

Carbon Species in the Crystal Structures of Uranium-Transition-Element Carbides, UMC_2

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The carbon species present in the ternary uranium-transition-metal carbide phases UMC_2 ($M = Fe, Cr, W, Mo$), prepared by arc melting, have been investigated by mild hydrolysis, thermal analysis, and X-ray and (for $M = W, Mo$) neutron powder diffraction. For $M = W$ and Mo , the Rietveld neutron-diffraction profile analyses confirm that UMC_2 ($M = W, Mo$) are isostructural at room temperature with orthorhombic ($Pnma$) unit cell dimensions $a = 5.612(2)$, $b = 3.241(1)$, $c = 10.956(3)$ Å for $UMoC_2$ and $a = 5.614(2)$, $b = 3.245(1)$, $c = 10.964(4)$ Å for UWC_2 . Accurate determinations of carbon positions establish that carbon-carbon interatomic distances correspond to the presence of C_1 rather than C_2 groups in both crystal structures. For $M = Fe$ and Cr , the hydrolysis, thermal, and X-ray results also show the presence of isolated C_1 carbon units. © 1988 Academic Press, Inc.

1. Introduction

For ternary uranium-carbide phases UMC_2 with a transition metal (e.g., $M = V, Cr, Mo, W, Mn, Tc, Re, Fe, Co, Ni$) (1-9), which may form from fission products during the use of carbide [(U, Pu)C] nuclear fuel elements, there is considerable interest in the nature of the carbon species, whether C_2^{2-} dipoles as in UC_2 (10) or C_1 methanide units or both. Following the X-ray single-crystal structure analysis of $UCrC_2$ and the establishment from powder data that UMC_2 ($M = Cr, Mo, W$) are isomorphous orthorhombic structures, Nowotny's implication (11) that UWC_2 and $UMoC_2$ also con-

tain anionic C_2 dipoles was at first accepted and extended to other members of the series for which orthorhombic lattice parameters have been determined (12).

However, since a single-crystal X-ray analysis (with extinction and anomalous dispersion corrections) indicated the absence of short acetylide C-C distances in $UMoC_2$, Cromer *et al.* (13) suggested that the same might be true for UWC_2 and $UCrC_2$. From studies of the free energy of formation, Naraine and Bell (2) concluded that $UMoC_2$ is the only low-temperature equilibrium ternary compound in the U-Mo-C system; above 1400°C, carbon vacancies lead to nonstoichiometry. By sin-

gle-crystal X-ray analysis of a new tetragonal structure (space group $P4/nmm$), Gerss and Jeitschko (14) established very recently that $UCoC_2$ contains unusually long (1.48 Å) C_2 units, even though hydrolysis yields 35% ethylene. This "anti"- $PbFCl$ -type structure for $UCoC_2$, with which Gerss and Jeitschko find $UFeC_2$ and $UNiC_2$ isotypic, has a unit cell quite distinct from the tetragonal one previously accepted for $UFeC_2$ (9, 12, 15).

Hydrolysis data as a probe of carbon structure has been used by Jeitschko and Gerss (16) to support their prediction of lengthy C-C distances in $UCoC_2$ and in a series of $LnCoC_2$ phases. Thus, for $DyCoC_2$, on which they carried out an X-ray crystal-structure analysis with minute crystals, the gases evolved during acid hydrolysis include 74% C_2H_6 but no C_2H_2 . The accompanying equal amounts of C_3H_8 and CH_4 were presumably the result of surface polymerization of C_4H_{10} followed by thermal decomposition under the relatively severe (hot 2N HCl) reaction conditions. Milder hydrolysis with water vapor at room temperature (17) could well generate near 100% C_2H_4 from units appropriate to C-C separations around 1.4 Å. Further support for the approach to anionic species determination by carefully controlled mild hydrolytic examination (17) has come from the X-ray confirmations (18) of the prediction of C_1 and C_2 units in Er_3C_{13} . For stable compounds that do not decompose peritectically, thermal analysis can also be helpful since phase changes may be expected when, as the temperature is lowered, C_2 dipoles align from a previously disordered or free-rotation structure. Also, neutron diffraction has advantages over X-ray diffraction for the direct location of carbon atoms, and thus for the determination of the carbon structural units, in compounds with X-ray scattering dominated by heavy metals (10, 19, 20).

