

## A Neutron Powder Diffraction Study of the $\kappa$ -Phase in the Co-W-C System

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The crystal structure of the  $\kappa$ -(Co-W-C) carbide has been refined from neutron powder diffraction data using the Rietveld profile analysis method. The results obtained are as follows: space group  $P6_3/mmc$  (No. 194), W(1) in  $12k$ :  $x=0.2038(3)$ ,  $z=0.0682(5)$ ; W(2) in  $6h$ :  $x=0.5497(4)$ ; W(3) in  $2a$ ; Co in  $6h$ :  $x=0.8868(9)$ ; C(1) in  $6g$ ; C(2) in  $2c$ . The  $2c$  position is only 41 % occupied, suggesting the approximate formula  $\text{Co}_3\text{W}_{10}\text{C}_{3.4}$ . The unit cell dimensions for the sample investigated were:  $a=7.8304(4)$  Å,  $c=7.8361(6)$  Å.

The occurrence of a hexagonal phase with a composition corresponding approximately to the formula  $\text{Co}_3\text{W}_{10}\text{C}_4$  was reported by Rautala and Norton,<sup>1</sup> who denoted this phase by the letter  $\kappa$ . The crystal structure of this carbide was examined by Schönberg<sup>2</sup> by X-ray powder diffraction methods. He proposed a structure with  $P6_3/mmc$  symmetry, involving 12 W on a  $12k$  position, 6 W and 6 Co distributed randomly between two  $6h$  positions, 6 C on  $6g$  and 2 C on  $2c$ . Pollock and Stadelmaier<sup>3</sup> reported phase analytical results indicating a lower carbon content than that corresponding to Schönberg's formula, they thus suggested that the  $2c$  position was vacant. In a series of studies, Nowotny, Benesovsky and coworkers<sup>4-7</sup> have investigated a large number of phases with crystal structures closely related to that of  $\kappa$ -(Co-W-C). Drawing the analogy with all such phases, Rogl and Nowotny<sup>7</sup> suggested that the  $2a$  position in the  $\kappa$ -(Co-W-C) structure was filled with metal atoms.

In connection with recent studies of the Co-W-C system made by Johansson<sup>8</sup> it was decided to examine the  $\kappa$ -(Co-W-C) structure more closely using neutron diffraction tech-

niques, particularly in view of the relatively large scattering length for carbon compared with that for tungsten and cobalt. The results of this study are reported in the present paper.

### EXPERIMENTAL DETAILS

*Preparation.* The starting materials for the synthesis of Co-W-C alloys were: tungsten powder from H.C. Starck, Berlin, claimed purity 99.95 %; tungsten monocarbide from H. C. Starck, Berlin, claimed purity 99.9 %; cobalt sponge from Johnson, Matthey & Co. Ltd., London; less than 15 ppm metallic impurities. The components were mixed by wet grinding in benzene in a tungsten carbide ball-mill, pressed into pellets and heated (after evaporation of the benzene) in a graphite tube resistance furnace under a protective atmosphere of argon. The samples were contained in zirconia crucibles and heated at 1750 °C for periods of about 7 h. The sample used for neutron diffraction measurements weighed about 30 g and was carefully ball-milled. An X-ray powder diffraction examination showed the sample to contain traces of  $(\text{Co,W})_6\text{C}$  and small amounts of tungsten metal.

*X-Ray diffraction.* Phase analyses and determinations of unit cell dimensions were made by X-ray powder diffraction. A Hägg-Guinier type camera (Philips XDC 700) with  $\text{CrK}\alpha_1$  radiation was used (silicon internal calibration standard:  $a=5.431065$  Å).<sup>9</sup> Unit cell dimensions were refined by the least-squares method using an IBM 1800 computer and a local program CELNE.<sup>10</sup>

*Neutron diffraction.* The neutron powder data were collected at room temperature ( $\sim 298$  K) at the R2 reactor, Studsvik, Sweden, using a Ferranti four-circle diffractometer modified to operate as a powder instrument. The reactor beam from a radial channel was passed through a double-crystal monochromator<sup>11</sup> using the 220 planes of two copper crystals to give a wavelength of 1.56 Å and a flux

at the specimen of  $10^6$  neutrons  $\text{cm}^{-2} \text{s}^{-1}$ . The specimen was contained in a 12 mm diameter vanadium tube of length 4 cm. The volume of powder irradiated was approximately  $3.5 \text{ cm}^3$ . The step-scan covered the range  $10-103^\circ$  (in  $2\theta$ ) in steps of  $0.08^\circ$ . Measuring time per point was about 12 min.

