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The Crystal Structures of V_2C and Ta_2C*

BY ALLEN L. BOWMAN, TERRY C. WALLACE, JOHN L. YARNELL, ROBERT G. WENZEL AND EDMUND K. STORMS
Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico, U.S.A.

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A neutron diffraction study of V_2C and Ta_2C has shown that V_2C has the *L'*3 structure, while Ta_2C has the *C*6 cadmium iodide antitype structure. The Ta_2C space group is $P\bar{3}m1$ (D^3_{3d}). Two tantalum atoms are in 2(*d*) with $z=0{\cdot}2537$ and one carbon atom is in 1(*a*).

Introduction

The structures of the metal hemicarbides V_2C, Nb_2C, Ta_2C, Mo_2C and W_2C are listed in modern reviews (Pearson, 1958; Smithells, 1962) as the hexagonal L'3-type structure. This structure requires that one carbon atom be distributed randomly between two equivalent sites. However, it has been shown recently from neutron-diffraction data (Parthé & Sadagopan, 1963) that the carbon distribution in Mo_2C is ordered, resulting in a different structure based on an orthorhombic unit cell. In this work the structures of V_2C and Ta_2C are determined from neutron-diffraction data.

Experimental

The carbide samples were prepared by heating the powdered elements in a graphite crucible in vacuum for several hours. The resulting sintered plugs were pulverized and screened to -325 mesh. Iron which was present as starting material was removed from the V_2C sample by hydrochloric acid extraction. The powders were heated and ground several times, Ta_2C at 1600° and V_2C at 1400°. X-ray powder patterns were taken in a 11·46 cm Debye–Scherrer camera, using copper $K\alpha$ radiation, $\lambda=1{\cdot}54051$ Å. The lattice parameters were obtained from the back-reflection lines by a least-squares extrapolation (Vogel & Kempter, 1959). Both patterns were indexed on a hexagonal cell, with $a_0=2{\cdot}9043\pm0{\cdot}0002$, $c_0=4{\cdot}5793\pm0{\cdot}0002$ Å for V_2C and $a_0=3{\cdot}1030\pm0{\cdot}0001$, $c_0=4{\cdot}9378\pm0{\cdot}0001$ Å for Ta_2C. The vanadium carbide sample had a small VC impurity in its powder pattern and an analyzed composition of $VC_{0.55}$, with <500 ppm oxygen and nitrogen. The V_2C phase thus should have a composition $VC_{0.50}$ (Storms & McNeal, 1962). The tantalum carbide sample had a small tantalum impurity and an analyzed composition of $TaC_{0.42}$, with <500 ppm oxygen and nitrogen. The Ta_2C phase thus should have a composition $TaC_{0.48}$ (Bowman, 1964).

The neutron-diffraction data were obtained at the Los Alamos Omega West Reactor. A monochromatic neutron beam was produced by reflection from an aluminum single crystal. The beam intensity was monitored by means of a thin fission counter. The samples were contained in a parallel-sided holder, made from a null-matrix (Ti–Zr) alloy (Sidhu, Heaton, Zauberis & Campos, 1956) with zero coherent scattering, and were located symmetrically between the incident and scattered beams. The samples intercepted the entire incident beam over the range of scattering angles employed. Soller slit collimators were placed between the monochromator and sample, and between the sample and BF_3 detector.

The data were recorded automatically as number of neutron counts per fixed number of monitor counts, at intervals of 0·2° in 2θ. Several separate runs were made and the results averaged. Calibration runs were made on nickel and niobium monoxide standards. A

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blank pattern, run on the empty sample holder, showed no diffraction peaks. The absorption factor, μt, was determined by transmission measurement at $2\theta=0$. The V_2C pattern was run from 10° to 90° at $\lambda=1{\cdot}3918$ Å, with the absorption factor $\mu t=0{\cdot}140$. The Ta_2C was run from 10° to 100° at $\lambda=1{\cdot}3030$ Å, with $\mu t=0{\cdot}128$. A second V_2C pattern was run from 6° to 40° at $\lambda=1{\cdot}14$ Å to confirm the initial finding of no low-angle lines, and hence no ordering of the carbon vacancies.

