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The Crystal Structure of the Molybdenum Cementite $Mo_{12}Fe_{22}C_{10}$ (ξ-Phase)

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The crystal structure of molybdenum cementite $Mo_{12}Fe_{22}C_{10}$ (ξ-phase) has been determined by means of a single crystal x-ray diffraction study of crystal fragments. The lattice parameters were found to be: $a = 10.865\ (3)$, $b = 7.767\ (2)$, $c = 6.559\ (2)$ Å and $\beta = 120.13\ (2)°$, space group C2/m; $Z = 1$. From the analysis of *Patterson* maps and difference *Fourier* analysis the atomic parameters were derived, yielding a residual of $R = 0.059$. The crystal structure contains octahedral and triangular prismatic groups which accommodate the carbon atoms in their voids, as is usually found in interstitial compounds. The octahedral building group consists of four Mo- and two Fe-atoms, the triangular prism is built up by four Fe- and two Mo-atoms. The mode of filling of the metal polyhedra is discussed.

(Keywords: Crystal structure; Complex carbides; Mo-cementite)

Die Kristallstruktur von Molybdän-Zementit, $Mo_{12}Fe_{22}C_{10}$ (*ξ-Phase*)

Die Kristallstruktur von Molybdän-Zementit, „$Mo_{12}Fe_{22}C_{10}$" (ξ-Phase) wird auf Grund von Einkristall-Beugungsaufnahmen unter Anwendung von *Patterson*- and Differential *Fourier*-Analysen bestimmt. In der monoklinen Elementarzelle ($a = 1.870$; $b = 7.67$; $c = 6.563$ Å, $\beta = 120.1°$) Raumgruppe C 2/m befindet sich eine Formeleinheit $Mo_{12}Fe_{22}C_{10}$ (oder $Z = 2$, $Mo_6Fe_{11}C_5$). Der R-Wert von 6% für 1200 Reflexe unterstreicht die Richtigkeit der Struktur, die aus oktaedrischen und trigonal prismatischen Gruppen aufgebaut ist. Die Oktaedergruppe besteht aus 4 Mo- und 2-Fe-Atomen, die trigonal prismatische Gruppe aus 4 Fe- und 2 Mo-Atomen. Die Kohlenstoffatome füllen die Lücken dieser Bauelemente, wie es für typische Einlagerungscarbide (Komplexcarbide) erwartet werden kann.

Introduction

Because of the significance of molybdenum-containing steels, quite a few investigations have been performed in the ternary system iron-molybdenum-carbon. Due to metastable phases and equilibria the results are not all consistent, although the existence of the complex carbides $Mo_{\sim 3}Fe_{\sim 3}C$ (η-carbide), $Mo_2Fe_{21}C_6$ (τ-carbide) and "$MoFe_2C$" (ξ-phase) is no longer questioned.

The ξ-phase complex carbide was discovered by *Kuo*[1] as well as by *Habraken*[2] and confirmed by *Dyson* et al.[3]. Nevertheless, there are discrepancies concerning the stability of the ξ-phase region and its chemical composition. Only recently did *Craig*[4] find and emphasize that the x-ray powder patterns of cementite Fe_3C and that of the ξ-phase "$MoFe_2C$" are very similar indeed. Considering this fact, the ξ-phase, henceforth called Mo-cementite, can easily be overlooked in iron base alloy. In addition, it has been shown[4] that the Mo-cementite also occasionally occurs in very fine precipitates which might be difficult to be discerned by metallographic techniques. From more recent studies[5] it has become obvious that the Mo-cementite is carbon-deficient as compared to the previously assumed composition. New measurements of single crystal materials by EDAX analysis indicate a slight increase of the atomic ratio Mo/Fe over 0.5.

Experimental

The preparation of single crystals and preliminary determination of structural parameters has already been described by *Wayne* and *Nowotny*[5]. Systematic extinctions in precession photographs limited the choice of space group to C2/m or C2/c. Subsequent refinement of the structure indicates the true space group as C2/m. It should be mentioned again, that all single crystal fragments used for x-ray precession photographs were identified after powdering as "$MoFe_2C$" according to patterns taken by previous work.