We report here an investigation of the structures of UMC_2 ($M = Fe, Cr, Mo, W$)

compounds (with some measurements on UWC_{2-x} compounds) prepared by high-temperature reaction of metal with UC_2 and by mild hydrolysis, thermal analysis, and X-ray diffraction; the room-temperature structures of $UMoC_2$ and UWC_2 have been examined in detail by neutron Rietveld powder-profile refinement.

2. Experimental

2.1 Preparation

Depleted uranium (>99%, Koch-Light Ltd.) was melted with Specpure (Johnson Matthey Ltd.) graphite rods in a small argon-arc furnace (21). Pieces (~0.4 g) of the nominal $UC_{2.0}$ so formed were then melted with appropriate stoichiometric quantities of Fe, Mo, W, and Cr (99.99%, Johnson Matthey Ltd.). Nonstoichiometric UWC_{2-x} compounds were prepared by direct fusion from weighed stoichiometric quantities; reaction yielded beads with negligible weight loss.

2.2 Hydrolytic and Structural Examination

After three meltings, beads of each compound were examined by X-ray powder photography, at room temperature and up to 1150°C (with a Pye-Unicam camera), and optical microscopy; details of the mild hydrolysis (17) and cooling (8) methods have been described previously. Parts of each preparation were then reexamined following annealing in a tantalum vacuum furnace at 1150 or 1350°C for 4 hr. An annealed sample of $UFeC_2$ was also examined (by Dr. T. C. Gibb, Department of Inorganic and Structural Chemistry, Leeds University) by Mössbauer spectroscopy (22).

2.3 Collection of Neutron-Diffraction Data

Neutron-diffraction powder patterns for $UMoC_2$ and UWC_2 were recorded at room

temperature on the CURRAN multi-counter diffractometer (wavelength 1.378 Å, 2θ range 5–107°, 2θ step increment 0.1°) on the DIDO reactor, AERE, Harwell, with the samples contained in a thin-walled 5-mm-diameter vanadium can and with a counting time of about 6 min per point. Other experimental conditions were as described earlier (10).

2.4 Rietveld Refinement of Neutron-Diffraction Data

For UMoC_2 , the starting point for the least-squares refinement was the orthorhombic structure described by Cromer *et al.* (13) but with the unit cell parameters given by Clark *et al.* (12). Refinement with a modified version (24) of the Rietveld powder-profile refinement program (25) incorporated the following crystal-structural and instrumental parameters as variables (33 variables in all):

(1) The orthorhombic (space group $Pnma$) unit cell parameters a , b and c .

(2) The x and z atomic positional coordinates for one uranium atom, one molybdenum atom, and two crystallographically independent carbon atoms (for each atom, the y -coordinate is fixed by symmetry at 0.25).

(3) The anisotropic thermal parameters B_{ij} for each of the four atoms, subject to the constraint (26) $B_{12} = B_{23} = 0.0$ for each atom.

(4) An overall scale factor, c .

(5) The three parameters U , V , and W in the equation $H^2 = U \tan^2 \theta + V \tan \theta + W$, where H is the full width at half-height of the Gaussian curve for the reflection at Bragg angle θ .

(6) A counter zero-point parameter, Z (25).

(7) A peak asymmetry parameter, P (25).

Starting values for the parameters were:

(1) Unit cell parameters from Clark *et al.* (12).

(2) Atomic positional coordinates from Cromer *et al.* (13).

(3) B_{ii} values from the isotropic temperature factors of Cromer *et al.* (13).

(4–7) Parameters determined as described before (10, 19). The neutron scattering amplitudes used were $b_U = 8.5$ fm, $b_{Mo} = 6.9$ fm, and $b_C = 6.65$ fm (27).

