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Structural Chemistry of Complex Carbides and Related Compounds*

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Complex carbides formed in ternary systems of a transition element (M), a B-group element (M'), and carbon and having a formula $M_2M'C$ (H-phase) or $M_3M'C$ (perovskite carbide) occur frequently. This reflects the simple geometry of the atomic arrangement of the metals and the filling mode by an interstitial stabilizer such as carbon or nitrogen. The phase relationship of the ternary combinations {Ti, Zr, Hf, V, Nb, Ta, Cr, Mn, and Ni}–aluminum–carbon was investigated. New complex carbides were found with the corresponding zirconium, hafnium, and tantalum combinations. The crystal structures in the case of Zr- and Hf-containing complex carbides can be characterized by a twelve-metal-layer sequence and by a ten-metal-layer sequence with carbon atoms again filling octahedral voids. The transition of structure types from TiC, Ti_2AlC, Ti_3SiC_2, $ZrAlC_2$, $Zr_2Al_3C_5$, to Al_4C_3 is also discussed.

Introduction

The structural chemistry of complex carbides and related compounds is governed to a wide extent by building groups such as [M_6C] (M = transition metal, C = carbon or another small nonmetal atom), octahedra, and triangular prisms, just as it is in the case of many binary transition metal carbides (*1*). Interestingly there are some structure types which combine both these building elements, such as the filled Re_3B type (*2*) or the κ-carbide type (*3*).

This paper mainly concentrates on these atomic arrangements. It was assumed for a long time that the accommodation of interstices (particularly carbon) was easier in triangular prisms rather than within octahedra, despite higher symmetry, making the metal prism more flexible. Similarly, as one can observe with binary transition metal carbides, extended defect structures may occur; that is, nonstoichiometry prevails. Occupancy and type of ordering or partial ordering cannot always be determined by X-ray diffraction experiments, which is sometimes also true for binary carbides containing heavy metal atoms. Thus neutron or electron diffraction methods have to be applied in order to locate unambiguously the atomic parameters for carbon or another interstitial nonmetal atom. In this way, subcarbides of transition metals, for example, have been investigated (*4*). In the meantime, a compilation by Holleck (*5*) concerning binary and ternary carbides and nitrides of transition elements and their phase relations appeared, which also covers the interstitial compounds of refractory metals. About 350 ternary carbide and nitride systems are represented in a fairly detailed manner.

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* Dedicated to Professor A. F. Wells on his 70th birthday.

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The Carbide $(V,Cr)_3C_{2-x}$

The occurrence of this complex carbide was reported in 1965 (*7*) when the formula VCr_2C_2 was proposed and the crystal structure was recognized to be of the filled Re_3B structure type. Representatives of this type occur widely. Considering VC_{1-x} as having carbon in octahedral voids and Cr_3C_2 with carbon in triangular prisms, VCr_2C_2 constitutes a fairly perfect topological sum of the binary carbides (Fig. 1). However, there was no differentiation with respect to ordering and occupancy of the carbon sites possible, although it was assumed that the vanadium octahedra would easier accommodate carbon because of the more favorable ratio r_C/r_M. Results of neutron diffraction investigations (*6*) confirm by and large the previous findings (*7, 8*) concerning structure type and atomic parameters (Table 1). A considerable improvement was achieved inasfar as the 4*c* site of vanadium was shown to be equally shared by vanadium and chromium (ratio about 1 : 1) and the 8*f* site for chromium was shared by some vanadium (ratio about 3 : 1). Furthermore, the occupancy of the vanadium-rich octahedral voids has been found to be 69%, while the chromium-rich triangular voids are occupied by 75% carbon. Almost single phase samples were obtained from a composition of 20.5 at% V, 42.0 at% Cr, and 37.5 at% C. Only a minor trace of Cr_7C_3 was present, for which the neutron diffraction profile has been corrected. From the obtained data the formula