The lattice parameters were found to be $a = 10.865$ (3), $b = 7.767$ (2), $c = 6.559$ (2) Å, and $\beta = 120.13$ (2)° from a least-squares refinement of 20 reflections in the angular range $46° < 2\theta < 59°$, each automatically centered on a Picker FACS-I diffractometer (Mo $K\alpha 1$, $\lambda = 0.70930$ Å). On the assumption of an interpolated density of ~ 8.5 g/cm^3 (out of the densities of Fe_3C, Mo_2C and Mo_3Fe_3C) one ends up with 11 formula units of "$MoFe_2C$" per unit cell. The space group C2/m allows the occupation of two-fold, four-fold, and eight-fold positions. Thus a formula $Mo_{12}Fe_{<24}C_{<12}$ appeared to be appropriate.

Over 1200 reflections in the range $2\theta < 60°$ were investigated using Zr-filtered Mo $K\alpha$ radiation at a take-off angle of 0.5° with the diffractometer operating in the ω-scan mode. Ten-second background counts were taken at both ends of a 1.4° θ–2θ offset with allowances for dispersion. A total of 716 data were considered observable according to the criterion $|F_0| > 3\sigma_F$. Intensity data were corrected for *Lorentz* and polarization effects and, since the crystal fragment was highly irregular in shape, an analytical (ψ-scan) absorption correction was applied. The maximum relative absorption correction was 18%.

The structure was solved by means of analysis of *Patterson* maps and difference *Fourier* analyses. The final full-matrix isotropic least-squares refinement[6] using a $1/\sigma^2$ weighting scheme, zerovalent scattering factors[7] and corrections for secondary extinction and anomalous dispersion, yielded a residual of $R = 0.059$ (data: parameter ratio = 26)*. The maximum extinction correction[8] was 36% of $|F_0|$ for the 022 reflection.

Results and Discussion

Table 1 presents the final atomic positional and isotropic thermal parameters. In view of the good agreement between observed and calculated structure factors the proposed atomic arrangement is most likely, which is also indicated by evaluation of the powder pattern given in Table 2.

Table 1. *Positional parameters and isotropic thermal parameters*

Atom	symm	10^4x	10^4y	10^4x	B
Mo(1)	(4i)	8830(1)	1/2	2828(2)	0.10(3)
Mo(2)	(8j)	884011)	1984(1)	372(2)	0.13(3)
Fe(1)	(2b)	0	1/2	0	0.19(7)
Fe(2)	(4i)	2656(2)	1/2	2095(4)	- 0.02(6)
Fe(3)	(8j)	3600(2)	1647(2)	6273(3)	0.08(4)
Fe(4)	(4h)	1/2	3374(3)	1/2	0.18(5)
Fe(5)	(4i)	3632(2)	1/2	6684(4)	0.08(6)
C(1)	(8j)	3013(11)	2506(15)	2992(18)	- 0.13(13)
C(2)	(2a)	0	0	0	0.35(33)

Variation of the metal site occupancies during the final stages of refinement showed that, within the standard deviations, there was no interchange of Fe and Mo. Accordingly, the resultant formula $Mo_{12}Fe_{22}C_{10}$ (or $2\,Mo_6Fe_{11}C_5$) meets the analytical observations, that the amount of carbon is slightly less than 25 at% C and the atomic ratio Mo/Fe somewhat higher than 0.5. There is no Mo/Fe substitution on the metal sites as it occurs in the neighboring η-carbide or in other related η-carbides such as the η-W—Fe—C carbide. In this connection it should be mentioned that the metastable τ-carbide $Mo_2Fe_{21}C_6$ exhibits a similar behavior as the Mo-cementite, insofar as no Mo/Fe exchange has been observed[9].

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* Lists for structure factors $|F_0|$ and $|F_c|$ can be obtained from the authors.

Table 2. *Evaluation of a powder diagram for the Mo-cementite of formula* $Mo_{12}Fe_{22}C_{10}$

f = faint; vw = very weak; w = weak; m = medium; st = strong.