Early cycles of refinement yielded an R value of 0.21 but some of the thermal parameters were nonpositive-definite. By application of only $\frac{1}{100}$ of each calculated shift to the thermal parameters in each cycle of refinement, R was reduced to 0.186 after 11 cycles, but nonpositive-definite thermal parameters still appeared again beyond this point. When the off-diagonal elements (B_{13}) of the thermal parameter matrix were fixed at 0.0 for each atom (so that the total number of least-squares variables was reduced to 29), an R value of 0.153 could be obtained with all the on-diagonal thermal parameters remaining positive. In the final cycles of refinement (Fig. 1), the parameter shifts did not exceed 3% of the estimated standard deviation. A repetition of the refinement, with initial unit cell parameters from Cromer *et al.* (13) instead of Clark *et al.* (12), did not change the result significantly.

For UWC_2 , the first starting point for attempted refinement was the structure described by Nowotny *et al.* (11), but with the unit cell parameters given by Clark *et al.* (12), and with neutron scattering amplitude for tungsten $b_W = 4.8$ fm (27). With the same 33 variables as for UMoC_2 , this did not reduce the R factor below 0.68. However, repetition of the refinement, starting from the structure described by Cromer *et al.* (13) for UMoC_2 , gave an R factor of 0.20 after four cycles. Further refinement then followed a closely similar pattern to that for UMoC_2 , giving a final R value of 0.165 with 29 variables (Fig. 2). Refinements in which regions of the profile with the least satisfactory agreement (50–52°, 80–83°) were ex-

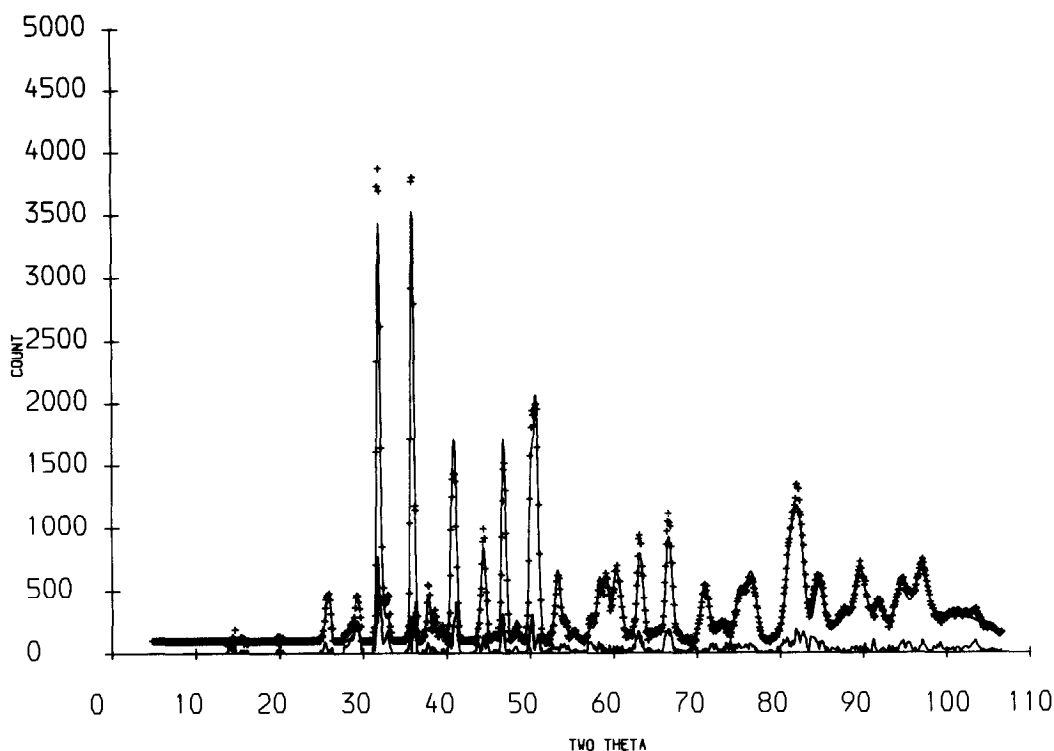


FIG. 1. Neutron powder-diffraction diagram for $UMoC_2$: solid line, calculated profile; crosses, experimental intensities; differences between these are shown in the bottom line.

cluded neither improved the overall agreement nor led to significantly different parameter values.

