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On the Crystal Chemistry of the Close Packed Transition Metal Carbides. I. The Crystal Structure of the ζ-V, Nb and Ta Carbides*

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The crystal structure of V_4C_3 was solved by single-crystal diffraction methods. The trigonal structure consists of 12 close packed metal atom layers with stacking sequence (*hhcc*)$_3$ or *ABABCACABCBC*. The carbon atoms which occupy octahedral interstices were not ordered in the single crystal examined. The other carbides Nb_4C_3 and Ta_4C_3 have the same metal atom arrangement. Due to the small scattering power of the C atoms no statement can be made on the C atom order in these compounds. The structure of the ζ-phase with ordered C atoms is isotypic with Sn_4P_3.

Introduction

The first reference to the existence of a ζ-phase was given by Lesser & Brauer (1958) who investigated the system Ta–C and found a new diffraction pattern in samples which were supposed to contain only a mixture of hexagonal subcarbide Ta_2C and cubic monocarbide TaC. The existence of this phase was verified by Zaplatynsky (1966) and later by Brizes & Tobin (1967) who gave for its composition $TaC_{0·74}$. The ζ-phase has been found also in the system Nb–C (Brauer & Lesser, 1959) and V–C (Storms & McNeal, 1962; Rassaerts, Benesovsky & Nowotny, 1966; Rudy, Windisch & Brukl, 1968) at approximately the same composition. All three ζ-phases are formed in a restricted temperature range in the two phase field T_2C–TC (T = V, Nb, Ta).

Experimental

Vanadium carbide samples of composition $VC_{0·62\pm0·01}$, $VC_{0·65\pm0·01}$, $VC_{0·69\pm0·01}$ and $VC_{0·71\pm0·01}$ were prepared by hot pressing mixtures of vanadium and graphite powder in carbon dies. The composition and limits of error have been determined by chemical analysis. X-ray powder pictures indicated that all samples contained mainly two phases: the subcarbide V_2C with hexagonal close packed metal atoms and the defect monocarbide $VC_{\sim0·75}$ with cubic close packed metal atoms. The amount of ζ-phase, identified from published *d* spacings (Storms & McNeal, 1962), was very small. To enrich the samples with ζ-phase the samples were encapsulated in quartz tubes, annealed at 1000 °C for up to 250 hr and then air cooled. It was never possible to obtain the ζ-phase without the other phases being present. It is obvious that under these circumstances a chemical analysis does not permit the determination of the true composition of the ζ-phase. However, after the metal atom arrangement of the ζ-phase was known it became possible to compare the intensities of the ζ-phase, V_2C and VC_{1-x} reflections and to determine the relative proportion of these three phases in a sample of known overall composition. For example, the sample $VC_{0·62}$ was found to contain 53% ζ-phase, 25% V_2C and 22% cubic $VC_{\sim0·75}$ (lower phase boundary of VC_{1-x} after Rudy, Windisch & Brukl, 1968). The composition of the ζ-phase was then calculated to be $VC_{0·67\pm0·02}$, in agreement with the result of metallographic examinations by Rudy, Windisch & Brukl (1968). The amount of oxygen, nitrogen and hydrogen present as impurities in the sample $VC_{0·62}$ was found to be: 0·77 wt% O, 0·05 wt% N, 0·002 wt% H. This corresponds to the composition: $VC_{0·62}O_{0·02}N_{0·002}H_{0·001}$. Interestingly enough the sample $VC_{0·65}$ contained much less ζ-phase than the sample $VC_{0·62}$ after identical heat treatment although the latter is further away from the ideal composition of the ζ-phase. This phenomenon together with the sluggishness of ζ-phase formation is probably connected with the close structural relationship between V_2C, ζ-phase and VC_{1-x}. It will be shown below that the structure of the ζ-phase consists of close packed V metal layers just as V_2C and VC_{1-x} and that it can be constructed of V_2C and VC building blocks.