Index	Int. obs.	$10^3 \sin^2\theta_{obs}$	Int. calc.
$(110)(\bar{1}10)$	-	-	0.7
(001)	f	40.5	4.1
$(\bar{2}01)$	-	-	1.1
$(\bar{1}11)$	-	-	1.0
(200)	-	-	0.6
(020)	-	-	0.1
(111)	-	-	0.2
$(\bar{3}11)$	-	-	0.1
$(\bar{2}02)$	-	-	0.8
(021)	vw	129.7	6.3
$(\bar{2}21)$	-	-	0.7
(220)	f	148.3	1.2
(201)			0.6
$(\bar{1}12)$			0.6
(310)	-	-	0.1
(002)	f	162.6	2.1
$(\bar{3}12)$	vw	170.7	2.8
$(\bar{4}01)$	vw	179.0	3.7
$(\bar{4}02)$	-	-	0.4
$(\bar{2}22)$	w^+	212.8	8.0
(130)	m	215.0	12.4
$(\bar{1}31)$	-	-	0.0
(400)	m^+	237.7	19.4
(221)			1.9
(112)	m^+	249.1	9.6
(022)		252.2	31.6
$(\bar{4}21)$	m	268.6	18.0
(311)			21.0
$(\bar{2}03)$	-	-	0.4
(131)	m	280.9	25.1
$(\bar{4}22)$	m	292.2	20.1
$(\bar{3}13)$	st	300.7	12.9
$(\bar{3}31)$			55.8
$(\bar{4}03)$	m	308.0	30.7
$(\bar{5}12)$	m	310.0	5.3
$(\bar{5}11)$			13.3
(202)	m	321.4	19.7
(420)	vw	326.5	3.1
$(\bar{1}32)$	m	329.2	21.0
$(\bar{1}13)$			4.1
(330)	f	334.0	2.5
$(\bar{3}32)$	-	-	0.3
(040)	vw	358	5.5
(003)	w^+	366.9	9.8
$(\bar{2}23)$			12.9
(401)	-	-	0.2
$(\bar{5}13)$	-	-	0.7
(510)	-	-	0.7
$(\bar{4}23)$	vw	397.8	2.4
(041)			2.9
$(\bar{6}02)$	vw	401.5	6.7
$(\bar{2}41)$			0.8
(222)	-	-	1.1
(240)	-	-	0.5
$(\bar{6}01)$	vw	427.3	2.9
(132)			0.1
(331)	-	-	0.1
(023)	-	-	0.3
$(\bar{6}03)$	-	-	0.1
(421)	w	466.2	8.9

Table 3 presents relevant interatomic distances and bond angles. C(1) fills the trigonal prismatic void in the smaller metal atom (mainly Fe) environment [average C(1)-*M* distance 2.072 Å] with the square faces capped at slightly longer distances. In the case of the large (preferentially Mo) environment, C(2) occupies octahedral voids [average C(2)-*M* = 2.019 Å].

The crystal structure of the Mo-cementite displays interesting aspects for interstitial compounds of transition element carbides. As expected from building groups within a considerable number of complex carbides[10]

Table 3. *Interatomic distances (Å), bond angles (°), and polyhedral edge lengths (Å)*

		Distance	Angle	Edge
Carbon Environments:				
C(1) trigonal prism				
C(1)-Fe(2)		1.980(12)		
C(1)-Fe(4)		1.982(10)		
C(1)-Fe(3)		2.017(11)		
C(1)-Fe(3)		2.144(11)		
C(1)-Mo(1)		2.144(12)		
C(1)-Mo(2)		2.165(11)		
capping atoms:				
(1)-Mo(2)		2.337(11)		
C(1)-Fe(5)		2.715(11)		
C(1)-Fe(5)		2.878(11)		
within the prisms:				
Fe(2)-C(1)-Fe(4)			82.3(4)	2.606(3)
Fe(2)-C(1)-Fe(3)			123.1(6)	3.514(3)
Fe(2)-C(1)-Fe(3)			73.3(4)	2.465(3)
Fe(2)-C(1)-Mo(1)			151.2(6)	3.994(1)
Fe(2)-C(1)-Mo(2)			85.8(4)	2.824(2)
Fe(4)-C(1)-Fe(3)			75.9(4)	2.458(2)
Fe(4)-C(1)-Fe(3)			119.6(5)	3.567(2)
Fe(4)-C(1)-Mo(1)			90.0(4)	2.921(2)
Fe(4)-C(1)-Mo(2)			152.3(6)	4.026(2)
Fe(3)-C(1)-Fe(3)			73.5(4)	2.491(3)
Fe(3)-C(1)-Mo(1)			81.1(4)	2.708(2)
Fe(3)-C(1)-Mo(2)			131.1(6)	3.807(2)
Fe(3)-C(1)-Mo(1)			133.3(6)	3.937(2)
Fe(3)-C(1)-Mo(2)			80.2(4)	2.774(2)
Mo(1)-C(1)-Mo(2)			88.4(4)	3.005(2)
C(2) octahedron				
C(2)-Fe(5)	2x	1.923(5)		
C(2)-Mo(2)	4x	2.067(1)		
Fe(5-C(2)-Mo(2)	4x		87.88(6)	2.770(2)
Fe(5)-C(2)-Mo(2)	4x		92.12(6)	2.875(2)
Mo(2)-C(2)-Mo(2)	2x		94.83(6)	3.044(2)
Mo(2)-C(2)-Mo(2)	2x		85.17(6)	2.797(2)
Fe(5)-C(2)-Fe(5)			180	3.845(5)
Mo(2)-C(2)-Mo(2)	2x		180	4.134(2)

