it would be useful to associate these results with the change in nitridation. To our knowledge no compositional ranges have been reported and correlated to the lattice parameter for yttrium nitride.

The reactions of aluminium trichloride with lithium nitride inside evacuated ampoules proceed very slowly through a melting process after which hexagonal wurtzite aluminium nitride and lithium chloride form as white solids.
These solids were then annealed for 12-15 hours to induce crystallinity. However in most cases at the end of annealing some grey aluminium metal was also observed (confirmed after XRD analysis (figure 2.12a)). Studies involving repeated synthesis of this product, each time using longer annealing periods, yield increasing aluminium metal content in the product. This suggests that the Al metal impurity might be formed during the annealing. When the same reaction was performed under a nitrogen pressure of ca. 2 atm. a pure phase of aluminium nitride was obtained after trituration with dried and degassed methanol (figure 2.12b). Details of this procedure are outlined in the experimental section 2.7.5. To investigate the tendency for aluminium nitride to lose nitrogen during annealing, three procedures have been performed. The first involved annealing of triturated and crystalline aluminium nitride product both under nitrogen pressure (ca. 2 atm.) and under vacuum inside an ampoule at 550 °C for 2 days. The second procedure involved annealing the same aluminium nitride under vacuum for 5 days at 550 °C and the third at 550 °C for 10 days. All these combinations have been performed simultaneously using the same size ampoules and the same mass of sample to insure similar physical conditions. After annealing the solids were analysed by combustion. All the results are represented in Table 2.5. These show that aluminium nitride looses all its nitrogen eventually to form aluminium metal and dinitrogen gas (figure 2.12c). Similar results were obtained when a commercial sample was treated under similar conditions.

Table 2.5  
Microanalytical data obtained for the samples of aluminium nitride annealed for different periods at 550 °C.

<table>
<thead>
<tr>
<th>Annealing timelength</th>
<th>Nitrogen composition/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>No annealing*</td>
<td>22.42</td>
</tr>
<tr>
<td>2 days</td>
<td></td>
</tr>
<tr>
<td>Under vacuum</td>
<td>8.73</td>
</tr>
<tr>
<td>Under nitrogen pressure (~2 atm)</td>
<td>17.80</td>
</tr>
<tr>
<td>5 days (vacuum)</td>
<td>4.51</td>
</tr>
<tr>
<td>10 days (vacuum)</td>
<td>0.97</td>
</tr>
</tbody>
</table>

*this excludes the annealing required to obtain the aluminium nitride product
Figure 2.12  *XRD patterns for triturated products from the reactions of aluminium trichloride with lithium nitride: (a) under vacuum annealed for 12-15 hours at 550 °C (c) under nitrogen pressure (~2 atm.) annealed for 12-15 hours at 550 °C (e) under vacuum and annealed for 10 days at 550 °C. Stick patterns are for hexagonal aluminium nitride and aluminium (b), hexagonal aluminium nitride (d) and aluminium (f).*
2.4.3 Formation of solid solutions

So far only synthesis of binary metal nitrides has been discussed in this chapter. There is an increasing interest in the synthetic application of more complicated materials such as bimetallic carbides and nitrides or transition metal carbonitrides. As an extension to this work, syntheses of such ternary homogeneous materials were investigated. This section will only discuss the work regarding bimetallic transition metal nitrides. The syntheses of transition metal carbonitrides and bimetallic transition metal carbides are discussed in chapter 3.

All the preparations of ternary solutions were attempted using three reagents each time (for example in order to prepare (Ti,V)N, TiCl₃, VCl₃ and Li₃N were used). After the reactions were complete the resultant solids were usually annealed at 550 °C. The resultant solids were triturated similarly to those of the binary transition metal nitrides. The most important aim of the analyses of these products was the assessment of homogeneity. This was performed using XRD and EDXA techniques, and for some selected examples, using PEELS.

Solid state metathetical reactions where two metal halides were reacted with a nitriding agent did not yield the desired homogeneous bimetallic transition metal nitrides. Inhomogeneous mixtures with varying compositions were obtained. The best results were obtained when the two transition metal halides used had similar melting points such as the pentachlorides of niobium and tantalum. In some other cases such as the reaction of a mixture of zirconium and vanadium chlorides (ZrCl₄ and VCl₃) with lithium nitride a mixture of separate phases of binary transition metal nitrides was obtained (figure 2.13).

Figure 2.14 shows TEM micrographs obtained from analysis performed on a ternary transition metal nitride (TiVN) formed using liquid tetrachlorides of titanium and vanadium reacting with lithium nitride. The electron diffraction experiments revealed grains of single crystal and polycrystalline patterns. The cubic structure of the crystals can be clearly observed in figures 2.14c-2.14e. Figure 2.14d shows a single crystal where the spots overly the rings in 0008/9. However the specific zone axis could not be assigned. In figure 2.14f also a single crystal has been observed with the spots overlying the rings in 0008/9 with the zone axis of [001]. Two TEM analyses have been used to obtain the a-
Figure 2.13 XRD pattern of triturated product from the reaction of zirconium tetrachloride/vanadium trichloride (1:1 molar mixture) with lithium nitride. The separation of binary phases of the two metal nitrides is clearly visible. Bottom stick patterns are for cubic zirconium nitride and vanadium nitride (dashed lines). Unidentified peaks represent substoichiometric phases.

The reactions of the liquid tetrachloride of titanium and vanadium with lithium nitride have been studied by Parkin et al. The two metal halides are miscible and have similar boiling points. After they are mixed together inside a Schlenk tube under a flow of nitrogen, lithium nitride is added to the mixture and the reaction initiates on contact of these reagents. Sometimes if the reaction does not initiate the mixture must be gently warmed up. X-ray powder diffraction patterns obtained for the products from these reactions suggest an intimate solid solution present. However the analyses performed using PEELS/ELNES showed that the solids were composed of several compositions the most abundant of which was within close stoichiometric proximity to the desired ratio of the transition metals. Some other bimetallic nitrides have also been formed using solid transition metal halides and lithium nitride as the reagents. The transition metal halides applied in these reactions were: tantalum pentachloride and niobium pentachloride, zirconium tetrachloride and niobium pentachloride.

Parameter of 4.22 Å and 4.23 Å (TiN\textsubscript{0.45-1.0} = 4.221-4.244 Å, VN\textsubscript{0.72-1.0} = 4.066-4.139 Å)\textsuperscript{152}, which is within the range of both binary transition metal nitrides.
Figure 2.14  TEM micrographs and electron diffraction patterns of TiVN sample prepared by reacting liquid tetrachlorides of titanium and vanadium with lithium nitride showing (a) polycrystalline and (c, e) single electron diffraction crystal patterns. For (e) the spots overly the rings in 0008/9 with zone axis of [001]. The crystals are shown accordingly (b, d, f).
2.5 THERMODYNAMIC CONSIDERATIONS

Transition metal halides react with a range of nitride precursors. The rate of reaction is determined by the nature of the nitriding reagent. This is due to large changes in the heats of reaction, dependent on the exact transition metal halide and nitride precursor used. Calculations obtained using Hess’s Law, assuming that the desired nitride is formed, show that there is a general trend throughout the transition metal block with the right hand side and heavier elements having greater potential exothermicity than those towards the top left (equations 2.11-2.13).

The most influential factors in the thermodynamics of these reactions are the oxidation state of the transition metal halide, the type of halide and the nitride precursors used. The co-formation of salt is the driving force in these reactions and can account for up to 90% of the SSM reaction enthalpy.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equations 2.11-2.13</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{TiCl}_3 + \text{Li}_3\text{N} \rightarrow \text{TiN} + 3\text{LiCl}$</td>
<td>$\Delta H_{298} = -676.8 \text{ kJ mole}^{-1}$</td>
</tr>
<tr>
<td>$\text{VCl}_3 + \text{Li}_3\text{N} \rightarrow \text{VN} + 3\text{LiCl}$</td>
<td>$\Delta H_{298} = -697.2 \text{ kJ mole}^{-1}$</td>
</tr>
<tr>
<td>$\text{MoCl}_3 + \text{Li}_3\text{N} \rightarrow \text{MoN}^* + 3\text{LiCl}$</td>
<td>$\Delta H_{298} = -741.6 \text{ kJ mole}^{-1}$</td>
</tr>
</tbody>
</table>

*For equation 2.13 the nitride produced decomposes to metal and dinitrogen during the reaction.

Equations 2.14-2.16 show changes in reaction enthalpies when using selected vanadium halides for reactions with lithium nitride.
Heats of reactions with different nitriding reagents, show a trend in exothermicity for the reaction with MClₙ in the order as shown below:

\[
\text{NaN}_3 > \text{Li}_3\text{N} > \text{Ca}_3\text{N}_2 > \text{Mg}_3\text{N}_2
\]

The reactions of rare earth halides with nitride precursors were also performed in this project. These combinations showed a marked decrease in reactivity. None of the halides used initiated with a filament. These reactions were studied more widely in our laboratory previously by A.L. Hector and I.P. Parkin et al. Reactions of lanthanide halides with calcium or magnesium nitrides required heating for several hours between 500 °C and 900 °C depending on the reagents used.

Many SSM reactions are propagative. Occurrence of a propagation wave in SSM processes is related to the maximum reaction temperature and the melting point of the co-product salt. The maximum adiabatic reaction temperature, \( T_{ad} \), can be found by correlating the reaction enthalpy and the heat capacities of the reagents and products. The sum and the integration of the heat capacities of the products is equal to the heat of reaction as shown in Formula 2.2. The assumption is that no energy is lost to the surroundings (an adiabatic process).

\[
\Delta H_r^o = \int_{T_{ma}}^{T_{ad}} \{ C_p(productX) + C_p(productY) \} \, dT
\]  

\text{Formula 2.2}
If the maximum adiabatic reaction temperature is above the melting or boiling points of any products then their heat of fusion and evaporation must be taken into account.

In the preparations of transition metal nitrides of Group 3–6 there is a marked trend in reactivity when the reactions are initiated with a filament. Group 3 trichlorides do not initiate at all (with Li₃N) while titanium trichloride reacts much slower than the trichlorides of vanadium and chromium.

An interesting point here is the reaction of scandium trichloride with lithium nitride. This reaction is thermodynamically at the crossover point for propagation and yet it does not propagate. The explanation to this is that some of the heat produced by the reaction is lost to the surroundings. Previous studies of SSM processes performed in our laboratory included thermocouple measurements to estimate the reaction temperatures and timescales. A thermocouple of composition Pt/13% Rh in Pt/Pt was placed inside reaction mixtures and the millivolts were measured and converted to degrees Celsius. The temperatures determined using this method were much lower than the theoretically calculated values. The products cooled back to ambient temperature within 5–10 seconds.

2.6 SUMMARY

Solid state metathesis routes to form binary metal nitrides via the combination of metal halides with various nitrides and azides of Group 1 and 2. This has been supported using various analytical techniques. The wide choice of reagents available provides room for experimental manipulation to modify the reaction conditions and in some cases control the reaction rates although the latter is more challenging.

Studies of the as prepared solids showed evidence of an elemental metathesis exchange reaction and the by-product formed was conveniently removed using cheap and readily available organic solvents such as methanol, THF or even distilled water.

Analysis performed using EELS showed little oxygen contamination in a number of selected samples. ELNES results performed on many samples prepared using SSM processes gave very useful information regarding the technique itself as well as on the nature of the samples. These are summarised below:
• Substitutions of the metal sub-lattice have a pronounced effect on the metal edge.
• Substitutions on the metal sublattice have small effects but the height of P1 reduces as the number of electrons increases.

2.7 EXPERIMENTAL

All reagent manipulations and weighings were carried out under an inert atmosphere in a Saffron Scientific nitrogen filled glove box. Standard Schlenk line techniques were applied (N₂, Ar). All reagents were used as supplied by Aldrich Chemical Co. and were a minimum of 99.9 % pure. Ampoules were made from Pyrex glass (mostly 1.2 cm diameter, 30 cm long, when NaN₃ was used: 1.35 cm diameter, 40 cm long) and were annealed before use and thoroughly flame dried under vacuum. In reactions where sodium azide was used no more than 0.05 g, 0.8 mmol of this reagent was used and reaction equations were salt balanced. All ampoules were sealed under vacuum.

Solvents were dried, distilled and degassed prior to their application.

X-ray powder diffraction patterns were determined on a Siemens D 5000 transmission powder diffractometer using germanium monochromated Cu-Kα₁ radiation (λ = 1.5406 Å). For indexing patterns TREOR and METRIC-LS programmes were used. SEM/EDXA was determined using a JEOL JSMM 820 microscope, with a Kevex Quantum Detector Delta 4, and a Hitachi SEM S-570. Nicolet 205 spectrometer was used to record IR spectra, using pressed KBr discs. Microanalyses were provided by the UCL departmental service. Microanalyses were determined by the departmental service. These were performed by vapourisation of an accurately weighed sample with some tin powder added for combustion aid, under an oxygen flow. GC was then used to analyse the nitrogen oxides, water and carbon dioxide formed.

TEM and electron diffraction investigations were performed on a JEOL 1200 EX or a JEOL 2000 FX microscope. The EELS spectra were recorded using GATAN 666 PEELS spectrometer on a VG Microscopes HB5 scanning transmission electron microscope operated at 100 keV or a Philips CM20 transmission electron microscope with a field emission gun operated at 200 keV.
For EELS and TEM analysis the samples were crushed in propan-2-ol, using a pestle and mortar. The crushed sample was spread onto a holey carbon film on a Cu grid.

*Ampoule reactions of Li₃N, Mg₃N₂ and Ca₃N₂ with anhydrous transition metal chlorides, MClₙ (n = 2, M = Cr; n = 3, M = Sc, Ti, V, Cr; n = 4, M = Zr, Hf, W; n = 5, M = Nb, Ta, Mo).*

Tantalum pentachloride, TaCl₅ (0.18 g, 0.5 mmol) and lithium nitride, 5/3Li₃N (0.03 g, 0.833 mmol), were ground together and sealed *in vacuo* in a large Pyrex ampoule (reactions carried out above 550 °C required quartz ampoules). The ampoule was placed into a tube furnace and the temperature ramped at 25 °C per minute from room temperature to 550 °C. In most cases for Li₃N and Ca₃N₂ and some of Mg₃N₂ a thermal flash reaction initiated within the 200-400 °C temperature range (for ScCl₃ and YCl₃ it occurred at 550 °C). The material spread over the wall inside the ampoule. The mixture was allowed to cool to ambient temperature and the ampoule was broken open. The material was washed with methanol (Group 3 nitride products were triturated with THF) and dried *in vacuo*. The residual black material was analysed using powder XRD, SEM/EDXA and FT-IR. Combustion analysis of the product from the reaction of chromium trichloride with lithium nitride (Cr₂N) revealed N = 8.8 wt.%, Cr₂N₀.₇₂ = 8.8 wt.%. Chemical yields were in the range of 60-80 %, the losses attributed to mechanical sources and incomplete reactions.

*Filament initiated reactions of Li₃N, Mg₃N₂ and Ca₃N₂ with anhydrous metal chlorides, MClₙ (n = 3, M = Ti, V, Mo; n = 4, M = Zr, Hf, W; n = 5, M = Nb, Ta, Mo; n = 6, M = W)*

These were carried out in same molar amounts as those performed inside ampoules. All mixtures were prepared and reacted, using a hot filament, in an agate pestle and mortar under a nitrogen atmosphere inside of a glove box. All reacted mixtures were then treated in the same way as those that were initiated inside a furnace.
Reactions of $NaN_3$ with anhydrous metal chlorides, $MCl_n$ (all as listed in previous procedure), inside ampoules

Sodium azide reaction mixtures were made up on a scale of 50 mg sodium azide with a 1:1 ratio of sodium to halogen in the anhydrous metal halide used. The reagents were ground together and sealed under vacuum in a large Pyrex ampoule. The ampoule was placed into a closed furnace (or a tube furnace with protective shields at the openings) inside a fume cupboard. The temperature was ramped at 25 °C per minute from ambient temperature until a thermal flash reaction was observed at 380 °C. The reaction released a lot of excess $N_2$ and the material was spread over the ampoule walls. The material was annealed at 550 °C for 2-5 hours. When the ampoule was cooled to room temperature it was broken open and the material was washed with methanol (5 x 6 ml) and dried in vacuo. The residual materials were analysed by powder XRD, SEM/EDXA and FT-IR.

Reactions of $Li_3N$, $NaN_3$, $Ca_3N_2$ and $Mg_3N_2$ with halides of aluminium (Cl, Br and I)

Aluminium trichloride, $AlCl_3$ (0.27 g, 2.0 mmol), and lithium nitride, $Li_3N$ (0.07 g, 2.0 mmol), were ground together and placed in a Pyrex ampoule, which was sealed under vacuum. The ampoule was placed in a furnace at room temperature, which was then raised to 500 °C. The reagents slowly reacted at varied temperatures and the product was annealed for 24–48 hours. The ampoule was then broken open and the product was washed with THF (2 x 5 ml), methanol (3 x 6 ml) and then THF (1 x 5 ml) again. It was dried under passing nitrogen and analysed using XRD, SEM/EDXA, FT-IR. Selected samples were also analysed using TEM, PEELS and ELNES. Combustion analysis of the product from the reaction of $AlCl_3$ with $Li_3N$, 17 hrs annealing at 500 °C, revealed $N = 18.7$ wt. %. $AlN$ requires $N = 34.17$ wt. %.
Reactions of anhydrous aluminium halides with \( \text{Li}_3\text{N} \) and \( \text{Ca}_3\text{N}_2 \) inside ampoules under raised nitrogen pressure

Anhydrous aluminium trichloride, (0.27 g, 2.0 mmol), and lithium nitride (ratio of Li to halogen 1:1) were ground together and placed in an ampoule consisting of 3 parts (chambers) connected by thin necks (as drawn below) (Diagram 2.1). This ampoule has to be at least 35 cm long, with walls 1.5-2 mm thick. The reagents were placed in chamber A and sodium azide was placed in chamber C (0.03 g, 0.45 mmol). Mixing of sodium azide with the reactants must be avoided. It was then sealed under vacuum and inside a fume cupboard chamber C was heated to 400 °C in a tube furnace to decompose sodium azide (dec. 365 °C\textsuperscript{169}). Care must be taken not to initiate the reaction of lithium nitride with aluminium halide in chamber A, which should be outside the furnace at that point. Then the ampoule and the furnace were cooled to room temperature. Chamber A was placed in the furnace and heated to 400 °C. The off-white solid formed was then annealed for 24 hours after which the temperature was raised to 550 °C and the product was annealed for a further 24 hours. The solid was treated with THF (2 x 6 ml), methanol (2 x 6 ml) and again with THF (1 x 6 ml). After drying under nitrogen flow the solid was analysed using XRD, FT-IR, SEM/EDXA, EELS, TEM and elemental microanalysis. (Microanalysis for product from the reaction of aluminium chloride with lithium nitride: N, 22.42; H, 0.18; C, 1.07 %. \( \text{AlN} \) requires N = 34.17 wt %.)

Diagram 2.1 3 chamber ampoule used in the reactions, where the nitrogen overpressure was used.
CHAPTER 3

PREPARATIONS OF TRANSITION METAL CARBIDES

3.1 INTRODUCTION

This chapter concerns the solid state metathetical preparations of transition metal carbides from saltlike carbides (e.g. CaC₂ or Al₄C₃) and transition metal halides. A number of carbon precursors are useful for this type of synthesis. Figure 1.1 in chapter 1 represents many of the existing transition metal carbide phases. It can be observed that a range of stoichiometries are known for transition metal carbides of Groups 5 to 7. The carbiding agents used in this chapter are highlighted in bold.

3.1.1 Potential carbiding reagents

1. Saltlike carbides. This group of carbides divides into methane (i), acetylene (ii) and propyne (iii) derivatives. Only some examples are represented.

   (i) Al₄C₃, Be₂C

   (ii) Li₃C₂, Na₂C₂, K₂C₂, Rb₂C₂, Cs₂C₂, MgC₂, CaC₂, SrC₂, BaC₂, MC₂ type phases of lanthanides and actinides

   (iii) Mg₂C₃

2. Organic precursors.

   Bu⁴Li, EtLi, MeLi,

   Some of the species listed above are not likely to form transition metal carbides from metathesis reactions. This may be due to their low reactivity and the
low exothermicity for the reaction. Magnesium carbide, for example, was shown to be completely unreactive with transition metal halides. Indeed unreacted transition metal halides and magnesium carbide could be isolated even after heating for prolonged time periods at elevated temperatures.

3.1.2 Aims and background

Solid state metathetical preparations of transition metal carbides have been reported in a conference abstract by Kaner et al. In Kaner’s work lithium acetylide, Li$_2$C$_2$, was reacted with a couple of transition metal halides to form metal carbides. Low temperature syntheses of metal carbides via solution routes using $n$-butyl lithium and metal chlorides have also been reported in a conference report. In this abstract metal halides were reacted with $n$-butyl lithium in hexane under an inert atmosphere to form $n$-butane, lithium chloride and black colloids which were air sensitive. The X-ray amorphous black colloids were then separated and dried. After annealing under vacuum crystalline carbides were obtained.

Chapter 2 discussed briefly the results from the synthesis of bimetallic transition metal nitrides. Great interest is concentrated at present on various bimetallic transition metal carbides and transition metal carbonitrides. Formations of intimate solutions of transition metal nitrides discussed in chapter 2 proved highly challenging. All carbonitrides of Groups 4 and 5 transition metals are potentially useful in industry as cemented carbides. Since their cubic carbides and nitrides are isotypical then complete miscibility occurs. One of the commercial methods of preparation of carbonitrides is by heating of the carbides and nitrides under vacuum at 1600-1800 °C. In this chapter the formations of intimate ternary solid solutions MM'C and MN$_4$C$_7$ by metathesis reactions are also presented.

This chapter reports the reactions of anhydrous transition metal halides with saltlike carbides. No parallel work has been reported previously. The aim of the work presented in this chapter is to provide a detailed investigation of the solid state metathetical syntheses of transition metal carbides. A number of reagent manipulations and reaction conditions were investigated. A selected number of samples were studied using TEM and EELS/ELNES.
3.2 SYNTHESIS

(i) Reactions performed inside ampoules (bulk reactions)

Reactions of transition metal halides with carbides of calcium, strontium and aluminium inside evacuated ampoules produce transition metal carbides and the co-product calcium, strontium or aluminium halide salt (Tables 3.1 and 3.2). The reactions of Group 2 carbides with transition metal halides were performed at 550 °C. However all the reactions initiated at a lower temperature, for example, the reactions of niobium pentachloride with calcium and strontium carbides initiated at ~200 °C, accompanying melting of the halide. The reaction of molybdenum trichloride with calcium carbide starts at ca. 470 °C (calcium carbide undergoes a structural change at 447 °C). The resulting grey to black solids were annealed for 2-5 days at 550 °C. A weak, red solid flame was observed after initiation in the reactions of molybdenum pentachloride and tungsten(IV) and (VI) chlorides with calcium and strontium carbides.

The reactions in which aluminium carbide was used as a reagent were performed inside quartz ampoules set at a temperature gradient of 100-1000 °C for 2-3 days to sublime the co-product aluminium trichloride to the cooler end of the ampoule, thereby separating it from the desired product. No thermal flash was observed in these reactions. The resulting products were triturated with dried and degassed tetrahydrofuran.