For both structures, the most significant correlations (derived from correlation matrices from the final refinement cycles) were between parameter shifts within the following groups:

- (i) Anisotropic thermal parameters (coefficients up to 0.6).
- (ii) Half-width parameters (coefficients greater than 0.9).
- (iii) Unit cell, zero-point, and asymmetry parameters (coefficients from 0.5 to 0.9).

Most correlation coefficients for atomic positional parameter shifts were less than 0.3.

Application of absorption corrections (coefficients μ in Table II calculated from

mass absorption coefficients U, 0.005; Mo, 0.009; W, 0.036; C, 0.00015 $cm^2 g^{-1}$) in accordance with the Hewat procedure (24) produced smaller corrections, ΔB , to the thermal parameters than the estimated standard deviations. Lists of observed and calculated intensities for both structures have been deposited.¹

¹ See NAPS document No. 04595 for 41 pages of supplementary materials from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance \$4.00 for microfiche copy or for photocopy, \$7.75 up to 20 pages plus \$0.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of \$15. Foreign orders add \$4.50 for postage and handling, for the first 20 pages, and \$1.00 for additional 10 pages of material. Remit \$1.50 for postage of any microfiche orders.

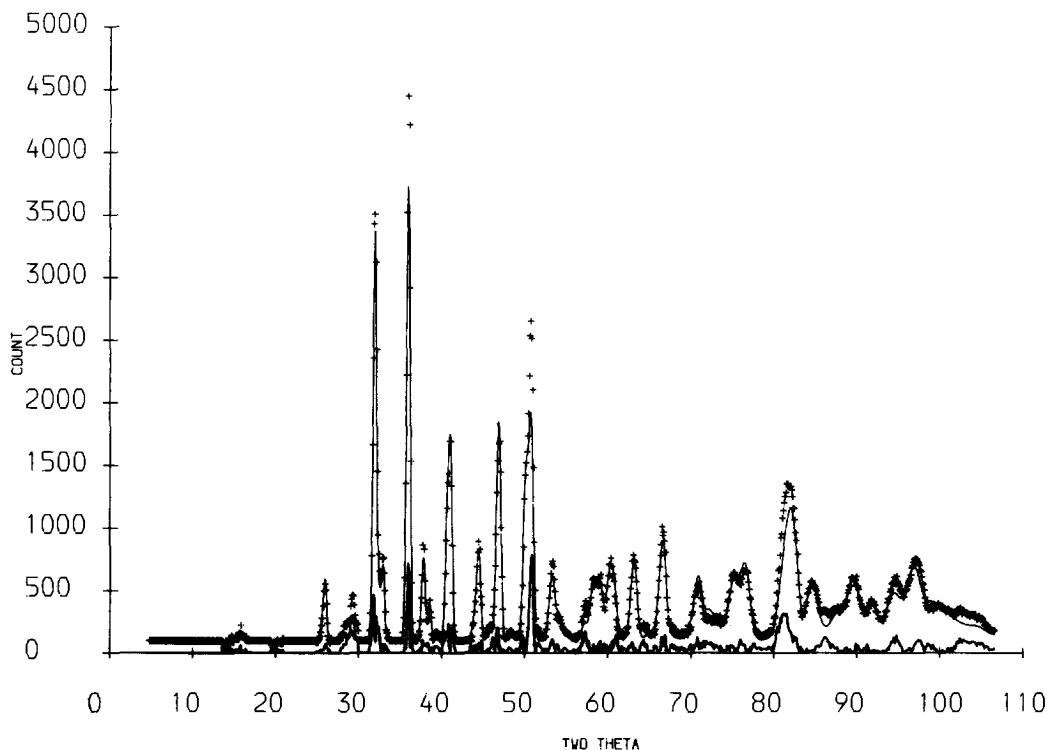


FIG. 2. Neutron powder-diffraction diagram for UWC_2 : solid line, calculated profile; crosses, experimental intensities; differences between these are shown in the bottom line.