Table 3 (continued)

		Distance		Angle	Edge
Iron environments:					
Fe(1)					
Fe(1)-Fe(3)	4x	2.481(2)			
Fe(1)-Fe(2)	2x	2.498(3)			
Fe(3)-Fe(1)-Fe(3)			2x	61.25(8)	2.528(4)
Fe(3)-Fe(1)-Fe(3)			2x	118.75(8)	4.270(4)
Fe(3)-Fe(1)-Fe(2)			2x	120.66(6)	4.326(3)
Fe(3)-Fe(1)-Fe(2)			2x	59.34(6)	2.465(3)
Fe(3)-Fe(1)-Fe(3)			2x	180	4.962(4)
Fe(2)-Fe(1)-Fe(2)				180	4.996(6)
Fe(2)					
Fe(2)-C(1)	2x	1.980(12)			
C(1)-Fe(2)-C(1)				149.0(6)	3.815(23)
Fe(3)					
Fe(3)-C(1)		2.017(11)			
Fe(3)-C(1)		2.144(11)			
C(1)-Fe(3)-C(1)				106.5(4)	3.335(21)
Fe(4)					
Fe(4)-C(1)	2x	1.982(11)			
C(1)-Fe(4)-C(1)				141.0(7)	3.736(21)
Fe(5)					
Fe(5)-C(2)		1.923(3)			
Molybdenum environments:					
Mo(1)					
Mo(1)-C(1)	2x	2.144(11)			
C(1)-Mo(1)-C(1)				128.1(6)	3.855(23)
Mo(2)					
Mo(2)-C(2)		2.067(1)			
Mo(2)-C(1)		2.165(11)			
Mo(2)-C(1)		2.337(11)			
C(2)-Mo(2)-C(1)				109.3(3)	3.452(11)
C(2)-Mo(2)-C(1)				133.5(3)	4.048(11)
C(1)-Mo(2)-C(1)				102.7(4)	3.518(22)

the interstices (carbon atoms) frequently fill transition metal octahedral or triangular prismatic voids. As can be seen from Figs. 1 and 2, the larger Mo-atoms form the transition metal octahedra, while the smaller Fe-atoms accommodate the carbon in a triangular prismatic surrounding [note the capping of the three prismatic faces by two Fe(5)'s and one Mo(2)]. The octahedral building group consists of four Mo- and two Fe-atoms, the triangular prism consists of four Fe- and two Mo-atoms. Fig. 3

