CARBIDES, INDUSTRIAL HARD

1. Introduction

The four most important carbides for the production of cemented carbides (a.k.a. hard metals) are tungsten carbide [12070-12-1] (WC), titanium carbide [12070-08-5] (TiC), tantalum carbide [12070-06-3] (TaC), and niobium carbide [12069-94-2] (NbC). The binary and ternary solid solutions of these carbides such as WC–TiC and WC–TiC–TaC (NbC) are also of great importance. Chromium carbide (3:2) [12012-35-0] (Cr_3C_2), molybdenum carbide [12011-97-1] (MoC), and molybdenum carbide (2:1) [12069-89-5] (Mo_2C), vanadium carbide [12070-10-9] (VC), hafnium carbide [12069-85-1] (HfC), and zirconium carbide [12020-14-3] (ZrC), have minor significance. Carbides and their solid solutions (the latter also herein referred to as mixed crystals) are generally combined with cobalt and used in the form of cemented carbides.

2. Preparation

In general, the carbides of metals of Groups 4–6 (IVB–VIB) are prepared by reaction of elementary carbon or hydrocarbons and metals and metal compounds at high temperatures. The process may be carried out in the presence of a protective gas, under vacuum, or in the presence of an auxiliary metal (menstruum).

2.1. Carburization by Fusion.

This method is used for the production of cast tungsten carbide eutectic alloy, chiefly for deposition by welding onto many types of machinery wear-surfaces, eg, on rotary rock-drill bits used in the petroleum, mining, and construction industries. Using rapid induction heating of tungsten metal powder and carbon under hydrogen in graphite crucibles, a fused eutectic (~4%C) is cast and chill-cooled and the mass crushed to produce preferred granular size ranges for use as filler for weldable hardfacing products.

$$3\,W + 2\,C \xrightarrow[H_2C]{2800^\circ C} W_2C\text{—}WC$$

2.2. Carburization by Thermal Diffusion.

Carburization of chemically processed metal or metal-compound powders is carried out through solid-state, thermal diffusion processes, either in protective gas or vacuum. Carbide solid solutions are prepared by the same methods. Most carbides are made by these processes, using loose or compacted mixtures of carbon and metal or metal-oxide powders. Halides of Group 5 (VB) metals recovered from ores by chlorination are similarly carburized.

$$W + C \xrightarrow[H_2]{1400-1600^\circ C} WC \tag{1}$$

$$Ta(H) + C \xrightarrow[H_2,\text{vacuum}]{1400-1500^\circ C} TaC + (H)$$

$$W + CH_4 \xrightarrow[H_2]{1400-1600^\circ C} WC + 2\,H_2$$

$$WO_3 + 4\,C \xrightarrow[H_2,CO]{1400-1600^\circ C} WC + 3\,CO \tag{2}$$

$$TiO_2 + 3\,C \xrightarrow[H_2,CO,\text{vacuum}]{1800-2000^\circ C} TiC + 2\,CO$$

$$Nb_2O_5 + 6\,C + CH_4 \xrightarrow[H_2]{1400-1700^\circ C} 2\,NbC + 5\,CO + 2\,H_2$$

2.3. Carburization by Menstruum Process.

The P. M. McKenna method of carburization (1) involves the use of mineral concentrates such as wolframite [1332-08-7] [$Fe(Mn)WO_4$] and microlite [12173-96-5] ($Ca_2Ta_2O_7$), ferroalloys such as iron tungstide (FeW) or high purity scrap metals in a high-temperature melt of auxiliary (menstruum) metal or metals, with carbon. Upon cooling, carbide crystals are dispersed throughout the metallic mass. The mass is then crushed and the carbide crystals isolated by dissolving the menstruum alloy in mineral acids. Further purification by elutriation follows.

$$Fe(Mn)WO_4 + 5\,C + Fe \xrightarrow{2300-2600^\circ C} WC + Fe(Mn) + Fe + 4\,Co + C$$

$$FeW + 2\,C \xrightarrow{2300-2600^\circ C} WC + Fe + C$$

$$TiO_2 + Fe + 4\,C \xrightarrow{2300-2600^\circ C} TiC + Fe + 2\,CO + C$$

$$FeW + Ti + Fe + 2\,C \xrightarrow{2300-2600^\circ C} (W,Ti)C + 2\,Fe + C$$

$$Ca_2Ta_2O_7 + Fe + 13\,C \xrightarrow{2300-2600^\circ C} 2TaC + Fe + 7CO + 2\,CaC_2 + C$$

2.4. Carburization by Exothermic Thermochemical Reaction.

Carburization of tungsten contained in tungsten mineral concentrates is accomplished by means of a simultaneous aluminothermic reduction and carburization (2,3). The reaction produces, upon cooling, a metallic mass in which tungsten carbide crystals are dispersed in a menstruum alloy. After crushing, WC crystals in the mass are isolated by dissolving the menstruum either in acidic ferric chloride solutions or mineral acids, followed by elutriation. The process has, since the 1960s, become an important source of primary WC for the manufacture of cemented hard carbides and other metallurgical products.

$$6\ \mathrm{Fe(Mn)WO_4} + 22\ \mathrm{Al} + 3\mathrm{CaC_2} + 3\ \mathrm{Fe_3O_4} \xrightarrow{2500-3000^\circ\mathrm{C}}$$

$$6\ \mathrm{WC} + 6\ \mathrm{Fe(Mn)} + 9\ \mathrm{Fe} + 3\ \mathrm{CaO} + 11\ \mathrm{Al_2O_3}$$

Titanium carbide may be prepared by a thermochemical reaction between finely divided carbon and titanium metal powder. The reaction proceeds exothermically.

$$\mathrm{Ti} + \mathrm{C} \xrightarrow{1700-2200^\circ\mathrm{C}} \mathrm{TiC}$$

Additionally, titanium carbonitride (TiCN) for use in cermets may be produced exothermically in a wide range of TiC–TiN solid solutions by reacting TiC and Ti powder-blends or powder compacts in low concentrations of nitrogen in vacuum. For example,

$$\mathrm{Ti} + \mathrm{N} \xrightarrow[\mathrm{N_2,vacuum}]{1500-1700^\circ\mathrm{C}} \mathrm{TiN}$$

$$\mathrm{TiC} + \mathrm{Ti} + \mathrm{N} \xrightarrow[\mathrm{N_2,vacuum}]{1500-1700^\circ\mathrm{C}} \mathrm{TiCN}$$

The use of titanium carbonitrides in Ti-based cermets marks a significant improvement in metal-cutting performance over TiC.

2.5. Reduction.

Reduction of halides using hydrogen–hydrocarbon mixtures is sometimes done in the presence of a graphite carrier or using metals possessing high melting points, ie, the van Arkel gas deposition method (4). If a plasma gun is employed, finely powdered (<1 µm) carbides are obtained (5) (see PLASMA TECHNOLOGY).

