Nitrides: Transition Metal Solid-State Chemistry

Walter Lengauer
TU-Wien—Laboratory of Physical Metallurgy, Vienna, Austria

1 INTRODUCTION

Together with the transition metal carbides and borides, the transition metal nitrides belong to a family of materials that features an unusual combination of outstanding properties, among which are exceptional hardness, high melting point, metallic luster with sometimes vivid colors, and simple metallic structures combined with excellent electrical and thermal conductivities. This combination of these properties has attracted considerable attention and has resulted in numerous technical applications.1–4 Lengauer5 has compiled several data and features of transition metal nitrides and carbonitrides. Many of the nitride phases closely resemble metallic alloys, with broad ranges of homogeneity, particularly if the structure of the metallic host lattice is one of the types encountered in typical metals. They often form solid solutions with structurally related compounds, such as other transition metal nitrides or carbides, and are easily wetted by liquid metals of the iron group.

The chemical stability of transition nitrides is considerable; they are not readily attacked by dilute acids except by oxidizing acids and hydrofluoric acid or alkaline solutions. The thermal stability is determined by their free energies of formation; the stability decreases with increasing group number. While TiN, ZrN, and HfN can be melted without decomposition at ambient pressure, the nitrides of the other groups decompose by liberating nitrogen before melting points are reached.

Table 1 gives a brief survey of the most important properties of the well-characterized binary transition metal nitrides with a maximum nitrogen content of 50 mol% N. It should, however, be emphasized that practically all properties are significantly influenced by the nitrogen to metal ratio (Section 6) and by impurities.

2 STRUCTURE AND BONDING

2.1 Structures: General Features

Transition metal nitrides, together with the structurally closely related transition metal carbides, belong to the family of “interstitial compounds” or alloys. The common features of this class of materials are the very simple metallic structures with the smaller nitrogen atoms in the interstitial voids of the frequently close-packed host lattice. The simple conceptual Hågg model, in which the basically metallic character of the host metal is thought to be only modified by insertion of nonmetal atoms into the voids, had to be substantially restructured in the light of modern bonding theories in order to account for the strong binding energies observed between transition metal atoms and nonmetal atoms. Nevertheless, the rather approximate interstitial alloy concept has proved helpful for gaining insight into the basic principles governing the structures of interstitial alloys and compounds.

Because of their structural similarities, transition metal nitrides usually form solid solutions with transition metal carbides. However, there are important differences, possibly owing to the different bonding character of nitrogen as compared to that of carbon. Transition metal carbides and nitrides generally have face-centered cubic (fcc) or hexagonal close-packed (hcp) metal lattices with nonmetal atoms more or less randomly distributed on the interstitial sites; deviations from this simple concept are much more frequently encountered with nitrides. If the immediate neighborhood of the nonmetal X (X = C, N) is considered, one can define the structural elements of interstitial alloys.6 In the group 4 and 5 transition metals, the common structural element of the nitrides and carbides is the T₆X octahedron. With increasing radius ratio rₓ/rₜ, the trigonal prismatic group T₆X is favored over the octahedral group. Therefore, the transition metal carbides of groups 6–9 feature trigonal prismatic T₆X elements in different crystallographic arrangements. In transition metal nitrides, a third structural element is occasionally observed, particularly in group 5 compounds, consisting of T₅X square pyramids. These prevail even in the complex nitrides, such as the Z-phases NbCrN, TaCrN, NbMoN, and TaMoN with the filled Θ-CuTi-type structure. With this square pyramid, which has lower symmetry than an octahedron, such nitrides have more complicated structures than the corresponding carbides.

Because of the formation of structural elements other than T₅X octahedra, the fcc structure of δ-nitrides is destabilized increasingly with increasing group number and, within a group, with increasing periodic number. For
Table 1: Bulk properties of important transition metal nitrides

<table>
<thead>
<tr>
<th>Nitride</th>
<th>Homogeneity range (a)</th>
<th>Structure (Bravais lattice)</th>
<th>Lattice parameter (nm)</th>
<th>Density (g cm(^{-3}))</th>
<th>Color</th>
<th>Microhardness (GPa)</th>
<th>Melting point (K)</th>
<th>Heat conduct. (W m(^{-1}) K(^{-1}))</th>
<th>Thermal exp. coefficient (K(^{-1})) at 1000 K</th>
<th>Electr. resistance ((\mu\Omega) cm)</th>
<th>Supercond. transition temp. (T_c) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN(_{1-x})</td>
<td>0.50</td>
<td>fcc</td>
<td>0.4215</td>
<td>–</td>
<td>Metallic gray</td>
<td>23</td>
<td>29</td>
<td>9.5</td>
<td>–</td>
<td>–</td>
<td>&lt;1</td>
</tr>
<tr>
<td>ZrN(_{1-x})</td>
<td>0.72</td>
<td>fcc</td>
<td>0.4585</td>
<td>–</td>
<td>Yellow</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>HfN(_{1-x})</td>
<td>0.85</td>
<td>fcc</td>
<td>0.4523</td>
<td>–</td>
<td>Light yellow</td>
<td>13.9 (0.94)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>8.7 (0.85)</td>
</tr>
<tr>
<td>VN(_{1-x})</td>
<td>0.70</td>
<td>fcc</td>
<td>0.4060</td>
<td>6.05</td>
<td>Brown yellow</td>
<td>13.0</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.7 (0.76)</td>
</tr>
<tr>
<td>NbN(_{1-x})</td>
<td>0.70</td>
<td>fcc</td>
<td>0.4380</td>
<td>6.04</td>
<td>Brown</td>
<td>5.7</td>
<td>2350</td>
<td>10.8</td>
<td>65</td>
<td>–</td>
<td>8.9</td>
</tr>
<tr>
<td>TaN(_{1-x})</td>
<td>0.72 (2200 K)</td>
<td>fcc</td>
<td>0.4345</td>
<td>–</td>
<td>Pale yellow</td>
<td>11.0</td>
<td>–</td>
<td>9.5 (0.92)</td>
<td>–</td>
<td>–</td>
<td>13.8 (0.84)</td>
</tr>
<tr>
<td>TaN</td>
<td>1.00</td>
<td>hex</td>
<td>0.5190</td>
<td>–</td>
<td>Gray yellow</td>
<td>32</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>8.9 (0.94)</td>
</tr>
<tr>
<td>CrN(_{1-x})</td>
<td>1.00 (1500 K)</td>
<td>fcc</td>
<td>0.4148</td>
<td>6.14</td>
<td>Gray</td>
<td>11</td>
<td>1300 (d)</td>
<td>2.3</td>
<td>640</td>
<td>(f)</td>
<td>–</td>
</tr>
<tr>
<td>CrN(_{1-x})</td>
<td>0.31 (c)</td>
<td>hcp</td>
<td>(a_0 = 0.4750^{[d]})</td>
<td>6.51</td>
<td>Gray</td>
<td>12 (d)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(c_0 = 0.4430^{[e]})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>MoN(_{1-x})</td>
<td>0.40</td>
<td>fcc</td>
<td>0.4139</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>MoN</td>
<td>0.62 (1200 K)</td>
<td>hex</td>
<td>(a_0 = 0.5745^{[c]})</td>
<td>9.1 (c)</td>
<td>Gray</td>
<td>17 (b)</td>
<td>–</td>
<td>9.3</td>
<td>–</td>
<td>–</td>
<td>5.08</td>
</tr>
<tr>
<td>MoN(_{1-x})</td>
<td>0.40</td>
<td>fcc</td>
<td>0.4162</td>
<td>9.84 (c)</td>
<td>Gray</td>
<td>17 (b)</td>
<td>–</td>
<td>9.3</td>
<td>–</td>
<td>–</td>
<td>5.08</td>
</tr>
</tbody>
</table>

(a) Nitrogen-rich phase boundary depends on nitrogen pressure.
(b) Exact composition phase boundary depends on nitrogen pressure.
(c) X-ray density.
(d) Decomposes.
(e) Calculated.
(f) Not superconducting.
(g) Exact composition unknown.
example, the nitrides of group 4, δ-TiN$_{1-x}$, δ-ZrN$_{1-x}$, and δ-HfN$_{1-x}$, crystallize in the sodium chloride structure. No low-temperature modifications of these stoichiometric nitrides are known. In group 5, all three metals form stoichiometric fcc nitrides also, but δ-VN$_{1.00}$ transforms below 205 K into a tetragonal modification, δ-NbN$_{1.00}$ changes below around 1320 °C into hexagonal η-NbN, and δ-TaN$_{1.00}$ converts below around 1920 °C congruently into hexagonal ε-TaN.