The presence of cobalt in the specimen meant that absorption was not negligible (experimental  $\mu R$  was 0.40). No correction for absorption was made, however. The estimated effect of this neglect on the refined value of the overall temperature factor is to increase it from 0.16 to  $0.25 \text{ \AA}^2$ . The effect on refined positional and occupancy parameters is likely to be insignificant.

The presence of  $(\text{Co}, \text{W})_6\text{C}$  and tungsten impurities resulted in troublesome additional peaks in the profile. The  $(\text{Co}, \text{W})_6\text{C}$  peaks were treated by calculating the  $2\theta$  regions most seriously affected and removing them from the profile. The tungsten peaks were treated partly in the same way and partly by making a run on pure tungsten and subtracting its estimated contributions from the profile.

## STRUCTURE REFINEMENT

The structure refinements were made on an IBM 370/155 computer at the Uppsala Data Center using a local modification NREF<sup>12</sup> of the full-matrix least-squares neutron powder profile analysis program of Rietveld.<sup>13</sup> The program assumes a Gaussian contribution from each reflection contributing to the profile, and minimizes the quantity  $\chi^2 = \sum_i w_i |y_i(\text{obs}) - \frac{1}{c} y_i(\text{calc})|^2$ , where  $w_i$  is the weighting function applied to  $y_i$ , the number of counts at  $2\theta$  (after subtraction of background), and  $c$  is a scale factor. Three  $R$  values are calculated by the program:

$$R_I = \frac{\sum_k |I_k(\text{obs}) - \frac{1}{c} I_k(\text{calc})|}{\sum_k I_k(\text{obs})}$$

$$R_{\text{profile}} = \frac{\sum_i |y_i(\text{obs}) - \frac{1}{c} y_i(\text{calc})|}{\sum_i |y_i(\text{obs})|}$$

$$R_{\text{profile}}(\text{weighted}) = \left[ \frac{\sum_i w_i |y_i(\text{obs}) - \frac{1}{c} y_i(\text{calc})|^2}{\sum_i w_i |y_i(\text{obs})|^2} \right]^{\frac{1}{2}}$$

where  $I_k$  denotes the integrated intensity of a reflexion  $k$ .  $R_I$  can be compared with the more familiar  $R(F^2)$  of single crystal work.

An initial structure refinement was made using Schönberg's<sup>2</sup> positional parameters with W in  $12k$ ,  $6h$  and  $2a$ ; Co in  $6h$  and C in  $6g$ . The refinement converged with the  $R$  values 0.117, 0.163 and 0.166.

In a subsequent series of refinements, the  $2c$  position was assumed to be occupied by carbon atoms and the occupancy allowed to refine. The agreement between observed and calculated intensities now improved considerably, with new  $R$  values: 0.078, 0.132 and 0.136. The degree of occupation for the  $2c$  position was found to be 0.415(17). In further attempts to improve the structural model, the occupancies of the  $12k$ ,  $6h$  and  $2a$  positions were also refined, but the results indicated no significant deviation from the metal atom distribution assumed initially.

The final structural data are presented in Table 1. These values were obtained from a refinement, where the refined parameters were the following: (a) *profile parameters*: halfwidth parameters (3),  $2\theta$  zero-point (1), wavelength (1). (b) *structural parameters*: scale factor (1), positional parameters (4),  $2c$  occupancy (1), overall isotropic temperature factor (1). The scattering lengths used were  $b_{\text{Co}} = 0.25 \times 10^{-14} \text{ m}$ ,  $b_{\text{W}} = 0.48 \times 10^{-14} \text{ m}$  and  $b_{\text{C}} = 0.665 \times 10^{-14} \text{ m}$ .<sup>14</sup> The profile fit obtained is shown in Fig. 1.