3. Results and Discussion

Temperatures of arrests as UMC_2 beads cool in the arc furnace are shown in Table I; the change with carbon content in the melting behavior of UWC_{2-x} is of particular interest in that a phase change at 1970°C in the $x = 1.75\text{--}1.80$ range is indicated. X-ray powder photographs of the arc-cast beads confirmed the metallographic analyses in showing that, while $UMoC_2$, UWC_2 , and $UCrC_2$ were single-phase preparations, $UFcC_2$ was multiphase and contained UC_2 , Fe, and $UFcC_2$; this sample became single-phase after annealing in vacuum at 1150°C for 48 hr. In Fig. 3 the acicular crystalline nature of these preparations is demonstrated.

Table II gives the refined structural parameters for $UMoC_2$ and UWC_2 derived

from the neutron-diffraction profile analysis. The comparatively high final R values are comparable with those derived for other carbide structures (10) from analogous data (3500 counts for highest peak maximum). Application of the neutron data to disordered structures of UWC_2 and of $UMoC_2$ in which C_1 and C_2 groups were present in the ratios implied by the hydrolysis results led to very much higher R values.

3.1 $UFcC_2$

The change in the phases present after annealing is apparent from the results of the mild hydrolysis investigation. Arc-cast unannealed specimens gave rise to 21% C_2H_6 , 6.2% C_2H_4 , and 69.1% C_2H_2 , but only 3.7% CH_4 . Since after annealing the sample produced 100% CH_4 , it is concluded that only isolated C_1 atom units are present in the

TABLE I
COOLING-CURVE ARREST DATA FOR UMC_2 PHASES

Composition	Arrest	
	Temp./°C ^a	Magnitude of effect ^a
UFeC ₂ ^b	1590	Large
	1455	Small
UCrC ₂	1660	Large
	1565	Small
	1330	Very small
	1280	Very small
UWC ₂	2185	Large with strong supercooling
UWC _{1.9}	2150	Large with strong supercooling
UWC _{1.8}	2190	Large
	1960	Small
UWC _{1.75}	2155	Large
UMoC ₂ ^c	1980	Small
	1995	Very large

^a Uncorrected for emissivity effects.

^b UFeC₂ is reported to melt at 1615°C.

^c UMoC₂ melts at 2350°C but with a eutectic at 2200°C with carbon.

structure of UFeC₂. Such behavior seems typical for ternary carbides that contain iron. Thus all the $LnFeC_2$ samples required lengthy annealing before Jeitschko and Gerss (16) obtained single-phase samples.

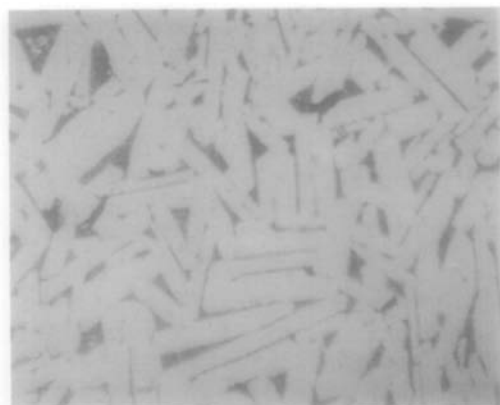


FIG. 3. Micrograph of acicular crystals of UWC₂ present in the arc-cast sample.

The Mössbauer spectrum of the annealed specimen contains isomer shifts at 0.351, 0.560, and 1.595 mm sec⁻¹ relative to an iron-foil standard; the two larger peaks at 0.351 and 0.560 mm sec⁻¹ suggest equal amounts of Fe O and Fe III, respectively, while the small peak is in a region characteristic of Fe II iron environments. X-ray examination at up to 1150°C revealed no structural change from the tetragonal cell determined at room temperature. The char-

