Carbides

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1. Survey

Most of the elements form binary compounds with carbon, all of which can be called carbides. The properties of these carbides are very different; therefore, like binary hydrides and nitrides, the carbides should be classified into groups. To avoid too many subdivisions, the following four types of carbides may be defined:

1. saltlike carbides of metallic elements, e.g., CaC₂
2. metal-like carbides of metallic elements, e.g., WC
3. diamond-like carbides, e.g., B₄C
4. carbides of nonmetallic elements, e.g., CO

This classification suggests another group: the elements that do not react with carbon, e.g., Sn.

Generally, the four groups of carbides can not be strictly separated from each other. Numerous carbides are in intermediate positions between these groups. One example is BeC₂ [57788-94-0]. It is a typical saltlike carbide and is decomposed by water. On the other hand, it may be viewed as a diamond-like carbide because of its hardness and other properties resembling those of SiC.

Figure 1 surveys the four types of carbides in the form of a periodic table. Elements that do not form binary compounds with carbon, or are not known to form carbides, are not shown. The carbides of the iron group and manganese are a subgroup of the metal-like carbides.

1.1. Saltlike Carbides

Saltlike carbides of metallic elements are the carbides of the elements of groups 1 – 3 and 11 – 13 (I – III, both A’s and B’s) of the periodic table, the lanthanides and actinides included. Exceptions are Ga, In, and Tl, which do not form carbides, and B₄C, which is a typical diamond-like carbide.

The saltlike carbides – also called ionic carbides – are attacked by water to form hydrocarbons. Most of these carbides form acetylene, e.g.:

\[
\text{CaC}_2 + 2 \text{H}_2\text{O} \rightarrow \text{Ca} (\text{OH})_2 + \text{C}_2\text{H}_2
\]
Figure 1. Survey of binary compounds of carbon with the elements.
These carbides can be viewed as salts of acetylene and may be called acetylides. The crystals contain $\text{C}_2\text{C}_0^-$ anions.

The carbides $\text{Be}_2\text{C}$ and $\text{Al}_4\text{C}_3$ form pure methane when hydrolyzed:

$$\text{Be}_2\text{C} + 4\text{H}_2\text{O} \rightarrow 2\text{Be(OH)}_2 + \text{CH}_4$$

$$\text{Al}_4\text{C}_3 + 12\text{H}_2\text{O} \rightarrow 4\text{Al(OH)}_3 + 3\text{CH}_4$$

In the crystal lattice of these carbides, the carbon atoms are isolated from each other, in contrast to the $\text{C}_2$ groups of the acetylides. The $\text{Be}_2\text{C}$ lattice is antiisotypical to that of $\text{CaF}_2$.

The carbide $\text{Mg}_2\text{C}_3$ can be decomposed by heating to form $\text{Mg}_2\text{C}_3$ and graphite. Hydrolysis of $\text{Mg}_2\text{C}_3$ yields propyne:

$$\text{Mg}_2\text{C}_3 + 4\text{H}_2\text{O} \rightarrow 2\text{Mg(OH)}_2 + \text{CH}_3\text{C}_0\text{C}_1\text{C}_1\text{CH}$$

In their carbides the lanthanides and actinides are mainly divalent. During hydrolysis they become trivalent, and hydrogen is formed in this reaction:

$$\text{M}^{2+} + \text{H}^+ \rightarrow \text{M}^{3+} + \text{H}_2$$

This hydrogen reacts with the acetylene also formed to produce a mixture of acetylene, methane, ethylene, and hydrogen.

Whereas the saltlike carbides of groups 1 and 2 are transparent and are not electrical conductors, the lanthanide and actinide carbides show some metallic behavior, an indication of a state intermediate between saltlike and metal-like carbides. The electrical conductivity and metallic luster may be due to the fact that the metals are divalent in their carbides and the third valence electron is available for metallic bonding.

One other subgroup of saltlike carbides should be mentioned: the alkali-metal – graphite compounds. They are formed by absorption of molten Na, K, Rb, and Cs by graphite. Compositions such as $\text{MC}_8$, $\text{MC}_{16}$, and $\text{MC}_{60}$ are known. These compounds are quite likely not chemical compounds, but merely adsorbtional compounds, and perhaps better not called carbides.

1.2. Metal-like Carbides

Metal-like carbides of metallic elements are the carbides of the transition elements of groups 4, 5, and 6 of the periodic table. These carbides, also called metallic carbides, are not attacked by water. The metallic character of these compounds is shown in their high thermal and electrical conductivity as well as in their metallic luster.

All the metallic carbides are stable at room temperature and resist attack by dilute acids as well as by alkaline and organic liquids. Their hardness and wear resistance are utilized in the cemented carbides (→ Hard Materials), which are sintered products of the carbides with cobalt or other metals. Because of their industrial significance, these carbides are described in more detail in Chapter 2.

The carbides of Mn, Fe, Co, and Ni are generally included in the metal-like carbides, although they are really better classified as a group on their own. These carbides are in an intermediate position between the metal-like carbides and the saltlike carbides. Their crystal structures are quite different from the structures of the metal-like carbides and the saltlike carbides. The pure compounds are attacked by water or dilute acids.

1.3. Diamond-like Carbides

Diamond-like carbides include, strictly speaking, only $\text{B}_4\text{C}$ and $\text{SiC}$. They are called diamond-like because of their extreme hardness, which is exceeded only by diamond itself. Sometimes the very hard $\text{Be}_2\text{C}$ is included in the diamond-like carbides. However, its hardness cannot be used industrially, because of its decomposition by water.

1.4. Carbides of Nonmetallic Elements

Such carbides as $\text{CO}$, $\text{CS}_2$, and $\text{CCl}_4$, the carbides of nonmetallic elements, have covalent, molecular character and are not discussed in this article.

1.5. Crystal Structure

The lattice structure of most carbides can be deduced from the structure of their most important group, the metal-like transition-metal carbides. Basically these carbides are cubic or hexagonal closest packings of metal atoms with the smaller carbon atoms in the interstitial sites.
Therefore, the transition-metal carbides can also be called interstitial carbides.

In 1931 Hägg [7] reported that the structure of the transition-metal carbides is determined by the radius ratio \( r = r_C/r_{\text{metal}} \). When \( r \) is less than 0.59, the metals form the simple structures just described, with the carbon atoms located at the octahedral interstices. If all interstices are occupied in a body-centered cubic (bcc) metal lattice, the result is the face-centered cubic (fcc) sodium chloride structure. All the carbides of transition-metal groups 4 and 5 crystallize in this B1 lattice. Tungsten carbide has a simple hexagonal structure with all of the trigonal prismatic interstitial sites occupied by carbon.

The B1 carbides, principally TiC, ZrC, HfC, and VC, tend to form defect structures in which the interstitial sites are not completely filled. Broad homogeneity ranges are the result, but some substructures with overlapping homogeneity ranges are indicated [8].

