# CARBIDES, (SURVEY)

## 1. Introduction

Carbon (qv) reacts with most elements of the Periodic Table to form a diverse group of compounds known as carbides, some of which are extremely important in technology. For example, calcium carbide, $CaC_2$, is a source of acetylene; silicon carbide, SiC, and boron carbide, $B_4C$, are used as abrasives (qv); tungsten carbide, WC, titanium carbide, TiC, and tantalum (niobium) carbide, TaC(NbC) find use as structural materials at extremely high temperatures or in corrosive atmospheres. Cementite, $Fe_3C$, and the multimetallic complexes $(Co,W)_6C$, $(Cr,Fe,Mo)_{23}C_6$, and $(Cr,Fe)_7C_3$ are the components in tool steels and Stellite-type alloys responsible for their hardness, wear resistance, and excellent cutting performance. The general properties and applications of the carbides, including emerging uses of these materials as catalysts, have been described (1). (See Tungsten and tungsten alloys; Tantalum and tantalum compounds; Niobium and niobium compounds; Titanium and titanium compounds).

Figure 1 provides a survey of the most important and well-known binary compounds of carbon, according to their position in the periodic system. These may be divided into four main groups: the saltlike, metallic, diamondlike, and volatile compounds of carbon, which have ionic, metallic, semiconductor, or

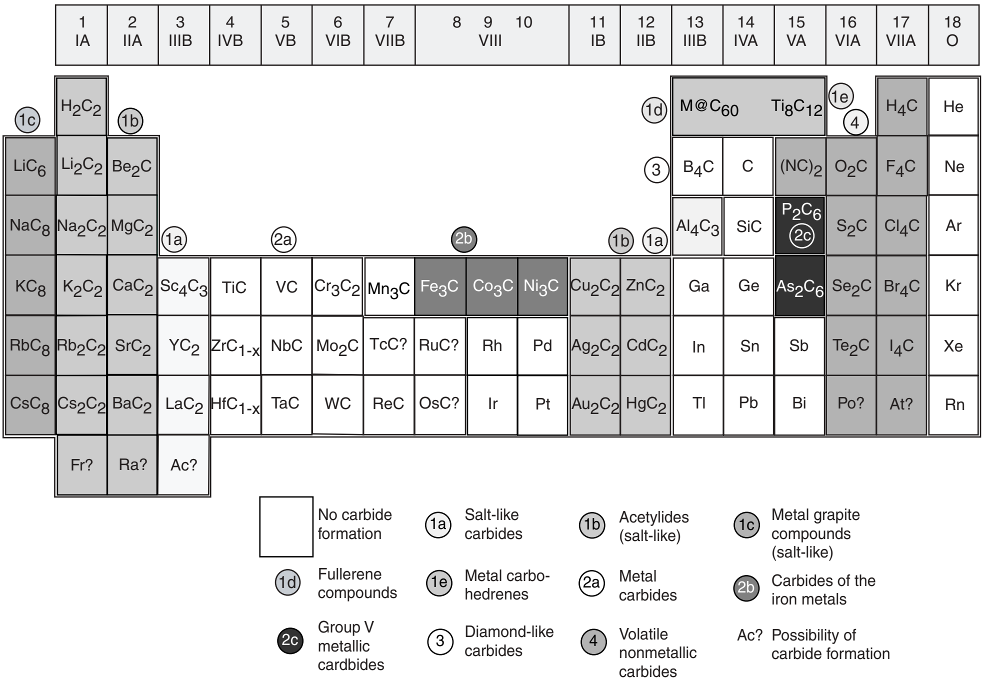


**Fig. 1.** Principal binary compounds of carbon.

covalent character, respectively. These and further subdivisions, used to characterize the compounds, are not rigid and there are a number of transitional cases. Whereas the members of Groups 2 (IIA) and 3 (IIIB) are classified as saltlike carbides, some of their properties, eg, $Be_2C$, with a very high degree of hardness, correspond to diamondlike carbides. Conversely, some monocarbides of Group 3 (IIIB), eg, scandium carbide, ScC, and uranium carbide, UC, as well as thorium carbide, ThC, have pronounced metallic characteristics.