The products from the reactions of transition metal halides with Group 2 carbides were triturated with water, dilute mineral acids and then washed with more water to remove the acid. **Equations 3.1-3.4 typify the reactions discussed in this chapter.** In many reactions co-formation of carbon was expected.

\[
\begin{align*}
\text{TiCl}_3 + \frac{3}{2}\text{CaC}_2 & \rightarrow \text{TiC} + \frac{3}{2}\text{CaCl}_2 + 2\text{C} \quad \text{eqn. 3.1} \\
\Delta H_{298} &= -566.2 \text{ kJ mole}^{-1}
\end{align*}
\]

\[
\begin{align*}
\text{ZrCl}_4 + \frac{1}{3}\text{Al}_4\text{C}_3 & \rightarrow \text{ZrC} + \frac{4}{3}\text{AlCl}_3 \quad \text{eqn. 3.2} \\
\Delta H_{298} &= +11.1 \text{ kJ mole}^{-1}
\end{align*}
\]
Scheme 3.1  Schematic equations typifying the SSM reactions discussed in this chapter.

\[
MX_n + n/2AC_2 \rightarrow MC + n/2AX_2 + (n-1)C \quad \text{eqn. 3.3*}
\]

[M = transition metals of Group 4 and 5 and W (for W, metal was also isolated in the final product); A = Ca, Sr; X = Cl, Br, I]

\[
MX_n + n/12Al_4C_3 \rightarrow MC_x + n/3AlX_3 + (3n/12-1)+(1-x)C \quad \text{eqn. 3.4*}
\]

[M = transition metals of Group 4 and 5 and Cr and W; X = Cl, Br, I]

*i these schematic equations are formulated for stoichiometric and substoichiometric monocarbides formations only

(ii)  Reactions initiated using a flame (propagation reactions)

The reactions of Group 5 and 6 transition metal halides with Group 2 carbides can also be initiated with flame or filament leading to the formation of transition metal carbides and the halide co-products (Table 3.3). An oxygen blow torch was used to produce a temperature ca. 800-900 °C. The reactions were initiated by applying the flame to the reagents. The flame was then immediately removed. Transition metal carbides of Group 6 formed using this method often contained some metal. The products were formed within 3-7 seconds of initiation. Initiation with flame, performed under a nitrogen atmosphere, resulted in highly crystalline products. Some of the co-product salt sublimed away. Filament initiation resulted in products, which were poorly crystalline. Products formed in the reactions initiated with flame or filament were not annealed. No reaction could be initiated between aluminium carbide and transition metal halide using flame or filament initiation.

X-ray powder diffraction patterns, FT-IR and SEM/EDXA were performed on both crude and triturated samples. A selected number of triturated samples were also analysed using TEM, PEELS/ELNES, microanalysis and electron probe measurements. Instruments used for analysis are listed in the experimental section.
Table 3.1  
Selected bulk reactions of transition metal halides with calcium or strontium carbide. * Literature lattice parameters were taken from references [18], [159] and [175].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products after annealing and trituration</th>
<th>(a_{\text{obs}}/\text{Å} \pm 0.001)</th>
<th>(a_{\text{id}}/\text{Å})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{TiCl}_3 + \text{CaC}_2)</td>
<td>(\text{TiC})</td>
<td>4.330</td>
<td>4.331</td>
</tr>
<tr>
<td>(\text{TiI}_4 + \text{CaC}_2)</td>
<td>(\text{TiC})</td>
<td>4.333</td>
<td>4.331</td>
</tr>
<tr>
<td>(\text{ZrCl}_4 + \text{CaC}_2)</td>
<td>(\text{ZrC})</td>
<td>4.690</td>
<td>4.698</td>
</tr>
<tr>
<td>(\text{ZrCl}_4 + \text{SrC}_2)</td>
<td>(\text{ZrC}^{a})</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>(\text{HfCl}_4 + \text{CaC}_2)</td>
<td>(\text{HfC})</td>
<td>4.632</td>
<td>4.643</td>
</tr>
<tr>
<td>(\text{VCl}_3 + \text{CaC}_2)</td>
<td>(\text{V}_8\text{C}_7)</td>
<td>4.165</td>
<td>4.165</td>
</tr>
<tr>
<td>(\text{VCl}_3 + \text{SrC}_2)</td>
<td>(\text{V}_8\text{C}_7)</td>
<td>4.159</td>
<td>4.165</td>
</tr>
<tr>
<td>(\text{NbCl}_5 + \text{CaC}_2)</td>
<td>(\text{NbC})</td>
<td>4.468</td>
<td>4.471</td>
</tr>
<tr>
<td>(\text{TaCl}_5 + \text{CaC}_2)</td>
<td>(\text{TaC})</td>
<td>4.451</td>
<td>4.456</td>
</tr>
<tr>
<td>(\text{CrCl}_3 + \text{CaC}_2)</td>
<td>(\text{CrC}_2^{a}, \text{Cr})</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>(\text{MoCl}_3 + \text{CaC}_2)</td>
<td>(\text{Mo}_2\text{C}[\text{Mo}])</td>
<td>(a = 3.003, , c = 4.735)</td>
<td>(a = 3.000, , c = 4.734)</td>
</tr>
<tr>
<td>(\text{MoCl}_5 + \text{CaC}_2)</td>
<td>(\text{Mo}_2\text{C}, \text{Mo})</td>
<td>((\text{Mo}_2\text{C}) , a = 3.001,, c = 4.731)</td>
<td>(a = 3.000, , c = 4.734)</td>
</tr>
<tr>
<td>(\text{MoCl}_3 + \text{SrC}_2)</td>
<td>(\text{Mo}_2\text{C}, \text{Mo})</td>
<td>((\text{Mo}_2\text{C}) , a = 3.006,, c = 4.733)</td>
<td>(a = 3.000, , c = 4.734)</td>
</tr>
<tr>
<td>(\text{MoCl}_5 + \text{SrC}_2)</td>
<td>(\text{Mo}_2\text{C}, \text{MoC})</td>
<td>((\text{Mo}_2\text{C}) , a = 3.002,, c = 4.736)</td>
<td>(a = 3.000, , c = 4.734)</td>
</tr>
<tr>
<td>(\text{WCl}_4 + \text{CaC}_2)</td>
<td>(\text{WC}^{a})</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>(\text{WCl}_4 + \text{SrC}_2)</td>
<td>(\text{WC})</td>
<td>(a = 2.901, , c = 2.836)</td>
<td>(a = 2.906, , c = 2.836)</td>
</tr>
</tbody>
</table>

* All the samples were cubic except for \(\text{Mo}_2\text{C}\) and WC, which were hexagonal. The reaction mixtures were brought to 550 °C and kept annealing for 2-5 days at that temperature.

* Samples poorly crystalline and lattice parameters have not been calculated.

[ ] - minor phases present.
Table 3.2  
Selected bulk reactions of transition metal halides with aluminium carbide.* All the literature lattice parameters were taken from reference [18], except for iron carbide, Fe₃C, which was taken from reference [175].

<table>
<thead>
<tr>
<th>Transition metal halide</th>
<th>Products after annealing and trituration</th>
<th>$a_{\text{obs}}/\text{Å}$ +/- 0.001</th>
<th>$a_{\text{lit}}/\text{Å}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCl₃</td>
<td>TiC</td>
<td>4.332</td>
<td>4.331</td>
</tr>
<tr>
<td>ZrCl₄</td>
<td>ZrC</td>
<td>4.692</td>
<td>4.698</td>
</tr>
<tr>
<td>HfCl₄</td>
<td>HfC</td>
<td>4.639</td>
<td>4.643</td>
</tr>
<tr>
<td>VCl₃</td>
<td>V₄C</td>
<td>4.165</td>
<td>4.165</td>
</tr>
<tr>
<td>NbCl₅</td>
<td>NbC</td>
<td>4.468</td>
<td>4.471</td>
</tr>
<tr>
<td>TaCl₅</td>
<td>TaC</td>
<td>4.456</td>
<td>4.456</td>
</tr>
<tr>
<td>CrCl₃</td>
<td>Cr₂C</td>
<td>$a = 2.87, b = 5.53, c = 11.66$</td>
<td>$a = 2.82, b = 5.53, c = 11.47$</td>
</tr>
<tr>
<td>CrCl₄</td>
<td>Cr₂C</td>
<td>$a = 2.87, b = 5.52, c = 11.60$</td>
<td>$a = 2.82, b = 5.53, c = 11.47$</td>
</tr>
<tr>
<td>MoCl₅</td>
<td>Mo₂C</td>
<td>$a = 3.010, c = 4.737$</td>
<td>$a = 3.000, c = 4.734$</td>
</tr>
<tr>
<td>MoCl₆</td>
<td>Mo₂C</td>
<td>$a = 3.010, c = 4.735$</td>
<td>$a = 3.000, c = 4.734$</td>
</tr>
<tr>
<td>WCl₄</td>
<td>WC</td>
<td>$a = 2.905, c = 2.845$</td>
<td>$a = 2.906, c = 2.836$</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>(Fe₃C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeCl₂</td>
<td>Fe₂C</td>
<td>$a = 5.085, b = 6.740, c = 4.522$</td>
<td>$a = 5.088, b = 6.744, c = 4.524$</td>
</tr>
<tr>
<td>FeBr₃</td>
<td>(Fe₃C)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*All the carbide products were cubic except for Cr₂C and Fe₃C which were orthorhombic, and Mo₂C and WC which were hexagonal. All the reaction mixtures were heated to 1000 °C and kept annealing at that temperature for 2-3 days.

3.4 CHARACTERISATION

3.4.1 X-ray powder diffraction

(i) Bulk reactions

Solid state metathesis reactions of transition metal halides with calcium carbide or strontium carbide yield highly crystalline transition metal carbides and calcium or strontium halides (figure 3.1, equations 3.3-3.4). The particle size of the carbide products as formed without annealing was of the order 50–1200 Å, as calculated from XRD line broadening using the Scherrer equation (Formula 2.1).
Table 3.3  Reactions of transition metal halides with calcium and strontium carbides
initiated with flame. * Literature lattice parameters were taken from references [18] and [175].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products after trituration</th>
<th>(a_{obs}/\text{Å} \pm 0.001)</th>
<th>(a_{abh}/\text{Å})</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrCl(_4) + CaC(_2)</td>
<td>Reaction incomplete</td>
<td>—</td>
<td>4.698</td>
</tr>
<tr>
<td>ZrCl(_4) + SrC(_2)</td>
<td>Reaction incomplete</td>
<td>—</td>
<td>4.698</td>
</tr>
<tr>
<td>HfCl(_4) + CaC(_2)</td>
<td>Reaction incomplete</td>
<td>—</td>
<td>4.643</td>
</tr>
<tr>
<td>VCl(_3) + CaC(_2)</td>
<td>V(_4)C(_7)</td>
<td>4.165</td>
<td>4.165</td>
</tr>
<tr>
<td>VCl(_3) + SrC(_2)</td>
<td>V(_6)C(_7)</td>
<td>4.164</td>
<td>4.165</td>
</tr>
<tr>
<td>NbCl(_5) + CaC(_2)</td>
<td>NbC</td>
<td>4.471</td>
<td>4.471</td>
</tr>
<tr>
<td>NbCl(_5) + SrC(_2)</td>
<td>NbC</td>
<td>4.462</td>
<td>4.471</td>
</tr>
<tr>
<td>TaCl(_5) + CaC(_2)</td>
<td>TaC</td>
<td>4.455</td>
<td>4.456</td>
</tr>
<tr>
<td>TaCl(_5) + SrC(_2)</td>
<td>TaC</td>
<td>4.440</td>
<td>4.456</td>
</tr>
<tr>
<td>CrCl(_3) + CaC(_2)</td>
<td>Cr</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>MoCl(_3) + CaC(_2)</td>
<td>Mo(_2)C (Mo)</td>
<td>((\text{Mo}_2\text{C}) a = 3.003, c = 4.735)</td>
<td>(a = 3.000, c = 4.734)</td>
</tr>
<tr>
<td>WCl(_4) + CaC(_2)</td>
<td>W(_2)C, W (WC)</td>
<td>((\text{W}_2\text{C}) a = 2.995, c = 4.725)</td>
<td>(a = 2.992, c = 4.722)</td>
</tr>
<tr>
<td>WCl(_4) + SrC(_2)</td>
<td>W(_2)C (W, WC)</td>
<td>((\text{W}_2\text{C}) a = 2.998, c = 4.729)</td>
<td>(a = 2.992, c = 4.722)</td>
</tr>
</tbody>
</table>

*The products were not annealed further after the reactions have ceased. All the samples were cubic except for Mo\(_2\)C, WC and W\(_2\)C, which were hexagonal.

X-ray patterns of crude and triturated products obtained from the reactions of transition metal halides and carbides of calcium or strontium showed that water washing was adequate for the removal of the co-products. The unannealed crude products of the reactions of transition metal halides with aluminium carbide performed within the 250-600 °C temperature range were X-ray amorphous and partly separated within the reaction ampoule as the aluminium chloride co-product sublimed to the colder end of the ampoule. Despite this the products were tritutated using dried and degassed diethyl ether followed by methanol.

The carbide product containing co-produced salt was annealed for 1-5 days, at 1000 °C for the reactions involving aluminium carbide. Annealing at 550 °C was also studied for selected reactions involving calcium or strontium carbide. In most reactions annealing was found to improve the crystallinity and improve oxidative stability, probably as a consequence of grain growth and reduced surface area.
Figure 3.1  XRD patterns of triturated products from the bulk reactions of molybdenum trichloride with aluminium carbide (a) and tantalum pentachloride with calcium carbide (b). Each pattern is followed by a standard stick pattern below for (a) molybdenum carbide, MoC, and (b) tantalum carbide, TaC.

Preparation of transition metal carbides using transition metal halides with different carbiding reagents such as aluminium, calcium or strontium carbide resulted in a range of particle sizes. The reactions with aluminium carbide yielded amorphous products. Crystalline products from this reaction started to show only
after 1-5 hours of annealing at 1000 °C. The products obtained from the bulk reactions of calcium or strontium carbide showed crystallite sizes between 50-1200 Å. In all cases annealing at 550 °C for 2-5 days induced greater crystallinity. Chapter 7 discusses various solid state metathetical preparations of carbides to obtain products with varied particle sizes using different reagents, reagent manipulations or reaction conditions.

Attempted solid state metathetical preparations of rare earth carbides using rare earth halides (La, Ce, Ho) with aluminium or calcium carbide did not yield the desired rare earth carbide products. Unreacted halide was the predominant aspect of the diffraction pattern.

(ii) Propagation reactions

Transition metal carbides prepared by reaction of Group 5 metal halide and strontium carbide or calcium carbide using flame initiation were highly crystalline and did not require any annealing. Figure 3.2a shows an XRD pattern of a crude sample from the reaction of tantalum pentachloride with calcium carbide. The hydrated calcium chloride peaks are very clear and disappear in the triturated sample (figure 3.2b). The reactions were performed without a closed environment using a flame from a gas torch with the reagents kept under a flow of nitrogen. Transition metal halides of Groups 6-8 also react with calcium and strontium carbides on flame initiation but the products are usually a mixed phase of the carbide and the metal or just the pure metal phase. Manipulations of the reaction mixture such as the addition of salt as an inert heat sink helped to obtain pure carbide phases of Groups 6-8 metals when using flame initiation (Table 3.3).

3.4.2 SEM/EDXA

SEM measurements of the crude and triturated unannealed samples from the bulk reactions of transition metal halides with carbon precursors showed contrasting morphology. The crude solids possessed agglomerates with smooth surfaces (figure 3.3a-b). The triturated samples had smaller sized agglomerates with sharper shapes (figure 3.3c-d). Transition metal carbides prepared using
solid state metathetical routes showed a narrow size distributions within the samples. The greatest average particle size disparities occurred between the corresponding transition metal carbides prepared using aluminium carbide in a bulk reaction and strontium carbide using flame for initiation. Figure 3.4 shows four samples of different transition metal carbides. These are characterised by variations in morphology and the size of agglomerates. These differences can be interpreted in terms of the thermodynamics of the reactions and the physical properties of the reagents and the products.
Figure 3.3  SEM micrographs showing: (a) surface of a particle of crude sample from a flame initiated reaction of niobium pentachloride with calcium carbide, (b) particle of crude sample from the bulk reaction of molybdenum trichloride with strontium carbide, (c) particle of a triturated sample from the bulk reaction of niobium pentachloride with calcium carbide, (d) close-up of a particle shown in (c).

EDXA analysis of the as prepared solids from the bulk and propagation reactions of transition metal halides with calcium or strontium carbide showed the presence of transition metal, carbon, chlorine, and calcium or strontium. However it was found that the presence of the transition metal on the surfaces of the particles was minimal in products obtained from bulk reactions. The reactions performed using flame initiation showed significantly more metal and less salt suggesting that much of the co-product sublimed away during the reaction. The as
prepared powders produced in the reactions of transition metal halides with aluminium carbide showed only the presence of transition metal by EDXA (carbon was below the detection threshold). The co-produced aluminium chloride salt was not in evidence presumably as the reaction was completed in an ampoule and all of the aluminium chloride sublimed to the cold end of the ampoule during the reaction. After trituration with water all the co-produced salt was removed and EDXA analysis showed only the presence of the transition element.

Figure 3.4  
*SEM micrographs showing: (a) vanadium carbide (V₂C₃) prepared using vanadium trichloride and strontium carbide using flame initiation, (b) surface of the particle shown in (a), (c) tantalum carbide (TaC) prepared using tantalum pentachloride with calcium carbide, (d) molybdenum carbide (Mo₂C) prepared using molybdenum trichloride and aluminium carbide.*
Despite the different reaction temperatures applied in the bulk solid state metathetical preparations of transition metal carbides the products showed significant similarity in morphology traversing through the transition metal block and was independent of the reagents used. All the transition metal carbides of Group 4-6 (except for Cr$_3$C$_2$) formed in this research have similar melting/decomposition points.

3.4.3 TEM analysis

TEM has not been used before to study products prepared using solid state metathetical reactions. A selected group of metal carbide samples prepared using transition metal halides and aluminium, calcium or strontium carbide were examined. Analysis of the microstructure and physical appearance has been performed and electron diffraction patterns obtained.

The samples analysed using TEM were TiC(1) and V$_6$C$_7$(1), prepared using the metal trihalides and aluminium carbide at 1000 °C for 2 days, and V$_6$C$_7$(2) and TaC(1) from the bulk reactions of vanadium trichloride and tantalum pentachloride with calcium carbide at 550 °C for 2 hours (Table 3.4). Titanium carbide, TiC(1), contained aggregates of grains of variable sizes. Figure 3.5 illustrates 3 dark-field TEM micrographs of different regions within the sample with the associated electron diffraction maps shown as inserts. Figure 3.5a shows a polycrystalline agglomerate with f.c.c. structure while figure 3.5b shows agglomerates with grains of about 30 nm in size. The structure is the same but the crystal is textured in the direction parallel to [022], which is indicated by the arrow on the electron diffraction map. Figure 3.5c shows a large crystal grain, which is highly faulted which can be observed as a non-uniform contrast in the dark-field image shown. These large crystals were very rare in the sample (average crystal size was estimated at 20 nm). The electron diffraction map represents a [111] diffraction pattern. Some extra spots were observed, which can be explained by the presence of ordered stacking faults in the f.c.c. structure. Some impurities were also observed in the TEM studies but these were not analysed more closely. The unidentified spots were expected to be due to titanium oxide or some free carbon present.
Figure 3.5  Dark-field TEM micrographs of titanium carbide (sample TiC1) produced using titanium trichloride and aluminium carbide. The analyses were performed on different regions within the same sample.
Table 3.4  Transition metal carbides analysed using TEM and EELS/ELNES.

<table>
<thead>
<tr>
<th>Carbide</th>
<th>Reaction/annealing conditions</th>
<th>Generalised TEM results</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC(1)</td>
<td>TiCl₃ + Al₄C₃/1000 °C, 2 days</td>
<td>f.c.c., fine aggregates mixed with large lumps, textured and spotted ring patterns obtained</td>
</tr>
<tr>
<td>V₈C₇(1)</td>
<td>VCl₃ + Al₄C₃/1000 °C, 2 days</td>
<td>f.c.c., polycrystalline pattern, needed single crystal to determine lattice parameter</td>
</tr>
<tr>
<td>V₈C₇(2)</td>
<td>VCl₃ + CaC₂/550 °C, 2 hours</td>
<td>f.c.c., 3 types of lumps/morphology, aggregates of small fine particles, single crystal and polycrystalline diffraction maps obtained</td>
</tr>
<tr>
<td>TaC(1)</td>
<td>TaCl₅ + CaC₂/550 °C, 2 hours</td>
<td>f.c.c., very fine aggregates; ring and spot patterns superimposed</td>
</tr>
</tbody>
</table>

The samples of vanadium carbide had an average grain size of 100 nm, for the sample prepared using aluminium carbide, and 20 nm, for the sample prepared using calcium carbide. These differences were attribute to the temperatures used for annealing of the products (Table 3.4). Variable grain shapes were observed for the sample V₈C₇(1) (figure 3.6). Some were regular polygons and others occurred as elongated grains often arranged in a chain configuration. Similar patterns were observed in the arrangement of particles in sample V₈C₇(2).

The interest in the analysis of vanadium carbide samples V₈C₇(1) and V₈C₇(2) was promoted by the unique structure of V₈C₇ and the bulk analysis obtained (V₈C₇(1): C = 13.75 %, calcd.: 17.07 % i.e.V₅C₆.). This is because vanadium carbide can occur in a range of stoichiometries in various structures (figure 1.1). Vanadium carbides of different stoichiometries give electron diffraction patterns with contrasts, for example, V₆C₅ has superlattice reflections at different positions. The strength of the diffraction spots of the samples is strongly dependent on the carbon deficiency. Despite the fact that the bulk analysis suggested a carbon deficiency, the lattice parameter determined from the X-ray powder diffraction pattern, showed a good match with the V₈C₇ stoichiometry (Table 3.2). TEM showed that there is no carbon deficiency.
present in the sample. The disagreement in the results has to be attributed either to the refractory nature of the carbide leading to incomplete combustion during microanalysis or to the presence of impurities in the sample. A small proportion of oxide phase was also detected. These to some extent would affect the bulk analysis.

In vanadium carbide, \( V_8C_7 \), the vanadium atoms occupy the same positions as they would possess in NaCl but the C vacancies are ordered. To represent the complete structure of vanadium carbide accurately, a supercell has to be presented composed of eight sodium chloride cells. Its atomic positions and space group were determined by de Novion et al. and Froidevaux and Rossier et al.\(^{177,178}\)

The electron diffraction pattern of vanadium carbide prepared using vanadium trichloride and aluminium carbide is in a good agreement with one simulated for a [111] diffraction pattern, which was referenced with respect to the supercell (figure 3.7). This shows that the grain has a composition close to the stoichiometry of \( V_8C_7 \). Few oxide grains have also been observed which can explain the low carbon composition determined via the bulk analysis.

Tantalum carbide (TaC(1)) prepared using the pentachloride and calcium carbide was composed of a very fine mesh of aggregates. These consisted of smooth layers of ‘plates’. Ring and spots electron diffraction patterns were superimposed.
3.4.4 ELNES/PEELS analysis

Electron energy loss spectroscopy (EELS) was another technique applied in this project for determining the lattice parameters and chemical compositions of cubic rock salt transition metal carbides of Group 4 and 5. A selection of transition metal carbides was used to obtain their ionisation edges and ELNES, which is sensitive to the lattice parameter and elemental composition of the carbide. The objectives behind this study were to parallel those for transition metal nitrides as discussed in detail in section 2.4.4. The sample analysed using the PEELS/ELNES technique was V₈C₇(1). This sample was already discussed in detail in section 3.4.3. This section discusses the PEELS results obtained and correlates them with results from previous analysis techniques. A commercial VC sample was used as a standard.

The main difficulty in PEELS analysis performed on sample V₈C₇(1) was due to the close proximity of the V L₂,₃ and O K edges (513 and 521 eV). To overcome these problems the ELNES technique has been utilised where the fine structure on the ionisation edges is ‘extracted’. The advantages of using ELNES technique are explained in detail in section 2.4.4.
Figures 3.8a-3.8b show strong C K and V L\textsubscript{2,3} ionisation edges for V\textsubscript{8}C\textsubscript{7}(1) and a commercial standard. The presence of the peaks at the same energies suggests identical lattice parameters for the two samples compared. The two samples were analysed for C K edges using different resolutions (V\textsubscript{8}C\textsubscript{7}(1) ~1.0 eV, standard ~0.3 eV) which partly explains the differences between the two spectra. The peak at ~284 eV for V\textsubscript{8}C\textsubscript{7}(1) is effectively lowered and broadened. Applying filtration removes the difference giving a satisfactory match. At the energy loss above 300 eV there are marked intensity differences, which is not very significant for the analysis intended.

Figure 3.8 EELS analyses of sample V\textsubscript{8}C\textsubscript{7}(1): (a): C K ionisation edges for sample V\textsubscript{8}C\textsubscript{7}(1) (~1 eV res.), prepared using vanadium trichloride and aluminium carbide and a commercial sample (~0.3 eV res.). (b): V L\textsubscript{2,3} ionisation edges for the samples in (a) at ~1.6 eV resolution (bottom fine line and middle thick line) and commercial sample at ~0.3 eV (top fine line).