When only one-half of the octahedral interstitial sites are occupied in an hexagonal-closest-packed (hcp) metal structure, the subcarbides – \( V_2C \), \( Nb_2C \), \( Ta_2C \), \( Mo_2C \), and \( W_2C \) – are obtained. This is a simplified interpretation, and in fact the subcarbides are more complex structures, as was shown by Nowotny [9]. Indeed, these structures are sometimes called Nowotny phases, to contrast them with the simpler Hägg phases.

When Hägg’s ratio exceeds 0.59, the simple phases can no longer be formed as before. Close to 0.59 and in the case of low carbon content, there are the compounds Cr\(_{23}C_6\) and Mn\(_{23}C_6\), which can still be viewed as interstitial structures. For higher values of \( r \) and higher carbon content, more complex structures, no longer interstitial compounds, are formed: \( M_2C_3 \), \( M_7C_3 \), \( M_3C_2 \). These stoichiometries are primarily found in the iron group. These more complex structures are less metallic than the Hägg phases. Hardness, melting point, and chemical resistance are markedly lower.

The structures of the saltlike carbides can also be deduced from the Hägg phases. When there are more carbon atoms than octahedral interstitial sites in the metal lattice, pairs of carbon atoms are formed. The CaC\(_2\) type is a tetragonally deformed B1 structure. The dicarbides of the lanthanides and actinides crystallize in this system. They lack metallic characteristics. The bcc carbides, \( M_2C_3 \), also contain \( C_2 \) groups, e.g., \( U_2C_3 \).

The structures of the diamond-like carbides SiC and B\(_4\)C differ from all structures described thus far. The carbide SiC has an expanded diamond lattice, whereas B\(_4\)C crystallizes in a rhombohedral lattice containing B\(_{12}\) icosahedrons and C\(_3\) chains.

### 1.6. General Production Processes

There are a number of general methods of producing carbides:

1. Nearly all carbides can be prepared at high temperature by direct reaction from the metal powder mixed with lamp black or graphite, e.g.:
   \[ W + C \rightarrow WC \]

   Generally the temperature is in the range 1000 – 1500 °C, and special furnaces are used. A protective atmosphere or vacuum is needed.

2. Instead of the pure metal, the oxide or hydride can be carburized with solid carbon:
   \[ Ta_2O_5 + 7C \rightarrow 2 TaC + 5 CO \]

   Large amounts of gas result from this reaction. Both processes 1 and 2 are solid-state reactions.

3. Carbides with high melting points can be prepared by a modified aluminothermic process:
   \[ 3Cr_2O_3 + 6Al + 4C \rightarrow 2 Cr_3C_2 + 3 Al_2O_3 \]

4. Instead of solid carbon, gaseous carbon compounds, such as CO or CH\(_4\), can be used. This process is important in the steel industry, where mainly iron, chromium, and manganese carbides are formed during fusion:
   \[ 3Fe + 2 CO \rightarrow Fe_3C + CO_2 \]

5. Reaction of metal chlorides with hydrocarbons in a hydrogen atmosphere produces carbides:
   \[ ZrC{l_2} + CH_4 \rightarrow ZrC + 4 HCl \]

   This method is used to produce layers of carbides on other materials by chemical vapor deposition (CVD → Thin Films).
Most of the saltlike carbides are prepared by processes 1 and 2, by heating the metals or oxides with carbon, e.g.:

\[ \text{CaO} + 3 \text{C} \rightarrow \text{CaC}_2 + \text{CO} \]

However, another, quite different process can also be used:

Reaction of acetylene with metals or salts dissolved in water or liquid ammonia or suspended in inert organic fluids forms simple or complex acetylides. Most are metastable but are stabilized by H₂O, NH₃, or acetylene itself. Cautious decomposition produces individual carbides:

\[ \text{Li(s)} + \text{NH}_3(l) + \text{C}_2\text{H}_2 \rightarrow \text{LiHC}_2\text{NH}_3 + 0.5 \text{H}_2 \]

\[ \text{LiHC}_2\text{NH}_3 \rightarrow \text{LiHC}_2 \rightarrow \text{Li}_2\text{C}_2 \]

Today this last method is primarily of laboratory interest.

### 1.7. Uses

The uses of carbides are as diverse as the types of carbides. Most important from an economic point of view are the carbides of the transition metals of groups 4, 5, and 6. The most important of these is tungsten carbide. The hardness and chemical resistance of these carbides are the basis for their use by the tool and machine industry in multitudinous applications as cemented carbides. The terms hardmetals and cemented carbides are synonymous. The term cermet is also used for some or all of these composites. Furthermore the term tungsten carbide is used because WC is the main constituent in most of these materials. These cemented carbides are sintered products of one or more carbides with a metallic binder, preferably the metal cobalt. There are many different combinations of carbides and binder metals. Factories producing cemented carbides are found in every industrial country; the world’s annual production is estimated at ca. 20 000 t in 1985. Some tungsten carbide combined with Cu or Ag is used in electrical contacts and in fuel cells.

The carbides of manganese and iron are never used alone like the harder transition-metal carbides, but rather are formed in alloys during fusion. These carbides, especially cementite, Fe₃C, are of fundamental importance because the individual carbides and the binary mixed carbides with V, Cr, Mo, and W are responsible for the hardness of steel, Stellites, and related alloys.

The most important saltlike carbide is CaC₂ (→ Calcium Carbide). One-half of the world’s annual production, several million tons, is converted to cyanamide (→ Cyanamides), which is used as fertilizer. Some 20% is used for acetylene production (→ Acetylene, Section 4.3.4.), and the remainder is used in steelmaking as a carburizing additive.

The monocarbides and dicarbides of uranium and thorium are used as nuclear fuels in high-temperature reactors. These carbides are not used as hard materials, although they do have some metallic character. Other saltlike carbides do not have industrial importance.

The carbides B₄C and SiC are used in large quantities as abrasives (→ Abrasives; → Boron Carbide, Boron Nitride, and Metal Borides → Silicon Carbide). Heating elements and many heat-resistant parts are made from SiC.

### 2. Metal-like Carbides of Industrial Importance

The important individual carbides of the transition metals and the mixed carbides of these metals are described in detail in the following. Tungsten carbide, WC, because of its importance in cemented carbides, or hardmetals, is described first. Thereafter, TiC, TaC, and NbC, which are also basic hard carbides, are described. The physical properties of these four carbides are given in Table 1. Finally, the carbides of Zr, Hf, V, Cr, and Mo are described. These last carbides are used only as additives in cemented carbides and have less importance. Their physical properties are given in Table 2.