Carbides are generally stable at high temperatures and thus can be prepared by the direct reaction of carbon with metals or metal-like materials at high temperatures. This does not apply to the acetylides and the alkali metal–graphite compounds, which although being carbon compounds, fit only marginally into the category of carbides. Similarly, the large class of coordination compounds, $ML_y$, known as organometallics are not typically considered carbides, even though the ligands, L, are attached to the metal center by metal–carbon bonds. The same applies to compounds such as $M_x$ @ $C_{60}$ or $M_x$ @ $C_{70}$, formed from diverse elements by association with fullerene structures (see Fullerenes) (2) and metallo-carbohedrene clusters such as $Ti_8C_{12}$, in which metals are part of the polyhedral cage (3). The volatile compounds of carbon are also excluded.

Table 1 contains an alphabetical listing of carbides referred to in the text.

## 2. Saltlike Carbides

This group comprises almost all carbides of Groups 1–3 (IA, IIA, and III B) of the Periodic Table. Beryllium carbide and $Al_4C_3$ may be considered as derivatives of

Table 1. **Carbide Compounds**[a]

| Carbide | CAS Registry Number | Formula |
|---|---|---|
| aluminum carbide (4:3) | [1299-86-1] | $Al_4C_3$ |
| arsenic carbide (2:6) | | $As_2C_6$ |
| beryllium carbide | [57788-94-0] | $Be_2C$ |
| boron carbide (4:1) | [12069-32-8] | $B_4C$ |
| calcium carbide (2:1) | [75-20-7] | $CaC_2$ |
| chromium carbide | [12011-60-8] | CrC |
| chromium carbide (3:2) | [12012-35-0] | $Cr_3C_2$ |
| chromium carbide (4:1) | [12075-40-7] | $Cr_4C$ |
| chromium carbide (7:3) | [12075-40-0] | $Cr_7C_3$ |
| chromium carbide (23:6) | [12105-81-6] | $Cr_{23}C_6$ |
| cobalt carbide (3:1) | [12011-59-5] | $Co_3C$ |
| cobalt tungsten carbide (6:6:1) | [12538-07-7] | $Co_6W_6C$ |
| hafnium carbide | [12069-85-1] | HfC |
| iron carbide | [12069-60-2] | FeC |
| iron carbide (2:1) | [12011-66-4] | $Fe_2C$ |
| iron carbide (3:1) | [12011-67-5]<br>[12169-32-3] | $Fe_3C$ |
| iron carbide (5:2) | [12127-45-6] | $Fe_5C_2$ |
| iron carbide (7:3) | [12075-42-2] | $Fe_7C_3$ |
| iron carbide (23:6) | [12012-72-5] | $Fe_{23}C_6$ |
| lanthanum carbide (1:2) | [12071-15-7] | $LaC_2$ |
| manganese carbide (3:1) | [12121-90-3] | $Mn_3C$ |
| manganese carbide (23:6) | [12266-65-8] | $Mn_{23}C_6$ |
| magnesium carbide (1:2) | [12122-46-2] | $MgC_2$ |
| magnesium carbide (2:3) | [12151-74-5] | $Mg_2C_3$ |
| molybdenum carbide | [12011-97-1] | MoC |
| molybdenum carbide (2:1) | [12069-89-5] | $Mo_2C$ |
| molybdenum carbide (23:6) | [12152-15-7] | $Mo_{23}C_6$ |
| nickel carbide | [12167-08-7] | NiC |
| nickel carbide (3:1) | [12012-02-1] | $Ni_3C$ |
| niobium carbide | [12069-94-2] | NbC |
| niobium carbide (2:1) | [12011-99-3] | $Nb_2C$ |
| plutonium carbide | [12070-03-0] | PuC |
| plutonium carbide (2:3) | [12076-56-1] | $Pu_2C_3$ |
| phosphorus carbide (2:6) | | $P_2C_6$ |
| scandium carbide | [12012-14-5] | ScS |
| silicon carbide | [409-21-2] | SiC |
| tantalum carbide | [12070-06-3] | TaC |
| tantalum carbide (2:1) | [12070-07-4] | $Ta_2C$ |
| thorium carbide | [12012-16-6] | ThC |
| thorium carbide (1:2) | [12071-31-7] | $ThC_2$ |
| titanium carbide | [12070-08-5] | TiC |
| tungsten carbide | [12070-12-1] | WC |
| tungsten carbide (2:1) | [12070-13-2] | $W_2C$ |
| uranium carbide | [12170-09-6] | UC |
| uranium carbide (1:2) | [12071-33-9] | $UC_2$ |
| uranium carbide (2:3) | [12076-62-9] | $U_2C_3$ |
| vanadium carbide | [12070-10-9] | VC |
| vanadium carbide (2:1) | [12012-17-8] | $V_2C$ |
| zirconium carbide | [12020-14-3] | ZrC |