The X-ray-diffraction intensity data were obtained on a Norelco X-ray Diffractometer, with a rotating flat specimen holder, using filtered copper radiation. A continuous scan rate of $\frac{1}{8}°$ min^{-1} was employed. The accumulated number of counts was recorded at intervals of $\frac{1}{2}°$ from the dekatron counting panel of a Norelco Electronic Circuit Panel. The powdered sample was lightly cemented in the specimen holder with a 1% solution of paraffin in benzene. A silicon standard was used for calibration purposes.

Results and discussion

The neutron-diffraction traces are shown in Fig. 1. Both patterns can be indexed on the same cells as the X-ray diffraction patterns. The V_2C patterns appear to be consistent with the L'3 structure type, while the presence of the 001 peak in the Ta_2C neutron-diffraction pattern requires another structure, probably the $C6$ type.

The neutron-diffraction data were fitted to the equation (Atoji, 1961; Sailor, Foote, Landon & Wood, 1956)

$$Y=B+\Sigma\left\{\frac{I_n}{s_n\sqrt{2\pi}}\exp\left[-\frac{1}{2s_n}(2\theta-b_n)^2\right]\right\} \qquad (1)$$

by the method of least squares (Moore & Zeigler, 1959), assuming zero error in the measurement of 2θ. Here Y is the number of neutron counts; I_n, s_n and b_n are the intensity, standard deviation and mean value of 2θ of the nth peak, respectively; and B is the background, arbitrarily assumed to be of the form $[a_0+a_1(2\theta)+a_2(2\theta)^2]$. The solutions were obtained in segments of 10° to 20° of 2θ, using unit weighting. These solutions included both the hemicarbide and impurity phase peaks.

The parameters b_n and s_n must obey the Bragg equation

$$\sin\frac{b}{2}=\frac{\lambda}{2d} \qquad (2)$$

and the equation (Caglioti, Paoletti & Ricci, 1958; Caglioti & Ricci, 1962)

$$s=(k_0+k_1\tan\theta+k_2\tan^2\theta)^{\frac{1}{2}}\,. \qquad (3)$$

Values for λ and the k's were obtained by the method of least squares from NbO and nickel standard patterns. Overlapping multiple peaks in the Ta_2C and V_2C patterns were resolved by using fixed values of b and/or s, obtained from equations (2) and (3), in the solution of equation (1). The computed values of I, s and b for V_2C and Ta_2C are listed in Tables 1 and 2 with their standard deviations. Fixed values of a and b are shown in parentheses.