$$(V_{0.46}Cr_{0.54})(V_{0.22}Cr_{0.78})_2C_{0.75}C_{0.69}$$

can be derived. The distance M–C in the octahedral voids of 2.00 Å is somewhat smaller than that in the surrounding triangular prismatic (2.20 Å). In this context it should be noted that in the metal parent structure of $Re_3B\square$ ($\square$ = void), boron atoms occupy fully the larger prismatic holes while the octahedra are empty. As was recently shown (*9*), the corresponding ordered Re_3B-type structure occurs, e.g., with $TaCo_2B$, where the metal atoms are ordered on (4*d*) and (8*f*) sites. Accordingly, the complex carbide $(V,Cr)_3C_{2-x}$ fits with regard to the metal ordering between the Re_3B- and the $TaCo_2B$-type structures. The linking of the octahedra and the triangular prisms for the ordered type is shown in Fig. 2. For the chromium borocarbide of the approximative formula Cr_7BC_4 (*10*), it was assumed that boron and some carbon filled the triangular prisms, leaving most of the carbon in the octahedral voids.

TABLE 1

CRYSTALLOGRAPHIC DATA FOR $(V_{0.46}Cr_{0.54})(V_{0.22}Cr_{0.78})_2C_{1.44}$, FILLED Re_3B-TYPE STRUCTURE, SPACE GROUP: *Cmcm* (No. 63): $a = 0.2876(1)$, $b = 0.9310(22)$, $c = 0.6987(7)$ nm

Atom	Site	*x*	*y*	*z*	*B* (10^2 nm^2)
Neutron diffraction data, $\lambda = 0.12$ nm $R_1 = 0.06$, $R_2 = 0.12$, $R_3 = 0.13$					
0.46V + 0.54Cr	4*c*	0	0.407(1)	$\frac{1}{4}$	0.19
0.22V + 0.78Cr	8*f*	0	0.144(1)	0.070(1)	0.12
0.75C	4*c*	0	0.7571(4)	$\frac{1}{4}$	0.30
0.69C	4*b*	0	0.5	0	0.17
X-Ray powder data (after P. Ettmayer *et al.*, 1966)					
V	4*c*	0	0.400	$\frac{1}{4}$	
Cr	8*f*	0	0.140	0.070	
C	4*c*	0	0.740	$\frac{1}{4}$	
C	4*b*	0	0.5	0	

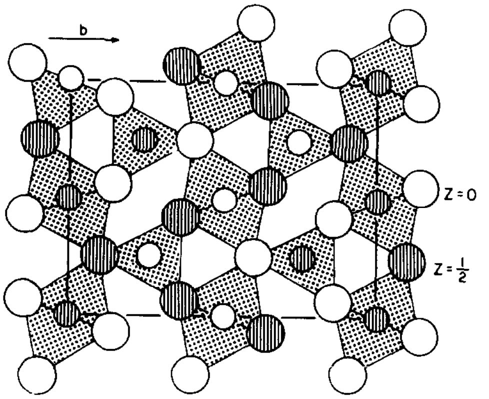

FIG. 1. Crystal structure of Re_3B (after W. B. Pearson). Large circles: metal atoms: small circles: nonmetal atoms.

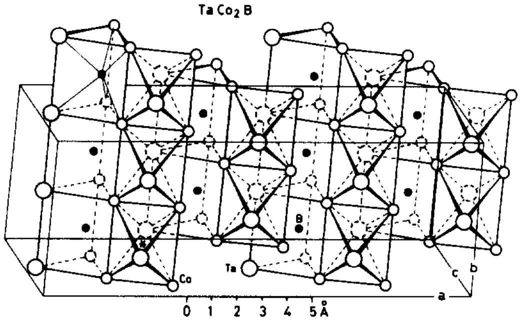

FIG. 2. Crystal structure of TaCo$_2$B (ordered Re$_3$B-type super structure).