Analysis of the V L\textsubscript{2,3} edges for both samples was also performed using different resolutions (V\textsubscript{8}C\textsubscript{7}(1) 1.6 eV, standard ~0.3 eV). The low resolution used for analysis of sample V\textsubscript{8}C\textsubscript{7} was due to the instrumental problems encountered at the time of the measurement. Figure 3.8b shows 1 V L\textsubscript{2,3} edge for V\textsubscript{8}C\textsubscript{7}(1) and 2 edges for the same standard used (higher fine line) one at a resolution of ~0.3 eV and lower after a 1.6 eV smoothing filter has been used. The main 2 peaks on these edges show good agreement but intensity beyond ~525 eV becomes indistinguishable. This difference is also purely an effect of the background and deconvolution errors. Unfortunately these errors made it difficult to test accurately the oxide contamination since the O K edge starts at ~532 eV. To
overcome the problem of the intensities the spectra were scaled to match in a 5 eV window before the O K edge threshold. Then they were subtracted. This technique revealed no presence of any rise in intensity in the spectrum in the ~532 eV region. The consistency of the intensity in this region allowed estimate of the possible oxygen contamination below 3 at.%.

3.3 DISCUSSION

Solid state metathetical reactions of anhydrous transition metal halides with Group 2 carbides and aluminium carbide initiate at temperatures related to a phase change of one of the reagents (melting, decomposition, structural rearrangement, equations 3.5-3.7). Most of the reactions discussed in this chapter were slow in comparison to the reactions of transition metal halides with Group 1 and 2 nitrides.

\[
\begin{align*}
12/5 \text{TaCl}_5 + 4 \text{Al}_4 \text{C}_3 & \rightarrow 12/5 \text{TaC} + 4 \text{AlCl}_3 + 3/5 \text{C} & \text{eqn. 3.5} \\
T_{in} & = 200-220 \, ^\circ \text{C} \\
2\text{MoCl}_3 + 3\text{CaC}_2 & \rightarrow \text{Mo}_2\text{C} + 3\text{CaCl}_2 + 5\text{C} & \text{eqn. 3.6} \\
T_{in} & = 450-460 \, ^\circ \text{C} \\
\text{NbCl}_5 + 5/2\text{SrC}_2 & \rightarrow \text{NbC} + 5/2\text{SrCl}_2 + 4\text{C} & \text{eqn. 3.7} \\
T_{in} & = 200-210 \, ^\circ \text{C}
\end{align*}
\]

\[m. \, pt \, \text{TaCl}_5 = 210 \, ^\circ \text{C}, \text{NbCl}_5 = 203 \, ^\circ \text{C}, \text{MoCl}_3 = 1027 \, ^\circ \text{C};^\text{28} \, \text{phase change of CaC}_2 \text{ occurs at } 447 \, ^\circ \text{C}^\text{18}\]

Products obtained from the reactions of transition metal halides with Group 1 and 2 carbides and aluminium carbide were analysed using various analytical techniques. Some of the results obtained were correlated where appropriate to provide a more substantial understanding of the reactions. One area of analysis that has already been discussed in chapter 2 is the study of product crystallite size and how solid state metathetical syntheses can be controlled to tune the reaction conditions to obtain products of desired crystallinity.

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One of the most important advantages of solid state metathetical reactions forming transition metal carbides, similar to the transition metal nitrides discussed in chapter 2, is that they lead after work-up to the formation of largely phase-pure products. Some reactions may form some metal due to the decomposition of the carbide but this can be avoided without complications. These reactions are always complete and the final triturated unannealed samples, when analysed, never showed evidence of the presence of unreacted starting reagents. The yields obtained from these reactions were generally very high the main losses attributed to the handling and impurity of starting reagents. Calcium carbide used in these reactions was 80 % pure, as assessed by the Aldrich Co. Strontium carbide was prepared from the elements at 800 °C and contains some minor oxide impurities. Products obtained from the reactions where calcium carbide and strontium carbide were used, were triturated with dilute acids, which removed the co-formed oxides in most cases to leave pure transition metal carbide.

Unlike the syntheses of transition metal nitrides using solid state metathetical routes the bulk preparations of transition metal carbides often required long periods of annealing, especially for reactions with aluminium carbide. Products even as stable as transition metal carbides when very poorly crystalline were found to undergo oxidative decomposition in air. Annealing the carbides synthesised using solid state metathetical preparations discussed in this work was very inefficient at low temperatures. No significant increase in crystallinity was observed when these products were annealed at 400 °C. Some progress was observed at temperatures above 500 °C.

Transition metal carbides of Groups 5 and 6, prepared using transition metal halides with calcium and strontium carbides by flame initiation, were highly crystalline as prepared and did not require any further annealing.

Reactions of Group 2 carbides with Group 6 transition metal halides yielded a mixture of transition metal carbides and metal. A number of approaches have been utilised to overcome this problem. Several transition metals can be washed away from the desired transition metal carbides using aqua regia. However control of the syntheses was attempted to prevent the formation of transition metal in the final product. The two easiest approaches were found to be:
spreading the reagents to prevent the 'overheating' of the mixture which decomposes some of the carbide product before it crystallises

addition of a salt diluent to act as an inert heat sink in the reaction mixture

Both approaches have been thoroughly tested and the first of them is related to in chapter 2 with relevance to the syntheses of thermally unstable transition metal nitrides (section 2.4). Both are discussed in more detail in chapter 7. The results show that not only do they succeed in halting the decomposition of the desired products but they can also be envisaged to synthesise completely different phases of transition metal carbides which would be otherwise inaccessible.

Preparations of transition metal carbides of Group 7 using solid state metathetical reactions were unsuccessful due to the poor thermal stability of the carbides. This comes into a conflict with the high temperatures required for the reactions to initiate as well as the high temperatures generated by these exothermic reactions. The only exception was the bulk reaction of iron trichloride with aluminium carbide at 700 °C yielding poorly crystalline iron carbide, Fe3C. Reactions involving iron halides and Group 2 carbides yielded austenite, (Fe,C).

One of the most notable phenomena of solid state preparations of transition metal carbides using transition metal halides and Group 2 carbides or aluminium carbide was the variation in product crystallinity. This was usually related to the mode of initiation, reaction rate and reagent combination (figure 3.9). Comparison of the crystallinity of the various products obtained from bulk and propagation reactions of these reagents lead to the following conclusions:

- these reactions can be used to yield transition metal carbides with a wide range of crystallinities from amorphous to highly crystalline
- in order to obtain crystalline samples from bulk reactions annealing is required
- products obtained from propagation reactions do not require further annealing to yield highly crystalline phases
- crystallinity of transition metal carbides discussed in this chapter can be categorised with respect to the carbon precursor in the following order starting with the most crystalline (all prepared without additional annealing):
Crystallinity of the products was determined using SEM and XRD using the Scherrer equation.

Reactions of transition metal halides with Group 2 carbides or aluminium carbide form transition metal carbides and on occasion some free carbon. The reactions where Group 2 carbides are used involve formation of excess amounts of carbon. However, no evidence of superstoichiometric phases was observed. The reactions always formed monostoichiometric transition metal carbides. The exception was the latter carbides of vanadium, chromium, molybdenum and iron, which form substoichiometric carbides, $V_8C_7$, $Cr_3C_2$, $Mo_2C$ and $Fe_3C$ despite the excess carbon available. The explanation for this is that for these elements the latter stoichiometric transition metal carbides are either thermally unstable ($MoC$) or they do not exist ($CrC$ and $FeC$). Substoichiometric molybdenum carbide, $Mo_2C$, exists in two forms. Solid state metathetical preparations discussed in this chapter always yielded the more thermally stable hexagonal close packed $\beta-Mo_2C$
with disordered carbon atoms. The ordered form of the carbide is the orthorhombic \(\alpha\)-Mo\(_2\)C. Elemental carbon impurities were observed in some of the products using PEELS. However most of the excess carbon tended to separate away from the carbide product during trituration by floating while most of the metal carbide product sank. The resulting solutions were decanted together with the floating 'graphitic carbon,' leaving the transition metal carbide.

3.4.1 Level of carburisation in transition metal carbides

X-ray powder diffraction patterns also helped in determining the stoichiometry of the transition metal carbides discussed in this chapter. The lattice parameters of transition metal carbides are related to their carbon composition in a linear fashion according to Vegard's Law.\(^{175}\) However the linear change of lattice parameter depends on the specific carbide. For example, the change in the lattice parameter of ZrC\(_x\), from \(x = 0.98\) to 0.55 is by only 0.006 Å while for NbC\(_x\), from \(x = 1.0\) to 0.77 is 0.029 Å. Therefore determination of the exact carbon content for zirconium carbide using X-ray diffraction patterns cannot be performed accurately since under the optimum conditions employed in this work the error limit for indexing is 0.004 Å.

Solid state metathetical preparations of transition metal carbides provide the possibility of controlling the stoichiometry of the final product. Carbides of Group 2 and aluminium carbide have been studied in this work as potential carbon precursors in these syntheses. Calcium and strontium carbides provide an excess quantity of carbon when reacted with transition metal halides to produce transition metal carbides and therefore cannot be expected to form any substoichiometric products. However aluminium carbide provides an insufficient amount of carbon in solid state metathetical reactions if it is made to react with low oxidation state (< 4) transition metal halides (equation 3.8).

\[
4\text{TiCl}_3 + \text{AlC}_3 \rightarrow 4\text{TiC}_{0.75} + 4\text{AlCl}_3 \quad \text{eqn. 3.8}
\]

Figure 3.10 shows the [200] X-ray diffraction peaks of vanadium carbide samples obtained from a variety of reaction approaches outlined below using
vanadium trichloride as the transition metal precursor. The main observation that can be made is that the crystallinity of the products varies progressively from the least crystalline carbide, obtained from the bulk reaction of vanadium trichloride with calcium carbide to the most crystalline carbide, which was obtained from the flame initiated reaction of strontium carbide. It can also be observed that the [200] peak shifts due to changes in the carbon composition of the carbides. For all interstitial transition metal monocarbides in general it can be expected that if aluminium carbide and a small molar proportion of calcium carbide are reacted with the transition metal halides, then higher substoichiometries of these carbides can be accessible, e.g. TiCₓ (where 1 ≥ x ≥ 0.75).

![Figure 3.10](image)

**Figure 3.10** [200] X-ray diffraction peaks of vanadium carbides prepared using vanadium trichloride and strontium carbide via a flame initiation (a) and in a bulk reaction (b), and using vanadium trichloride with calcium carbide via a flame initiation (c) and in a bulk reaction (d).

One other method that could be studied in order to form substoichiometric transition metal carbides is the so-called double salt metathesis where a specific amount of Group 1 or 2 metal is added to the mixture to be reacted with some of the transition metal halide to form a Group 1 or 2 metal halide and the transition metal while the remainder of the transition metal halide would react with the silicide reagents. In a system where a transition metal halide reacts with aluminium carbide some lithium or calcium can be added and it is possible that the following process might occur:
4ZrCl$_4$ + Al$_4$C$_3$ + 4Li $\rightarrow$ 4ZrC$_{0.75}$ + 4AlCl$_3$ + 4LiCl \hspace{1cm} \text{eqn. 3.9}

No work has been performed to confirm that this hypothesis works.

3.4.2 Formation of bimetallic transition metal carbides and transition metal carbonitrides

An attempt was made to produce intimate ternary solutions of transition metal carbides and transition metal carbonitrides. The carbide and nitride precursors used for the syntheses of carbonitrides were always pre-annealed together for 7 days at 550 °C inside an evacuated ampoule prior to use. Five reagents were used in such syntheses – calcium carbide, aluminium carbide, lithium nitride, magnesium nitride and calcium nitride.

The reactions where lithium nitride was used in combination with calcium carbide or aluminium carbide yielded inhomogeneous mixtures of solids on every occasion. The central three rows in figure 3.11 show the metal, carbon and nitrogen ionisation edges obtained from PEELS analyses of vanadium carbonitride prepared using lithium nitride and aluminium carbide of molar ratios 3 : 1 respectively in a form of a chart. The top and bottom rows of the figure show reference patterns for VC$_{0.9}$ and VN. This analysis shows patterns consistent with ternary products containing variable carbon, nitrogen and vanadium compositions. Notably the composition of an individual grain was homogeneous whilst between grains inhomogeneity resulted. Oxygen contamination in the sample has not been analysed since the V L$_{2,3}$ edges and O K edge lie in close proximity (~513 and 521 eV cf.~532 eV). The ELNES technique is an option to solve this problem. It has already been discussed in more detail in section 2.3.4. This technique uses the fine structure present on the edges and is closely related to XANES. The fine structure is sensitive to the site symmetry and the lattice parameter of the product analysed. The correlation of EDXA and PEELS analyses allowed identification of three main phases present within the sample. The most abundant phase contained high ratios of nitrogen with less carbon present. The other two main phases were close to the extremes in carbon and nitrogen ratios respectively. It can be concluded that the binary solids are
miscible using these solid state metathetical reactions. However intimate solutions could not be obtained. Annealing the inhomogeneous mixtures at temperatures from 550 °C to 1000 °C for up to 14 days have done little to improve the macroscale homogeneity of these products.

The investigations performed in an attempt to form bimetallic transition metal carbides, MM'C, using two carefully pre-ground transition metal halides and carbon precursors showed limited success in forming solid solutions. The
best results were obtained when the two transition metal halides used had similar melting points, for example, the pentachlorides of niobium and tantalum. It was also important for the two metals to form the same carbide structural type. Carbides of niobium and tantalum form the same cubic rocksalt structure when synthesised using solid state metathetical routes. The reaction of these two pentachlorides with calcium carbide at 210 °C inside an ampoule has lead to the formation of a homogeneous solid solution of these transition metal carbides. After annealing the crude products at 550 °C for 4 days a crystalline single phase bimetallic carbide was observed using XRD. Molybdenum pentachloride (m. pt. 194 °C, \( \cdot \). similar to NbCl\(_5\) and TaCl\(_5\)) forms hexagonal Mo\(_2\)C when reacted with calcium or aluminium carbide. Attempts to form homogeneous solutions of Group 5 transition metal carbides with molybdenum carbide were unsuccessful. In both cases (Nb/Mo and Ta/Mo) two structures were observed in the final product cubic rocksalt, representing a phase with a small proportion of molybdenum and the other, hexagonal, with molybdenum as the major transition metal present. Annealing of these mixtures at temperatures up to 1000 °C for 2-3 weeks has not helped to form homogeneous mixtures of these solids. Figure 3.12 shows an SEM of the intended Ti\(_{0.75}\)V\(_{0.25}\)C, from the reaction of titanium trichloride, vanadium trichloride and aluminium carbide at 1000 °C for 2 days, which in fact proved to be a mixture of ternary carbides with the most common ranges from Ti\(_{0.6}\)V\(_{0.4}\)C to Ti\(_{0.9}\)V\(_{0.1}\)C, as assessed using EDXA. The first clear observation made using SEM was the great contrast in morphology of this solid (and several other bimetallic transition metal carbides prepared using solid state metathetical reactions) when compared with the binary transition metal carbides that were discussed previously (section 3.4.2). These products lacked the presence of the individual well defined particles. In these products instead the particles were in the form of ‘flakes’ arranged in an unsystematic mesh with many features, which had little in common with each other.
TEM analyses performed on two areas of the sample Ti$_{0.75}$V$_{0.25}$C showed single crystal grains forming conglomerations (figure 3.13). The cubic $a$-parameters obtained from these two regions using electron diffraction experiments varied considerably at 4.22 Å (figure 3.13a) and 4.30 Å (figure 3.13b) (TiC$_{0.61}$-1.0 = 4.313-4.328 Å, VC$_{0.73}$-0.87 = 4.131-4.166 Å$^{175}$). However both represent values consistent with presence of two different solid solutions of two binary carbides of titanium and vanadium.

All the reactions discussed so far in this section to form ternary species form primarily the binary species with some incorporation of the second metal into their lattice. Hence a true solid solution was not formed. Further dissolution of these species to form homogeneous solid solution is practically impossible since they are in the solid state and the annealing temperatures used were far too low. It is possible that adding very little of a low melting point salt (e.g. LiCl, m. pt. 613 °C$^{21}$) to the starting reagents might help to form homogeneous solid solutions. However addition of small quantities of such salt to reaction mixtures of transition metal halides and calcium carbide reduce the crystallinity of the final product.
The most successful reactions to form ternary solid solutions were those in which a pre-annealed mixture of calcium carbide and calcium nitride was employed. Annealing of the reagents was performed for a few days at 550-600 °C. A colour change was observed with the mixture becoming dark grey. It is difficult to explain what has happened to the mixture and whether some kind of a reaction has occurred. However calcium carbide undergoes a structural change at 447 °C which is most probably relevant to this observation. Analysis by XRD of this calcium carbide and nitride mixture was unhelpful as the reagent mix decomposed in air.

All the reactions of transition metal halides with a mixture of calcium carbide and calcium nitride were performed at temperatures up to 550 °C. The reactions initiated rapidly often being assisted by a dark red thermal flash (Table 3.5). After the initiation the resultant solids were annealed at 550 °C for up to 4 days. Figure 3.14 shows the [111] X-ray diffraction peaks for two tantalum carbonitrides prepared using tantalum pentachloride, calcium carbide and nitride where the molar ratio of the carbon and nitrogen precursors was manipulated. The difference in the peak shifts illustrates that these have a different composition of nitrogen and carbon.

Figure 3.13 TEM micrographs collected from two regions of sample Ti0.75V0.25C with a-parameters of 4.22 Å for (a) and 4.30 Å for (b).
Table 3.5  
**Bulk reactions of transition metal halides with two calcium nitride/calcium carbides mixes.***

<table>
<thead>
<tr>
<th>Transition metal halide</th>
<th>Reaction</th>
<th>Product after trituration and annealing</th>
<th>$a_{calc} / \text{Å} \pm 0.001$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VCl₅⁺</td>
<td>Red light, initiation at 370 °C</td>
<td>V(C,N)</td>
<td>4.134</td>
</tr>
<tr>
<td>TaCl₅⁺</td>
<td>Red thermal flash, initiation at 250 °C</td>
<td>Ta(C₁₆N₁₆)</td>
<td>4.429</td>
</tr>
<tr>
<td>ZrCl₅⁺</td>
<td>Red thermal flash, initiation at 340 °C</td>
<td>ZrCN</td>
<td>4.61</td>
</tr>
<tr>
<td>NbCl₅⁺</td>
<td>Red thermal flash, initiation at 220 °C</td>
<td>NbCN</td>
<td>4.418</td>
</tr>
<tr>
<td>TaCl₅⁺</td>
<td>Red thermal flash, initiation at 220 °C</td>
<td>TaC₁₂N₁₂⁺</td>
<td>4.397</td>
</tr>
<tr>
<td>ZrCl₅⁺</td>
<td>Red thermal flash, initiation at 340 °C</td>
<td>ZrCN⁺⁺</td>
<td>—</td>
</tr>
</tbody>
</table>

*All the products were annealed at 550 °C for 12-96 hours.

$n = 1.7 \times 10^{-3}$ moles Ca₃N₂/0.78 $\times 10^{-3}$ moles CaC₂, $m = 2.36 \times 10^{-3}$ moles Ca₃N₂/0.625 $\times 10^{-3}$ moles CaC₂).

$x₁ > x₂$, $y₁ < y₂$, sample poorly crystalline and the lattice parameter could not be calculated using the XRD pattern.

---

**Figure 3.14**  
[111] X-ray powder diffraction peaks for: (a) tantalum carbide prepared using tantalum pentachloride and calcium carbide using flame initiation, (b) tantalum nitride prepared using tantalum pentachloride and lithium nitride in a bulk reaction, (c-d) tantalum carbonitrides prepared using tantalum pentachloride and preannealed mixtures of calcium carbide and calcium nitride of varied molar ratios (bulk reactions) (Table 3.5).
3.5 THERMODYNAMIC CONSIDERATIONS

Transition metal carbides can be produced from a range of transition metal halides and three carbide precursors (Al₄C₃, CaC₂, SrC₂) via solid state metathetical routes. The precursors available for such synthesis have varying thermodynamic stabilities. Hess’s Law has been used to determine the exothermicity of some reactions. A relationship was found between the reaction rates and the calculated exothermicities for the reactions in which carbides of calcium, strontium and aluminium were used (Equations 3.8-3.11). Although the calculated reaction enthalpies for the reaction of magnesium carbide with transition metal halides are the most exothermic these reactions did not propagate.

\[
\begin{align*}
2\text{MoCl}_5 + 5\text{MgC}_2 &\rightarrow \text{Mo}_2\text{C} + 5\text{MgCl}_2 + 9\text{C} \quad \text{eqn. 3.8} \\
\Delta H_{298}^{\circ} &\approx -3586.8 \text{ kJ mole}^{-1} \quad \text{(no reaction)} \hfill \\
2\text{MoCl}_5 + 5\text{CaC}_2 &\rightarrow \text{Mo}_2\text{C} + 5\text{CaCl}_2 + 9\text{C} \quad \text{eqn. 3.9} \\
\Delta H_{298}^{\circ} &\approx -2676.7 \text{ kJ mole}^{-1} \quad \text{(fast bulk or propagation reaction)} \\
2\text{MoCl}_5 + 5\text{SrC}_2 &\rightarrow \text{Mo}_2\text{C} + 5\text{SrCl}_2 + 9\text{C} \quad \text{eqn. 3.10} \\
\Delta H_{298}^{\circ} &\approx -2720.7 \text{ kJ mole}^{-1} \quad \text{(fast bulk or propagation reaction)} \\
2\text{MoCl}_5 + 5/6\text{Al}_4\text{C}_3 &\rightarrow \text{Mo}_2\text{C} + 10/6\text{AlCl}_3 + 9/6\text{C} \quad \text{eqn. 3.11} \\
\Delta H_{298}^{\circ} &\approx -1176.4 \text{ kJ mole}^{-1} \quad \text{(slow bulk reaction, no propagation reaction)}
\end{align*}
\]

Another factor influencing the rates of solid state metathetical reactions, which must be taken into account is the mode of initiation of the reaction. It has been observed that reactions initiated at the melting point of one of the reagents tended to be more rapid than those caused by decomposition or structural change. This is exemplified by equations 3.12-3.13. This may also be due to the fact that transition metal halides that melt below 450 °C (point of structure change in CaC₂) tend to be of higher oxidation states. Solid state metathetical preparations are driven to their completion by the formation of co-product salt, which in these reactions can account for up to 90 % of the reaction enthalpy.\textsuperscript{117} Therefore
reactions involving more volatile (higher oxidation state) halides are typically more exothermic and more rapid due to the fact that more co-produced salt is formed.

\[
\begin{align*}
2\text{MoCl}_3 + 5\text{CaC}_2 & \rightarrow \text{Mo}_2\text{C} + 5\text{CaCl}_2 + 9\text{C} \quad \text{eqn. 3.12} \\
T_m &= 210 \, ^\circ \text{C} \\
2\text{MoCl}_3 + 3\text{CaC}_2 & \rightarrow \text{Mo}_2\text{C} + 3\text{CaCl}_2 + 5\text{C} \quad \text{eqn. 3.13} \\
T_m &= 470 \, ^\circ \text{C}
\end{align*}
\]

\[\text{m. pt. MoCl}_3 = 194 \, ^\circ \text{C}, \text{m. pt. MoCl}_3 = 1027 \, ^\circ \text{C}\]

Four principal factors are important in determining the rates in solid state metathetical preparations of transition metal carbides:

- Oxidation state (melting point) of transition metal halide
- Carbide precursor used ($\Delta H_f = \text{CaC}_2 > \text{SrC}_2 > \text{Al}_4\text{C}_3 > \text{MgC}_2$)
- Halide used
- Transition metal involved

Interestingly, transition metal halides react with carbides of calcium and strontium when initiated with flame under a nitrogen atmosphere giving transition metal carbides of variable purity (Table 3.3). Some of these reactions are incomplete (Group 4 transition metal halides). Group 5 transition metal halides produce highly crystalline transition metal carbides under these conditions. Group 6 transition metal carbides were obtained with some incorporation of an additional phase of transition metal. Transition metal carbides of groups 7-9 were not obtained at all using this method. The products obtained from these flame initiated reactions are more crystalline than those obtained by reacting the corresponding reagents inside of ampoules and then annealed for a long period. Attempts to initiate the reactions of Group 4-6 transition metal halides with Group 2 carbides using a filament failed with the reactions occurring only at the point source, when the filament temperature used was 900 °C. The most likely
explanation for this is that the filament provides heat only very locally at the tip of the wire. Flame provides heat required for initiation over a large surface area of the reactants.

