JOURNAL OF SOLID STATE CHEMISTRY **49**, 118–122 (1983)

A Neutron Powder Diffraction Study of the κ Phase in the Fe–W–C System

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Received January 3, 1983, in revised form February 28, 1983

The crystal structure of the κ-carbide in the Fe–W–C system has been refined from neutron powder diffraction data using the Rietveld profile analysis method. κ-(Fe–W–C) is isostructural with κ-(Co–W–C); space group $P6_3/mmc$; unit cell dimensions a = 7.7982(2) Å, c = 7.8298(4) Å. The structure refinement indicates Fe/W substitution at two of the tungsten sites, and 46% vacancies at one of the carbon sites. The composition corresponds to the formula $Fe_{3+x}W_{10-x}C_{4-y}$, with x = 0.57(3) and y = 0.46(1).

Introduction

The occurrence of κ-type carbides in the ternary systems {Fe,Co,Ni}–W–C was first reported by Rautala and Norton (*1*). No unit cell dimensions were given, however, for the iron- and nickel-containing κ phases. These data were later supplied by Kuo for the phase κ-(Ni–W–C) (*2*) and by Pollock and Stadelmaier for the phase κ-(Fe–W–C) (*3*). The observed unit cell volumes show an interesting trend: they increase in the order Fe→Co→Ni, whereas the opposite would have been expected on the basis of the atomic radii of the elements concerned. Similar trends have also been observed among other κ phases (*4–6*). In an earlier investigation, the structure of the κ phase in the Co–W–C system was determined (*7*), and the present study of the κ phase in the Fe–W–C system was embarked upon primarily to investigate the cause of the abovementioned unit cell volume anomaly.

Experimental Details

Preparation

The starting material for the syntheses of the κ-(Fe–W–C) alloys were tungsten powder from H. C. Starck, Berlin (claimed purity 99.95%); tungsten monocarbide powder from H. C. Starck, Berlin (claimed purity 99.9%); iron sponge from Johnson & Matthey, London (less than 10 ppm metallic impurities). The iron sponge initially contained considerable amounts of oxygen as surface oxide; this was removed by hydrogen reduction at 600°C for 1 hr. 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 con-

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0022-4596/83 $3.00

tained in zirconia crucibles and heated at 1600°C for periods of about 50 hr. After the heat treatments, the zirconia crucibles were seen from X-ray powder photographs to be coated with zirconium carbide. It was very difficult to maintain a constant carbon activity in the furnace during the reaction period. Despite numerous attempts, it was impossible to obtain a κ-carbide sample free from neighboring phases in the Fe–W–C system. A previous accurate determination of neutron diffraction data for W_2C (*8*) made it possible to correct the κ-phase diffraction data for the presence of W_2C; a two-phase sample containing W_2C could thus be taken for the neutron diffraction experiment.

X-Ray Diffraction

Phase analysis and determination of unit cell dimensions were made by X-ray powder diffraction using a Guinier–Hägg-type focusing camera with $CrK\alpha_1$ radiation and Si ($a = 5.431065$ Å) (*9*) as internal standard. Unit cell dimensions were refined using the local program CELNE (*10*).

Neutron Diffraction

The neutron powder data were collected using the same equipment and under the same experimental conditions as those described in Ref. (*7*) (the step-scan now covered the 2θ range 8.08–109.12°). Absorption correction was made after the refinements according to a suggestion by Hewat (*11*). The experimental μR was 0.37, giving $\Delta B = 0.08$ Å^2; this quantity was added to the temperature factors obtained in the final refinement.

Chemical Analysis

Tungsten. Tungsten was determined as WO_3 according to Ref. (*12*).

Iron. Iron was present in several locations following the determination of the tungsten content: (i) in the filtrate from the cinchonine–benzoinoxime precipitate of tungsten; (ii) in a smaller amount in the remainder from the purification of WO_3; (iii) in very small amounts in the filtrate after this purification. After several stages of purification according to Nydahl (*13*), the three parts were brought together; the iron was reduced in a cadmium reductor and its amount determined by titration with cerium(IV) sulfate. The procedure was checked by analyzing a known mixture of tungsten and iron; this indicated the relative accuracy to be 0.1% for the tungsten analysis and 0.2–0.3% for the iron analysis.

Carbon. Carbon was determined as CO_2 in a Strölein Monomat 300 apparatus using standard techniques.

The result of the analysis was 85.84(9)% W, 10.06(3)% Fe, and 2.22(3)% C. This gives a total of 98.12(10)%. A check for impurities was made by X-ray fluorescence spectrometry, and the following elements were detected: Zr ~ 1%, Ca ~ 0.2%, and Si ~ 0.2%. It seems likely that zirconium and at least part of the calcium comes from the calcium-stabilized zirconia crucible used in the synthesis. The presence of silicon may be due to accidental contamination by silica-containing insulation material inside the furnace. Oxygen was not determined. Assuming Zr to be present as zirconium carbide, and Ca and Si to be bound to oxygen, the calculated oxygen content would be ~0.3%.