#### 2.1. Tungsten Carbide

There are two hexagonal carbides in the tungsten – carbon system (Fig. 2): the monocarbide, WC, and the subcarbide [12070-13-2], W₂C. The hexagonal WC, also called α-WC, decomposes at its incongruent melting point of 2776 °C. Its range of homogeneity is extremely narrow: from 49.5 to 50.5 mol % C.
The subcarbide, $W_2C$, probably has three modifications. The highest temperature modification melts without decomposition at $\approx 2800$ °C. The “eutectic” of $W_2C$ and WC is known as cast or fused tungsten carbide. The solid eutectic mixture is sometimes incorrectly called $W_2C$. In addition to these two industrial carbides, there is a substoichiometric face-centered cubic WC$_{1-x}$ phase, also called $\beta$-WC, which is unstable at room temperature, forming only above 2530 °C. The phase diagram is made more complicated by this additional compound and the $W_2C$ modifications, mainly in the high-temperature range. Although many have investigated the tungsten – carbon system, unanswered questions remain.

Table 1. Physical properties* of WC, TiC, TaC, and NbC

<table>
<thead>
<tr>
<th>Property</th>
<th>WC</th>
<th>TiC</th>
<th>TaC</th>
<th>NbC</th>
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<td>[12070-08-5]</td>
<td>[12070-06-3]</td>
<td>[12069-94-2]</td>
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<td>Carbon content (theory), wt %</td>
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<td>20.05</td>
<td>6.23</td>
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<td>Crystal structure</td>
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<td>fcc, B1</td>
<td>fcc, B1</td>
<td>fcc, B1</td>
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<td>445.5</td>
<td>447.0</td>
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<td>Density, g/cm$^3$</td>
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<td>14.48</td>
<td>7.78</td>
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<td>3985</td>
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<td>≈ 3000</td>
<td>1800</td>
<td>2000</td>
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<td>550</td>
<td>240 – 390</td>
<td>350 – 400</td>
<td>300 – 400</td>
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<td>338</td>
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<td>− 141.0</td>
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<td>+ 6.7</td>
<td>+ 9.3</td>
<td>+ 15.3</td>
</tr>
</tbody>
</table>

*Properties given without a temperature are for room temperature.

The subcarbide, $W_2C$, probably has three modifications. The highest temperature modification melts without decomposition at $\approx 2800$ °C. The “eutectic” of $W_2C$ and WC is known as cast or fused tungsten carbide. The solid eutectic mixture is sometimes incorrectly called $W_2C$. In addition to these two industrial carbides, there is a substoichiometric face-centered cubic WC$_{1-x}$ phase, also called $\beta$-WC, which is unstable at room temperature, forming only above 2530 °C. The phase diagram is made more complicated by this additional compound and the $W_2C$ modifications, mainly in the high-temperature range. Although many have investigated the tungsten – carbon system, unanswered questions remain.

Table 2. Physical properties* of ZrC, HfC, VC, Cr$_3$C$_2$, and Mo$_2$C

<table>
<thead>
<tr>
<th>Property</th>
<th>ZrC</th>
<th>HfC</th>
<th>VC</th>
<th>Cr$_3$C$_2$</th>
<th>Mo$_2$C</th>
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<td>Specific heat, J mol$^{-1}$ K$^{-1}$</td>
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<td>− 25.2</td>
<td>+ 26.2</td>
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<td>—</td>
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</table>

*Properties given without a temperature are for room temperature.
Properties. Commercial monocarbide, WC, the raw material for the powder-metallurgy industry, is a gray metallic powder. Its average grain size is between 0.5 and 20 μm. In addition, very small quantities are prepared with smaller or coarser size for special applications. The carbide is insoluble in water and dilute acids, but is dissolved by hot mixtures of HNO₃ and HF. It is oxidized in air above 600 °C. Although it is stable in dry hydrogen up to its melting temperature, wet hydrogen decarburizes it. Chlorine attacks WC above 400 °C, while fluorine attacks WC at room temperature.

Hardness, combined with high modulus of elasticity, is the most important mechanical property of WC. The microhardness is anisotropic [10], [11] and, because of this, values ranging between 1000 and 2500 kg/mm² can be found in the literature.

The chemical resistance of the subcarbide W₂C is less than that of WC. The subcarbide is dissolved by HNO₃ – HF mixtures even at room temperature. It may be distinguished from WC by its reaction with alkaline potassium hexacyanoferrate (Murakami’s reagent): W₂C turns yellow to brown, whereas WC remains gray. The microhardness of the subcarbide is higher than that of WC, but W₂C is not used alone industrially because it is too brittle.

Because eutectic W₂C – WC is prepared by a fusion process, it is not produced as a powder in the micron range. The grains are much coarser, up to several millimeters. The carbon content can vary from 3.5 to 4.5 wt %, corresponding to 50 – 90 % of W₂C or 10 – 50 % of WC in this “eutectic”.

Preparation. Most of the world’s annual production of 15 000 – 20 000 t of WC is made by direct carburization of tungsten metal with carbon. Mixtures of metal and lamp black, or even graphite, are heated to temperatures between 1400 and 2000 °C in a hydrogen atmosphere or vacuum. Electrical walking-beam or pusher-type furnaces or gas-fired muffle furnaces are used. Carbon tube furnaces are needed for the high-temperature range, and batch-type induction furnaces are needed for vacuum processing.

After purity, the most important property of the carbide is grain size, because the grain size significantly affects the mechanical properties of WC products. Fine-grained powders cannot be made from coarser powders only by milling. Intensive milling changes carbon and oxygen contents, the shape of the grains, and the grain size distribution. Therefore, the grain size is better determined by the processing parameters during reduction and carburization: temperature, reaction time, humidity, flow rate of the hydrogen, and several other factors. Most importantly, the grain size of the starting material must be selected to produce the desired end product. Generally, powders become coarser when converted from oxide to metal to carbide.

The chemical nature of the starting materials and the intermediate steps also affect the physical properties of the final carbide. Possible starting materials are tungstic acid [7783-03-1], H₂WO₄, and ammonium paratungstate or APT [11120-25-5], (NH₄)₁₀W₁₂O₄₁·5H₂O. The intermediates are yellow oxide (WO₃), blue oxide (W₂O₅, simplified), and brown oxide (WO₂). Various ways of processing are illustrated in Figure 3 by the flow sheet, which contains 12 different production lines.

The following are typical production lines:

1. Fine tungstic acid powder is reduced directly to metal by dry hydrogen at 750 °C. Metal
particles with an average size of 0.7 – 0.8 μm are obtained. These are carburized at 1400 °C to produce 1-μm carbide.

2. Ammonium paratungstate is calcined at 700 °C in a stream of nitrogen to give blue oxide, which is reduced at 800 °C. The metal is carburized at 1400 °C to produce carbide of 2 – 5 μm.

3. Ammonium paratungstate is roasted at 800 °C in air to produce WO₃. This is reduced by wet hydrogen at 950 °C. Carburizing at 1600 °C produces carbide of 10 – 20 μm.