[a] Stoichiometry indicated in paranthesis

methane ($C^{4-}$ anion) and most carbides with $C_2$ groups (chiefly ${C_2}^{2-}$ anions) as derivatives of acetylene. This finding is supported to some extent by the following hydrolysis reactions:

$$Be_2C + 4\ H_2O \rightarrow 2\ Be(OH)_2 + CH_4 \tag{1}$$

$$Al_4C_3 + 12\ H_2O \rightarrow 4\ Al(OH)_3 + 3\ CH_4 \tag{2}$$

$$CaC_2 + 2\ H_2O \rightarrow Ca(OH)_2 + C_2H_2 \tag{3}$$

Propyne is obtained from $Mg_2C_3$ (probably ${C_3}^{4-}$ anions), formed by thermal decomposition of $MgC_2$, with separation of graphite:

$$Mg_2C_3 + 4\,H_2O \rightarrow 2\,Mg(OH)_2 + CH_3C{\equiv}CH \tag{4}$$

In their pure state, the carbides of Groups 1 (IA) and 2 (IIA) are characterized by their transparency and lack of conductivity. The carbides of Group 3 (IIIB) (Sc, Y, the lanthanides, and the actinides) are opaque. Some of them, depending on their composition, show metallic luster and electroconductivity. The $M^{2+}$ cation may exist in the $MC_2$ phases of this group, and the remaining valence electron apparently imparts partly metallic character to these compounds. Methane, ethylene, and hydrogen, as well as acetylene, are formed during the hydrolysis of the Group 3 (IIIB) carbides of varying composition, $M_3C$, MC, $M_2C_3$, and $MC_2$.

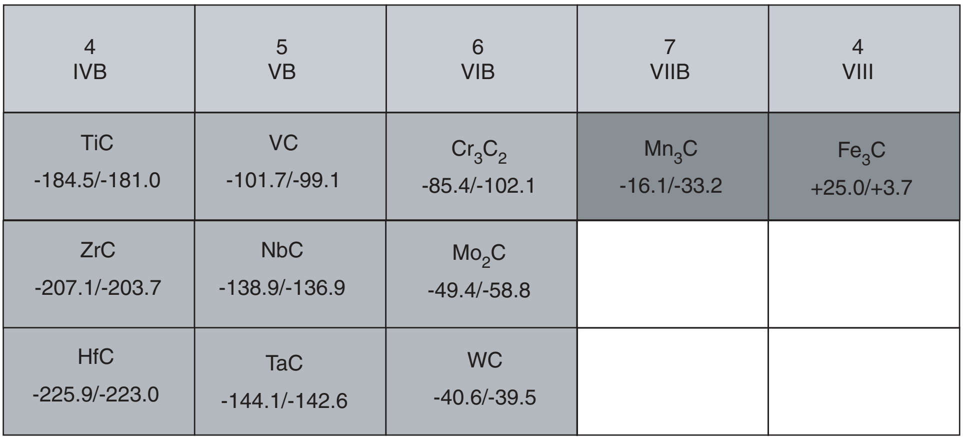
Formally, the term acetylides applies to carbides precipitated from aqueous solutions or from solutions in aqueous ammonia by reaction of metal ions with acetylene (4). These include compounds of Cu, Ag, Au, Na, K, Rb, Cs, Zn, Cd, Hg, Pd, Os, Ce, Al, Mg, etc. Because they require additives such as $H_2$, $H_2O$, $NH_3$, $C_2H_2$, and metal salts for stabilization, it is doubtful whether they can be considered as pure metal–carbon compounds and described as carbides.