Table 1. Structure data for  $\kappa$ -(Co-W-C). Space group  $P6_3/mmc$  (No. 194);  $a = 7.8304(4) \text{ \AA}$ ,  $c = 7.8361(6) \text{ \AA}$ . Overall temperature factor  $B = 0.16(5) \text{ \AA}^2$ .

Atom	Position	$x$ ( $y = 2x$ )	$z$	Occupancy
W(1)	$12k$	0.2038(3)	0.0682(5)	1
W(2)	$6h$	0.5497(4)	$\frac{1}{2}$	1
W(3)	$2a$	0	0	1
Co	$6h$	0.8868(9)	$\frac{1}{2}$	1
C(1)	$6g$	$\frac{1}{2}$	0	1
C(2)	$2c$	$\frac{1}{2}$	$\frac{1}{2}$	0.415(17)

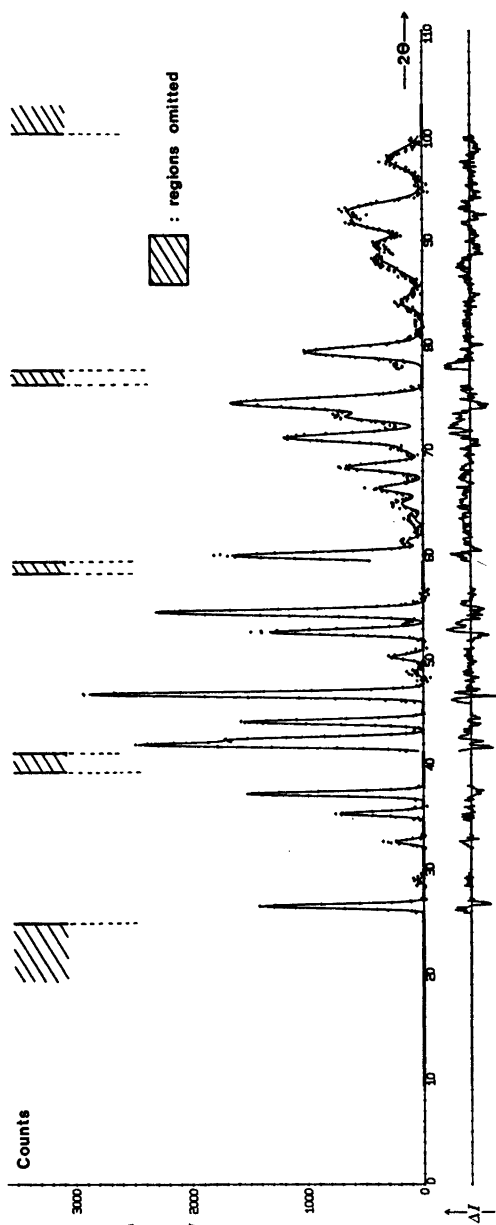


Fig. 1. Neutron powder profile fit for  $\kappa$ -(Co-W-C).

#### DISCUSSION OF THE STRUCTURE

A projection of the  $\kappa$ -(Co-W-C) structure along the hexagonal axis is shown in Fig. 2. The carbon atoms have only tungsten atoms as their nearest neighbours: in an octahedral

configuration for the  $6g$  carbon atoms, and in a trigonal prismatic configuration for the  $2c$  carbon atoms. The tungsten atoms situated at  $2a$  are surrounded icosahedrally by six  $12k$  tungsten atoms and six cobalt atoms. The metal atoms at the  $12k$  and  $6h$  positions have more irregular coordinations. A list of interatomic distances is given in Table 2.

Although the  $\kappa$ -(Co-W-C) structure has been the subject of much discussion in the past, the only experimental basis was Schönberg's<sup>2</sup> X-ray powder diffraction analysis reported in 1954. Schönberg succeeded in determining the positional parameters for the  $12k$  and the two  $6h$  type metal atoms but failed to observe that the  $2a$  position is also filled with metal atoms. The missing  $2a$  atoms probably forced him to assume a random distribution of cobalt and tungsten atoms on the two  $6h$  positions, in order to obtain a reasonable agreement between observed and calculated intensities. It should be pointed out that the analysis of the powder diffraction data is particularly difficult because of the numerous overlaps among the lines, brought about by the nearly equal lengths of the  $a$  and the  $c$  axes.

As regards the number and distribution of the carbon atoms in the structure, Schönberg's proposal was based solely on considerations of the available space in the unit cell, combined with the value for the carbon content as determined by chemical analysis.