Solid state reactions of transition metal halides with calcium carbide using flame initiation showed a great shift in reaction rates throughout the transition metal Groups 4-9. In general the propagation wave is faster for the latter transition metal halides. Group 4 halides propagated very slowly and the reactions were most often incomplete. Group 5 pentahalides reacted with calcium carbide rapidly giving crystalline Group 5 carbides and calcium chloride. A slow propagation wave was observed for the reaction of vanadium trichloride with calcium carbide when initiated with a flame. The reactions of Group 6-9 transition metal carbides occurred even more rapidly with some of the co-product subliming away giving a mixture of transition metal carbide and transition metal, or pure transition metal in the final product. Heats of reactions of 3 Group 4-6 transition metal trichlorides with calcium carbide show that reaction exothermicities can be empirically related to rates of propagation reactions (equation 3.14-3.16).

\[
\begin{align*}
\text{TiCl}_3 + \frac{3}{2}\text{CaC}_2 & \rightarrow \text{TiC} + \frac{3}{2}\text{CaCl}_2 + 2\text{C} \\
\Delta H_{298}^\circ &= -566.2 \text{ kJ mole}^{-1} \quad \text{(slow incomplete reaction)} \\
\text{VCl}_3 + \frac{3}{2}\text{CaC}_2 & \rightarrow \frac{1}{8}\text{V}_8\text{C}_7 + \frac{3}{2}\text{CaCl}_2 + \frac{17}{8}\text{C} \\
\Delta H_{298}^\circ &= -624.1 \text{ kJ mole}^{-1} \quad \text{(slow complete reaction)} \\
\text{MoCl}_3 + \frac{3}{2}\text{CaC}_2 & \rightarrow \frac{1}{2}\text{Mo}_2\text{C} + \frac{3}{2}\text{CaCl}_2 + \frac{5}{2}\text{C} \\
\Delta H_{298}^\circ &= -741.1 \text{ kJ mole}^{-1} \quad \text{(rapid complete reaction)}
\end{align*}
\]

3.6 SUMMARY

Solid state metathetical routes can be utilised for convenient preparations of transition metal carbides using a choice of metal halides and carbide precursors to control product particle size. Most of these preparations are an improvement over commercial routes with their low energy inputs, high reaction rates leading
to comparably phase pure products. Many reagent manipulations, such as addition of salt or spreading the reagents, applied to transition metal nitride formations have been repeated in the solid state metathetical syntheses of transition metal carbides. These show that product particle size can be modified by small changes in reaction conditions. These studies are further discussed in chapter 7.

Due to the novelty of metathetical preparations of transition metal carbides, studies of the as prepared solids were performed in more detail than those performed on products from the preparations of transition metal nitrides. All the by-products formed were either removed via sublimation in the process of the reaction or by using inexpensive solvents such as water or dilute mineral acids.

EELS analysis performed on a selection of cubic rocksalt transition metal carbides produced via solid state metathetical preparations showed little or no oxygen contamination. ELNES analysis was used to study a selection of samples. Products from the reactions of three carbide precursors (CaC₂, SrC₂, Al₄C₃) with transition metal halides were investigated. The samples produced were also used to study the ELNES technique and the following conclusions were extracted:

- Substitution on the metal sublattice has a principal effect on the shape of the C K ionisation edge
- Substitution on metal and non-metal sublattice has a more complex effect on the metal L₂,3 ionisation edge
- Substitution on metal or non-metal sublattice degrades the splitting of the white line present in the Ti and V L₂,3 ionisation edges

3.7 EXPERIMENTAL

All manipulations and analysis were performed as generalised in Chapter 2. Calcium carbide was purchased from Aldrich Chemical Co and was 80% pure. Strontium carbide was synthesised by reacting strontium metal with graphite at 800°C inside an evacuated ampoule.¹⁴⁰ Ampoules used in all the reactions were made from quartz or Pyrex (1 cm diameter, 20 cm long). Distilled water was used
to dilute HCl acid to 5% which was then applied in the purification of the crude products.

*Ampoule reactions of CaC₂ and SrC₂ with anhydrous metal halides, MCl₂ (M = Cr, Fe), MCl₃ (M = Ti, V, Cr, Mo, Fe), MCl₄ (M = Zr, Hf, W), MCl₅ (M = Nb, Ta, Mo), WCl₆, TiI₄, FeBr₂.*

Tantalum pentachloride, TaCl₅ (0.18 g, 0.5 mmol), and calcium carbide, \( \frac{5}{2} \text{CaC}_2 \) (0.08 g, 1.25 mmol), were ground together and heated inside an evacuated Pyrex glass ampoule. A rapid bulk reaction initiated within the 200-450 °C range. The temperature was ramped to 500-550 °C, left for an hour and allowed to cool to ambient temperature. The solids were triturated with methanol (5 x 6 ml), water and dilute mineral acid, dried *in vacuo* and analysed by powder X-ray diffraction, SEX/EDXA and FTIR. (Microanalysis: reaction of niobium pentachloride with calcium carbide, C, 11.13; H, 0.16; N, 0.11. Calcd.: NbC, 11.43 wt.%, ∴NbC₀.₉₇). Chemical yields were variable at 65–85 % with losses attributed to mechanical sources and incomplete reaction.

*Flame initiated reactions of CaC₂ and SrC₂ with anhydrous metal halides, MXₙ (n = 3, M = V, Mo, Cr; n = 4, M = W, n = 5, M = Nb, Ta, Mo; n = 6, M = W)*

Tantalum pentachloride, TaCl₅ (0.27 g, 0.75 mmol), and calcium carbide, \( \frac{5}{2} \text{CaC}_2 \) (0.12 g, 1.875 mmol), were ground together and placed on an asbestos plate in air. The reaction was initiated by application of a flame from a gas torch at *ca.* 1000 °C. This initiation sparked off a very rapid high temperature reaction, which left a partly fused powder and caused some of the salt produced to sublime. The solids formed in this way were triturated with methanol (5 x 6 ml), water and dilute mineral acid. Then they were dried *in vacuo* for analysis by powder XRD, SEM/EDXA and FTIR.
Ampoule reactions of aluminium carbide with anhydrous metal chlorides, $MCl_n$
($n = 2$, $M = Cr, Fe$; $n = 3$, $M = Ti, V, Cr, Mo, Fe$; $n = 4$, $M = Zr, Hf, W$; $n = 5$, $M = Nb, Ta, Mo$; $n = 6$, $M = W$), and iron dibromide

Tantalum pentachloride, $TaCl_5$ (0.32 g, 0.9 mmol), and $5/12Al_4C_3$ (0.05 g, 0.375 mmol) were ground together and placed into a tube furnace inside a long sealed off and evacuated quartz ampoule. The ampoule was placed with 1/3 of its length outside the furnace at 500 °C. The mixture was left for 2-3 hours and then the temperature was raised to 1000 °C to anneal for 2-3 days. The aluminium chloride co-product separated from the desired carbide by sublimation to the cool end of the ampoule. The carbide was still be triturated with THF (2 x 5 ml) and methanol (1 x 10 ml). When the black or grey solid was dried in vacuo it was analysed using XRD, SEM/EDXA, FT-IR, elemental microanalysis and in many cases PEELS and TEM. (Microanalysis: reaction of vanadium trichloride with aluminium carbide, C 13.75, H 0.21, N 0.19 %; Calcd. $V_8C_7$ C = 17.07 % $\therefore V_8C_{5.64}$; reaction of molybdenum trichloride with aluminium carbide, C 6.66, H 0.0, N 0.0 %; Calcd. $Mo_2C$ C = 5.88 % $\therefore Mo_2C_{1.1}$; reaction of tungsten tetrachloride with aluminium carbide, C 6.64, H 0.14, 0.0 %; Calcd. $WC$ C = 6.12 % $\therefore WC_{1.08}$.)
CHAPTER 4

PREPARATIONS OF TRANSITION METAL SILICIDES

4.1 INTRODUCTION

Transition metal silicides are a group of compounds of considerable importance as ceramic materials. The most studied transition metal silicide is molybdenum disilicide. This is due to its utilisation as a high temperature material. Figure 1.3 shows most of the existing phases of transition metal silicides.

Solid state metathetical processes provide a choice of reagents for the preparations of metal silicides. In previous work a number of transition metal halides were used to produce transition metal silicides in reactions with magnesium silicide, $\text{Mg}_2\text{Si}$. The work presented in this chapter discusses the reactions of transition metal halides with silicides of lithium, calcium and magnesium ($\text{Li}_2\text{Si}$, $\text{CaSi}_2$ and $\text{Mg}_2\text{Si}$). There is a range of siliciding reagents, which were not studied in this work. These include metal rich silicides of calcium ($\text{Ca}_2\text{Si}$ or $\text{CaSi}$), which can also be envisaged to produce metal rich silicides.

One of the main problems in preparations of metal silicides is the co-formation of silicon, which cannot be removed easily using laboratory techniques. In this work a new approach was developed to synthesise transition metal disilicides using solid state metathesis. Variation of the ratio of metal to silicon by using mixed precursors, such as, magnesium and calcium silicides enabled the synthesis of a range of metal or silicon rich phases with no elemental silicon impurity. The molar ratio of these reagents required for various reactions is presented in section 4.2.

Metal silicides produced via solid state metathetical pathways using transition metal halides and Group 1 and 2 metal silicides were analysed by XRD,
FT-IR and SEM/EDXA. Results regarding control of the experiments are discussed in detail in chapter 7.

4.2 SYNTHESIS

(i) **Reactions performed inside ampoules (bulk reactions)**

Reactions of Group 4-6 transition metal halides with silicides of lithium and calcium or a calcium silicide/magnesium silicide mix inside sealed, evacuated ampoules at a temperature of 550 °C produce transition metal silicides and co-product salt of Group 1 or 2 metal (Table 4.1-4.2). All the reactions initiated at the melting point of the transition metal halide and propagated with a yellow to orange thermal flash. In all the reactions much of the co-product (LiCl, MgCl$_2$ or CaCl$_2$) sublimed away to the cooler end of the ampoule leaving a partially fused grey solid. After opening the ampoule the product was triturated with methanol. Some of the products were annealed for up to 24 hours but this was not necessary to obtain crystalline products, since the as-formed materials were generally crystalline. Most of the reactions of Group 6 transition metal halides with siliciding reagents also yielded some transition metal as a minor phase.

Reactions of transition metal halides with magnesium silicide inside sealed and evacuated quartz ampoules produced poorly crystalline transition metal silicides, which then required annealing to produce crystalline solids. All of these reactions initiated within the 200-700 °C temperature range. The reactions of the most volatile transition metal halides (NbCl$_5$, TaCl$_5$, MoCl$_5$) occurred with a thermal flash. After the initiation the reacted mixtures were brought to a temperature of 800 °C and annealed for 2-8 hours. The resulting grey, partially fused solids were triturated with methanol to remove the co-product salt. All of the products identified were transition metal silicides (Table 4.3).

The reactions of magnesium silicide with lower oxidation state transition metal halides (< +4) were very slow and often they required high temperatures to proceed. Magnesium silicide also provides an insufficient amount of silicon to produce stoichiometric transition metal disilicides (equations 4.1-4.2).
TaCl₃ + 5/4Mg₂Si → TaSi₁₂₅* + 5/4MgCl₂  
MoCl₃ + 3/4Mg₂Si → MoSi₀.₇₅* + 3/4MgCl₂  

*Note the equations show the stoichiometric reactions. In actuality MSi₂ phases were seen from the reactions as well as metal.

Table 4.1  
Reactions of transition metal halides with lithium and calcium silicides initiated with flame (fl), filament (fil), by grinding (gr), or performed inside evacuated ampoules (bk).*  
Literature lattice parameters were taken from reference [159].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products after annealing and trituration</th>
<th>a_{ab} Å / ±0.001</th>
<th>a_{bc} Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiI₄ + CaSi₂ (bk)</td>
<td>TiSi₂</td>
<td>a = 8.261, b = 8.547,</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 4.795</td>
<td>a = 8.269, b = 8.553,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c = 4.798</td>
</tr>
<tr>
<td>ZrCl₄ + CaSi₂ (fil)</td>
<td>ZrSi₂ [Si]</td>
<td>a = 3.697, b = 14.744,</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 3.665</td>
<td>a = 3.696, b = 14.751,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c = 3.665</td>
</tr>
<tr>
<td>ZrCl₄ + Li₃Si (fl)</td>
<td>ZrSi₂</td>
<td>a = 3.691, b = 14.722,</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 3.659</td>
<td>a = 3.696, b = 14.751,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c = 3.665</td>
</tr>
<tr>
<td>VCl₃ + CaSi₂ (fil)</td>
<td>VSi₂</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>NbCl₅ + Li₃Si (fil)</td>
<td>NbSi₃</td>
<td>a = 4.776, c = 6.552</td>
<td>a = 4.797, c = 6.592</td>
</tr>
<tr>
<td>NbCl₅ + CaSi₂ (bk)</td>
<td>NbSi₂ [Si]</td>
<td>a = 4.791, c = 6.581</td>
<td>a = 4.797, c = 6.592</td>
</tr>
<tr>
<td>NbCl₅ + CaSi₂ (fil)</td>
<td>NbSi₂, Si</td>
<td>(NbSi₂) a = 4.787,</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 6.575</td>
<td>a = 4.797, c = 6.592</td>
</tr>
<tr>
<td>TaCl₅ + Li₃Si (fl)</td>
<td>TaSi₁₂</td>
<td>a = 4.777, c = 6.558</td>
<td>a = 4.784, c = 6.570</td>
</tr>
<tr>
<td>TaCl₅ + Li₃Si (bk)</td>
<td>TaSi₁₂</td>
<td>a = 4.777, c = 6.560</td>
<td>a = 4.784, c = 6.570</td>
</tr>
<tr>
<td>MoCl₅ + Li₃Si (gr)</td>
<td>Mo, Si [MoSi₂]</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>MoCl₅ + Li₃Si (bk)</td>
<td>Mo, Si [MoSi₂]</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>MoCl₅ + CaSi₂ (bk)</td>
<td>Mo, Si</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>WCl₅ + CaSi₂ (fil)</td>
<td>W, Si</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>

*Bulk reaction mixtures were heated to 550 °C. Some products were annealed for up to 24 hours at 550 °C. Products obtained from the reactions initiated with flame, filament or by grinding were not annealed.

*sample poorly crystalline and the lattice parameters were not calculated. [-] - minor phases present
Table 4.2  Reactions of transition metal halides with calcium silicide/magnesium silicide mix initiated with flame (fl), filament (fil) or performed inside evacuated ampoules (bk).

*Literature lattice parameters taken from reference [159].

<table>
<thead>
<tr>
<th>Transition metal halide</th>
<th>Products after trituration</th>
<th>$a_{obs}/\text{Å} +/-0.002$</th>
<th>$a_{lat}/\text{Å}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCl$_3$ (bk)</td>
<td>TiSi$_2$ [Ti$_2$Si$_3$]</td>
<td>(TiSi$_2$) $a = 8.273$, $b = 8.554$, $c = 4.800$</td>
<td>$a = 8.269$, $b = 8.553$, $c = 4.798$</td>
</tr>
<tr>
<td>ZrCl$_4$ (fil)</td>
<td>ZrSi$_2$</td>
<td>$a = 3.698$, $b = 14.743$, $c = 3.665$</td>
<td>$a = 3.696$, $b = 14.751$, $c = 3.665$</td>
</tr>
<tr>
<td>ZrCl$_4$ (fl)</td>
<td>ZrSi$_2$</td>
<td>$a = 3.698$, $b = 14.742$, $c = 3.665$</td>
<td>$a = 3.696$, $b = 14.751$, $c = 3.665$</td>
</tr>
<tr>
<td>HfCl$_4$ (bk)</td>
<td>HfSi$_2$</td>
<td>$a = 3.670$, $b = 14.521$, $c = 3.633$</td>
<td>$a = 3.680$, $b = 14.556$, $c = 3.649$</td>
</tr>
<tr>
<td>VCl$_5$ (bk)</td>
<td>VSi$_2$</td>
<td>$a = 4.578$, $c = 6.373$</td>
<td>$a = 4.572$, $c = 6.373$</td>
</tr>
<tr>
<td>NbCl$_5$ (bk)</td>
<td>NbSi$_2$ [Si]</td>
<td>(NbSi$_2$) $a = 4.786$, $c = 6.567$</td>
<td>$a = 4.797$, $c = 6.592$</td>
</tr>
<tr>
<td>NbCl$_5$ (fl)</td>
<td>NbSi$_2$</td>
<td>$a = 4.794$, $c = 6.582$</td>
<td>$a = 4.797$, $c = 6.592$</td>
</tr>
<tr>
<td>TaCl$_5$ (bk)</td>
<td>TaSi$_2$</td>
<td>$a = 4.771$, $c = 6.556$</td>
<td>$a = 4.784$, $c = 6.570$</td>
</tr>
<tr>
<td>TaCl$_5$ (fl)</td>
<td>TaSi$_2$ [Ta$_2$Si$_3$]</td>
<td>$a = 4.776$, $c = 6.560$</td>
<td>$a = 4.784$, $c = 6.570$</td>
</tr>
<tr>
<td>TaCl$_5$ (fil)</td>
<td>TaSi$_2$</td>
<td>$a = 4.786$, $c = 6.576$</td>
<td>$a = 4.784$, $c = 6.570$</td>
</tr>
<tr>
<td>CrCl$_3$ (bk)</td>
<td>CrSi$_2$, Cr</td>
<td>(CrSi$_2$) $a = 4.425$, $c = 6.354$</td>
<td>$a = 4.428$, $c = 6.369$</td>
</tr>
<tr>
<td>MoCl$_5$ (bk)</td>
<td>MoSi$_2$, Mo</td>
<td>(MoSi$_2$) $a = 3.198$, $c = 7.836$</td>
<td>$a = 3.205$, $c = 7.845$</td>
</tr>
<tr>
<td>MoCl$_5$ (fil)</td>
<td>MoSi$_2$ [Mo]</td>
<td>$a = 3.201$, $c = 7.839$</td>
<td>$a = 3.205$, $c = 7.845$</td>
</tr>
<tr>
<td>WCl$_4$ (bk)</td>
<td>W, Si [WSi$_2$]</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>FeCl$_3$ (bk)</td>
<td>FeSi$^\alpha$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>LaCl$_3$ (bk)</td>
<td>LaSi$_3$</td>
<td>$a = 4.298$, $c = 13.861$</td>
<td>$a = 4.281$, $c = 13.75$</td>
</tr>
</tbody>
</table>

*The molar ratio of calcium silicide and magnesium silicide was manipulated to obtain fully stoichiometric transition metal disilicides. For example for zirconium disilicide: $3ZrCl_4 + 2Mg_2Si + 2CaSi_2$. The reaction mixtures were heated to 550 °C and then cooled down before trituration. Some were annealed for up to 24 hours. Products obtained from the reactions initiated with flame or filament were not annealed.

*sample poorly crystalline and the lattice parameters were not calculated. [l]– minor phases present.

Calcium silicide is more reactive than magnesium silicide in these solid state metathetical reactions and often lowers the temperatures required for reaction initiation. It also raises reaction exothermicities increasing the maximum reaction temperature and on most occasions giving more crystalline products. Although calcium silicide is silicon rich and provides excess silicon, an exact tuned ratio of magnesium silicide to calcium silicide, dependent on the transition
metal halide used, provides a fully stoichiometric disilicide. For example, for the formation of tantalum disilicide from tantalum pentachloride, the ratio is 4 : 1 (equations 4.3-4.5).

\[
\begin{align*}
\text{TaCl}_3 + \frac{5}{4}\text{Mg}_2\text{Si} & \rightarrow \text{TaSi}_{1.25} + \frac{5}{4}\text{MgCl}_2 & \text{eqn. 4.3} \\
\text{TaCl}_3 + \frac{5}{2}\text{CaSi}_2 & \rightarrow \text{TaSi}_2 + \frac{5}{4}\text{CaCl}_2 + \frac{1}{2}\text{Si} & \text{eqn. 4.4} \\
(\frac{1.25 \times 4 + 5 \times 1}{5}) &= 2 & \therefore \text{TaSi}_2 \\
\text{thus:} \\
(4\text{TaCl}_3 + 5\text{Mg}_2\text{Si}) + (1\text{TaCl}_3 + \frac{5}{2}\text{CaSi}_2) & \rightarrow \text{5TaSi}_2 + 10\text{MgCl}_2 + \frac{5}{2}\text{CaCl}_2 & \text{eqn. 4.5}
\end{align*}
\]

During the preparation of the reagent mixture inside the nitrogen filled glove box the two silicon precursors, magnesium silicide and calcium silicide, were always thoroughly pre-ground together before adding the transition metal halides.

Table 4.3 Reactions of transition metal halides with magnesium silicide initiated with a filament (fil), a flame (fl) or performed inside evacuated quartz ampoules (bk).* Literature lattice parameters were taken from reference [159].

<table>
<thead>
<tr>
<th>Transition metal halide</th>
<th>Products after annealing and trituration</th>
<th>(a_{obs}/\text{Å} +/- 0.001)</th>
<th>(a_{lat}/\text{Å})</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCl₃ (bk)</td>
<td>TiSi₂⁺</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>VCl₃ (bk)</td>
<td>VSi₂, VsSi₃</td>
<td>(a = 4.573, c = 6.376)</td>
<td>(a = 4.572, c = 6.373)</td>
</tr>
<tr>
<td>NbCl₅ (fl)</td>
<td>NbSi₂</td>
<td>(a = 4.783, c = 6.566)</td>
<td>(a = 4.797, c = 6.592)</td>
</tr>
<tr>
<td>MoCl₅ (bk)</td>
<td>MoSi₂, Mo</td>
<td>(a = 3.201, c = 7.838)</td>
<td>(a = 3.205, c = 7.845)</td>
</tr>
<tr>
<td>TaCl₅ (fl)</td>
<td>TaSi₂⁺</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

*All the reactions initiated at 200-700 °C and the solids were then annealed at 800 °C for 2-8 hours.

⁺sample poorly crystalline and the lattice parameters were not calculated.
(ii) Reactions initiated with a flame or a filament (propagation reactions)

Reactions of transition metal halides with silicides of lithium and calcium, or a calcium silicide/magnesium silicide mix, can also be initiated with a flame or a filament (Tables 4.1 and 4.2). After the initiation, the reactions propagate very rapidly with a bright orange flash to produce a partially fused solid. Some of the co-product salt is sublimed away from the products. Magnesium silicide reacted only with a selection of transition metal halides under these conditions (Table 4.3). The reactions that worked were completed within 2-5 seconds of initiation and resulted in highly crystalline products. These products were tritutrated in the same way as the materials obtained from the reactions performed inside ampoules.

All of the reactions discussed in this chapter can be generalised by equations 4.6-4.8. The yields obtained from these preparations were generally high (80-90 %); the exceptions were the reactions of the most volatile transition metal halides with magnesium silicide, in which some of the transition metal halide sublimed away from the silicide reagent before reacting. In these cases the resultant excess magnesium silicide decomposed during washing with water and the resulting products were easily removed with dilute acid.

Scheme 4.1 Schematic equations typifying the SSM reactions discussed in this chapter.

\[
\begin{align*}
MX_n + n/2Li_2Si &\rightarrow MSi_{2x} + nLiCl + [(n/2-2) + 2(1-x)]Si \quad \text{eqn. 4.6} \\
MX_n + n/4Mg_2Si &\rightarrow MSi_{2x} + n/2MgCl_2 \quad \text{eqn. 4.7} \\
MX_n + n/2CaSi_2 &\rightarrow MSi_{2x} + n/2CaCl_2 + [(2n/2-2) + 2(1-x)]Si \quad \text{eqn. 4.8}
\end{align*}
\]

X-ray powder diffraction patterns, FT-IR and SEM/EDXA were performed for both crude and tritutrated samples. Details regarding the instruments used in characterisation are included in the experimental section.
4.3 CHARACTERISATION

4.3.1 X-ray powder diffraction

(i) Bulk reactions

Solid state metathesis reactions of transition metal halides with Group 1 and 2 silicides performed inside evacuated ampoules at temperatures between 200 °C and 400 °C yield transition metal silicides and the corresponding Group 1 and 2 halides (Tables 4.1-4.3). Group 6 silicides were usually obtained with some additional transition metal phase (figure 4.1). The co-formation of the parent transition metal was later prevented by the addition of a small amount of diluent salt such as magnesium chloride, which was ground together with the reagents before initiating the reaction. These pre-reaction work-ups are discussed more closely in chapter 7. The reactions in which calcium silicide was used yielded some silicon as the co-product. Products obtained from the reactions in which calcium or lithium silicide were used tended to be more crystalline than those obtained from the reactions with magnesium silicide (crystallite size of the order 400-1400 Å cf 200-300 Å as calculated from XRD line broadening using the Scherrer equation).