A number of hard materials, including TiC, Ti(C,N), Zr(C,N), TiN, and alumina, ($\mathrm{Al_2O_3}$), are produced by reduction from metal-halide precursors as thin coatings (3–20 µm) directly onto metalcutting insert surfaces by chemical vapor deposition (CVD), in gaseous atmospheres containing various combinations of nitrogen, hydrocarbon gases, eg, methane, and oxygen, at ~1000°C. These coatings reduce cutting temperatures and the various abrasive and chemical wear processes, increase tool life, and allow higher machining speeds, thereby increasing metalcutting productivity. Titanium nitrides, TiN, titanium carbonitrides, TiCN, titanium aluminum nitrides, TiAlN, titanium diborides, $\mathrm{TiB_2}$, and chromium nitrides, CrN are also deposited, with tool life and metalcutting productivity benefits, by the physical vapor deposition (PVD) process. The following typify the CVD process:

$$\mathrm{TiCl_4 + CH_4 \xrightarrow[H_2]{1000^\circ C} TiC + 4\,HCl}$$

$$\mathrm{TiCl_4 + CH_4 + 1{-}2\,N_2 \xrightarrow[H_2]{1000^\circ C} TiCN + 4\,HCl}$$

$$\mathrm{TiCl_4 + 1{-}2\,N_2 + 2\,H_2 \xrightarrow[H_2]{1000^\circ C} TiN + 4\,HCl}$$

$$\mathrm{2\,AlCl_3 + 3\,H_2O \xrightarrow[H_2]{1000^\circ C} Al_2O_3 + 6\,HCl}$$

3. Tungsten Carbide

Traditionally, tungsten ore is chemically processed to ammonium paratungstate [1311-93-9], $[(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O]$ and tungsten oxides (W_xO). These compounds are then hydrogen-reduced to tungsten [7440-33-7] metal powder (see TUNGSTEN AND TUNGSTEN ALLOYS; TUNGSTEN COMPOUNDS). The fine tungsten powders are blended with carbon and heated in a hydrogen atmosphere between 1400 and 1500°C to produce tungsten carbide particles having sizes varying from 0.5 to 30 μm. Each particle is composed of numerous tungsten carbide crystals. Small amounts of vanadium, chromium, or tantalum are sometimes added to tungsten and carbon powders before carburization to produce very fine (<1 μm) WC powders.

The characteristics of WC, especially grain size, are determined by purity, particle shape and grain size of the starting material, and the conditions employed for reduction and carburization. The course of the reaction $WO_3 \rightarrow W \rightarrow WC$ is dependent on temperature, gas-flow rates, water-vapor concentration in the gas, and the depth of the powder bed. All these factors affect the coarsening of the grain.

Selection of suitable tungsten-containing raw materials and modification of the reduction and carburization conditions permit the preparation of the WC powder in various grain sizes. The following examples are illustrative: (*1*) very pure tungstic acid of fine (<0.1 μm) grain size is reduced in dry hydrogen at ~800°C, and the fine (<0.5 μm) tungsten powder obtained gives very fine (<1 μm) grained WC on carburization at 1350–1400°C; (*2*) calcined coarse (<2 μm) WO_3, after reduction with hydrogen in the presence of water vapor at 900–950°C, provides tungsten powder (<6 μm) from which coarse (<10 μm) crystalline WC powder can be prepared by carburization at 1600°C.

The WC leaving the furnace is light gray with a bluish tinge. It is generally caked and must be broken up, milled, and screened before use. It should contain ~6.1–6.25 wt% total C, of which 0.03–0.15 wt% is in the free, unbound state. The theoretical C-content is 6.13 wt%. The great bulk of WC powder used in the manufacture of cemented carbides exceeds ~2 μm in average particle size before conversion to powder grades by milling. During the sintering process, which follows milling and compacting, WC crystal growth occurs in the semiliquid binder alloy, during which the largest crystals may reach 10 μm or more, while the underlying ground mass may range from 1 to 10 μm, depending on the grade composition and the intended application. At the high particle size end of this broad spectrum lie coarser initial WC particle sizes, used in the manufacture of coarser sintered microstructures for mining, construction, and transportation tools. At the lower particle-size end, finer initial WC particle sizes, generally 1–2 µm, enter the picture, yielding finer sintered microstructures (eg, ∼1–6 µm WC crystals), designed to provide combinations of both high strength and high flank-wear resistance, especially for metalcutting and metalforming applications.

In recent years, efforts to achieve higher levels of both sintered strength and wear resistance, using an initial submicron WC particle size typically in the <1-µm range, and sometimes in "ultrafine" or "nanosized" ranges, typically <0.4-µm average particle size, have resulted in much finer sintered microstructures together with increases in transverse rupture strengths. Special WC powder processing controls necessary for the production of initial WC in submicron sizes are demanding. Many control parameters in WC-powder processes influence initial WC particle size and particle size range. They include the characteristics of tungsten-precurser materials, such as ammonium paratungstate and its reduction parameters to form tungsten metal powder, the purity and stream velocity of hydrogen or other gases used in reduction or carburizing furnaces, temperature profiles used in both, the gas–solid contact efficiency in processing furnaces, and choices of processing equipment. Equipment and process departures made by some manufacturers to produce submicron particle sizes include, inter alia, a rotary carburizing furnace with a carbon-rich atmosphere, gaseous

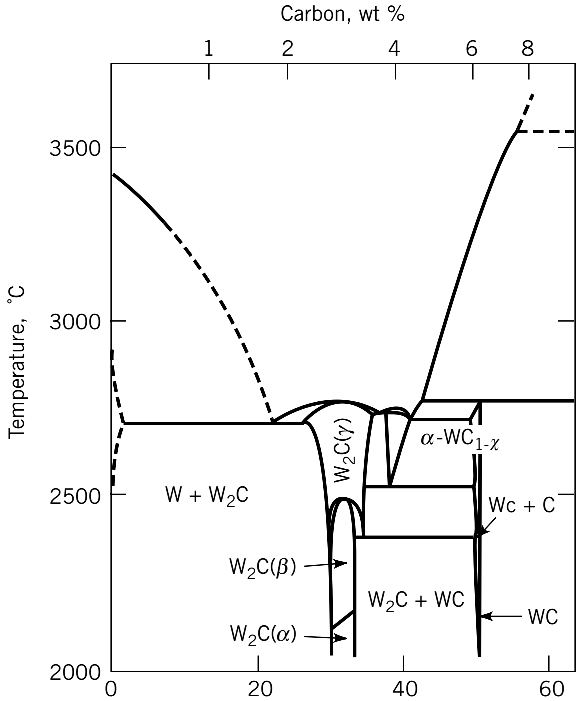

Fig. 1. Phase diagram for W–C.

fluid-bed carburizers, a chemical vapor reaction (CVR) process, fluid-bed gas carburization of dry-powder mixtures of cobalt and tungsten, and a continuous interconnected tungsten reduction and carburization complex. At the same time, enormous increases in the specific surface of WC powder, which must accompany reductions in particle size into the submicron ranges, introduce problems related to powder flow, compacting, sensitivity to adsorption of ambient gases, and other surface related behavior.

The P. M. McKenna aluminothermic process proceeds from tungsten–mineral concentrates, scheelite, wolframite or ferberite, or mixtures of them, to produce tungsten carbide crystals and crystal fragments ranging in size from ~840–44 μm. Macrocrystalline WC, as grown in a menstruum alloy, forms well-developed, angular crystals having a triangular habit. The crystals always contain a perfectly stoichiometric bound-carbon content and are monocrystalline. Both in initially coarse form, and after size-reduction by milling, macrocrystalline WC has comparatively low specific surface and is entirely free of W_2C. Powders are prepared over a wide range of particle sizes, from granular screen-sized ranges to micron-sized powders.

Both macrocrystalline WC and the fused WC–W_2C eutectic (Fig. 1) are important in the manufacture of diamond drill bits used in the mining, oil and gas, and construction industries, and in hardfacing rods and electrodes. The properties of WC are listed in Table 1.