In group 6, these fcc nitrides are increasingly less stable: fcc CrN is nearly a line compound (i.e., one with a very narrow range of stoichiometry) at low temperature with a reduced thermochemical stability; it transforms below approximately 280 K into a tetragonal antiferromagnetic compound. In γ-MoN$_{1-x}$, apparently does not occur with a nitrogen content even approaching the ideal composition MoN$_{1.00}$ (except perhaps at very high pressures) but it is rather in the vicinity of MoN$_{0.50}$. fcc MoN$_{0.30}$ also transforms into a tetragonal modification with an ordered arrangement of nitrogen atoms in the interstitial sites. This tendency proceeds further in the Mn–N and Fe–N systems, where ferromagnetic fcc phases with the stoichiometry T$_{3/4}$N are observed with an ordered arrangement of N atoms. Ordered manganese nitride phases with respect to the arrangements of nitrogen and a concurrent tetragonal distortion of the metal host lattice are found. An fcc MnN$_{1-x}$ can be prepared by high-rate reactive sputtering.

An extensive compilation of nitride phases is contained in Pearson’s handbook and in the ASM binary phase diagram compilation.

The different stacking of close-packed metal layers can be described by the Jagodzinski–Wyckoff notation, where close-packed stacking ABC, ABC, ... is designated as ‘‘c’’ and hcp stacking AB, AB, ... is designated as ‘‘h’’. Figure 1 shows these structures and lists several metal nitride and carbide phases that can be described with this formalism.

### 2.2 Bonding

The bonding in transition metal carbides and nitrides can be described as a mixture of metallic, covalent, and ionic components. The metallic character is immediately noticed in the high electrical conductivities of these compounds. The bonding mechanism was described extensively by a variety of approaches for calculating the density of states (DOS) and, hence, the electron density, in fcc transition metal nitrides, carbides, and oxides. In the DOS of these compounds, there is a minimum at a valence electron concentration (VEC) of eight that corresponds to the stoichiometric composition of group 4 carbides TiC, ZrC, and HfC. Figure 2 compares the decomposed and the total DOS of TiN and TiC with respect to the s, p, and d bands. At low energies of <0 Ryd, the s band is characterized by a large contribution of the nonmetal 2s state. Above 0 Ryd, the p band follows and there is a significant contribution of d states to this band, too. At higher energies, the d band composed of d states follows with the Fermi energy $E_F$ located well within this band. The DOS at $E_F$ is higher for TiN than for TiC, consistent with the observed superconducting properties (TiN, $T_c = 5.4$ K; TiC, $T_c < 1.2$ K) and room-temperature electrical conductivities (Section 6.3).

An illustrative picture of covalent bonding in these compounds can be drawn in the molecular orbital (MO) scheme where atomic orbitals of atoms are combined to form bonding and antibonding states. Figure 3 shows a schematic drawing of these bonds between metal d and nonmetal p orbitals in the (100) plane of the fcc structure, which can be decomposed into two different bonding symmetries, $t_{2g}$ and $e_g$. It can be shown that the calculated electron densities in this plane reflect the change of $e_g$ bonding symmetry in TiC to $t_{2g}$ bonding symmetry in TiN. Thus, the exchange in bonding strength from a strong Ti–C interaction in TiC toward a more pronounced Ti–Ti interaction in TiN is to be expected.
The ionic contribution to the binding mechanism of transition metal nitrides and carbides can be estimated from the charge transfer from the metal atom to the nonmetal atom. It is about half an electron per atom, which contributes to the electrostatic interaction of metal and nonmetal.

The bonding of 4d transition metal nitrides and carbides can be treated in a very similar way; the nonmetal contribution to the electron density is about the same, whereby the contribution from 4d electrons causes a greater spatial extension of electron density than in 3d compounds. In 5d transition metal nitrides and carbides, relativistic effects owing to the heavy cores have to be taken into account.

3 PREPARATION

Transition metal nitrides can be prepared by allowing the metal or the metal hydride in powdered or compact form to react with molecular or atomic nitrogen or flowing ammonia (equations 1–3):

$$\text{Ti} + \frac{1}{2} \text{N}_2 \rightarrow \text{TiN} \quad (1)$$

$$\text{ZrH}_2 + \frac{1}{2} \text{N}_2 \rightarrow \text{ZrN} + \text{H}_2 \quad (2)$$

$$\text{Mo} + \text{NH}_3 \rightarrow \text{MoN} + \frac{3}{2} \text{H}_2 \quad (3)$$

$$\text{TiO}_2 + 2\text{C} + \frac{1}{2} \text{N}_2 \rightarrow \text{TiN} + 2\text{CO} \quad (6)$$

The pressure of molecular nitrogen at a given temperature that is necessary to obtain a specific nitride phase is defined by the nitrogen potential (partial free energy of nitrogen) of the nitride. In flowing ammonia, very high nitrogen potentials can be maintained. However, the decomposition of ammonia by the reaction (equation 4)

$$2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2 \quad (4)$$

is very fast at increased temperatures, which are necessary for diffusion of nitrogen in the nitrides, if bulk samples have to be prepared. Hence, the amount of decomposed ammonia is high. The nitriding potential of ammonia according to equation 4 is (equation 5)

$$\text{RT} \cdot \ln(p\text{N}_2) = -\Delta G = \text{RT} \cdot \ln p \left( \frac{3}{2} x \right) + 2\text{RT} \cdot \ln p(1 - x)$$

where \(\Delta G\) is the free energy of the above decomposition reaction and \(x\) is the portion of ammonia that has decomposed. The smaller the portion \(x\), the higher is the nitriding potential of ammonia.

The formation of nitrides from oxides is performed in the presence of carbon as a reducing agent, according to the overall reaction (equation 6)
This reaction usually proceeds over several intermediate products and the resulting nitride may contain oxygen and carbon.

For the preparation of nitrides from metal powders, the exothermic heat of formation can be utilized in the self-sustaining high-temperature synthesis (SHS) process. If the reaction is exothermic enough, that is, if the heat generated is sufficient to reach the reaction temperature, then the starting material is converted to the nitride and the heat is dissipated. For the preparation of large crystals, zone-annealing techniques were developed. Similar to the zone-melting process, a heated zone is passed along a rod in a nitrogen atmosphere. The starting materials are either solid-state sintered nitride powders or metal powders pressed into rods. The applied temperatures must be very high (about 3000 °C) in order to overcome the low diffusivity of nitrogen in nitrides, but they must not exceed the melting temperatures of the compounds in order to avoid incongruent melting and decomposition. Crystals on the order of 1 cm² were produced by this technique. While they still may show some concentration gradients, they are suitable for solid-state investigations such as neutron diffractometry.

A great variety of methods were applied to the preparation of nitride layers. These can be divided into three main groups:

- Chemical vapor deposition (CVD)—a volatile transition metal compound such as a chloride is reacted in the gas phase with ammonia, nitrogen/hydrogen, or ammonia/hydrogen/nitrogen mixtures. The high-melting nitride that forms as a reaction product in the gas phase nucleates on any solid present, for example, hardmetals, and forms compact strongly adhering layers at temperatures around 1000 °C.
- Physical vapor deposition (PVD)—the transition metal is evaporated by electron beam or plasma heating or sputtered by glow discharge and reacted with low-pressure nitrogen (typically in the range of 10⁻⁴ mbar). Numerous modifications of PVD methods have been developed. The nitride layers that are deposited on the substrate often have high lattice defect concentrations and hence exhibit significant deviations from generally known bulk values (lattice parameters, hardness, composition, etc.).
- Surface nitridation is widely used for surface hardening and can be achieved by subjecting the material surface to the action of ammonia, molecular or atomic nitrogen, or nitrogen ions. Casehardening techniques also make use of cyanide salt baths to form nitrides or carbonitrides on material surfaces. Reactive plasma techniques and high-pressure techniques were developed to keep the workpiece temperature low and to avoid thermally induced changes in the workpiece. Laser irradiation together with an N₂ jet directed on the heated spot is employed for locally limited heating of the sample. This nitridation method is applicable to titanium alloys (e.g., Ti₆Al₄V) used to create wear- and corrosion-resistant layers on steam turbine blades for protection against droplets having supersonic velocity.

4 CHARACTERIZATION

4.1 Chemical Analysis

Several procedures can be applied for the analysis of nitrogen and impurities such as oxygen and carbides in nitrides.