We assume that the formation of the ζ-phase is favored by the presence of the hexagonal V_2C phase. This could explain its faster formation in $VC_{0·62}$ samples and further explains why the ζ-phase was found to grow epitaxically on the V_2C phase. Among 50 crystals investigated (obtained by crushing the bulk specimen $VC_{0·62}$) none was found to consist of ζ-phase only. Even the best crystal we could separate (~20μ of size) had a tiny V_2C crystal attached. Later it was found that both have a common 00.1 plane. With this crystal we determined the unit-cell dimensions and the space group of the ζ-phase. However, because of the epitaxic intergrowth we could not rely on the F^2 values obtained from the Weissenberg photographs. Instead,

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* Part II, Parthé & Yvon (1970). *Acta Cryst.* B**25**, 153.

intensities from a powder diffractometer pattern were measured with a planimeter and subsequently used for the structure refinement.

Structure determination

Weissenberg and precession photographs of a ζ-phase single crystal (epitaxically intergrown with V_2C) could be indexed with a hexagonal unit cell. The lattice parameters, refined from powder diffraction data using the least-squares program by Mueller, Heaton & Miller (1960) and Gvildys (1965) are:

$$a_H = 2{\cdot}917 \pm 0{\cdot}001\text{Å},$$
$$c_H = 27{\cdot}83 \ \pm 0{\cdot}01\text{Å and } c_H/a_H = 9{\cdot}541.$$

The systematic absences among the observed reflections are *hkl* with $-h+k+l \neq 3n$ which leads to possible space groups $R3$, $R\overline{3}$, $R32$, $R3m$ and $R\overline{3}m$. The symmetry of the structure is thus trigonal and instead of the above given hexagonal unit cell one can use a one-third smaller rhombohedral unit cell with the parameters

$$a_R = 9{\cdot}428 \pm 0{\cdot}007\text{Å},$$
$$\alpha = 17°48' \pm 1'.$$

Our structure proposal was predicated on the following observations:

(*a*) The hexagonal *a* axis of the ζ-phase is almost identical to the *a* axis of V_2C ($a = 2{\cdot}910$Å).

(*b*) A great number of *d*-spacings in V_2C and VC_{1-x} coincide with the *d*-spacings of the ζ-phase.

(*c*) The only 00.*l* reflections observed are the 00.12 and 00.24 and the *d*-spacing for the 00.12 corresponds roughly to the distance between the metal atom layers in V_2C and VC_{1-x}.

All this suggests that the metal atom arrangement in the ζ-phase is also close-packed with 12 layers per cell. Simple considerations show that there is only one 12 layer stacking sequence which has the observed trigonal symmetry. This stacking arrangement can be denoted by the letter sequence *ABABCACABCBC* or by the Jagodzinski–Wyckoff symbol $(hhcc)_3$. The carbon atoms occupy octahedral interstices. The structure proposal disregarding any possible carbon atom ordering is thus given by:

$R\overline{3}m$ (D^5_{3d})
6V in 6 (*c*) with $z \sim \frac{1}{8}$
6V in 6 (*c*) with $z \sim \frac{7}{24}$

Table 1. *Powder intensity calculation and list of observed and calculated F values for* V_4C_{3-x} ($x = 0{\cdot}33$) *with random carbon atom arrangement*

Cu $K\alpha_1$ radiation ($\lambda = 1{\cdot}5405$ Å).