The existence of a borocarbide of composition close to "Cr$_7$BC$_4$" was confirmed by Steurer (*11*), who also determined its region of stability to be within 1550 and 1710°C. A recent neutron powder diffraction study (Table 2) showed that carbon atoms fill the smaller octahedral voids (occupancy 85%), sharing the 4*c* site at the centers of triangular prisms with boron atoms. A more precise formula is $Cr_3(B_{0.44}C_{0.56})C_{0.85}$. A neutron powder diffraction investigation of another isotypic interstitial phase, namely, $Cr_3(C,N)_2$ (Table 3), revealed a statistical occupation of carbon and nitrogen atoms in octahedral sites but full occupation of carbons within the larger triangular chromium prisms: $Cr_3C(C_{0.52}N_{0.48})$. Thus for all these isotypic interstitial phases $(V,Cr)_3C_{2-x}$, $Cr_3(B,C)_2)Cr_3(C,N)_2$ the neutron diffraction experiments confirmed the earlier assumption (*7*, *8*) made from arguments of structural chemistry that the smaller nonmetal atoms are filling the octahedral voids.

It is well known from various examples that filling of voids by interstitials depends on the size of the metal atoms forming the parent lattice. Thus the nature of interstitials may vary considerably. This occurs with the suboxide phases {Zr,Hf}$_3${Fe, Co,Ni}O which also crystallize with the filled Re$_3$B-type structure (*12*, *13*). The iron metal elements, small in size compared to zirconium or hafnium, act here as interstitial fillers of the triangular prisms; oxygen

TABLE 2

CRYSTALLOGRAPHIC DATA FOR $Cr_3(B_{0.44}C_{0.56}C_{0.85}$, SPACE GROUP *Cmcm*. D_{2h}^{17} (NO. 63); FILLED Re$_3$B-TYPE LATTICE PARAMETERS: $a = 0.2857(1)$, $b = 0.9233(11)$, $c = 0.6967(5)$ nm, $V = 0.1838(3)$ nm3

Atom	Site	*x*	*y*	*z*	Occupancy	*B* (10^2 nm^2)
			Neutron diffraction data (Ref. *33*)			
Cr1	8*f*	0	0.1422(7)	0.0715(6)	1.00	0.43
Cr2	4*c*	0	0.4067(9)	$\frac{1}{4}$	1.00	0.70
C B	4*c*	0	0.7563(5)	$\frac{1}{4}$	0.44 0.56	0.49
C	4*b*	0.5	0	0	0.85	0.19
Residual value $R_n = 0.07$						
			X-Ray powder data (Ref. *10*)^a			
Cr1	8*f*	0	0.142	0.069		
Cr2	4*c*	0	0.406	$\frac{1}{4}$		
(B,C)	4*c*	0	0.755	$\frac{1}{4}$		
(B,C)	4*b*	$\frac{1}{2}$	0	0		
Residual value: $R_x^{(F0kl)} = 0.08$						

Note. The standard deviations are given in parentheses; individual isotropic temperature factors are expressed as $T = \exp\{-0.25.10^{-2}B(\sin\theta/\lambda^2)\}$; $\lambda = 0.120$ nm.

^{a} Lattice parameters: $a = 0.2870(2)$, $b = 0.9260(5)$, $c = 0.6982(5)$ nm, $V = 0.1855$ nm^3, $D_m = 6.30$ kg/dm^3.