- Combustion analysis according to the Dumas method—the sample is heated at temperatures of up to 1200 °C in oxygen and/or with oxidizing agents such as V₂O₅, CuO, or Cu₂O. The evolved N₂ is measured either volumetrically in an azometror or via a gas chromatograph equipped with a thermconductivity detector. With the latter equipment, C and H can also be determined simultaneously via the combustion products CO₂ and H₂O. The accuracy of the method is better than 1 rel%N for finely powdered samples if combustion can be completed within a rather short time span.

- Carrier gas hot extraction—the sample is heated to more than 2000 °C in the presence of carbon and an auxiliary bath of metal such as platinum and in a stream of a carrier gas such as He. Nitrogen is liberated as N₂ and is usually measured in a thermconductivity cell. Oxygen combines with C to give CO and can thus be analyzed. Because of the high temperatures involved, the method is suitable for powder samples with larger grain size or even for small solid pieces. The accuracy of the method is on the order of 1–2 rel%N.

- Kjeldahl analysis—this involves the dissolution of nitrides in acids whereby the nitrogen is converted into ammonium ions. The dissolution process may be time consuming as some nitrides, such as δ-TiN₁₋ₓ, are chemically very stable against acids and must be dissolved using severe conditions such as by the action of hydrofluoric acid in polytetrafluoroethylene (PTFE) containers at 100–200 °C. It is doubtful whether all of the nitrogen can be converted into NH₄⁺, so systematic errors may arise.

4.2 Physical Analysis

Among the microphysical methods used for the analysis of nitrogen in nitrides, for example, electron probe microanalysis (EPMA), Auger electron spectroscopy (AES), ultraviolet X-ray spectroscopy (UPS), X-ray spectroscopy (XPS), secondary ion-mass spectrometry (SIMS) or secondary ion-neutral mass spectrometry (SNMS), and Rutherford backscattering (RBS), EPMA is considered to have the highest reproducibility and accuracy, provided that the lateral resolution of only a few microns is sufficient. The
main problem in EPMA is the rather low energy of $N_{K\alpha}$ radiation. Even with windowless detector systems, a high background-to-peak ratio together with low net intensities is the result.22 High-accuracy EPMA requires external or internal standardization22,23 together with a wavelength-dispersive spectrometer equipped with high-quality crystals (e.g., W–Si multilayer or lead stearate crystals). For standardization, diffusion couples were used in which diffusion layers are broadened.24–26 Such samples can even be prepared in single-phase form upon increase of diffusion time so that the gross chemical composition is the same as the phase composition, a necessary prerequisite for application of different analyzing techniques and for true standardization.27 By such a method, single-phase standards of $\epsilon$-TaN,28 $\delta$-CrN,29 and $\zeta$-Hf$_4$N$_{3-x}$30,31 were prepared. These phases have a very narrow homogeneity range, at least at certain temperatures.

Neutron activation analysis (NAA) making use of the nuclear reaction $^{15}$N$(n,2n)^{13}$N can be applied for bulk determination of nitrogen.

5 THERMODYNAMICS AND SPECIFIC STRUCTURAL FEATURES

5.1 Nitrogen Partial Pressure

The nitrogen partial pressure of the transition metal nitrides is a function of temperature and increases substantially with increasing group number. This is reflected in the Richardson diagram shown in Figure 4. The lower (the more negative) the free energy of formation, the lower is the equilibrium nitrogen pressure of the nitride. Group 4 nitrides can easily be obtained by nitridation of the metals with molecular nitrogen under low pressures even at high temperatures, whereas for the group 5 nitrides, the nitrogen pressure must already exceed normal pressure at temperatures above 1400 °C, and even higher pressures or more energetic nitriding conditions must prevail for the preparation of group 6 nitrides.

The nitrogen pressure determines the composition of the nitride if equilibrium is attained. Thermochemical models were established that correctly predict pressure–temperature–composition ($p$–$T$–$x$) relationships for nitride phases.

Nitride phases with a nonmetal to metal ratio greater than 1 were obtained with high-pressure nitrogen or at high nitrogen potentials, such as those prevailing in flowing ammonia or ionic nitrogen atmospheres. Either an extension of the mononitride phase field to compositions $N/T > 1$ was observed, such as in the Nb–N, Hf–N, and Ta–N systems, or distinct nitride phases were found such as in the Zr–N, Hf–N, Nb–N, and Ta–N systems.33–35 Thermodynamic models were also used for these phases to establish the stability regions and to supply data for preparation at extremely high nitrogen pressures and high temperatures.33

Ion implantation techniques can lead to nitrides having extremely high nitrogen to metal ratios, such as TiN$_{1.5}$, but these phases are probably metastable.

5.2 Phase Equilibria and Structural Features

Several of the transition metal–nitrogen systems are not yet fully established. This is especially the case for some of the metals in groups 6–9, probably because of the lower technical relevance of the nitrides and the high nitrogen pressures needed for equilibrium investigations.

For nitrides of a composition exceeding $[N]/[Me] = 1$, that is, containing more than 50 mol% N, which can be obtained at increased nitrogen activity,33,34 an introduction into a phase diagram is not possible. Such nitrides, for example, cubic Zr$_3$N$_4$ and Hf$_3$N$_4$36 as well as Ta$_3$N$_5$,37 were prepared in small bulk samples by diamond anvil cell preparation; some others, for example, orthorhombic Zr$_3$N$_4$, Ta$_3$N$_5$, and Mo$_5$N$_6$, were prepared with high-pressure nitridation or reaction with ammonia.38–40 and several niobium and tantalum nitrides were generated in the form of a band in diffusion couples35 or in the form of thin films.41 Some further details on some of these nitrides are given in Section 6.8.

5.2.1 The Ti–N System

The distinctive features of the Ti–N system42 are a consequence of the high solubility of nitrogen in $\alpha$-Ti; it consists of the three subnitride phases $\eta$-Ti$_3$N$_{2-x}$, $\zeta$-Ti$_i$N$_{3-x}$, and $\epsilon$-Ti$_2$N and the fcc phase $\delta$-TiN$_{1-x}$ with the sodium chloride structure. $\eta$-Ti$_3$N$_{2-x}$ and $\zeta$-Ti$_i$N$_{3-x}$ were found to be isostructural with the hafnium subnitride phases and are characterized by metal atom layers comprising cubic and hexagonal stacking sequences (Figure 1). Figure 5 shows the phase diagram of the Ti–N system.

In $\delta$-TiN$_{0.50}$, the random distribution of nitrogen atoms undergoes an ordering process43 below about 880 °C, with a concurrent tetragonal distortion of the metal lattice. The consequently formed $\delta'$-TiN$_{0.5}$ phase is only formed from $\delta$-TiN$_{1-x}$ by lattice distortion; it is not an equilibrium phase (e.g., it is not formed in isothermal diffusion couples in the form of a phase band). Figure 6 shows a diffusion couple44 that was prepared by nitridation of Ti metal in a first step and then annealed in order to form the $\delta'$-TiN$_{0.5}$ phase within the nitrogen-poor region of $\delta$-TiN$_{1-x}$. The metallographic appearance of a hatched region confirms the above-mentioned formation of the $\delta'$-TiN$_{0.5}$ phase.

A possible Ti$_3$N$_4$ phase has so far only been proposed by calculation, contrary to Zr$_3$N$_4$ and Hf$_3$N$_4$, which were obtained in an anvil cell.36
5.2.2 The Zr–N System

The solid solution of nitrogen in Zr, α-Zr(N), exists up to a composition of about 33 mol% N. The phase diagram of the Zr–N system is characterized by the presence of only one nitride phase, δ-ZrN\(_{1-x}\), up to a composition of [N]/[Zr] = 1. It should be mentioned that none of the subnitride phases that exist in the neighboring systems Ti–N and Hf–N occur here. In Massalski’s compilation\(^{11}\) (Figure 7), the Zr\(_3\)N\(_4\) phase\(^{36,45}\) has not been included. This phase was prepared at high nitrogen pressure and temperature (15.6–18 GPa, 2500–2800 K) in an anvil cell and could thus be characterized in more detail\(^{36}\). It crystallizes in space group \(I\bar{4} 3d\) (no. 220) with a lattice parameter of 0.6740 nm. Further properties are given in Section 6.8.

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**Figure 4** Richardson diagram of various transition metal mononitrides (together with other nitrides) giving the free energy of formation as a function of temperature. (Reproduced from Ref. 4. P. Ettmayer and W. Lengauer, ‘Nitrides’ in *Ullmann’s Encyclopedia of Industrial Chemistry*. pp. 341. 1991. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)
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5.2.3 The Hf–N System

Besides the fcc \( \delta'\)-HfN\(_{0.5}\), the Hf–N system contains two subnitride phases, \( \eta\)-Hf\(_2\)N\(_{2.5}\) and \( \zeta\)-Hf\(_3\)N\(_{3.5}\). Only a few phase equilibria studies were performed for this system. Figure 7 shows the compiled phase diagram together with results from diffusion couples.\(^{30,31}\) The homogeneity ranges of the subnitride phases could be established; the decomposition temperatures of these phases, however, need to be reinvestigated.