Tungsten oxides can also be carburized directly with carbon, e.g.,

\[ \text{WO}_3 + 4 \text{C} \rightarrow \text{WC} + 3 \text{CO} \]

In this case, the intermediate metal step is omitted. The disadvantage is the difficulty in obtaining the correct carbon content in the carbide, since the CO itself reacts with oxide to form metal to a degree that cannot be calculated. Therefore, this process is used only to produce technical grades. Tungstic acid, ammonium paratungstate, or even scheelite (natural or artificial) can be treated in the same way.

\[ \text{CaWO}_4 + 4 \text{C} \rightarrow \text{CaO} + 3 \text{CO} + \text{WC} \]

However, when scheelite is heated with carbon, the resulting cake must be leached with acid to isolate the carbide, and this carbide is of low quality because of its high level of impurities.

Tungsten metal can be carburized by carbon-containing gases, usually carbon monoxide or methane. Gas-phase carburization is done preferably in the temperature range 800 – 900 °C. Therefore, the grains do not become much coarser. For example, WC of 0.3 – 0.4 μm is obtained from 0.3-μm metal. Such fine carbides are often called submicron carbides. Tungsten oxide can also be reduced and carburized in one step by CO or CH₄, but the product is always slightly deficient in combined carbon. When CO is used, water is not present in the furnace atmosphere as a byproduct of reduction. Because grain growth of tungsten during reduction is induced mainly by water vapor and high temperature, extremely fine WC can be made. These powders can be used as catalysts in fuel cells.

Another method of preparing fine WC is the reaction of tungsten metal or oxide with CH₄ and H₂ in a plasma reactor [12]. Carbide having a grain size of 0.1 μm or less, sometimes called ultrafine carbide, is obtained. The plasma technology and the use of such ultrafine WC are still being developed.

Numerous other ways to prepare WC have been developed. Some are modifications of the processes just described; others are entirely different. Most still need to be improved and are not yet in use on an industrial scale:

1. In the Axel – Johnson process, tungsten ore, ferrotungsten, or tungsten scrap is treated with chlorine to form WCl₆, which is reduced by H₂ in a gas-phase reaction. The fine metal formed by this reaction is carburized by a conventional process [13].

2. A mixture of WO₃ and carbon is heated in a two-stage rotary furnace. In the first stage the oxide is reduced to metal in a stream of nitrogen, and in the second stage WC is formed at higher temperature in a stream of hydrogen [14].

3. A mixture of WO₃, Co₃O₄, and carbon is reduced in H₂. After carburization, the mixture of WC and cobalt metal can be sintered directly to cemented carbides. The WC grains have a uniform, fine size, which is a result of the coreduction of the oxides [15].

All methods of preparation described thus far are solid-state or gas-phase reactions. The preparation of cast tungsten carbide is the only method involving fusion. A mixture of tungsten metal and carbon or tungsten carbide is heated in a carbon tube or high-frequency furnace to ca. 2800 °C. The molten eutectic is quenched in water or otherwise cooled rapidly to produce a fine crystalline structure.

Uses. Tungsten carbide is by far the carbide most used in cemented carbides: About 90 % of
the world’s production of carbide tools are tungsten carbide-based sinter alloys. Of these, 50% are so-called straight grades, tungsten carbide – cobalt products consisting of 70 – 95 wt % of tungsten carbide. There are many, many uses for cemented carbides of various compositions. The greatest demand is for cutting and drilling tools, mining machinery, and wear-resistant parts of all kinds. Some examples illustrate the broad field of applications: milling cutters, cutting tips and drills, sawing teeth and blades, drawing and heading dies, rolls, nozzles, sealing rings, balls for ball mills, balls for ballpoint pens, tire studs, and even scratch-proof watchcases. Protective surface coatings are made from cast tungsten carbide.

The mechanical properties of the cemented carbides depend primarily on the grain size of the tungsten carbide. Generally speaking, smaller grain sizes produce greater hardness but lower crack resistance. The cobalt content also affects the mechanical properties, and the properties of the cemented carbide can be adjusted to the mechanical requirements over a wide range.

**Toxicology.** Tungsten carbide and the other carbides of the transition metals are not known to be toxic in themselves. However, nearly all of these carbides are used in combination with cobalt metal, and cobalt dust is carcinogenic. Therefore, mixtures for the powder-metallurgical preparation of cemented carbides are classified as dangerous materials in some countries.

### 2.2. Titanium Carbide

The face-centered cubic monocarbide TiC is the only carbide in the titanium – carbon system. It melts without decomposition at ca. 3000 °C. Its range of homogeneity is very broad, ranging from 35 mol % to just below 50 mol % carbon. The composition with the highest melting point and the largest lattice constant contains less carbon than stoichiometric TiC (see Fig. 4). Because of this, undesired low-carbon phases cannot be formed during sintering of cemented carbides when TiC is present, unlike the case for the straight WC – Co grades. Titanium carbide forms solid solutions with all other cubic transition-metal carbides of groups 4 and 5. In addition, it is the host lattice for hexagonal WC in the most important industrial solid-solution carbide, (W,Ti)C (see Section 3.1).

At elevated temperatures, TiC and Ti metal react with oxygen and nitrogen to form TiO and TiN, the structures of which are isotypical to the lattice of TiC. Therefore, many TiC powders contain small amounts of N and O, to an extent of 1 % or more, and may be viewed as Ti(C, N, O) mixed crystals.

Commercial TiC is a gray powder usually having an average grain size of 2 – 10 μm. It is very resistant to acids, oxidation, and heat. However, it is dissolved easily by mixtures of HNO₃ and HF. In hydrogen it can be heated to its melting point without decomposition. Titanium carbide is the hardest of all the transition-metal carbides.

**Preparation.** Most commercial TiC is made by the reaction of TiO₂ with carbon. Intimate mixtures of pure TiO₂ and carbon are heated to 2000 °C or above in a hydrogen atmosphere. Large quantities of CO are produced. After the resulting cake is milled, the material contains up to 1 wt % each of free carbon, nitrogen, and oxygen. The amounts of these elements must be reduced in a second step, usually a vacuum
heating process. Nitrogen and oxygen contents are decreased to less than 0.1 wt % each. The free carbon content is usually in the range 0.2 – 0.4 wt %, and the combined carbon is 19.5 wt % max., somewhat less than the stoichiometric content of 20.05 wt %.

Titanium metal can be carburized with carbon. Titanium sponge, or even finely divided scrap, is used. The process is exothermic, and therefore, exact temperature control is not possible. As a result, the cake is sometimes extremely dense and can merely be broken down or milled only with difficulty. Carbon, nitrogen, and oxygen contents must be adjusted in a subsequent process.

Very coarse, comparatively pure TiC is prepared by the auxiliary metal bath technique [16]. Titanium metal, ferrotitanium, or even titanium alloy scrap is dissolved along with graphite in molten metal, preferably iron or nickel. After this mixture is cooled, TiC is isolated by dissolving the auxiliary metal with a nonoxidizing acid (menstruum process).