TABLE 3

CRYSTALLOGRAPHIC DATA FOR Cr_3C ($C_{0.52}N_{0.48}$), SPACE GROUP *Cmcm*, D^{17}_{2h} (No. 63); FILLED Re_3B-TYPE, LATTICE PARAMETERS: a = 0.2833(1), b = 0.9249(27), c = 0.6937(5) nm, V = 0.1818(5) nm^3

Atom	Site	x	y	z	occ.	B (10^2 nm^2)
Neutron diffraction data (Ref. *33*)						
Cr1	8*f*	0	0.1428(7)	0.0728(6)	1.00	0.04
Cr2	4*c*	0	0.4078(9)	$\frac{1}{4}$	1.00	0.32
C	4*c*	0	0.7559(5)	$\frac{1}{4}$	1.00	0.47
C N	4*b*	$\frac{1}{2}$	0	0	0.52(2) 0.48(2)	0.96
Residual value R_1 = 0.057, R_2 = 0.128, R_3 = 0.150						
X-Ray powder data (Ref. *8*)[a]						
Cr1	8*f*	0	0.140	0.07		
Cr2	4*c*	0	0.400	$\frac{1}{4}$		
(C,N)	4*c*	0	0.740	$\frac{1}{4}$		
(C,N)	4*b*	$\frac{1}{2}$	0	0		

Note. The standard deviations are given in parentheses; individual isotropic temperature factors are expressed as $T = \exp\{-0.25.10^{-2}B(\sin\theta/\lambda)^2\}$; λ_n = 0.120 nm.

[a] Lattice parameters: a = 0.284, b = 0.925, c = 0.695 nm, V = 0.1825 nm^3.

as a "true" interstitial atom in the metallic state occupies the octahedral holes, but very likely not completely filling them. In the above-mentioned case there is no problem in determining the occupancy of the triangular prismatic holes by X-ray diffraction, which then makes the filling of the octahedral voids by oxygen obvious.

κ(Kappa) Carbides and Oxides

At this point another class of complex oxides such as $Zr_9Os_4O_3$ and $Hf_9Os_4O_3$ can be discussed (*14*). They crystallize with κ-carbide structure type, which occurs with borides, carbides, and oxides, but obviously not with nitrides (Table 4). The κ-carbide structure is illustrated in Fig. 3, from which the octahedral and triangular voids are immediately visible. Because of the *c*/*a* ratio, which is always close to 1, the array and subsequently the holes are fairly regular. In contrast to the first assumption, where carbon is to fill in octahedral and triangular prismatic holes (*15*), it is more likely that the carbon is only filling the octahedra because the other type of voids appeared to be too large for accommodation of carbon atoms (*3*). The following occupancy and metal ordering was proposed: (12*k*) and (6*h*) for the tungsten atoms, and random metal mixture on (2*a*) and another (6*h*) site for cobalt (*3*). This suggestion was later essentially confirmed by neutron diffraction (*16*); however, there was a hint for a fractional occupation of the triangular voids. In a more general way the κ-phases were considered a result of filling or partial filling of the octahedral, triangular prismatic, and icosahedral voids of a parent structure $M_9M'_3$ (*17*).

Among complex carbides and nitrides two classes occur, namely, confining to ternary systems, M–M'–C(N), where M and M' are both transition metals, or M' is a metametal, such as aluminum or a nonmetal. $W_{2-x}Re_xC_{1-x}$ solid solutions between W_2C and Re-metal (*18*) belong to the one type, the H-phase Ti_2AlC to the other. But there are complex carbides such as perovskite carbides, η-carbides, etc., where M' is either another transition metal or a metametal.

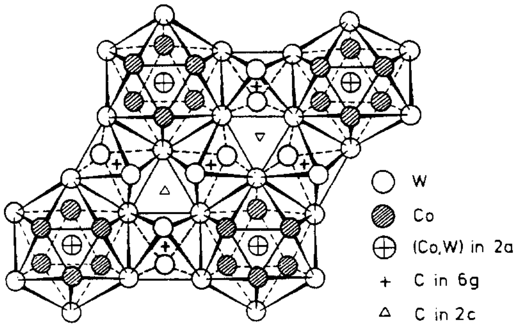

FIG. 3. Crystal structure of $W_9Co_3C_3$ (κ-carbide) (*16*).