An attempt to estimate the W_2C content was made as follows. Starting from the original sample, two additional samples were prepared by adding 20 and 40% W_2C, respectively. Powder diffraction films were recorded for the three samples, and the intensities of the W_2C reflections relative to the κ-phase reflections determined. Assuming a linear relationship between W_2C content and those relative intensities, the W_2C content was estimated to be 8(2)%.

Structure Refinement

The structure refinements were performed with a NORD 100 computer using a local multiphase version PULXN (*14*) of the full-matrix least-squares neutron powder profile analysis program of Rietveld (*15*). The profile shape is here assumed to be Gaussian with a correction for asymmetry. For a definition of the agreement indices R_I, R_P, and R_{wP}, see (*7*).

An initial structure refinement was made using the atomic coordinates of κ-(Co–W–C) (*7*) as starting values for the positional parameters (with iron replacing cobalt). Unit cell dimensions for κ-(Fe–W–C) and W_2C obtained from the X-ray measurements were used, and only the neutron wavelength was refined. Since W_2C was present only in minor amounts no attempt was made to refine its structural parameters. Values were taken from (*8*) and only an overall occupation parameter (*14*) for all atoms (taking account of different atom-site multiplicities) was refined for this phase. The refinement converged with *R* values 0.068, 0.096, and 0.115, respectively. In the subsequent refinements, the possibility of iron substitution at the 2*a* position was tested. This improved the agreement between observed and calculated intensities considerably, to give the new *R* values 0.034, 0.069, and 0.082. The degree of iron substitution was found to be 41%. In further attempts to improve the model, the occupancies of the 12*k* and the two 6*h* sites were allowed to refine. Some iron substitution at the 6*h* position was indicated; this site was initially assumed to be occupied by tungsten only. The possibility of carbon being present at the octahedral 4*f* site ($z \sim 0.59$) instead of at the trigonal prismatic 2*c* site was also tested; no significant improvement of the initial model was indicated.

Final structural data are presented in Table I. These values were obtained from a refinement where the refined parameters

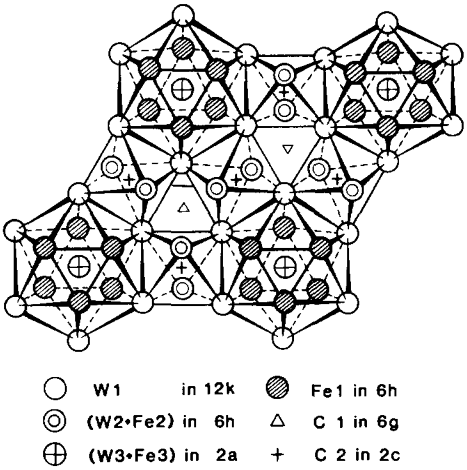

FIG. 1. The structure of κ-(Fe–W–C) projected along the hexagonal axis.

TABLE I

STRUCTURE DATA FOR κ-(Fe–W–C) (STANDARD DEVIATIONS GIVEN IN PARENTHESES. SPACE GROUP $P6_3/mmc$ (No. 194), $Z = 2$. CELL DIMENSIONS: $a = 7.7987(2)$ Å, $c = 7.8298(4)$ Å)

Atom	Position	$x(y = 2x)$	z	Occupation (%)	B(Å^2)
W(1)	12*k*	0.2008(2)	0.0673(3)	100	0.41(4)
W(2)	6*h*	0.5507(3)	$\frac{1}{4}$	95.9(8)	
W(3)	2*a*	0	0	55(1)	
Fe(1)	6*h*	0.8925(1)	$\frac{1}{4}$	100	0.47(3)
Fe(2)	6*h*	0.5507(3)	$\frac{1}{4}$	4.1(8)	
Fe(3)	2*a*	0	0	45(1)	
C(1)	6*g*	$\frac{1}{2}$	0	100	0.50(4)
C(2)	2*c*	$\frac{1}{3}$	$\frac{1}{4}$	54(1)	

were the following: (a) *profile parameters:* half-width parameters (3), 2θ zero-point (1), wavelength (1), asymmetry parameter (1); (b) *structural parameters:* scale factor (1), overall occupation parameter for W_2C (1), positional parameters (4), occupation parameters (3), isotropic temperature factors (3). The scattering lengths used were $b_{Fe} = 9.5$ fm, $b_W = 4.8$ fm, and $b_C = 6.65$ fm (*16*). The final R values were 0.031, 0.065, and 0.077 (expected $R = 0.050$). The refined overall occupation parameter for W_2C indicated its content to be 9.0(2)%. A list of observed and calculated intensities for all points in the profile has been deposited at the Institute of Chemistry, Uppsala, and can be obtained on request.