An Hf\(_3\)N\(_4\) phase with the same structure as Zr\(_3\)N\(_4\)\(^{36}\) but with a lattice parameter of 0.6701 nm, and thus smaller than the corresponding Zr nitride, was synthesized at 18 GPa at 2800 K in a diamond anvil cell by laser heating. Some properties of Hf\(_3\)N\(_4\) are given in Section 6.8.

5.2.4 The V–N System

In the V–N system, the phases \( \beta\)-V\(_2\)N and \( \delta\)-VN\(_{1-x}\) have cph and fcc structures, respectively. Carlsson et al.\(^{47}\) have reviewed the V–N system and reinvestigated the vanadium-rich portion. Compiled data and results of a phase diagram study based on diffusion couples\(^{48}\) were used to construct the phase diagram shown in Figure 8.

Stoichiometric VN undergoes a phase transition into a tetragonal phase below 205 K.\(^{7}\) At a composition of around VN\(_{0.80}\), a transition into a tetragonal phase occurs at 500 °C. Two different versions of the phase diagram at temperatures below 500 °C were reported,\(^{51,52}\) one with a eutectic and one with a peritectic phase reaction between tetragonal VN\(_{0.83}\) and \( \delta\)-VN\(_{1-x}\).

5.2.5 The Nb–N System

Brauer et al.\(^{53,54}\) made careful studies on \( p-T-x \) relationships in the Nb–N system. In recent years, the phase reactions in this system were investigated by high-temperature X-ray diffraction as well as by use of diffusion couples.\(^{35,49,55,56}\) The phase reactions could be assumed as

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**Figure 5** Phase diagram of the Ti–N system. (Reproduced from Ref. 42. © Elsevier, 1991.)

**Figure 6** Reannealed diffusion couple showing the formation of the \( \delta'\)-TiN\(_{0.5}\) phase\(^{44}\)
of the $\delta$-NbN$_{1-x}$ phase can be extended beyond N/Nb = 1. At even higher nitrogen pressure, the phase Nb$_3$N$_6$ can be prepared.\textsuperscript{35} Nb$_3$N$_6$ is isotypic with Ta$_3$N$_6$ and features T$_5$N square pyramidal structural elements. These structural elements were not observed in the analogous carbide systems and are probably linked to the higher electron concentration in nitrides.

5.2.6 The Ta–N System

The lower stability of the tantalum nitride phases as compared to the nitrides of the group 4 metals is reflected in their substantially higher equilibrium pressures (Figure 8).\textsuperscript{58} In order to prepare the high-temperature fcc phase $\delta$-TaN$_{1-x}$, the nitrogen pressure must exceed 10 bar, but it can be stabilized at lower pressures and temperatures by minute amounts of carbon. It is the hardest known transition metal nitride phase. The Ta$_2$N phase belongs to the $\epsilon$-Fe$_2$N type at low temperatures and undergoes an order–disorder transition to an L3 type between 1600 and 2000 °C. The often-cited melting point of TaN of 2950 °C is probably incorrect and has to be attributed to Ta$_2$N. TaN is expected to melt at about 2800–3000 °C and nitrogen equilibrium pressures of 1–3 kbar. The $\Theta$-TaN phase with a WC-type structure is often observed in the reaction products of Ta powder with nitrogen or ammonia at temperatures below 1100 °C and is believed by Brauer et al.\textsuperscript{57} to be a high-pressure phase that is metastable under normal conditions. $\varepsilon$-TaN has a structure not encountered in carbides, featuring an arrangement of Ta$_2$N squared pyramids. There are three stoichiometric phases in the Ta–N system with decreasing metallic character. Red Ta$_x$N$_5$ is nonmetallic and was synthesized by the reaction of TaCl$_5$ with NH$_3$. In this rhombohedral phase, the nitrogen atoms are situated in the centers of tetrahedra, while the tantalum atoms are still sixfold coordinated by nitrogen atoms in the form of slightly distorted octahedra. Orthorhombic $\eta$-Ta$_2$N$_3$ was prepared in different types of a high-pressure apparatus at 9–20 GPa nitrogen pressures and temperatures up to 2000 K.\textsuperscript{37,58–60} This compound can contain some small amount of nitrogen. Because of the closure of pores after metallographic preparation, a self-healing mechanism was reported.\textsuperscript{37} Further data are given in Section 6.8.

5.2.7 The Cr–N System

The Cr–N system is characterized by the nitride phases $\beta$-Cr$_2$N$_{1-x}$ and $\delta$-CrN. The former has an appreciable homogeneity range. The arrangement of the metal atoms is cph and the nitrogen atoms are distributed in an ordered arrangement in the interstitial voids corresponding to the $\epsilon$-Fe$_2$N-type structure. CrN crystallizes in the sodium chloride-type structure and its homogeneity range at low temperature is rather narrow, whereas it is substantially broadened above about 1230 °C.

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![Figure 7 Phase diagrams of group 4 transition metal–nitrogen systems. (a) Zr–N (Ref. 11. Reproduced by permission of Materials Information Society/ASM International), (b) Hf–N. (Reproduced from Ref. 30. © Elsevier, 1993.]

Near the composition NbN, at least three phases were observed. For $\eta$-NbN, two different structures were proposed with respect to the nitrogen positions. It contains trigonal prismatic and octahedral T$_5$N structure elements and features a metal layer sequence AABB. $\eta$-NbN undergoes a phase transition at about 1320 °C (depending on the nitrogen pressure) into fcc $\delta$-NbN$_{1-x}$ with a sodium chloride structure. Another phase, $\delta$'-NbN$_{0.97}$, is most probably oxygen stabilized or occurs as a metastable phase with phase transitions and is not included in the phase diagram. By reacting Nb powder with nitrogen under high pressure, the composition...
Dilute acids readily dissolve Cr$_2$N$_{1-x}$, whereas CrN appears to withstand acid attack for prolonged periods. CrN is paramagnetic at room temperatures and undergoes a paramagnetic–antiferromagnetic first-order transition at temperatures between 276 and 286 K, depending on the composition. The phase equilibria in the Cr–N system are strongly dependent on the nitrogen pressure. A phase diagram based on literature data is shown in Figure 8.

![Phase diagram of group 5 transition metal–nitrogen systems](image_url)

**Figure 8** Phase diagram of group 5 transition metal–nitrogen systems. (a) V–N (Ref. 48. Reproduced by permission of Materials Information Society/ASM International), (b) Nb–N (Reprinted from Ref. 49. © 2000, with permission from Elsevier), and (c) Ta–N. (Reproduced from Ref. 50. © Elsevier, 1998.)
As fcc–\(\text{Mo}_2\text{N}_{1-x}\) was reported to exist at nitrogen contents above 33 at% and as it forms solid solutions with fcc \(\delta\)-CrN, it can be assumed to be basically of the fcc \(\delta\)-nitride type. This compound undergoes an ordering transition of the nitrogen atoms and a concurrent tetragonal distortion of the metal lattice into \(\beta\)-Mo\(_2\)N between 400 and 850 °C, depending on the composition. A hexagonal phase, Mo\(_2\)N, which would be expected by analogy with the other transition metal nitride systems, appears to be thermodynamically less stable than the cubic phase, because in the ternary system Mo–C–N, the compositional range of the hexagonal solid solution Mo\(_2\)(C\(_x\),N\(_{1-x}\)) extends from Mo\(_2\)C to approximately Mo\(_2\)(C\(_{0.35}\)N\(_{0.65}\)).

Another phase, \(\delta\)-MoN, with a structure similar to that of WC, was prepared by various methods including nitridation of Mo powder with flowing ammonia and reaction of MoCl\(_5\) with NH\(_3\). It was structurally characterized to have several types of ordered arrangements of nitrogen in the centers of trigonal prismatic structure elements.

While at least 15 different nitride phases with compositions ranging between W\(_2\)N and W\(_3\) have been reported, none of them appears to be very well characterized. Some theoretical calculation of phase stabilities of tungsten nitrides have been carried out. As for the Mo–N system, an fcc nitride W\(_{1-x}\) appears to exist, as nitridation experiments under pressure in the Mo–W–N system have shown that the fcc Mo\(_{1-x}\) phase is able to form extended solid solutions with the isotypic phase W\(_{1-x}\). The pressure required to bring molecular nitrogen to reaction with tungsten at such temperatures, where kinetics are favorable, appears to be possible in diamond anvil cells. It is quite probable that another phase, WN with a WC-type structure, exists; at least it was shown that nitrogen stabilizes the quaternary solid solution (Mo,W)(C,N) with a WC-type structure. Except for the solubility of nitrogen in bcc WN, no reliable data for this system are available.