TABLE 4

κ-PHASES (BORIDES, CARBIDES, OXIDES, METALLIDES)

	a (Å)	*c* (Å)	*c*/*a*		*a* (Å)	*c* (Å)	
Mo–Mn–Al–C	7.87_6	7.86_7	0.999	$Zr_9Mo_4O_3$	8.653–	8.476–	0.979–
Mo–Fe–Al–C	7.84_9	7.84_8	1.000		8.684	8.449	0.973
Mo–Co–Al–C	7.95_0	7.84_3	0.986	$Hf_9Mo_4O_3$	8.60_9	8.53_6	0.99_1
Mo–Ni–Al–C	7.89_3	7.85_0	0.995	$Zr_9W_4O_3$	8.67_4	8.49_1	0.97_9
$Mo_{12}Cu_3Al_{11}C_6$	7.95_2	7.86_5	1.010	$Hf_9W_4O_3$	8.59_5	8.44_4	0.98_2
W–Mn–Al–C	7.90_3	7.78_7	0.986	$Zr_9Re_4O_3$	8.56_8	8.49_8	0.99_2
W–Fe–Al–C	7.89_5	7.85_7	0.995	$Hf_9Re_4O_3$	8.53_5	8.38_5	0.98_2
W–Mn–C	7.75_6	7.75_6	1.000				
$W_9Mn_3C_4$	7.76_4	7.77_5	1.001	Zr–Mo–Fe	8.68_5	8.44_4	0.97_2
$W_9Fe_3C_3$	7.81_0	7.81_6	1.000	Zr–Mo–Co	8.72_5	8.50_3	0.97_5
$W_9Co_3C_3$	7.82_6	7.82_6	1.000	Petkov *et al.*	8.73	8.54	0.98
$W_9Co_3C_4$	7.82_6	7.82_6	1.000	Zr–Mo–Ni	8.74_8	8.50_7	0.97_3
$W_{10}Co_3C_4$	7.84_8	7.84_8	1.000	Hf–Mo–Fe	8.61_1	8.41_1	0.97_7
$W_{16}Ni_3C_6$	7.81_8	7.81_8	1.000	Hf–Mo–Co	8.63_2	8.47_2	0.98_2
W–Ni–C	7.84_8	7.84_8	1.000	Hf–Mo–Ni	8.65_2	8.49_8	0.98_2
				Hf–W–Fe	8.60_1	8.39_9	0.97_7
Zr–Mo–B	8.63_4	8.56_8	0.99_2	Hf–W–Co	8.62_8	8.48_1	0.98_3
Zr–W–B	8.61_9	8.63_5	1.00_2	Hf–W–Ni	8.64_5	8.49_8	0.98_3
Hf–Mo–B	8.56_5	8.49_3	0.99_1				
Hf–W–B	8.59_2	8.49_1	0.98_8				

H-Phases and Perovskite Phases and New Complex Carbides Within the Zr–Al–C and Hf–Al–C Systems

As was mentioned earlier (*19*), the stability of the perovskite carbide varies depending on the transition element–aluminum–carbon system. With regard to the corresponding ternary combinations of Sc, Ti, V, Cr, Mn, and Ni, there is an obvious competition between the H-phase carbide and the perovskite carbide. In the system Mn-Al-C it has been shown that Mn_3AlC having perovskite-type structure is the only ternary carbide (*19, 20*). In this context the ternary system nickel–aluminum–carbon has also been studied. From the studies by Hütter and Stadelmaier (*21*) on the one hand and Fritscher (*22*) on the other, it was not quite clear whether Ni_3AlC_x was a solid solution of carbon in γ' or a separate ternary phase (perovskite). It was found (*23*) that γ' dissolves 7–8 at% carbon at 1000°C, but no ternary carbide occurs (Fig. 4).