TABLE II
RESULTS OF RIETVELD NEUTRON POWDER PROFILE REFINEMENTS FOR UMoC₂ AND UWC₂

Parameter ^a	UMoC ₂	UWC ₂
<i>a</i>	5.612(2)	5.614(2)
<i>b</i>	3.241(1)	3.245(1)
<i>c</i>	10.956(3)	10.964(4)
<i>x</i> (U)	0.0809(15)	0.0804(14)
<i>z</i> (U)	0.1433(6)	0.1428(6)
<i>x</i> (M)	0.4158(17)	0.4089(23)
<i>z</i> (M)	0.8977(7)	0.8956(10)
<i>x</i> (C(1))	0.1600(15)	0.1588(14)
<i>z</i> (C(1))	0.7487(8)	0.7470(9)
<i>x</i> (C(2))	0.7444(15)	0.7425(15)
<i>z</i> (C(2))	0.0072(7)	0.0122(7)
<i>B</i> ₁₁ (U)	0.22(0.31)	0.14(0.32)
<i>B</i> ₂₂ (U)	0.04(0.35)	0.19(0.36)
<i>B</i> ₃₃ (U)	0.24(0.36)	0.21(0.33)
<i>B</i> ₁₁ (M)	0.30(0.36)	0.05(0.50)
<i>B</i> ₂₂ (M)	0.31(0.43)	0.48(0.56)
<i>B</i> ₃₃ (M)	0.50(0.36)	0.48(0.46)
<i>B</i> ₁₁ (C(1))	0.69(0.36)	0.65(0.35)
<i>B</i> ₂₂ (C(1))	0.58(0.40)	0.61(0.41)
<i>B</i> ₃₃ (C(1))	0.56(0.44)	0.61(0.44)
<i>B</i> ₁₁ (C(2))	0.22(0.44)	0.15(0.46)
<i>B</i> ₂₂ (C(2))	0.03(0.47)	0.10(0.47)
<i>B</i> ₃₃ (C(2))	0.16(0.44)	0.09(0.41)
μ	0.03	0.13
ΔB	0.001	0.003
<i>R</i>	0.153	0.165
<i>R</i> _w	0.179	0.192

Note. Unit cell dimensions *a*, *b*, and *c* (Å), fractional atomic coordinates *x* and *z*, anisotropic temperature factors *B*_{*ii*} (Å²), absorption coefficients μ (cm⁻¹), absorption corrections ΔB , unweighted (*R*) and weighted (*R*_w) agreement factors.

^a *M* = Mo or W.

acterization by Gerss and Jeitschko (14) of a new actinoid-transition-metal carbide structure type in their analysis of UCoC_2 , with which UFeC_2 was said to be isotypic, may mean that UFeC_2 is polymorphic.

3.2 UCrC_2

The X-ray pattern for UCrC_2 from room temperature up to 800°C could be indexed on an orthorhombic unit cell (11); at 850°C the pattern corresponded to a tetragonal cell, $a = 3.56$, $c = 15.87$ Å, close to the $a = 3.636$, $c = 15.739$ Å cell reported earlier by Nowotny (11, 23) for a ternary phase of this composition. Although the cooling-curve technique had limited reliability in the region below 850°C , small arrests on the arc-cast beads were detected at the melting point and in the range 1280 – 1350°C (Table I). The most positive evidence for the presence of C_1 units in the orthorhombic structure was the 95% methane in the gases evolved during mild hydrolysis.

3.3 UWC_2

As the carbon stoichiometry in UWC_{2-x} was varied between $\text{UWC}_{1.75}$ and $\text{UWC}_{2.0}$, differences in the cooling curves pointed to a phase change at about 1960 – 1980°C for carbon-deficient specimens in the range $\text{C}_{1.80}$ – $\text{C}_{1.75}$. Above $\text{C}_{1.80}$, only a freezing point was observed, which reached a maximum at 2185°C for UWC_2 . The hydrolysis, carried out only on arc-cast nonannealed material, produced a mixture of 54% methane and 46% C_2 hydrocarbons. Since the metallographic and X-ray analyses together showed UWC_2 to be single-phase with well-formed acicular crystals, there arose the possibility that two types of carbon unit coexist in the crystal structure, about one-half as isolated carbon atoms and the other half as carbon pairs (12). This possibility prompted the neutron diffraction study.

A successful neutron powder profile refinement of the UWC_2 data enabled the unit cell parameters to be determined with im-

proved precision. Furthermore, the new atomic positional parameters confirm that UWC_2 is effectively isostructural with UMoC_2 and indicate unequivocally that UWC_2 does not contain short acetylenic C–C bonds.