5.2.9 The Mn–N, Fe–N, Ni–N, and Co–N Systems

The Mn–N system bears some resemblance to the Cr and Fe nitride systems. The correspondence to the Cr–N system manifests itself by the existence of the Mn\(_2\)N\(_{1-x}\) phase with a cph arrangement of Mn atoms as well as two nearly cubic phases with compositions \(\eta\)-Mn\(_3\)N\(_4\) and \(\delta\)-Mn\(_6\)N\(_5\).

Similarity to the Fe–N system is reflected by the extensive solid solubility of nitrogen, particularly in the fcc manganese (austenite) phase and the occurrence of a ferromagnetic Mn\(_4\)N phase. The nitrides with higher nitrogen contents, \(\eta\)-Mn\(_3\)N\(_3\) and \(\delta\)-Mn\(_6\)N\(_5\), can only be prepared by the reaction of ammonia with manganese powder at rather low temperature, suggesting that the equilibrium pressures of nitrogen are very high even at moderate temperatures. \(\eta\)-Mn\(_4\)N\(_3\) resembles in its structure the ordered phases Mn\(_3\)N\(_3\) and \(\beta\)-Mn\(_4\)N\(_3\), where ordering of the nitrogen atoms at the interstitial sites is accompanied by a tetragonal distortion of the cubic lattice. The \(\Theta\)-Mn\(_6\)N\(_3\) phase

---

comes very close to the stoichiometric composition MnN but still has a clearly visible tetragonality of the basically fcc lattice. CrN apparently stabilizes an fcc solid solution extending from CrN up to (Cr$_{0.2}$Mn$_{0.8}$)N$_{1-x}$ at 1000 °C and 800 bar N$_2$.\(^67\)

The solubility of nitrogen in austenite (γ-Fe) is much higher than that in α-Fe, and in this respect, nitrogen behaves similarly to carbon. Upon cooling of nitrogen-containing austenite, a structure develops that is similar to pearlite and is consequently called nitrogen pearlite. Unlike carbon, nitrogen forms an ordered Fe$_4$N phase that is ferromagnetic below 480–508 °C. At about 680 °C, Fe$_4$N transforms into ε-Fe$_2$N$_{1-x}$, and in that respect, the close similarity to the Mn–N system becomes apparent. Besides ε-Fe$_2$N with an ordered arrangement of nitrogen atoms on the interstitial sites between the hexagonally arranged metal atoms, the ζ-Fe$_2$N phase with a slightly higher nitrogen content and an orthorhombic distortion of the cph metal lattice was reported. Figure 10 presents the Fe–N phase diagram with pressure isobars.\(^68\)

Various iron nitrides and carbonitrides are formed during case hardening of steels and alloyed steels.\(^69\) These iron nitrides are hard, highly wear resistant, and usually do not lead to dimensional changes in the case-hardened items.

While there are no phase diagrams available for the Co–N and Ni–N systems, it can be supposed that they are similar to the Fe–N system but with even higher equilibrium pressures. Several phases were prepared by the reaction of flowing ammonia with Co and Ni powder.\(^57\)

5.2.10 Ternary and Higher Order Nitride Systems

Binary transition metal nitrides can form ternary solid solutions with each other\(^70\) if they are isostructural and if their lattice parameters differ by no more than about 10–15%. δ-VN$_{1-x}$ and δ-ZrN$_{1-x}$ do not form extensive solid solutions with each other and the inter(solubility of δ-VN$_{1-x}$ and δ-HfN$_{1-x}$ is not complete, either.

Ternary phases with structures different from those of the phases of the binary boundary systems are more the exception than the rule. Such phases were reported in the systems Nb–Mo–N, Ta–Mo–N, Nb–Ta–N, Zr–V–N, Nb–Cr–N, and Ta–Cr–N. Information about ternary transition metal–nitrogen systems is often available for specific temperatures only.\(^57\) This is even more the case for quaternary nitride systems, which play a role in the production of carbonitride cermets (see Section 7) where quaternary compounds of the types (Ti,Mo)(C,N) and (Ti,W)(C,N) are of interest (see Carbides: Transition-Metal Solid-State Chemistry), as well as in layer technology where titanium nitride-based coatings of the type Ti(C,B,N) are prepared by magnetron sputtering. Layers consisting of ternary compounds in the systems Ti–Al–N, Cr–Al–N, Ti–V–N, Ti–Si–N, and Ti–Cr–N also have favorable properties with respect to performance in cutting tools\(^51–78\) (see Section 7).

A further group of ternary nitrides is of the type R$_2$Fe$_{17}$Nx, where R is a rare earth element such as Sm, Ce, or Nd and x indicates the variable nitrogen content. These phases have been prepared by nitridation at relatively low temperatures and up to 15 MPa N$_2$, under which conditions the nitrogen content can reach $x = 3$. They are closely related to
borides and carbides with similar formulas and have attracted considerable interest for hard-magnetic applications.\textsuperscript{79} It was reported that these phases can reach compositions where $x = 6$, using a combination of hydrogen and nitrogen treatments.

Additional generally interesting phases from the crystal chemistry viewpoint are the H-phases,\textsuperscript{80} for example, Ti$_2$AlN, nitrogen perovskites, filled $\beta$-manganese-type phases, and Nowotny\textsuperscript{8} phases.

6 PROPERTIES OF FCC TRANSITION METAL NITRIDES

For carbonitrides, see Carbidess: Transition-Metal Solid-State Chemistry\textsuperscript{1}.

6.1 Melting Points

Melting points of various nitrides\textsuperscript{81} were measured under nitrogen pressures up to 300 bar. The nitrogen pressure has to be chosen in such a way as to be equal to the nitrogen equilibrium pressure of the nitride at its melting point. The melting point temperatures of the various nitrides can reach more than $3000\, ^\circ\text{C}$ and can be read from the phase diagrams given in Section 5.2.

6.2 Color

Many mononitrides exhibit vivid colors of a bright metallic appearance that depends on the N/T ratio. Table 1 lists the colors of the mononitrides and gives some idea of their color-composition interdependency. These colors can be observed in bulk samples and have an important role when thin films\textsuperscript{77,82} are produced for ornamental purposes.

6.3 Thermal and Electrical Properties

Interestingly, the transition metal carbides and nitrides do not show the expected decrease in heat conductivities with temperature but instead display an increase.\textsuperscript{83} Figure 11 illustrates this property for the group 4 nitrides and shows a comparison with group 4 carbides and carbonitrides. The substitution of nitrogen by carbon in group 4 transition metal nitrides significantly reduces the heat conductivities.

The electrical conductivities of transition metal carbides and nitrides are greatly influenced by the nonmetal/metal ratio; as this ratio approaches unity, the electrical conductivity reaches a maximum. This is shown for $\delta$-TiN$_{1-x}$ in Figure 12.\textsuperscript{85} A similar behavior can be observed for other carbides and nitrides. The electrical conductivities of these compounds decrease linearly with increasing temperature.\textsuperscript{84}

The phenomenon of superconductivity is common for all fcc transition metal nitrides of groups 4 and 5 and is also observed in fcc MoN$_{1-x}$ and hexagonal MoN. $\delta$-NbN$_{1-x}$ shows the highest superconducting transition temperature of 17 K, which was the highest known of any material for several decades. It is noteworthy that hexagonal $\delta$-MoN also has one of the highest superconducting transition temperatures (15 K) of these materials,\textsuperscript{64} and fcc $\gamma$-MoN$_{1.00}$, although never prepared with a stoichiometric composition, was predicted theoretically to have a $T_c$ of up to 30 K. All transition metal nitrides are type II (hard) superconductors. For several fcc nitrides, such as $\delta$-TiN$_{1-x}$, $\delta$-ZrN$_{1-x}$, and $\delta$-VN$_{1-x}$, $T_c$ increases linearly with increasing nitrogen content up to $[\text{N}]/[\text{T}] = 1$.\textsuperscript{86} $\delta$-NbN$_{1-x}$ shows a much weaker increase. The $T_c$ data reported for $\delta$-HfN$_{1-x}$ are contradictory as to whether an increase
or a decrease occurs. This is probably because δ-HfN_{1−x} can apparently exist with a hyperstoichiometric composition. Figure 13 shows the normalized $T_c$ of several fcc nitrides (where the highest $T_c$ of each compound is equal to 1) and Table 1 shows the highest $T_c$ for each compound for the given composition.