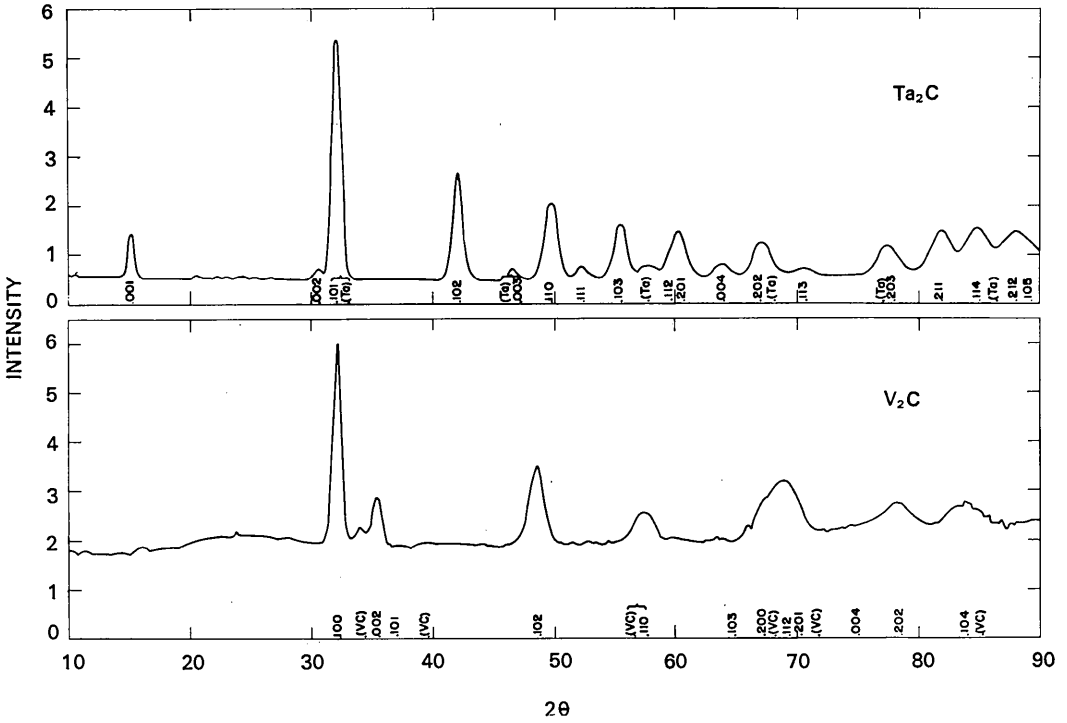

Fig. 1. Neutron-diffraction traces of V_2C and Ta_2C.

The observed neutron intensities were fitted to trial structures by least-squares solutions of the equation (Bacon, 1962)

$$I=K\frac{\exp(-\mu t\sec\theta)}{\sin^2 2\theta}\exp\left(-2B\frac{\sin^2\theta}{\lambda^2}\right)jF^2 . \quad (4)$$

Each peak was weighted by its inverse variance. Unobserved peaks were included in the calculations with intensities equal to the uncertainty of the background.

The observed X-ray intensities were fitted to the same structures by least-squares solution of the equation (*International Tables for X-ray Crystallography*, 1959)

$$I=K\frac{(1+\cos^2 2\theta)}{\sin^2\theta\cos\theta}\exp\left(-2B\frac{\sin^2\theta}{\lambda^2}\right)jF^2 , \quad (5)$$

using unit weighting and ignoring unobserved peaks. An agreement index is defined by

$$R=\Sigma(w|I_{obs}-I_{calc}|)/\Sigma(wI_{obs}) . \quad (6)$$

The V_2C patterns were fitted to the $L'3$ structure, $P6_3/mmc$ with 2V in $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ and 1C in (000), with $K=43{\cdot}6\pm1{\cdot}1$, $B=0{\cdot}97\pm0{\cdot}15$, $R=0{\cdot}048$ for the neutron-diffraction pattern and $K=0{\cdot}0075\pm0{\cdot}0004$, $B=0{\cdot}89\pm0{\cdot}40$, $R=0{\cdot}086$ for the X-ray-diffraction pattern. The Ta_2C patterns were fitted to the $C6$ structure, $P\bar{3}1m$ with 2Ta in $(\frac{1}{3}, \frac{2}{3}, z)$ and 1C in (000), with $K=56{\cdot}3\pm1{\cdot}0$, $B=0{\cdot}53\pm0{\cdot}07$, $z=0{\cdot}2537\pm0{\cdot}0009$, $R=0{\cdot}045$ for the neutron diffraction pattern and $K=0{\cdot}00050\pm0{\cdot}00003$, $B=-2{\cdot}1\pm0{\cdot}5$, $z=0{\cdot}267\pm0{\cdot}014$, $R=0{\cdot}104$ for the X-ray diffraction pattern. The poorer fit of the X-ray diffraction data is similar to that obtained for silicon and NbO standards.

The interatomic distances are listed in Table 3. Each carbon atom is surrounded by six metal atoms in a regular octahedron. Each metal atom has three equidistant carbon neighbors, randomly distributed among

Table 1. *Summary of experimental data — vanadium carbide*

		Neutron ($\lambda=1{\cdot}3918$ Å)				X-ray (Cu $K\alpha$)	
hkl	*d*	*s*	*b*	I_{obs}	I_{calc}	I_{obs}	I_{calc}
100	2·513 Å	0·384±0·004°	32·147±0·003°	375±5	373	124	139
002	2·289	0·422±0·021	35·381±0·019	106±6	118	194	177
101	2·203	not observed		3±4	9	874	872
102	1·692	0·646±0·012	48·548±0·010	250±5	251	120	148
110	1·451	0·781±0·031	(57·327)	103±12	78	132	132
103	1·304	not observed		3±10	3	132	107
200	1·257	(0·880)	(67·256)	111±9	97		
112	1·225	(0·930)	(69·204)	221±8	211	92	93
201	1·212	not observed		3±10	3	58	78
004	1·144	(1·207)	(74·914)	8±6	17		
202	1·102	1·099±0·075	(78·365)	105±8	114	56	27
104	1·041	1·245±0·086	(83·862)	126±13	142		