Extremely fine TiC is made in a plasma reaction of TiCl₄, H₂, and CH₄.

Layers of TiC on other materials may be produced by controlled vapor deposition from a mixture of TiCl₄, H₂, and CH₄.

Uses. Titanium carbide is the hardest carbide of the commercial transition-metal carbides, but it is too brittle to be used alone. However, it is the most important additional carbide in tungsten-based cemented carbides for cutting steel. Although toughness is decreased a little by the addition of TiC, the hardness and especially the heat resistance are increased significantly. Normal steel-cutting grades contain 5 – 30 wt % of TiC. Furthermore, TiC is the basic carbide for the formation of solid solutions with all other transition-metal carbides used in cemented carbides. In tungsten-free hardmetals, TiC is used in combination with molybdenum carbide and nickel binder metal.

Titanium carbide in combination with steel alloy forms a special type of hard alloy called Ferro-TiC. Tungsten-based cemented carbides can be replaced by this material in some cases. TiC was the first carbide material used for coatings on cutting tips made from normal cemented carbides. Even though the thickness of such a layer is in the range of only a few microns, the life of the cutting tools is increased markedly. Some TiC is used in combination with oxides in ceramic cutting tools (Al₂O₃ – TiC).

2.3. Tantalum Carbide

In general, the phase relationships in the systems of group 5 metals and carbon are complex. The system Ta – C (Fig. 5) is typical for the group. This system is characterized by several subcarbides, with lower carbon contents, in addition to the monocarbide, TaC. The face-centered cubic monocarbide melts without decomposition near 4000 °C, one of the highest melting points known. The broad range of homogeneity extends from 43 to 50 mol % C. The subcarbide Ta₂C decomposes at its incongruent melting point. There are two modifications, a high-temperature phase, with disordered L' 3 structure, and a low-temperature phase, of C6 type. The transformation temperature is near 2000 °C. In addition, there is a metastable Ta₅C₂, which is sometimes called the Brauer or ζ-phase. Similar phases are also found in the V – C and Nb – C systems, although the structure of the carbides is still not completely resolved [17].

![Figure 5. Tantalum – carbon phase diagram [3]](image-url)
The monocarbide, TaC, is the only phase of commercial interest. It is a brown powder, usually of 1 – 5 μm average grain size. Sintered and polished pieces have a yellow-golden sheen. The chemical resistance is high. The monocarbide is stable in nonoxidizing acids, although it is attacked easily by a mixture of HNO₃ and HF and by oxidizing salt melts. It can be heated up to 3000 °C in hydrogen or nitrogen, but it is oxidized rapidly in air at 800 °C.

**Preparation.** The method most used for preparation is based on the reaction of tantalum oxide with carbon:

\[ \text{Ta}_2\text{O}_5 + 7\text{C} \rightarrow 2\text{TaC} + 5\text{CO} \]

Intimate mixtures of oxide and carbon are pressed into graphite boats and heated at 1700 °C in hydrogen. Usually the product is deficient in bound carbon, and this must be adjusted in a second step. Tantalum metal can also be used for direct carburization with carbon. Very pure monocarbide for scientific use is obtained by the reaction of tantalum hydride with carbon.

A commercial grade of lower purity can be made by melting ferrotantalum or tantalum-containing scrap and slag in a metal bath with an excess of carbon. After the mixture is cooled, the auxiliary metal is dissolved with acid to free tantalum carbide. An additional step to adjust the carbon content is also necessary in this process.

**Uses.** Because of its extremely high melting point, some TaC is used in high-temperature techniques, but the main application is in hardmetals. Although TaC is the most expensive of all the carbides normally used in cemented carbides, consumption is still increasing because of the marked improvement in the properties of cemented carbides containing TaC. The world’s annual demand can be estimated to be ca. 500 t.

There are two quite different reasons for this use of TaC. First, small amounts of TaC, in the range of 0.2 – 2.0 wt %, are added to straight WC – Co grades in which fine-grained WC, 1.5 μm or less, is used. In these grades, often there is an undesired grain growth of the carbide phase during sintering because of the sintering time and temperature and probably some still unknown factors. This grain growth is inhibited to a great extent by TaC. Although there are other, cheaper compounds that retard grain growth, TaC is preferred because it is the only compound known to have no negative effects. The second reason for using TaC in cemented carbides is based on the great improvement in cutting tools, mainly in long-chipping steel cutting grades. In this second case the TaC content ranges from 2 to 15 wt %, and even more in some special cases. Thermal shock resistance, hot hardness, and resistance against cratering and oxidation are all increased markedly.

2.4. Niobium Carbide

The phase relationships in the system niobium – carbon are quite similar to those in the system tantalum – carbon. However, because of the close similarity, there is some doubt about the correctness of the phase diagram. The face-centered cubic monocarbide, NbC, melts without decomposition at ca. 3600 °C. It has a range of homogeneity from ca. 40 to almost 50 mol %; the stoichiometric value of 50 % is never reached. The subcarbide Nb₂C decomposes at its melting point of ca. 3000 °C. It exists in several modifications, the number and structure of which are a point of uncertainty. The other open question is the existence of an additional ζ-phase, Nb₃C₂.

The monocarbide, NbC, is the only phase used industrially. It is a gray-brown powder of normally less than 10 μm average grain size. Sintered pieces show a lavender tint. The chemical reactivity is similar to that of TaC, but NbC is less resistant to nitrogen. Heating the carbide in ammonia produces the nitride.

**Preparation.** Niobium monocarbide, NbC, is made in the same way as TaC: by carburization of the oxide, hydride, or metal at 1500 °C. The auxiliary metal bath technique can also be used. Most NbC is not produced as a single pure compound because demand for pure NbC is small. Nearly all of the NbC is used in combination with TaC; therefore, mixtures of Nb₂O₅ and Ta₂O₅, in various ratios, are carburized together. The resulting products are true mixed crystals of NbC and TaC. Any ratio can be prepared, but the usual commercial compositions contain 10, 20, or 50 wt % NbC.

**Uses.** Only small quantities of pure NbC are needed. Some is used in special grades of
cemented carbides in combination with Al₂O₃ (cermets). Another use is the reduction of Nb₂O₅ by NbC to niobium metal, a process carried out at 1600 °C under vacuum or hydrogen.

Most of the NbC is used in combination with TaC in hardmetals. When used with TaC, the NbC improves the properties of the sintered material just like pure TaC does. At the same time, NbC is much less expensive than TaC. However, NbC is said to decrease the strength when it is added in large amounts. The limit and the degree of toughness loss are not known exactly. In any case, NbC is never used alone, and the content of NbC in the TaC ranges from less than 1 to 50 wt %.