X-ray diffraction patterns of crude and triturated products obtained from the reactions of transition metal halides and Group 1 and 2 silicides showed that washing with water successfully removed the co-produced salts. The products obtained from the reactions of transition metal halides with lithium and calcium silicides were crystalline and did not require any annealing (equation 4.9).

\[
\text{VCl}_3 + \frac{3}{2}\text{CaSi}_2 \rightarrow \text{VSi}_2 + \frac{3}{2}\text{CaCl}_2 + \text{Si}
\]

eqn. 4.9
Figure 4.1  XRD pattern of the triturated sample from the bulk reaction of molybdenum pentachloride with a calcium silicide/magnesium silicide mix. Bottom stick diffraction patterns for molybdenum disilicide and molybdenum (dashed lines) have been shown. The remaining unidentified low intensity peaks are all due to Mo$_5$Si$_3$.

The reactions of low oxidation state transition metal halides ($< +4$) with magnesium silicide required several hours of annealing to complete the SSM process. Some metal silicides may have formed within minutes, for example the reaction of magnesium silicide with tantalum pentachloride as a rapid colour change was observed at ca. 200 °C. However the products from such reactions could not be identified because they were amorphous. Some unreacted transition metal halides were detected on the ampoule walls after they were opened. This suggests that these reactions occur slowly and after initiation at raised temperatures under vacuum some of the volatile reagents escape from the reaction mixture. As a result excess magnesium silicide should be present in the reaction mixture. In many cases triturated solids evolved a lot of gas due to the decomposition of unreacted magnesium silicide. Whether these reactions are incomplete or the transition metal halide sublimes to the cooler end of the ampoule could not be determined. To yield crystalline products for X-ray powder
diffraction analysis the solids had to be reacted/annealed to at least 700 °C for several hours after the critical metathesis reaction.

The products obtained from the reactions of Group 4 and 5 transition metal halides with mixed calcium and magnesium silicides at appropriate ratios (as discussed in section 4.2) contained pure phases of Group 4 and 5 transition metal disilicides (figure 4.2). No metal or silicon was found using X-ray powder diffraction analysis. However the reactions of Group 6 transition metal halides with a mix of these siliciding reagents produced some undesired transition metal phase.

The starting reagent magnesium silicide and calcium silicide mix contained two components with different molar amounts of silicon. Therefore, it was expected that products obtained from such reactions might contain a mixture of silicides with varied stoichiometry. The stoichiometry was best investigated using SEM/EDXA to identify the atomic percentages of metal and silicon throughout different particles of each sample. Nevertheless, X-ray powder diffraction patterns can also be helpful for determining stoichiometric homogeneity since if the sample is not homogeneous then broadened or even 'doublet' peaks will be observed. X-ray powder diffraction patterns determined for all these samples showed sharp peaks, suggesting both homogeneity and high crystallinity (figure 4.2). In fact, after performing some repeat test reactions it was concluded that most of these silicides (Group 5-8) prepared using this method were crystalline (crystallite size or the order 300-1000 Å, calculated from XRD line broadening) without any annealing.

(ii) Propagation reactions

Reactions of transition metal halides with lithium or calcium silicide, or a calcium silicide/magnesium silicide mix were also initiated using a filament or a flame from a gas torch (Tables 4.1-4.3). The products obtained from such reactions were highly crystalline. Group 4 and 5 transition metal disilicides prepared using transition metal halides and lithium or magnesium silicide, or calcium silicide/magnesium silicide mix were all obtained as pure single phases. All samples, including those obtained using a mix of calcium silicide and magnesium silicide, showed homogeneous stoichiometry when analysed using
Figure 4.2  XRD patterns for tantalum disilicides formed using tantalum pentachloride and calcium silicide/magnesium silicide mixes of variable molar ratios. The desired stoichiometries of these products were TaSi$_{1.99}$ (a) and TaSi$_{1.70}$ (b). Fully inserted in a box (c) is the $[111]$ diffraction peak for the TaSi$_{1.99}$ and TaSi$_{1.70}$ predicted phases formed (dashed line in the stick pattern for tantalum disilicide pointed below). Stoichiometric tantalum disilicide is shown in the stick pattern.

EDXA. The reactions of molybdenum pentachloride and tungsten tetrachloride with calcium silicide/magnesium silicide mix yielded the disilicides, Group 2 salts and the metals. However when magnesium chloride was used as an inert heat sink in similar reactions, pure molybdenum disilicide was obtained after trituration of the ‘as-prepared’ product with water. Details regarding the amount of salt used in the reaction of molybdenum pentachloride with calcium silicide/magnesium silicide mix are represented in scheme 4.2.
Reagent combination: MoCl₅ : CaSi₂ : Mg₂Si  
Molar ratio: 9 : 2.5 : 10
Initiation temperature: 180 °C
Products: MoSi₂, CaCl₂, MgCl₂, Mo, Si

Scheme 4.2. Preparations of molybdenum silicide (MoSi₂₅, x ≈ 0.9). Reactions performed with and without the use of magnesium chloride as an inert heat sink.

Reaction of iron trichloride and a calcium silicide/magnesium silicide mix led to the formation of iron silicide (FeSi). It should be noted that this phase could only be obtained phase pure when some salt was added to the reagents to act as an inert heat sink, in the absence of salt, some iron metal and silicon were produced.

X-ray powder diffraction patterns of these products revealed that with the appropriate choice of reagents it is possible to ‘tune’ the particle size of the material. Altering the reaction conditions or manipulating the reagent mixtures, for example by spreading the reagents, could also affect the product microstructure. This is discussed more widely in chapter 7 along with results obtained from the solid state metathetical synthesis of borides, carbides and nitrides.

4.3.2 SEM/EDXA

SEM measurements of the crude products from the reactions of transition metal halides with lithium, calcium and magnesium silicide or a calcium silicide/magnesium silicide mix always showed a smooth and homogeneous coating of the co-produced salts (figure 4.3a-b). However there was a significant contrast in the size of the agglomerates observed in different samples. Products obtained from the reactions of Group 5 or 6 transition metal halides with lithium and calcium silicide had larger agglomerates than the products from the reactions where magnesium silicide was used.

SEM photographs obtained for triturated products from the reactions of transition metal halides with lithium and calcium silicide or magnesium silicide/calcium silicide mix also showed varied morphology (figure 4.3c-d). Unlike the crude samples these were usually composed of agglomerates with
sharper shapes and usually smaller size. The particle size distribution was usually small within the samples, with the exception for some Group 4 silicides. The products obtained from the reactions of transition metal halides with magnesium silicide were in the form of very small agglomerates and sometimes contained impurities.

Figure 4.3  SEM micrographs of crude product from the reaction of tantalum pentachloride with a calcium silicide/magnesium silicide mix initiated with a flame (a-b), and triturated products from the same reaction (c), and the bulk reaction of titanium trichloride with a calcium silicide/magnesium silicide mix (d).
The particle sizes of the products obtained from the reactions of transition metal halides with silicide precursors, initiated using flame or filament or performed in bulk syntheses, did not vary as much as the products from the reactions forming transition metal carbides, discussed in chapter 3. However, some of the products from the reactions initiated with a filament had a greater particle size distribution within the same sample than those obtained by initiating a reaction using a flame or by heating inside an ampoule.

EDXA analysis of the crude products from the reactions of transition metal halides with Group 1 and 2 silicides showed the presence of transition metal, silicon, Group 1 or 2 metal and a halogen (figure 4.4a). Surfaces of these solids contained much more of the Group 1 and 2 metals and the halogens than transition metal and silicon. This may be due to the nature of solid state metathetical processes where the salt produced remains molten for some time throughout the reaction. Presumably the silicide forms within this molten flux. On cooling, the salt solidifies around the solid transition metal silicide and coats it. All triturated solids showed only metal and silicon present (figure 4.4b).

Transition metal silicides prepared using transition metal halides and calcium silicide/magnesium silicide mix were analysed for their homogeneity. The reasons for this were discussed in section 4.3.1. A selected group of samples were used to explore homogeneity; these showed little variation in the atomic ratios of transition metal to silicon.

The SEM/EDXA system was also used to perform linescan analyses on a few samples. Figure 4.5 shows the results obtained from analysis of tantalum disilicide prepared from lithium silicide and tantalum pentachloride in a bulk reaction after trituration. The patterns for tantalum and silicon show a relationship in the presence of the two elements on the sample surface. The samples were also cross-analysed for oxygen content. All showed some oxygen contamination.
Figure 4.4  EDXA analyses of surface of crude product from the reaction of tantalum pentachloride with a calcium silicide/magnesium silicide mix (a) and triturated product from the reaction of niobium pentachloride with a calcium silicide/magnesium silicide mix (b). Note that in (a) most of the coating of the particle is composed of the co-product salts.
Figure 4.5  
Linescan analysis of tantalum (a) and silicon (b) across the surface of triturated product from the bulk reaction of tantalum pentachloride with lithium silicide.

4.4 DISCUSSION

Solid state metathetical reactions of transition metal halides with Group 1 and 2 silicides yield transition metal disilicides. Some reactions also yield metal as a result of partial decomposition of the product due to the high reaction temperatures. This can be prevented by an appropriate work-up procedure such as spreading the reagents or adding a diluent salt of Group 1 or 2 metal. These procedures are discussed in detail in chapter 7. The reaction of iron (III) chloride with magnesium silicide yielded stoichiometric, poorly crystalline iron silicide, FeSi. The reactions in which magnesium silicide was used tended to be incomplete with some of the unreacted magnesium silicide hydrolysing during work-up by trituration with water. Further some of the transition metal halide sublimed to the cooler end of the ampoule during the reaction. This was only observed for the volatile transition metal halides such as the pentachlorides of niobium, tantalum, and molybdenum. The reactions in which magnesium silicide was used required various initiation temperatures (Table 4.2) but due to the poor crystallinity of the products the reacted solids were all annealed at 700 °C for several hours. This procedure was not necessary when the silicides of lithium or calcium were used as precursors because the products were crystalline within seconds after initiating the reactions. Here the initiations also depended on the melting points of the transition metal halides. Notably the as made materials
using lithium silicide, calcium silicide and a calcium silicide/magnesium silicide mix were crystalline as formed.

The reactions of transition metal halides with calcium silicide also produced silicon as a co-product. This was due to the excess silicon provided by calcium silicide, CaSi₂, in these reactions. Magnesium silicide, Mg₂Si, provides an insufficient quantity of silicon in these reactions to produce stoichiometric transition metal disilicides. Therefore using a mixture of these reagents in ratios determined according to the calculations discussed in section 4.2.1 allows the use of calcium and magnesium silicides to produce stoichiometric transition metal disilicides. It also enables control of the ratio of the transition metal and silicon within these disilicides in order to obtain substoichiometric disilicides (MSi₂ₓ, where x < 1) as represented in equations 4.10-4.11. This is discussed in detail in section 4.4.1.

\[
\begin{align*}
\text{VCl}_3 + \frac{3}{2}\text{CaSi}_2 & \rightarrow \text{VSi}_3 + \frac{3}{2}\text{CaCl}_2 \quad \text{eqn. 4.10} \\
\text{VCl}_3 + \frac{3}{4}\text{Mg}_2\text{Si} & \rightarrow \text{VSi}_{0.75} + \frac{3}{2}\text{MgCl}_2 \quad \text{eqn. 4.11}
\end{align*}
\]

\[(0.75 \times 2) + (3 \times 1)/3 = 1.5 \quad : \quad \text{molar ratio of Mg}_2\text{Si} : \text{CaSi}_2 \text{ required: } 2 : 1\]

Reactions of transition metal halides with lithium silicide and calcium silicide/magnesium silicide mix were also initiated with flame and/or filament. Some of these reactions also initiated on grinding. The products obtained from the reactions initiated with a filament were less crystalline than those obtained from the corresponding bulk reactions performed inside evacuated ampoules. The reactions of transition metal halides with calcium silicide, initiated with a flame or a filament, producing highly crystalline transition metal disilicides. However, silicon was always formed as a co-product. Since it is very difficult to remove silicon from the final products, this combination of reagents does not offer any advantages and was not studied any further.

The products obtained from the reactions discussed in this chapter were analysed using X-ray powder diffraction, FT-IR and SEM/EDXA for correlative studies. These included analyses of phase purity, crystallite and particle size,
stoichiometry and product homogeneity. The analyses were always performed both on triturated and as prepared samples.

SEM and XRD analyses on selected samples have shown that trituration removes the co-product salt and leaves crystalline phase-pure products. The particles in the as prepared products were characterised by a smooth morphology and rounded shapes with little surface detail. Triturated products were rough, possessed sharpened edges and more surface details were observed. The particle shapes were more angular and more cubical. Crystallinity of products from these reactions was improved by annealing the solids at 500 °C prior to trituration.

The yields obtained from all the reactions were high, in the order of 80-90%. Most of the losses in yields were due to triturations and mechanical handling. All the reactions were performed on a small scale.

4.4.1 Control of stoichiometry in transition metal disilicides

Formations of substoichiometric transition metal carbides and nitrides have already been discussed in previous chapters. The possibility of controlling the extent of carbon or nitrogen deficiency in transition metal carbides and nitrides obtained from solid state metathetical reactions is somewhat limited. However, the availability of mixed silicide precursors (Mg$_2$Si and CaSi$_2$) for these reactions allowed the formation of transition metal disilicides with a range of substoichiometries. These investigations were conducted in much more detail than the studies performed with the formations of transition metal carbides and nitrides. In all the reactions performed the aim was to control and obtain the desired stoichiometry of the final product. The method of calculating the molar ratios of these reagents required to obtain transition metal disilicide of desired stoichiometry is explained in section 4.2.1.

Since silicon is above the threshold of the EDXA system used it was possible to analyse a selection of transition metal disilicides produced by the reactions discussed in this chapter for stoichiometry and homogeneity. Products from the reactions of titanium trichloride, Group 5 chlorides and molybdenum tri- and pentachloride with a calcium silicide/magnesium silicide mix were studied. Particular emphasis was placed on the products, which were formed in the reactions where the M/Si ratio was manipulated. EDXA analyses of these
products showed that they were homogeneous and that the M/Si ratio in the final product can be conveniently manipulated. These results have not been obtained for the product of the reaction between titanium trichloride and the calcium silicide/magnesium silicide mix. In this exceptional case EDXA has showed on spot analysis regions across the product surface, which had Si : Ti ratios of 4 : 1. This may be due to the poor mixing of the reagents prior to initiating the reaction. However in most spot analyses this product possessed the M/Si ratio of ~1 : 1.85.

Results obtained from the reactions of transition metal halides with varied calcium silicide and magnesium silicide ratios have shown that the stoichiometry of transition metal disilicides prepared using these reagents can be ‘tuned’ (figure 4.2 and 4.6). These investigations were performed for the formations of disilicides of zirconium, tantalum, vanadium and molybdenum and are illustrated in Table 4.4. The reactions where more magnesium silicide was used yielded less crystalline solids. The extent of these manipulations is limited by the range of stoichiometries accessible before a structural phase change into a more metal rich system occurs. When too much magnesium silicide was added to the reagent mixture to yield highly silicon deficient transition metal disilicide then either a more metal rich phase was produced (for example V₅Si₅) or a mixture of these two silicides was obtained in the final product. Nevertheless the reactions that were performed to produce transition metal disilicides of varied silicon composition have shown that varying the ratio of calcium and magnesium silicides affects the stoichiometry of the final product. The changes in the M/Si ratio are illustrated by the lattice parameters of the products, which are linearly sensitive to the occupancy level according to Vegard’s Law. The solids produced in these reactions were annealed at 550 °C for 2 to 3 days. This was not necessary to obtain crystalline products, but additional annealing increases the degree of crystallinity, making X-ray diffraction peaks sharper, and therefore, the lattice parameter calculations of the final products more accurate. It must be noted here that even large changes in the M/Si ratio in the final product give only small shifts in the lattice parameters of transition metal disilicides.
Table 4.4  
*Bulk reactions of ZrCl₄, TaCl₅ and MoCl₃ with a calcium silicide/magnesium silicide mix with different ratios used to vary the substoichiometry of transition metal disilicide formed.*

<table>
<thead>
<tr>
<th>Transition metal halide</th>
<th>Desired stoichiometry</th>
<th>Products after annealing and trituration</th>
<th>( a_{\text{obs}}/\text{Å} )</th>
<th>Cell volume (( \text{Å}^3 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrCl₄</td>
<td>ZrSi₁.₉</td>
<td>ZrSi₂₁</td>
<td>( a = 3.699, )( b = 14.741, )( c = 3.666 )</td>
<td>199.855</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZrCl₄</td>
<td>ZrSi₁.₈</td>
<td>ZrSi₂₁</td>
<td>( a = 3.696, )( b = 14.737, )( c = 3.665 )</td>
<td>199.625</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZrCl₄</td>
<td>ZrSi₁.₇</td>
<td>ZrSi₂₁</td>
<td>( a = 3.693, )( b = 14.722, )( c = 3.661 )</td>
<td>199.064</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZrCl₄</td>
<td>ZrSi₁.₆</td>
<td>ZrSi₂₁</td>
<td>( a = 3.689, )( b = 14.718, )( c = 3.660 )</td>
<td>198.746</td>
</tr>
<tr>
<td>TaCl₅</td>
<td>TaSi₁.₉</td>
<td>TaSi₂₁</td>
<td>( a = 4.775, )( c = 6.557 )</td>
<td>129.460</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TaCl₅</td>
<td>TaSi₁.₈</td>
<td>TaSi₂₁</td>
<td>( a = 4.774, )( c = 6.557 )</td>
<td>129.435</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TaCl₅</td>
<td>TaSi₁.₇</td>
<td>TaSi₂₈</td>
<td>( a = 4.774, )( c = 6.556 )</td>
<td>129.396</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TaCl₅</td>
<td>TaSi₁.₆</td>
<td>TaSi₂₁</td>
<td>( a = 4.771, )( c = 6.553 )</td>
<td>129.164</td>
</tr>
<tr>
<td>MoCl₃</td>
<td>MoSi₁.₉</td>
<td>MoSi₂₈</td>
<td>( a = 3.206, )( c = 7.854 )</td>
<td>80.736</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MoCl₃</td>
<td>MoSi₁.₇</td>
<td>MoSi₂₁</td>
<td>( a = 3.202, )( c = 7.842 )</td>
<td>80.415</td>
</tr>
</tbody>
</table>

*To stop the co-formation of molybdenum in the reactions where molybdenum trichloride was used, magnesium chloride was added to act as an inert heat sink. All the reaction mixtures were brought to 550 °C and kept annealing for 2 to 3 days to yield highly crystalline solids.*
Figure 4.6  [101] X-ray powder diffraction peaks (with reference stick) of molybdenum disilicides formed using molybdenum trichloride and varied molar ratios of calcium silicide/magnesium silicide mix to 'tune' the disilicide product stoichiometry (MoSi$_{1.70}$ (a), MoSi$_{1.80}$ (b) MoSi$_{1.90}$ (c)). Note the shifts in the peaks showing varying stoichiometry.

4.5 THERMODYNAMIC CONSIDERATIONS

Transition metal silicides were prepared via bulk solid state metathesis using a variety of both silicon and transition metal precursors. Reactions involving calcium and lithium silicides were far more violent than those of magnesium silicide. However, it proved impossible to compare these reactions quantitatively, as the heats of formations for lithium and calcium silicides are not published in readily available texts. The heat of formation of magnesium silicide and the melting points for all three siliciding reagents used are listed in Table 4.5. It is observed that the melting points of these reagents are high, therefore, these reactions initiate at the melting/decomposition point of the transition metal halide precursor.
Table 4.5  
Melting points and heats of formations of silicide precursors used in this work

<table>
<thead>
<tr>
<th>silicide</th>
<th>Melting point/°C</th>
<th>$\Delta H_{298} \text{kJ mole}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$Si</td>
<td>760</td>
<td>—</td>
</tr>
<tr>
<td>Mg$_2$Si</td>
<td>1085</td>
<td>79.1</td>
</tr>
<tr>
<td>CaSi$_2$</td>
<td>980</td>
<td>—</td>
</tr>
</tbody>
</table>

4.6 SUMMARY

Solid state metathetical routes to transition metal silicides using transition metal halides and Group 1 and 2 silicides lead to the formation of fused solids composed of transition metal silicides and Group 1 or 2 metal halides. After appropriate trituration of these solids pure transition metal silicides are conveniently obtained. The reactions are characterised by their fast rates and high exothermicity even by the solid state metathetical standards. The products are usually crystalline but a range of varied crystallinities has been observed throughout the samples when pre-experimental work-ups were performed. These included additions of salt or spreading the reagents. It was also possible to produce nanocrystalline samples of transition metal silicides. Solid state metathetical preparations of transition metal silicides discussed in this chapter have no equal counterparts among currently utilised commercial preparations where input of energy, timing, equipment and simplicity of performance are concerned.

Analysis performed on crude and triturated products from solid state metathetical preparations of transition metal silicides have shown evidence for an elemental exchange reaction. In bulk reactions performed inside Pyrex ampoules some of the co-products were observed on the walls of the ampoules after the reactions. The remainder of these co-products were removed successfully using water.

A very interesting point is that despite the range of stoichiometry and number of possible structures available for each Group 4 and 5 transition metal silicide, solid state metathetical preparations were capable of forming the MSi$_{2-x}$ phase. However the silicon content in MSi$_{2-x}$ could be manipulated within
various ranges depending on the particular transition metal. Some products from the reactions contain some metal, although it was possible to avoid formation of such impurities. Investigation using magnesium chloride as an inert heat sink proved that Group 1 and 2 salts can be utilised in solid state metathetical preparations of transition metal silicides without incorporation of metal. Metal phases can also be removed from the final product in some cases by trituration with aqua regia.\textsuperscript{74}

This chapter explores widely the use of calcium disilicide as a precursor for solid state metathetical preparations of transition metal disilicides using the halides as the transition metal precursors. Excess silicon in this reagent combination required the use of metal rich magnesium silicide, Mg\textsubscript{2}Si, to counter-balance the transition metal to silicon ratio. This solution has proved not only successful in obtaining transition metal disilicides without the excess silicon present, but it also allowed control of the level of substoichiometry in the desired disilicides. Interestingly, calcium forms several silicides in various stoichiometries (CaSi, Ca\textsubscript{2}Si). These are rare on the commercial market. However, monostoichiometric calcium silicide provides the accurate quantity of silicon to produce pure stoichiometric transition metal disilicides using transition metal tetrahalides. The co-formation of calcium halides makes these reactions potentially highly exothermic.

4.7 EXPERIMENTAL

All reagents manipulations and weighings were performed as generalised in Chapter 2. All reagents were purchased from Aldrich Chemical Co.

Solvents were dried, distilled and degassed prior to use.

Ampoules were made from quartz (0.5 cm diameter, 12–15 cm long) and sealed with the reactants under vacuum.

X-Ray diffraction patterns were determined on a Siemens D 5000 transmission powder diffractometer using germanium monochromated Cu-K\textalpha\textsubscript{1} radiation (\(\lambda = 1.5406\) A). TREOR and METRIC-LS indexing programmes were used to determine lattice parameters. SEM/EDXA were obtained on a JEOL JSM 820 instrument using Kevex detector and software and a Hitachi SEM S-570. EDXA were obtained over many regions of the sample surface (point and whole
screen analysis) for regional homogeneity. FT-IR spectra were recorded on a Nicolet 205 instrument using pressed KBr discs.

Reactions of magnesium silicide with anhydrous metal chlorides, $MCl_n$ ($n = 2, M = Cr, Fe; n = 3, M = Ti, V, Cr, Mo, Fe; n = 4, Zr, Hf, W; n = 5, M = Nb, Ta, Mo; n = 6, M = 6$) inside ampoules.

Anhydrous tantalum pentachloride, $TaCl_5$ (0.32 g, 0.9 mmol), and magnesium silicide, $4/5Mg_2Si$ (0.09 g, 1.125 mmol) were ground together and placed inside a Pyrex ampoule which was then sealed under vacuum (quartz ampoules were used if the temperature required for the reaction was above 550 °C. The ampoule was then placed in a furnace and heated to the temperature required. At ca. 200 °C the reagents reacted with a thermal flash, spreading some of the solid over the walls of the ampoule. The grey solid was annealed for 5 hours at 550 °C. Most other products were annealed for longer (1-3 days) and often at higher temperatures (700-900 °C). The ampoule was then broken open and the crude product was triturated with water (4 x 6 ml), dilute mineral non-oxidising acid (2 x 6 ml) and promptly rinsed with water (2 x 6 ml). It was then dried in vacuo. The product was analysed using XRD, FT-IR, SEM/EDXA.