hk l	d_{calc}	I_{cal}	I_{obs}		F_{cal}	$\lvert F\rvert_{obs}$
00· 3	9·28 Å	0·2	—		−2·4	—
00· 6	4·64	<0·1	<1·0		3·1	2·2†
00· 9	3·09	0·1	<1·0		−6·4	5·8†
10· 1	2·516	5·2	6·9	C: $(100)_{V_2C}$	33·6	40·9*
01· 2	2·486	21·4	18·9		−69·1	66·6
10· 4	2·375	7·2	5·8	C: $(111)_{VC}$	−41·7	39·6*
00·12	2·319	38·2	32·0		−169·4	175·4
01· 5	2·300	88·0	72·5	C: $(002)_{V_2C}$	−148·5	145·5*
10· 7	2·132	100·0	100·0		169·1	184·8
01· 8	2·044	8·9	8·4		52·3	55·8
10·10	1·871	18·5	12·6		82·2	75·1
00·15	1·855	<0·1	<1·0		8·2	9·2†
01·11	1·788	5·6	3·4		−47·7	40·5
10·13	1·633	3·5	2·1		−40·6	35·1
01·14	1·562	14·8	9·9		88·4	79·5
00·18	1·546	<0·1	<1·0		−6·4	5·9†
11· 0	1·459	43·1	37·0	C: $(220)_{VC}$	161·8	164·3*
11· 3	1·441	<0·1	<1·0		−1·6	13·1†
10·16	1·433	2·2	2·5		37·1	43·7
11· 6	1·391	<0·1	<1·0		1·8	14·3†
01·17	1·374	19·5	16·8		115·4	116·9
00·21	1·325	<0·1	<1·0		10·7	39·2†
11· 9	1·319	<0·1	<1·0		−4·1	15·5†
10·19	1·267	14·7	14·7		−108·5	116·9
02· 1	1·262	0·6	<1·5	C: $(200)_{V_2C}$	22·8	27·4*†
20· 2	1·258	2·6	2·1		−46·5	44·5
02· 4	1·243	0·9	<1·5		−27·7	26·1†
11·12	1·235	30·0	29·0		−112·7	116·9
20· 5	1·232	11·4	10·5		−97·8	101·2
01·20	1·219	1·1	<1·5	C: $\{(11{\cdot}2)_{V_2C}$	−30·7	28·0*†
02· 7	1·204	14·5	11·9	$(20{\cdot}1)_{V_2C}$	111·3	109·4
20· 8	1·187	1·4	<1·5		34·6	28·6*†
00·24	1·160	6·4	5·5	C: $(222)_{VC}$	130·9	133·3
02·10	1·150	3·5	2·5		55·5	52·3

† One half of the *F* value obtained from the smallest observable intensity value.
* Values obtained by subtracting from observed intensity the intensity of coinciding V_2C or VC_{1-x} line.