Table 1. **Physical Properties of Primary Carbides**

Property	WC	TiC	TaC	NbC
mol wt	195.87	59.91	192.96	104.92
carbon, wt%	6.13	20.05	6.23	11.45
crystal structure	hex, Bh	fcc, B1	fcc, B1	fcc, B1
lattice constants, nm	$a = 0.29065$ $c = 0.28366$	0.43305	0.4454	0.4470
density, g/cm^3	15.7	4.93	14.48	7.78
mp, °C	2720	2940	3825	3613
microhardness, kg/mm^2	1200–2500	3000	1800	2000
modulus of elasticity, N/mm^2[a]	696,000	451,000	285,000	338,000
transverse rupture strength, N/mm^2[b]	550–600	240–400	350–450	300–400
coefficient of thermal expansion, K^{-1}	$a = 5.2 \times 10^{-6}$ $c = 7.3 \times 10^{-6}$	7.74×10^{-6}	6.29×10^{-6}	6.65×10^{-6}
thermal conductivity, W/(m · k)	121	21	22	14
heat of formation, $\Delta H_{f,\,298}$, kJ/mol[c]	−40.2	−183.4	−146.5	−140.7
specific heat, J/(mol ·)c	39.8	47.7	36.4	36.8
electrical resistivity, μΩ · cm	19	68	25	35
superconducting temperature, <K	1.28	1.15	9.7	11.1
Hall constant, cm^3/(A · s)	-21.8×10^{-4}	-15.0×10^{-4}	-1.1×10^{-4}	-1.3×10^{-4}
magnetic susceptibility	+10	+6.7	+9.3	+15.3

[a] Face-centered cubic = fcc and hexagonal = hex.

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

[c] To convert J to cal, divide by 4.184.

4. Titanium Carbide

On an industrial scale, TiC is produced most often through the reaction of TiO_2 with carbon black (see TITANIUM AND TITANIUM ALLOYS; TITANIUM COMPOUNDS).

In industrial production of titanium carbide, pure (99.8%, with minor impurities of Si, Fe, S, P, and alkalies) titanium oxide [13463-67-7] (TiO_2), in the dry or wet state is mixed in 68.5/31.5 ratio with carbon black or finely milled low ash graphite. The dry mixture is pressed into blocks that are heated in a horizontal or vertical carbon-tube furnace at 1900–2300°C; hydrogen that is free of oxygen and nitrogen serves as protective gas. In the vertical push-type furnaces, the liberated CO itself provides protection.

Titanium carbide is generally obtained in the form of gray, well-sintered lumps that are broken up in jaw-crushers and fine-milled in ball mills. Technical-grade TiC contains 0.5–1.5 wt% graphite, in addition to 0.5–1 wt% oxygen and nitrogen and 0.1 wt% impurities, such as Fe, Si, S, and P. The oxygen and nitrogen content may be reduced to 0.1–0.3 wt% by heating the impure carbides under high vacuum for several hours at 2000–2500°C, or less expensively, by formation of solid WC solutions, with or without the use of Mo_2C or Cr_3C_2.

Titanium carbide is also prepared by the menstruum method (6), starting with ferrotitanium (TiO_2), or titanium [7440-32-6] (Ti), metal. Comparatively low levels of oxygen and nitrogen, 0.1 and 0.3 wt%, respectively, are achieved without double processing because of strong outgassing under high temperature liquid menstruum alloy. Menstruum-made TiC strongly reflects the cubic crystal form, initially ranging in size from ~149 down through 44 μm. Among TiC produced by various processes, the combined carbon content of mestruum-process unmilled crystals at 19.7% (theoretical 20.05 wt%) is comparatively high, while free carbon content at 0.1 wt% is comparatively low. Oxygen content of TiC made by the carbothermic process is slightly higher than that for menstruum-made TiC, while free carbon at ~0.6 wt% is higher and combined carbon at 19.0 wt% minimum is lower. As is true with all of the major primary monocarbides and notably in the case of TiC, the closeness of combined carbon content to theoretical carbon content is a useful single-value surrogate indicator of purity and hardness. Properties of titanium carbide are listed in Table 1; the Ti–C phase diagram is shown in Figure 2.

The relatively high hardness and the cubic lattice of titanium carbide, the latter providing strong solvent power for forming solid solutions (mixed crystals) with WC (as well as with NbC and TaC), give it high importance in cemented carbide metal-cutting compositions. With WC as solute, TiC forms a continuous mixed-crystal series up to a maximum of ~25 TiC–75 WC wt%, which is a saturated end member sometimes called $WTiC_2$. In steel machining applications TiC imparts crater wear resistance, generally entering such compositions in the form of a WC–TiC mixed crystal rather than as TiC. As TiC added in any form to cemented carbide compositions decreases transverse rupture strength and thermal shock resistance, its use is generally limited to a maximum of ~10 wt%. After the advent of hard coatings, the modern cemented carbide substrates generally have a maximum of ~2 wt% TiC. Titanium carbide, together with titanium carbonitride, TiCN, are the dominant hard phases in uncoated

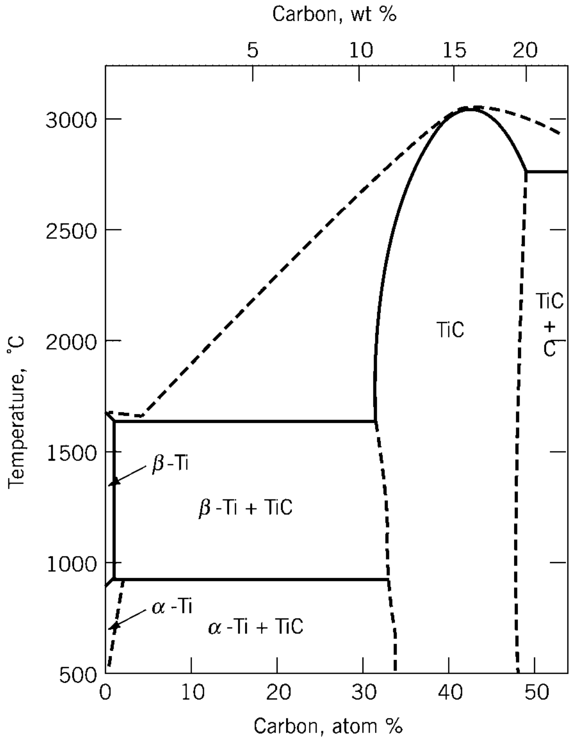

Fig. 2. Phase diagram for Ti–C.

cermet alloys, added for their high chemical stability in metalcutting tools and corrosion-resistant wear and heat-resistant parts.

5. Tantalum Carbide

On an industrial scale, TaC is prepared from tantalum [7440-25-7] (Ta) metal or tantalum hydride [12026-09-4], (Ta_2H, powder), tantalum pentoxide [1314-61-0], Ta_2O_5, high purity scrap obtained in the preparation of ductile Ta, or from ferrotantalum–niobium. The chemical and metallurgical industry produces refined Ta_2O_5 from tantalite mineral concentrate and sometimes from columbite mineral concentrate, and to a lesser extent from microlite mineral concentrate, the latter mineral from the higher tantalum end of the calcium tantalate–calcium niobate solid-solution comprising the microlite–pyrochlore solid-solution mineral series. Until the mid-1980s and the collapse in tin prices, accumulations of Ta- and Nb-containing slags from Southeast Asian tin smelters were a significant resource for Ta (and Nb) oxide recovery, however are now of little importance. The ores are decomposed and separated by fractional crystallization of the double fluorides, fractional distillation of the pentachlorides, or by solvent extraction of the HF-containing solutions. The metals are prepared mainly by alkali metal reduction or fusion electrolysis of the halides.