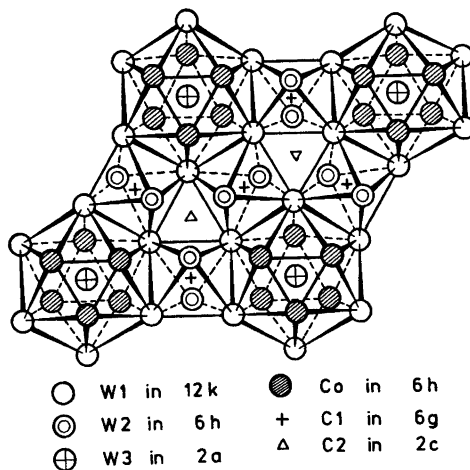


Fig. 2. The structure of  $\kappa$ -(Co-W-C) projected along the hexagonal axis.

Table 2. Interatomic distances (Å) in  $\kappa$ -(Co-W-C). Distances up to 3.8 Å are included. When greater than one, the number of equivalent distances from a central atom to its neighbours precedes the notation for the neighbouring atom.

W(1)–2C(1)	2.124(2)	W(2)–2C(1)	2.072(2)
C(2)	2.262(4)	2Co	2.587(6)
Co	2.780(5)	2W(2)	2.746(10)
2Co	2.790(5)	C(2)	2.935(6)
W(3)	2.815(4)		
W(1)	2.849(9)	W(3)–6Co	2.489(4)
2W(2)	2.928(5)		
2W(1)	2.964(5)	Co–2Co	2.660(10)
2W(2)	3.006(5)	4C(1)	3.334(6)
2W(1)	3.043(5)		
		C(1)–2C(2)	2.991(1)

In a general survey of alloy structures, Kripyakevich<sup>15,16</sup> pointed out the close relationship between the metal atom lattices in  $\kappa$ -(Co-W-C) and  $Mn_3Al_{10}$ ,<sup>17</sup> the icosahedral hole at  $2a$  being filled with aluminium atoms in  $Mn_3Al_{10}$  but empty in the  $\kappa$ -carbide according to Schönberg. This relationship was further emphasized by Reiffenstein, Nowotny and Benesovsky,<sup>4</sup> who prepared a number of  $\kappa$ -carbides in quaternary systems of the types Mo-(Mn, Fe, Co, Ni, Cu)-Al-C and W-(Mn, Fe)-Al-C. In the structures of these carbides, Reiffenstein *et al.* assumed that the icosahedral  $2a$  position is occupied by aluminium atoms, while the carbon atoms occupy the octahedral  $6g$  position, leaving the trigonal prismatic  $2c$  position empty. In later studies, Rogl, Nowotny and Benesovsky<sup>5-7</sup> discovered the occurrence of  $\kappa$ -type phases composed of only transition metal components in many of the ternary systems {Zr, Hf}-(Mo, W)-{Fe, Co, Ni}. They were also able to identify a number of  $\kappa$ -borides and  $\kappa$ -oxides in the systems {Zr, Hf}, {Mo, W, Re, Os}-B and {Zr, Hf}-{Mo, W, Re}-O. A single crystal structure determination of  $\kappa$ -(Hf-Mo-B) gave the following results:<sup>8</sup> the  $12k$  position is occupied by hafnium atoms, the distribution of hafnium and molybdenum atoms on the two  $6h$  positions is completely ordered, molybdenum atoms occupy the  $2a$  position, and the boron atoms occupy the  $2c$  position. For the  $\kappa$ -phases formed by metallic components only, a distribution of the atoms similar to that in the  $\kappa$ -borides was assumed, with iron, cobalt or nickel replacing the boron atoms on the  $2c$  site. This suggestion was supported<sup>8</sup> by qualitative powder diffraction

intensity data for  $Hf_2Mo_4Co$ . The structures of these phases are accordingly close counterparts of the  $Co_4Al_{10}$  structure,<sup>18</sup> where, in contrast to  $Mn_3Al_{10}$ , the  $2c$  position is also filled. For the  $\kappa$ -oxides, on the other hand, Rogl *et al.* suggested that the  $2c$  position is empty, and the oxygen atoms occupy only the octahedral  $6g$  position.