The alkali metal–graphite compounds formed by graphite absorption of the fused metals Na, K, Rb, and Cs, represent a special type of metal–carbon compound (5). These are intercalation compounds with formulas such as $MC_8$, $MC_{16}$, and $MC_{60}$. They become strongly graphitic as the carbon content increases, with their color changing from brown to gray to black.

## 3. Metallic Carbides

This class of compounds comprises the interstitial carbides of the transition metals of Groups 4–6 (IVB–VIB) (see CARBIDES, INDUSTRIAL HARD) and the carbides of metals of Groups 7–10 (VIIB–VIII). The metalloconductive carbides $P_2C_6$ and $As_2C_6$ are also included, as well as some members of the lanthanide and actinide series. Their standard heat of formation and free energy of formation are reported in Figure 2. It is seen that the thermodynamic stability of the compounds is high toward the left in the Periodic Table and decreases in moving to the right.

**3.1. Group 4–6 (IVB–VIB) Metals.** The early transition elements possess relatively large atomic radii and carbon resides in the interstitial cavities between metal atoms. In these interstitial carbides, the metal atoms form



| 4<br>IVB | 5<br>VB | 6<br>VIB | 7<br>VIIB | 4<br>VIII |
|---|---|---|---|---|
| TiC<br>-184.5/-181.0 | VC<br>-101.7/-99.1 | $Cr_3C_2$<br>-85.4/-102.1 | $Mn_3C$<br>-16.1/-33.2 | $Fe_3C$<br>+25.0/+3.7 |
| ZrC<br>-207.1/-203.7 | NbC<br>-138.9/-136.9 | $Mo_2C$<br>-49.4/-58.8 | | |
| HfC<br>-225.9/-223.0 | TaC<br>-144.1/-142.6 | WC<br>-40.6/-39.5 | | |

**Fig. 2.** Thermodynamic properties of metallic carbides (ΔH°298/ΔG°298). Values in kJ/mol of metal.

relatively simple structures commonly found among pure metals: hexagonal closed-packed (hcp), face-centered cubic (fcc), and simple hexagonal (hex) structures. The major structure not adopted by carbides is the body-centered cubic (bcc) structure, because this lattice does not accommodate a large interstitial site. In Groups 4 and 5 (IVB and VB), and some of the rare earth carbides the preferred structure is the B1 NaCl structure, where carbon occupies every octahedral site in an fcc arrangement of metal atoms. The resulting stoichiometry is MC, exemplified by TiC, ZrC, HfC, VC, NbC, TaC, UC, and PuC. There is often some carbon deficiency in these substances, which may be disordered, as in the $MC_{1-x}$ phases, or ordered, as in the compounds, $V_8C_7$, $Nb_4C_3$, etc. In Group 5 (V B), the stoichiometry $M_2C$ appears, eg, $V_2C$, $Nb_2C$, and $Ta_2C$, which becomes most favorable for Group 6 (VIB), eg, $Mo_2C$, and $W_2C$. In this structure, carbon randomly occupies one-half of the octahedral sites in an hcp arrangement of metal atoms. Again, substoichiometry may occur, as well as the formation of ordered vacancies. At high temperatures $MoC_{1-x}$ and $WC_{1-x}$ ($x \sim 0.5$) phases having an fcc arrangement of metal atoms are observed. Group 6 (VIB) also shows retention of the MC stoichiometry, MoC, WC, and (Mo,W)C. However, here carbon does not occupy the octahedral holes of the B1 structure, but rather the more spacious trigonal prismatic sites in a hex arrangement of metal atoms.