Reactions of magnesium silicide/calcium silicide mixture with anhydrous metal chlorides (as listed in previous procedure) performed inside ampoules.

To obtain the desired stoichiometric product (MSi$_2$) appropriate molar ratio of CaSi$_2$ and Mg$_2$Si were used. These molar ratios were calculated as described in section 4.2.1.

Magnesium silicide, Mg$_2$Si (0.05 g, 0.625 mmol), and calcium silicide, CaSi$_2$ (0.03 g, 0.3 mmol), were ground together. Tantalum pentachloride, $TaCl_5$ (0.22 g, 0.615 mmol) was added and the mixture was reground. Care had to be taken since these reactions are very spontaneous and highly exothermic. The reactants were placed inside an ampoule, which was then sealed under vacuum. The ampoule was placed inside a tube furnace at room temperature in a fume cupboard and the temperature was quickly raised (furnace ramped at 100 °C per minute) till reaction occurred with a thermal flash. The ampoule was then cooled.
to room temperature and broken open. The grey to black partially fused solid was treated with water and analysed using XRD, SEM/EDXA, FT-IR.

Flame (or filament) initiated reactions of calcium silicide/magnesium silicide mix with anhydrous transition metal chlorides, $MCl_n$ ($n = 3, M = V, Mo; n = 5, M = Nb, Ta, Mo$)

Reaction mixtures were prepared as in the previous procedure and initiated using a hot filament placed in the mixture, inside glove box, and removed after initiation. The reaction was completed in a nitrogen filled glovebox. For flame initiation the reactant mixtures were taken out of the glove box and immediately initiated on an asbestos platform using a blow torch, which was removed immediately after initiation. This procedure can also be performed with the reactants placed on an open Pyrex tube under a nitrogen flow.
CHAPTER 5

PREPARATIONS OF METAL BORIDES

5.1 INTRODUCTION

Despite the numerous boron containing starting materials available for SSM reactions, only magnesium diboride has been previously used. This chapter discusses the reactions of transition metal halides with aluminium diboride. Figure 1.4 outlines known transition metal borides.

5.1.1 Potential boride precursors

There are numerous Group 1 and 2 borides available as potential boride precursors for solid state metathetical preparations of transition metal borides. Some of these are listed below.

1. Alkali metal borides:
   
   LiB4, LiB6, LiB10, NaB5, NaB15, KB6, RbB6, CsB6

2. Alkaline earth metal borides:
   
   Be4B, Be2B, BeB2, BeB3, BeB6, BeB12, MgB2, MgB4, MgB6, MgB7, Mg2B14, MgB12 CaB4, CaB6, SrB6, BaB6

3. Aluminium borides:
   
   AlB2, α-AlB12, γ-AlB12, SiB6

4. Ternary metal borides:
   
   MgAlB14
5.1.2 Aims and background

This chapter discusses the reactions of transition metal halides with magnesium diboride, MgB₂, and aluminium diboride, AlB₂. Some work on the reactions of transition metal halides with magnesium diboride has been performed previously.¹¹⁶,¹⁷⁹,¹⁸⁰

The reagent magnesium diboride provides a fixed amount of boron, as illustrated in salt balanced equations 5.1-5.2. If the transition metal halide has an oxidation number higher than +2 excess boron is incorporated into the product. Most transition metal halides of Groups 4, 5 and 6 are commonly found in the forms of tri-, tetra- and pentachlorides.

\[
\begin{align*}
\text{VCl}_3 + \frac{3}{2}\text{MgB}_2 & \rightarrow \text{VB}_2 + \frac{3}{2}\text{MgCl}_2 + \text{B} & \text{eqn 5.1} \\
\text{TaCl}_5 + \frac{5}{2}\text{MgB}_2 & \rightarrow \text{TaB}_2 + \frac{5}{2}\text{MgCl}_2 + 3\text{B} & \text{eqn. 5.2}
\end{align*}
\]

Aluminium diboride provides an alternative boron source for the synthesis of transition metal diborides using solid state metathetical routes.

The aim of the work presented in this chapter is to provide a detailed look at the reactions of transition metal halides with aluminium diboride via solid state metathetical routes. The results are closely related to work performed previously on the reactions of transition metal halides with magnesium diboride.

5.2 SYNTHESIS

Reactions of transition metal halides with aluminium diboride inside an evacuated ampoule with a temperature gradient of 150-900 °C for 2-5 days produces transition metal borides and aluminium trichloride. The aluminium trichloride sublimes to the cooler end of the ampoule (Table 5.1). No thermal flash was observed in any of the reactions. The black solids did not require any trituration and pure borides were obtained for a number of reactions. Some reactions did not occur, for example, combination of tantalum pentachloride with
aluminium diboride. In this case the tantalum halide sublimed to the cooler end of the ampoule before reacting. The yields in most reactions were, however, generally high with losses attributed mainly to mechanical handling. **Equation 5.3** typifies the SSM reactions discussed in this chapter.

\[
3/nMX_a + n/3AlB_2 \rightarrow 3/nMB_{2x} + n/3AlX_3 + [(2n/3-2) + 2(1-x)]B \quad \text{eqn. 5.3}
\]

\[
[M = V, Cr, Mo, W, Fe, Co, La, Ce, Ho; X = Cl or I]
\]

All the products prepared using transition metal halides and aluminium diboride were analysed using X-ray powder diffraction, FT-IR and SEM/EDXA. No trituration of the products was required in these syntheses. Instruments used for analyses are listed in the experimental section.

### 5.3 CHARACTERISATION

#### 5.3.1 X-ray powder diffraction

Solid state metathetical reactions of transition metal halides with aluminium diboride for 1 h at 550 °C yield poorly crystalline transition metal diborides, most of which are obtained as single phases (particle size of the order 20-150 Å, as calculated from XRD line broadening using the Scherrer equation). The products were annealed at 900 °C for 2-5 days to induce better crystallinity (**figure 5.1**). Transition metal diborides required much shorter annealing periods to induce crystallinity than the transition metal carbides, reported in chapter 3. This is probably due to the more refractory nature of transition metal carbides. Using lower oxidation state transition metal halides (which generally have higher melting points) helps to obtain more crystalline products. This has been observed from the reactions of chromium trichloride and chromium dichloride with aluminium diboride. The first reaction yielded a more crystalline product. However the difference was still marginal.
Table 5.1  Bulk reactions of transition metal halides with aluminium diboride. Note no elemental boron was observed by XRD. *Literature lattice parameters were taken from reference [159].

<table>
<thead>
<tr>
<th>Transition metal halides</th>
<th>Products after annealing and trituration</th>
<th>$a_{o/b}$/Å $\pm$0.0006</th>
<th>$a_{l/a}$/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrCl$_4$</td>
<td>No reaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VCl$_3$</td>
<td>VB$_2$</td>
<td>$a = 2.997, c = 3.056$</td>
<td>$a = 2.998, b = 3.056$</td>
</tr>
<tr>
<td>NbCl$_5$</td>
<td>No reaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TaCl$_5$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CrCl$_3$</td>
<td>CrB$_2$</td>
<td>$a = 2.967, c = 3.066$</td>
<td>$a = 2.973, c = 3.071$</td>
</tr>
<tr>
<td>MoCl$_3$</td>
<td>Mo$_2$B$_6$ [MoB]</td>
<td>$a = 3.011, c = 20.890$</td>
<td></td>
</tr>
<tr>
<td>WCl$_4$</td>
<td>WB$_2^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeBr$_3$</td>
<td>FeB$^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoCl$_3$</td>
<td>CoB</td>
<td>$a = 3.948, b = 5.248,$</td>
<td>$a = 3.948, b = 5.243,$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c = 3.039$</td>
<td>$c = 3.037$</td>
</tr>
<tr>
<td>LaCl$_3$</td>
<td>LaB$_6$</td>
<td>$a = 4.148$</td>
<td>$a = 4.153$</td>
</tr>
</tbody>
</table>

*All the reaction mixtures were brought to 900 °C with a temperature gradient of 150-900 °C within the ampoule, and were annealed for 2-5 days.

*Sample poorly crystalline and the lattice parameters were not calculated. [ ] - minor phases present.

Figure 5.1  XRD pattern of chromium diboride prepared using chromium trichloride and aluminium diboride in a bulk reaction at 800 °C for 5 days with the standard stick pattern below.
5.3.2 SEM/EDXA

SEM measurements of the samples prepared from the reactions of transition metal halides with aluminium diboride possessed similar morphology. The solids consisted of micron sized agglomerates (figure 5.2). A narrow particle size distribution was evident within each sample.

![SEM micrographs of triturated products from the bulk reactions of vanadium trichloride (a) and chromium trichloride (b) with aluminium diboride.](image)

EDXA analysis of the as prepared products from the reactions of transition metal halides with aluminium diboride showed the presence of transition metal. No aluminium or chlorine was detected. Some of the products analysed using SEM showed the presence of more than one phase. EDXA analysis performed on such products showed that one of the phases contained the transition metal whilst the other contained no elements above the threshold of the EDXA system used. It was found that the mixed phase products were obtained from higher oxidation state transition metal halides, i.e. MX₃-MX₆. The combination of these halides with aluminium diboride provides excess boron in solid state metathetical reactions. It was concluded that the secondary unidentifiable phase present in these solids is elemental boron.
5.4 DISCUSSION

Solid state metathetical reactions of transition metal halides and aluminium diboride, performed in quartz ampoules, yield transition metal diborides and aluminium halides. Initiation temperatures were not related to a phase change of the halides used. This may be due to the high thermal stability of the diboride precursor (m. pt. AlB$_2$ = 1710 °C$^{76}$). More volatile transition metal halides sublimed to the cooler end of the ampoule preventing reaction with aluminium diboride. Those transition metal halides that remained in the reagent mixture at 550-600 °C reacted slowly to yield poorly crystalline transition metal diborides, which then required further annealing to produce a crystalline product. The challenge in these reactions is to keep the transition metal halides within the reaction mixture. Even the least volatile transition metal halides tend to sublime under vacuum at temperatures below 550 °C. To avoid this, experiments were performed where the reagents were kept in the coolest part of the ampoule. This improved these reactions greatly but did not solve the problem of encouraging more volatile transition metal halides, such as niobium pentachloride, to react before sublimation. Attempts to initiate the reactions using a flame or filament failed. This is probably a consequence of the high thermal stability of aluminium diboride.

The products obtained from the reactions of transition metal halides and aluminium diboride were analysed using X-ray powder diffraction, FT-IR and SEM/EDXA. Correlation of all the analytical results show that the transition metal diborides formed were poorly crystalline with micron sized agglomerates. The agglomerates were of a sharp, angular nature and had a narrow particle size distribution within each sample. It has been observed that annealing the transition metal diboride samples at 550 °C was very effective in increasing crystallinity. This is in contrast to the case with transition metal carbides. This can be attributed to the more refractory nature of the carbides.

Reactions of transition metal halides with aluminium diboride have also been performed with lithium chloride and magnesium chloride acting as an inert heat sink. Addition of minimal amounts of Group 1 or 2 salts such as chlorides of
lithium or magnesium (molar ratio AlB$_2$ : salt, 12-15 : 1) reduces the rates of these reactions leading to the formation of amorphous transition metal diborides with aluminium halide subliming to the cooler end of the ampoule. Addition of greater quantities of the salts leads to failure of these reactions and, when the temperature is raised, the transition metal halide used invariably sublimes to the cooler end of the ampoule instead of reacting.

All the reactions were performed on a very small scale (0.1 g, 0.002 moles AlB$_2$). The yields obtained in these reactions are essentially 100 % although some minor losses were observed due to handling and mechanical factors. Performing the reactions of transition metal halides with aluminium diboride on a larger scale is difficult to envisage due to the air-sensitive nature of the reagents and large furnaces would be required to perform such reactions. It is expected that large scale preparations of transition metal diborides using this approach would yield purer products of greater particle size.

Syntheses of transition metal diborides have also been performed using magnesium boride as a boron precursor. However, in most of such reactions, this precursor provides excess boron when combined with most of the commonly available transition metal halides. This has already been discussed in section 5.1.2. Aluminium diboride can be reacted with all transition metal halides with oxidation state +3 leaving no excess boron in the product (equation 5.4). This provides a great advantage since this oxidation state is very common in transition metal halide chemistry. Using transition metal halides of higher oxidation state leaves excess boron in the products (equation 5.5). This boron cannot be readily separated from the transition metal product.

\[
\begin{align*}
\text{VCl}_3 + \text{AlB}_2 & \rightarrow \text{VB}_2 + \text{AlCl}_3 \quad \text{eqn. 5.4} \\
\text{ZrCl}_4 + 4/3\text{AlB}_2 & \rightarrow \text{ZrB}_2 + 4/3\text{AlCl}_3 + 2/3\text{B} \quad \text{eqn. 5.5}
\end{align*}
\]
5.5 THERMODYNAMIC CONSIDERATIONS

This chapter considers the reactions of transition metal halides with just one new boron precursor - aluminium diboride. Aluminium diboride is a comparatively inert compound for solid state metathetical reactions. It melts at a high temperature (1710 °C) and has a lower heat of formation than magnesium diboride ($\Delta H_{298}^{\circ} \text{MgB}_2 = -92.0 \text{ kJ mole}^{-1}$, $\Delta H_{298}^{\circ} \text{AlB}_2 = -151.2 \text{ kJ mole}^{-1}$). Thus it is of no surprise that it resisted reacting with some of the transition metal halides. It reacts only at high temperatures with the less volatile transition metal halides such as the di- and trichlorides of chromium to form amorphous transition metal diborides, which require further annealing to increase the degree of crystallinity. Due to the high chemical stability of aluminium diboride at low temperatures, thermodynamic calculations showing that higher oxidation state transition metal halides are more likely to react are irrelevant and unreliable. Therefore thermodynamic calculations are not going to be discussed in this chapter any further.

5.6 SUMMARY

Solid state metathetical routes to transition metal borides using low oxidation state transition metal halides ($\text{MX}_n$, $n < 4$) and aluminium diboride yield poorly crystalline, but pure, transition metal borides. These can be annealed at low temperatures (500-550 °C) to induce greater crystallinity. No trituration of the products is required since the co-product aluminium halide sublimes to the cooler end of the ampoule. The reactions discussed in this chapter are slow, compared with other solid state metathetical reactions.

The reactions of transition metal halides with aluminium diboride can also be used to obtain amorphous transition metal diborides, by the addition of very small amounts of Group 1 or 2 salts (such as lithium chloride or magnesium chloride). The salt limits the reaction rate and an amorphous product is produced. Adding larger quantities of diluent salts prohibits these reactions and, when the temperature is raised, the transition metal halide sublimes to the cooler end of the ampoule.
Despite the rich stoichiometry and structural chemistry of Groups 5 and 6 transition metal borides (for example for chromium: $\alpha, \beta$-Cr$_2$B, Cr$_3$B$_3$, $\delta, \zeta$-CrB, Cr$_3$B$_4$, Cr$_2$B$_3$, CrB$_2$, CrB$_4$ exist) solid state metathetical preparations of these products do not produce mixed phases but just the diborides. The only exception was the reaction of molybdenum trichloride with aluminium diboride (Table 5.1).

5.7 EXPERIMENTAL

All manipulations were performed under an inert atmosphere inside a Saffron Scientific nitrogen filled glove box or using Schlenk line techniques. All reagents were supplied by Aldrich Chemical Co. and used as supplied.

Solvents were dried, distilled and degassed prior to their use.

Ampoules were made from Pyrex (1 cm diameter, 25 cm long) or quartz (0.7 cm diameter, 25 cm long) depending on the reagents used. They were flame dried under internal vacuum and sealed with the reactants in vacuo.

X-ray diffraction patterns were recorded using a Siemens D5000 transmission powder diffractometer with germanium monochromated Cu-K$_{\alpha 1}$ radiation ($\lambda = 1.5406 \text{ Å}$). TREOR and METRIC-LS programmes were used for indexing. A Nicolet 205 FT-IR was used to record IR spectrum using KBr discs. SEM/EDXA were performed using a JEOL JSM 820 instrument with Kevex detector and software, and a Hitachi SEM S-570. EDXA were measured on many point regions across the sample (also compared with whole screen tests) and tested for regional homogeneity of the sample.

Reactions of aluminium diboride with anhydrous transition metal halides CrCl$_2$, CoCl$_2$, FeBr$_2$, VCl$_3$, CrCl$_3$, MoCl$_5$, LaCl$_3$, WCl$_4$ inside ampoule

Aluminium diboride, AlB$_2$ (0.05 g, 1.0 mmol), and transition metal halide (1 : 3 ratio of aluminium to halide) were ground together and placed in a quartz ampoule which was then evacuated and sealed. The ampoule was placed with 2/3 of its length inside a tube furnace at ambient temperature to obtain a temperature gradient when the furnace is switched on. The temperature was then raised to 1000 °C and left for 3-4 days to anneal the black solid produced. Aluminium halide
co-product separated away to the cooler end of the ampoule via sublimation. The solid was triturated with THF (2 x 6 ml), methanol (1 x 6 ml) and THF again (1 x 5 ml). After drying under vacuum it was analysed using XRD, SEM/EDXA and FT-IR.
CHAPTER 6

PREPARATIONS OF TRANSITION METAL CARBIDES AND SILICIDES USING METAL OXIDES AS PRECURSORS

6.1 INTRODUCTION

Chapters 2-5 of this thesis concentrated on solid state metathetical preparations of ceramic materials using metal halides and main group elements precursors, such as lithium nitride and aluminium carbide. The great driving force involved in these reactions is the formation of the co-produced salts such as lithium and calcium chloride. Group 1 and 2 oxides also have high heats of formations. It is expected that the reactions of transition metal oxides with main group element precursors such as calcium carbide are likely to be energetically favourable despite the stability of the transition metal oxide. Equation 6.1 shows the calculated enthalpy of reaction for molybdenum trioxide with calcium carbide.

\[
\text{MoO}_3 + 3\text{CaC}_2 \rightarrow \frac{1}{2}\text{Mo}_2\text{C} + 3\text{CaO} + 3/2\text{C}, \quad \text{eqn. 6.1}
\]

\[\Delta H_{298} = -1007.5 \text{ kJ mole}^{-1}\]

6.1.1 Some commonly available transition metal oxides

A wide variety of transition metal oxides are commercially available. The oxides highlighted in bold were used as reagents in the syntheses discussed in this chapter.

1. Binary transition metal oxides:

\[\text{TiO}_2, \text{ZrO}_2, \text{HfO}_2, \text{V}_2\text{O}_3, \text{V}_2\text{O}_5, \text{Nb}_2\text{O}_5, \text{Ta}_2\text{O}_5, \text{MoO}_3, \text{WO}_3\]
2. Ternary $A_2M_3O_7$ oxides ($A = \text{alkali or alkali earth metal, } M = \text{transition metal}$)

$Li_2TiO_3, LiTaO_3, NaV_2O_4, LiNbO_3, Li_2MoO_4, CaTiO_3, CaZrO_3$

3. Ternary mixed transition metal oxides:

$HfTiO_4, Zr(WO_4)_2$

4. Ternary lanthanide transition metal oxides

$La_2(ZrO_3)_3, La_2(WO_4)_3, CeZrO_4, Ce_2(WO_4)_3$,

The successes or failures of reactions discussed in this chapter are related to the thermodynamic stabilities of the starting reagents and the co-formation of other products.

6.1.2 Aims and background

Solid state metathetical preparations of chromium nitrides using chromium oxide and lithium nitride has been previously reported. The co-product lithium oxide, was removed using water or methanol. This chapter discusses the reactions of metal oxides with Group 1 and 2 metal carbides and silicides. No previous work has, to our knowledge, been reported on any similar processes. Most metal oxides are commonly available and inexpensive, therefore potential wide scale production of carbides and silicides, which are of great commercial demand, using oxides gives a new scope to solid state metathesis. All the products were analysed using X-ray powder diffraction, FT-IR and SEM/EDXA. A selected group of transition metal carbides produced in the reactions discussed in this chapter were also analysed using TEM, PEELS/ELNES and combustion analysis.
6.2 SYNTHESIS

(i) Reactions performed inside an ampoule (bulk reactions).

Solid state metathetical reactions of binary and ternary metal oxides of Group 5, molybdenum and tungsten with Group 2 carbides lead to formation of transition metal carbides and Group 1 and 2 oxides (Table 6.1, equations 6.2-6.3).

\[
\begin{align*}
1/2\text{Ta}_2\text{O}_5 + 5/2\text{CaC}_2 & \rightarrow \text{TaC} + 5/2\text{CaO} + 4\text{C} & \text{eqn. 6.2} \\
1/2\text{Ta}_2\text{O}_5 + 5/2\text{SrC}_2 & \rightarrow \text{TaC} + 5/2\text{SrO} + 4\text{C} & \text{eqn. 6.3}
\end{align*}
\]

\[ T = 900-1000 ^\circ\text{C}, 12-96 \text{ hours} \]

Table 6.1. Bulk reactions of binary and ternary metal oxides with carbides of Group 2 elements. *Literature lattice parameters were taken from references [18] and [159].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products after annealing and trituration</th>
<th>( a_{\text{obs}}/\text{Å} ) +/−0.001</th>
<th>( a_{\text{id}}/\text{Å} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{LiTiO}_3 + \text{CaC}_2 )</td>
<td>( \text{CaTiO}_3 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{V}_2\text{O}_3 + \text{CaC}_2 )</td>
<td>( \text{V}_4\text{C}_7 )</td>
<td>4.159</td>
<td>4.165</td>
</tr>
<tr>
<td>( \text{NaVO}_3 + \text{CaC}_2 )</td>
<td>( \text{V}_4\text{C}_7 )</td>
<td>4.161</td>
<td>4.165</td>
</tr>
<tr>
<td>( \text{NaVO}_3 + \text{SrC}_2 )</td>
<td>( \text{V}_4\text{C}_7 )</td>
<td>4.165</td>
<td>4.165</td>
</tr>
<tr>
<td>( \text{Nb}_2\text{O}_5 + \text{CaC}_2 )</td>
<td>( \text{NbC} )</td>
<td>4.462</td>
<td>4.471</td>
</tr>
<tr>
<td>( \text{Nb}_2\text{O}_5 + \text{SrC}_2 )</td>
<td>( \text{NbC} )</td>
<td>4.467</td>
<td>4.471</td>
</tr>
<tr>
<td>( \text{LiNbO}_3 + \text{SrC}_2 )</td>
<td>( \text{NbC} )</td>
<td>4.462</td>
<td>4.471</td>
</tr>
<tr>
<td>( \text{Ta}_2\text{O}_5 + \text{CaC}_2 )</td>
<td>( \text{TaC} )</td>
<td>4.446</td>
<td>4.456</td>
</tr>
<tr>
<td>( \text{LiTaO}_3 + \text{CaC}_2 )</td>
<td>( \text{TaC} )</td>
<td>4.448</td>
<td>4.456</td>
</tr>
<tr>
<td>( \text{MoO}_3 + \text{CaC}_2 )</td>
<td>( \text{Mo}_2\text{C} )</td>
<td>( a = 4.730, b = 6.017, c = 5.208 )</td>
<td>( a = 4.732, b = 6.037, c = 5.204 )</td>
</tr>
<tr>
<td>( \text{Li}_2\text{MoO}_4 + \text{CaC}_2 )</td>
<td>( \text{Mo}_2\text{C} )</td>
<td>( a = 4.733, b = 6.006, c = 5.203 )</td>
<td>( a = 4.732, b = 6.037, c = 5.204 )</td>
</tr>
<tr>
<td>( \text{Li}_2\text{WO}_4 + \text{CaC}_2 )</td>
<td>( \text{WC} )</td>
<td>( a = 2.901, c = 2.838 )</td>
<td>( a = 2.906, c = 2.838 )</td>
</tr>
</tbody>
</table>

*All the reaction mixtures were brought to 900-1000 °C and were annealed for 12-96 hours.
The co-produced alkali metal oxides (equations 6.2-6.3) can be removed using water and dilute mineral acids. All the reactions initiate between 480 °C and 650 °C. Solids isolated from reactions performed at low temperatures (500-550 °C) showed amorphous products and some unreacted transition metal oxide after 7-10 days of annealing. If the temperature was raised to 1000 °C, and the solids formed annealed for 12-96 hours, transition metal carbides and the co-product were obtained. Some of the reactions attempted tended to result in undesired products. One example of that is the reaction of lithium titanate with calcium carbide, which resulted in the final product calcium titanate as a result of an elemental reaction process. No such results were observed in any reactions involving Group 5 and 6 oxides. Both binary and ternary transition metal precursors yielded transition metal carbide products.