Tantalum carbide is produced by carburization of the element or the oxide with carbon, in a manner similar to the preparation of WC or TiC. Final carburization in a vacuum gives a golden yellow carbide, free of oxygen and nitrogen, that contains 6.1–6.3 wt% C and 0–0.2 wt% graphite.

The McKenna menstruum carburization process (7) for preparation of TaC parallels that for menstrum-made WC. The golden colored crystals produced have a specific gravity of ~14.2 and a bound-carbon content of 6.2–6.3 wt%. Starting material may be low niobium tantalite or microlite concentrates or high purity tantalum scrap. Low levels of niobium carbide in solid solution with TaC occur when tantalite is used and is of economic benefit, as NbC is widely used as a partial substitute for TaC in cemented carbide manufacture. The properties of TaC are given in Table 1; the Ta–C phase diagram is shown in Figure 3.

WC–TiC–Co grades originally developed for machining long-chip materials have been largely replaced by WC–TiC–TaC(NbC)–Co grades that show higher hot-hardness and better thermal-shock resistance. This, as well as the addition of small (0.5–2 wt%) quantities of TaC to straight WC–Co alloys to prevent grain growth, brought TaC to a position of importance (among the hard carbides), particularly in thermal shock resistant compositions for steel machining. The major area of tantalum metal consumption is electronic components, notably capacitors, and its uses are many and are growing.

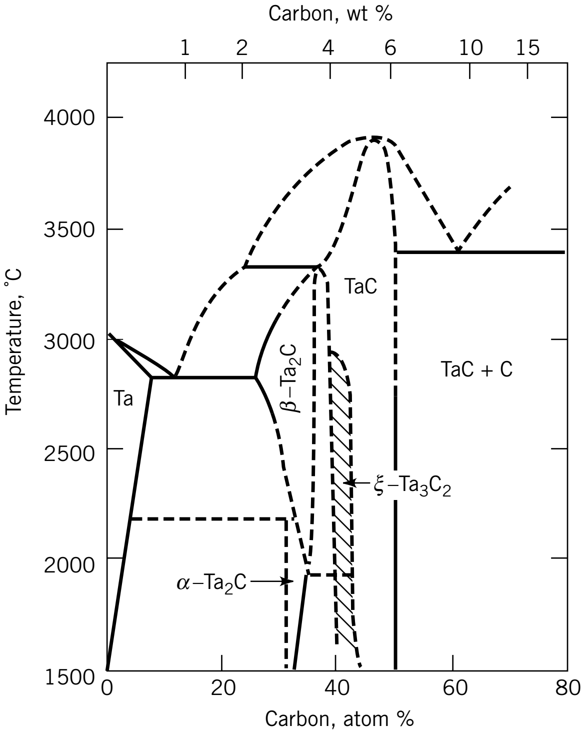

Fig. 3. Phase diagram for Ta–C.

6. Niobium Carbide

The preparation of niobium [7440-03-1], Nb, metal and niobium pentoxide [1313-96-8], Nb_2O_5, is very similar to that of tantalum (see NIOBIUM AND NIOBIUM COMPOUNDS). Niobium carbide is prepared most often by the carburization of Nb_2O_5 with carbon black, and less frequently by reaction of niobium and carbon. The preparation of NbC has special importance because it is used on an industrial scale as a reducing agent to prepare niobium metal. In this process, finely divided mixtures of Nb_2O_5 and carbon black are pressed into cylindrical blocks in large hydraulic presses and converted to NbC in high frequency furnaces in the presence of hydrogen or under vacuum at 1600–1800°C. The carbide may then be mixed with further quantities of the oxide in induction-heated vacuum furnaces and processed to technical-grade niobium metal containing 1–3 wt% O_2, 0.5–1 wt% free graphite.

The menstruum method for niobium carbide (7) may use mineral concentrates of columbite, a niobium-dominant member of the continuous mineral solid-solution series of iron–manganese niobate, or columbite, and iron–manganese tantalate, or tantalite. Since pure end members of the series are rare, the carbide made from columbite is a mixed crystal rich in NbC with low levels of TaC. The production of NbC essentially free of TaC may use ferroniobium as a starting material, of which large quantities are produced in Brazil from calcium niobate, i.e. the mineral pyrochlore, for the production of niobium steels. Pyrochlore lies at the niobium-rich end of a continuous mineral solid-solution series of calcium niobate, or pyrochlore, and calcium tantalate, or microlite. Mixed crystals of NbC carrying subordinate levels of TaC are used in steel-cutting compositions as partial replacements of TaC or TaC-rich TaC–NbC mixed crystals. Such partial replacements of TaC by NbC may result in savings in raw material costs as well as in prior chemical separation of Ta and Nb oxides.

7. Auxiliary Carbides

7.1. Chromium Carbide. Cr_3C_2, the chromium carbide having the highest carbon level, is used as an additive in the preparation of cobalt or nickel-cemented WC or TiC-based carbide alloys designed for corrosion-resistant applications (see CORROSION AND CORROSION CONTROL). Lower carbon forms, eg, chromium carbide (7:3) [12075-40-0], (Cr_7C_3), are not suitable for these purposes. However, Cr_3C_2 is unstable in cobalt or nickel cemented alloys, tending to react with binder metals to produce brittle binary carbides. Lower carbon chromium carbides, however, are useful in reducing binder attack in corrosive applications. Chromium carbide is also used in cemented alloys as a grain-growth inhibitor.

Chromium carbide can be best prepared from pure chromic oxide [1308-38-9], (Cr_2O_3) (see CHROMIUM COMPOUNDS). Compacts containing 74 wt% Cr_2O_3 and 26 wt% carbon black can be heated in carbon-tube furnaces at 1600°C in the presence of hydrogen, giving a carbide containing 13–13.3 wt% total C and 0.1–0.3 wt% free C.

Table 2. **Physical Properties of Auxiliary Carbides**

Property	Cr_3C_2	β-Mo_2C	η-MoC	VC	HfC	ZrC
mol wt	180.05	203.91	107.96	62.96	190.51	103.23
carbon, wt%	13.33	5.89	11.3	19.08	6.30	11.64
crystal structure[a]	rhom, $D5_{10}$	hex, L′3	hex, L′3	fcc, B1	fcc, B1	fcc, B1
lattice constants, nm	$a = 1.147$ $b = 0.554$ $c = 0.283$	$a = 0.3$ $c = 0.4734$	$a = 0.298$ $c = 0.281$	0.4165	0.4648	0.4698
density, g/cm^3	6.68	9.18	9.15	5.36	12.3	6.46
microhardness, kg/mm^2	1350	1500	2200	2900	2600	2700
modulus of elasticity, N/mm^2[b]	373,000	533,000		422,000	352,000	348,000
mp, °C	1810	2520	2600	2684	3820	3420
coefficient of thermal expansion, K^{-1}	10.3×10^{-6}	7.8×10^{-6}		7.2×10^{-6}	6.59×10^{-6}	6.73×10^{-6}
heat of formation $\Delta H_{f,\ 298}$, kJ/mol[c]	−94.2	−49		−124.8	−230.3	−196.8
specific heat, J/(mol · K)c	32.7	30.3		32.3	37.4	37.8
electrical resistivity, μΩ · cm	75	71		60	37	42
superconducting temperature, <K	<1.2	2.78		<1.2	<1.2	<1.2
Hall constant, $cm^3/(A \cdot s)$	-0.47×10^{-4}	-0.85×10^{-4}		-0.48×10^{-4}	-12.4×10^{-4}	-9.42×10^{-4}
magnetic susceptibility				+28	−25.2	−23

[a] rhom = rhombohedral, hex = hexagonal, fcc = face-centered cubic.