The Group 4–6 (IVB–VIB) carbides are thermodynamically very stable, exhibiting high heats of formation, great hardness, elevated melting points, and resistance to hydrolysis by weak acids. At the same time, they have values of electrical conductivity, Hall coefficients, magnetic susceptibility, and heat capacity in the range of metals (6).

**3.2. Group 7–10 (VIIB, VIII) Metals.** Carbides of these metals are generally less stable than those of the earlier transition metals. The noble metals of the second and third row (Rh, Pd, Ir, Pt) do not form carbides at all. In moving to the right in the Periodic Table the size of the atoms decreases, and the metal lattice is no longer able to accomodate interstitial carbon atoms while maintaining close-packed or near close-packed metal atoms. Thus, complex structures arise, eg, $Mn_8C_3$ is triclinic, $Mn_4C$ is tetragonal, while $Mn_3C$, $Fe_3C$, and $Co_3C$ are orthorhombic. The chromium carbides occupy an intermediate position in this respect, eg, $Cr_3C_2$, is also orthorhombic. Group 7–10 (VI B–VIII) compounds also differ markedly in chemical and physical behavior from the interstitial carbides. Hardness values and melting points are lower and chemical stability to mineral acids is also no longer apparent. However, the materials are still robust; as mentioned earlier, they are of technological importance as components in high speed tool steels and advanced alloys.

**3.3. Properties and Nature of Bonding in the Metallic Carbides.** The metallic carbides are interesting materials that combine the physical properties of ceramics (qv) with the electronic nature of metals. Thus, they are hard and strong, but at the same time, good conductors of heat and electricity.

The crystal structure and stoichiometry of the materials are determined from two contributions, geometric and electronic. The geometric factor is derived from the empirical observation (7) that simple interstitial carbides, nitrides, borides, and hydrides are formed for small ratios of nonmetal (X) to metal radii, $r_X/r_M < 0.59$, ie, the Hägg rule. When this ratio is $>0.59$, as in the Group 7–10 (VI B–VIII) metals, the structure becomes more complex to compensate for the loss of metal–metal interactions. Although there are minor exceptions, the Hägg rule provides a useful basis for predicting structure.

There is also an electronic factor that contributes to the bonding properties of the materials (8). The materials behave electronically as though their electron density increased by alloying. In forming carbide alloys, carbon combines its valence *sp* electrons with the metal *spd* band. Engel-Brewer theory may be used to predict the crystal structures of the materials based on the total number of valence *sp* electrons. Thus, with increasing *sp* electrons, crystal structure is predicted to change from bcc → hcp → fcc, as observed in the series $Nb \rightarrow Nb_2C \rightarrow MoC_{1-x}$ or $Ta \rightarrow Ta_2C \rightarrow WC_{1-x}$. An increase in band occupancy, first to bonding levels and then to antibonding levels, is also indicated by the occurrence of a maximum in melting point at Group 5 (VB) for the carbides, rather than at Group 6 (VIB) for the pure metals. Furthermore, increased metal/nonmetal ratios ($MC \rightarrow M_2C \rightarrow M_3C$) in moving to the right in the Periodic Table suggests rejection of carbon by the metal. This occurs from increased filling of the antibonding portion of the electronic band.