### 2.5. Zirconium Carbide

The monocarbide ZrC is the only compound in the zirconium – carbon system. It has a face-centered cubic crystal structure, and the range of homogeneity reaches from 38 to 50 mol % C. Zirconium carbide melts without decomposition at ca. 3400 °C. The phase boundaries in the Zr – C system are extremely sensitive to oxygen, nitrogen, and probably even more to other impurities. On the other hand, ZrC is difficult to prepare free from oxygen and nitrogen because the lattices of ZrC, ZrO, and ZrN are isotypical. As a result there have been many misinterpretations of the phase diagram in the past, and some disagreements still must be clarified.

The carbide is a gray powder. Its chemical resistance is somewhat lower than that of TiC. It is dissolved by cold HNO₃ or a cold mixture of H₃PO₄ and dilute H₂SO₄. It can be heated in hydrogen up to its melting point, but it is attacked by oxygen at 500 °C. When the carbide is heated in nitrogen above 1500 °C, the nitride is formed.

**Preparation.** Zirconium carbide is made mostly by heating mixtures of ZrO₂ and carbon at 1800 – 2400 °C in hydrogen or under vacuum. The carbon content must be adjusted in a second step. The metal, in the form of a sponge, or the hydride can be carburized with carbon at a temperature as low as 1400 – 1600 °C. Up to 1800 °C, the carbide getters oxygen, and oxygen-free material is difficult to obtain. Very pure ZrC, for scientific use, can be made by the gas-phase reaction of ZrCl₄, H₂, and a hydrocarbon.

**Use.** Up to now only small quantities of ZrC have been used in hardmetals. This may be due to the comparatively high price of ZrC as well as to its insufficient heat resistance. ZrC forms solid solutions with all other transition-metal carbides. Therefore, the demand of ZrC may increase. Other than use in cemented carbides, there is no use of importance.

### 2.6. Hafnium Carbide

The hafnium – carbon system and the properties of the carbide are similar to those of zirconium. The only phase is the face-centered cubic monocarbide, HfC. The broad range of homogeneity extends from 37.5 to 50 mol % C. The carbide melts at ca. 3900 °C without decomposition. Its chemical reactivity seems to be similar to that of ZrC, but little information is to be found in the literature.

**Preparation.** Hafnium dioxide can be carburized like ZrO₂ in hydrogen or under vacuum at 1800 – 2200 °C. If hafnium metal or hydride is used for carburization, a temperature of 1600 – 1700 °C is sufficient. When the oxide is the starting material, a second step for adjustment of carbon content and reduction of the oxygen content is necessary. This second step is often not necessary if the metal or hydride is the starting material.

**Uses.** Hafnium oxide or metal is a byproduct in the production of zirconium for nuclear reactors. Therefore, hafnium is available in sufficient quantities, and HfC has become attractive for cemented carbides. Tantalum carbide, TaC, in steel-cutting tools or as grain-growth inhibitor may be replaced by HfC. An HfC – NbC solid solution seems to be the most effective. Coatings of HfC on normal hardmetal tools increase the oxidation resistance. Such coatings are made by chemical vapor deposition (CVD) with HfCl₄ and a carbonizing gas.

### 2.7. Vanadium Carbide

Vanadium forms the same phases with carbon as tantalum and niobium. The face-centered cubic monocarbide, VC, exists over a broad range of homogeneity, from 43 to 49 mol % C. It melts...
without decomposition at ca. 2800 °C. There are two modifications of the subcarbide, V\(_2\)C, the orthorhombic low-temperature \(\alpha\)-phase and the hexagonal high-temperature \(\beta\)-phase. The latter decomposes on melting. Furthermore, there is a metastable \(\zeta\)-phase, V\(_3\)C\(_2\). Often a V\(_4\)C\(_3\) phase has been described in the literature, but this phase is only found in vanadium-containing steel alloys. Probably it is not a distinct phase, but rather a solid solution of carbide, oxide, and nitride, the structures of which are isotypical.

The only phase of commercial interest is the monocarbide, VC. It is a gray powder with a grain size usually of several micrometers. It is resistant to cold acids, except HNO\(_3\), but it is easily dissolved by hot oxidizing acids. The monocarbide can be heated to its melting point in hydrogen, but in air it is oxidized rapidly at 800 °C.

Preparation. Vanadium monocarbide is made mostly by heating V\(_2\)O\(_3\) or V\(_2\)O\(_5\) with carbon at 1500 – 1700 °C in hydrogen. Ammonium vanadate also can be used as the starting material. A second treatment under vacuum is necessary in every case to adjust the carbon content and to reduce the oxygen level. Because of the great stability of the V(C,O,N) mixed crystal, oxygen-free material is difficult to prepare. Very pure VC is best made by the reaction of vanadium metal with carbon under vacuum.

Uses. Vanadium monocarbide is too brittle to be used alone in cemented carbides. Some special grades were made with VC – TiC mixed crystals with nickel or iron binder, but this was done temporarily only when there was a shortage of tungsten. Small quantities of VC are used to inhibit grain growth in tungsten carbide – cobalt hardmetals. The effectiveness is higher than that of TaC, but the toughness of the sintered material is lower when > 0.5 % VC is added. Large quantities of VC are contained in steel alloys where it forms during melting.

2.8. Chromium Carbide

The phase relationships in the chromium – carbon system are quite different from those of the other metals of group 6 as well as those of the metals of groups 4 and 5. Hägg’s ratio of the atomic radii is 0.609 in the case of chromium and carbon; thus, the critical figure of 0.59 is exceeded and a simple closest packed structure can no longer form. There are three chromium carbides in the system (Fig. 6). The cubic carbide

---

Figure 6. Chromium – carbon phase diagram [6]
**Cr$_{23}$C$_6$** [12105-81-6] is a complex D$_8^4$ type with 116 atoms in the unit cell. It decomposes on melting at ca. 1500 °C. This Cr$_{23}$C$_6$ is sometimes formulated incorrectly as Cr$_2$C. The hexagonal Cr$_7$C$_3$ [12075-40-0] melts without decomposition at ca. 1800 °C, whereas the orthorhombic Cr$_3$C$_2$ [12012-35-0] decomposes at its melting temperature of ca. 1900 °C. All three phases have very narrow ranges of homogeneity. There are hints of the existence of one or more additional phases in the high-temperature range. These phases and some uncertainties in the phase boundaries between the known carbides are still a matter of discussion. Very little is known about the properties of Cr$_{23}$C$_6$ and Cr$_7$C$_3$ because these carbides are not prepared as pure compounds and are never used alone. They form during melting of steel and ferrous alloys, and they exist probably in the form of mixed crystals with iron and other metallic carbides. The carbide Cr$_3$C$_2$ is the only phase produced as such. It is a gray powder of a grain size normally less than 10 μm. It is insoluble in cold HCl, but dissolves in hot oxidizing acids and in H$_2$O$_2$. It has the greatest resistance to oxidation of all metal-like carbides. It is stable in air up to 1000 °C because of a very dense and firm oxide layer that forms on its surface.