### 6.4 Thermal Expansion

The thermal expansion of various transition metal nitrides was measured at both low temperatures \(^{87} (8–300 \text{ K})\) and high temperatures \(^{88} (\text{up to 1500 K})\). According to the polynomial expression fit of the low-temperature lattice parameters, δ-VN_{1−x} exhibits negative thermal expansion at temperatures below 55 K for the composition VN_{0.96} and below 41 K for the composition VN_{0.72}. At these temperatures, the lattice parameter is a minimum. An even more pronounced minimum was found for ScN at 107 K. \(^{87}\) The high-temperature thermal expansion data are summarized in Figure 14. \(^{88}\) Interestingly, considering its low-temperature thermal expansion behavior, δ-VN_{1−x} has the highest high-temperature expansion coefficient among these compounds, up to $11 \times 10^{-6} \text{ K}^{-1}$ at 1100 K.

### 6.5 Nitrogen Diffusivities

In transition metal nitrides, nitrogen diffusion proceeds via a vacancy mechanism in the nonmetal sublattice. The vacancy concentration is a function of composition within the homogeneity range of the fcc phases, and hence, the nitrogen diffusivity is most probably composition dependent as well. \(^{89}\) In this respect, the Ti–N\(^{90}\), Nb–N\(^{91}\) and Cr–N\(^{29}\) systems were investigated in detail.

Figure 15 shows the nitrogen diffusivities in titanium nitride at three different temperatures determined from high-precision EPMA line scans \(^{27}\) in diffusion couples (nitrided Ti sheet). \(^{90}\) Because of the identical slope of the three lines, the concentration dependency of the diffusivity was found to be temperature independent in this temperature interval.

Figure 16 shows the concentration-dependent diffusivity in CrN\(^{29}\). Generally, diffusivity studies were conducted by investigating nitride layer growth as a function of time, which gives the average nitrogen diffusivity in the various phases. A parabolic relationship, $d = k t^{0.5}$, holds for this layer growth, where $d$ is the layer thickness, $k$ a constant, and $t$ the diffusion time. The parabolic behavior indicates that the nitride layer growth is indeed diffusion controlled. By use of wedge-type samples, the thickness of diffusion layers is increased if the sample thickness increases. Such a deviation from the parabolic law (if different thicknesses are compared) can be used to establish the nitrogen diffusivities in all the phases at a given temperature. \(^{24,26}\) An example of such a wedge-type sample is shown in Figure 17 for the Hf–N system. \(^{80}\)

Nitrogen diffusion in nitrides such as δ-TiN_{1−x}, δ-ZrN_{1−x}, and δ-HfN_{1−x} has an activation energy of 2–4 eV. Although the metal diffusivity in transition metal nitrides is not yet investigated in detail, the activation energy of that process is...
A modified Boltzmann–Matano analysis, carried out on nitrogen diffusion profiles measured by EPMA, yielded a composition-dependent diffusion coefficient for N diffusion expressed as (equation 7)

\[ D = f \nu^2 d \exp\left(-\frac{E}{k_B T}\right) \exp(A(c^+ - c)) \text{cm}^2\text{s}^{-1} \] (7)

where \( f = 1/12 \), for fcc compounds, \( \nu \) is the jump frequency of the N atom, \( d \) the mean distance between lattice planes, \( E \) the activation energy, \( k_B \) the Boltzmann constant, \( A \) a parameter for the steepness of concentration dependency, \( c \) the concentration, and \( c^+ \) is the maximum concentration; \( (c^+ - c) = x \) in the formula \( \text{MeN}_x \).

### Table 2: Diffusion data for nitrogen in transition metal nitrides

<table>
<thead>
<tr>
<th>Compound</th>
<th>( D_0 ) (cm(^2)·s(^{-1}))</th>
<th>( E ) (eV)</th>
<th>( A ) (cm(^{-3}) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \delta )-TiN(_{1-x} )</td>
<td>0.03</td>
<td>2.4</td>
<td>6.5</td>
</tr>
<tr>
<td>( \delta )-HfN(_{1-x} )</td>
<td>0.02</td>
<td>2.70</td>
<td>-</td>
</tr>
<tr>
<td>( \gamma )-Hf(<em>4)N(</em>{1-x} )</td>
<td>0.14</td>
<td>2.74</td>
<td>-</td>
</tr>
<tr>
<td>( \eta )-Hf(_2)N(_2-x )</td>
<td>0.54</td>
<td>2.73</td>
<td>-</td>
</tr>
<tr>
<td>( \delta )-VN(_{1-x} )</td>
<td>12.7</td>
<td>2.93</td>
<td>-</td>
</tr>
<tr>
<td>( \beta )-VN(_2)N</td>
<td>13.6</td>
<td>2.92</td>
<td>-</td>
</tr>
<tr>
<td>( \delta )-NbN(_{1-x} )</td>
<td>0.68 (-1.10)</td>
<td>3.20</td>
<td>20</td>
</tr>
<tr>
<td>( \beta )-Nb(_2)N</td>
<td>120</td>
<td>4.0</td>
<td>-</td>
</tr>
<tr>
<td>( \delta )-TaN(_{1-x} )</td>
<td>3.4</td>
<td>3.6</td>
<td>-</td>
</tr>
<tr>
<td>( \beta )-Ta(_2)N</td>
<td>1.4</td>
<td>3.3</td>
<td>-</td>
</tr>
<tr>
<td>( \delta )-CrN(_{1-x} )</td>
<td>0.18</td>
<td>2.92</td>
<td>184</td>
</tr>
<tr>
<td>( \beta )-Cr(_2)N</td>
<td>3.51</td>
<td>2.68</td>
<td>-</td>
</tr>
</tbody>
</table>

### 6.6 Elastic Properties

Transition metal nitrides exhibit high Young’s moduli, appreciably higher than the elastic moduli of the transition metals. As can be seen from Figure 18, the Young’s moduli of \( \delta \)-TiN\(_{1-x} \) and \( \delta \)-ZrN\(_{1-x} \) increase with increasing nitrogen to metal ratio, whereas for \( \delta \)-HfN\(_{1-x} \), the modulus remains approximately constant. Several of these data were obtained from thin layers. It is well known that in layers large deviations from bulk properties (lattice parameter, composition) may occur, due probably to the high concentration of defects particularly in PVD layers, while in bulk samples, pores can drastically influence the results.

The elastic properties of a variety of transition metal nitrides were critically reviewed by Kral et al. The temperature dependence of \( \delta \)-TiN\(_{1-x} \) and of TiC\(_{0.6}\)N\(_{0.4}\) is shown in Figure 19. Up to the maximum investigation temperatures, the moduli lower only slightly upon increasing temperature, both indicating the stiffness of the materials and that softening of the lattice occurs at even higher temperatures.

### 6.7 Hardness

Some transition metal nitrides are among the hardest materials known. Figure 20 shows hardness versus composition for \( \delta \)-TiN\(_{1-x} \) and for the group 5 transition metal nitrides. The hardness decreases with increasing nitrogen content for the group 5 nitrides. This behavior can probably be explained by electronically induced lattice softening as a result of the generation of antibonding states. It is known from band structure calculations that in fcc transition metal compounds with more than eight valence electrons, antibonding states are successively occupied. Indeed, in \( \delta \)-TiN\(_{1-x} \), a maximum in
Figure 16  Temperature dependence of diffusion coefficients for the Cr–N system obtained from layer growth and concentration profiles: □: δ-CrN1−x from layer growth (different concentration ranges for different temperatures), □: δ-CrN1−x from concentration profile fitting (lower dashed line CrN1.00, upper dashed line CrN0.67), ○: β-Cr2N from concentration profile fitting, ●: β-Cr2N from layer growth, ▲: α-Cr(N) from layer growth. (Reproduced from Ref. 29. J. Phase Equilib., vol. 20, 1999, p. 35, ‘Phase equilibria and multiphase reaction diffusion in the Cr–C and Cr–N systems’, W. Mayr, W. Lengauer, D. Rafaja, J. Bauer, and M. Bohn. With kind permission from Springer Science and Business Media.)