By analogy with all these  $\kappa$ -phases, Rogl and Nowotny<sup>7</sup> proposed that the ternary  $\kappa$ -carbides also have a metal lattice of the  $Mn_3Al_{10}$  type, with the icosahedral  $2a$  hole filled, and an ordered distribution of the two types of metal atom on the two  $6h$  sites. As far as the carbon atoms are concerned, Rogl and Nowotny observed that a situation intermediate between the boride and the oxide structures is conceivable, but they favoured a distribution of the carbon atoms on the octahedral  $6g$  site exclusively.

The present results are in good agreement with the proposal by Rogl and Nowotny regarding the  $Mn_3Al_{10}$ -type metal sublattice. The neutron diffraction data clearly demonstrate that the  $2a$  icosahedral holes are filled with tungsten atoms, and the ordered distribution of the tungsten and cobalt atoms on the  $6h$  positions is also evident. The ordered distribution provides a near environment of tungsten atoms only about the carbon atoms. This conforms with the well-known rule for carbides in steel and other transition metal alloys: the carbon atoms tend to be associated with those metal atoms which have the lowest group number in the periodic table.

While the neutron data show clearly that the  $6g$  position is filled with carbon atoms, the

interpretation of the scattering power associated with the  $2c$  position is less definitive. Assuming carbon atoms in  $2c$ , the scattering power observed corresponds to about 41 % occupation. The structure would then contain carbon atoms in both octahedral and trigonal prismatic coordination simultaneously. This is perhaps not surprising, since octahedral coordination occurs in  $W_2C$ , and trigonal prismatic coordination in WC. The W–C distances for the  $6g$  carbon atoms agree closely with those in  $W_2C$ , while the W–C distances for carbon atoms in  $2c$  are appreciably larger than those in WC. This difference might be associated with the vacancy formation on the  $2c$  site.

If, on the other hand, the scattering power at  $2c$  were due to cobalt atoms, full occupancy has to be assumed. The corresponding W–Co distances would then be abnormally short, and furthermore, the W/Co atomic ratio in the carbide would be 2.5. In all previous determinations of the W/Co ratio in  $\kappa$ -(Co-W-C),<sup>1-3</sup> it has been found to be 3 or larger, and recent microprobe measurements<sup>8</sup> have given values of the order of 3.5. It is conceivable that higher W/Co ratios might be obtained through a partial W/Co substitution on the  $6h$  cobalt site, but the present neutron diffraction data do not support this hypothesis.

Accordingly, the safest conclusion seems to be that the  $2c$  position is partially occupied by carbon atoms. Although less likely, the possibility of a  $2c$  occupation by a mixture of carbon and cobalt atoms cannot be entirely ruled out, however.

It should be mentioned that  $\kappa$ -(Co-W-C) has a range of homogeneity.<sup>8</sup> This is indicated by small but significant differences in lattice parameters observed for this carbide between alloys from the various two- and three-phase areas surrounding the  $\kappa$ -phase in the Co-W-C equilibrium diagram. The variations in composition may be connected with a varying carbon atom occupation of  $2c$ , with Co/W substitution in the metal lattice, or perhaps with both mechanisms operating simultaneously. In this context, an interesting observation by Rogl *et al.*<sup>6</sup> is worth mentioning. For the  $\kappa$ -phases formed between transition metal components only, the unit cell volumes are abnormally small by comparison with the corresponding  $\kappa$ -borides, where iron, cobalt

and nickel atoms have been replaced by boron atoms on the  $2c$  position. Furthermore, the unit cell volumes for iron-, cobalt-, and nickel-containing  $\kappa$ -phases increase in the order mentioned, while a decrease should be expected judging from the normal size for iron, cobalt and nickel atoms. A similar situation occurs among the  $\kappa$ -carbides, where  $\kappa$ -(Fe-W-C)<sup>8</sup> has a smaller unit cell volume than  $\kappa$ -(Co-W-C).

In order to investigate these problems in more detail, a study of  $\kappa$ -(Fe-W-C) has been started using both diffraction methods and <sup>57</sup>Fe Mössbauer spectroscopy. The latter technique will hopefully provide additional structural information not accessible by X-ray or neutron diffraction measurements.

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