In contrast to the Ti–Al–C system where a stable H-phase carbide does exist, there were no such carbides found for Zr(Hf)–Al–C, although Zr may substitute for quite a few niobium in Nb_2AlC. A dimensional analysis has recently been made by Pearson (*24*) for H-phase carbides. On the basis of Pauling's equation $R(n) = R(1) - 0.3 \log n$ (n = valence/CN) and all radii referred to C.N. = 12, it was found that for most of the H-phase carbides Hägg's condition for interstitial compounds $R_C/R_M < 0.59$ holds. There are, however, exceptions, such as Cr_2AlC. It was recognized from the two degrees of freedom, c/a ratio, and the z parameter in the [0001] direction that the relation $zc\,6^{1/2} = a$ for a fixed length $D_M + D_C$ in the octahedron controls the structure. In

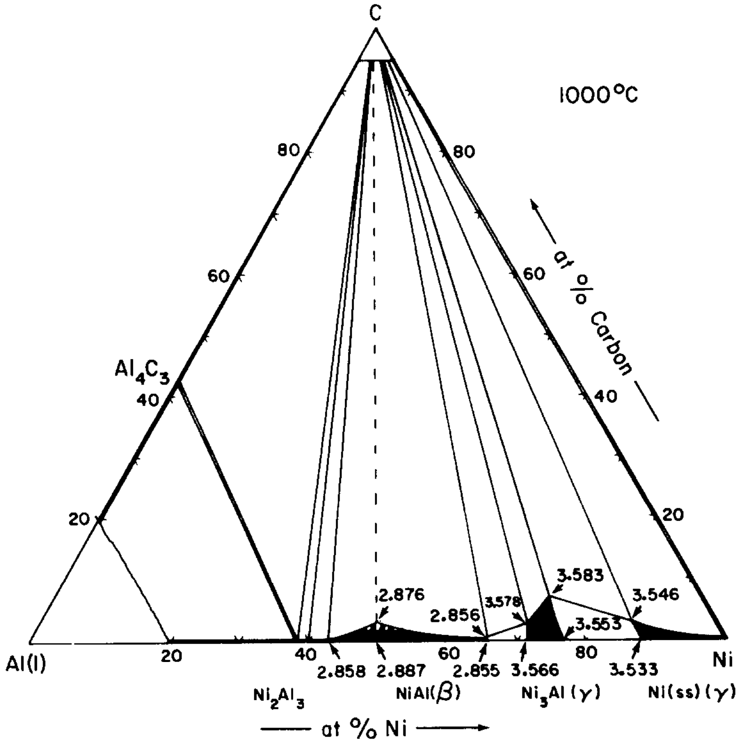

FIG. 4. Ternary system Ni–Al–C, isothermal section at 1000°C, parameter in Å.

this manner, the transition metal *d* band is maintained as in the elemental transition metal.

On the basis of the configurational electronic model of matter (*25*) the ductility of carbides could be improved by adding to them an electron donor which may promote a delocalization of the sp^3 state of carbon, and the complex carbides in the titanium–aluminum–carbon system became of interest (*26*). Considerable hardness values (2100 kg/mm^2) have been reported for the H-phase Ti_2AlC and the perovskite-phase Ti_3AlC by Russian authors (*26, 27*). However, these results could not be corroborated until now (*28*). Thus microhardness was found to be around 900 kg/mm^2 (Knoop, 50 g, 30 sec) for Ti_2AlC and modified H-phases such as $(Ti,V)_2AlC$. Such modified H-phases have been obtained by substitution of the transition element according to solid solutions $(T,T')_2AlC$ (*29*). As indicated in Table 5, complete solid solutions form between the H-phases Ti–V, V–Cr, Ti–Nb, V–Nb, Ti–Ta, and V–Ta, which mainly reflects the size factor.