Ideas on bonding have evolved considerably over the years (9). Early models considered bonding to arise from resonance between different covalent canonical forms. The hardness and brittleness of the compounds was attributed to the presence of directed covalent bonds, and the electrical conductivity to the existence of resonance structures. An opposing view, based on the high electronegativity of carbon compared to metals, held that the bonding was ionic in nature. This explained the refractory nature and the B1 NaCl structure of many of the compounds, but did not account for the instability of carbides beyond Group 6 (VIB). The instability was explained by band structure models suggesting that in compounds of the late transition metals, filling of the antibonding portion of the *d*-band occurred. This finding was consistent with electron donation from carbon

Table 2. **Physical Properties of Diamondlike Carbides and Nonmetallic Hard Materials**

| Compound | Molecular formula | Density, g/mL | mp, °C | Micro hardness[a] | Transverse rupture strength, N/mm$^{2b}$ | Compression strength, N/mm$^{2b}$ | Modulus of elasticity, N/mm$^{2b}$ | Heat conductivity, W/(cm·K) | Coefficient of thermal expansion, $\beta \times 10^{-6}$ | Electrical resistivity, $\mu\Omega \cdot cm$ |
|---|---|---|---|---|---|---|---|---|---|---|
| diamond | $C$ | 3.52 | 3800 dec | 7600 | ~300 | ~2000 | ~900,000 | 1.14 | 0.9–1.18 | $10^{18}$ |
| boron carbide | $B_4C$ | 2.52 | 2450 | 2940 | 500 | 1800 | 450,000 | 0.27 | 6.0 | $10^{4}$ |
| silicon carbide | $SiC$ | 3.2 | 2300 dec | 2580 | <400[b] | 1400 | 480,000 | 0.15 | 5.7 | $10^{3}$ |
| beryllium carbide | $Be_2C$ | 2.42 | 2300 | 2690 | | 740 | 350,000 | 0.21 | 7.4 | $10^{3}$ |
| alumina, sintered | $Al_2O_3$ | 3.9 | 2050 | 2080 | <700[c] | 3000 | 400,000 | 0.19 | 7.8 | $10^{18}$ |
| boron nitride, cubic | $BN$ | 3.45 | 2730[d] | 4700 | | | 600,000 | | | $10^{16}$ |
| aluminum nitride | $AlN$ | 3.26 | 2250 | 1230 | | | 350,000 | | | $10^{13}$ |
| silicon nitride | $Si_3N_4$ | 3.44 | 1900 | 1700 | <750[c] | | 210,000 | 0.18 | 2.4 | $10^{16}$ |
| silicon boride | $SiB_6$ | 2.43 | 1950 | 2300 | ~100 | | 330,000 | | 6.3 | $10^{5}$ |

[a] See HARDNESS.

[b] To convert N/mm$^2$ (MPa) to psi, multiply by 145.

[c] Hot-pressed.

[d] Transition from cubic to hexagonal ~1650°C.

to metal. The direction of electron transfer has been controversial, both theoretically and experimentally (10). Rigid-band models and tight-binding linear combination of atomic orbitals (LCAO) models suggest electron transfer from carbon to metal, which is supported by the known chemical behavior of the compounds and similarities in the shapes of the valence bands. However, augmented plane wave (APW) and related calculations suggest electron donation in the opposite direction, and this is confirmed experimentally by X-ray photoelectron spectroscopy and near-edge X-ray absorption fine structure spectroscopy (11). These difficulties may be resolved by considering a narrowing of the *d*-band in forming the later transition metal carbides (12). This results in greater occupation of the band, as deduced chemically, with simultaneous transfer of electrons from metal to nonmetal, as observed physically.

## 4. Diamondlike Carbides

This group of materials include the main group compounds silicon carbide and boron carbide (see SILICON CARBIDE BORON COMPOUNDS. Beryllium carbide, which has a high degree of hardness, can also be included (see BERYLLIUM COMPOUNDS). These materials have electrical resistivity in the range of semiconductors, and the bonding is largely covalent. Diamond itself may be considered a carbide of carbon because of its chemical structure, although its conductivity is low.

Table 2 summarizes the properties of the so-called nonmetallic hard materials, including diamond, the diamondlike carbides $B_4C$, SiC, and $Be_2C$. Also included in this category are corundum, $Al_2O_3$, cubic boron nitride, BN, aluminum nitride, AlN, silicon nitride, $Si_3N_4$, and silicon boride, $SiB_6$ (13).

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