TABLE II

INTERATOMIC DISTANCES (Å) IN κ-(Fe–W–C) (DISTANCES SHORTER THAN 3.80 Å ARE LISTED. ESTIMATED STANDARD DEVIATIONS ARE GIVEN IN PARENTHESES. SITES W(2) AND W(3) ARE PARTIALLY OCCUPIED BY IRON)

W(1)–	2 C(1)	2.126(1)	Fe(1)–	2 W(3)	2.437(1)
	C(2)	2.292(2)		2 Fe(1)	2.514(1)
	2 Fe(1)	2.752(2)		2 W(2)	2.642(2)
	W(3)	2.763(2)		4 W(1)	2.752(2)
	Fe(1)	2.785(2)		2 W(1)	2.785(2)
	W(1)	2.862(4)		4 C(1)	3.367(1)
	2 W(1)	2.909(2)	C(1)–	2 W(2)	2.074(1)
	2 W(2)	2.935(2)		4 W(1)	2.126(1)
	2 W(2)	3.004(2)		2 C(2)	2.983(1)
	2 W(1)	3.101(3)		4 Fe(1)	3.367(1)
W(2)–	2 C(1)	2.074(1)	C(2)–	6 W(1)	2.292(2)
	2 Fe(1)	2.642(2)		3 W(2)	2.936(1)
	2 W(2)	2.713(1)		6 C(1)	2.983(1)
	4 W(1)	2.935(2)			
	C(2)	2.936(1)			
	4 W(1)	3.004(2)			
W(3)–	6 Fe(1)	2.437(1)			
	6 W(1)	2.763(2)			

Discussion

As mentioned in the Introduction, the κ-type carbides show unexpected behavior in their unit cell volumes. The κ phase in the Fe–W–C system has a smaller volume than in the Co–W–C system. The cobalt-containing κ phase has an ordered metal–atom distribution with tungsten at the 12*k*, 2*a*, and one of the 6*h* sites, and with cobalt on the other 6*h* site (*7*). In contrast, the κ phase in the Fe–W–C system exhibits iron substitution at both the 2*a* site and at the tungsten 6*h* site. Since the atomic radius of tungsten is much larger than that of iron, Fe/W substitution causes a decrease in the unit cell volume. This explains the smaller cell volume of κ-(Fe–W–C) as compared to that of κ-(Co–W–C). As seen from Table I, the degree of iron substitution is 45(1)% at the 2*a* site and 4.1(8)% at the 6*h* site. The occupation of carbon at the 2*c* site is 54(1)%. This corresponds to the formula $Fe_{3.57(3)}W_{9.43(3)}C_{3.54(1)}$. This formula can be compared with the results obtained from the chemical analysis. By subtraction of 9.0% W_2C from the chemical analytical data, assuming Zr to be present as $ZrC_{0.9}$ and disregarding the Ca and Si impurities, the chemical formula obtained is $Fe_{3.65}W_{9.35}C_{3.45}$. Considering the somewhat uncertain character of the corrections made, the agreement between the two chemical formulae is quite satisfactory, and the occurrence of Fe/W substitution must be regarded as well established.

A ^{57}Fe Mössbauer investigation of κ-(Fe–W–C) has also been performed (*17*), and the results completely confirm the iron substitutions reported in the present paper.

A comparison between the interatomic distances in κ-(Fe–W–C) (see Table II) and those in κ-(Co–W–C) (*7*) shows a close agreement. The largest deviation occurs in the W(3)–Fe(1) distance (2.437 Å) compared with the corresponding W(3)–Co distance (2.489 Å). This is explained, however, by the iron substitution at the W(3) position.

The position 2*c* is only partially occupied by carbon. This site is also partially occupied in κ-(Co–W–C) but to a somewhat smaller extent (41%). However, in conformity with κ-(Co–W–C), the κ phase in the Fe–W–C system has a range of homogeneity. The composition of the sample used for the present investigation lies in the two-phase field κ + W_2C, while the sample used for the κ-(Co–W–C) study lay in the three-phase field κ + M_6C + W. This might be the reason for the slightly higher carbon content observed in κ-(Fe–W–C).

Acknowledgments

The authors are most grateful to Professor F. Nydahl and Dr. Lilly Gustafsson, Department of Analytical Chemistry, University of Uppsala, for their skilled analysis of the tungsten and iron content, and to Sandvik AB, Hard Metal Division, Stockholm, through the kind auspices of Dr. B. Uhrenius, for the carbon analysis. Financial support from the Swedish Natural Science Research Council is gratefully acknowledged.

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