3.4 UMoC_2

Of all the preparative reactions studied, that between UC_2 and Mo was the smoothest and easiest to carry out, with single-phase products achieved by cooling from the liquid state. While Naraine and Bell (2) have confirmed the single-phase as-cast material for alloys containing 46–50 at% carbon, they also showed that only the UMoC_2 composition remained single-phase when annealed at 1400°C ; this suggests that a metastable carbon-deficient phase can be quenched from high temperatures. Our X-ray analysis showed a single-phase orthorhombic material, isostructural with UWC_2 , $a = 5.62$, $b = 3.23$, $c = 10.90$ Å. The hydrocarbon gases produced by hydrolysis, 36% methane and 64% a mixture of ethane, ethylene, and acetylene, implied the presence of a mixed carbon structure, one-third isolated carbon atoms and two-thirds C_2 pairs.

However, profile refinement of the neutron powder data (Table II) confirms that UMoC_2 is isostructural with UWC_2 and has the crystal structure proposed by Cromer *et al.* (13) rather than that suggested by Nowotny *et al.* (11). In particular, with more accurate metal–carbon and carbon–carbon interatomic distances than from X-ray diffraction (Table III), the neutron analysis indicates the absence of short (acetylenic) carbon–carbon bonds for the composition UMoC_2 .

4. Summary and Conclusions

The apparent discrepancy between the hydrolysis and neutron-diffraction results for UMoC_2 and UWC_2 deserves some com-

TABLE III
INTERATOMIC DISTANCES (Å) IN $UMoC_2$ AND UWC_2

	$UMoC_2$ X-ray (13)	$UMoC_2$ neutron	UWC_2 neutron
U-2C(1)	2.40(3)	2.420(9)	2.428(8)
U-2C(1)	2.51(3)	2.464(9)	2.466(8)
U-C(2)	2.39(3)	2.406(11)	2.376(11)
U-2C(2)	2.48(2)	2.511(8)	2.551(8)
U-2M	3.274(4)	3.287(11)	3.321(13)
U-M	3.279(3)	3.282(11)	3.278(14)
U-2U	3.249(5)	3.241(1)	3.245(1)
M-C(1)	2.11(3)	2.110(13)	2.101(15)
M-C(1)	2.20(3)	2.174(13)	2.151(14)
M-2C(2)	2.16(2)	2.126(8)	2.092(9)
M-C(2)	2.20(3)	2.200(12)	2.268(14)
M-2M	2.902(4)	2.923(10)	2.987(13)
M-2U	3.274(4)	3.287(11)	3.321(13)
M-U	3.279(3)	3.282(11)	3.278(14)
C(1)-2C(1)	2.813(1)	2.806(12)	2.808(11)
C(1)-2C(1)	3.249(5)	3.241(1)	3.245(1)
C(1)-C(2)	2.87(4)	2.844(12)	2.881(12)
C(1)-M	2.11(3)	2.110(13)	2.101(15)
C(1)-M	2.20(3)	2.174(13)	2.151(14)
C(1)-2U	2.40(3)	2.420(9)	2.428(8)
C(1)-2U	2.51(3)	2.464(9)	2.466(8)
C(2)-C(1)	2.88(4)	2.844(12)	2.881(12)
C(2)-2C(2)	3.24(5)	3.241(1)	3.245(1)
C(2)-2M	2.16(2)	2.126(8)	2.092(9)
C(2)-M	2.20(3)	2.200(12)	2.268(14)
C(2)-U	2.39(3)	2.406(11)	2.377(11)
C(2)-2U	2.48(2)	2.511(8)	2.551(8)

Note. $M = Mo$ or W . Atom numbering scheme is as by Cromer *et al.* (13).