Table 2. *Summary of experimental data — tantalum carbide*

		Neutron ($\lambda=1{\cdot}3030$ Å)				X-ray (Cu $K\alpha$)	
hkl	*d*	*s*	*b*	I_{obs}	I_{calc}	I_{obs}	I_{calc}
001	4·950 Å	0·255±0·008°	15·125±0·008°	574±19	566		
100	2·688	not observed		(3)	2	278	243
002	2·468	(0·338)	30·607±0·044	177±16	199	296	269
101	2·362	0·341±0·004	32·027±0·007	3837±100	3862	1170	1191
102	1·818	0·429±0·005	42·003±0·005	2231±24	2246	290	240
003	1·646	(0·479)	(46·633)	69±66	96		
110	1·551	0·511±0·007	49·669±0·006	1948±26	1918	260	281
111	1·508	(0·538)	52·207±0·039	328±20	327		
103	1·403	0·528±0·010	55·333±0·009	1366±30	1387	350	295
200	1·344	not observed		(9)	1	94	44
112	1·314	(0·621)	(59·464)	391±59	367	322	336
201	1·296	0·605±0·021	60·364±0·026	1276±58	1268	218	268
004	1·232	(0·673)	63·832±0·048	354±27	426	48	48
202	1·180	(0·718)	(67·014)	1091±28	1045	126	91
113	1·129	(0·778)	70·508±0·066	316±25	302		
104	1·122	not observed		(6)	7		
203	1·041	(0·862)	(77·500)	1071±86	864		
210	1·016	not observed		(89)	1		
211	0·994	0·880±0·024	81·873±0·022	1743±50	1713		
005	0·988	not observed		(89)	18		
114	0·968	0·845±0·039	84·755±0·036	1659±103	1818		
212	0·939	(1·035)	(87·892)	1458±145	1550		
105	0·928	(1·063)	89·203±0·181	659±75	829		

Table 3. *Interatomic distances*

	V_2C	
V–C	(3)	2·029 Å
C–C	(1)	2·288
V–V	(6)	2·836

	Ta_2C	
Ta–C	(6)	2·186 Å
Ta–Ta	(3)	3·021
	(3)	3·080

the apices of a trigonal prism in V_2C, and forming one triangular face of the prism in Ta_2C. Thus V_2C, Ta_2C and Mo_2C have structures based on a hexagonal closest-packed metal lattice, with the carbon atoms filling one half of the octahedral holes, randomly in V_2C and in different ordered arrangements in Ta_2C and Mo_2C.

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Structural Changes Caused by the Neutron Irradiation of σ Phases

BY C. G. WILSON AND M. H. PARSELLE

Royal Military College of Science, Shrivenham, Swindon, Wilts., England.

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The effect of fast neutron bombardment on the structure of three σ phases, MoRe55, MoRe68 and WRe50, has been studied by X-ray diffractometry. Radiation damage consisting of (i) line broadening, (ii) changes in unit-cell dimensions and (iii) disordering were observed, the magnitude of the effects depending on the total fast-neutron dose. It is suggested that the irradiation creates clusters of defects causing line broadening and that the change in unit-cell size is caused by the disordering of atoms of different radii.

Introduction

The study of the effect of fast-neutron irradiation of alloys has been mainly confined to simple cubic structures such as Cu_3Au (Adam, Green & Dugdale, 1952, Blewitt & Coltman, 1954), $MnNi_3$ (Aronin, 1954), Fe_3Al (Saenko, 1964), *etc.*, the interest being in the disordering or ordering produced. In the irradiation of some uranium-based alloys phase transformations have been reported (Konabeevsky, Pravdyuk & Kutaitsev, 1956; Bleiberg 1959). Enhanced precipitation with consequent changes in mechanical hardness have also been reported (Kernohan, Billington & Lewis, 1956). Incidental to these effects have been changes in lattice parameter and increased lattice strain, but the importance of the relation of crystal structure to the nature of the radiation damage has not been emphasized except in the special case of uranium growth (Cottrell, 1960) and more recently with BeO (Yakel & Borie, 1963). In view of the importance of focusing collisions (Goland, 1962), which involve the preferential deposition of energy along simple crystallographic direc-