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

[c] To convert J to cal, divide by 4.184.

Chromium carbide is important in powder preparations designed for thermal spray applications of corrosion and wear-resistant coatings on tool and machine parts. Lower carbon carbides of chromium are important in hardfacing rods and electrodes for weld-applied overlays on machine wear surfaces. However, these carbides are usually formed *in situ* from Cr and C in the rod and not added as preformed carbides. The properties of Cr_3C_2 are listed in Table 2.

7.2. Molybdenum Carbide. Mo_2C can be prepared by the carburization of molybdenum trioxide [1313-27-5] (MoO_3), and molybdenum dioxide [18868-43-4] (MoO_2), with carbon black or, more conveniently, by the reaction of molybdenum [7439-98-7], Mo, powder (93.4 wt%) and carbon black or charcoal (~6.6 wt%) at 1350–1500°C, in the presence of hydrogen (see MOLYBDENUM AND MOLYBDENUM ALLOYS). The carbide formed contains 5.9–6.1 wt% total C and 0.05–0.25 wt% free C. The physical properties are listed in Table 2. There are two molybdenum carbides having higher carbon contents, ie, the cubic MoC_{1-x}, a high-temperature phase often described as Mo_3C_{2-x}, and the hexagonal η-molybdenum carbide [12011-97-1] (MoC), a low temperature phase. Both carbides tend to decompose to graphite and β-molybdenum carbide (2:1) [12069-89-5], (Mo_2C). The latter can be stabilized by W (8), N (9), or W + N (10) so that (Mo,W)C (11) or (Mo,W)(C,N) (10) mixed crystals are formed.

Ferromolybdenum additives to the menstruum method for the production of WC crystals stabilize molybdenum monocarbide, MoC, in a (W,Mo)C mixed crystal. In much the same manner, but with ferrotitanium additives to the menstruum process for TiC, MoC is stabilized in a (Ti,Mo)C mixed crystal. The lower carbon molybdenum carbide, Mo_2C, finds its chief use as an additive to nickel or Ni–Co bonded TiC and TiCN based cermet compositions. Mo_2C, unstable in Ni or Ni–Co binder, reacts with the carbide phase to increase the bond strength between the binder and carbide or carbonitride phases.

7.3. Vanadium Carbide. Vanadium pentoxide [1314-62-1] (V_2O_5), or vanadium trioxide [1314-34-7] (VO_3), are the most satisfactory oxides for the preparation of VC. Vanadium pentoxide is best prepared by igniting chemically pure ammonium vanadate [7803-55-6] (NH_4VO_3), in the presence of moist oxygen to avoid reaction with nitrogen; V_2O_3 is obtained by reduction of V_2O_5 with hydrogen (see VANADIUM COMPOUNDS).

Vanadium carbide is prepared by the reaction of the elements under vacuum. In this process V_2O_5 is reduced at a high temperature with calcium [7440-70-2] and the product is melted in an arc furnace in the presence of argon producing a 99.9% pure material. Vanadium powder of equal purity may be prepared by hydriding and crushing vanadium metal turnings. Vacuum carburization removes nitrogen and oxygen, which are generally present up to 0.5–1 wt% in carbides obtained from vanadium oxides. The properties of VC are given in Table 2.

Although VC is very hard, it is very brittle and has, therefore, been used only in special cemented carbides. For example, submicrometer straight WC–Co alloys are prepared using ~0.5 wt% VC as a grain–growth inhibitor. TiC–VC–Ni–Fe cemented carbides were used in Germany during World War II as tungsten carbide–cobalt-free cutting tool alloys. Small quantities of VC are sometimes used in TiCN–Ni based cermets.

7.4. Hafnium Carbide. The minerals, chiefly zircon, ie, zirconium silicate, and baddeleyite, ie, zirconium oxide, are the sole industrial resources of hafnium metal, a minor constituent of both minerals at a ratio of 1 part hafnium to ~50 parts zirconium. The carbide of hafnium is mutually miscible with the carbides of Zr and Ti, the metal's Group 4 (IVB) comembers. A similar solid-solution relationship between Zr and Hf applies in the mineral forms noted above, placing any possibility of mineral separation at the preliminary ore-dressing stage beyond reach. The need of pure zirconium [7440-67-7] for nuclear reactors prompted the large-scale separation of hafnium [7440-58-6] from zirconium. This in turn made sufficient quantities of hafnium dioxide [12055-23-1] (HfO_2), or Hf metal sponge available for production of HfC for use in cemented carbides (see HAFNIUM AND HAFNIUM COMPOUNDS).

Hafnium carbide can be prepared industrially from hydrided hafnium sponge at 1500–1700°C or from HfO_2 at 2000–2200°C by carburization in vacuum in the presence of hydrogen. The resulting carbide contains almost the theoretical quantity of carbon, 6.30 wt% C, of which a maximum of 0.1 wt% is unbound.

The properties of HfC are listed in Table 2. Addition of HfC as NbC–HfC or TaC–HfC solid solutions to WC–TiC–Co alloys has been shown to improve the hardness (12).

7.5. Zirconium Carbide. ZrC may be prepared by igniting a mixture of 78.8 wt% annealed zirconium oxide [1314-23-4] (ZrO_2) and 21.2 wt% charcoal under hydrogen in a graphite crucible in a carbon-tube furnace at 2400°C. The carbide obtained has the following composition: 11.3 wt% chemically bound C, traces of free C, 88.3 wt% Zr, and 0.3 wt% ($O_2 + N_2$). Alternatively, a pressed mixture of ZrO_2 and carbon black may be induction heated in a graphite crucible in the presence of H_2 at 1800°C, and then comminuted and annealed at 1700–1900°C, under vacuum, after addition of 1–2 wt% carbon black. The product contains 11.8 wt% C (~0.5 wt% free C).

The physical properties of ZrC are listed in Table 2. While zirconium carbide (the "red carbide"), as well as zirconium carbonitride, could effectively replace titanium carbide and carbonitride in steel-cutting compositions, their use in cemented carbides has so far not been wide.

7.6. Solid Solutions of the Major Hard Carbides. Essentially straight WC–Co alloys are of paramount importance in manufacturing industries for machining short-chipping materials, as well as for a host of tools and wear parts across a broad spectrum of industrial applications, including metalworking, metal and coal mining, transportation and construction industries. At the same time, the cubic carbides TiC, TaC, and NbC are relied upon to impart thermal stability and crater resistance to cemented carbide metalcutting tools, most effectively when added to metalcutting compositions as preformed solid solutions (mixed crystals). However, WC, among all carbides, supplies the preeminent platform for a wide variety of tools, owing to its superior bonding strength with cobalt and Co–Ni binders, its comparatively good fracture toughness among the carbides, and its superior thermal conductivity. However, WC is less refractory than the cubic carbides, additions of which, in the form of preformed solid solutions of preferred combinations, make up for the deficiency in machining applications that generate high tool tip temperatures. While the use of preformed solid solutions does not entirely replace random reactions between the carbides, which occur in any case during sintering, it greatly reduces dependence on *in-situ*, intercarbide reactions, thus carrying the desired intercarbide reactions closer to completion than would otherwise be the case.