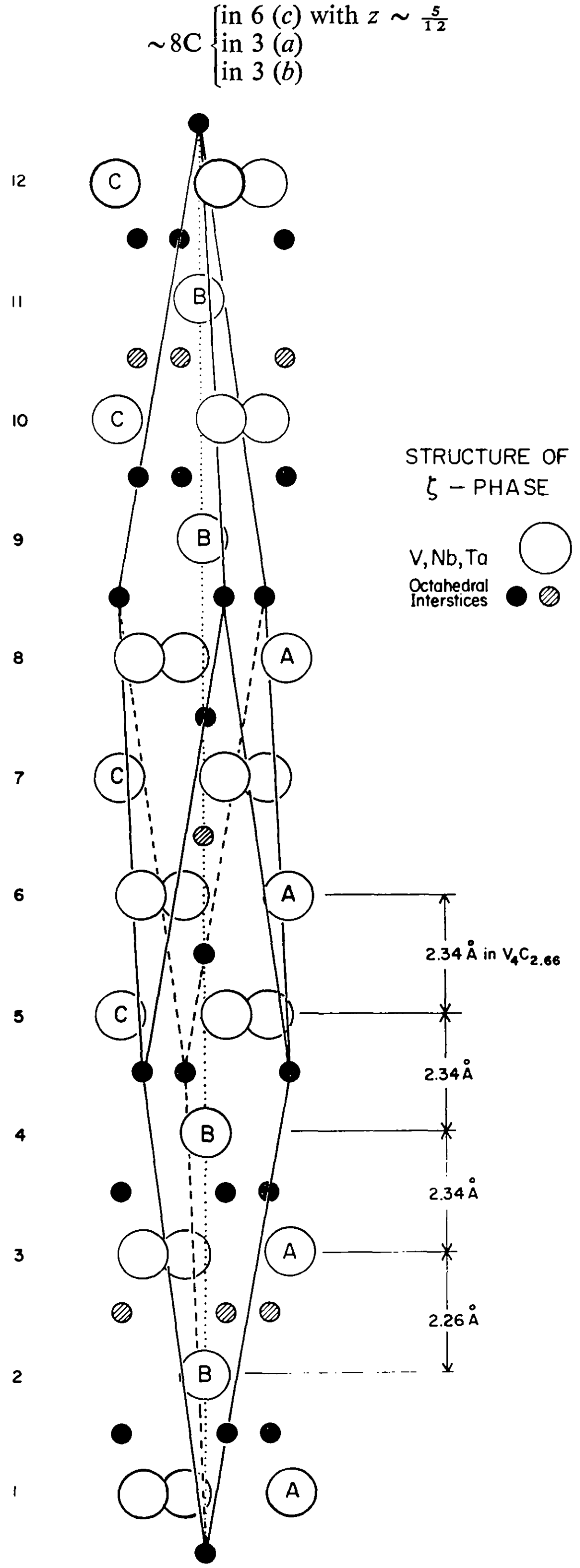

Fig. 1. The structure of the ζ-phase. For maximum carbon content the composition of the ζ-phase is T_4C_3. In this case the 3(*b*) positions indicated by small shaded circles are not occupied. This is probably the case with Ta_4C_3.

A powder intensity calculation using the program by Yvon, Jeitschko & Parthé (1969) showed that the proposed structure was essentially correct but needed refinement.

As discussed in more detail in part II (Parthé & Yvon, 1970) there exist certain restrictions on the C atom arrangement in close packed transition metal carbides which depend on the particular stacking sequence of the metal layers. For stacking *hhcc* the composition with the highest carbon content is T_4C_3 (T means transition metal atom). This composition allows only for one ordered carbon atom arrangement 6C in 6 (*c*) with $z \sim \frac{5}{12}$ and 3C in 3(*a*). If, however, the carbon atoms are distributed randomly, point position 3(*b*) is also partly occupied. A way to find out quickly whether or not the carbon atoms are ordered is provided by the 0.03 reflection which should be observable if the defects are ordered. In all Weissenberg and powder photographs no trace of the 00.3 reflection could be detected. Consequently we have concluded that the eight carbon atoms are randomly distributed over all twelve octahedral interstices.

The parameters which we have refined are the three *z* parameters of the vanadium metal and carbon positions. As stated above, due to the intergrowth of the single crystals we had difficulties in making the proper absorption corrections and decided to rely only on powder reflection intensities. Using 21 properly corrected F_{obs} values in the full-matrix least-squares program by Gantzel, Sparks & Trueblood (1961) we obtained the following final parameters and their estimated standard deviations:

$$\begin{aligned} z_{V_I} &= 0{\cdot}1265\ (0{\cdot}0006) \\ z_{V_{II}} &= 0{\cdot}291\ \ (0{\cdot}001) \\ z_C &= 0{\cdot}417\ \ (0{\cdot}005) \end{aligned}$$

An overall temperature factor of $0{\cdot}5 \, . \, 10^{-16}$ cm³ was assumed.

$$\text{The residual } R_{21} = \frac{\Sigma\big||F_{\text{obs}}| - |F_{\text{calc}}|\big|}{\Sigma|F_{\text{obs}}|} = 5{\cdot}4\,\% \, .$$

This does not include the *F* values of unobserved intensities. Taking these into account, the *R* value becomes 12%. A list of the powder diffraction line intensities and of the F_{obs} and F_{calc} values for $V_4C_{2{\cdot}67}$ is given in Table 1.