Figure 18  Young’s modulus of bulk and layered group 4 transition metal nitrides. (Reproduced from Ref. 92. © Elsevier, 1987.)

microhardness is found at the composition δ-TiN0.67, corresponding to 7.3 valence electrons. This is also reflected in the hardness of titanium and zirconium carbonitrides with 50 mol% C+N, which show a maximum for [C]/([C]+[N]) = 1, that is, VEC = 8 for the pure carbide, whereas the hardness is lowered as carbon is replaced by nitrogen. An increasing VEC arising from increasing nitrogen content would then lead to a decrease in hardness when the number of valence electrons exceeds eight. For δ-HfN1−x, a smooth increase in microhardness with increasing nitrogen content is observed. This, however, is probably a result of the difference in electronic states owing to 5f electrons. Also, the carbide Hf(C,N) does not show such a pronounced maximum at [C]/([C]+[N]) = 1 as do Ti and Zr carbonitrides.

6.8 Properties of Nitrides with a Nitrogen Content Exceeding 50 mol%

In recent years, bulk nitrides with a nitrogen content significantly exceeding 50 mol% N have been prepared. They have very interesting properties of which Table 3 gives an overview. Even the preparation in form of thin very hard layers was successful. Tests showed that such layers outperform conventional coatings; hence, a technical application would seem likely to occur in due course.
Figure 19  Elastic constants $E$, $B$, and $G$ as a function of temperature (a) for TiN and (b) for TiC$_{0.6}$N$_{0.4}$.

Figure 20  (a) HV0.3 Microhardness of $\delta$-TiN (Reproduced from Ref. 85. © Elsevier, 1992) and HV0.01 microhardness (b) of group 5 transition metal nitrides as a function of composition. (Reproduced from Ref. 5. Books: W. Lengauer in R. Riedel: Handbook of Ceramic Hard Materials. pp. 202. 2000. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)
Table 3  Structure data and solid-state properties of bulk transition metal nitrides with [N]/[Me] > 1 and some low amount of oxygen

<table>
<thead>
<tr>
<th></th>
<th>Zr₃N₄ [U3]</th>
<th>Hf₃N₄</th>
<th>Ta₃N₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>220 cubic</td>
<td>220 cubic</td>
<td>62 orthorhombic U2S3</td>
</tr>
<tr>
<td>Structure type</td>
<td>Th3P4</td>
<td>Th3P4</td>
<td>a = 8.1911(17)</td>
</tr>
<tr>
<td>Lattice parameter(s)</td>
<td>a = 0.6740(6) nm</td>
<td>a = 0.6701(6) nm</td>
<td>b = 8.1830(17)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c = 2.9823(3)</td>
</tr>
<tr>
<td>Density</td>
<td>7.159 g cm⁻³</td>
<td>13.058 g cm⁻³</td>
<td>13.42 g cm⁻³</td>
</tr>
<tr>
<td>Hardness</td>
<td>HV(1) = 12.0(6)(e) GPa</td>
<td>ca. 35 GPa(5)</td>
<td>16 GPa(5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>97</td>
<td>ca. 30 GPa(5)</td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>394(24)(d) GPa</td>
<td>223(2) GPa(4)c</td>
<td>322(3) GPa(4)c</td>
</tr>
<tr>
<td>Bulk modulus</td>
<td>217(20)(d) GPa</td>
<td>227(7) GPa(99)</td>
<td>176(6) GPa(4)c</td>
</tr>
<tr>
<td></td>
<td>219(13) GPa(98)</td>
<td></td>
<td>281(15) GPa(4)c</td>
</tr>
<tr>
<td>Shear modulus</td>
<td>163(9)(d) GPa</td>
<td>319(6) GPa(59)</td>
<td>87(1) GPa(4)c</td>
</tr>
<tr>
<td></td>
<td></td>
<td>123(2) GPa(4)c</td>
<td>0.29(1)(c)GPa</td>
</tr>
<tr>
<td>Poisson ratio</td>
<td>0.20(4)(d)</td>
<td>0.31(1)(d)</td>
<td>0.31(1)(d)</td>
</tr>
</tbody>
</table>

(a) Porous sample (10% porosity).
(b) Estimated from elastic properties.
(c) Measured for a porous sample with the volume fraction porosity (VFP) of 18%.
(d) For dense material, derived from experimental data for porous sample using a theoretical approach taking into account the porosity influence.
(e) Porous sample: VFP = 25–30%.
(f) For dense material, estimated from the dependence of HV on porosity and from the elastic shear modulus for dense material.

7 USES

Nitrides and carbonitrides in form of powders play an important role in hardmetals (cemented carbides). The reader is also referred to the article on Carbides of this Encyclopedia (see Carbides: Transition-Metal Solid-State Chemistry).

7.1 Functional-Gradient Hardmetals with Carbonitrides, Interaction of Nitrogen with Hardmetals

The interaction of nitrogen with hardmetals (cemented carbides) containing nitride and carbonitride-forming metals such as Ti, Ta, and Nb can be exploited to form near-surface gradients in order to enhance the performance of the hardmetals and to supply specific surface conditions for a better adherence of coatings. By means of the appropriate application of nitrogen atmospheres upon sintering, this interaction leads to various forms of near-surface microstructures in functional-gradient hardmetals (see also Carbides: Transition-Metal Solid-State Chemistry). The microstructures can be tailored in order to adjust hardness and toughness of the materials.

Upon appropriate application of nitrogen pressure, nitrogen-enriched or nitrogen-depleted near-surface regions can be established. Figure 21 shows these microstructures.

These surface regions have a higher hardness than the bulk if the nitrogen is enriched because of the formation of hard nitrides. Contrarily, the hardness is lowered but toughness is increased in nitrogen-depleted surface region free of fcc carbonitrides. Figure 22 shows this behavior for the two types (compare with Figure 21). In fact, a variety of different near-surface microstructures is possible, depending on the composition and process parameters of the sintering regime. Even nitrogen enrichment below a tough surface layer is possible. Functional-gradient hardmetals show excellent performance in some specific cutting applications.

In hexagonal tungsten carbide (WC), nitrogen can be introduced in order to form a carbonitride W(C,N). By means of the appropriate application of nitrogen powders and application of nitrogen pressures up to 160 MPa at temperatures up to 1500 °C, W(C,N) powders with 20 mol% N could be prepared. W(C,N) can also be prepared by ammonia synthesis with and without addition of CH₄ at ambient pressure and temperatures up to 1300 °C with nitrogen contents up to 5 mol% N. Exploiting the ability of WC to form W(C,N) by nitridation at high nitrogen pressures, WC powders with particles covering a nitrided rim have recently successfully employed to obtain fine-grained WC–Co hardmetals. Nitrogen serves as a transient grain-growth inhibitor as long as the nitrided surface exists. Upon liquid-phase sintering, this nitrided rim is dissolved in the eutectic, nitrogen is outgassed, and a pore-free hardmetal body can be obtained.
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Figure 21 Microstructures of functional-gradient hardmetals with (a) a nitrogen-enriched (WC-depleted) zone (light-optical microscope image) and (b) a nitrogen-depleted (WC-enriched) zone (SEM image).

Figure 22 Hardness HV0.025 of surface zones of functional-gradient hardmetals as a function of distance. (a) Hardness of the nitrogen-enriched surface region (regular gradient) of a functional-gradient hardmetal and (b) hardness of a nitrogen-depleted WC-rich surface zone (fcc-free zone) and hardness of a WC-rich surface zone with inner Ti(C,N) enrichment, “inverse gradient”. (Reproduced from Ref. 106. © Plansee, 2005.)

7.2 Cermets—Cemented Carbonitrides

Cermets\textsuperscript{112–116} are cemented carbonitrides in which only a cubic hard phase without free hexagonal WC is present (see also Carbides: Transition-Metal Solid-State Chemistry). However, there is no boundary between a typical cemented carbide (hardmetal), that is, pure WC–Co, on the one hand and a typical cermet on the other: the microstructures can contain both free WC and fcc phases. In some hardmetal grades, Ti-based fcc carbides and carbonitrides are added in order to improve the performance, for example, in interrupted cutting processes. Cermets can be produced by liquid-phase sintering of blends of a variety of compounds such as TiN, TiC, WC, Mo\textsubscript{2}C, Ti(C,N), (Ti,W)\textsubscript{C}, (Ti,W)(C,N), (Ti,Mo)(C,N), (Ta,Nb)\textsubscript{C}, VC, Cr\textsubscript{3}C\textsubscript{2}, and so on together with binder metals such as Co, Ni, or Co/Ni. After sintering, quaternary hard phases based on (Ti,W)(C,N) and (Ti,Mo)(C,N) or a combination thereof forms. Further metal constituents of the starting formulation such as Ta, Nb, Cr, and V are introduced into the hard-phase particles upon sintering. Cr also dissolves in substantial amount in the binder phase.