Preformed solid solutions of the major carbides used for metalcutting applications fall mainly into two categories: those between the solute, WC, and one or more of the solvent cubic carbides, and a number of preferred combinations of two or more cubic carbides, without WC. The former case often prevails, as TiC, the strongest solute among the cubic carbides for WC, forms the most widely used solid solution series for steel machining applications, ranging mainly from WC–TiC 50:50 to WC–TiC 75:25. TaC–NbC mixed crystals are commonly preformed, as also TaC–NbC–TiC formulations to preferred rations, as well as WC–TiC–TaC(NbC), WC–TaC(NbC), and (W,Mo)CN. In addition to providing closer approaches to compositional equilibrium in the form of sintered carbides, these solid solutions carry the additional advantages over monocarbides of improved strength and hardness.

Solid solutions are produced by thermal diffusion of blends of the primary carbides, which themselves have been formed initially either by metal–carbon thermal diffusion or by reduction-diffusion reactions from pure oxides. In a third stage, the resulting preformed solid solution powders are then annealed in vacuum furnaces, with hydrogen, in order to attain acceptable levels of intercarbide reactions as well as to achieve low levels of residual (ie, unreacted or free) carbon, oxygen, and nitrogen. Low levels of cobalt or other binder metals are sometimes added to such preformed solid solution powders prior to annealing, as a means of promoting the diffusion of residual carbon and of lowering oxygen and nitrogen.

Alternatively, preformed carbide solid solutions produced by the menstruum method proceed directly from blends of mineral concentrates, or from ferroalloys or from blends of these, to macrocrystalline mixed crystals. By this method, blends of mineral concentrates containing natural association of Ta and Nb oxides with usually minor Ti, and, if WC is desired in the crystal, tungsten mineral concentrates, are the precursor materials, without prior chemical separation of the primary metal oxides or the subsequent formation of separate monocarbides. The same general procedure applies to the production of members of the TiC–WC solid solution series, in which high-temperature menstruum melts provide complete solid solutioning and low levels of oxygen, nitrogen, and residual free carbon in a single operation. Precursor materials for the menstruum-made WC–TiC solid solution series may be blends of tungsten mineral concentrates and rutile (TiO_2) mineral concentrates. Carbide solid solutions of metals in Groups 4 (IVB), 5 (VB), and 6 (VIB) are thus produced by both the thermal diffusion and menstruum methods.

Carbonitride solid solutioning is illustrated by TiC–cermet history. Cermet metalcutting tools and corrosion-resistant components were for some years based on Ni-bonded TiC, strengthened by additions of Mo, either as metal powder or as molybdenum carbide, Mo_2C, which during sintering reacted with TiC to form Ti(Mo)C at the surfaces of TiC crystals, thereby strengthening the TiC–Ni bond. Subsequent development of titanium nitride, TiN, led to both partial and total replacement of TiC by Ti(C,N), reinforced by additions of Mo_2C, which yielded a sintered microstructural refinement and high hardness, attributed both to nitrogen and solid solutioning effects. Wider use of cermets followed Ti carbonitride developments. Production is by diffusion annealing of TiC and TiN in vacuum furnaces or by vacuum heating of TiC and Ti with nitrogen.

Carburization. Metal oxide mixtures with carbon black having additives such as Co, Ni, Fe, or Cr(0.5–1%) to promote diffusion, may undergo carburization.

$$WO_3 + TiO_2 + C \xrightarrow[H_2,CO]{1600-1800^\circ C} (W,Ti)C + CO$$

$$WO_3 + TiO_2 + Ta_2O_5 + C \xrightarrow[H_2]{1600-1800^\circ C} (W,Ti,Ta)C + CO$$

$$MoO_3 + WO_3 + C + (Fe,Ni,Co) \xrightarrow[H_2,CO,CH_4]{1000-1200^\circ C} (Mo,W)C + CO + (Fe,Ni,Co)$$

Metal powder mixtures with carbon black may also undergo carburization.

$$W + Ta + C \xrightarrow[H_2,vacuum]{1500-1600^\circ C} (W,Ta)C$$

$$Hf + Ta + C \xrightarrow[H_2,vacuum]{1600-1800^\circ C} (Hf,Ti)C$$

Diffusion Annealing. Mixed preformed carbides can be diffusion annealed at temperatures giving solid solutions. Additives, such as Co, Ni, Fe, or Cr (0.5–1%) promote diffusion.

$$WC + TiC \xrightarrow[H_2,vacuum]{1600-1900^\circ C} (W,Ti)C$$

$$WC + TiC + TaC(NbC) \xrightarrow[H_2,vacuum]{1600-1800^\circ C} (W,Ti,Ta,Nb)C$$

$$HfC + TiC + WC \xrightarrow[H_2,vacuum]{1600-1900^\circ C} (Hf,Ti,W)C$$

$$TiN + TiC \xrightarrow[vacuum]{1600-1800^\circ C} Ti(C,N)$$

Menstruum Carburization. Mineral concentrates, ferroalloys, primary metals, or high purity scrap may also be carburized (13).

$$Fe(Mn)WO_4 + TiO_2 + Fe + C \xrightarrow{2300-2600^\circ C} (W,Ti)C + Fe(Mn) + Fe + CO + C$$

$$WFe + TiFe + C \xrightarrow{2300-2600^\circ C} (W,Ti)C + Fe + C$$

$$(Fe,Mn)(Ta,Nb)_2O_6 + Fe + C \xrightarrow{2300-2600^\circ C} (Ta,Nb)C + Fe(Mn) + Fe + CO + C$$

The monocarbides of Groups 4 (IVB) and 5 (VB) metals are completely miscible except for ZrC–VC and HfC–VC (Fig. 4). At 1400–1500°C, WC is soluble in the carbides of Groups 4 (IVB) and 5 (VB) 25–60 wt%, and at higher (1800–2400°C) temperatures even up to 90 wt% (14,15). WC itself, like the other

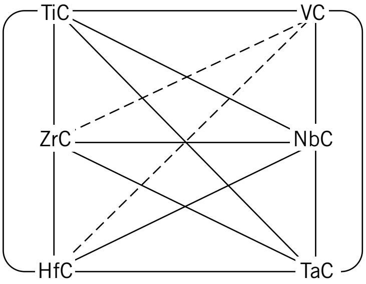

Fig. 4. Schematic illustrating the solid solubility between carbides. Solid line = complete solubility; dashed line = limited solubility.

carbides of Group 6 (VIB), has practically no solubility for face-centered cubic (fcc) carbides. The cubic solid solutions, which are saturated at higher temperatures and contain a high percentage of WC, are very stable. The hexagonal WC forms complete series of solid solutions with the hexagonal MoC.

The pseudoternary system WC–TiC–TaC is especially important in the metallurgy of cemented carbides (16). Figure 5 shows the phase distribution and thus the solubility ratios at 1450°C, which is the typical cemented carbide sintering temperature; at 2200°C, which is the preferred temperature for the formation of pure solid solutions having high WC content; and at 2500°C showing a hypothetical curve, maximum solubility. It is obvious that TiC is a better solvent for WC than TaC, ie, TaC additives in ternary solid solutions reduce the solubility for WC. The more spherical TiC–TaC–WC solid-solution grains can be readily distinguished from the angular WC in the microstructure.