The corresponding ζ-phases in the system Nb–C and Ta–C have the same crystal structure. The exact carbon defect of these compounds has not been determined. Due to the small scattering power of C, no statement could be made on the order of the C atoms. The lattice constants are:

Nb_4C_3, $a = 3{\cdot}14 \pm 0{\cdot}01$, $c = 30{\cdot}1 \pm 0{\cdot}1$ Å, $c/a = 9{\cdot}58$;
Ta_4C_3, $a = 3{\cdot}116 \pm 0{\cdot}005$, $c = 30{\cdot}00 \pm 0{\cdot}05$ Å, $c/a = 9{\cdot}62$.

Discussion of the structure

The ζ-phase with a structure as shown in Fig. 1 belongs to the Hägg compounds which are characterized by close packed metal atoms with carbon or nitrogen atoms in the octahedral interstices. The structure can be described as being composed of structural blocks of hexagonal V_2C (metal layers 1–2–3–4, 5–6–7–8, 9–10–11–12) or cubic VC (metal layers 11–12–1–2, 3–4–5–6, 7–8–9–10). The interlayer distances 2–3, 6–7 and 10–11 correspond roughly to the interlayer distance in V_2C (2·28 Å) while the interlayer distances 4–5, 8–9 and 12–1 are much closer to the distances between the hexagonal layers in cubic $VC_{\sim 0\cdot 75}$ (2·38 Å).

The twelve metal layer stacking of the ζ-phase which is described by the Jagodzinski symbol $(hhcc)_3$ has not yet been found with elemental structures, but has been reported for one phosphide, two sulfides and one gallide: Sn_4P_3 (Olofsson, 1967); ZnS 12*R* (Haussühl & Müller, 1963), the mineral smythite Fe_3S_4 (Erd, Evans & Richter, 1957) and the high temperature form of $PuGa_3$ (Larson, Cromer & Roof, 1965).

Sn_4P_3 and probably also Sn_4As_3 are isostructural with the stoichiometric ζ-carbides with ordered vacancies. The shaded circles in Fig. 1 corresponding to point position 3(*b*) of space group $R\bar{3}m$ are not occupied. V_4C_{3-x}, however, was found to be carbon deficient and did not show any ordering of the C atoms. The octahedral interstices on equipoint 3(*b*) are here partly occupied by C atoms.

ZnS 12*R* can be described as a close packed $(hhcc)_3$ arrangement of Zn atoms with sulfur atoms located not in the octahedral but in the tetrahedral interstices. Zn and S atom positions are interchangeable. Thus one can equally well describe the structure as $(hhcc)_3$ arrangement of S atoms with Zn atoms placed in the tetrahedral interstices.

The structure of Fe_3S_4 is more closely related to the structure of the ζ-phase. The sulfur atoms form close packed layers which are stacked like the metal atom layers in the ζ-phase. The Fe atoms occupy the octahedral interstices of the sulfur atoms but have a different arrangement of the carbon atoms in the ζ-phase. Only the NiAs-like octahedral holes are filled with Fe atoms while the NaCl-like holes remain empty.

In the high temperature form of $PuGa_3$ the Pu atoms are positioned in the centers of Kagomé nets formed by the Ga atoms.

Problems relating to the composition and formation of the ζ-phases

An interesting feature of the ζ-phase V_4C_{3-x} is its considerable carbon deficiency. The fact that the maximum carbon content of 42·8 at.% is not reached is certainly related to the defect character of the transition metal carbides in general. It appears well established that the stoichiometric composition TC is reached in none of the cubic monocarbides (T = V, Nb, Ta).

VC_{1-x} in particular deviates considerably having the carbon rich boundary located at ~ 47 at.% C ($VC_{0\cdot 89}$; Rudy, Windisch & Brukl, 1968). Since the structure of V_4C_{3-x} contains 50% cubic stacking of metal layers a similar defect in C atoms can be anticipated to occur in the ζ-phase. In the case of cubic TaC_{1-x} the carbon rich boundary is located much closer to the ideal composition: 49·8 at.% ($\triangleq TaC_{0\cdot 99}$). In fact, a C analysis of the Ta_4C_{3-x} phase gave a composition $TaC_{0\cdot 74}$ (Brizes & Tobin, 1967) in perfect agreement with the assumption of almost no carbon vacancies in the cubic stacking sequences, thus giving ideal composition T_4C_3 for the ζ-phase in the Ta–C system. In this context it is worth mentioning that the lattice parameters of V_4C_{3-x} were found to be identical in samples having different C/V (or V_2C/VC) ratios. Also different heat treatment did not have any influence. Thus, the ζ-phase seems to have a well defined C-composition, varying only little with the temperature and overall C-composition of the sample in which it is being formed.