Complex, Al-containing carbides having a higher amount of carbon have been newly detected with $Zr(Hf)AlC_2$ and $Zr_2(Hf)_2Al_3C_{5-x}$. It has been shown that the structural elements are nevertheless closely

TABLE 5

LATTICE PARAMETERS OF MODIFIED H-PHASES (nm)

	a	*c*	*M*:*M'*
$(Ti,V)_2Al\ C$	0.2975	1.339_3	1:1
$(Ti,Nb)_2Al\ C$	0.307_7	1.38_0	1:1
$(Ti,Ta)_2Al\ C$	0.3058_5	1.3779_7	0.8:1.2
$(V,Nb)_2Al\ C$	0.304_5	1.35_0	1:1
$(V,Ta)_2Al\ C$	0.2976_5	1.338_0	1.3:0.7
$(V,Cr)_2Al\ C$	0.2893	1.297_0	1:1

related to those which occur in binary carbides (*30*). As compared to the H-phase or Ti_3SiC_2-type structures, the degree of filling of the voids is higher, inasmuch as one can consider the triangular voids of the above-mentioned structure types as already filled by the metametal or nonmetal (Si). Figure 5 illustrates the array showing the stepwise development in the [11$\bar{2}$0] plane from the metallic transition metal carbide type (TiC) to the nonmetallic carbide Al_4C_3 structure type, where one already encounters the presence of $[M_4C]$ building groups besides $[M_6C]$ groups. The metal layer stacking for the $ZrAlC_2$-type structure, which has been independently reported by Michalenko *et al.* (*31*), is

$$A_cB_aC_bA_bC_aB_cA_bC_aB_cA_cB_aC_b.$$

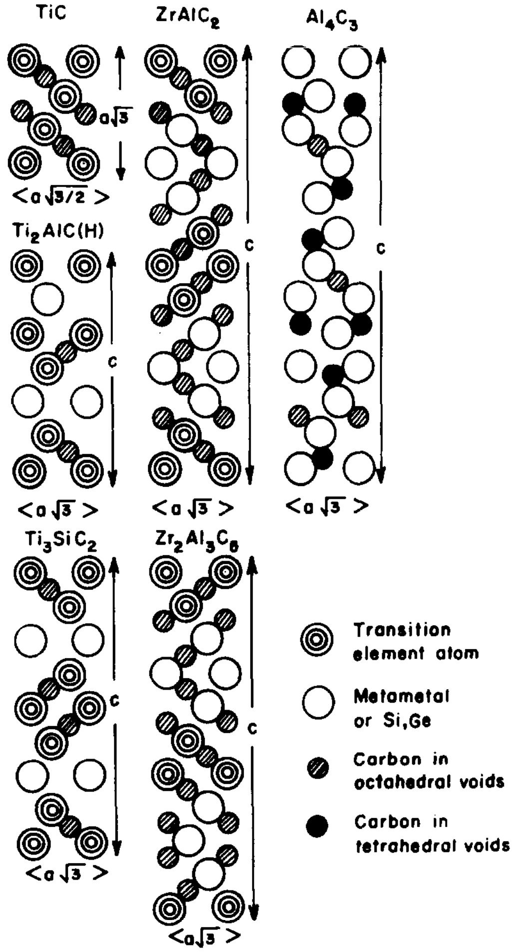

FIG. 5. Atomic arrangement in the (11$\bar{2}$0) plane of complex carbides and Al_4C_3. The atomic arrangement of TiC in the corresponding plane is also shown.

For the crystal structure proposed for $Zr_2Al_3C_{5-x}$ the stacking was found to be

$$A_cB_aC_bA_cB_aC_aB_cA_bC_aB_c,$$

which means a 10-layer stacking of the metal atoms for the latter complex carbide and a 12-layer stacking for the former. As was pointed out earlier (*32*) with the γ''-$MoC_{1-x}(\eta)$-type structure, carbon defects can be expected at the positions C_bA_b, B_aC_a, and B_cA_c because of carbon–carbon repulsion at those near distances.

Complex carbides having a lower amount of carbon and exhibiting a smaller ratio r_C/r_M, such as Ta_5Al_3C, are characterized, as expected, by filling of the octahedral voids (*30*).

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