A Neutron Powder Diffraction Study of W_2C

ANDERS HÅRSTA, STIG RUNDQVIST and JOHN O. THOMAS

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

In connection with studies of $\varkappa$-type transition metal carbides,[1] it became desirable to obtain accurate crystallographic data for W_2C to be used in subsequent structure refinements of $\varkappa$-carbides from multiphase X-ray and neutron diffraction data.[2] The crystal structure of W_2C can be described as a slightly distorted hexagonal close-packing of tungsten atoms, with carbon atoms occupying half of the octahedral interstices. The carbon atoms may be distributed in an ordered manner, the type and degree of ordering depending on temperature.[3,4]

We decided to investigate the W_2C structure by neutron diffraction in samples prepared under the same thermal conditions as those employed for the $\varkappa$-carbide syntheses. The results of a crystal structure refinement, together with some phase-analytical information, are reported in the present communication.

W_2C was synthesized from tungsten powder (H. C. Starck, Berlin, claimed purity 99.95 %) and tungsten monocarbide powder (H. C. Starck, Berlin, claimed purity 99.9 %). Appropriate mixtures of the powders were pressed into pellets, placed in zirconia crucibles and heated in a graphite tube resistance furnace at 1650 °C for 30 – 50 h. The products were examined by X-ray powder diffraction, and the composition was adjusted until a sample was finally obtained for which only very faint traces of WC were discernible on heavily overexposed powder films. The sample was ground to a fine powder in a tungsten carbide ball mill.

Chemical analysis was made as follows. Tungsten was determined by firing samples at 720 °C in air and weighing as WO_3. Carbon was determined as CO_2 in a LECO IR-12 instrument, and oxygen as CO in a Ströhlein Monomat 300 apparatus using standard techniques.

Neutron diffraction data were collected using the same equipment and experimental conditions as described in Ref. 1. The intensities were corrected for absorption using an experimental μR of 0.35. Refinement of the structure was carried out using a local modification NREF[5] of the full-matrix least squares powder profile analysis program of Rietveld.[6]

The neutron diffraction data indicated ordering of the carbon atoms corresponding to an ε-Fe_2N type structure. This is in agreement with results reported by Yvon, Nowotny and Benesovsky[7] for W_2C samples subjected to different heat-treatments between 2400 °C and 2100 °C. They observed that the carbon atoms were only partially ordered in samples quenched from higher temperatures.

The ideal ε-Fe_2N type structure of W_2C can be described in the space group $P\bar{3}1m$ (No. 162), with W in 6*k*: $x \sim 0.33$, $z \sim 0.25$; C(1) in 2*d* and C(2) in 1*a*. Preliminary calculations based on this structure model gave a poor agreement between observed and calculated intensities, indicating disorder and/or vacancies in the carbon atom sublattice. Refinement of the occupancy parameters for the two carbon positions indicated carbon deficiency and led to a substantially improved agreement. Introducing disorder by allowing carbon occupation of the remaining octahedral interstices at 2*c* and 1*b* (and a corresponding number of vacancies at 2*d* and 1*a* to retain the ideal 2/1 tungsten/carbon atomic ratio) also improved the agreement considerably. A model incorporating both types of defect structure simultaneously was therefore used in the final refinement, where the occupation parameters for all four types of octahedral carbon positions were allowed to vary. From the values returned by the program after convergence, the composition of the W_2C phase was calculated to be $W_2C_{0.85}$. To substantiate this result the sample was chemically analyzed. The result obtained: tungsten 96.77 %, carbon 2.83 %, corresponds to a W/C atomic ratio of 2/0.90. Unfortunately, the finely ground powder had been stored unprotected in air for more than a year before the chemical analysis was made. We suspected that some oxidation might have occurred. Analysis revealed an oxygen content of 0.5 %. Since the chemical state of the oxygen present could not easily be determined, the true composition of the W_2C phase remained somewhat uncertain.

A second W_2C sample (containing traces of WC) was synthesized under the same conditions as previously, now taking the necessary precautions to protect the sample as far as possible from air before analysis. Chemical analysis of the new sample gave (including estimated maximum errors): tungsten 97.14 ± 0.04 %, carbon 2.82 ± 0.03 %, oxygen 0.12 ± 0.02 %. Disregarding the impurities, this corresponds to a composition of $W_2C_{0.89 \pm 0.01}$ for the W_2C phase. Even if all oxygen present was dissolved interstitially in W_2C, the tungsten/non-metal atomic ratio would still be much larger than 2/1.

Neutron diffraction data were also recorded for the second sample, with much improved counting statistics following an improvement in the experimental facilities. Structure refinement was carried

Table 1. Structure data for W_2C. Space group $P\bar{3}1m$ (No. 162); $a=5.1852(4)$ Å, $c=4.7232(5)$ Å (24 °C).

Atom	Position	x	y	z	B(Å^2)	Occupancy (%)
W	6*k*	0.335(1)	0	0.2521(5)	0.11(8)	100
C(1)	2*d*	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{2}$	0.19(8)	65(1)
C(2)	1*a*	0	0	0		100
C(3)	2*c*	$\frac{1}{3}$	$\frac{2}{3}$	0		12(1)

out in the same manner as before, and the results agreed within experimental error with those obtained for the first sample. The following parameters were refined (*a*) *profile parameters:* half-width parameters (3), 2θ-zeropoint (1), wavelength (1); (*b*) *structural parameters:* scale factor (1), positional parameters (2), isotropic temperature factors (2), 2*c* and 2*d* occupancies (2). The occupancy for 1*a* tended to increase beyond 100 % and that for 1*b* tended to become negative. In the final refinement cycles these parameters were fixed at 100 and 0 %, respectively. Two isotropic temperature factors were refined, one for tungsten and one for carbon atoms. The scattering lengths used were: $b_W = 0.48 \times 10^{-14}$ m and $b_C = 0.665 \times 10^{-14}$ m.[8] The final R-values (for definitions, see Ref. 1) were: $R_I = 0.058$, $R_P = 0.144$, $R_{wP} = 0.122$. Unit cell dimensions were determined from X-ray powder films recorded in a Philips XDC-700 camera with Cu$K\alpha_1$ radiation and silicon ($a = 5.431065$ Å)[9] as internal calibration standard. The cell dimensions were refined by the least-squares program CELNE.[10]

The structure data are presented in Table 1. Corresponding interatomic distances (Å) are: W – 12 W: 2.90, 2.92 (×2), 2.93, 2.94 (×2), 2.99 (×4), 3.01 (×2); W – 2 C(1): 2.09; W – 2 C(3): 2.09; W – C(2): 2.11.

The phase analysis and the structure refinement consistently show that the W_2C phase is carbon-deficient under the conditions of synthesis employed in the present study. The presence of trace amounts of WC in the samples ensures that the composition of the W_2C phase must lie at the carbon-rich limit of the homogeneity range. It should be stressed, however, that the formula $W_2C_{0.89}$ does not necessarily represent the limiting composition at 1650 °C, since the cooling-rate for samples in the furnace was only moderately large (room temperature attained in about 10 min), while the carbon diffusion rate might initially be quite high during the cooling process.

A third W_2C sample was prepared under the same thermal conditions as before for the purpose of estimating the width of the homogeneity range. X-Ray phase analysis now indicated faint traces of α-W. Chemical analysis gave a composition of $W_2C_{0.86\pm0.01}$. The unit cell dimensions [$a = 5.1833(5)$ Å, $c = 4.7240(6)$ Å] were barely significantly different from those found for the carbon-rich preparations.

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