7.7. Carbides of the Actinides, Uranium, and Thorium. The carbides of uranium and thorium are used as nuclear fuels and breeder materials for gas-cooled, graphite-moderated reactors (see NUCLEAR REACTORS). The actinide

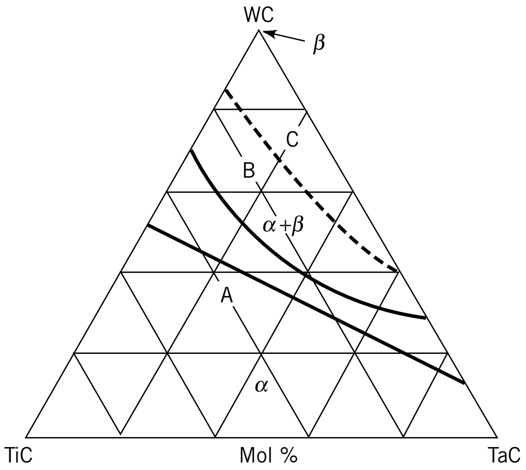

Fig. 5. Phase distribution in the system WC–TiC–TaC at A, 1450°C; B, 2200°C; and C, 2500°C. Dashed line = hypothetical solubility; solid line = experimental solubility.

Table 3. **Physical Properties of Uranium and Thorium Carbides**

Property	UC	UC_2	ThC	ThC_2
mol wt	250.08	262.09	244.06	256.07
carbon, wt%	4.8	9.16	4.92	9.37
crystal structure[a]	fcc, B1	tetr, C11a	fcc, B1	mon
lattice constants, nm	0.49597	$a = 0.3524$ $c = 0.5996$	0.5346	$a = 0.6691$ $b = 0.4231$ $c = 0.6744$
$\beta = 103°50'$				
density, g/cm^3	13.63	11.86	10.64	8.65
microhardness, kg/mm^2	920	620	850	600
mp, °C	2560	ca 2500	2625	2655
heat of formation, $\Delta H_{f,298}$, kJ/mol[b]	−97.1	−96.3	−29.3	−125.2
specific heat, J/(mol · K)[b]	50.2	58.6		
electrical resistivity, μΩ · cm	40	90	25	30
magnetic susceptibility	+3.15	+3.40		

[a] tetr = tetragonal; mon = monoclinic cubic.
[b] To convert J to cal, divide by 4.184.

carbides are prepared by the reaction of metal or metal hydride powders with carbon or preferably by the reduction of the oxides uranium dioxide [1344-57-6] (UO_2), triuranium octaoxide [1344-59-8] (U_3O_8), or thorium dioxide [1314-20-1] (ThO_2) at 1800–2200°C in carbon-tube furnaces in the presence of hydrogen or in vacuum furnaces. Hot pressing and arc melting are very suitable methods for the preparation of homogeneous compacts, especially if followed by heat treatment in a tungsten-tube furnace in the presence of argon.

The properties of the uranium carbide [12070-09-6] (UC), uranium carbide (1:2) [12071-33-9], thorium carbide [12012-16-7] (ThC), and thorium carbide (1:2) [12071-31-7] (ThC_2), are given in Table 3; the phase diagram for the system U–C is shown in Figure 6. Coefficient of thermal expansion for UC is $9.1 \times 10^{-6} K^{-1}$, and its thermal conductivity is 25 W/(m · K).

Uranium carbide (UC) is comparatively stable whereas UC_2, especially in powder form, hydrolyzes rapidly in moist air. The latter is used in the form of pellets or annealed spherical particles, coated with pyrographite, as a nuclear fuel for high temperature reactors. For breeder reactors using thorium [7440-29-1], it should be noted that UC and ThC form a continuous series of solid solutions, whereas UC_2 and ThC_2 have limited mutual solubility. Furthermore, UC can be stabilized with regard to its carbon content, even at high temperatures, by the formation of solid solutions with ZrC, HfC, NbC, or TaC so that no higher carbides are formed (17). Uranium carbides and plutonium carbides show a high degree of mutual miscibility (see ACTINIDES AND TRANSACTINIDES).

7.8. Carbides of the Iron Group Metals. The carbides of iron, nickel, cobalt, and manganese have lower melting points, lower hardness, and different structures than the hard metallic materials. Nonetheless, these carbides, particularly iron carbide and the double carbides with other transition metals, are of great technical importance as hardening components of alloy steels and cast iron.

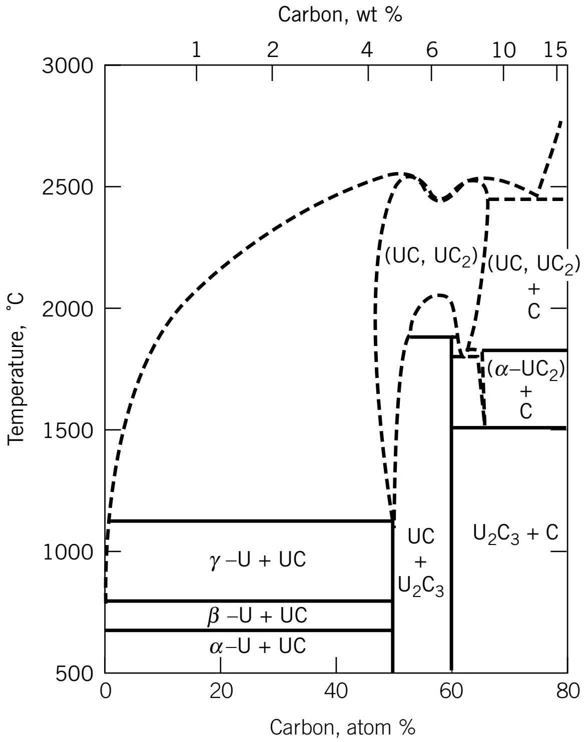

Fig. 6. Phase diagram for U–C.

The iron–carbon system contains the orthorhombic iron carbide (3:1) [12011-67-5] (Fe_3C), which melts congruently and represents the cementite in steel metallurgy. The existence of other carbides, eg, iron carbide (2:1) [12011-66-4] (Fe_2C), iron carbide (5:2) [12127-45-6] (Fe_5C_2), and iron carbide (7:3) [12075-42-2] (Fe_7C_3), are doubtful (see STEEL).

Iron carbide (3:1) (Fe_3C); mol wt 179.56; carbon 6.69 wt%; density 7.64 g/cm^3; mp 1650°C; is obtained from high carbon iron melts as a dark gray air-sensitive powder by anodic isolation with hydrochloric acid. In the microstructure of steels, cementite appears in the form of etch-resistant grain borders, needles, or lamellae. Fe_3C powder cannot be sintered with binder metals to produce cemented carbides because Fe_3C reacts with the binder phase. The hard components in alloy steels, such as chromium steels, are double carbides of the formulas $(Cr,Fe)_{23}C_6$, $(Fe,Cr)_7C_3$, or $(Fe,Cr)_3C_2$, that derive from the binary chromium carbides, and can also contain tungsten or molybdenum. These double carbides are related to η-carbides, ternary compounds of the general formula $M_3M'_3C$ where $M =$ iron metal; $M' =$ refractory transition metal.

The complex iron carbonitride is the hard component in steels that have been annealed with ammonia (nitrided steels). Complex carbonitrides with iron metals are also present in superalloys in the form of precipitates.