ment. From the hydrolysis data it would appear that $UMoC_2$ and UWC_2 , while being isostructural, contain varying ratios of C_1 and C_2 units, dependent upon preparation temperature, annealing conditions, and (for carbon-deficient samples) deficiency from 50 at% carbon. While X-ray diffraction may not be a very sensitive probe of such mixed carbon structures, neutron diffraction unambiguously establishes the presence of isolated carbon atoms. A possible explanation is that hydrolysis is performed on very small samples of the preparation which, de-

spite the X-ray results, may contain trace amounts of unreacted UC_2 ; since this hydrolyzes much more rapidly than the ternary carbide, the data will be biased. However, this explanation is hard to sustain in light of an apparently simple relationship (Fig. 4) between the percentage of evolved methane and the atomic radius of M in UMC_2 . It may be that, in nonannealed samples, the existence of nonstoichiometric phases, as implied by cooling curves and high-temperature X-ray analyses, is responsible for the disagreement. Previously we have shown that at high temperatures $2C_1 \rightarrow C_2^{2-}$ is favored (12) while Naraine and Bell (2) have detected C_1 vacancies in $UMoC_2$; formation of these would be favored by a mechanism such as that in (12) and would lead to catenated defects.

For structures formed when smaller atoms Fe, Mn, and Cr are inserted into the UC_2 structure, agreement between the several approaches is better; these small atoms lead to decatenated structures and wholly isolated C_1 units. Thus it might be argued that, as UC_2 dissolves these smaller atoms, there is sufficient strain on the C_2 units to lead to instability and C_2 decatenation. Conversely, substitution of Cr_2 by U in $Cr(Cr)_2C_2$ leads to a breakdown of the carbon chains known to be present in the chromium carbide. Interestingly, Gerss and Jeitschko (14) report that their hydrolysis of $UCoC_2$ (in 2N HCl, more vigorous than our aqueous hydrolysis of the Fe, Cr, W, Mo, and other carbides) yielded 62% C_2 hydrocarbons; our observation of some C_2 hydrocarbons from $UFeC_2$ applied only to unannealed material.

So far in the absence of the preparation of single crystals suitable for a combined mild hydrolysis and X-ray and neutron-diffraction study of stoichiometric and nonstoichiometric compounds, there is a strong balance of evidence that the stoichiometric UMC_2 ($M = Cr, Fe, Mn, Mo, W$) all exist as monocarbides.

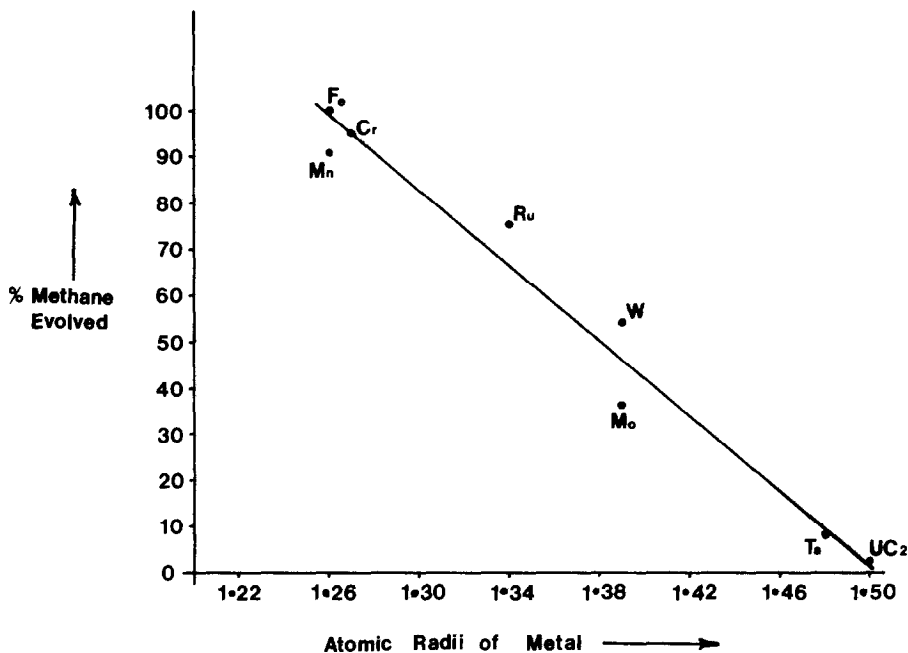


FIG. 4. Graph of percentage methane evolved in hydrolysis of UMC_2 phases as a function of M atomic radius.

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