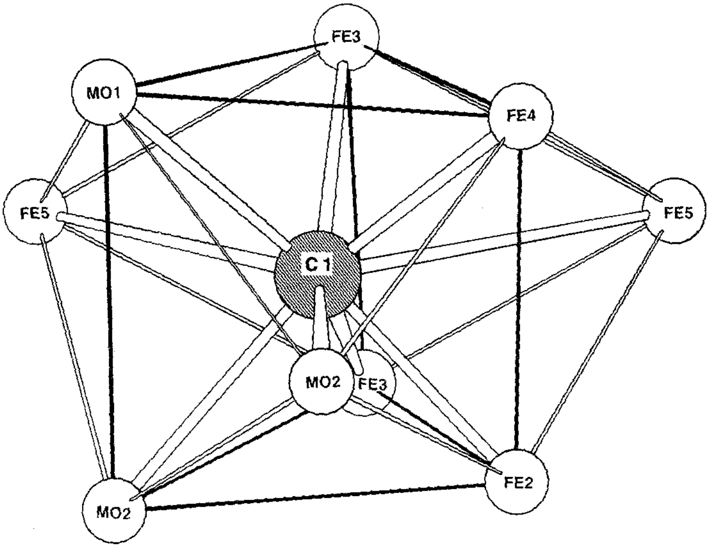

Fig. 1. Small metal (preferentially Fe) environment with C(1) atom in the trigonal prismatic void (note the tricapped faces)

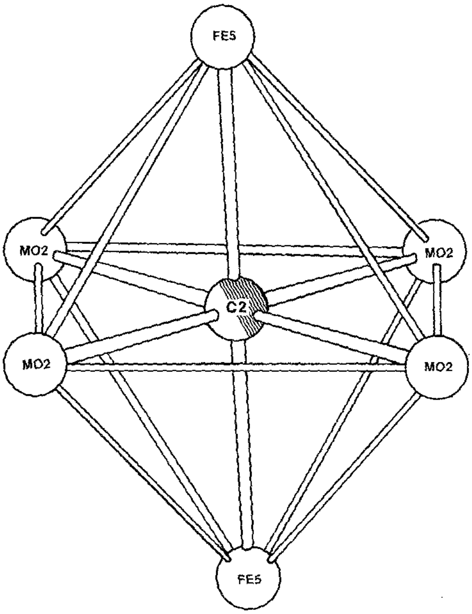

Fig. 2. Large metal (preferentially Mo) environment with C(2) atom in the octahedral void

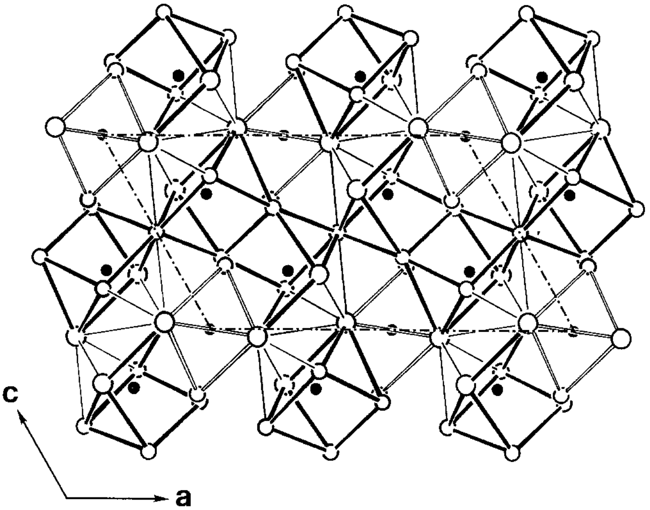

Fig. 3. Projection of the structure of $Mo_{12}Fe_{22}C_{10}$ onto the *ac* plane; small filled circles are C atoms, smaller open circles are Fe, larger open circles are Mo

is a projection of the structure onto the *ac* plane. It also is of interest to note, in view of topochemical reactions[7], that in the competing binary carbides Mo_2C and Fe_3C the octahedral environment dominates in Mo_2C, the triangular prismatic in the cementite. This fact reflects in the observed distances Mo—C and Fe—C with the crystal structure of $Mo_{12}Fe_{22}C_{10}$ (Table 3). Fig. 3 also makes clear that there are still voids unoccupied in 0 1/2 1/2 etc. which is proven by a difference *Fourier* analysis. Filling this site by iron, which would make the atomic ratio Mo/Fe = 0.5, leads, however, to large discrepancies for the calculated intensities, particularly at low angles. Besides the metal octahedron and the triangular prism, the tetrahedral configuration of the iron atoms in Fig. 3 has to be discussed. Because of the small size of this void, no carbon can be accommodated. In essence, these three metal polyhedra are also found in M_7C_3 carbides, which are derived from the Cr_7C_3 type structure [for example $(Cr, Mn, Fe)_7C_3$]. In this case the triangular prisms are filled while the tetrahedral and octahedral voids are empty[8].

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