Figure 23 shows a microstructure of a modern cermet. In Figure 23(a), the grain size of the hard carbonitride particles is below 1 \( \mu \text{m} \), whereas the microstructure of the cermet shown in 23(b) is substantially coarser. The hard-phase particles of cermets often exhibit a so-called core-rim-type structure, which means that in principal two quaternary carbonitrides exist. The core of these particles is Ti and N enriched and the rim is C- and W- or Mo-rich relative to the core. Often an inner rim is found that has a substantial higher amount of W. All these constituents have an fcc structure with a lattice parameter very close to each other so they cannot be distinguished by X-ray diffraction. In scanning electron microscopy images that are atomic mass sensitive, they appear as dark or even black core (light elements—Ti), white inner
rim (heavy elements—W), and gray outer rim (mixture of light and heavy elements).

The characteristics and the following advantages of cermets used for metal-cutting operations (turning, milling, and drilling) can be summarized as follows (Table 4).

Table 4 Some characteristics and accompanying advantages of cermets used for metal-cutting operations

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Advantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low specific density</td>
<td>High tool rotation</td>
</tr>
<tr>
<td>Low friction, low tendency to stick</td>
<td>High surface quality of workpiece</td>
</tr>
<tr>
<td>Low thermal conductivity</td>
<td>Dry machining</td>
</tr>
<tr>
<td>High heat resistance</td>
<td>High cutting speed</td>
</tr>
<tr>
<td>High performance without coating</td>
<td>Sharp cutting edge</td>
</tr>
<tr>
<td>Long tool life</td>
<td>Lower tooling costs</td>
</tr>
<tr>
<td>Low flank wear</td>
<td>High dimensional accuracy</td>
</tr>
<tr>
<td>Low-risk raw materials</td>
<td>Safe supply</td>
</tr>
</tbody>
</table>

The workpiece materials for which cermets are employed are mainly high and low alloyed and unalloyed steels, ferritic and martensitic corrosion-resistant steels, ferritic/martensitic and duplex stainless steels, cast iron grades (with the exception of gray cast iron), as well as pearlitic and ferritic cast iron grades. Cermets are much less suited for machining of hardened steels and noniron materials such as aluminum alloys, brass, Inconel, and titanium alloys. Examples of products in which cermets are used as cutting materials are connecting rods and shafts for engines. Because of their increased brittleness as compared to WC–Co hardmetals, cermets should only be used on highly stable machines without vibration and by application of a low depth of cut. The workpieces should be free of scale. Interrupted cutting is a problem for cermets. Their specific density is less than a half of the specific weight of hardmetals; hence, high rotation speeds of cermet cutters are possible.

Table 5 contains some important data for industrial grades of cermets. The hard phase is Ti(C,N) based, and for the starting formulation, tungsten, molybdenum, niobium, and/or tantalum carbides are added.

7.3 Wear-Resistant Layers

In order to increase the service life of hardmetal tools for cutting and milling operations, they are coated with CVD- and PVD-produced transition metal nitride layers. The coatings are composed mainly of δ-TiN$_{1-x}$, Ti(C,N), (Ti,Al)N, (Ti,Si)N, and (Ti,Cr,Si)N, occasionally with some other elements such as V and B added. Nitride-coated tool tips result in a better surface finish of the workpiece owing to both a decrease in diffusion welding between tool tip and workpiece and an increase in thermal oxidation resistance. The total layer thickness is generally 5–20 μm. Often, layers of the above-mentioned nitrides are combined with layers of Al$_2$O$_3$. Figure 24 shows a multilayer coating including δ-TiN$_{1-x}$ layers on a WC–Co hardmetal.

In recent years, very interesting coatings have been developed in the Ti–Al–N system. Previously, only PVD was capable of producing thermodynamically unstable fcc (Ti,Al)N coatings. However, it was shown that CVD methods working around 800–1000°C can also be used to form coatings of fcc Ti$_{1-x}$Al$_x$N with $x$ up to 0.9. Such layers have excellent performance in turning and milling operations of steel. Figure 25 shows a fractograph of a Ti$_{1-x}$Al$_x$N coating on a hardmetal substrate. Upon introduction of carbon, Ti$_{1-x}$Al$_x$(C,N) coatings can be prepared by CVD at temperatures of 800–850°C. The nitride has only a low carbon content of 2 mol%, but the layer covers some portion of amorphous carbon. These layers, too, show excellent cutting performance in milling tests. The hardness of these nitride and carbonitride layers is
Table 5  Important solid-state properties of industrial cermet grades.

<table>
<thead>
<tr>
<th></th>
<th>Grade 1</th>
<th>Grade 2</th>
<th>Grade 3</th>
<th>Grade 4</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binder phase content Co + Ni</td>
<td>6.0</td>
<td>12.2</td>
<td>14.1</td>
<td>15.4</td>
<td>wt%</td>
</tr>
<tr>
<td>Specific density</td>
<td>6.40</td>
<td>6.60</td>
<td>6.40</td>
<td>7.00</td>
<td>g·cm⁻³</td>
</tr>
<tr>
<td>Vickers hardness</td>
<td>1780</td>
<td>1620</td>
<td>1630</td>
<td>1580</td>
<td>MPa</td>
</tr>
<tr>
<td>Transverse rupture strength</td>
<td>1500</td>
<td>1800</td>
<td>2000</td>
<td>2000</td>
<td>MPa</td>
</tr>
<tr>
<td>Compressive strength</td>
<td>4000</td>
<td>5000</td>
<td>4700</td>
<td>4600</td>
<td>MPa</td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>448</td>
<td>445</td>
<td>425</td>
<td>430</td>
<td>GPa</td>
</tr>
<tr>
<td>Fracture toughness</td>
<td>10.3</td>
<td>8.0</td>
<td>8.0</td>
<td>10.0</td>
<td>MPa·m⁴/²</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>11</td>
<td>19</td>
<td>15</td>
<td>14</td>
<td>W·m⁻¹K⁻¹</td>
</tr>
<tr>
<td>Thermal expansion coefficient</td>
<td>8.3</td>
<td>9.0</td>
<td>7.6</td>
<td>9.4</td>
<td>10⁻⁶ K⁻¹</td>
</tr>
</tbody>
</table>

Courtesy of Kennametal Technologies, Mistelgau and Ceratizit, Luxemburg.

Figure 24  CVD multilayer coating on WC–Co hardmetal with yellow TiN₁₋ₓ as top and bottom layer. Following the bottom layer, a Ti(C,N) layer (gray) was deposited, in turn followed by a black Al₂O₃ layer (invisible in the light-optical microscope)

Figure 25  Fractograph of a Ti₅₆Al₄₄N coating on a hardmetal (WC–Co). (Courtesy of Dr. Ingolf Endler, Fraunhofer IKTS Dresden, Germany.)

around 3000 HV0.01. Even higher hardnesses of up to 4100 HV0.01 can be obtained if Al is replaced by Si to form Ti₁₋ₓSiₓN and Ti₁₋ₓSiₓ(C,N) coatings. These are no longer single phase, but contain in fact crystalline titanium nitride and titanium silicide and amorphous silicon nitride, whereas in the C-containing coatings, Ti(C,N) and Si(C,N) coexist. The increased hardness stems from the partially

nanocrystalline nature of the phases. A problem of the Si-containing coatings is their weaker adherence to the hardmetal substrate.

Bright golden yellow δ-TiN₁₋ₓ is also used for ornamental layers; for example, on watch cases where the combination of color with increased scratch resistance is exploited.

By PVD methods, it is possible to prepare a huge variety of multielement nitride layers. The metals are introduced upon appropriate choice of the sputter targets. The layers can be single phase, multiphase, and multiphase nanostructured as well as amorphous, for instance, in the Ti–Si–N system where nanocrystalline TiN and amorphous Si₃N₄ coexist. Other examples of layers prepared with PVD are Cr- and V-containing nitride-based coatings.

7.4 Diffusion Barriers

Because of their chemical inertness, high electrical conductivities, and the ease with which they can be deposited as layers, transition metal nitrides, for example, titanium, zirconium, tantalum, niobium, and tungsten nitrides, and also their ternary forms such as (Ti,Zr)N and (Ti,Ta)N are excellent candidates for use in multilayer metallizations of integrated circuits. In these devices, interdiffusion between the different metals, compound layers, or thin metal wires during thermal load with soldering and packaging operations must be avoided, otherwise degradation of the multilayer arrangement will occur. In order to protect these layers against interdiffusion, very thin nitride layers (<100 nm) can be deposited by PVD methods. These layers are stable up to 600 °C (depending on the time and the substrate) and prevent the layers from undergoing structural changes.

8 REFERENCES