**Preparation.** The carbide Cr$_3$C$_2$ is made by heating mixtures of Cr$_2$O$_3$ and carbon up to 1600 °C in hydrogen. Below 1300 °C, primarily Cr$_7$C$_3$ is formed. The following equations demonstrate how complicated the process of carburization is:

\[
3 \text{Cr}_2\text{O}_3 + 13 \text{C} \rightarrow 2 \text{Cr}_3\text{C}_2 + 9 \text{CO}
\]

\[
5 \text{Cr}_2\text{O}_3 + 27 \text{Cr}_3\text{C}_2 \rightarrow 13 \text{Cr}_7\text{C}_3 + 15 \text{CO}
\]

\[
\text{Cr}_2\text{O}_3 + 3 \text{Cr}_3\text{C}_2 \rightarrow \text{Cr}_2\text{C}_6 + 3 \text{CO}
\]

\[
3 \text{Cr}_2\text{O}_3 + 3 \text{Cr}_3\text{C}_2 \rightarrow 13 \text{Cr} + 6 \text{CO}
\]

Oxygen-free Cr$_3$C$_2$ with the stoichiometric carbon content is difficult to obtain if the starting material is the oxide. Very pure Cr$_3$C$_2$ can be made by the carburization of chromium metal powder.

**Uses.** Some Cr$_3$C$_2$ is used in hardmetals in special tools with great resistance to acids and salts. In these grades the carbide is bound with nickel. Small quantities of Cr$_3$C$_2$ are used as a grain-growth inhibitor in WC – Co cemented carbides. Considerable amounts of the eutectic Cr$_7$C$_3$ – Cr$_3$C$_2$ are used in welding electrodes for hard facing.

The greatest demand for chromium carbides is in steel, Stellite, and related alloys. In such cases, pure chromium carbides are not used; instead, chromium metal is added to the melt together with carbon-containing additives.

2.9. Molybdenum Carbide

Although much work has been done on the molybdenum – carbon system, there are still uncertainties and disagreements. The existence of at least four phases seems to be assured (Fig. 7). The hexagonal Mo$_2$C is the only phase stable at room temperature. Its range of homogeneity is very narrow and lies between 33 and 34 mol % C. The orthorhombic Mo$_2$C phase is stable only above 1475 °C. It melts without decomposition at ca. 2400 °C. Two carbon-rich phases, ca. 39 mol % C, exist only at high temperature, a hexagonal one above 1655 °C and a cubic one above 1960 °C. Both phases are designated as MoC$_{1-x}$ by some authors and as MoC or Mo$_3$C$_2$ by other authors. Below their decomposition temperatures these phases break down into Mo$_2$C and C. Hexagonal MoC$_{1-x}$ is isotypical with WC and can be stabilized by the inclusion of tungsten. More phases have been observed in the system, but probably all of them were oxygen-containing mixed phases.

The only phase of commercial interest is the hexagonal Mo$_2$C. It is a gray powder in the micron range. It is resistant to nonoxidizing acids but is dissolved by HNO$_3$ or by hot H$_2$SO$_4$. It is stable in hydrogen, but it is oxidized in air at 500 °C.

**Preparation.** Although MoO$_3$ or MoO$_2$ can be carburized with carbon at 1500 °C, a carbide with the correct carbon content and a low oxygen content is difficult to obtain. Pure Mo$_2$C is best made by heating molybdenum metal powder with carbon in hydrogen at ca. 1500 °C.

**Uses.** Mo$_2$C is used in special cemented carbide grades containing TiC and nickel metal.
Such grades were the first tungsten-free hardmetals. Attempts have been made to replace tungsten partially with Mo – W mixed crystals. Most Mo₂C is used in steel alloys, where it forms during melting.

3. Mixed Carbides

The commercial carbides of groups 4, 5, and 6 form numerous mixed carbides with each other. The formation of these solid solutions depends on the lattice constants of the carbides and corresponds to the Hume – Rothery rule on the atomic volumes. Only a few of the metallic carbides do not conform to these conditions and, thus, do not form a continuous series of solid solutions. The cubic monocarbides of the metals of groups 4 and 5 are completely miscible, except the pairs ZrC – VC and HfC – VC, which are soluble in each other only to a limited extent. Limited miscibility is found between TiC and the carbides of Cr, Mo, and W, but there are still some uncertainties about the TiC – WC system. Solid solutions of three or more carbides also exist. The host lattice of the mixed carbides is usually TiC. The hexagonal WC has only a negligible capability to receive cubic carbides into solid solution.

The use of mixed crystals in cemented carbides offers several advantages. Mixed crystals are harder and tougher than single, unalloyed carbides. The contents of oxygen, nitrogen, and free graphite are distinctly lowered by autopurification during the diffusion process; the wettability by cobalt and other binder metals is increased.

The temperatures for the preparation of mixed crystals are ca. 500 °C higher than the normal sintering temperatures for hardmetals. Therefore,
an exact formation of mixed crystals cannot be attained by mixing the individual carbides with the binder metal before sintering: the mixed carbides must be prepared in a separate process.

The mixed carbides can be prepared by the processes used for the preparation of the single carbides. Mixtures of the oxides and carbon are heated up to 1800 – 2000 °C in hydrogen, mostly in high-frequency induction furnaces. A second step under vacuum is always necessary to adjust the carbon content. The mixed metal powders can be treated with carbon in the same way. In addition, the reaction of metal oxide with another metal carbide and additional carbon is used, for example:

\[ \text{TiO}_2 + \text{WC} + 3\text{C} \rightarrow 2(\text{Ti}, \text{W})\text{C} + 2\text{CO} \]

Very pure mixed carbides are best made by heating mixtures of the single carbides at 2000 °C under vacuum. The process of diffusion can be accelerated by the addition of cobalt, nickel, iron, or chromium metal in the range 0.5 – 1.0 wt %:

\[ \text{TiC} + \text{TaC} \rightarrow 2(\text{Ti,Ta})\text{C} \]

Pure mixed crystals are also made by the auxiliary metal bath technique (menstruum process, see Preparation).

### 3.1. Tungsten – Titanium Carbide

The most important mixed carbide in cemented carbides is tungsten – titanium carbide. The ternary system is not yet known in all its details. The uncertainties in the Ti – C system caused by the isotypical TiO and TiN phases are observed in the Ti – W – C system as well. The solid solubility of WC in the cubic lattice of TiC is limited and depends on the temperature:

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>1500</th>
<th>2000</th>
<th>2400</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC, wt %</td>
<td>60</td>
<td>80</td>
<td>90</td>
</tr>
<tr>
<td>WC, mol %</td>
<td>31</td>
<td>55</td>
<td>73</td>
</tr>
</tbody>
</table>

Above 2600 °C, there is probably complete miscibility.