Solid state metathetical reactions of binary and ternary transition metal oxides with lithium silicide lead to formation of transition metal silicides and the Group 1 metal oxide co-product (Table 6.2, equation 6.4). The reaction mixtures were brought to 550 °C and then cooled down. The final products were triturated with water and methanol. All the reactions were extremely rapid and highly exothermic proceeding with a yellow thermal flash.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products after trituration</th>
<th>$a_{obs}$/Å +/-0.001</th>
<th>$a_{lab}$/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{V}_2\text{O}_3 + \text{Mg}_2\text{Si}/\text{CaSi}_2$</td>
<td>VSi$_2$ [V$_x$Si$_y$]</td>
<td>$a = 4.565, c = 6.363$</td>
<td>$a = 4.572, c = 6.373$</td>
</tr>
<tr>
<td>$\text{V}_2\text{O}_3 + \text{Mg}_2\text{Si}/\text{CaSi}_2$</td>
<td>VSi$_2$</td>
<td>$a = 4.568, c = 6.369$</td>
<td>$a = 4.572, c = 6.373$</td>
</tr>
<tr>
<td>$\text{Nb}_2\text{O}_5 + \text{Mg}_2\text{Si}/\text{CaSi}_2$</td>
<td>NbSi$_2$</td>
<td>$a = 4.776, c = 6.555$</td>
<td>$a = 4.797, c = 6.592$</td>
</tr>
<tr>
<td>$\text{Nb}_2\text{O}_5 + \text{Li}_2\text{Si}$</td>
<td>NbSi$_2$</td>
<td>$a = 4.787, c = 6.584$</td>
<td>$a = 4.797, c = 6.592$</td>
</tr>
<tr>
<td>$\text{LiNbO}_3 + \text{Li}_2\text{Si}$</td>
<td>NbSi$_2$</td>
<td>$a = 4.792, c = 6.590$</td>
<td>$a = 4.797, c = 6.592$</td>
</tr>
<tr>
<td>$\text{Ta}_2\text{O}_5 + \text{Mg}_2\text{Si}/\text{CaSi}_2$</td>
<td>TaSi$_2$</td>
<td>$a = 4.777, c = 6.564$</td>
<td>$a = 4.784, c = 6.570$</td>
</tr>
<tr>
<td>$\text{LiTaO}_3 + \text{Li}_2\text{Si}$</td>
<td>TaSi$_2$</td>
<td>$a = 4.777, c = 6.564$</td>
<td>$a = 4.784, c = 6.570$</td>
</tr>
<tr>
<td>$\text{Li}_3\text{MoO}_4 + \text{Mg}_2\text{Si}/\text{CaSi}_2$</td>
<td>MoSi$_2$ [Mo$_x$Si$_y$, Mo]</td>
<td>$a = 3.199, c = 7.839$</td>
<td>$a = 3.205, c = 7.845$</td>
</tr>
</tbody>
</table>

*All reaction mixtures were brought to 550 °C and then cooled down before trituration. [] - minor phases present.

Table 6.2 Bulk reactions of binary and ternary metal oxides with lithium silicide and a calcium silicide/magnesium silicide mix. The ratios of the silicide precursors were 'tuned' to obtain stoichiometric transition metal disilicides. * Literature lattice parameters taken from reference [159].
The reactions of binary and ternary oxides with calcium silicide/magnesium silicide mix, listed in Table 6.2, performed inside evacuated ampoules initiated at temperatures below 500 °C (equation 6.5). The molar ratios of the two silicide precursors were determined as shown in chapter 4 and were aimed to form stoichiometric transition metal disilicides unless specifically stated (equation 6.5). No thermal flash was observed in any of these reactions. The products were triturated with dilute mineral acids and distilled water to remove the co-product oxides of calcium and magnesium, and in some cases of lithium when the ternary oxides were used as precursors.

\[
\begin{align*}
V_2O_3 + 3Li_2Si & \rightarrow 3Li_2O + 2VSi_{2x} & \text{eqn. 6.4} \\
V_2O_3 + CaSi_2 + Mg_2Si & \rightarrow 2VSi_{2x} + CaO + 2MgO & \text{eqn. 6.5}
\end{align*}
\]

\[x = 0.75\]

(ii) Reactions initiated using flame or filament (propagation reactions)

Solid state metathetical reactions of ternary metal oxides (i.e. Li$_2$MoO$_4$) and transition metal oxides (i.e. MO$_3$) with lithium silicide and calcium silicide/magnesium silicide mix could be initiated with a flame or a filament (Table 6.3). The reactions of lithium silicide with transition metal oxides of Groups 5 and 6 initiated violently on grinding the precursors and propagated very rapidly to form transition metal disilicides. The reaction of molybdenum trioxide with lithium silicide included some molybdenum metal impurity. This can be avoided by careful spreading of the reagents inside the ampoule. The reactions of ternary oxides with lithium silicide were less rapid and no initiation was observed on grinding. Flame initiation was usually applied. The consequent propagation was much slower. In all reactions initiated using flame or filament some of the co-product separated to the edges of the fused masses. Some sublimation was also observed.
Table 6.3  Propagation reactions initiated with flame (fl), filament (fil) or by grinding (gr) of binary and ternary metal oxides with lithium silicide or calcium silicide/magnesium silicide mix. Literature lattice parameters were taken from reference [159].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products</th>
<th>$a_{obs}$/Å +/-0.001</th>
<th>$a_{true}$/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_2O_5 + Mg_2Si/CaSi_2 (fl)$</td>
<td>$VSi_2$</td>
<td>$a = 4.569, c = 6.369$</td>
<td>$a = 4.572, c = 6.373$</td>
</tr>
<tr>
<td>$Nb_2O_5 + Mg_2Si/CaSi_2 (fl)$</td>
<td>$NbSi_2 [NbSi_3]$</td>
<td>$a = 4.801, c = 6.596$</td>
<td>$a = 4.797, c = 6.592$</td>
</tr>
<tr>
<td>$Nb_2O_5 + Li_2Si$ (gr)</td>
<td>$NbSi_3 [NbSi_3]$</td>
<td>$a = 7.512, c = 5.247$</td>
<td>$a = 7.536, c = 5.248$</td>
</tr>
<tr>
<td>$LiNbO_3 + Mg_2Si/CaSi_2 (fl)$</td>
<td>$NbSi_2 [NbSi_3]$</td>
<td>$a = 7.527, c = 5.249$</td>
<td>$a = 7.536, c = 5.248$</td>
</tr>
<tr>
<td>$Ta_2O_5 + Mg_2Si/CaSi_2 (fil)$</td>
<td>$TaSi_2$</td>
<td>$a = 4.776, c = 6.560$</td>
<td>$a = 4.784, c = 6.570$</td>
</tr>
<tr>
<td>$Ta_2O_5 + Mg_2Si/CaSi_2 (fil)$</td>
<td>$TaSi_2 [Si]$</td>
<td>$a = 4.776, c = 6.561$</td>
<td>$a = 4.784, c = 6.570$</td>
</tr>
<tr>
<td>$MoO_3 + Li_2Si$ (gr)</td>
<td>$Mo, MoSi_3$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$Li_2MoO_4 + Li_2Si$ (fl)</td>
<td>$MoSi_2$,</td>
<td>$a = 3.198, c = 7.830$</td>
<td>$a = 3.205, c = 7.845$</td>
</tr>
<tr>
<td></td>
<td>$MoSi_3$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$Li_2MoO_4 + Mg_2Si/CaSi_2 (fl)$</td>
<td>$MoSi_2 [Mo]$</td>
<td>$a = 3.203, c = 7.840$</td>
<td>$a = 3.205, c = 7.845$</td>
</tr>
</tbody>
</table>

*All the products were ready for trituration after the propagation reactions have ceased. No annealing was required. "lattice parameters of the main product were not calculated due to presence of multiple lattice peaks of secondary phases. [] – minor phases present.

The reactions of Group 6 transition metal oxides with calcium silicide/magnesium silicide mix, initiated with a flame or a filament, formed transition metal disilicides and calcium oxide. The reactions were always incomplete and some of the magnesium silicide used remained in the mixture, hydrolysing when the products were triturated with water. The resultant magnesium oxide was removed using dilute mineral acids. The significance of these reactions was determined by the fact that incomplete reaction does not allow control of the silicon content in the final product and leaves some unreacted oxides in the final mixture.

The reactions of binary and ternary metal oxides with carbides of Group 2, initiated with a flame or a filament, failed to propagate. Some reaction was noted at the tip of the filament.
6.3 CHARACTERISATION

6.3.1 X-ray powder diffraction

(i) Bulk reactions

Carbides. Solid state metathetical reactions of binary transition metal oxides and ternary Group 1 metal transition metal oxides with carbides of Group 2 metals yield amorphous transition metal carbides and the co-product Group 1 metal oxides. The carbides became crystalline after annealing at 1000 °C for 12-96 hours (equation 6.4). The co-products were successfully removed with dilute acids and distilled water (figure 6.1). The particle size of the products was of the order 50-400 Å, as calculated from the XRD line broadening using the Scherrer equation.

\[
\text{Ta}_2\text{O}_5 + 5\text{CaC}_2 \rightarrow 2\text{TaC} + 5\text{CaO} + 8\text{C}
\]  eqn. 6.4

Silicides. The X-ray diffraction analyses of the products from the reactions of binary and ternary oxides with lithium silicide or calcium silicide/magnesium silicide mix, listed in Tables 6.2 and 6.3, showed highly crystalline transition metal disilicides and Group 1 and 2 metal oxides. Analyses of triturated solids revealed pure transition metal disilicides (figure 6.1). The products did not require any additional annealing but keeping the crude products at a temperature of 550 °C for 1-2 days improved their crystallinity considerably. The particle size of the products was of the order 200-700 Å, as calculated from XRD line broadening using the Scherrer equation.

(ii) Propagation reactions

Transition metal silicides prepared using solid state metathetical processes from binary and ternary metal oxides and lithium silicide or calcium silicide/magnesium silicide mix using a flame or a filament were also crystalline. No additional annealing was performed on any of these solids. The crystallite sizes in
Figure 6.1  XRD patterns of triturated products from the bulk reactions of lithium niobate with strontium carbide (a), lithium molybdate with calcium carbide (b) and niobium (V) oxide with a calcium silicide/magnesium silicide mix (c). Bottom stick patterns are for cubic niobium carbide, NbC in (a), hexagonal molybdenum carbide, Mo$_2$C in (b) and niobium disilicide, NbSi$_2$ in (c).
these solids were of the order 100-600 Å as calculated from the XRD line broadening using the Scherrer equation.

6.3.2 SEM

**Carbides.** Transition metal carbides obtained from the bulk reactions of Group 1 metal transition metal oxides and transition metal oxides with Group 2 carbides were analysed by SEM. This showed no evidence of melting. All the solids analysed had particles with rough and sharp surfaces (figure 6.2). Triturated products possessed similar morphology with generally smaller agglomerates compared to the crude samples. No differences were observed in the nature of products whether they were formed using calcium carbide or strontium carbide as a carbon precursor.

**Silicides.** SEM measurements of the crude and triturated products from the bulk reactions of transition metal oxides with lithium silicide and calcium silicide/magnesium silicide mix showed similar morphology (figure 6.3). All the products possessed rough angular particles. This suggests that the reactions were not assisted by melting. The products showed narrow particle size distributions within the samples. The products obtained from the reactions where lithium silicide was used as a silicon precursor were more crystalline than the products from the reactions where a calcium silicide/magnesium silicide mix was used. SEM measurements of triturated products showed evidence that trituration with acids reduces the size of the agglomerates.

Transition metal silicides obtained from the reactions of transition metal oxides with lithium silicide and calcium silicide/magnesium silicide mix, when initiated with a flame (no annealing), possessed particle sizes of dimensions comparable to those obtained from the corresponding reactions performed inside ampoules (2-3 days, 550 °C). Products obtained from similar reactions initiated with a filament had smaller size agglomerates (most commonly by a factor of 3) and, as EDXA analysis has confirmed, frequently contained impurities. It has also been observed that products obtained from these reactions possessed wider particle
Figure 6.2  SEM micrographs of transition metal carbides: (a-c) cubic tantalum carbide, TaC, prepared using tantalum (V) oxide and calcium carbide, (d) vanadium carbide, VₓCₙ, prepared using vanadium (III) oxide and calcium carbide, (e) niobium carbide, NbC, prepared using niobium (V) oxide and calcium carbide. All reactions were performed inside evacuated ampoules.
Figure 6.3  SEM micrographs of transition metal disilicides: crude (a-b), and triturated (c-d) product from the bulk reaction of tantalum (V) oxide with a calcium silicide/magnesium silicide mix. (e-f) triturated product from the reaction of vanadium (V) oxide with a calcium silicide/magnesium silicide mix initiated with a flame.
size distributions within the same samples. SEM measurements of triturated products showed smaller size agglomerates than the as prepared products discussed earlier.

6.3.3 EDXA

**Carbides.** EDXA analyses of the as prepared products from the reactions of transition metal oxides with Group 2 carbides showed the presence of transition metal, Group 2 metal and oxygen. The concentration of oxygen varied in these solids throughout different particles suggesting that the ratio of product and co-product was inconsistent. EDXA analyses of triturated products showed that trituration removes the co-product from these solids.

**Silicides.** EDXA analysis of the as prepared solids from the reactions of transition metal oxides with lithium silicide and calcium silicide/magnesium silicide mix showed the presence of Group 1 and 2 metals, transition metals, silicon and oxygen. Analyses performed on various individual particles have shown that there is a great variation in abundance of the product and co-product within the solid. Some particles contained mainly the product, others the co-product and some were an intimate mix of the two. The corresponding triturated products showed, when analysed using EDXA that the trituration removed the co-products leaving pure transition metal disilicides (figure 6.4). EDXA analyses also gave evidence that the products are homogeneous.

The SEM/EDXA system has also been used to perform linescan tests on a selected number of samples discussed in this chapter. Figure 6.5 shows the patterns obtained from the analysis of tantalum disilicide produced using tantalum (V) oxide and lithium silicide. There is a clear relationship between the two patterns showing that tantalum and silicon are part of the same compound. The sample has also been analysed for oxygen contamination. Some oxygen has been found on the sample surface. The pattern obtained for this element showed a relationship with the other two elements indicating that the surface of tantalum disilicide has been partially oxidised.
Figure 6.4  *EDXA analysis of triturated product from the bulk reaction of tantalum (V) oxide with a calcium silicide/magnesium silicide mix.*

Figure 6.5  *Linescan measurements for tantalum and silicon, performed on the surface of tantalum disilicide prepared using tantalum (V) oxide and a calcium silicide/magnesium silicide mix.*
Figure 6.6  TEM micrographs of niobium carbide, (a), prepared using lithium niobate and strontium carbide, and tantalum carbide, (b), prepared using lithium tantalate and calcium carbide.

6.3.3 TEM

TEM analyses have been performed on niobium carbide prepared using lithium niobate and strontium carbide, and tantalum carbide prepared using lithium tantalate and calcium carbide both at 1000 °C inside sealed quartz ampoules and annealed for 36 hours (figure 6.6). Tantalum carbide had agglomerates of average size ca. 400 nm with the crystals varying in size from 20 nm to 120 nm. The cubic a-parameter was found to be 4.435 Å (TaC$_{0.70-0.99}$ = 4.410-4.456 Å$^{175}$), corresponding to TaC$_{0.86}$. Niobium carbide had larger agglomerates, which were composed of a mesh of small crystals of average size between 20 and 50 nm. The cubic a-parameter was found to be 4.458 Å (NbC$_{0.77-0.99}$ = 4.432-4.471 Å$^{175}$), corresponding to NbC$_{0.92}$.

Electron diffraction patterns for both samples showed the presence of polycrystalline grains with crystals randomly arranged.
6.4 DISCUSSION

Solid state metathetical reactions of transition metal oxides and Group 1 metal transition metal oxides with lithium silicide or a calcium silicide/magnesium silicide mix, performed inside ampoules, yield transition metal silicides and oxides of Group 1 and 2 metals (equations 6.4-6.5). The reactions initiated at various temperatures. The initiation temperatures were generally higher for the reactions where the ternary oxides were used as precursors. The co-produced Group 1 and 2 oxides started to react with the glass walls of the ampoule at high temperatures when the products were annealed. Care had to be taken not to keep the products annealing for too long (up to 4 days) at high temperatures (up to 1000 °C) as the ampoule could crumble exposing the products to oxidation.

The reactions of Group 5 and 6 transition metal oxides with lithium silicide also initiated on grinding or by using a flame or a filament for initiation. This caused an orange propagation wave. Use of a flame for initiation produced reactions that were the most rapid of all. These also yielded the most crystalline products.

Transition metal oxides and ternary metal oxides also react with carbides of calcium and strontium (equations 6.2-6.3). The reactions were slow, with the grey reagent mixtures transforming to black solids (~30 seconds) at temperatures between 450 °C and 550 °C. Crystalline products were only obtained after the solids were annealed for at least 6 hours at 900-1000 °C. In these reactions care was taken not to keep the solids annealing for too long (2-3 days) as the co-produced oxides of Group 1 and 2 started to react with the quartz glass ampoules used at raised temperatures. None of the reactions of transition metal oxides with Group 2 carbides propagated on initiation with a flame or a filament. The reaction occurred only at the point source of the heated filament.

The analytical results on the products obtained from the reactions discussed in this chapter have given evidence that these synthesis routes can be envisaged to form carbides and disilicides of transition metals with a wide range of particle sizes. However for an individual reaction a narrow particle size distribution was
observed. The X-ray diffraction, SEM and for a selected group of samples, TEM were used to determine particle sizes.

Analyses of all the products have shown that these solid state metathetical reactions, despite their rapid nature, generally yield pure phases after the co-product has been removed. No initial unreacted reagents were observed in crude products when analysed using XRD and EDXA. Addition of water and dilute mineral acid during triturating did not promote vigorous hydrolysis reactions of unreacted carbide or silicide precursors, which suggested that these precursors have already reacted with the oxide precursors. The yields obtained from these reactions were high with small losses, which were due to the mechanical handling. All the reactions were performed on a very small scale (e. g. ~0.0007 moles of Ca$_3$N$_2$).

The structural chemistry of transition metal silicides is very rich spanning through varied stoichiometries from cubic through hexagonal, tetragonal to orthorhombic. Still the solid state metathetical preparations discussed in this chapter mostly can lead to formation of single transition metal disilicide phases. The major problem to challenge these syntheses was the decomposition of the product during the reaction leading to formation of some transition metal. Some transition metals can be removed using aqua regia but the slow decomposition of transition metal silicides in acids impelled us to use alternative routes. In the reactions, where the products desired were found to decompose, the procedure was repeated by spreading the reagents before initiation. These types of manipulations are discussed in more detail in chapter 7. Their main drawback is a consequent reduction of crystallinity in the final product.

EDXA analyses of tantalum disilicides prepared using tantalum (V) oxide and calcium silicide/magnesium silicide mixes with various ratios of the two siliciding reagents have shown that homogeneous mixtures of various stoichiometries have been obtained. The tantalum to silicon ratio in the final products from these reactions showed close consistency (within 5%) with the desired stoichiometry calculated before the reactions.
6.5 THERMODYNAMIC CONSIDERATIONS

Solid state metathetical reactions of binary and ternary metal oxides with Group 1 and 2 silicides and Group 2 carbides lead to the formation of transition metal silicides and carbides. These SSM processes show a marked variation in reaction rates. The reactions forming transition metal silicides were in general a lot more rapid than the reactions forming transition metal carbides. No variation in reaction rates was observed in the reactions of calcium carbide and strontium carbide with ternary metal oxides. Equations 6.5 and 6.6 give the reactions of lithium tantalate with calcium and strontium carbides along with their enthalpies. The reaction enthalpies, calculated using Hess' Law, reveal some variation in exothermicities.

\[
\begin{align*}
2\text{LiTaO}_3 + 5\text{CaC}_2 &\rightarrow 2\text{TaC} + \text{Li}_2\text{O} + 5\text{CaO} + 8\text{C} & \text{eqn. 6.5} \\
\Delta H_{298} &= -922 \text{ kJ mole}^{-1} \\
2\text{LiTaO}_3 + 5\text{SrC}_2 &\rightarrow 2\text{TaC} + \text{Li}_2\text{O} + 5\text{SrO} + 8\text{C} & \text{eqn. 6.6} \\
\Delta H_{298} &= -790.3 \text{ kJ mole}^{-1}
\end{align*}
\]

All the reactions (equations 6.5-6.6) forming transition metal carbides were very slow. Attempts to initiate these reactions with a filament were unsuccessful.

6.6 SUMMARY

Solid state metathetical routes can be used for preparations of binary transition metal carbides and silicides by combining and heating mixtures of the precursors that were previously discussed in this chapter. These can be generalised as follows:

(i) **Preparations of transition metal carbides**
- Group 2 metal carbides as carbon precursors
- Binary transition metal oxides as transition metal precursors
- Ternary Group 1 metal transition metal oxides as transition metal precursors
(ii) **Preparations of transition metal disilicides**

- Group 1 and 2 metal silicides as silicon precursors
- A mix of calcium silicide and magnesium silicide as a silicon precursor to obtain transition metal disilicides of accurate stoichiometry or substoichiometry
- Binary transition metal oxides as transition metal precursors
- Ternary Group 1 metal transition metal oxides as transition metal precursors

Preparations of transition metal disilicides of desired substoichiometry using transition metal oxides and calcium silicide/magnesium silicide mix have been proven possible using tantalum (V) oxide as an example. However more oxides should be studied for these types of reactions. Tantalum disilicides produced in similar reactions where tantalum pentachloride has been used instead of the oxide, discussed in chapter 4, were a lot more crystalline.

### 6.7 EXPERIMENTAL

All manipulations and weighings were performed as generalised in Chapter 2. Quartz glass ampoules (0.6-0.8 cm diameter, 15 cm long, 2-3 mm thick walls) were annealed prior to use and flame dried under vacuum. Calcium carbide purchased from Aldrich Chemical Co. was 80 % pure. Strontium carbide was prepared by heating the elements at 800 °C (above the melting point of Strontium metal, m. pt. Sr ~750 °C).

Dilute hydrochloric acid (5 %) was used for all triturations. After treatment with acid the remaining solids were always rinsed with distilled water and dried under vacuum.

Lenton Thermal Designs programmable tube furnace, ramped at 100 °C per minute, was used to initiate the reactions.
Reactions of calcium carbide and strontium carbide with binary metal oxides, TiO₂, V₂O₅, Nb₂O₅, Ta₂O₅, MoO₃, WO₃, and ternary metal oxides, HfZrO₄, Li₂TiO₃, Na₂VO₄, LiNbO₃, LiTaO₃, Li₂MoO₄, Li₂WO₄ inside ampoules

Lithium niobate, LiNbO₃ (0.2 g, 1.35 mmol), and calcium carbide, 3/2CaC₂ (0.13 g, 2.0 mmol), were ground together, placed inside an ampoule which was then evacuated and sealed. The ampoule was then placed in a tube furnace at room temperature, which was then rapidly raised to 1000–1100 °C and kept annealing for 2-5 days. In the reaction some white residue settled on the cooler parts of the ampoule and the solid at the hotter end of the ampoule turned black at ca. 450 °C. The product was triturated with dilute acid (3 x 6 ml), rinsed with distilled water (3 x 10 ml) and then dried in vacuo. The resultant black solid was analysed using XRD, SEM/EDXA, FT-IR, EELS, TEM, electron diffraction and elemental microanalysis. (Microanalysis: reaction of tantalum (V) oxide with calcium carbide, C, 5.69; H, 0.21; N, 0.31. Calcd.: TaC, C, 6.22 wt.%, .*.TaC₉₁; reaction of lithium tungstate (lithium tungsten (VI) oxide) with calcium carbide, C, 6.67; H, 0.10; N, 1.26. Calcd.: WC, C, 6.12 wt.% .*.WC₁₀ and some free carbon.)

Reactions of lithium silicide, Li₂Si, and magnesium silicide/calcium silicide, Mg₂Si/CaSi₂ mixture with binary metal oxides, V₂O₅, Nb₂O₅, Ta₂O₅, WO₃ and ternary metal oxides, LiNbO₃, LiTaO₃, Li₂MoO₄, inside ampoules

All manipulations and weighings of reagents were performed as generalised in previous experimental. The reactions in general required less time to anneal than the reactions discussed in section 6.7.1.