Concerning the carbon atom arrangement in V_4C_{3-x} it is rather surprising that there is no evidence for ordering. For the subcarbides T_2C and the defect monocarbides TC_{1-x} (T = V, Nb, Ta) recent work revealed a great number of distinct phases with ordered C-atom arrangements. Only the high temperature modifications have randomly distributed C atoms in the metal atom framework. Annealing samples containing the ζ-phase at low temperatures (600–700° C) for several weeks did not bring about C-ordering in any of the three phases VC_{1-x}, V_4C_{3-x}, V_2C. This fact indicates that the order–disorder transition in vanadium carbides is not a function of the temperature alone, but might be also influenced by the microstructure of the sample investigated. Even the different distances between the metal layers observed in V_4C_{3-x} (Fig. 1) do not necessarily indicate an ordering tendency, since cubic stacking in disordered $VC_{0\cdot 75}$ and hexagonal stacking in disordered V_2C show similar differences in the layer–layer distances.

Further, it should be noted that during the course of these studies unexpected kinetic effects have been observed. It was found that the powder diffraction patterns of sample $VC_{0\cdot 62}$ containing the three carbide phases changed with the time of storage at room temperature. Diffraction photographs were taken of the same powder specimen with the same camera during a time span of two weeks after the final heat treatment, in intervals of several days. It was found that with storage

(*a*) the V_2C and VC_{1-x} lines become diffuse while the ζ-phase lines remain sharp and

(*b*) the lattice parameter of VC_{1-x} changes from 4·137 to 4·145 Å.

A powder film made after three months did not differ from that obtained after two weeks; it still contained diffuse V_2C and VC_{1-x} diffraction lines. Reactions at room temperature have also been observed by Rudy (1968) in the system Ta–C.

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On the Crystal Chemistry of the Close Packed Transition Metal Carbides. II. A Proposal for the Notation of the Different Crystal Structures*

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To counteract the prevailing confusion in the notation of the close packed transition metal carbides a notation is proposed which is based on the structural features of the carbide phases. It consists of the Jagodzinski–Wyckoff symbol for the stacking sequence of the close packed metal atom layers followed by the space group of the compound to distinguish between different arrangements of the carbon atoms on the octahedral interstices. The known close packed carbide types are reviewed and their new notation is given. It is found that in the case of the NaCl defect structures there exist two different structure types which although not homometric yet give rise to identical powder diffraction patterns. A distinction between both types in principle is possible only with single-crystal diffraction data.

Introduction

During the last fifteen years, the structures and phase relationships of the refractory transition metal carbides have been studied quite intensively (for review see Kieffer & Benesovsky, 1963; Storms, 1967; Goldschmidt, 1967; Nowotny & Benesovsky, 1968). Nearly all occurring carbide structures have already been solved. For the most part they are simple structures consisting of an arrangement of close-packed transition metal atoms with carbon atoms positioned in the octahedral interstices. Quite often not all of the available octahedral interstices are occupied and the remaining carbon atoms can then have ordered arrangements which may require unit cells which are a multiple of the earlier assumed repetitive units. The ordering of the carbon atoms leads to superstructure lines. These may be seen in X-ray diffraction patterns of Sc, Ti and V carbides but not at all in the X-ray patterns of carbides with heavier transition metals. In the latter case, only neutron and electron diffraction experiments will permit the determination of the supercell and the C atom arrangement. Certain carbides, depending on temperature and carbon content, show a variety of ordered carbide structures, with some of the phase changes occurring at very high temperature as indi-

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