Saturated mixed crystals prepared at high temperatures become supersaturated when used in hardmetal production because of the comparatively low sintering temperatures, only 1400 – 1500 °C. Therefore, very fine WC crystals precipitate in the metal binder phase, thus strongly influencing the properties of the hardmetal. The mechanisms are still a matter of discussion. The W – Ti mixed crystals used in industry generally contain 50 or 70 wt % W.

### 3.2. Other Mixed Carbides

Another important mixed carbide for cemented carbides is tungsten – tantalum carbide. The solubility of cubic TaC in hexagonal WC is negligible, but WC has a limited solubility in TaC that depends strongly on the temperature:

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>1500</th>
<th>1800</th>
<th>2000</th>
<th>2500</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC, wt %</td>
<td>10</td>
<td>20</td>
<td>27</td>
<td>70</td>
</tr>
</tbody>
</table>

Because the solubility of WC in TaC decreases rapidly as the temperature is lowered, WC crystals always precipitate from the solid solutions during cooling. Therefore, preparation of single-phase (W,Ta)C mixed crystals is almost impossible, and unlike other mixed carbides, (W, Ta) C is usually marketed with the additional designation double phase.

The (W, Ti, Ta)C mixed crystal may be viewed as a combination of (W, Ti)C and (W, Ta)C mixed crystals. It is used in considerable quantities in cutting tools for steel and related long-chipping materials. Sometimes this mixed crystal is called “triple carbide”, which is incorrect because in nearly every case, TaC – NbC mixtures, not pure TaC, are used. The system W – Ti – Ta – Nb – C is not yet known in all its details. There are some isothermal sections in the quasiternary system WC – TiC – TaC [18], but the effects of the addition of NbC to this system are not known exactly.

Another important mixed crystal is titanium – molybdenum carbide (Ti,Mo)C. It is used in tungsten-free hardmetals with nickel binder for special steel cutting tools.

From the nine commercial carbides of the transition metals, 36 combinations of double carbides can be formed. Some of these are attracting growing interest, for example (W,Mo)C as a partial substitute for WC, or (Zr,Hf)C and...
(Zr,Nb)C as substitutes for TaC. All the double carbides are being intensively investigated [19], [20]. Mixed crystals of three transition-metal carbides, such as (Ti,Nb,Ta)C, number a total of 84, and 126 combinations are possible from four carbides, for example, (Ti,W,Hf,Zr)C. The knowledge about most of these systems is still quite limited.

3.3. Carbonitrides

The face-centered cubic monocarbides of groups 4 and 5 are isotypical with the face-centered cubic nitrides of the same groups, and because of this, there is complete miscibility between a metal carbide and metal nitride. The situation for Ta (C,N) is more complex because the usual form of TaN is hexagonal, the cubic TaN being stable only at high temperature and pressure.

With some limitations all carbonitride compounds can be used in cemented carbides [21]. A special application is scratchproof watchcases, because some carbonitrides are colored. The tint depends on the C : N ratio. For example, Nb (C, N) is violet at high carbon contents but yellow at high nitrogen contents. Another special application is coating of normal cemented carbides with layers of carbonitrides, usually Ti(C,N), by chemical vapor deposition (CVD). Carbonitrides can best be made by heating mixtures of the single carbides and nitrides in argon or under vacuum at 1600 – 1800 °C.

3.4. Mixed Carbonitrides

By methods similar to those used in the production of solid solutions of carbides or carbonitrides, a large number of mixed crystals can be prepared with various metals and nonmetals in one lattice. Only a few of them have been investigated up to now, and still fewer are used commercially. However, interest is growing. For example, (W,Mo)(C,N) with a nickel binder has properties comparable to those of WC – Co cemented carbides and can be used as a partial substitute for tungsten. The mixed carbonitride (Ti,Mo)(C,N) with a nickel alloy binder can be made to have an extremely fine carbide structure because of a spinodal decomposition of the carbonitrides. Both (Ti,W)(C,N) and (Ti,Ta)(C,N) have excellent heat-resistant properties.

4. Carbides of the Iron Group and Manganese

The carbides of Fe, Co, Ni, and Mn are usually classified as metallic carbides or metal-like carbides like the carbides of groups 4, 5, and 6. However, in fact, they are different from the transition-metal carbides, and their metallic characteristics are less pronounced. Hardness, melting points, and electrical conductivity are all distinctly lower. The crystal structures are not the simple interstitial Hågg phases, but rather much more complex structures, similar to those of the chromium carbides.

The carbides of Fe, Co, Ni, and Mn are neither prepared nor used alone. They are formed in iron and steel alloys during the melting process, and they can be isolated from these products by anodic oxidation of the metals. The carbides are important because they are the hardening phases in steel alloys, Stellites, cast iron, and related materials.

In the iron – carbon system there is probably only one phase, the orthorhombic Fe₃C, which is called cementite [12011-67-5]. Preparation of the pure carbide from the elements has not been achieved up to now. When Fe₃C is isolated electrolytically from alloys and sintered with cobalt metal, it decomposes. In alloy steels, the “iron carbide” is mostly included in mixed crystals with chromium carbides: (Fe,Cr)₂₃C₆, (Fe, Cr)₇C₃, and (Fe,Cr)₃C₂.

Cobalt and nickel form only the carbides Co₃C and Ni₃C, which are isotypical to Fe₃C. In the manganese – carbon system, three carbides are formed: Mn₃C is isotypical to Fe₃C, and Mn₇C₃ and Mn₂₃C₆ are isotypical to the corresponding chromium carbides.

5. Complex Carbides

A great number of ternary and quaternary phases can be formed between carbon and two or three metals, one a transition metal. In addition, the elements S, P, and As can be included.

These so-called complex carbides are a group of their own. They are not solid solutions of one
carbide in the lattice of another carbide. Each has its own typical structure, which in all cases is much more complicated than the simple Hägg phases of the transition-metal carbides.

Numerous complex carbides have been investigated [9], and all were found to contain octahedral or, less often, trigonal prismatic M₆C groups. M is always a transition metal, and six such atoms surround a central carbon atom. The octahedrons are linked by common corners, edges, or faces. The resulting interstitial sites can be occupied by other metals. Many distinct crystal structures can be formed under these conditions. The most important are perowskite carbides such as Ti₃AlC, β-Mn carbides such as Ta₅Al₂C, κ-carbides such as W₁₆Ni₃C₆, η-carbides such as W₃Co₃C, H-phases or Cr₇Al₂C-type carbides such as Zr₂AlC, V₃AsC-type carbides such as W₃Co₃C, and Mn₅Si₃-type carbides such as Nb₅Ga₃C₀.₂. Complex carbides can be best prepared by heating mixtures of the single carbides and metals for an extended period of time. Mechanical pressure or gas pressure is helpful.

Of commercial interest are mainly the η-carbides, which are formed in alloy steels and in Stellites. In hardmetals, η-carbides, such as W₃Co₃C and W₄Co₃C, form because of carbon deficiency, these phases causing a decrease in toughness.

References

General References

Further Reading