Reactions of lithium silicide and calcium silicide/magnesium silicide mix with transition metal oxides (MoO₃, V₂O₅, Nb₂O₅, WO₃, Ta₂O₅, LiTaO₃, LiNbO₃, Li₂MoO₄) initiated with a flame or a filament

All weighings and manipulations of reagents were performed as described in previous reactions. The reactions were initiated using a filament inside a nitrogen-filled glove box. Alternatively a flame (supplied from an oxygen fuelled blow
torch) was used to initiate the reactions. After successful initiation the reactions propagated with an orange combustion wave.
CHAPTER 7

CONTROL OF CRYSTALLITE SIZE IN PRODUCTS FORMED USING SSM

7.1 INTRODUCTION

Chapters 2-6 discussed the formation of four groups of ceramic materials, borides, carbides, nitrides and silicides, using metal halides and metal oxides as metal precursors.

This chapter discusses investigations performed to study the nature of SSM reactions and attempts to control these reactions to obtain products with desired crystallite sizes. The reagents used for each particular study are outlined in subsections of this chapter, where appropriate. Experimental details, if different from the methods used in chapters 2-6, are always outlined prior to the discussion of results.

7.1.1 Aims and background

One of the major factors influencing the commercial application of particular syntheses of ceramic materials is whether the final product particle and crystallite size can be controlled. Scientists work on new synthetical pathways, that yield products rapidly and cheaply with the desired particle and crystallite size. Results discussed in this chapter will present the reader with evidence that the solid state metathetical route to ceramic materials is one such new pathway. This has been achieved by a number of experimental manipulations and work-ups as well as controlling the reaction conditions. Section 7.2 discusses fully results from investigative experiments performed with the aim to control the final product crystallite size using solid state metathetical reactions.
Transition metal borides, carbides, nitrides and silicides prepared using solid state metathetical reactions studied in this project were often poorly crystalline and, as a result, often required further annealing for identification. Commercially, these solids are usually annealed at very high temperatures, often in excess of 1600 °C. This is the case especially with carbides and the most refractory nitrides. For example, the crystallite size of hexagonal boron nitride powders starts to increase only slightly at 1600 °C if a growth promoter such as boric oxide is added to promote crystallization. However higher temperatures are required to effectively raise the crystallinity of boron nitride. Section 7.2.7 will concentrate on the effects of annealing the products formed using solid state metathetical reactions at 550 °C over different timescales. The degree of crystallinity was assessed using XRD from the line broadening using the Scherrer equation (Formula 2.1). For some selected samples the particles were also observed using SEM. In all cases these observational analyses were performed before and after annealing. This chapter will concentrate on thorough analyses of crystallite sizes of the SSM products. Their particle sizes were not analysed in detail, however similar trends have been observed (SEM).

7.2 CONTROL OF PRODUCT CRYSTALLITE SIZE

Several types of manipulations and work-ups were performed on solid state metathetical reactions discussed in chapters 2-5 in order to influence crystallite size. These are described and discussed in the following subsections.

7.2.1 Spreading the reagents

The reagents can be either spread inside a reaction vessel over a large area or placed inside it in a relatively compact bulk. The effect in the first case is that there is more contact with the surroundings, which therefore absorb more reaction enthalpy. When the reagents are spread the heat released from the reaction is more delocalised and the cooling rate increases. This reduces the extent of crystallization of the product.
The reaction of vanadium trichloride with lithium nitride performed in bulk inside an evacuated ampoule at 550 °C for 1 hour initiated at ~400 °C and yields highly crystalline vanadium nitride with a small proportion of vanadium subnitride phase, V₂N, present. An orange thermal flash is observed during the reaction. However if the same reaction is repeated with the reagents spread along the inside of the evacuated ampoule the reaction initiates at a higher temperature (ca. 430-440 °C) with a weaker thermal flash (red). The resulting products have poorer crystallinity and the undesired subnitride phase disappears, leaving after work-up phase pure stoichiometric vanadium nitride, VN. Similar results have been obtained for the reactions of tantalum pentachloride with lithium nitride.

The bulk reaction of chromium trichloride with lithium nitride inside an evacuated ampoule produces a mixture of highly crystalline phases of chromium and chromium nitrides, CrN and Cr₂N, initiating with an orange thermal flash at a temperature of 300-350 °C. However if the same reagents are spread along the inside of the ampoule the reaction initiates at the much higher temperature of 445 °C with a low temperature thermal flash producing only highly crystalline chromium subnitride, Cr₂N (figure 7.1).

7.2.2 Varying the reaction scale

Formation of vanadium nitride using solid state metathetical reactions on variable reaction scales has been performed (Table 7.1). Increasing the reaction scale decreases the cooling rate of the combustion products and increases the time allowed for crystallization. It can also help to complete the reactions. Reactions forming transition metal silicides from parent transition metal halides and magnesium silicide have frequently been reported to be incomplete. SHS reactions, the main characteristics of which in many ways resemble SSM reactions, are aided if their combustion is performed on a large scale, giving products of higher quality.

The reaction of vanadium trichloride with lithium nitride has been repeated four times, varying the reaction scale (Table 7.1). The reactions were all performed simultaneously in a bulk process without extra annealing. X-ray
diffraction analyses of the trititated products revealed that variation of the reaction scale has a similar effect on the crystallite size as spreading the reagents as discussed in the previous section. Increase of the reaction scale leads to formation of more crystalline products. The main problem in this investigation was that reaction scales were limited as dinitrogen gas was released which inside small and closed vessels was hazardous.

![XRD pattern for chromium subnitride, Cr$_3$N, prepared by initiating a bulk reaction of chromium trichloride with lithium nitride at 445 °C with the reagents spread along the ampoule. Standard stick pattern for the subnitride has been assigned below.](image)

**Figure 7.1** XRD pattern for chromium subnitride, Cr$_3$N, prepared by initiating a bulk reaction of chromium trichloride with lithium nitride at 445 °C with the reagents spread along the ampoule. Standard stick pattern for the subnitride has been assigned below.

<table>
<thead>
<tr>
<th>Quantity of Li$_3$N applied/moles</th>
<th>Crystallite size of VN formed/A</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5.7 \times 10^{-4}$</td>
<td>180</td>
</tr>
<tr>
<td>$2.0 \times 10^{-3}$</td>
<td>250</td>
</tr>
<tr>
<td>$2.6 \times 10^{-3}$</td>
<td>280</td>
</tr>
<tr>
<td>$2.9 \times 10^{-3}$</td>
<td>280</td>
</tr>
</tbody>
</table>

**Table 7.1** Representation of varying crystallite sizes of vanadium nitrides, VN, from a number of reactions of vanadium trichloride with lithium nitride performed at various scales. The samples were not annealed. *The Scherrer equation (Formula 2.1) has been used to calculate crystallite sizes.*
It is not expected that there would be a linear relationship between the reaction scales and final product crystallite size. When the reaction scale is very small, minute changes will have an influence. However if the reaction scale is comparatively large further increases should have little effect. It is also necessary to note that increasing the reaction scale has an effect on the final product crystallite size only if the reaction is very rapid. For example the solids obtained from the reactions of molybdenum trichloride with aluminium carbide, performed on various scales without annealing, were all amorphous.

7.2.3 Mode of initiation

It has already been discussed in previous chapters that the three modes of initiation exercised in these reactions yield products with varying degrees of crystallinity. Bulk reactions tend to give products of higher crystallinity than those initiated at a point source with a filament. Thus if the reaction can be initiated by a filament then this method can be utilised to form products with lower crystallinity while bulk reactions can be used to produce more crystalline products. Bulk reactions have a thermal boost provided by heating the whole reaction mixture. Since the temperature of the surroundings is much higher in the bulk reactions than in the filament reactions the rate of cooling of the product mixture is also reduced in bulk reactions.

Solid state metathetical reactions initiated with a flame source produce the most crystalline solids (figure 7.2). This is probably due to the initial input of energy being higher in these reactions than in the corresponding reactions initiated with a filament. The resulting reaction is more rapid and at a higher temperature. A filament provides the energy input on a very local scale promoting a far slower propagation than flame initiation, which in the systems studied tended to cover the whole reaction mixture.

X-ray diffraction patterns of triturated products from the reactions of calcium silicide/magnesium silicide mix with tantalum pentachloride, performed using all three modes of initiation have been used to determine the crystallite sizes using the Scherrer equation. The reaction initiated using a filament showed
average crystallite size of 220 Å. The product from the reaction initiated using a flame had average crystallite size of 480 Å and the bulk reaction 640 Å. No further annealing of the products was performed.

Figure 7.2  [200] X-ray diffraction peaks of titanium nitrides prepared using titanium trichloride and lithium nitride initiated with a filament (a), performed inside an evacuated ampoule (bulk reaction) (b), or initiated with a flame under a nitrogen flow (c).

7.2.4 Using a diluent

Adding a diluent salt such as magnesium chloride to act as an inert heat sink in solid state metathetical reactions has been investigated in detail in this study. The addition of various anhydrous alkaline metal salts to the given mixture reduces the crystallite size of the product as a consequence of a lower reaction temperature. The diluent absorbs some of the reaction enthalpy and increases the path length for diffusion of the reacting components. The magnitude of these effects can also be manipulated. Varying the diluent salt or the reagent/diluent molar ratios modifies the overall effect. There are a number of Group 1 and 2 halides available with different heat capacities enabling a range of diluency. Care must be taken in the preparation of products from salt-added reactions to ensure the initial powders are
intimate mixtures, particularly when producing solids with narrow particle size distributions.

Reactions of transition metal halides with lithium nitride performed inside evacuated ampoules with additional salts, such as the chlorides of lithium, caesium, calcium or magnesium, produce transition metal nitrides, which are of lower crystallinity than the solids obtained from the corresponding reactions performed without the addition of salts. Table 7.2 shows the crystallite sizes of the products from the reactions of vanadium trichloride with lithium nitride using varying molar concentrations of magnesium chloride, calculated using the Scherrer equation from the X-ray powder diffraction patterns. Manipulation of the molar ratio of the diluents and the reagents enabled products to be obtained with a range of crystallite sizes. The reactions where more salt was used, yielded low crystallinity or amorphous solids but those in which very little salt was added, yielded crystalline products although their crystallinity was lower than that of the products obtained from the reactions where no diluents were added. It is also expected that using other Group 1 and 2 salts in the same molar ratios in the reactions with scales kept constant would lead to effects of variable magnitudes. This is due to the differing heats of fusion and melting points of Group 1 and 2 salts (m. pt. LiCl = 613 °C, m. pt. MgCl₂ = 708 °C).
solids are lowered. This is highly advantageous when thermally unstable products are desired. Magnesium chloride used in the reactions of transition metal halides with lithium nitride may simply reduce the crystallite size of the final nitride products but when magnesium nitride is used in place of lithium nitride, thermally unstable nitrides can be produced. These include:

$$\text{CrN, Mo}_2\text{N, W}_2\text{N, Mn}_3\text{N}_2, \text{Mn}_4\text{N, Fe}_2\text{N(Fe}_2\text{N), Co}_2\text{N}_0.67, \text{InN}$$

Combustion analyses for the products from the reaction of manganese diiodide with magnesium nitride in magnesium chloride diluent, Mn$_3$N$_2$, revealed N = 15.02 wt.% (Mn$_3$N$_{2.07}$) and the reaction of chromium dichloride with magnesium nitride in magnesium chloride diluent, CrN, revealed N = 16.2 wt.% (CrN$_{0.72}$). These phases have not been reported previously from solid state metathetical processes. After spreading the reagents and magnesium chloride evenly inside an evacuated ampoule it was possible to initiate a very slow solid state metathetical reaction by raising the temperature of the furnace very slowly to the minimum level required for the reaction to proceed. The molar ratios of magnesium chloride and the nitride precursor used in these reactions are outlined in Table 7.3. In all these reactions reagents were spread along the length of the ampoule prior to initiation. Many products formed in this way were amorphous or nanocrystalline and their lattice parameters were not calculated.

SEM measurements were performed on a selection of thermally unstable transition metal nitrides prepared using magnesium chloride as an inert heat sink. These showed that particle sizes were much smaller than those of more stable transition metal nitrides obtained from reactions where no diluent was used (figure 7.3).

Addition of magnesium chloride as a diluent in solid state metathetical processes has also been applied in the preparation of transition metal carbides and silicides using transition metal halides and carbides or silicides of Group 2. The reactions of calcium carbide with halides of Group 6 metals, initiated with a flame or performed inside an evacuated ampoule lead to the formation of transition metal carbides, transition metal and the co-product. However, if they are repeated inside an evacuated ampoule, with the addition of a small quantity of magnesium chloride,
the reaction yields poorly crystalline carbides of Group 6 transition metals and the co-product salt. If the same reaction is initiated with flame, crystalline products are formed. Further annealing of the as-prepared solids induces better crystallinity within 2-5 days and the phase-pure transition metal carbide desired is isolated from the salt simply by washing with distilled water.

Figure 7.3
SEM micrographs of products from the reactions of hafnium tetrachloride with lithium nitride and sodium azide (a), and molybdenum trichloride with magnesium nitride in magnesium chloride as an inert heat sink (× 2.5 moles of magnesium nitride) (b).

Reactions of halides of molybdenum and tungsten with calcium carbide in the presence of magnesium chloride inside of evacuated ampoules have also been performed using well spread reagents (Table 7.4). The temperature was raised to 550 °C at a slow rate and the products, which began to form very slowly at ca. 400-500 °C were annealed for one week. These new reaction conditions lead to the formation of two nanocrystalline cubic carbides, Mo$_2$C and WC. The reason for their formation in this particular case cannot be explained at present. Table 7.4 illustrates some of the reactions carried out in an attempt to form these products using various other reaction conditions. The hexagonal carbides of molybdenum and tungsten were always favoured except for this unique case.
Table 7.3  
Reactions of transition metal halides with magnesium nitride performed with magnesium chloride acting as an inert heat sink. * Literature lattice parameters were taken from reference [19].

<table>
<thead>
<tr>
<th>Transition metal halide</th>
<th>Conditions</th>
<th>Products after trituration</th>
<th>( a_{obs}/\text{Å} )</th>
<th>( a_{std}/\text{Å} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrCl(_2)</td>
<td>( T_{bulk} = 350^\circ\text{C}, 1 \text{ h}; 500^\circ\text{C}, 1.5 \text{ h}; 1.5 \text{ equiv. MgCl}_2 )</td>
<td>CrN(^a)</td>
<td>4.150</td>
<td>4.150</td>
</tr>
<tr>
<td>CrCl(_3)</td>
<td>( T_{bulk} = 350^\circ\text{C}, 1 \text{ h}; 500^\circ\text{C}, 1.5 \text{ h}; 1.5 \text{ equiv. MgCl}_2 )</td>
<td>CrN (Cr(_2)N)(^a)</td>
<td>( a = 4.147 ) (+/-0.002)</td>
<td>4.150</td>
</tr>
<tr>
<td>MoCl(_3)</td>
<td>( T_{bulk} = ) raised from 350 °C to 410 °C at 5 °C every 12 minutes and maintained at 400 °C for 5 hrs; 2.5 equiv. MgCl(_2)</td>
<td>Mo(_2)N(^b)</td>
<td>4.158</td>
<td>4.163</td>
</tr>
<tr>
<td>WCl(_4)</td>
<td>( T_{bulk} = ) raised from 330 °C to 375 °C at 5 °C every 12 minutes and maintained for 7 hrs; 3.5 equiv. MgCl(_2)</td>
<td>W(_2)N(^c)</td>
<td>4.119</td>
<td>4.126</td>
</tr>
<tr>
<td>MnCl(_2)</td>
<td>( T_{bulk} = ) raised from 330 °C to 400 °C within 90 min., maintained at 400 °C for 120 min.; 2.8 equiv. MgCl(_2)</td>
<td>Mn(_3)N(_2), Mn(^a)</td>
<td>( a = 2.957, c = 12.221 ) (+/-0.002)</td>
<td>( a = 2.966, c = 12.243 )</td>
</tr>
<tr>
<td>MnI(_2)</td>
<td>( T_{bulk} = ) raised from 330 °C to 400 °C within 90 min., maintained at 400 °C for 120 min.; 3 equiv. MgCl(_2)</td>
<td>Mn(_3)N(_2)(^a)</td>
<td>( a = 2.961, c = 12.238 ) (+/-0.001)</td>
<td>( a = 2.966, c = 12.243 )</td>
</tr>
<tr>
<td>FeCl(_3)</td>
<td>( T_{bulk} = ) raised from 290 °C to 360 °C within 60 min., maintained at 360 °C for 90 min.; 5.5 equiv. MgCl(_2)</td>
<td>Fe(_2)N (Fe(_3)N, Fe)(^b)</td>
<td>( a = 2.684, c = 4.350 ) (+/-0.01)</td>
<td>( a = 2.695, c = 4.362 )</td>
</tr>
<tr>
<td>CoCl(_2)</td>
<td>( T_{bulk} = ) raised from 310 °C to 330 °C within 60 min., maintained at 330 °C for 60 min.; 7.5 equiv. MgCl(_2)</td>
<td>Co(<em>2)N(</em>{0.67})(^b)</td>
<td>( a = 2.651, c = 4.352 ) (+/-0.008)</td>
<td>( a = 2.658, c = 4.356 )</td>
</tr>
</tbody>
</table>

* Molar quantities of the diluent are expressed as a ratio with respect to the amount of magnesium nitride used in the 'conditions' column. All the reagents were spread evenly inside the evacuated ampoules prior to initiating any reaction.

\(^a\)crystalline phase obtained, \(^b\)nanocrystalline phase obtained, \(^c\)amorphous phase obtained (lattice parameters calculated for these products are expected to be inaccurate)
Table 7.4  Bulk reactions of transition metal halides with calcium carbide where magnesium chloride (st) or spreading technique (spr) have been used to prevent decomposition of the carbide to metal and carbon during the reaction or to form cubic carbides of molybdenum and tungsten. * Literature lattice parameters were taken from reference [175].

<table>
<thead>
<tr>
<th>Transition metal halide</th>
<th>Salt (st) or spreading (spr)</th>
<th>Products after annealing and trituration</th>
<th>( a_{\text{obs}}/\text{Å} ) (-0.01)</th>
<th>( a_{\text{tal}}/\text{Å} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoCl(_3)</td>
<td>Spr</td>
<td>cubic Mo-C</td>
<td>4.26</td>
<td>4.28</td>
</tr>
<tr>
<td>MoCl(_3)</td>
<td>St ((\times 0.4))</td>
<td>amorphous product formed</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>MoCl(_3)</td>
<td>St ((\times 4))</td>
<td>no reaction</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>WCl(_4)</td>
<td>Spr</td>
<td>cubic WC</td>
<td>4.192</td>
<td>WCo(_{0.5-0.8}) = 4.16-4.22</td>
</tr>
<tr>
<td>WCl(_4)</td>
<td>St ((\times 0.4))</td>
<td>no reaction</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>WCl(_4)</td>
<td>St ((\times 3))</td>
<td>hexagonal WC</td>
<td>(a = 2.902,) (c = 2.834)</td>
<td>(a = 2.906,) (c = 2.836)</td>
</tr>
</tbody>
</table>

*The amounts of magnesium chloride added are expressed as a molar function of calcium carbide used. The reaction mixtures were annealed for various time periods ranging from one to ten days.

7.2.5  Selection of SSM precursors

SSM processes provide a versatile choice of reagents to form borides, carbides, nitrides and silicides of transition metals. The diversity of choice surrounds both the transition metal and main group element precursors. Since all these reagents possess a wide range of thermodynamic stabilities their application to particular syntheses can be tailored to the desired product. These demands can include the control of particle and crystallite sizes of the final product. One of the key concerns in controlling the crystallite sizes of the products in solid state metathetical reactions is the control of the reaction enthalpy. The formation of the co-product is the driving force in these reactions, providing up to 90 % of the reaction enthalpy (which is responsible for the crystallisation of the products). Thus selecting the reagents for the syntheses of a product allows a ‘selection’ of the reaction enthalpies and therefore also to some extent the crystallite size of the final product. For example, to produce a poorly crystalline transition metal nitride,
magnesium nitride can be used instead of lithium nitride. Also a low oxidation state transition metal halide can be used for the enhancement of this effect, as the reaction is then less exothermic as less co-produced salt is formed.

Some nitriding reagents, such as sodium azide, react via an explosive decomposition even when the green reaction mixture is spread over the reaction vessel. Therefore the products formed are less fused and more spread allowing more rapid cooling. The transition metal nitrides obtained from the reactions of sodium azide with transition metal halides are poorly crystalline or amorphous.

The effects on the crystallite size of the products formed using solid state metathetical reactions with various reagents have already been discussed in chapters 2-6. In this section only an outline summary has been provided in form of a table to show the average crystallite sizes of vanadium nitrides prepared using vanadium trichloride and various nitriding agents as an example (Table 7.5). For each of the four groups of compounds studied only the two extreme borderline figures are represented for each one.

Table 7.5  
Representation of crystallite sizes of vanadium nitrides, VN, obtained from the reactions of vanadium trichloride with various nitriding precursors. * The crystallite sizes were calculated using the Scherrer equation (Formula 2.1).  

<table>
<thead>
<tr>
<th>Nitriding precursor</th>
<th>Crystallite size/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₃N</td>
<td>400</td>
</tr>
<tr>
<td>Mg₃N₂</td>
<td>50</td>
</tr>
<tr>
<td>Ca₃N₂</td>
<td>120</td>
</tr>
<tr>
<td>NaN₃*</td>
<td>—</td>
</tr>
<tr>
<td>Li₃N/NaN₃ (mol. ratio 3 : 1)</td>
<td>560</td>
</tr>
</tbody>
</table>

*The products were annealed for 2 hours at 550 °C.

*Sample very poorly crystalline and the crystallite size could not be calculated.

7.2.6 Increase in pressure

This work has shown that a rise in pressure during reaction produces crystalline products more rapidly during annealing than if performed under vacuum.
However the laboratory equipment available to us allowed such pressure manipulations to be only within ~0-2.5 atmospheres at 550 °C. Nitrogen was used as the gas providing the pressure. Thus all the investigations have only been performed on the syntheses of transition metal nitrides. The reagents were placed inside an ampoule which contains several thin necks dividing the vessel into several (3 or 4) chambers (Diagram 2.1). The experimental procedure has been described in section 2.7 for the synthesis of aluminium nitride, using aluminium trichloride and lithium nitride, under nitrogen pressure.

The investigations of solid state metathetical reactions forming transition metal nitrides performed under nitrogen pressure have provided two very important observations. Firstly, the nitrogen pressure present in the synthesis of zirconium nitride using zirconium tetrachloride and lithium nitride has provided a product with much greater crystallinity. The difference in the crystallite sizes was of the order of 2-3 times. A second observation, studied by microanalysis, has shown that the use of nitrogen pressure helps to prevent nitrogen loss from the nitride. This has been studied for the reactions of aluminium trichloride with lithium nitride and is discussed in detail in chapter 2, section 2.4.3. SEM measurements of the particles from these products were taken. It has been observed again that the presence of nitrogen pressure helped to produce more crystalline solids in these reactions.

7.2.7 Annealing the as prepared SSM products

Annealing the as-prepared products of SSM reactions generally showed a marked increase in their crystallinity. The rate of crystallisation was highly dependent on the temperature used and the annealing conditions. The most common annealing temperatures used were 550 °C and 1000 °C. The lower temperature was suitable for annealing transition metal nitrides, which showed a substantial improvement in crystallinity over a period of a few hours. However transition metal carbides required much higher temperatures for annealing and only at 1000 °C did they show a rise in the degree of crystallinity. At 550 °C they had to be annealed for 7-10 days to gain any marked increase in crystallite size.
Transition metal silicides and borides have not been studied thoroughly in this type of investigation. However, initial observations have suggested that the crystal growth in these two groups of SSM prepared materials becomes quite efficient at temperatures as low as 550 °C.

There are also other possible manipulations that can be performed with the reagents before reacting them which may help in either inducing or reducing the crystallinity of the final product in solid state metathetical reactions. One such approach may be pressure pressing the reagents before the reaction takes place. This is due to the higher density of reacting particles obtained. Less of the reaction enthalpy is lost to the surroundings also making the reaction more rapid. The path length for diffusion of reacting components also becomes reduced. However, diffusion might then be hampered in a more packed solid.
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