In the nickel–carbon and cobalt–carbon systems, the nickel carbide (3:1) [12012-02-1] (Ni_3C) and cobalt carbide (3:1) [12011-59-5] (Co_3C) are isomorphous with Fe_3C and exist only at low temperatures. The manganese–carbon system contains manganese carbide (3:1) [12121-90-3] (Mn_3C), isomorphous with Fe_3C, and manganese carbide (23:6) [12266-65-8] ($Mn_{23}C_6$), isomorphous with chromium carbide (23:6) [12105-81-6] ($Cr_{23}C_6$). These binary carbides occur frequently in the form of carbide solid solutions or double carbides with other transition metals in alloy steels, superalloys, and special hard metals.

7.9. Complex Carbides. Complex carbides are ternary or quaternary intermetallic phases containing carbon and two or more metals. One metal can be a refractory transition metal; the second may be a metal from the iron or A groups. Nonmetals can also be incorporated.

Complex carbides are very numerous. Many newer compounds of this class have been discovered and their structures elucidated (18). The octahedron M_6C is typical where the metals arrange around a central carbon atom. The octahedra may be connected via corners, edges, or faces. Trigonal prismatic polyhedra also occur. Defining T as transition metal and M as metal or main group nonmetal, the complex carbides can be classified as: (*1*) T_3M_2C, which has a filled β-manganese structure, eg, Mo_3Al_2C, W_3Re_2C; (*2*) T_2MC, *H*-phases, eg, Cr_2AlC, Ta_2GaC, Ti_2SC; (*3*) T_3MC, perovskite carbides which have the filled Cu_3Au-structure, eg, Ti_3AlC, VRu_3C, URh_3C; (*4*) T_3M_3C, T_2M_4C, η-carbides that have the filled Ti2Ni structure, eg, Co_3W_3C, Ni_2Mo_4C; and (*5*) κ-carbides, eg, $W_9Co_3C_4$, $Mo_{12}Cu_3Al_{11}C_6$.

The preferred method for synthesis of complex carbides is the powder metallurgy technique. Hot-pressed powder mixtures must be subjected to prolonged annealing treatments. If low melting or volatile components are present, autoclaves are used.

The η-carbides are not specifically synthesized, but are of technical importance, occurring in alloy steels, stellites, or as embrittling phases in cemented carbides. Other complex carbides in the form of precipitates may form in multicomponent alloys or in high temperature reactor fuels by reaction between the fission products and the moderator graphite, ie, pyrographite-coated fuel kernels.

8. Quality Control Methods for Primary Carbides

Analytical control of primary hard carbides for cemented carbides is normally done on a production-lot basis, with powder samples of uniformly blended lots being issued routinely to control laboratories, which, among major carbide producers commonly have widely diverse analytical capabilities, while more numerous smaller carbide producers rely on independent laboratories. The rapid growth of semi-automatic analytical equipment over the past decades has resulted in large cost savings as well as faster delivery of results.

At the primary carbide stage, control of WC and the principal cubic carbides, TiC, TaC, and NbC, as well as the solid solutions of these, accounts for the bulk of control-lab volume. Combined carbon, among all determinations being the most indicative of purity and hardness, is determined by automated combustion with oxygen and the measurement of resultant CO_2 by infrared detection or by thermal conductivity, as typified by the Leco apparatus. Free (or residual) carbon is determined by decomposition in HNO_3–HF and subsequent filtration to separate carbon. Average particle size is also routine, for which a common method is measurement of air flow through a compacted powder bed, as typified by the Fisher Sub-Sieve particle size analyzer. In the case of submicron or ultrafine WC powder, particle size measurement is based on a determination of the surface area of the powder sample as measured by the volume of gas absorbed under liquid nitrogen and subsequently desorbed, which is then converted to particle size. As in the case of combined carbon, specific gravity is a fundamental indicator of purity among the major hard-metal monocarbides, although unlike the carbon analysis this determination may enter the picture mainly in combination with other tests. For average particle sizes exceeding $\sim 2\ \mu m$, the pycnometer method with sample in water is used for specific gravity determination. For submicron or ultrafine WC powders, a problem of thorough wetting of very high surface area powders is met by the use of a helium pycnometer, replacing water with helium. The primary solid-solution carbides are of course subject to all of the tests noted above, and are also analyzed by X-ray diffraction for composition and purity.

The abrasive nature of carbide powders carries a potential for low-level, accumulative pick up of impurity metals during contact with processing equipment, notably when powders are in the coarser, primary form. This effect is lessened by a selection of special alloys for critical machine components, accumulations of which are of least effect on ultimate properties, eg, the use of cemented tungsten carbide parts for selected crushing and milling machinery components, as well as of high-hardness ferrous alloys elsewhere. Given normalized acceptable pick-up levels, analyses for selected iron-group metals as well as other metals may be made at intervals, relying on the atomic absorption method for trace metals, inductively coupled plasma method for trace and compositional levels, and on X-ray fluorescence for higher concentrations (19).

Also in the important but nonroutine analytical category, surface examinations may be made of samples in either powder form or in diamond-polished, cemented-alloy form at high magnifications by scanning electron microscope. Such observations include crystal or particle forms, particle surface condition, degree of particle attachment, and particle or crystal size ranges. Qualitative determinations by X-ray line scans may also be made across selected phase areas in polished samples. Observations on a coaser basis are also made by binocular microscope.

9. Economic Aspects

Three categories of metallurgical refining support manufacturers of cemented carbides. The first involves extraction from ore concentrates of tungsten minerals to produce tungstic oxide, WO_3, or ammonium paratungstate (APT), and the extraction from ore concentrates of Ti, Ta, and Nb minerals to produce refined oxides of titanium, tantalum, or niobium. The second step converts WO_3, APT, and oxides of titanium, tantalum, and niobium to the respective primary carbides or solid solutions of these metals. A third category of refining combines the first two steps to convert mineral concentrates of these metals directly into primary carbides. These refining categories also apply in general to the production of the auxiliary carbides.

Some refining, traditionally the conversion of the metal oxides to carbides, is carried out by the cemented carbide manufacturers themselves, chiefly by larger, more vertically integrated companies, while smaller cemented carbide manufacturers obtain their supplies either from independent refiners specializing in primary metal powders, carbides, nitrides, carbonitrides, and many lower volume accessory materials used in cemented carbide production or from the more integrated cemented carbide manufacturers. Consolidation within the cemented carbide industry is however an important ongoing evolution, one aspect of which is growth in cross-supply arrangements between larger companies of primary carbides and other precursor materials, in a mutual search for cost savings.

Recently, many of the advances in the preparation of primary carbides have favored metalcutting and metalworking components in the manufacturing industries rather than the resource industries, eg, the mining and processing of coal and hard minerals, exploration for and development of oil and gas fields, and agriculture. That unalloyed WC has been virtually the sole carbide used in these latter fields suggests that great tool opportunities may yet lie ahead in these fields. For metalcutting and metalworking fields, an ongoing development of production methods for carbides and carbonitrides in the form of chemical vapor- and physical vapor-deposited coatings on cemented carbide tool components stand out as a major leap forward for the cemented carbide tool industry, increasing productivity and profitability. A further important advance in carbide metallurgy has been seen in the development of submicron and ultrafine WC powders, which, in cemented carbide form, reach combinations of high strength and high hardness. Ongoing developments have motivated new independent enterprises specializing in this field, thus creating a potential for a new line of independent suppliers to the industry.

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